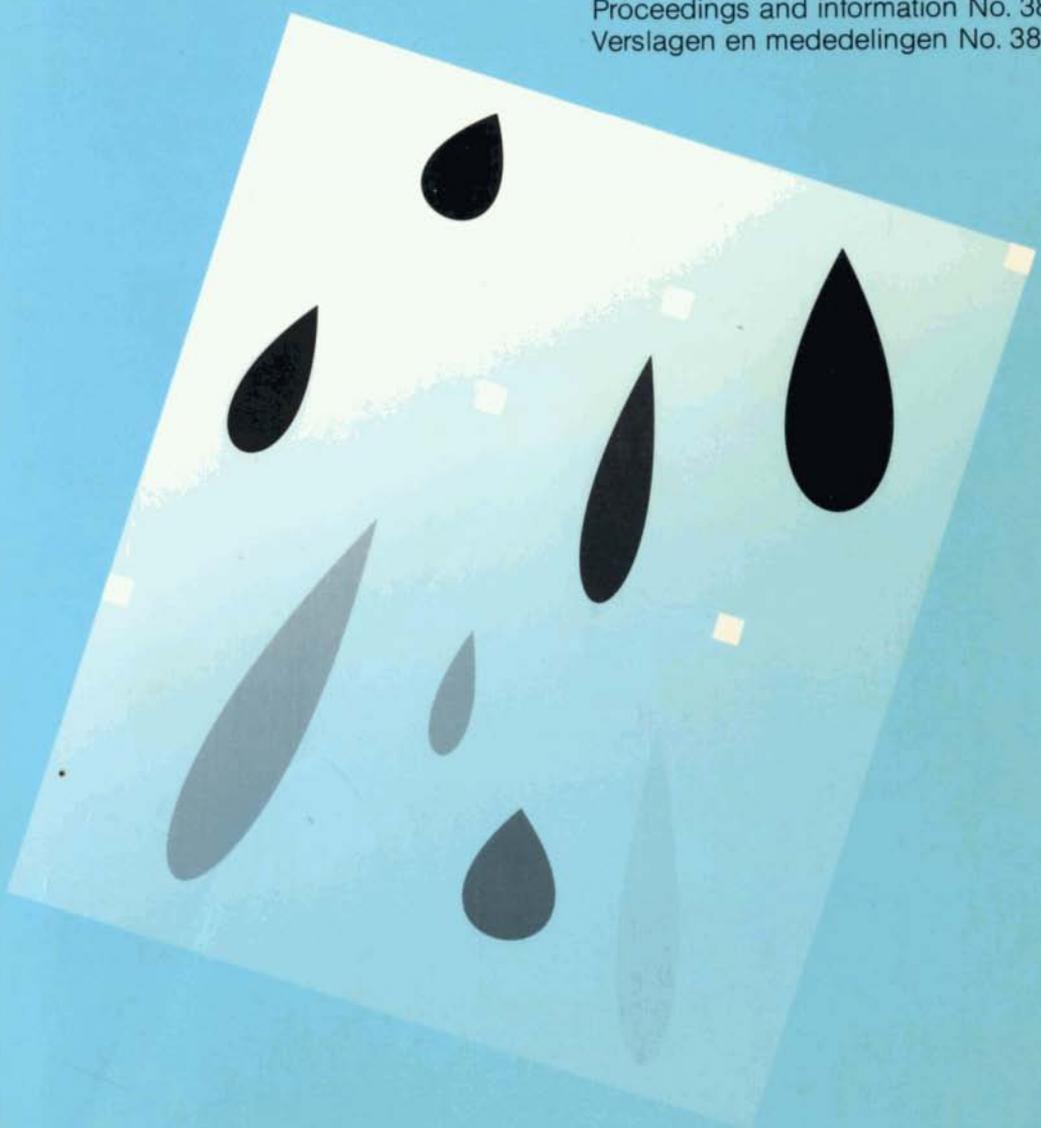


Netherlands
organization for
applied scientific
research

TNO Committee
on Hydrological
Research

National Institute of Public
Health and Environmental
Hygiene



Vulnerability of soil and groundwater to pollutants

Proceedings and information No. 38
Verslagen en mededelingen No. 38

Vulnerability of soil and groundwater to pollutants

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Editors

W. van Duijvenbooden
H. G. van Waegeningh

International Conference
Noordwijk aan Zee, The Netherlands
March 30 – April 3, 1987

Organized by
National Institute of Public Health
and Environmental Hygiene

The Hague 1987

Vulnerability of soil and groundwater to pollutants:
proceedings of the International Conference on March 30 –
April 3, 1987 at Noordwijk aan Zee / (ed. by W. van Duijven-
bouden and H. G. van Waegeningh) – The Hague: TNO
Committee on Hydrological Research. – 111. – (Proceedings
and Information / TNO Committee on Hydrological Research;
no. 38)

Met lit. opg., reg.

ISBN 90-6743-109-5

SISO 614.62 UDC 504.4.05+504.53.05

Trefw.: bodemverontreiniging / grondwaterverontreiniging

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SCIENTIFIC RESEARCH TNO, 1987.

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**INTRODUCTION, SUMMARY, CONCLUSIONS AND
RECOMMENDATIONS**

PREFACE

Expansion and intensification of human activities give cause to dispersion of pollutants in the subsurface environment. Today, acid rain, hazardous chemical wastes, fertilizers, pesticides, solvents, manure and sewage sludge are, amongst other things, a serious threat to soil and groundwater. In numerous cases they have a severe impact on the quality of these natural resources. Therefore, existing groundwater and soil protection policies and strategies have to be reconsidered, and new ones have to be developed. To this end many research programmes have to be carried out.

It was against this background that the National Institute for Public Health and Environmental Hygiene (RIVM) of the Netherlands arranged the International Conference on the Vulnerability of Soil and Groundwater to Pollutants. This conference was held at Noordwijk aan Zee in March/April 1987.

The conference focused on one of the essential elements in the wide range of research topics involved, namely the vulnerability of soil and groundwater to pollutants with respect to their multifunctional character. Subjects covered were: criteria for protection, monitoring strategies, mapping, collection, interpretation and use of data in modelling and subsurface behaviour of pollutants.

Special attention was given to the interaction between top soils and groundwater bodies, as well as to the spatial and temporal variability of parameters.

The main objective of the conference was to stimulate the exchange of information and points of view, on the topics mentioned, between researchers, especially hydrogeologists and soil scientists, active in the field of soil and groundwater quality.

In this respect the conference was attended by about 250 scientists from 26 countries all over the world. In total 111 papers and posters were presented during several plenary and

parallel sessions and poster presentations. All these presentations are included in the proceedings. They have been grouped according to the six topics of the conference:

- topic 1 Criteria for protection of soil and groundwater
- topic 2 Monitoring strategies for the quality of soil and groundwater
- topic 3 Vulnerability mapping
- topic 4 Vulnerability in relation to subsurface behaviour of inorganic pollutants
- topic 5 Vulnerability in relation to subsurface behaviour of organic pollutants
- topic 6 Use of data required for modelling effects on soil and groundwater quality.

Besides, the first chapter of this book includes a general introduction and the conclusions and recommendations drawn by the chairmen at the end of the conference.

The organization of the conference was only possible due to the valuable and active support of several national and international organizations and a lot of well-known scientists from all over the world.

Programme, topics and presentations were screened by the Scientific Committee, which consisted of the following members:

- | | |
|-------------------------------------|---|
| J.J. Meulenkamp
(chairman) | National Institute of Public Health and
Environmental Hygiene, Bilthoven, The
Netherlands |
| W. van Duijvenbooden
(secretary) | National Institute of Public Health and
Environmental Hygiene, Bilthoven, The
Netherlands |
| J. Bouma | Agricultural University, Wageningen,
The Netherlands |
| W. Cramer | National Institute of Public Health and
Environmental Hygiene, Bilthoven, The
Netherlands |

- A. Pekdeger, Geological Institute, University of Kiel, Federal Republic of Germany (geochemistry aspects)
- H.A.M. de Kruijff, National Institute of Public Health and Environmental Hygiene, Bilthoven, The Netherlands (ecological aspects)
- H. Wiechmann, University of Bonn, Federal Republic of Germany (soil aspects)
- Ph.E. LaMoreaux, Environmental Institute for Waste Management Studies, Tuscaloosa, USA (groundwater quality aspects)
- W. Cramer/J.E.T. Moen, National Institute of Public Health and Environmental Hygiene, Bilthoven/Ministry of Housing, Physical Planning and Environment, Leidschendam, The Netherlands (implementation of soil protection policies)

TOPIC 2

chairman:

E. Romijn, Provincial Waterboard of Gelderland, The Netherlands

co-chairman:

S.S.D. Foster, British Geological Survey, Wallingford, United Kingdom

invited speakers:

J. Vrba, Stavebni Geologie n.p., Prague, Czechoslovakia

W. van Duijvenbooden, National Institute of Public Health and Environmental Hygiene, Bilthoven, The Netherlands

TOPIC 3

chairman:

Ph.E. LaMoreaux, Environmental Institute for Waste Management Studies, Tuscaloosa, USA

co-chairman:

J. Vrba, Stavebni Geologie n.p., Prague, Czechoslovakia

invited speakers:

- Y. Bachmat, Hydrological Service, Jerusalem, Israel
- A. Breeuwsma/W. van Duijvenbooden, Soil Survey Institute, Wageningen/National Institute of Public Health and Environmental Hygiene, Bilthoven, The Netherlands
- L.J. Andersen, Geological Survey, Copenhagen, Denmark

Due to illness mr LaMoreaux was unable to attend the meeting. For this reason he has been replaced by mr J.Vrba and mr Vrba by mr W. Cramer.

TOPIC 4

chairman:

H. Wiechmann, University of Bonn, Federal Republic of Germany

co-chairman:

K. Harmsen, Institute for Soil Fertility, Haren, The Netherlands

invited speakers:

- S. van der Zee, Agricultural University, Wageningen, The Netherlands
- H. Kerdiijk/A.J. de Groot, Delft Hydraulics Laboratory, Delft/Institute for Soil Fertility, Haren, The Netherlands

TOPIC 5

chairman:

E. Custodio, Curso Internacionale de Hydrologie Subterranea, Barcelona, Spain

co-chairman:

J.P.G. Loch, National Institute of Public Health and Environmental Hygiene, Bilthoven, The Netherlands

invited speakers:

- I. Scheunert, Gesellschaft fur Strahlen und Umweltforschung mbH, Munchen, Neuherberg, Federal Republic of Germany

P. Friesel, Institute of Water-, Soil- and Air
Hygiene, Berlin, Federal Republic of Germany

TOPIC 6

chairman:

J.J. Fried, European Institute for Water, Stras-
bourg, France

co-chairman:

J. Bouma, Agricultural University, Wageningen,
The Netherlands

invited speakers:

W. de Vries, Soil Survey Institute, Wageningen,
The Netherlands

A. Bourg, National Geological Survey, Orleans,
France

W.T. Piver, National Institute of Environmental
Health Sciences, USA

The enthousiastic participation in and contribution to the conference of chairmen and speakers as well as participants conduced considerably to the success of the conference. In this respect special attention should be given to Prof.Dr. G. Matthes, who summarized the conference and prepared the general conclusions and recommendations.

The organizers wish to thank mr Andre Berends of the RIVM and the Congress Office of the Dutch Royal Society of Engineers for their valuable assistance to the organization of the conference, and mr J.C. Hooghart of the TNO-Committee on Hydrological Research for his assistance in compiling these proceedings.

Finally the organizers acknowledge the following sponsoring organizations:

VROM	Ministry of Housing, Physical Planning and Environ- ment, The Netherlands
IAH	International Association of Hydrogeologists
IAHS	International Association of Hydrological Sciences
ISSS	International Society of Soil Science

GEC Commission of the European Communities
 UNESCO United Nations Educational, Scientific and Cultural
 Organization
 WHO World Health Organization.

The Organizing Committee:

W. van Duijvenbooden National Institute of Public Health and
 (chairman) Environmental Hygiene, Bilthoven,
 The Netherlands

I.D. van der Meiden National Institute of Public Health and
 (secretary) Environmental Hygiene, Bilthoven,
 The Netherlands

H.G. van Waegeningh National Institute of Public Health and
 Environmental Hygiene, Bilthoven,
 The Netherlands

H.J. Colenbrander TNO Committee on Hydrological Research,
 (advisor) The Hague, The Netherlands

W.J. Willems Ministry of Housing, Physical Planning
 (advisor) and Environment, Leidschendam, The
 Netherlands.

WELCOME

R.B.J.C. van Noort

Director General of the National Institute of Public Health
and Environmental Hygiene

Ladies and Gentlemen,

It is with great pleasure that I welcome you at the beginning of this International Conference on the Vulnerability of Soil and Groundwater to Pollutants, organized by The Netherlands' National Institute of Public Health and Environmental Hygiene and sponsored by a number of international organizations.

A special word of welcome to mr Evers, Deputy Director-General of the Directorate-General for Environmental Protection of the Dutch Ministry of Housing, Physical Planning and Environment, who will officially open this conference in a few minutes, to the representatives of the sponsoring organizations and to the members of the Scientific Committee.

It is just six years ago that the former National Institute for Water Supply, which now forms part of the RIVM, organized the world's first International Symposium on the Quality of Groundwater. At the end of that symposium Prof. Huisman suggested that other governments, international agencies, learned societies and the like keep the flame burning and make sure that another congress on this subject, or perhaps better: a meeting of specialists on part of the subject matter, would be organized in the near future.

In fact, I've noticed with pleasure that after this symposium several of the suggested meetings have been held, including even a "First International Conference on Groundwater Quality Research".

And now in the next few days we will be here together with more than 200 participants from 25 countries all over the world, which makes this conference a real international event. In contrast with the symposium in 1981, this conference is not primarily directed to hydrogeologists but

also to soil scientists active in the field of soil and groundwater quality. The main objective of the conference is to stimulate the exchange of information and points of view between these researchers. The Organizing Committee with the valuable assistance of the Scientific Committee, and last but not least with the cooperation of the numerous authors, succeeded in making up an interesting but rather full programme, covering six topics, divided into six plenary and 17 parallel sessions. During these sessions 84 papers will be presented: in addition to this there will be poster presentations. In view of the fact that various activities will take place simultaneously, you are strongly advised to study the programme carefully and make a plan of the activities you wish to attend. Furthermore I have to ask for your cooperation and discipline to adjust to the programme and the time schedule. The chairmen will be very strict in this respect. On the other hand, I trust that there will be ample opportunity to discuss the several subjects in smaller groups outside the scheduled meetings. I would like to ask your special attention for the poster presentations. However, it is possible to go and see the poster presentations till coming Thursday.

The proceedings of the conference will appear in print in the course of June 1987. The proceedings will include the summary and conclusions of the chairmen and the main conclusions and recommendations given by Prof. G. Matthes during the closing session on Thursday. For questions you can always contact the Congress Office and the members of the Organizing Committee.

I would like to express my gratitude to the EC, the Ministry of Housing, Physical Planning and Environment and the KLM for their financial support, and to all those who by joined effort made this conference possible.

Ladies and Gentlemen, I wish you a couple of interesting days and a pleasant stay in this country.

OPENING ADDRESS

F.W.R. Evers

Deputy Director General Environmental Protection

Ministry of Housing, Physical Planning and Environment

Mr Chairman, ladies and gentlemen,

Originally the minister had the intention of opening this conference. Unfortunately the minister is prevented from coming here due to a stay abroad. Therefore I have the honour of performing this task.

This conference deals with the vulnerability of soil and groundwater to pollutants. Pollution of soil and groundwater is a world-wide problem both in developing countries as well as in countries with intensive agricultural and industrial activities. I will take the opportunity to inform you about some aspects of the Dutch protection policy. The protection of soil and groundwater is an integrated part of our environmental policy.

Since January 1st of this year the Soil Protection Act has become effective. This act defines the soil as the solid part of the earth including the liquid and gaseous components as well as the organisms living in it. The idea behind this definition is, that groundwater protection is impossible without protecting the soil as a whole. In a densely populated country as The Netherlands the soil has many functions which are interfering with each other both in space and in time. For example groundwater abstracted at a pumping station for public water supply may have been recharged years ago in agricultural and urbanized areas elsewhere. Furthermore changes of soil use are frequently occurring in The Netherlands. Therefore the preservation of this so called multifunctionality of the soil is a main objective of our environmental policy.

The leading thought behind this policy is to behave ourselves as 'guest in our own house' in order to keep as many options as possible open for future soil use.

The Soil Protection Act will be implemented in the forthcoming years. A

distinction is made in establishing a general protection level and a specific protection level based on a different acceptance of pollution risks.

The general protection level will be implemented by the national government on the following priority pollution sources: manuring of farming land, disposal of solid and liquid wastes and underground storage tanks.

The establishment of the specific protection level is laid in the hands of the twelve provincial authorities. For example groundwater protection areas around pumping stations for public water supply must be realized at January 1st in 1989. The provinces are obliged to draw up an ordinance and a protection plan. This groundwater protection plan must contain the policy objectives towards local and diffuse pollution sources in these protection areas.

The protection of soil and groundwater requires as much as possible a sound scientific base. The international exchange of information and ideas is very valuable in this respect to learn from experiences obtained in other countries. In spite of the differences in magnitude of actual pollution and in soil and hydrological setting in the various countries, the nature of the problem is fundamentally the same. This conference covers a wide and complicated field ranging from sources and nature of pollution, its behaviour in soil and groundwater to modelling and vulnerability mapping.

It is of utmost importance that study of these topics takes into account the soil as a whole. For example groundwater specialists must not see the solid part of the soil as an inert filter medium or define the upper soil layers simply as covering layers. On the other hand soil scientists who focus themselves to the topsoil must realise that leaching of substances to deeper layers does not mean that they really have disappeared. This conference has the pretention to integrate these fields.

Finally, I will add something to the subject of vulnerability. Vulnerability has not only scientific but also policy aspects. Scientifically speaking, statements can be given about the vulnerability of soil and groundwater based on the soil characteristics and pollutant behaviour in different regions. However, the amount of available data governs the accuracy of these statements. From the view of policy making differences

in vulnerability may be used in setting priorities for combating pollution sources. This is a legitimate use of vulnerability studies but it makes high demands on the scientific base of the studies with respect to schematization, accuracy and presentation. The use of vulnerability studies must always be done in a sensible way, taking into account the inevitable limits connected with them.

This conference aims at stimulating the exchange of information between - amongst others - the top soil specialists and the aquifer-oriented specialists. I hope this exchange will be fruitful and lead to useful results.

I am looking forward to the conclusions and recommendations by professor Matthes.

Mr Chairman, ladies and gentlemen, I wish you a successful meeting.

SOIL POLLUTION: AN APPEAL FOR A NEW AWARENESS OF EARTH'S
INTOXICATION

B.C.J. Zoeteman

Director Environmental Division of the National Institute
of Public Health and Environmental Hygiene

1. STANDING-UP MAKES THE WORLD BIGGER

As long as 10,000 years ago man began to interact with nature when the neolithic revolution took off. In South-west Asia human settlements started for the first time to grow crops and to raise cattle instead of collecting plants and hunting animals. It took another 4,000 years before this neolithic revolution reached The Netherlands and Belgium. It seems as if man's awareness of the larger ecosystem in which he lives became more and more clouded as man stopped hunting and devoted his activities to the development of agriculture around his settlement. The early steps in the cultivation of land were relatively harmless to nature, but interaction between the farmer and his land changed gradually from respect and understanding to manipulation and exploitation. Man behaves like a little child that is creeping in a flower-garden without noticing the destruction he leaves behind. Mechanization and industrialization of agriculture are initiated by a desire to force the power of photosynthesis into the constraints of scientifically optimized egoism. Man and its technology became the enemy of nature. Instead of multifunctional farms, each farmer is forced to specialize in raising either pigs or chicken and to grow corn or sugarbeets. Shortterm output maximization, sustained by over-irrigation, excess use of fertilizer and application of a wide range of pesticides, has superseded the original organic function of the farm which was an integral part of the landscape. I take the example of the agricultural industry, as the farmer is the most important manager of the European environment. Even in The Netherlands with its high population density the farmers control about 70% of the landsurface. The farmers will be the first to develop the new awareness that a farm can be seen as a living entity in which chemical

substances should be recirculated as much as possible instead of being dumped and burried. If the soil is intoxicated the farmer's products cannot be sold and their private wells do no longer deliver potable drinking water. And as I will show you, we are very close to that situation. For many decades man has been creeping through nature's garden as an ignorant baby. Yet the natural boundaries of self-purification and absorbtive capacity of the soil are becoming visible and time has come that man stands up to see that the world is bigger than his own garden or farm, that all chemicals do not disappear in the soil, but show up somewhere else in the larger organism of the landscape in which the individual farm is embedded. Only by developing an integrated understanding of the cycling of chemicals in air, water and soil, man will be able to overcome the present ecological crisis. Maybe we first have to accept the hypothesis of James Lovelock (1979) that earth is a living organism, a thought that goes back to the old cultures of the Greek, the Egyptians and the Persians. Once we have accepted the existance of a global living organism we might be closer to the idea that we have to harmonize our economic goals with those of the organisms we live in, such as the drainage area of a river, the landscape of the Rhine delta, the village or the individual farm. Everywhere we have to search for the living cells that are part of the living organs and the larger living organism of the landscape. And each time we have to define the magnitude of chemical cycles that can be identified in those cells, organs and organisms in order to see if the natural processes can support these cycles and if these cycles are sufficiently closed. Man must take up his role as a partner of nature before it is too late. I will illustrate this for the case of soil and groundwater pollution. But first I will present to you some more general thoughts on integrated environmental management and research.

2. INTEGRATION TRENDS IN RESEARCH AND POLICY MAKING

The concept of integrated management of environmental entities must be preceeded by an integrated view on the relationship between research, policy-making and inspection. Generally speaking environmental policy-making and enforcement can be divided into 4 phases (Winsemius,

1986). Firstly there is the phase of identification of a problem followed by the second phase of regulating the problem by laws or other measures. Once these measures are accepted the phase of problem solving starts with e.g. the construction of treatment and recycling facilities. Finally one reaches the phase of control of the situation aimed at. Figure 1 shows these 4 phases and the interaction of research, policy-making and inspection with these 4 phases. Research has to contribute primarily to the identification of new problems and it will subsequently help to define the scope of the problem and possible ways to manage it. Finally research is needed to support the control function of the environmental inspectorate. A more detailed look at the type of research activities needed can be obtained by approaching the environmental research process in a similar way. Environmental research can also be divided into 4 phases (Figure 2):

- identification;
- process analysis;
- system simulation;
- system control.

After the "identification" of an environmental problem by analytical chemists or toxicologists and once the scope of the problem is clear, the second phase starts with the "analysis of the types of processes" that determine the emission, transport, transformation and effect of the substance of interest in order to obtain mathematical equations that quantify the contribution of these processes to the problem. Once these mathematical equations are known the third phase of "system simulation" starts. The research team will try to develop a system that integrates mathematical models which can simulate the problem and the effects of possible counter measures in terms of cost and ecological or health impacts. Once such a simulation system is operational the final phase of "system control" starts, which is characterized by the routine use of the simulation system of a particular compound for policy-making and enforcement. The four phases of the environmental research process, as illustrated in Figure 2, can also be used to characterize the subsequent developments in instrumental analysis activities. In the first phase analytical techniques are developed and applied in an ad-hoc way. During the second phase monitoring networks are installed and operated as much as possible in an automated way. The third phase is characterized by a

routine functioning of automated monitoring systems and refinements in the accuracy and sensitivity of measurements and data handling. Finally in the fourth phase the number of sampling points, of quality parameters etc. is rationalized and automated ways of advanced data processing and data presentation are operational. Generally, monitoring networks for surface water quality and air quality have reached this stage in a number of countries, while soil or groundwater quality monitoring is still in the second and third phase. In future the use of monitoring networks to identify trends in environmental quality, to illustrate the relationship between air, water and soil and to calibrate integrated models that simulate environmental quality changes will be an essential instrument for the integrated management of the environmental entities which I mentioned earlier.

3. THE NATIONAL GROUNDWATER QUALITY MONITORING NETWORK

This paper focusses on the results of changes in groundwater quality in The Netherlands. Since 1981 RIVM operates a national groundwater quality network that consists of 370 sampling sites with filters at a depth of 10 and 25 metres below surface (v. Duijvenbooden et al., 1985). Monitoring of groundwater is quite different from monitoring the quality of surface water or air. The time-space dimensions of phenomena in the soil in comparison to water and are illustrated in Figure 3. Generally undeeper groundwater flows 1,000 times slower than river water. This results in local pollution patterns of point sources. However diffuse sources and ubiquitous pollutants can also result in a widespread occurrence of pollutants in groundwater as is the case for acidifying compounds like SO_4 , NO_3 and NH_4 . Although the groundwater quality network is operational only for a few years and groundwater flows rather slowly through the soil, it is astonishing that dramatic changes in groundwater quality can already be detected. A striking example gives Figure 4, which depicts a rapid acidification of the shallow aquifers in sandy soils. For 207 sampling sites in sandy soils and at a depth of 10m below surface the proportion of samples with a pH below 4 increased from 1 till 5% in the periode 1981-1985 and reached a value of 10% in 1986. Similar trends were found at a depth of 25 m. This unexpected rapid increase in acidity

is also reflected in changes of other quality parameters. Nitrate levels steadily increased in groundwaters although the rate of increase is dependent on different types of landuse as given in Table 1.

Table 1: Mean nitrate concentrations (mg N/l) of groundwater at 10 m below landsurface (sandy soils) in The Netherlands

Type of landuse	1981	1985
Arable land	19	24
Grass land	1.7	3.2
Natural area	1.5	1.8

As Table 1 shows, high nitrate levels are primarily due to agricultural use of the land. This is further confirmed by the statistical correlation of low pH values with NO_3 and SO_4 , while decreasing pH-values are correlated with Na and Cl. In 20% of the sampling sites in sandy soils nitrate levels and potassion levels exceed at a depth of 10m the quality standard for potable water (resp. 11,3 mg N/l and 12 mg/l). Parallel to these increased levels pH lowering has resulted in very high aluminium levels up to 10-30 mg/l at pH=4.

4. CAUSES OF THE RAPID GROUNDWATER QUALITY DEGRADATION

As illustrated by Table 1, agriculture is a major source of soil contamination. Particularly organic manure has contributed to the growing burden of waste materials as indicated in more detail in Table 2.

Table 2: Development in sources of waste in The Netherlands (CBS, 1986)

Source of waste problem	6 10 ⁶ ton/year	
	1975	1984
Agricultural waste	77	97
- cows	64	79
- pigs	12	16
- chicken	1	2
Domestic waste	3.5	3.8
Industrial waste	2.8	4.2

This Table further illustrates the historic changes in the quantitative contribution of the three main sources of soil contamination. As these waste streams have shown up till recently a tendency to grow, it may be expected that the rapid acidification of shallow aquifers will continue the coming decades.

5. IMPACT OF GROUNDWATER ACIDIFICATION

Groundwater acidification has an impact on the natural ecosystems which have developed in the drainage area of brooks and creeks that are typical for the sandy soils in which groundwater acidification is found in The Netherlands. Particularly in the central part of the country, called Veluwe, pH values of brooks started to decrease since the beginning of this decade. A number of 15 sampling sites in brooks was monitored for acidity in 1981 and 1986; 12 out of these 15 showed a lower pH in 1986. Already more than 50% of the samples in brooks, taken up-stream of waste water discharges, showed a pH of <6 and 9% showed pH values between 4 and 4.5. Examples of these brooks are: Heelsumsebeek, Renkumsebeek and Heerdersprengen. These lower pH values result in a complete absence of fish and amphibians in these ecosystems and a drastic change in vegetation and soil organisms of these brook valleys. In the province of Noord-Brabant artificial lakes, created in former sandpits, already show pH values as low as 3-4. These lakes are completely dead as a result of drainage water originating from the acidified aquifer.

Of course there will also be an impact of acid groundwater on the potable water supply. The most dramatic actual problem is that most of the farmers on the sandy soils, which have private wells for their supply of potable water, drink water with nitrate levels that far exceed drinking water standards. Levels up to 50 mg N/l are no exception. It is estimated that at least 20-30,000 farms are involved.

Most of the treatment plants of public water supplies in the vulnerable areas have no facilities for adequate acid neutralization. Furthermore

Al-removal cannot be achieved easily by iron-coagulation. Problems of this kind may be expected for about 80 pumping stations within a period of 10-30 years. Among all these new problems I have to mention also a positive point. Most of the treatment sludge of groundwater pumping stations has to be classified as chemical waste because of the high arsenic content. Increased acidity of groundwater immobilizes the arsenic and will result in cleaner sludges as far as arsenic is concerned.

6. VULNERABILITY OF GROUNDWATER FOR CONTAMINATION

This brief description of the rapid quality change in certain undep groundwaters and its impact on local ecosystems and potable water supply illustrate the toxifying effect of over-exploitation of agricultural land on the living entity of the farm and the landscape. It is the ignorance of the larger organism which hosts us, which has created this critical situation. As soon as we start to become parasites this will be the end of the symbiosis. This will affect our agricultural economy, our health and finally our society as a whole. The specific signs depicted by the groundwater quality network point at a problem of a much wider scope which will either revolutionize the present agricultural practice or which will lead to the intoxication of Earth's most fertile soils. Social changes, unfortunately, take time. There is an urgent need to reduce on short term the polluting activities at those soils which are most vulnerable for groundwater contamination. For this purpose RIVM, in collaboration with the Soil Survey Institute and the National Geological Survey has very recently finalized the production of maps that characterize the protective ability of the soil layers that cover the upper aquifers in The Netherlands. A distinction was made between the unsaturated zone and the water saturated parts of the covering layers. In this way it is possible to gain an insight into the vulnerability of the shallow groundwater close to the phreatic groundwater level, as well as of the groundwater in the upper aquifer. The choice of soil characteristics was limited by the availability of sufficient data on national level. The data are presented in 12 different maps at a scale 1:400,000 and include:

- total thickness of the covering layers;
- thickness of the unsaturated zone;
- organic matter content;
- clay content;
- CaCO₃ content;
- cation exchange capacity (CEC).

For interpretation of data several vertical profiles were made. These profiles were also of importance when calculating the residence time of water. The maps can be used to determine the areas vulnerable to leaching of heavy metals, organic micropollutants and nitrate to groundwater. Type of pollutant and research purpose determine which single value maps are of importance in a special case. In general vulnerable areas are found in the central and eastern part of The Netherlands. The thickness of the unsaturated zone is of importance when monitoring the vulnerability of the groundwater for nitrate pollution (Veluwe, South-Limburg, South-East Brabant and Achterhoek. CEC, organic matter, clay and residence time are of importance for leaching of heavy metals, while the map on organic matter gives some information on vulnerability to organic micropollutants (Gelderland, Overijssel, East-Brabant).

Mr Evers, it is with great pleasure and proudness that I can offer you the first copies of these 12 maps which have just arrived from the printer. We hope that these maps become an important tool for planners, policy-makers and licensing authorities and that they will be used to reverse the rapid intoxication of the precious soil and groundwater of resources of this country.

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Gast in eigen huis

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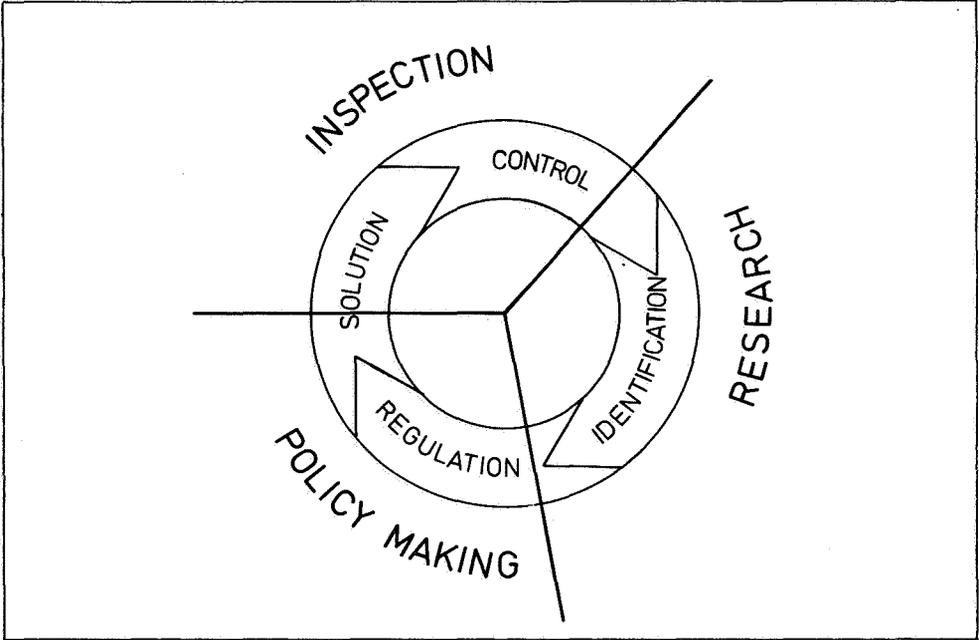


FIG. 1
POSITION OF RESEARCH IN THE POLICY LIFE CYCLE

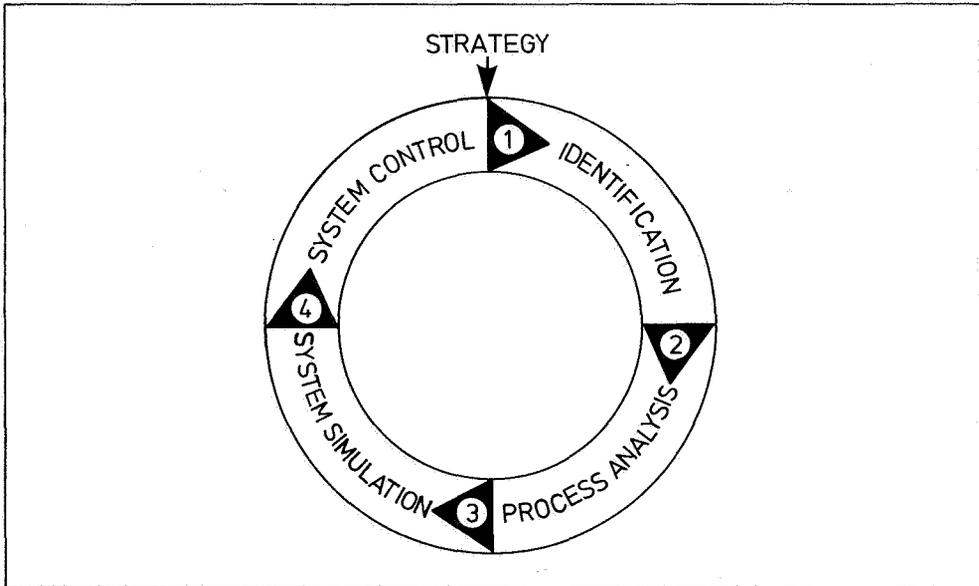


FIG. 2
THE RESEARCH LIFE-CYCLE

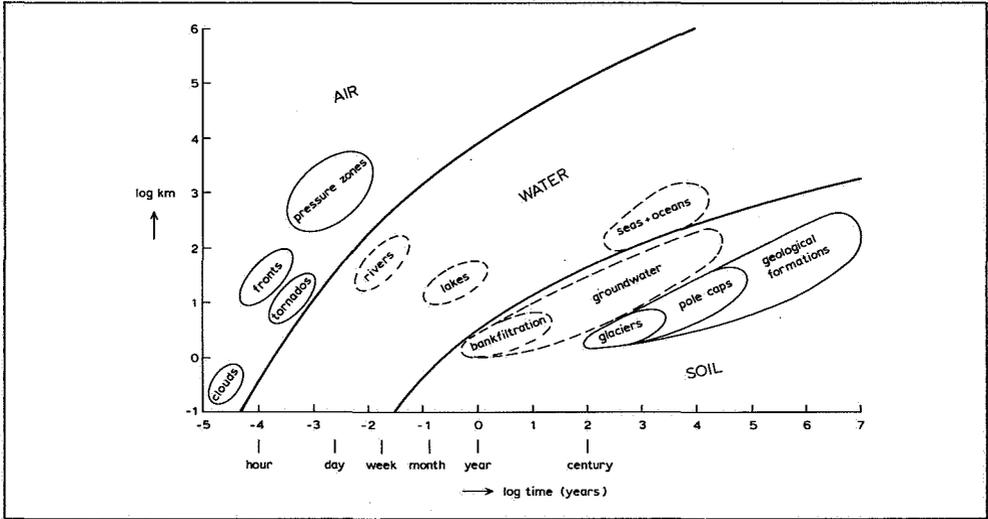


FIG. 3
TIME-SPACE DIMENSIONS OF NATURAL PHENOMENA

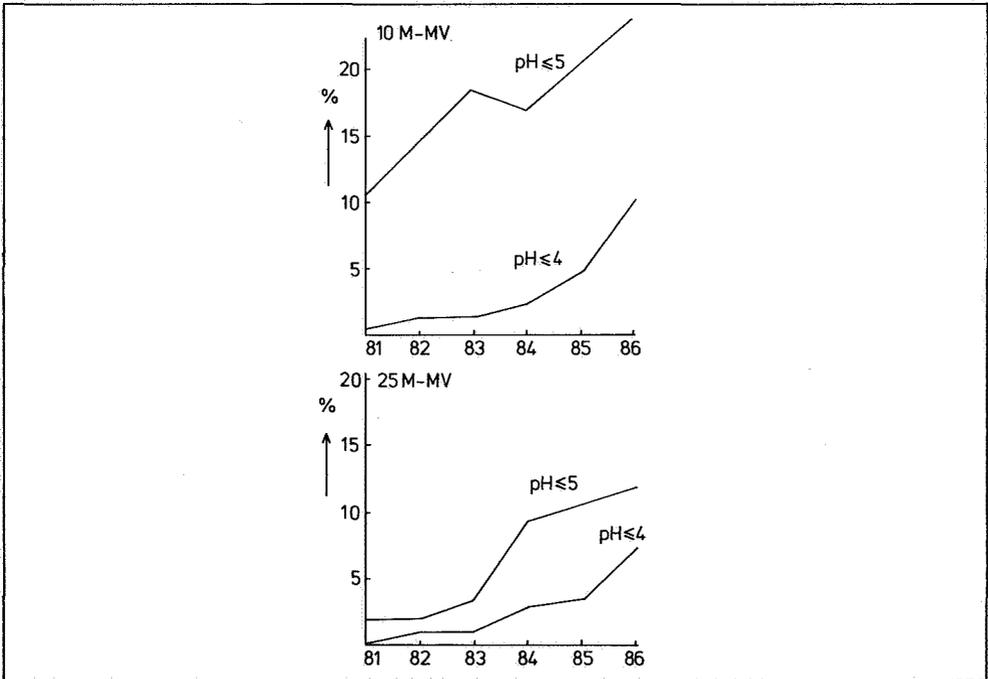


FIG. 4
NATIONAL GROUNDWATER QUALITY NETWORK
PERCENTAGE OF OBSERVATIONS $pH \leq 5$ RESP $pH \leq 4$
FOR SANDY SOILS (207 MEASURING POINTS) ON 10 AND 25 M

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

G. Matthes

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The International Conference on the Vulnerability of Soil and Groundwater to Pollutants is one of the many positive results of the International Symposium on Quality of Groundwater held in 1981 at Noordwijkerhout, The Netherlands. This former meeting brought the science community - as far as it is involved in groundwater - to realize the importance of man's various influences on the quality of groundwater. It added a new dimension to the knowledge of man's impact on groundwater by expanding the spectrum of the point and linear sources of groundwater pollution, which had raised public attention by spectacular damages, to that of diffuse sources with creeping effects on water quality. At that time mainly the effects of fertilizers and liquid animal manure (with respect to nitrate problems) and of pesticides (with respect to organic micropollutants) were discussed. However, in the last years, beginning in Scandinavia the detrimental effects of acid precipitation on the pH and on the aluminium content of groundwater became more and more obvious (Eriksson 1986). This development caused a revision of views: soil and the impact of man on the soil quality had to be considered more and more. Thus, interdisciplinary activities started in many places and it was only a consequence of this development that this conference is a joint meeting of soil scientists, of hydrogeologists and of experts of related disciplines. It is another consequence that people coming from different backgrounds run into scientific language barriers. These can only be overcome by clear definitions which can be accepted from a scientific as well as from a socio-economic or political viewpoint. It is not meaningful to separate scientific approaches from the socio-economic or political background, because the two fields interact and very often political demands do not consider in the right way the natural laws which can not be debated and overvoted by human groups or interests.

In his opening address Dr Zoeteman (1987) mentioned the neolithic revolution 10,000 years ago when the collector and hunter population turned into an agricultural population. The possibility to grow crops and to raise cattle enabled man to develop an ever-increasing population density. The impact of man on the environment can not be separated from the development of population densities. This has been shown in an impressive graph by Stumm & Morgan (1981). The introduction of fertilizers into modern agriculture in the middle of the last century stopped the permanent threat and the presence of famine in Europe, which had caused severe crises in various nations up to that years. At the same time public water supply in the industrialized areas in Europe had to give up river water as its basic resource and turned to use groundwater.

The development and use of pesticides allowed the harvesting and preservation of crops in an extent never expected in former decades. The industrial revolution combined with modern medical services has prolonged individual life expectancy of man in most countries. However, there are still areas on the world where famine and water-borne diseases are severe problems, which restrict the quality of life. These pressing problems are in a great extent connected with the availability of water of good quality.

These facts can not be used as arguments for overfertilizing and misuse of chemicals and energy but they may relativate some of the puristic approaches which are very often used in environmental discussions.

An overall concept of the fluxes of substances on the earth has to be aware of the law of mass conservation and the second law of thermodynamics which mean in this context that the substances produced by man as the chemicals or processed by man as the heavy metals tend to distribute in the environment. There is only the biosphere which seemingly does not follow thermodynamic laws (De Kruijf & Schouten, 1987) however, the reason for this paradox is the solar energy which allows the biosphere to form highly structuralized organic compounds from low energy primary components.

The concept of an integrated environmental management follows the 4 phases of identification, regulation solution and control, for which the present task is defined by identification, process analysis, system simulation and system control (Zoeteman, 1987). In the 1981 symposium on Quality of Groundwater the stage of identification predominated, whereas seen from the main topics, this conference focussed on process analysis including installation of monitoring networks, system simulation and system control. It is a need from the side of policy and decisionmakers to have maps of a suitable scale (1:400.000 or similar scales) which provide informations on thickness of covering impervious layers and of the total unsaturated zone, on content of organic matter, clay and calcium carbonate as well as cation exchange capacity (CEC) in both unsaturated and saturated zone. It is hoped that these maps may be used as important tools for planners, policy makers and licensing authorities and that they will help to prevent further intoxication and deterioration of soils and groundwater resources.

On its subsurface path water interacts with soil and rocks establishing the properties of water and vice versa the properties of soils and rocks.

The soil in its strict sense is "the upper layer of the terrestrial part of the earth crust, mainly consisting of weathered minerals and organic substances usually confined in depth to one or a few metres, on which plants are growing and organisms are living". It has a filter function for groundwater and surface water and an ecological function especially with respect to nutrient cycling (De Haan, 1987). It is the basis for plant production, the effectivity of which is controlled by the fertility status of soil either due to natural soil fertility or achieved by plant nutrient elements in manures and fertilizers. It has been shown by various contributions that surplus of available nutrients deteriorate not only the groundwater due to the leaching of unused substances, but - and this has to be stressed here - soil is changed in its physico-chemical status by the interference of compound properties. The filter function of soils due to processes like sorption, precipitation and microbial decay and enrichment of pore solutions by desorption - dissolution, or microbial formation of compounds is the major control of the quality of groundwater. This filter can be

destroyed by overloading, which results in the break-through of pollutants into deeper horizons and finally into groundwater.

Besides the chemical impacts on soil quality, for which many examples have presented and discussed here, the aspect of physical impacts on soil quality has to be considered as well (Wiechmann 1987). Both chemical and physical impacts result in changes of soil structures including compaction and decrease of permeability, which cause increased surface runoff and erosion as well as changed infiltration and percolation conditions. Therefore soil as such has to be protected not only from the standpoint of groundwater protection.

Soil is a very important ecological compartment and its beneficial effects on groundwater quality depend to a large extent on its ecosystem consisting of soil flora and fauna. Soil flora includes algae, fungi, yeasts, bacteria and actinomycetes which strongly contribute to the subterranean fluxes of substances, mainly by kinetic effects enhancing the turnover velocity of substances. The contribution of the soil fauna, which includes unicellulars as well as developed forms of animals, e.g. worms, snails and moles, is less obvious but cannot be separated from the overall soil biological effects. It has been pointed out by De Kruijf & Schouten (1987) that ecosystems are less or more vulnerable to natural or man-made stresses. They exhibit considerable resistance in their general response to stresses like acid deposition, heavy metals or micropollutants based on the internal forces to maintain essential characteristics (e.g. composition of the population) within the limits of the system. Thus, the vulnerability of ecosystems with respect to stresses can be defined by the inability to cope with the combined natural and man-made stress. Ecosystems undergoing long term stress may reach a point of no return where the removal of stress will not lead to the restoration of the initial situation. Unfortunately, due to the heterogeneity of the cybernetic processes in soil-water systems, it is not yet possible to define numerical limits of reactions to stress.

In discussing the ecosystems of soils those of aquifers including very deep strata have also to be considered. There is no doubt that microorganisms are present in these compartments and that they

contribute to the quality of deep groundwater by mineralisation reactions with respect to the carbon, sulphur and nitrogen cycle (Matthess 1982). There is little known on the impact of man on the microbial populations and the protection of subsurface ecosystems will have to include this aspect into its approach.

In aquifers different, however similar approaches and definitions are valid. A rational definition of groundwater pollution combines the alteration of groundwater quality due to the addition of a substance to water with the lessening of its usage-value (Bachmat & Collin, 1987; Matthess 1982). This definition, which is not generally accepted by environmentalists and decision makers, allows to define goals for groundwater protection binding them to maximum permissible concentrations or to requirements of the user. From this basic definition vulnerability of groundwater can be defined by the sensitivity of its quality to anthropogenic activities causing pollution (Bachmat & Collin, 1987). It should be an intrinsic property of the aquifer system considered and clearly defined by the pollutant or activity to be referred to (Foster 1987).

Again - similar to the soil systems - pollution of groundwater does not only affect the chemical properties but also the physical properties of the aquifer system. The rigorous evaluation of the salt water encroachment proved to be not satisfying as long as the hydraulic conductivity of the respective aquifers were considered as more or less constant. However, recent field and laboratory observations in Israel proved that hydraulic conductivity changes considerably when fresh water is replaced by salt water due to rock/water interaction (Goldenberg et al. 1986). Observations in four artificial aquifers constructed at the Leichtweiss-Institut für Wasserbau at Braunschweig Technical University showed the clogging effect of leachates from sanitary landfills. Scanning electron microscope surveys indicate that the necks between the pores are closed, thus the hydraulic conductivity is diminished rapidly (Betz et al. 1983). This should be kept in mind if in situ treatments of polluted groundwater are discussed which involve the precipitation of substances in the porous media.

The treatment of complex subsurface processes which affect the behaviour of pollutants in the soil water-system and the rock/water-system can be achieved only by using models of various types. These models may aim at the characterisation of organic chemicals with respect to admission policies, with the behaviour of substances as nitrate or phosphate with respect to the operational use of fertilizers, or as descriptive or predictive models for the evaluation of pollution cases or clean-up procedures. Finally they may be used for producing vulnerability maps. All these models need input data which include hydraulic characteristics (hydraulic conductivity in the unsaturated and saturated zone, porosity and dispersivity), geometric data (thickness and extent of unsaturated and saturated zones), furthermore solubility, persistence (half-lives) and transport characteristics of pollutants (K_d -values).

It has been pointed out by various authors that the content of natural organic substances is a major control for the solubility of organic pollutants and their K_d -values, which affect the mobility of a substance with respect to water (Pekdeger et al. 1987). Natural organic substances also interfere with the persistence of substances.

From the literature half-life data of many organic substances are available for soil environments, but very few data from groundwater. Friesel (1987) deduced from the lower microbial population density, assumed to be 2 orders of magnitude lower in groundwater than in the biological active soils, that half-lives of organic substances should correspondingly be longer in groundwater than in soils. Furthermore, it has been observed that biological degradation of organic pollutants needs threshold concentrations, below which apparently no further degradation occurs. It is open to what extent the nature, the concentration and the overall mass balance of natural organic substances are controlling the degradation behaviour of pollutants. There is a big gap of knowledge on this important aspect.

Nitrate is reduced in groundwater mediated by microorganisms and in the presence of degradable organic carbon. This beneficial effect may end if the amount of biodegradable organic materials is used up. It is still open, whether these substances are primary components of the aquifer

materials or whether they are permanently entrained by seepage and groundwater. It is a crucial task to define these substances, but it is to be kept in mind that even in sands with so low an organic carbon content of 0.001 weight-% the total mass of solid organic carbon is in the order of 10,000 times higher than that dissolved in the aqueous phase.

The following recommendations follow the topics in this conference.

Criteria for protection of soil and groundwater need clear, generally accepted definitions of the compartments to be considered that means soil, the deeper parts of the unsaturated zone (transition zone) and the aquifer (groundwater zone), definitions of pollution of soil and water and definitions of the vulnerability of soils, ecosystems and groundwater. In this context reference or target levels should be defined. Maximum permissible concentrations (as used in drinking water regulations) may be helpful. It is necessary to define the scientific basis and setting-up procedures of such reference levels, so that they may be more transparent and debatable. The demand, that the detection level should be the maximum permissible concentration, should be inspected since, as Friesel (1987) has pointed out, persistent chemicals will show up in all aquifers provided these are part of the hydrological cycle and given a detection level low enough.

Monitoring strategies for the quality of soil and groundwater are developed on national, provincial and local levels, their tasks being identification, control and solving of problems. The benefits and necessities for networks on a provincial or local level are evident due to the direct connection between the user of land and water resources on one side and detrimental activities of man at the other side (or due to a direct monetarian and health related interest).

Groundwater quality monitoring networks on a national scale are useful tools for the definition of long term changes in water quality. The handicap of sampling groundwater from not pumped observation wells due to vertical and horizontal variations of water quality in the different flow lines is overcome by the regional comparison of the local data,

which give confidence that the observed trends and changes are not of a local character. It is a difficult task to define the spectrum of data to be collected routinely. This might be done by a system analysis approach which has been addressed in topic 6.

In the monitoring concept routine measurements of the unsaturated zone should be included. Such integrated monitoring installations should be preferentially installed in recharge areas of major aquifer systems. For the installation and development of monitoring networks international exchange of experiences and - to some extent - standardization should be encouraged. This includes the analysis of cost-benefit-relationships, which were presented for the Netherlands in a convincing manner by Van Duijvenbooden (1987).

Vulnerability mapping includes thematic maps showing the intrinsic properties of soils and aquifers with respect to the various groups of pollutants, which are readily available or can be produced. But the combination of these thematic maps to vulnerability maps can only be meaningful if they are restricted to a certain pollutant or group of pollutants. A universal, all purpose map can not be produced. Mis-use or mis-interpretation of vulnerability maps by non-expert users, decision-makers and planners should be prevented by including experts in the evaluation of such maps, thus using it as an interactive tool.

The evaluation of vulnerability in relation to subsurface behaviour of inorganic and organic pollutants makes it necessary to group pollutants according to their chemical properties and environmental behaviour, since even the environmental behaviour of the relative low number of thousand organic chemicals, which presumably may show up in groundwater (Friesel 1987), can not be investigated individually. There is still the need for pilot (or model) substances, easy to measure and to observe in the hydrological and soil system.

The operational use of the degradation and the sorption-desorption (retardation) concept does not mean that the processes involved are fully understood in all cases. Therefore research on this field should be encouraged. It is necessary to perform this work not only in the

laboratory, but also in the field scale, because the extrapolation from point observations of pollutant behaviour to their regional behaviour is not a trivial task.

Different kinds of models are available as tools for the description of pollutant behaviour. They are meanwhile integrated parts of scientific and practical approaches. For rational use of this tool system analyses should be included in the setting up of modelling procedures to make sure that the complexity of the model and the availability of data are balanced in a way adequate to the given problem.

International efforts should be encouraged to establish the compatibility of data banks and the coherence of data.

It is a great pleasure to thank our hosts for the organisation of this conference in the beautiful environment of Noordwijk. The lectures and discussions as well as the posters gave insight into recent developments of the vulnerable soil- and aquifer-systems we all depend on. The enormous task we have to deal with needs the joint efforts of science community on an international level. Therefore future international cooperation and exchange of methods, experiences and results should be encouraged. One possible way is conferences like our recent conference. As a topic for an international conference in near future I propose: "Changes of hydraulic properties due to soil and aquifer pollution and physical impacts".

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CONCLUSIONS ON TOPIC I: CRITERIA FOR PROTECTION OF SOIL
AND GROUNDWATER

F.A.M. de Haan and A. Pekdeger

The main aim of this session with the above title was setting the framework for the entire conference. This made it unavoidable that the subjects to be treated could be discussed only in a very general and necessarily superficial way.

Nevertheless a number of important points were revealed already at that time, which became of increasing interest and importance throughout this conference. These points will not separately be treated here for the individual contribution of all speakers, but just summarized for the entire session.

One of the important points to be mentioned was possibly not so much a disagreement, but at least some lack of agreement on a number of definitions.

There appeared to be common appreciation of the necessity for protection of soil and groundwater. Especially against the background of the ever-increasing need for land for waste disposal, as one of the major point sources for pollution. In this respect, the practical impossibility of taking leached pollutants out of the hydrological cycle if the waste would not be isolated at the top (at least in climates with a precipitation surplus) was mentioned in the discussion. In a comparable way as necessity for protection was commonly appreciated, also the objects to be protected, viz. soil and groundwater, did not give rise to problems with respect to subject delineation. Fortunately it became increasingly apparent that indeed soil and groundwater, including their mutual interdependencies, have to be taken into consideration.

In this meeting of predominantly physicists, chemists and hydrogeologists the description of "soil ecosystem" initiated already some commotion in the audience. This, however, seemed to grow exponentially when an attempt was made to combine the concepts of "soil ecosystem" and "vulnerability". Upon closer consideration, however, I think that the interpretation of vulnerability by the physicist and the biologist did not differ so much in essence, although they were

approaching the subject from a positive and negative side respectively. This is probably the correct place to mention that also three posters were included into this session. These are emphasizing on the developments of ways and methods in order to quantify the vulnerability of parts and components of the soil ecosystem. And this brings me to my main conclusion: the problems actually start if one tries to translate qualitative concepts into a quantitative framework. It will be clear that this has to do everything with standardization. In this connection: standardization of soil and water (either surface water or groundwater). I can happily, or at least conveniently, live with the qualitative description of the concept of multifunctionality; as you know by now, this is the general point of departure in Dutch soil protection policy. There is indeed not much reason for disagreement or misunderstanding if this concept is interpreted as: "keep all options open".

The subject becomes already a little bit more touchy if one attempts to extrapolate this point of departure in terms of soil and groundwater quality. Of course, again no disagreement: "a good soil quality and a good water quality" is required or at least desirable.

Here a new problem is intruding, namely the fact that processes preserving water quality are sometimes adversely affecting soil quality, and vice versa. This in turn makes that interests in soil quality and water quality are sometimes interfering and even conflicting. An illustrative example in this respect is the former use of sewage farms for treatment of wastewater. Whereas the wastewater may be purified in this manner to a very high degree, this method may in the end lead to polluted soil, at least for persistent pollutants.

This actually means that in the discussion about a definition of vulnerability, several aspects do seriously influence its practical meaning, of which the subject for protection (soil and/or water) and the compound against which protection is required, take key positions. Using the colours applied in our vulnerability maps so far, this would imply that the entire globe should be kept white with respect to persistent pollutants, because every situation has to be considered vulnerable in this respect.

In the Dutch policy of soil protection, soil and groundwater are considered as a unity, which facilitates the protection of the combination. Nevertheless, the relationship between soil quality and

soil composition (e.g. in terms of contents of contaminants) still remains an extremely complicated one. As many of us did realize already prior to this conference, but we certainly all appreciate this complexity now.

It is apparent that soil quality evaluation should necessarily be based upon the interpretation of compound's presence in soil in view of the resulting effects to be expected. This holds as well in relation to groundwater and surface water quality, in relation to the soil ecosystem functioning, as for instance in relation to growth of natural vegetations and agricultural crops.

As a consequence this implies that effect-oriented evaluation of the quality of soil and groundwater will be the only way out in order to achieve a correct and unambiguous interpretation of their composition. However, the knowledge to arrive at such quantitative evaluation is still lacking to a substantial degree. This is so despite our present approaches, valiantly indicated with abbreviations like DRASTIC or GOD. As long as such effect-oriented soil and groundwater quality evaluation can not be given a profound and sound basis, source-limitation has to be considered as the only acceptable alternative left. This would then mean that not just "as soon as possible" but already tomorrow an equilibrium should be achieved between the addition of potentially hazardous compounds to soil and their discharge, thus leading to a steady state situation of pollutants in the system, at a level which is acceptable for the many functions that soil and groundwater have.

This conclusion does sound reasonable and hence will be commonly acceptable for broad layers in society. However, it must be realized that there is still a pitfall in it. The pitfall is that also for the acceptability of this steady state content one needs quantitative information about the no-effect level in soil, which are again standard values that still have to be established. In final conclusion this means that for the time being we have to accept careful handling of soil and groundwater and some "crippled" criteria and standards as to only way out.

CONCLUSIONS ON TOPIC 2: MONITORING STRATEGIES FOR THE
QUALITY OF SOIL AND GROUNDWATER

E. Romijn and S.S.D. Foster

At first two general statements should be put forward:

1. The establishment and maintenance of a monitoring network is (very) expensive.
2. There is always lack of data of the desired type on the desired place and at the desired moment.

Main question therefore is how to come to an optimal network taking into account information needs and information costs (Bachmat & Collin; Kelly et al.; de Kwaadsteniet).

As a principle, our efforts should be used to solve the problems of today. But what about the problems of tomorrow? What kind of problems do we face the next 10 years? A direct interaction between datacollection and problem formulation is needed. Collected data open our eyes for the existing problems and problems lead to design of monitoring networks.

Therefore we should at least design different types of networks:

- a. Networks for research needs. Main goals: to get insight in behaviour of pollutants and effects of remedial tactics (Kleijn & De Vries);
- b. Local networks for safeguarding and early warning, mainly around strongly polluted sites or around soil & groundwater protection areas (Van Beek et al.; Kerndorff et al; Landa & Mazac, Veul & Posthumus);
- c. Networks for monitoring trends in soil and groundwater quality on a regional or national base. These are designed for planning purposes with respect to groundwater resources development or strategies with respect to environmental hygiene. With these networks forecasting of especially diffuse pollutions should be made possible and also forecasts of effects of remedial measures taken on a regional or national scale (Van Beek, Van Duijvenbooden, Korkman, Tadolini, Vrba).

Several times the need for integrated monitoring networks was expressed (Van Duijvenbooden; Vrba) We should be able to follow the pollutants on their way e.g. from atmosphere, through vegetation and soil, through the unsaturated zone to the groundwater (and then to seepage zones where to polluted groundwater deteriorates the surface water). With the obtained knowledge, we will be able to tackle the pollution problems in the most effective way, that is by handling and removing the sources of the pollutants.

CONCLUSIONS ON TOPIC 3: VULNERABILITY MAPPING

W. Cramer and J. Vrba

There are three important tools used by soil scientists and groundwater hydrologists in soil and groundwater protection management: monitoring, modelling and mapping. These 3 M's are essential for an adequate implementation of soil protection policies. And so is vulnerability mapping.

On the topic of vulnerability mapping 18 papers were presented, including three invited papers. However, some papers didn't address the topic. Throughout the papers different approaches have been followed using different definitions and criteria with respect to the vague term "vulnerability". Furthermore, it has been clearly demonstrated that approaches in vulnerability mapping are to some extent defined by the specific problem at hand, for example nitrate leaching to groundwater.

In the presentations as well as in the discussions it has been noted that vulnerability maps should be prepared with care to avoid misinterpretation or even abuse by non-specialists, for instance planners or decision makers. Some even argue that no maps should be presented indicating vulnerability, because of possible abuse. That may be the case indeed. But this holds also for the presentation of the results of any scientific work and it is not specific for vulnerability mapping. And therefore the expressed fear is not a reason for not making vulnerability maps but a reason for making good maps.

In all papers on vulnerability mapping the covering soil layers have been considered as a purifying filter for the groundwater in the main aquifer. No attention has been paid to the vulnerability of the top soil itself. However, for an integrated soil and groundwater protection concept it is necessary to assess and to depict also the vulnerability of the upper soil layers.

Special attention should also be paid to vulnerability assessment and mapping in karstic and fractured rock terrains.

The presentations and discussions in this conference have confirmed again that there is not such a thing as a standardized vulnerability map like a soil map, a geological map or a hydrogeological map. And there isn't also some sort of a universal algorithm to produce maps to suit one's purpose. Therefore, there seems to be no reason to look for it. Vulnerability mapping is a matter of "bespoke tailoring" rather than "ready made". Every time again, we have to measure the problem and produce a map that fits. Every time we have to select, evaluate and present the relevant data carefully. For that purpose it is of great importance to develop and maintain accessible databases on the physical, chemical and biological properties of soil and groundwater, the sources of pollution and the nature and behaviour of pollutants. In this context it should be pointed out that soil maps and hydrogeological maps have proven to be indispensable for vulnerability mapping.

There are at least three types or groups of vulnerability maps:

Type 1: single value maps, depicting intrinsic data of soil and groundwater relevant for vulnerability assessment.

These maps could be looked upon as geographical representations of input data for methods for environmental impact assessment.

Type 2: management maps, which are a geographical representation of information relevant for specific management or policy decisions to be made in the context of environmental policy and/or physical planning.

These maps include information on the polluting sources, emissions, probability of occurrence, objects to protect, groundwater protection areas, environmental properties to be effected and the actual vulnerability assessment. It should be clear that such a management tool has to be developed in cooperation with those who are involved with decision-making and management. These maps could be used for instance:

- to set priorities in policy development and implementation;
- to develop and implement areal differentiated protection policies;
- to select sites for certain activities, and
- to take protective or mitigating measures.

Finally, one could distinguish a third type of vulnerability map, the educational map or the "wall paper" map. It is of great importance to

address politicians, industries, farmers, students, other groups and the general public, convincingly and continuously, on the functions and the vulnerability of soil and groundwater. A greater public awareness of the problems will make it easier to protect these natural resources more adequately against man-induced stresses. Firstly, by creating more understanding for protective measures, and secondly, by making the actors of the activities themselves feel more responsible for the preservation of soil and groundwater quality. A vulnerability map illustrating the vulnerability of soil and groundwater in general terms could serve such a purpose.

CONCLUSIONS ON TOPIC 4: VULNERABILITY IN RELATION TO SUBSURFACE
BEHAVIOUR OF INORGANIC POLLUTANTS

H. Wiechmann and K. Harmsen

Considering this topic I had the problem to define the subsurface. Asking agriculturists, subsurface is the plough layer and the subsoil 20 cm below it. Soil scientists are looking mostly to a depth of 2 meters and hydrogeologists consider zones in 20, 40, 60 or more meters depth. Despite of nearly 20 presentations and posters the link between soils and geological parent material was missed. This was somewhat concealed by the contributions of Dutch colleagues related to sandy and loamy soils with very shallow groundwater table. More problems grow up very quickly and strategies of monitoring and preventing vulnerability are actually needed. But are soils and their groundwater at deep groundwater levels out of danger? The risk of groundwater pollution by exceeding suffering capacity or changing the relation between sorption and desorption in fifty or hundred years was mentioned but not intensively interpreted.

In many cases "soil type" was used, but only the soil material was characterized by some parameters. Vulnerability of groundwater depends on the amount and the quality of recharge. This is related in a high degree to conditions of soil surface and of root zone. Regarding the rising problems with nitrogen and phosphorus, discussion of soil management and fertilizing practices has urgently to be included. The upper layers with their chemical and especially physical conditions are the only filters which can eventually be restored. This may additionally involve not only how to prevent soil contamination but also how to prepare soils to prevent vulnerability.

Soil scientists, hydrogeologists and other disciplines have to explain processes occurring in the black box in the transition zone between root zone and aquifer. Especially information about the influence of soil life and activity has to be quantified. Even if more than 90% of soil life is concentrated in the top soil many presentations pointed out the important role of microorganisms in the deeper unsaturated and saturated zones. The effect on nitrogen loss by denitrification, mobilisation of

heavy metals and phosphorus and on forming soluble organic substances may be very significant.

In our investigations we can't overlook special cases or events with spectacular damages to soil and groundwater, but we have to take more into consideration the creeping negative effects. Estimations in predicting and modelling vulnerability have been pointed out. But we are far away to rule out general recommendations.

General recommendations - there should be no misunderstanding - are not possible for pollutants at all. But it is impossible to consider each single pollutant. We have to find out detectable categories of soils and pollutants. These can be soils with sorbing capacity, mainly due to organic matter, soils with different amounts of variable charged sesquioxides or special reducing conditions. On the other hand pollutants have to be grouped to their ability to form charged or uncharged complexes to their affinity to be sorbed in a specific way and to their precipitation as insoluble compounds.

We are on a right way, but it's a long way.

CONCLUSIONS ON TOPIC 5: VULNERABILITY IN RELATION TO SUBSURFACE
BEHAVIOUR OF ORGANIC POLLUTANTS

E. Custodio and J.P.G. Loch

Conference papers and well known recent literature show that man-made organic pollutants not only are a real threat to soil and groundwater resources, but an increasing number of enough well documented cases exists.

Both diffuse and concentrated contaminations of organic substances appear, but those of diffuse origin are more concerning since generally they affect a wide area, even a whole region, and the consequences manifest slowly and delayed.

Presented problems deal mainly with agriculture-related use of pesticides and with the household and industrial use of chlorinated organics, but oil and refuse-related contaminants are also of concern, as also are the spread over the ground of a wide variety of decomposing organic matter cumulated in the bottom of polluted rivers when a flood occurs.

Main conclusions from conference papers and discussions can be grouped under various headings:

The concept of vulnerability itself has been discussed. In relation to organic substances pollution, vulnerability is a comprehensive concept and cannot be separated into soil and groundwater, since both are deeply related, and even in areas devoid of true soil, the role of the solid, liquid and gas phases of the unsaturated zone is of paramount importance. It seems that the only important thing in respect to vulnerability to organic substances pollution is whether a given pollutant is fully degraded or not.

In this respect decay times under existing conditions is the key issue. Transport retarding properties such as sorption are important in the aspect they contribute opportunities for degradation in the soil, both high sorption itself does not reduce vulnerability, except when sorption implies incredible fixation. Small turnover time systems may be less vulnerable in practice, even if highly pervious, than systems presenting

portions little pervious and highly sorbing, that may become a long lasting problem.

During the decay processes diverse organic substances of decreasing complexity may appear. The paths, the type and number of substances and their toxicity is in many instances poorly known. Some of them may be even more troublesome than the original substances, would they move to groundwater or the degradation process is interrupted.

The early detection and observation of soil and groundwater pollution by organic substances is costly, difficult and time consuming, specially for organizations devoid of expert teams and sophisticated analytical means. In some instances the observation of companion substances or easily detected degradation products can be a helpful warning and indicators of organic pollution. Only preliminary studies exist. Agriculture-derived problems may be tracked through contributed onic substances. Also, the much greater diffusivity of organic substances and its by-products in the gas phase of the unsaturated zone would be used to detect pollutions in the liquid phase.

Quantitative studies of organic pollutant transport rely on well established equations, but needed parameters and constants are frequently poorly known. Furthermore, the definition of suitable boundary conditions and solution methods is a very specialized field. Frequently the answer to a given problem is a time-consuming process. Simplified calculation methods, calibrated against well known case studies and much more sophisticated calculation methods, are lacking. Misapplication of simple calculation methods is a danger if professionals who apply them are not fully aware of the limits of validity and the assumptions involved, but it does not decrease its intrinsic usefulness. There are every time better approaches to find intrinsic transport properties of organic pollutants that, linked to measurable soil and water characteristics, yield more accurate transport parameters suitable at least for preliminary calculations or to interpolate values. However, numerous uncertainties remain. Given the large number of potentially polluting substances, published data does not cover the wide spectrum of possibilities. It is not clear if it is possible to found intrinsic properties of chemically similar substances.

When dealing with already polluted aquifers there is the dilemma of just abandoning it for drinking purposes, though avoiding the spread of the contaminants, or to try to restore them. Abandoning a polluted aquifer is something that must duly be considered in regional water plans. There is the need of an alternative water source of enough good quality. But even in that case, duly consideration has to be given to the strategic value of local aquifers, specially when other water sources or the water transportation systems are vulnerable to accidental pollution or breakdowns. It seems that in densely populated areas, common in any of the European countries, the strategic role of local aquifers cannot be overlooked. But restoration of contaminated aquifers is a large and costly process. It is not enough to replace groundwater, or wait until waisted water is renovelated. Pollutants have to be desorbed and it may mean several leachings. Only an exponential decreasing approach to initial quality is possible. Simple rules of thumb generally do not yield satisfactory results. Efficient processes of reclaiming an aquifer polluted by organic compounds have to duly take into account the water flow system under natural and influencial conditions, the detailed local geology, the whole of the water saturated zone and the water and air in the unsaturated zone, the soil, and sometimes the existence and separate movement of other liquid phases formed by the organic pollutants, both continuous and dispersed. It is not uncommon that to decontaminate an aquifer, the most important action to be applied is to clean-up the gasphase of the unsaturated zone. Stagnant zones pose long lasting problems, and only careful and detailed consideration of the flow system may help in the solution.

Degradation of organic substances in the soil, specially pesticides, is fairly well documented. But much less is known in the rest of the less active unsaturated zone and little can be said about degradation in the saturated zone, in which, in many instances, long residence times can be expected. The right consideration of the rate of degradation is essential to plan decontamination processes.

It is not clear yet if organic pollutant extraction can be accelerated in practice and economically by influencing desorption constants. This is a field for research.

CONCLUSIONS ON TOPIC 6: USE OF DATA REQUIRED FOR MODELING
QUALITY OF SOIL AND GROUNDWATER

J.J. Fried and J. Bouma

Discussing this topic, two main questions were posed:

- a. What kind of parameters do we need for what problem?
- b. What kind of data do we need for what model?

which led us to the following conclusions.

As there is a strong interaction between Problem, Data and Modelling, we need a system analysis approach. In this approach it is not necessary to measure all parameters for a given problem and a selection is made of the parameters needed.

There is a relationship between scarcity and quality of data and the cost of data collection.

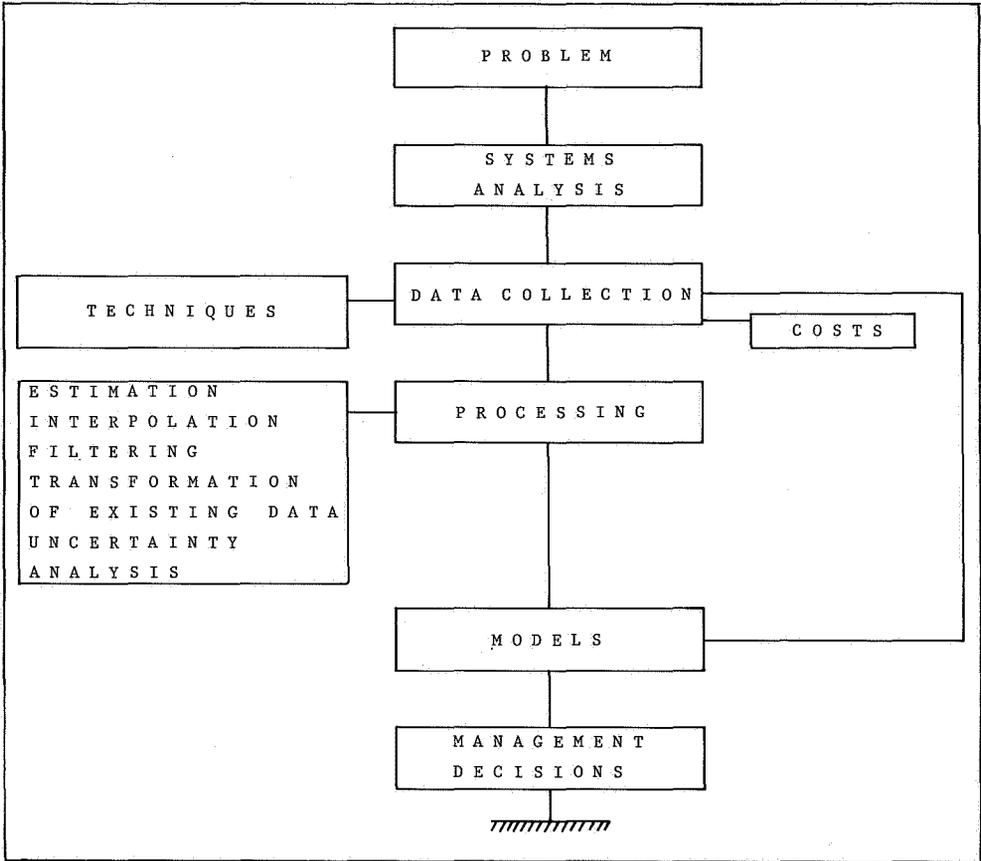
The complexity of the models and the data required should be in balance with the availability and quality of the data.

Alternative approaches are either to use a less complex model or to collect more data, taking into account the results of estimation.

When dealing with the technical aspects of data collection, it should be stressed that the experience of the data collector is a non quantifiable important input.

In order to use the data in models, processing should be given major attention. Processing methods and tools are usually known. Here three aspects have been stressed:

1. The significance of point values for regional estimates;
2. Uncertainty analysis of the input data, which is needed to have an estimate of the validity of the proposed solution;
3. Compatibility of databanks and coherence of the data.



**TOPIC 1: CRITERIA FOR PROTECTION OF SOIL AND
GROUNDWATER**

SOIL QUALITY IN RELATION TO SOIL FUNCTIONS

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1. INTRODUCTION

Soil constitutes the basis for an important part of life on earth. According to rough estimates, about one half of the total volume of what can be indicated with the common name "living organisms" prevails on or in soil. The human race as part of the global biological entity is completely dependent on soil as the basis for its living conditions. Basis should then be interpreted not only in its literal sense of providing a life platform by its consistency. In addition to its bearing capacity and bearing function, soil has many other properties and functions which enable mankind to live and redeem the prerequisites in this respect.

Following the earliest concepts applied in soil science, soil can be defined, or at least satisfactorily described as: "the upper layer of the terrestrial part of the earth-crust, mainly consisting of weathered minerals and organic matter, usually confined in depth to one or a few meters, on which plants are growing and in which organisms are living". This definition clearly reflects emphasis on edaphic interest. When groundwater and deeper soil layers (and even geological formations) are considered, consequently the depth of interest has to be extended. As discussed by De Haan and Van Riemsdijk (1985), present concern about soil protection measures also comprises submerged soils, thus inducing not only a deepening but also a broadening of the area of interest as compared to the original concept of soil.

In the development of the earth itself and of life on earth, soil is and has always been an inconstant, permanently changing continuum of material and biological interplay. The results of these interactions, combined with

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differences in the original material, are reflected in a vast variety of soil types as they appear to us at present.

In addition to natural factors and processes, man also has greatly influenced soil conditions. Such actions were mainly aimed at improving production of food and fiber, both in a quantitative and a qualitative way. However, human activities in relation to soil not only led to beneficial but also to adverse effects. So additional to the ever-occurring natural erosion of soil, the accelerated erosion became apparent. Extending the comparison to a nowadays urgent environmental problem, it can be mentioned that growth of plants and the activity of soil organisms inherently induce natural acidification, but human contribution to acid deposition causes soil acidification in an accelerated way (Van Grinsven et al., 1986). Many compounds come or are brought into the soil, which may cause undesirable effects, either on short or on long term.

The dangers involved in uncautious use and treatment of soil have been recognized for long. Almost a century ago Shaler wrote the following warning, quoted by Balfour (1975): "If mankind cannot devise and enforce ways of dealing with the earth, which will preserve the source of life, we must look forward to a time - remote it may be, yet clearly discernible - when our kind, having wasted its great inheritance, will fade from the earth because of the ruin it has accomplished". These words still sound alarming and must have done even more so (presumably with a shade of exaggeration) when they were written first. Nevertheless it can not be denied that the message involved became of growing realistic significance ever since that time.

Whereas Shaler referred specifically to the physical decline of soil by increasing erosion, we have to face at present also chemical deterioration, generally indicated as pollution of soil. Its severeness causes a necessity for soil protection. The development and establishment of protective rules and measures requires insight in the complex interdependency of soil properties, processes, and conditions required for proper functioning of soil.

In this respect the large variety of soil as mentioned above implies a concurrent variation in vulnerability. This should also be taken into account when considering soil protection. At the mean time, however, information must be available with respect to criteria for soil quality. Such criteria, in turn, are necessarily related to soil functions.

2. FUNCTIONS OF SOIL

Although the above-mentioned bearing function of soil is of prime importance, the soil quality criteria involved in this respect are predominantly confined to physical and not so much to chemical conditions. It is interesting to note that when the soil bearing capacity insuffices for certain purposes, it may be increased by specific measures, e.g. compaction. Compaction as commonly applied in soil engineering and road construction may thus considerably improve bearing properties. However, comparable degrees of soil compaction sometimes resulting from the use of heavy machineries in agriculture, can be disastrous for the soil physical conditions required for plant root development and water management. This example is mentioned here because it clearly demonstrates that a proper evaluation of soil properties can be achieved only with account of the function of soil at the time and place under consideration.

Under specific conditions also the chemical composition of soil plays a role with respect to its bearing function. Prime examples in this respect are given by former waste disposal sites that were used for urban purposes. When people become aware that their homes are located on what in the related journalistic terminology is indicated as "poisoning waste", their anxiety may grow to dramatic degrees. Although the effects involved may be much more of psychosomatic nature than physically health-threatening, the situation may easily be derailed, thus forcing politicians and administrators to drastic measures like complete destruction of the houses involved. Fortunately such situations are limited to a number of specific locations. They nevertheless have generated the lesson that great caution must be taken when assigning functions to soil that is not unsuspected from a chemical quality point of view. In this context it might be mentioned that not only vulnerability of the soil itself, but also vulnerability with respect to its use should be distinguished.

Soil has many other functions for which the soil composition, and hence its chemical quality is of prime consideration. Listing a few of the most evident ones:

- the plant production function
- the filter function for groundwater and surface water
- the ecological functioning with special emphasis on nutrient cycling.

Production of food and fiber is dependent on the fertility status of soil. Optimum requirements for plant growth may be met with natural soil fertility or achieved by addition of plant nutrient elements in manure and fertilizers. Both quantitative and qualitative aspects of plant growth are of importance, and influenced by compound availability in soil. Abundant availability may adversely affect both aspects of crop production, and thus damage the production function of soil. The term "availability" is used deliberately in this context, in order to indicate that in most cases not so much the mere compound presence in soil is of significance but more its physico-chemical status as resulting from the interference of compound properties and soil properties (De Haan et al., 1986).

An important part of groundwater and surface water has been in contact with soil and may thus reflect in its composition the results of such passage. No need to say that groundwater quality is highly important when this water will be used for drinking water purposes. Of course also surface water must meet certain quality requirements in order to perform as valuable environmental compartment. The nature and intensity of the interactions of water and dissolved components, with soil constituents during the passage through soil layers is determining for the results of this mutual influence. This may lead to indifference as in the complete absence of any interaction, to the removal of compounds from the liquid phase by processes like adsorption, precipitation and biological decay, or to enrichment of the liquid phase with compounds by desorption from the soil solid phase, by dissolution of solid phase constituents or by compound formation as the result of biological action. Here again it are the system properties and conditions that are decisive with respect to the final result. When discussing the filter function of soil in relation to water quality, all aspects mentioned should be given consideration; so the attention should not be limited merely to removal of compounds from the liquid phase, as the somewhat narrower meaning of the word "filter" might possibly suggest.

The ecological functioning of soil directly refers to the way in which the soil ecosystem operates. The soil ecosystem is then described, in line with the generally accepted definition of an ecosystem, as the whole of the biotic soil community including its mutual relationships and interdependencies. It thus embraces the complexity of interactions between biotic and abiotic components of soil. Although the results themselves of these interactions are highly

dependent on the chemical and physical conditions of the system, these are now considered of second order of importance as emphasis is given to soil life. Soil life comprises all organisms which spend one or more stages of their development in soil. Usually a distinction is made in this respect between soil flora and soil fauna. The soil flora is constituted by algae, fungi, yeasts, bacteria and actinomycetes. Plant roots, although of importance in the soil ecosystem, are not considered part of the soil flora. The soil fauna consists of primitive and highly developed forms of life. Samples of the first are amoebae and other unicellulars, of the second earthworms, snails and slugs, and moles. The most important part of the ecological functioning of soil to the preservation of life is its contribution to the cycling of elements, especially of nitrogen, carbon, sulphur and phosphorus. A quantitative evaluation of the ecological functioning of soil is up till now hard to achieve. In this respect both sum- or collective parameters (e.g. respiratory activity) and single parameters (e.g. content or activity of certain compounds) can be used. While quantitative evaluation of the soil ecosystem is still under development, assessment of boundary conditions for proper soil functioning in this respect is even further away.

Soil may, and usually does perform various functions simultaneously. Because the requirements involved are sometimes conflicting to a certain degree, it may be necessary to introduce a hierarchy of functions in the practice of soil protection policy. Clear examples in this respect are the restrictions that can be imposed in The Netherlands on agricultural activities in groundwater protection areas. The ban on the use of specified pesticides and of groundwater for irrigation purposes are such measures, aimed at the qualitative and quantitative management, respectively, of the underlying groundwater. The Dutch governmental policy with respect to soil protection took the so-called "multifunctionality" as a main point of departure. Since this policy and its implementations will be discussed elsewhere, it is only mentioned here that the inadmissibility of irreversible damage to soil takes a key position in the approach.

All soil functions do have their specific requirements with respect to soil quality. This will inclusively be treated in fair detail in the specialist sessions of this conference, with the vulnerability of the soil system as a central theme. This general session will focus attention on the development of criteria to be

applied in the protection of soil and groundwater. This subject will be described from different points of view which are more or less concurrent with putting emphasis on one specific soil function or soil use. Prior to this, the next section presents an elaboration of soil quality evaluation in general terms. As this evaluation focuses on soil composition, chemical aspects are given predominant consideration. Moreover, the approach is strongly effect-oriented.

3. RELATIONSHIP BETWEEN SOIL QUALITY AND EFFECTS

As discussed by De Haan et al. (1986) a quantitative evaluation of soil quality should preferably be based on effects that can be expected from the presence and behaviour of compounds in soil. When soil functioning is hampered, the compounds involved can be considered as pollutants or contaminants. An important practical consequence of the central rôle of contaminant behaviour is that soil quality evaluation usually can not be based on single value interpretation of contaminant content. Since the resulting effects are controlled by many system parameters (e.g. bonding capacity and bonding strength, solubility, pH, redoxpotential, etcetera) proper evaluation should apply sliding scales, in which the effectiveness of the contaminant in relation to soil functioning is expressed. With respect to phytotoxicity of copper in soil this has been worked out fairly detailed by Lexmond (1981). Taking such an approach, it soon becomes apparent that many pathways are involved in the interpretation of the effect of a contaminant from the point of its mere presence in soil (e.g. expressed as a content value) on its way to the organism or object of interest where the effect is exerting itself. At the same time it becomes evident that quantitative information about transfer and transition factors and coefficients constitutes a prerequisite in order to put these links.

Figure 1, taken from Van Genderen (1987), presents in a schematic way the relationships involved for contaminants of which the occurrence in soil may adversely affect humans, plants and animals, including soil organisms. With respect to soil quality evaluation, the following question must now be answered: which content of a certain compound in soil, C_s , is acceptable in order to safeguard desirable conditions of the three groups of organisms mentioned before? It will be clear that this problem is closely related to the risk analysis

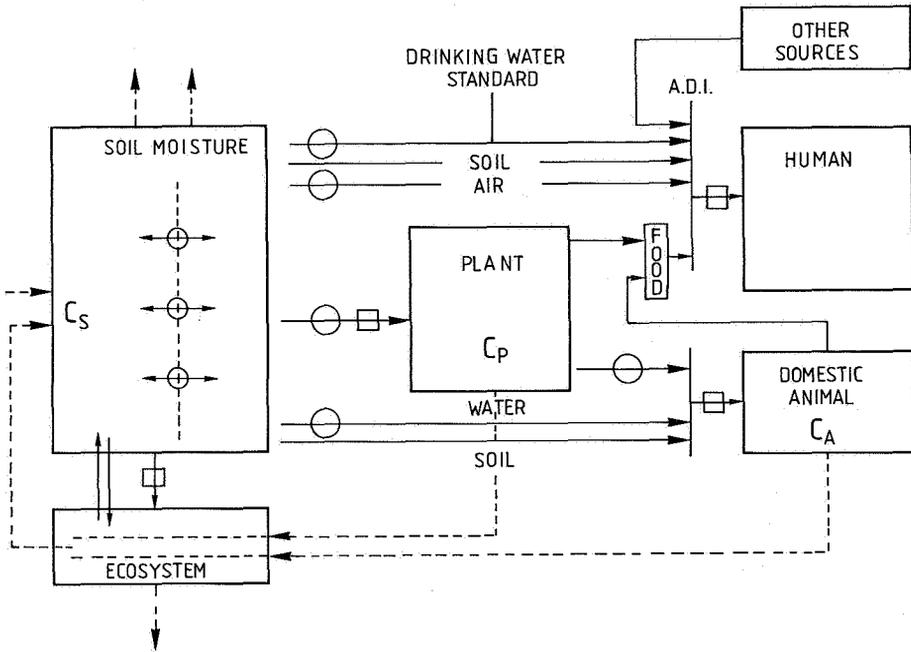


Figure 1. Pathways for contaminants from soil to other compartments and groups of organisms (after Van Genderen, 1987). For most compounds the distribution over solid phase and liquid phase (soil moisture) is of prime concern.

Rounds refer to required information about transfer coefficients. Squares to the same about dose-effect relationships.

as applied in health and toxicological considerations. This implies that once the exposure-effect relationships are known, the question is transferred to the assessment of the exposure of the organism of interest.

Sometimes the exposure can be determined in a relatively simple way as in the case of many soil organisms. Then usually the concentration (or rather the activity) in the soil solution is of major importance since the exposure dose is found as the product of the time of exposure and this solution concentration. This means that the relationship between solid phase content and the solution concentration is of prime concern. Soil chemistry provides a basis to arrive at

such relationships for different contaminants and various soil systems. Adsorption and desorption isotherms are the common way of expression, whereas the distribution coefficient, $K_{s,l}$, provides a useful parameter to characterize this type of interaction between the solid and liquid phase of soil.

The concentration in the soil solution is also highly significant with respect to leaching and as a consequence the composition of surface water and groundwater, and with respect to uptake of compounds by plant roots. In relation to the latter, the uptake mechanisms involved are in general of fairly complicated nature (e.g. preferential or discriminating uptake) and hence the compound content of plants, C_p , can usually not simply be derived from transpiration fluxes and solution concentration values.

Whereas the liquid phase concentration thus in general plays the most important part, a few examples can be given where the exposure, or part of it, is directly governed by the content of the solid phase. These are limited to situations where the exposure results from ingestion of contaminated soil or dust, as is the case with earthworms (Ma Wei-chun, 1983), with grazing animals (Bremner, 1981), and with "pica" (direct soil uptake by children, Brunekreef, 1985). Normally, however, the way of exposure is much more complicated as is indicated in figure 1.

Taking an anthropocentric approach one might say that the upper limit of the exposure of human beings is given by the ADI, the acceptable daily intake of the contaminant of interest. This, however, is constituted by a number of different contributions, so the first question to be answered refers to the part of the ADI that can be reserved for soil and its derivatives. As shown in figure 1, then there are still at least four soil-related sources for ADI contributions, namely drinking water, direct soil ingestion, inhalation of air that can be contaminated by soil, and the uptake with food. The latter pathway again is in itself pretty complicated as it is composed of many different edible plants and animal products. The possible contamination of animal products in turn is depending on several different contributions as indicated in the picture.

The rounds in the connecting lines of figure 1 refer to a need for quantitative information about transfer factors of contaminants from the soil to other compartments and organisms indicated. The squares indicate a need for quantitative information about dose-effect relationships in order to estimate the eventual effects for humans, animals, plants and the soil

ecosystem. The dotted lines back to soil indicate that part of the contaminants is cycling in the system as in the case of persistent constituents like e.g. heavy metals and slowly degradable organic compounds.

4. POSSIBLE WAYS TO PROCEED

Unfortunately the scheme of figure 1 so far presents a qualitative picture only of the relationships involved in soil quality evaluation. It is evident that a complete quantitative elaboration of all questions involved for the numerous compounds of interest and the unlimited variety of soil types would require the concerted efforts of many generations of research work. As time is urging other ways of approach are apparently necessary. Keywords in this respect are: standardization (or schematization) and modeling.

As mentioned by Van Genderen (1987) standardization of food packages as applied in health considerations is a first start to bring one important pathway of human exposure in line. Critical evaluation, and if necessary adjustment of drinking water standards another.

The complexity of the problem area forces to modeling approaches. Recent developments in this field are promising, e.g. in relation to the characterization of organic chemicals with respect to admission policies (Jury et al., 1983, 1984).

In the mean time further development and introduction of rules and measures for protection of soil against proceeding damage is a necessity. In this respect it must be realized that soil is the final sink for many environmental contaminants. This favours policies directed towards the limitations of further contaminant additions to soil. A steady state of contaminant content of soil is reached when supply and removal of a compound under consideration are in balance (cf. also the contribution of Van der Zee et al. to this conference). Care should be taken that this steady state content is not damaging for soil functioning. Because of the great differences in vulnerability of soil with respect to such damage, it is self-evident that the most vulnerable situations deserve priority in protection considerations.

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FUNDAMENTAL CONCEPTS IN AQUIFER VULNERABILITY,
POLLUTION RISK AND PROTECTION STRATEGY

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ABSTRACT

Improving the protection of groundwater against serious pollution is an urgent but difficult task, involving rather complex and poorly defined concepts. During infiltration through soils and transport in aquifers many contaminants are naturally attenuated, but not all subsurface environments are equally effective in this respect. Moreover certain contaminants are mobile and persistent in most environments. If protection strategies are not to be unnecessarily restrictive, aquifer pollution vulnerability, which can be considered an intrinsic characteristic, needs to be ranked and mapped. The differing roles of the soil, unsaturated and saturated zones, in providing natural defence of groundwater quality and reducing aquifer vulnerability, are discussed. Groundwater pollution risk is most logically defined in terms of the interaction between aquifer vulnerability and the pollution loading that is, or will be, applied to the subsurface. High pollution risk should require implementation of a realistic protection strategy. The options in this respect are considered.

1. INTRODUCTION

1.1 Importance of groundwater supplies

Worldwide, groundwater is a major source of urban water-supply, both for

domestic and industrial uses, normally requiring only minimal treatment. This is true equally of industrialised and developing nations, and of arid and humid regions. In most cases relatively high yielding boreholes (10-100 l/s) have been developed progressively with increasing demand and are widely-distributed within and on the fringes of urban areas, and in adjacent areas of intensively-cultivated agricultural land. Groundwater can also be important for agricultural irrigation and in rural water-supply, the latter frequently from large numbers of lower yielding boreholes (up to 5 l/s) drilled on an uncontrolled basis, providing completely untreated and infrequently monitored supplies.

1.2 Need for groundwater protection

In view of the importance of groundwater supplies and the extensive reliance upon them as an economical and safe source of drinking water, aquifer protection to minimise deterioration of their quality should receive detailed attention because of:-

- a. the increasing chemical diversity of potential groundwater pollutants manufactured, used and disposed of by mankind in recent decades,
- b. the widespread disposal of domestic and industrial effluents to the ground, especially in developing nations, due to the high cost of alternative arrangements,
- c. the enormous increase in the application of fertilisers and pesticides to agricultural land in all industrialised and some developing nations since the 1950s and 1970s respectively,
- d. the potentially insidious health effects associated with the pollution of groundwater supplies, consequent upon slow but persistent increases in concentration of contaminants with uncertain toxicology,
- e. the impracticability of providing comprehensive treatment to remove pollutants at large numbers of individually small groundwater sources,
- f. the fact that rehabilitation of polluted aquifers will always be expensive and protracted, and may often prove impracticable, leading to abandonment of valuable groundwater resources at considerable economic cost.

Nevertheless there is still all too widespread complacency about ground-

water pollution risks and insufficient action on aquifer protection. One of the main reasons is that groundwater movement, and pollutant migration from the land surface to production boreholes, tends to be a relatively slow process in many aquifers. This means that it can take many years, even decades, before the full impact of a pollution episode, involving a persistent contaminant, becomes fully apparent in groundwater supplies, even though it will by then have affected very large volumes of the aquifer. This situation is compounded by difficulties in sampling groundwater systems to give early warning of the onset of pollution (Parker & Foster, 1986).

1.3 Health criteria for pollution control

In general it will not be practicable to prevent all pollution. The question of how much contamination is tolerable arises. The water quality standards and guidelines for potable or other uses thus, in effect, become the design criteria for groundwater pollution protection. It is, therefore, of relevance to consider how the (current) WHO 1984 guidelines for drinking water quality relate to groundwater contamination. In so doing it is important to appreciate that the guidelines are based on two separate criteria; health implications (toxic, carcinogenic, mutagenic effects), which are of primary importance, and aesthetic grounds (taste, odour, colour), which are of secondary importance providing the consumer will accept the water and not revert to a superficially-better source of much higher public-health risk.

Among the inorganic constituents of health significance, by far and away the most widespread is nitrate, because of its high mobility and stability in aerobic groundwater systems. Others, generally of natural origin, such as fluoride, arsenic and selenium, occur quite widely and may be mobilised by imposed stresses on aquifers. The hazardous heavy metals tend to be immobilised by precipitation, or other processes, but migrate significantly in groundwater systems of low pH and Eh. Numerous of the inorganic constituents listed in the guidelines on aesthetic grounds occur widely at elevated levels in groundwater; often naturally, sometimes due to pollution. Most notable amongst these are chloride,

iron, manganese, sodium, and sulphate.

As regards organic constituents, current guidelines do not yet cover the full range of synthetic organic compounds known to be potential water pollutants of health significance, because there is not sufficient medical evidence to make firm recommendations. Among listed compounds, those that appear from current evidence to represent the greatest threat to groundwater quality are some of the chlorinated alkanes, alkenes and benzenes, which are relatively mobile and persistent in groundwater. These compounds are now used very widely as industrial and domestic solvents or disinfectants. None of the listed pesticides appear on current evidence to present a major hazard to groundwater, although only limited investigation and monitoring have been carried out. Moreover, other pesticide compounds are known to be mobile in groundwater, highly toxic in terms of acceptable daily intake, but not yet listed in the WHO guidelines. The bacteriological standards for drinking water are also of direct relevance because groundwater is often consumed with minimal disinfection, especially in developing nations.

1.4 Concept of groundwater pollution risk

The most logical approach to the definition of groundwater pollution risk is to conceive of it as the interaction (Figure 1) between:

- a. the natural vulnerability of the aquifer, and,
- b. the pollution loading that is, or will be, applied on the subsurface environment as a result of human activity.

Adopting this scheme we can have high vulnerability but no pollution risk, because of the absence of significant pollution loading, and vice versa. Both are perfectly consistent in practice. Moreover, the pollution loading can be controlled or modified but not the aquifer vulnerability.

Other considerations will determine whether this risk of aquifer pollution will result in serious threat to groundwater already developed, or designated, for water-supply:

- a. the magnitude of the pollution episode,
 - b. the value of the groundwater resources,
- both of which, in turn, depend on a series of related factors (Figure 1).

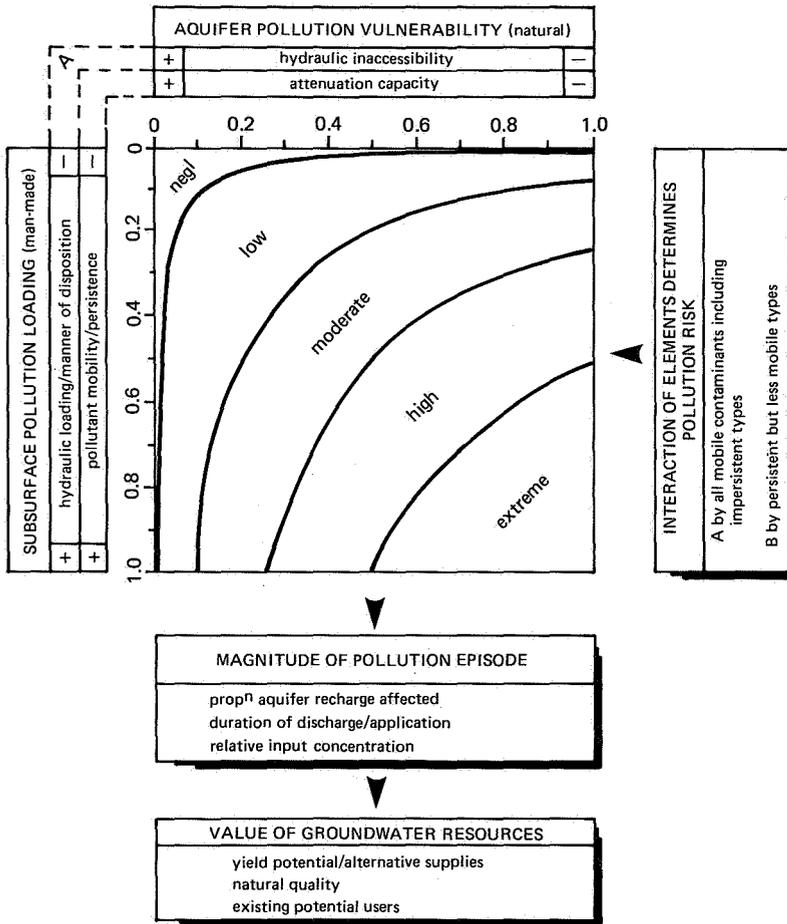


Figure 1. *General conceptual scheme for groundwater pollution risk assessment*

2. GROUNDWATER POLLUTION RISK ASSESSMENT

2.1 Aquifer Pollution Vulnerability

The term aquifer pollution vulnerability is used to represent the intrinsic characteristics which determine the sensitivity of various parts of an aquifer to being adversely affected by an imposed contaminant load. It is in effect the inverse of the pollutant assimilation

capacity of a receiving water-body in the jargon of river quality management.

Aquifer vulnerability can be helpfully subdivided into various semi-independent components. A basic and logical subdivision (Figure 1) is into:

- a. inaccessibility of the saturated zone, in a hydraulic sense, to penetration of mobile pollutants,
- b. attenuation capacity, as a result of physicochemical retention or reaction of pollutants.

These two components of aquifer vulnerability interact primarily with the following respective components of subsurface pollution loading:

- a. the manner of pollutant disposition, especially in relation to any by-pass of the soil and/or unsaturated zone, and the magnitude of associated hydraulic loading,
- b. the physicochemical mobility and persistence of the pollutant.

2.2 Importance of Unsaturated Zone

The unsaturated zone is of special importance since it represents the first line of natural defence against groundwater pollution. This is not only because of its strategic position between the land surface and the groundwater table (from which water-supplies are abstracted), but also because it normally has a favourable environment for pollutant attenuation or elimination (Figure 2).

Unsaturated zone water movement is normally slow and restricted to the smaller pores with larger specific surface, the chemical condition is normally aerobic and frequently alkaline. This results in considerable potential for:

- a. interception, sorption and elimination of pathogenic bacteria and viruses,
- b. attenuation of heavy metals, and other inorganic chemicals, through precipitation (as carbonates, sulphides or hydroxides), sorption or cation exchange,
- c. sorption and biodegradation of many natural and synthetic hydrocarbon compounds.

Such processes will, in the main, continue below in the saturated zone

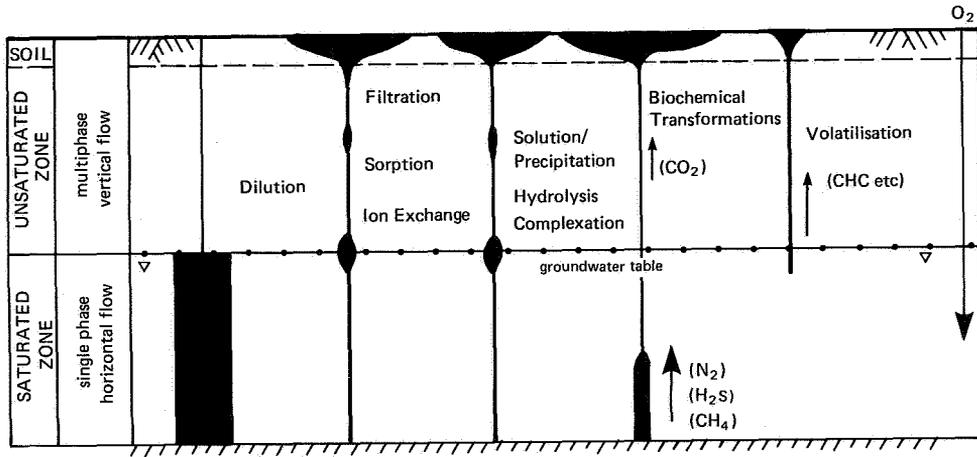


Figure 2. Processes causing pollutant attenuation in groundwater systems and their relative importance in the soil, above, and below the water-table (modified after Gowler, 1983).

of aquifers but generally at much lower rates (Figure 2). In this zone reduction of pollutant concentrations will primarily depend on dilution, resulting from hydrodynamic dispersion, which will not be a reliable control for highly toxic contaminants.

It is, therefore, essential that the unsaturated zone be fully considered in the evaluation of aquifer vulnerability. Should it be ignored, evaluations will be excessively conservative. However, the role of the unsaturated zone can be complex and its ability to attenuate pollutants difficult to predict. Marked changes in the behaviour of certain contaminants occur if the polluting activity has sufficient organic or acidic loading to bring about an overall change in the Eh or pH of the unsaturated zone. Moreover, in the case of persistent, mobile pollutants the unsaturated zone merely introduces a large time-lag before arrival at the water-table, without any beneficial attenuation. In many other cases the degree of attenuation will be highly dependent upon the flow regime and residence time.

Unsaturated vertical hydraulic conductivity is a function of prevailing matrix potential and moisture content. In the case of fissured rocks, for example, the variation can be dramatic, since fissures only retain

and conduct water at very low matrix potential. Thus while natural flow rates in the unsaturated zone of almost all formations do not generally exceed 0.2 m/d in the short-term (and less when averaged over longer periods), water flow and pollutant penetration rates in fissured formations may be more than an order-of-magnitude higher, given artificial hydraulic surcharging.

Although simplistic, it is generally reasonable to assume that, under conditions of natural rainfall infiltration, unsaturated zone transit time will be a function of the annual infiltration rate and a moisture content approaching the (specific) retention after prolonged drainage (Figure 3). Since the latter varies little amongst soil and rock types compared with the climatic variations of the former, under natural conditions the transit time (for a given unsaturated zone thickness) is essentially controlled by climatic type. An indication of the sensitivity of this transit time to hydraulic loading may be obtained by assuming that, under conditions of gross surcharging, it will become a function of effective porosity and saturated vertical hydraulic conductivity (Figure 3). In practice this case will rarely be reached under field conditions, but nevertheless in most strata (other than fine-grained unconsolidated sediments) great sensitivity is exhibited, with radical reductions in unsaturated zone transit time. Thus lithological character, and especially the grade of consolidation and degree of fissuring, will be key factors in the assessment of aquifer pollution vulnerability.

2.3 Significance of Soil Zone

Most of the processes causing pollutant elimination and attenuation in aquifers occur at much higher rates in the biologically-active soil zone (Figure 2), as a result of its higher clay mineral and organic content, and very much larger bacterial population.

In many point sources of contamination, however, the subsurface pollutant load is applied below the soil zone at the base of excavations, such as pits, trenches, lagoons, soakaways and quarries, and so the attenuation capacity of the zone does not contribute to reducing the

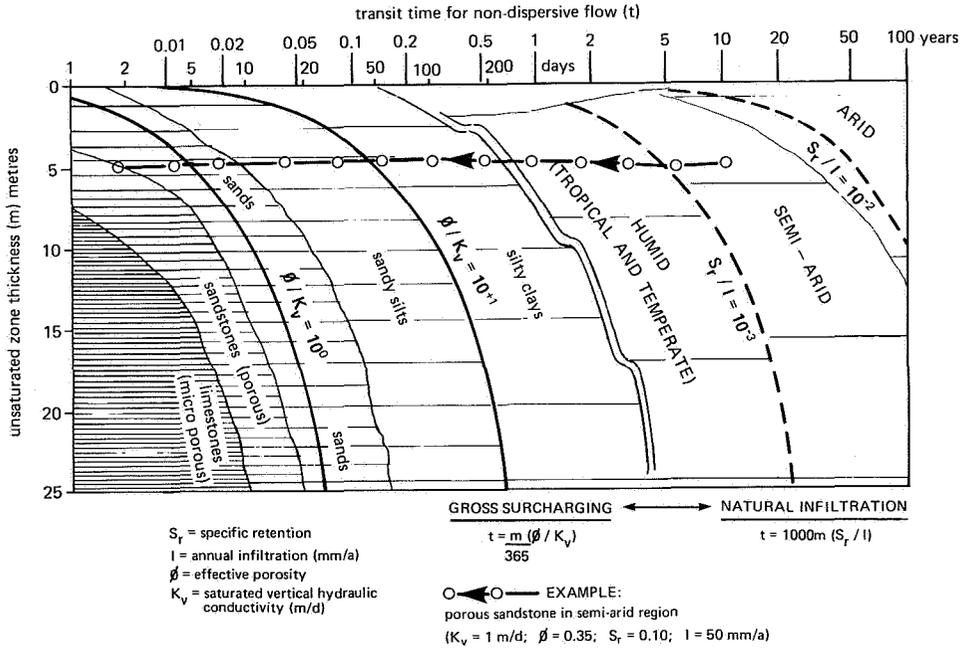


Figure 3. *Highly-simplified estimation of unsaturated zone transit time illustrating sensitivity to hydraulic surcharge.*

overall aquifer vulnerability. The position is different for most diffuse pollution sources. For example, the characteristics of the soil zone will strongly influence the scale of nutrient and pesticide leaching from a given agricultural land-use and management practice and whether acidic aerial deposition is neutralised. Thus it is preferable not to incorporate soil attenuation capacity into aquifer vulnerability. This is especially the case where the soil zone and superficial cover are of distinct geological origin and not derived by the weathering of the underlying aquifer. For the purpose of groundwater pollution risk assessment the soil zone can, in practice, either be allowed for indirectly when estimating the subsurface pollution load from diffuse sources, or directly in combination with aquifer vulnerability the resulting categories applying only to diffuse source pollution.

2.4 Organisational Basis of Risk Assessment

In view of the complexity of factors affecting pollutant migration in groundwater systems, the potential significance of detailed hydrogeological factors, and the uniqueness of each field situation, it might appear more logical to treat each polluting activity in a given hydrogeological environment on individual merit and undertake field investigations to assess pollution risk. This, however, is a very costly approach and, in most instances, a simpler assessment procedure is required, at least initially. Such a procedure could utilise basic data normally available, to produce a map of aquifer vulnerability and, thereby, identify principal groundwater pollution risks.

Scientifically, it is more consistent to evaluate vulnerability to pollution by each class of contaminants (nutrients, pathogens, micro-organics, heavy metals, etc.) individually, or (failing this) by each group of polluting activities (unsewered sanitation, agricultural land-use practice, industrial effluent disposal, etc.) separately. The latter has been attempted for some activities (e.g. Sellar & Canter, 1980; le Grand 1983, Carter et al 1987). Pursuing this approach to its logical conclusion would generate a series of specific vulnerability maps which could be compiled into an aquifer vulnerability atlas.

Normally, however, there will be insufficient resources and/or inadequate data to achieve this ideal, but less refined and more generalised systems of aquifer vulnerability mapping can still be technically valid and of practical use at reconnaissance level, and have progressively been developed (Albinet & Margat, 1970; Haertle, 1983; Aller et al, 1985).

A system developed and used by the author and known as GOD (although this in no way should be taken as implying its infallibility) is illustrated in Figure 4. It relates primarily to vulnerability of ingress of pollutants to the saturated zone and not to lateral transport within that zone and is based on the identification of:

- a. groundwater occurrence
- b. overall aquifer class in terms of grade of consolidation and lithological character,
- c. depth to groundwater table or strike.

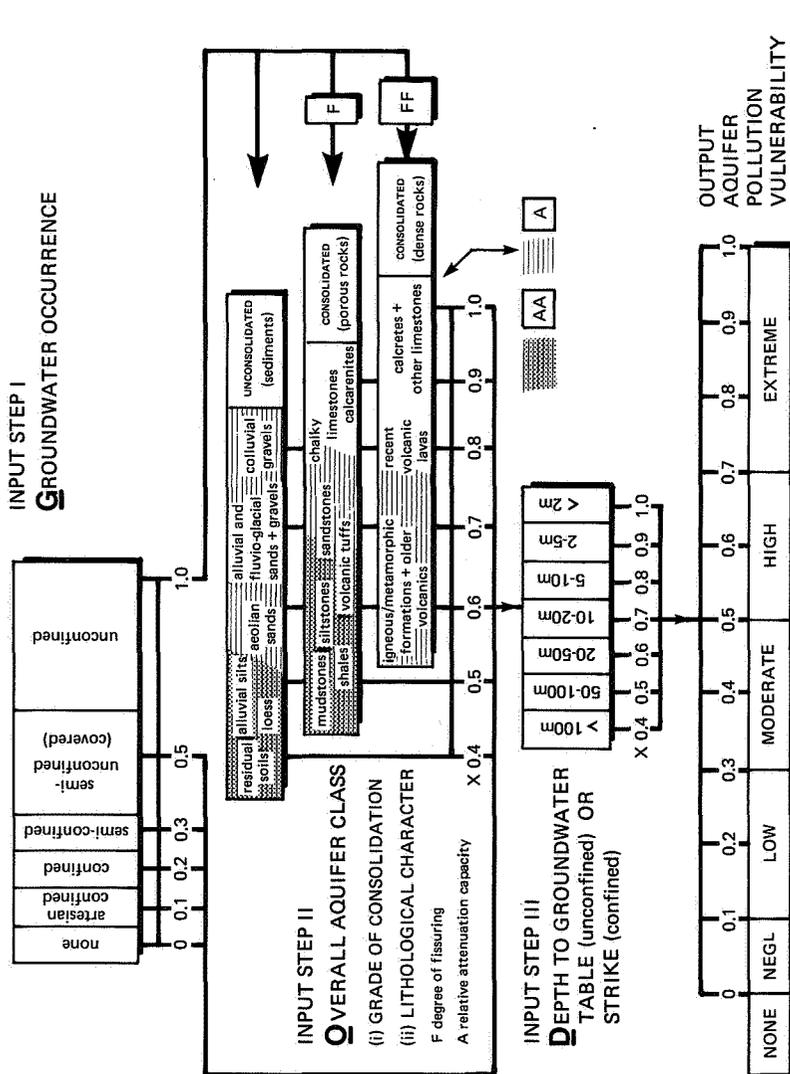


Figure 4. GOD empirical system for the rapid assessment of aquifer pollution vulnerability.

Each step leads to a ranking on a scale up to unity, the product of which is the final score for aquifer vulnerability in relative, qualitative terms, with a qualifying suffix indicating degree of fissuring and attenuation capacity, both of which may interact sensitively with corresponding components of the pollutant loading. This suffix will also be a qualitative measure of the relative tendency for lateral pollutant transport in the saturated zone. One of the frequent problems encountered in applying most methods of aquifer vulnerability assessment is the stratification or layering of many geological deposits, which can occur both above and below the groundwater table. This is allowed for, to some extent, in the system described by the selection at the groundwater occurrence step, but only the presence of lower permeability cover or confining beds is considered.

A fairly comprehensive list of potentially-polluting activities is presented in Table 1, and their characteristics classified. The importance of the differentiation between readily-identifiable point sources and non-point (diffuse or regional) pollution, and the significance of hydraulic loading and bypass of the soil zone have already been discussed. It should also be noted that climatic conditions and natural infiltration to groundwater are taken into consideration in the estimation of pollutant and hydraulic loading.

While there will be significant uncertainties in relation to some activities, it should prove possible in many cases to rank the principal components of the subsurface pollution loading they generate, in a similar way to those of aquifer vulnerability, and record them by inventory with supporting location map at the same scale. The coexistence of high rankings for subsurface pollutant loading and aquifer pollution vulnerability would define and focus attention upon high risk situations.

3. AQUIFER PROTECTION STRATEGIES

3.1 Overall Philosophy

The aquifer vulnerability map and groundwater pollution risk assessment will provide a useful framework within which to designate priorities for

Activity	Character of Pollution Load			
	Distribution Category	Main Types of Pollutant	Hydraulic Surcharge	Soil Zone Bypass
<u>Urbanization</u>				
unsewered sanitation	u/r P-D	n f o	+	*
leaking sewers ^a	u P-L	o f n	+	*
sewage oxidation lagoons ^a	u/r P	o f n	++	*
sewage land discharge ^a	u/r P-D	n s o f	+	
sewage to losing river ^a	u/r P-L	n o f	++	*
leaching refuse landfill/tips ^a	u/r P	o s h		*
fuel storage tanks	u/r P-D	o		*
highway drainage soakaways	u/r P-D	s o	+	*
<u>Industrial</u>				
leaking tanks/pipelines ^b	u P-D	o h		*
accidental spillages	u P-D	o h	+	
process water/effluent lagoons	u P	o h s	++	*
effluent land discharge	u P-D	o h s	+	
effluents to losing river	u P-L	o h s	++	*
leaching residue tips	u/r P	o h s		*
soakaway drainage	u/r P	o h	++	*
aerial fallout	u/r R	s o		
<u>Agricultural^c</u>				
soil cultivation				
with agrochemicals	r D-R	n o		
and with irrigation	r D-R	n o s	+	
with sludge/slurry	r D	n o s		
with wastewater irrigation	r D	n o s f	+	
livestock rearing/crop processing				
unlined effluent lagoons	r P	f o n	++	*
effluent land discharge	r P-D	n s o f		
effluents to losing river	r P-L	o n f	++	*

u/r	urban/rural	^a can include industrial components
P/L/D/R	point/line/diffuse/regional	^b can also occur in non-industrial areas
n	nutrient compounds	^c intensification presents main pollution risk
f	faecal pathogens	
o	micro-organic compounds and/or organic load	
s	salinity	
h	heavy metals	

Table 1. *Summary of principal activities potentially generating subsurface pollution loading.*

the implementation of pollution protection and control measures, but in some instances field investigations and monitoring will be required to resolve uncertainties. While a wide range of human activities are likely to generate some subsurface pollution load (Table 1), relatively few activities in the more vulnerable areas are often found to be responsible for the major groundwater pollution threat.

The options available for groundwater pollution control and quality management within designated areas include:

- a. strict inventory, control and even prohibition on the production and/or use of certain hazardous chemicals,
- b. control over human settlement, industrial activity or agricultural land-use,
- c. modification to land management practices, and to the design of urban and industrial installations to reduce or eliminate subsurface pollutant loading,
- d. allow groundwater quality degradation and providing treatment, or prohibiting the use, of groundwater supplies.

Under idealised conditions the entire recharge area to each and every source of potable groundwater supply could be accurately defined and human settlement, industrial activity and land-use controlled throughout these areas to conserve fully the natural groundwater quality.

However, in many situations this is found to be impracticable because of:

- a. too large an area is implicated,
- b. potentially-polluting activities predate identification of groundwater supply interests,
- c. complex hydrogeological conditions and/or varying hydraulic stresses render accurate catchment definition impossible,
- d. very large and growing numbers of small, and often private, groundwater sources are involved.

The latter two factors are especially true of the situation in most developing nations (Foster, 1985).

The most realistic and effective approach to the conservation of groundwater quality will, thus, generally require the combination of two strategies:

- a. overall *resource* protection, involving some control of all activities affecting aquifers, and especially their entire recharge area,

- b. special protection areas (SPAs) directly around major *sources* of potable groundwater (Blau, 1981; van Waegeningh, 1985).

3.2 Designation of Special Protection Areas

In view of the major constraints on human activity and land-use which will be imposed in special protection areas, they should be as small as possible but as large as necessary. A sound understanding of natural groundwater flow regimes and recharge areas, together with the modifications induced by abstraction, are essential for the effective designation of special protection areas. In certain cases this will require field investigation because a more detailed knowledge is often needed than was acquired during the original development of the groundwater supply source. In heterogenous aquifers, and especially in the karst (Paloc, 1985), identification of the features responsible for the major groundwater flows and forming the principal pollution pathways is essential, since it is vital to protect these from direct ingress of contaminants.

Confusion often appears to enter into discussions of the criteria on which to base the dimensions of special protection zones around important groundwater sources. Two completely independent approaches are possible depending upon what type of pollutant we are trying to protect against:

- a. the delay zone approach, which should strictly only relate to the elimination of microbiological and degradable pollutants of known aquifer half-life, and is based upon preventing such pollutants from entering the aquifer in a zone where the residence time (normally for a conservative non-reactive tracer and without consideration of the unsaturated zone) would be insufficient for its decay to insignificant concentrations,
- b. the dilution area approach, which is suitable for all contaminants but especially appropriate for persistent and mobile pollutants, and is based upon the necessary area or radius free from the pollution so as to achieve the required dilution to acceptable contaminant concentrations.

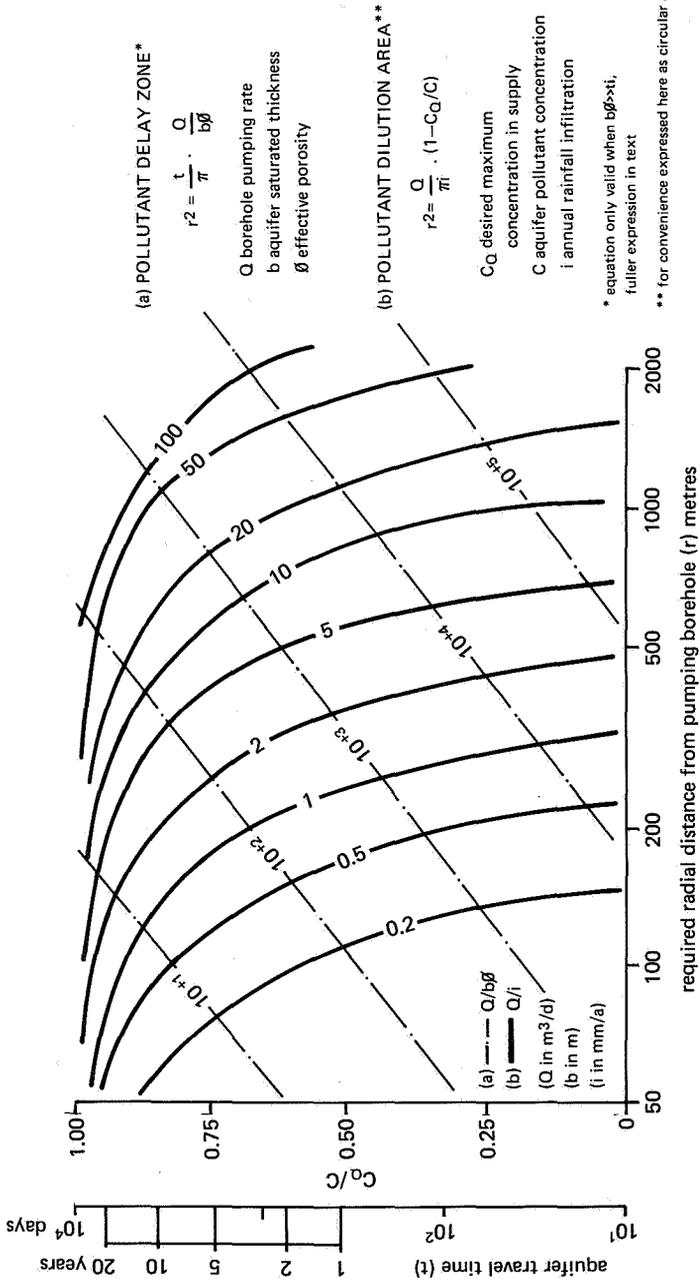


Figure 5. Grossly simplified method for estimating size of SPAs (special protection areas) based on pollutant delay or dilution.

The dimensions of both types of protection zone will vary with the rate of groundwater abstraction. An indication of the relative size of such zones in homogenous aquifers of low hydraulic gradient can be derived from Figure 5, but this also demonstrates the sensitivity of the former to errors in the estimation of effective porosity and saturated thickness, which can easily occur in practice. Fuller expressions for the required dimensions of pollutant delay zones, considering the effect of local infiltration and of hydraulic gradient respectively, can be found elsewhere (van Waegeningh, 1985; Skinner, 1985). However, the effectiveness of the former and the estimation of the latter become progressively more unreliable as hydrogeological conditions and groundwater hydraulics become more complex. As a result some water and environmental authorities prefer to opt for empirical sizing criteria or even fixed dimensions for special protection areas.

On a more rigorous basis, it is evident that the dimensions of special protection areas will increase markedly for fissured aquifers in the delay zone approach and if rainfall is low and/or required dilution factor high in the dilution area approach. Moreover, it is perhaps questionable whether the delay zone approach in practice proves effective as a result of pollutant degradation or simply allows more time for dispersion and retention to occur, and for remedial operational or control measures to be implemented.

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GEOCHEMICAL CRITERIA FOR MAKING A RISK
ASSESSMENT OF HAZARDOUS SUBSTANCES IN
GROUNDWATER

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ABSTRACT

In this paper, main concepts for making risk assessments on hazardous chemicals with the help of their geochemical properties are described. Two extremely different groups of hazardous chemicals are chosen, namely nonpolar organic chemicals and heavy metals. In the case of nonpolar organic substances, the half life and the adsorptions-desorption behaviour due to organic content in the aquifer are the most important factors affecting the spread in groundwater after hazardous contamination. A simple model including both properties is introduced using the degradation constant and the retardation factor calculated from the adsorption constant K_{OC} . In the case of heavy metals, the solution/precipitation behaviour and adsorption-desorption behaviour are to be taken into account.

1. INTRODUCTION

The principle of groundwater protection in the F.R.G. is defined in the § 34,2 Wasserhaushaltsgesetz. Substances have to be deposited in a way that no hazardous contamination of groundwater or other negative influences on its properties can be predicted after human experience. These regulations were made to protect the groundwater which is the most important source of drinking water in the F.R.Germany. The

protection of drinking water against contamination is applied by the assessment of groundwater protection zones around the discharge wells. The correct delimitation of the groundwater protection zones must be established on the correct prediction of the possible groundwater contaminants, chemicals or bacteria and viruses (Pekdeger & Schröter, 1986). This is only possible by the application of modern scientific methods and knowledge (Matthess et al., 1985). The need for the correct prediction of the behaviour of pollutants in groundwater has become more important since the number of potential pollutants increased in the recent years (Duijvenboden et al., 1981). On the other hand, protection of groundwater against contamination may lead to collisions with the interests of agriculture and industry. Therefore arguments based on scientific knowledge are necessary. Using the physico-chemical properties of a contaminant, the extent of a contamination in an aquifer with known geochemical characteristics, can be predicted.

The concept used here is based on the guidelines for protection zones in the F.R.Germany, in which three different zones are subdivided with increasing obligations for the land users with increasing proximity to the wells. Zone III is dimensioned over the whole catchment area. For catchment areas greater than 2 km in diameter, zone III is subdivided into IIIa (2 km) and III b (2 km up to the end of the catchment area). Protection zone II is defined by the flow distance of groundwater which is reached after 50 days. Zone I is the area around the wells and belongs to the water works. Such calculations must consider besides hydraulic aspects, which are often applied solely, the geochemical processes in the underground.

The most important properties and processes which influence the concentration of chemicals in the environment are solubility, precipitation-or coprecipitation, microbial or physico-chemical degradation, adsorption/desorption and hydraulic properties like hydrodynamic dispersion. A chemi-

cal is the more dangerous for the environment, the higher its mobility in the aquifer is and the lower the degradation constant is. Two extremely different groups of hazardous chemicals are mainly to be considered because of their different geochemical properties, namely nonpolar organic chemicals and heavy metals.

2. NONPOLAR ORGANIC SUBSTANCES

In the case of nonpolar organic chemicals, precipitation behaviour can be neglected. The solubility of the most of non-polar organic substances is higher than the drinking water standard.

2.1 Degradation

For the description of the degradation of the non polar organic substances, results from laboratory and field-studies are available, most of them for pesticides in soils. These data can be used to calculate half lives and degradation rates with the help of the first order degradation equation (Equation 1). Only few data are available for degradation in groundwater. Half lives observed in groundwater are 1-3 times higher than in soils or surface waters, e.g. for triacines the half lives in soils were between 22 - 380 d depending on temperature and pH-conditions, whereas the half live measured in an aquifer was 2460 d.

$$c = c_0 * e^{-\lambda \cdot t} \quad (1)$$

2.2 Solubility and Adsorption

The solubility of nonpolar organic substances can be derived from empirical regression equations between solubility and the octanol/water distribution coefficient K_{ow} (Table 1).

Nonpolar organic substances are mainly adsorbed by organic material. This leads to the definition of a distribution coefficient of a substance between solid organic substances and water K_{OC} . The distribution coefficient of a substance between water and solid (K_d) is related to the K_{OC} and the solid organic carbon content C_{OC} by

$$K_d = C_{OC} \cdot K_{OC} \quad (2)$$

The aptitude for adsorption of non polar organic chemicals as for example chlorinated hydrocarbons is positively correlated to their solubility in organic solvents. With the help of K_{OW} therefore the distribution coefficient K_{OC} can be estimated (Table 2).

As a result of continuous adsorption-desorption processes, the transport of contaminants is retarded with respect to water flow. This can be formulated in a one dimensional retardation equation (Equation 3).

$$R_d = \frac{v_a}{v_s} = 1 + \frac{\bar{\rho}_b}{n} K_d \quad (3)$$

where

v_s = mean transport velocity of the substance

v_a = mean flow velocity of the water

$\bar{\rho}_b$ = the bulk density

n = the porosity of the aquifer

For K_{OC} values greater than 0 v_s is lower than v_a , the movement of the substance is retarded with respect to the movement of water. The relative mobility of a substance with respect to the transport medium water can be predicted with the help of K_d values measured under controlled conditions in the laboratory or calculated with the relationships listed in Table 2. Thus, retardation factors can be used for an evaluation of the propagation velocity of a contaminant in the underground.

Table 2. Regression Equations for the relations between K_{ow} , K_{oc} and solubility calculated by different authors

Correlation	Equation	n	r ²	Source
$K_{oc} - K_{ow}$	$\log K_{oc} = 0,524 \log K_{ow} + 0,618$	30	0,84	(1)
$K_{oc} - K_{ow}$	$\log K_{oc} = 1,00 \log K_{ow} - 0,21$	10	1,00	(2)
$K_{oc} - K_{ow}$	$\log K_{oc} = 0,72 \log K_{ow} + 0,5$	-	0,95	(3)
$K_{oc} - S$	$\log K_{oc} = -0,54 \log S + 0,44$	10	0,94	(2)

where

n: number of cases; r: correlation coefficient;

1: Briggs (1973); 2: Karickhoff et al. (1979);

3: Giger et al. (1983)

2.3 Model for Risk Assessment

Neglecting it's toxic potential, the pollution potential of an organic substance increases with decreasing adsorption behaviour and increasing half life. These parameters depend on the geochemical conditions of the underground. Dilution processes, caused by adsorption/desorption and hydrodynamic dispersion, are not considered in this case. These processes include an additional security factor.

The retardation of a transported substance provides an extended degradation period compared to the transport period of a contamination to a well, calculated from hydraulic properties of the underground.

The calculations for predicting the potential of health danger are based on limits defined by the concept of drinking water protection zones as used in the F.R. Germany. The potential contaminants in a protection zone have to be classified in such a way that in the case of an accidental spill or continuous application, the contamination should decrease below TVO-limits before it reaches a well. To rule out any danger potential for a drinking water well, as input data, we have to consider the highest possible concentra-

tion, the solubility of a specific substance. Using the degradation and retardation, the chemicals can be classified for their use, transport and handling in a given distance from a water well (in our case in a water protection zone, Figure 1). All handling and transport of hazardous chemicals is forbidden in protection zone I and II. As seen in fig. 1, many pesticides and most of the halogenated hydrocarbons are a potential danger in a water catchment area due to their geochemical behaviour in groundwater. For the calculation, the lowest half lives and the highest retardation factors were chosen from the literature, to model the worst case. With this kind of model calculations, it can be seen that only a few chemicals can be tolerated in a groundwater-protection zone (1-3 km from the well). The results of the calculations shown in Figure 1 are based on a flow velocity of 1 m/d and organic content of the aquifer material of 0.1 %. Lower organic content or higher flow velocities would increase the potential risk of a chemical. The input concentration has been calculated as the highest possible value (solubility), to lower the risk of a potential contamination, the quantity of a possible contaminant should be kept to a minimum.

3. HEAVY METALLS

The model shown above is not appropriate for all contaminant groups. Other chemicals like heavy metals, anionic and cationic pollutants react more intensively with the groundwater and aquifer material. They are influenced by the geochemical reactions in the underground and participate in the water/rock interactions of the subsurface. The speciation of these chemicals, e.g. heavy metals, depend strongly on Eh/pH- conditions of the subsurface (Figure 2). Depending on their speciation, the adsorption/desorption and dissolution/precipitation can be quite different. Geochemical computer models based on thermodynamics allow to define the specia-

tion of heavy metals, if the chemical properties of a groundwater are known. Of great importance for the heavy metals is the specific adsorption to different underground materials - sands, clays, organic substance, oxides and hydroxides of iron and manganese. The aspect of specific adsorption has not yet been studied very thoroughly, although this kind of stable bounding is very important for the retention of heavy metals in subsurface.

Here, some conclusions from our work on the transport behaviour of cadmium are given as an example of the complexity of the problem (Isenbeck et al., 1985, Isenbeck et al., in press):

- The solubility of cadmium depends on the chemical properties of the water. The most important factors which lead to cadmium precipitation are increasing HCO_3 -content and pH-value.
- Adsorption/desorption behaviour of cadmium can be described by the freundlich isotherm. The calculated adsorption constant k is very low. ($k = 0.2$, $1/n \approx 1.00$)
- The transport behaviour of cadmium in porous media is influenced by both processes mentioned above. It depends on the geochemical properties of the groundwater and the aquifer material.
- Carbonate content in the aquifer material leads to total precipitation, no cadmium is transported. As the sands were comparable in their organic substance, amorphous Fe- and Mn hydroxide and oxide content, this effect is specific for carbonate. Cadmium immobilization by secondary minerals on the surface of a fissure as e.g. carbonate minerals, was also shown in a fractured rock aquifer.
- The description of the transport velocity by straight forward methods using retardation factors or FREUNDLICH isotherms is not appropriate.

Models for heavy metal transport have to include simultaneously parameters describing specific dissolution-/precipitation behaviour and adsorption behaviour.

4. CONCLUSIONS

Geochemical criteria can be used for the risk assessment of a groundwater contamination by hazardous substances. Some of these parameters are described in literature in great detail, although in most cases with very limited description of the environmental conditions. The results of these investigations show great variations, caused by varying test methods and environments. Most of these data are derived from soil investigations. The possibility of transferring data from soil investigations to aquifer conditions is limited due to the lack of overlapping investigations. The extrapolation of data from one environment to another by standardization of parameter data as e.g. the definition of a K_{OC} -value, has to be seen as a simplification.

Therefore the results of the model-calculations introduced here for nonpolar organic contaminants have to be interpreted as rough evaluations only giving an idea of the complex problem. Nevertheless this idea helps us solving our problems in practical applications.

The first step for the assessment of groundwater contamination must be a good description of the hydrogeological situation. The most important features like the distribution of permeabilities, groundwater flow velocities and resulting dispersivities must be wellknown to calculate the transport time and dilution of possible contaminants. The baseline for that work is at least more sufficient than the data for the physico-chemical behaviour of many contaminants and the transport processes related to aquifer properties which are still missing or incomplete. In the field of evaluating the highest permissible concentrations of toxic substances for drinking water, lots of work has still to be done. For the correct prediction of groundwater contamination, the scientific background has to be improved for a better understanding and accurate modelling of the transport processes.

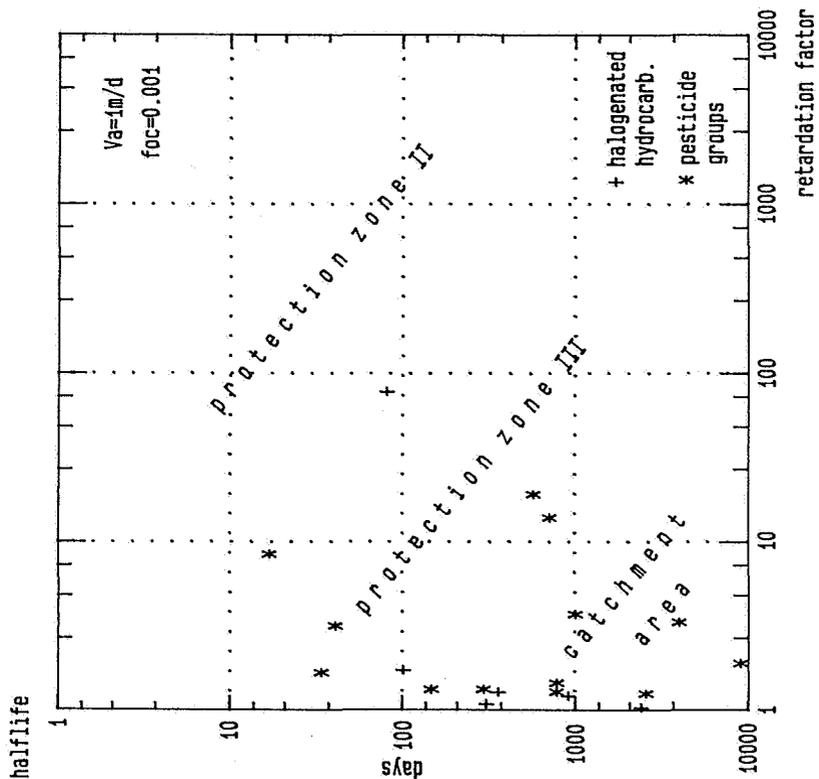


Figure 2. Model of risk assessment for non-polar organic substance in groundwater protection zones

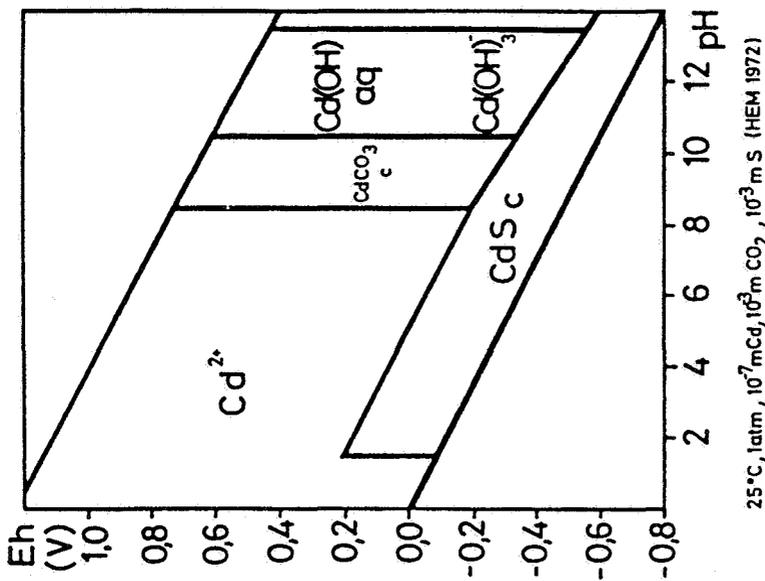


Figure 1. Eh/pH - Stability diagram for Cadmium in natural waters

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ON THE PROBLEM OF MEASURING VULNERABILITY OF SOIL ECOSYSTEMS

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ABSTRACT

Ecosystems are more or less vulnerable to natural and man-made stresses and exhibit considerable uniformity in their general responses. The ecosystem distress syndrome is manifest through changes in various essential ecosystem characteristics and follow a series of stages -alarm, resistance, and exhaustion. The ability of a soil ecosystem to cope stresses may be measured in biological monitoring systems through indicators such as environmental capacity, unicity of species and systems, distribution of r- and K-strategists and nutrient cycle characteristics.

1. INTRODUCTION

Earth is continuously changing (see De Haan, this volume) and so is life on earth and in the soil. Causes or factors responsible for the changes are of great diversity and its importance may vary with the scale of its working sphere. There are continuous interactions between biological and abiotic phenomena such as climate and other smaller scale natural processes. One could wonder whether such processes are at random, are connected by laws of chance or are guided by global processes we do not yet understand. Lovelock (1979) proposed his quite controversial Gaia-hypothesis and gave additional arguments for its existence in subsequent papers. One aspect in this hypothesis is the maintenance of certain chemical distribution equilibria that seemingly do not follow thermodynamic laws. Only by the presence of feedback mechanisms and active processes such equilibria can be maintained. An example is the distribution of chemicals in the air (O_2 , N, CO_2) which as it is, is

fundamental for the existence of all life on earth. Additional information and data are necessary to support this Gaia-hypothesis. If, however, the hypothesis is essentially acceptable, it then defines some general contours for all ecosystems. Even more important, the capacity in general terms may be present to react on or counteract activities induced by man and affecting on a global scale the functioning of the earth. Such reactions by feedback mechanisms have of course its bearings on parts of the system earth. Although this hypothesis has led to heated confrontations of pro's and contra's which are not yet ended, we consider it as a framework and as a set of unknown factors that may exercise direct or indirect influences on ecosystems.

The functioning of ecosystems is naturally strongly dependent on series of other less global factors including man-induced factors such as acid deposition, phosphates in freshwater, heavy metals, organic micropollutants etc. We consider stress as an external factor, force or stimulus that causes changes in ecosystems. The vulnerability of an ecosystem may be defined as the inability to cope with stress factors including natural factors, and is based on the internal forces to maintain essential ecosystem characteristics within the limits of the system. Vulnerability is a resultant of essential ecosystem capacities such as stability, persistence (to changes from one type to another), susceptibility (of populations and communities to pollutants and other man-made disturbances), and restoration potential (i.e. the potential of individuals, populations and communities to recover from a stress and to restore to an original situation). For instance if an ecosystem is characterized by high diversity and is able to maintain its original diversity despite natural calamities or man-made stress factors, then it is not very vulnerable.

2. BEHAVIOUR OF ECOSYSTEMS UNDER STRESS

Ecosystem responses may give rise to a sequence of events in which it is possible to observe 3 stages: 1) initial effects of a stress, an alarm or primary reaction; 2) feedback mechanisms that are triggered at the

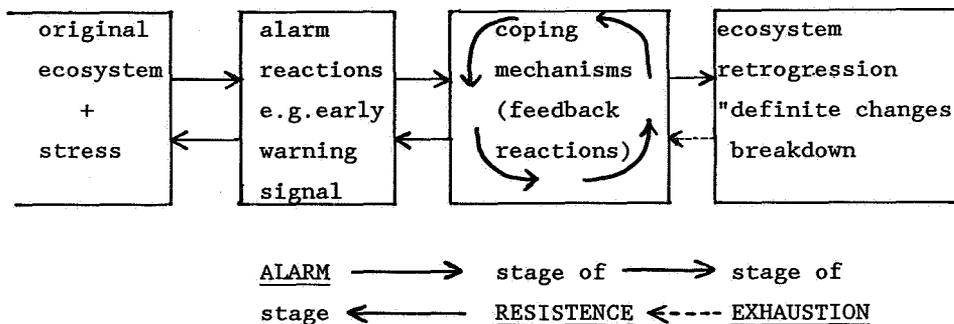


Figure 1. *Three stages of responses to stress in ecosystems.*

(Redrawn from De Kruijf et al., 1987, after Rapport et al. '84)

ecosystem level to mitigate the effect of stress, i.e. the stage of coping or resistance, and; 3) in those cases where the coping mechanisms are finally in-adequate leading to the breakdown of the ecosystem the stage of exhaustion.

2.1 Alarm Reactions

The earliest indications of ecosystem response to stress may be found in abnormal fluctuations in sensitive populations or communities, abnormalities in reproduction, changes in the distribution of sensitive species, and in the case of contaminant stress, biochemical or histological abnormalities within populations and organisms. Such early-warning symptoms manifest themselves primarily at the reproductive and species-specific levels. The disappearance or alteration in the species composition and size spectrum in lichens may serve as an early-warning indicator of chronic air pollution in forested ecosystems (Hawksworth and Rose 1976; De Wit, 1984). Failure in reproduction and the mortality of cormorants revealed the serious impacts of PCB's in the Dutch Wadden Sea (Koeman et al, 1973). More rarely, ecosystem-level effects are detectable prior to changes in species or populations. In a study of the effects of toxic substances on terrestrial ecosystems, O'Neill et al. (1977) reported that the first signs of disturbance were detectable in increased nutrient leaching, well before any change in population or community parameters was noted. This is also occurring in areas subject to acid deposition, with accelerated leaching of foliar and soil calcium and magnesium. Some biochemical early-warning

indicators of stress that function primarily at the organismal level might also apply at the ecosystem level.

2.2 Coping Mechanisms

While ecologists still debate the point (Rapport et al. 1985), it seems clear that ecosystems have cybernetic mechanisms which operate to counteract the impact of stressors, at least to some extent. These mechanisms maybe chemical or biological in nature and in certain instances entail deactivation of the stressor itself. The ecosystems ability to cope with specific stresses appears, in part, to be a function of its evolutionary history. Ecosystems which have evolved in relatively unstable environments are more likely to resist moderate stresses from human impact, especially those which mimic natural stress. Several examples may be found (see Rapport et al. 1985, a.o.) There are also suggestions (Margaleff, 1975) that ecosystems that never have gone through the selection of serious environmental stress, such as tropical forests and coral reefs will be the first to succumb, as adequate tested coping mechanisms are lacking. The precise mechanisms whereby ecosystems resist or cope with stress vary. One mechanism involves the replacement of the more stress sensitive species by functionally similar, but more resistant species. This congeneric homeostasis (Hill and Wiegert, 1980) preserves overall functional properties of the ecosystem such as productivity and nutrient cycling. Another mechanism involves external biogeochemical feedback loops which may be an expression of Gaia-mechanisms as well. In terrestrial ecosystems, chemical feedback involves the conversion of toxic compounds to less deleterious forms. Heavy metals are chelated in soil organic matter and gaseous SO_2 is converted to sulphate. Plants may exhibit genetical or physiological adaptation to stress such as heavy metals (Verkley, 1985). Biological as well as non-biological processes are involved. Throughout the resistance phase, there may be an increase in community respiration which reflects the dissipation of energy to cope with stress (Lugo 1978). This constitutes a drain on the energy available to do useful work in the ecosystem and these changes in energy flow provide an indicator of stress (Odum 1967). Indexing the energy drain by the ratio of respiration to biomass yields an indicator of broad applicability

since the changes in energy flow presumably are affected by many different types of stress. The community metabolism approach to stress is reviewed by Lugo (1978).

2.3 Ecosystem Retrogression

For any homeostatic system, homeostasis cannot be maintained indefinitely if stress is sufficiently prolonged or intense. For cases in which ecosystem breakdown occurs, the removal of the stress may no longer be sufficient to restore the system to its initial state. During the coping stages new equilibria between species may have settled leading to the removal of some species or changes in general ecosystem characteristics. Eutrophic freshwaters are examples of such new systems, usually characterized by the presence of less great predators and the abundance of a few species, thus suggesting simplified ecosystems. Still, surprisingly restoration could be induced, thus suggesting that some mechanisms strongly dominated but that other mechanisms and species were only seemingly absent. Restoration of an ecosystem using all original elements does not necessarily lead to a system that is completely similar to the original ecosystem. Small changes in abiotic factors may lead to different expressions and performances of all species present compared to the original situations. Because several of human induced stresses lead to depletion of chemicals or irreversible changes in chemical composition in soil systems, the soil ecosystems may especially be subject to such changes and as a consequence may never return to the original system. It may be discussed whether it is at all necessary to require return to original ecosystems or that it would be sufficient to arrive at some ecosystem that bear characteristics essentially similar to the original system.

3. RETROGRESSION AND RESTORATION

Measurement of vulnerability of an ecosystem at least needs a notion of the stage, in which the ecosystem is. Is the ecosystem in the resistance stage and -if possible to indicate- where, or is the system already broken down so far that return to an original or comparable situation is not possible without human assistance. Suggestions for further

monitoring the vulnerability of such ecosystems needs elaboration of stages of development downwards to a possible breakdown. Very little is known about the various steps or substages within the coping phase. What are, in theory the global steps which an ecosystem undergoes when stress is imposed on such systems by e.g. discharges of nutrients, acid deposition, or toxic chemicals. One of the reasons of lack of knowledge is that symptoms often become manifest in a later stage and processes could not be followed. Regier and Cowell (1972) suggest that stress usually produces the same ecosystem effects independent of the nature of the stress. Stress or combinations of stress, lead for instance to reduction of stability and diversity, elimination of long-living, larger species (K-strategists) and a tendency to offer greater opportunities for survival of shortliving opportunistic species (r-strategists). Especially this last aspect -favouring short-living species- is considered a consequence of nutrient enrichment. Such changes do not implicitly mean complete disappearance of species or weak links from the ecosystem scene.

The various steps that lead to breakdown of ecosystems do not necessarily occur sequentially. Some steps do take much time and occur simultaneously with other smaller steps. Fig. 2. represents a simplified scheme just to indicate the stepwise process under the influence of a stressor that ultimately leads to an ecosystem of lower complexity in a dynamic steady state situation adapted to the stressor. The expression of all species and possible processes is variable and depend on abiotic factors as well as the interactions. When one or a few species or processes disappear irreversibly from the ecosystem than a certain "point-of-no-return" will be reached, i.e. a point from which it will be impossible to return to the original situation or a comparable one, at least without outside -human- help (actual ecosystem breakdown). Indicating whether an ecosystem is under stress and than to identify what breakdown processes are taking place in the resistance stage is difficult. Nevertheless, a systematic approach to the rehabilitation or restoration of damaged ecosystems and the maintenance of ecosystem health requires an identification of the major effects or symptoms of stress, in order to judge the state of health of the environment. Vulnerability of ecosystems defines the actual effects of stresses and the time scale of the breakdown phenomenon or the rehabilitation

processes. It is necessary to measure biological variables to collect information on the vulnerability, on the actual state of the environment and on the development breakdown or restoration.

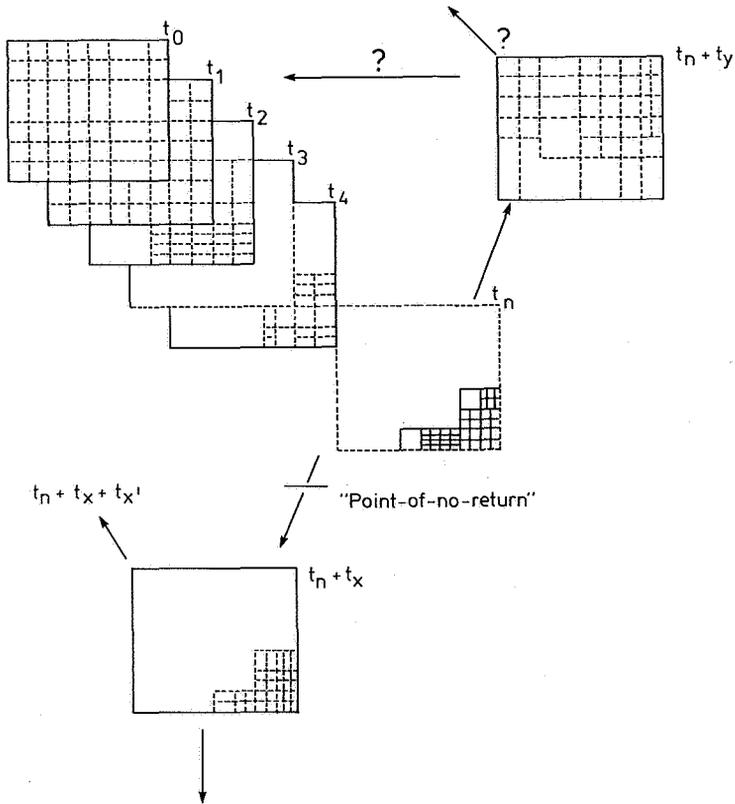


Figure 2. Schematic presentation of breakdown of an ecosystem (from De Kruijf et al., 1987). An imaginary ecosystem contains 41 species in different abundancies (t_0). Under stress the ecosystem undergoes a series of changes, t , t_0 , t_n , where at t_n still all 41 species are present, though the relative abundancies and thus also processes have drastically changed as indicated. An additional step leads to a retrogressed or broken down ecosystem ($t_n + t$). Return to t_0 or $t_n + t_y$ which is a system with the same species as t_0 but at other abundancies is, from this point on not possible. Removal of stress factors may ultimately lead to a new more simple ecosystem, $t_n + t_x + t_x'$, but without human help the system will be definitely of a more simple nature and an impoverished version of t_0 .

4. APPROACHES FOR MEASURING VULNERABILITY

Monitoring biological variables may serve different goals and functions (De Kruijf, 1987, GESAMP, 1980). In this case we are especially interested in the vulnerability of soil ecosystems to stressors or man-made forces, and how to measure that vulnerability. Ecosystems exhibit considerable uniformity in their general response to various stresses, thus indicators sufficiently sensitive to measure such responses may be applied in a general monitoring system.

Monitoring biological variables requires a number of conditions:

- i) Goals and functions should be clearly defined.
- ii) For instance the time-scale of ecosystem phenomena should be matched by adequate parameters.
- iii) If stresses are taken away by measures, stressed ecosystems may return to some ecosystems comparable with an original ecosystem. However, reference systems are scarce certainly in overpopulated countries in the world, thus absolute and good comparison with original systems will be difficult and usually based on deduction and estimations.
- iv) All ecosystem parameters whether under stress or under natural conditions demonstrate natural variability of numbers and intensity (of processes). Indicators for ecosystem must produce general information on the one hand, but should be sufficiently sensitive on the other hand to enable distinction between natural variations and variations due to stress.
- v) Choices of ecosystem parameters maybe based on two different approaches which are sometimes clearly at odds (Gairns and Pratt, 1986). One approach studies ecosystem structure as the sum of interacting species, many of which usually differ from site to site even in healthy ecosystems. Careful examination of resident species can reveal changes in dominant flora and fauna, loss of rare species, changes in relative abundance of taxa and changes in diversity with changes in the ambient environment.

The other approach studies ecosystem functions by tracing the flow of matter and energy through processing compartments (producers,

herbivores, carnivores, detritus, detritivores). The system is seen as a series of "black boxes", and adverse effects are inferred from changes in processing rates of the various compartments regardless of the identities of the resident species. Estimates of functional responses (e.g. detritus processing), however, ignore the processing organisms. Huge species lists do not indicate the actual functioning of the ecosystem. As organisms ultimately integrate the environmental impacts the route to be followed is to link species to community structure and to specific functions. Indicators representation for such integrated information demand new approaches and new technologies.

Nevertheless taking into account the various drawbacks and limitations of indicators and the conditions to be met by monitoring systems for measuring vulnerability of soil ecosystems, some areas are suggested below which could provide useful parameters.

4.1 Environmental Capacity

The Environmental (also known as receiving, absorption or assimilation) Capacity is defined as a property of the environment, a measurement of its ability to accommodate a particular activity or rate of an activity such as the discharge of contaminants, without unacceptable impact. (GESAMP, 1986). The Environmental Capacity can be apportioned for various uses. This property which include such aspects as vulnerability of the biotic parts but also abiotic factors is extensively worked out in a report on Marine Pollution (GESAMP, 1986). As with other general principles this system seems quite worthwhile to be considered for adaptation to the soil ecosystems.

4.2 Nutrient Cycles and Productivity

From the perspective of trophodynamic studies, rates of nutrient cycling and productivity are of primary importance. A measure in this respect could be the C/N ratio or the Mn contents (Swift et al., 1979). However, an ecosystem could appear unchanged if nutrient cycling and productivity remain relatively unaffected, although the partaking components may change considerably. The composition of species participating in nutrient cycles and productivity may change measurably

due to stress and thus may provide a useful indicator. Increase or decrease in nutrient cycling and productivity also may provide an indication of coping reactions.

4.3 Stability, Complexity, Resistance and Resilience

Definitions of these intrinsic characteristics of ecosystems are still much in debate (Holling, 1973; Zonneveld, 1977; McIntosh, 1982), but it is not our intention to extend the debate. Stability as the outcome of regulatory processes to maintain an expected equilibrium of the system within its tolerance limits, may be measurable if the major processes and the tolerance limits are known. Complexity of the relations, between organisms, populations, communities and abiotic characteristics forms indication of the various pathways of processes and dependencies. Quantification may lead to measurable parameters with sufficient sensitivity. Resistance and resilience include such properties as buffering capacity, stand by and restoration capacity but are theoretical described intrinsic characteristics that at present are difficult to transform into quantifiable parameters.

4.4 Unicity of Species and Ecosystems

Species and ecosystems may be rare and rather unique in one geographical area but abundant in another. Extreme characteristics of abiotic systems as for instance the natural or man-induced presence of high heavy metal concentrations often induce special composed ecosystems. Such ecosystems either are themselves rather unique or some of the species may. Uniqueness of species or ecosystems, either in a regional or a global context, indicate to particular situations where special soil characteristics as well as other influences may occur. This provides information on its history, the mechanisms, and the development to such special ecosystems and thus to their vulnerability.

4.5 Distribution of r- and K-strategists

As mentioned above stress is manifest by reductions in stability and diversity, elimination of the longer-lived larger species (K-

strategists), and a tendency to favor shorts-lived opportunistic species (r-strategists), at least in aquatic ecosystems under stress. Apparently the ratio between K-strategists and r-strategists changes toward the latter. If a profile of a normal ecosystem is drawn based on specific parameters, a ratio of r- and K-strategists within trophic levels can be quantified. The rate of change of this ratio in ecosystems under stress could be an indicator of the vulnerability of ecosystems. This requires adequate information on species diversity, but not necessarily huge lists where species could be placed on the r- to K-strategy continuum.

4.6 Functional classification

In addition to the ratio between r- and K-strategists also ratio's between generalists and specialists could be considered. Most promising is the ratio between functional groups of soil animals within a taxonomic larger group. An example on Collembola is given by Van Straaten et al.(1985), but also other groups such as nematodes (Sohlenius and Wasilewska, 1984) and acari or groups characterized by large morphological and physiological variations could be used.

4.7 Ecosystem profile

A soil ecosystem profile includes at least basic semi-quantitative information on functional groups, structural parameters, ratio's and ecosystem processes. A general profile could be used to check, based on an extensive set of criteria, whether that system may fall under a category very vulnerable ecosystems or just the reverse. In this context mathematical models together with further development of theoretical ecological concepts could be stimulating and productive.

5. CONCLUDING REMARKS

Several theories exist on how to approach measurement of such difficult to define ideas as vulnerability of (soil)ecosystems. Compared to terrestrial and aquatic ecosystems basic knowledge on soil ecosystems is fragmentary. Approaches as suggested above may lead to an acceleration of the development of ideas and notions concerning vulnerability, to the translation of such ideas into widely applicable tools in this context and also may help to direct basic and applied research to support such developments.

ACKNOWLEDGEMENTS

We like to thank Mrs. M.P.M. van Dijk-de Bruijn for patiently typing various drafts of the manuscript.

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CRITERIA FOR PROTECTION OF SOIL AND
GROUNDWATER -- SOIL ASPECTS

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ABSTRACT

Because of manifold demands on soils it's only possible to give a short introduction to aspects of soil vulnerability. Major requirements are the conservation of infiltration and percolation to prevent soil erosion.

Assessing the effect of pollutants to soils the type of bonding is of main interest. With only few exceptions the pollutants concentration is too low to form mineral precipitates. Injuring cations and anions react with charged and uncharged surfaces on sesquioxides, organic matter and clay minerals. Specific bondings predominate, therefore ion exchange equilibria can't be calculated in a simple way. Some of these difficulties are pointed out with heavy metals, acid precipitation, nitrate and phosphate.

Regarding the importance of sesquioxides and humic substances as sorbents the influence of reducing conditions may be significant to the mobility of pollutants.

Activity of soil organisms can be restricted by pesticides. We are lacking in precise estimations of these effects. Until now the observed damages have been reversible.

The mobility of immitted radionuclides is related to the reaction with soils. Some transferfactors in respect to plant uptake are available, but they are very roughly estimated.

1. INTRODUCTION

Considering the theme of the conference there is no soil but only soils which are connected with each other. Like a soil type with the characteristic combination of horizons as expression of distinct processes, we have to recognize the associated soils in a landscape with specific functional interactions.

Demands on soils never have been so manifold as today. Therefore the division of this theme is very difficult. There is no doubt about the principle:

From the soils and on the soils we are living

The possibilities in studying vulnerability of soils and preventing their injury may follow different guide-lines:

Processes with integrated biological and physico-chemical reactions involved in vulnerability of soils.

soil compaction

runoff

infiltration, percolation

water tension and
water movement
(soil solution)

diffusion
mass flow

transformation
of organic matter

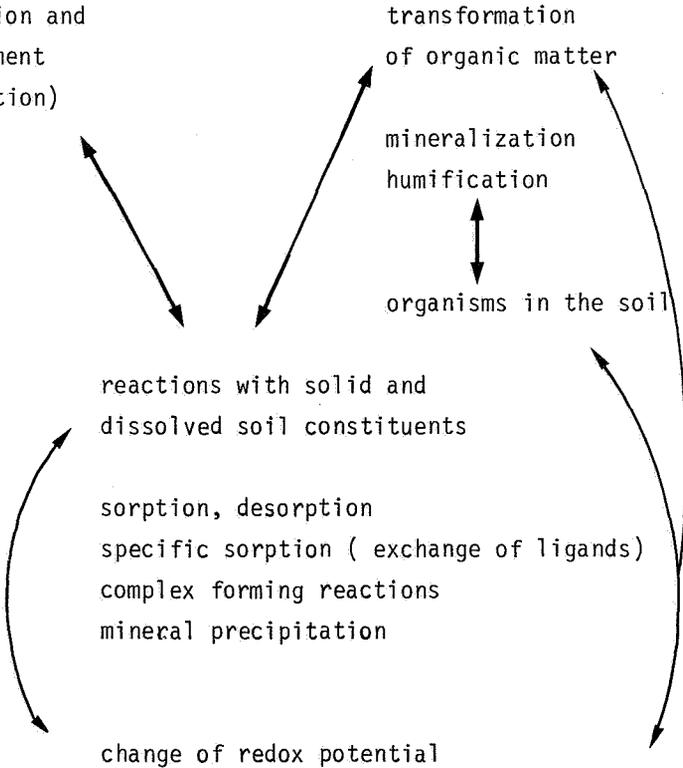
mineralization
humification

organisms in the soil

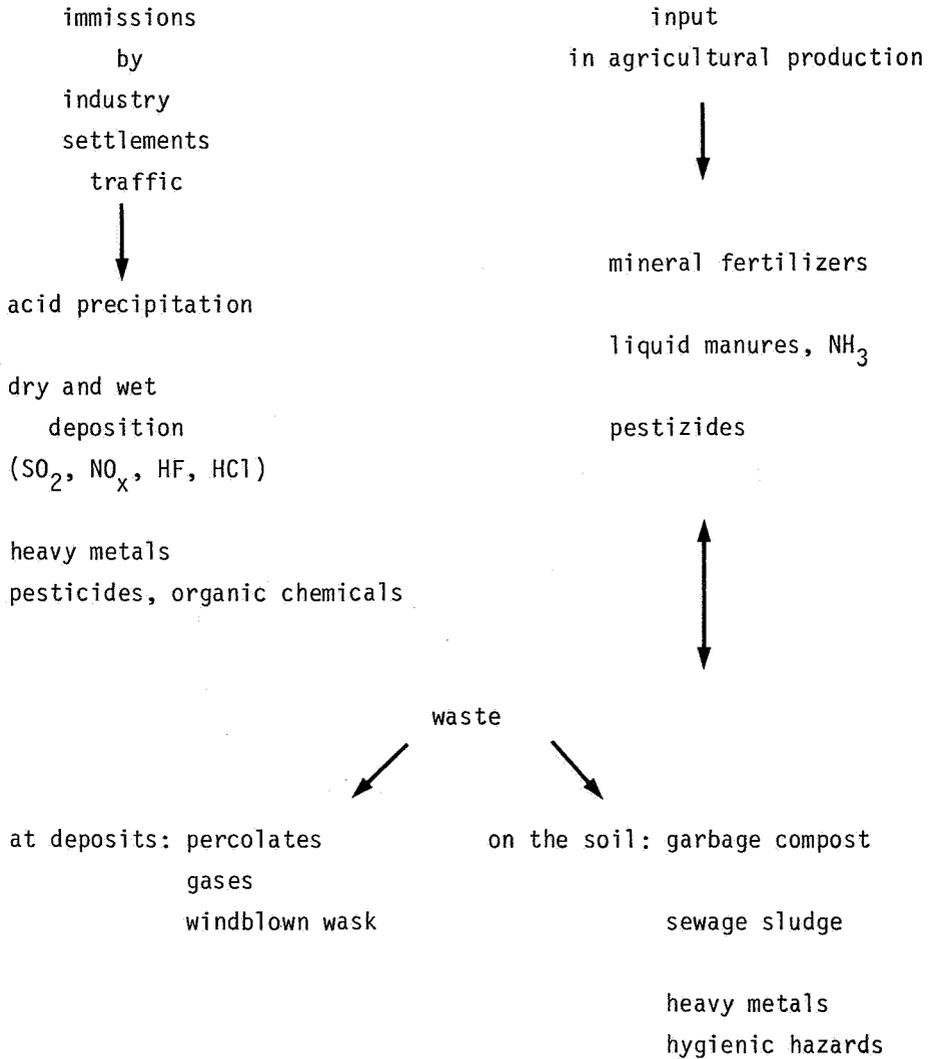
reactions with solid and
dissolved soil constituents

sorption, desorption
specific sorption (exchange of ligands)
complex forming reactions
mineral precipitation

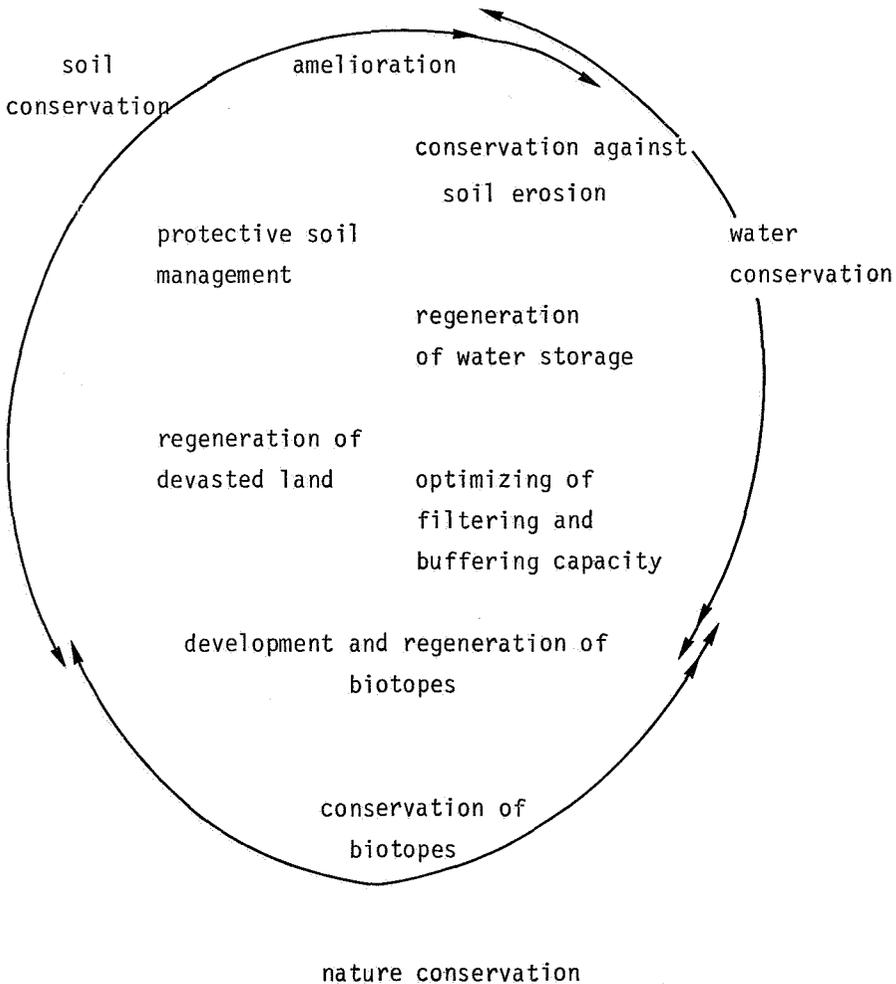
change of redox potential



Pathways and kind of pollutants.



Forms of technical conservation management



It's impossible to review all aspects of vulnerability of soils, so I want to discuss only a few examples where problems are obviously and further information is needed.

Soils are different in respect to parent rocks, weathering and soil formation and to land use. From the first it is unreasonable to discuss vulnerability and concepts for soil conservation without regarding the using. Soil conservation is related to soil using.

Conservation or regeneration of special biotopes needs special knowledge about specific - may be very one-sided - conditions. Agricultural practices require another management than forestry production.

2. SOIL PROTECTION

2.1 Physical conditions

Who wants to prevent soil damages has to conserve the soil. Soil erosion is always injurious it may be enhanced when the phosphorus-rich top soil or polluted soil material reacts with waters. Until now soil erosion in Germany was not regarded as a main problem in agricultural cropland.

In connection with large sized fields due to consolidation in large areas, with high-power tillage and one sided crop-rotations problems grow up. Because former methods of erosion control were not very effective we nowadays try to adjust the Wischmeier-formula to predetermine soil loss by erosion. Especially the R (erosivity)-, K (soil conditions)- and the C (soil- and crop management)- factor should be studied and fitted to our climatic conditions (Wischmeier a. Smith, 1978; Schwertmann, 1982). Nevertheless we should try to keep on all soils a good infiltration and percolation rate. Crop rotations with mainly maize for silage or with more than 30% sugar beets cause damages to soil structure due to using heavy harvesting machines, late tillage of wet soils and deep mixing of the soils. Despite of leaving straw and leaves of sugar beets at the field the content of organic matter is low, aggregates formed by biological activity are absent and compacted subsoils are common. Silting up at the surface, restricted infiltration and considerable run-off is visible in our loess-soils. But we have to remember the better soil structure, the higher resistance against compaction and the better infiltration combined with higher yields in slightly eroded Alfisols. These findings twenty years ago by Grosse in the loess area of Lower Saxony was the reason for deep ploughing-amelioration to get a clay content of more than 18% in the whole soil which is necessary to build up a crumbly struc-

ture. Unfortunately the yield response was too low and the disturbance in the deeply mixed soils caused many negative effects, so the amelioration of loess soils is now only done by deep loosening.

2.2 Filtering and buffering

Favourable conditions of soils rise generally with a deep root zone and/or with the filter space and in regard to contamination of groundwater with the rapidity of percolation. Reactions with organic and inorganic pollutants are mostly surface reactions, therefore the equilibration is influenced by concentration of soil solution as well as by reaction time (= rapidity of percolation) and distribution of soil solution. Concentration and transport of dissolved compounds are different in soil water bound with high and low tension. These differences are very pronounced in soils with well developed wide pore space due to aggregation or in sands under specific conditions.

Only in some cases concentrations in soil solution are high enough to form precipitates. An exception is the formation of heavy metal carbonates and sometimes hydroxides in calcareous soils or of heavy metal sulfides under reducing conditions. Both are labile equilibria because dissolution or oxidation occurs at pH values lower 7 and redox-potentials more than -50 mV.

Involved in these mentioned surface reactions are clay minerals, sesquioxides and humified organic matter. With regard to the latter we have to consider complexation by humic substances additionally.

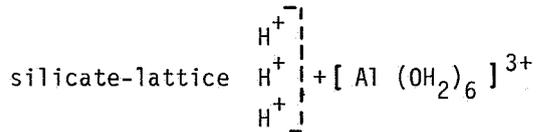
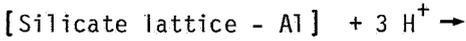
If equilibrium is reached it could be expected that conformity with laws of ion exchange would be valid. Unfortunately there are more exceptions than regularities. This is true for anions as well as for cations regarding the most interesting pollutants. Large organic molecules are often bound by van der Waal - forces. In this case organic matter is very active, so it's not surprising to find high concentrations of organic pollutants in organic surface layers. Sometimes these substances may be partly bound with low energy by van der Waal - forces and with higher energy by Coulomb - forces. Desorption is very

easy in the first case and lower in the second. If soil fauna feeds organic matter, if humification and/or mixing with the soil occurs the binding forces are more strongly and availability and solubility decreased. Regardless of origin of negative charge due to permanent lattice charge or of pH-dependent variable charge, more or less all pollutants behave exceptional.

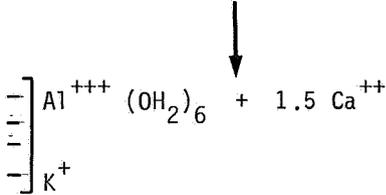
2.2.1 Sorption of cationic pollutants

Pushes of H^+ -ions in soil solution due to acid precipitation or mineralization and nitrification led to pH-values below 5. Under these conditions Al is exchanged from the silicate lattice. This is a very slow reaction but irreversible. In soils this reaction is marked by a very high buffering capacity (store of weatherable silicates) and very slow buffering rate. Released trivalent is adsorbed exchanging basic cations. Base saturation is lowered and toxic Al-monomeres appear in soils.

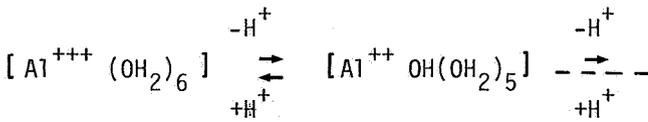
Polymerisation of monomeric Al to large Hydroxo-Al-complexes forms non-exchangeable compounds. These polymeres are blocking negatively charged permanent sites but variable charge is enhanced because of variable charge at attached $(OH)_2$ -groups. These reaction involves buffering soil acidity, irreversible decrease in permanent exchange capacity and an increase in variable charge (Ulrich, 1981).



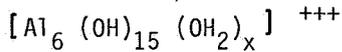
irreversible exchange of Al from weatherable silicates



Base desaturation



polymerization



non exchangeable Hydroxo-Al-polymers
with variable charge

Regarding the cation exchange reactions several unregularities are known. This is expressed by a simple selectivity coefficient or by the Gaponcoefficient.

$$\left(\frac{\text{Me}_x^+}{\text{Me}_y^+} \right)_{\text{ex.}} = k \cdot \left(\frac{\text{Me}_x^+}{\text{Me}_y^+} \right)_{\text{sol.}}$$

$$k = 1 \quad \text{Me}_y \text{ selective}$$

$$k = 1 \quad \text{Me}_x \text{ selective}$$

$$\left(\frac{\text{Me}_x^+}{\text{Me}_z^{++}} \right)_{\text{ex.}} = k \left(\frac{\text{Me}_x^+}{\sqrt{\text{Me}_z^{++}}} \right)_{\text{sol.}} \quad \text{Gapon equation}$$

Concerning the sorption of heavy metals in soils nobody was successful in exact prediction. Heavy metal cations are apparently sorbed in an un-specific way to a less extent. A more pronounced specific sorption is found at the humified organic matter and at sesquioxides. With organic matter all transitions to real complexes are possible, while sorption on sesquioxide-surfaces with variable charge occurs below the point of zero charge too. Grouping the sesquioxides Mn-rich oxides are mostly effective.

Often the desorption decreased with reaction time. Obviously the bonding strenght enhanced with time without changing the properties of the adsorbing matrix. Sorption of heavy metals can be described therefore by isotherms of the Langmuir type.

Because of marked specific influence of the behaviour of element and adsorbent it is impossible to give detailed informations about impending damages to soil biology, plant growth and quality or groundwater pollution. The given limits of total heavy metal contents in soils in respect to sewage sludge application are only weakly founded.

Complex forming with organic Ligands is pronounced with heavy metals.

Stability and mobility of these complexes is very different. Low molecular weight is mainly correlated with higher parts of acid groups, therefore these substances play an important role in heavy metal mobility.

Humified organic matter contains on its polymeres or macromolecules a large number of active groups. So it is possible that the same molecule may act as an sorbed anion at sesquioxides and as an complex forming reagent to heavy metals. Most extractants are less selective to separate all fractions according to their special bonding type. The definition of organic matter - or sesquioxide - bound heavy metals may be fluid. On the other hand this may be of great interest in respect to different desorption to soil solution.

2.2.2 Redoxpotential

It will be understandable that all reactions which are influencing the sphere - biological activity - decomposition and humification of organic matter - changing the kind of sesquioxides - are influencing the mode of immobilization and mobilization of heavy metals too. Especially effective and simultaneous very much incalculable are redox processes. Decreasing redox-potentials result often in restricted decomposition and forming of mobile organic acids of low molecular weight. This and the reducing of iron and manganese oxides led to higher mobilization of heavy metals unless the reducing of sulfate to sulfide causes heavy metal precipitation and very strong immobilization.

In fields of dumped dredged mud from harbour the very high contamination was harmless as long as percolation was low and a deeper layer was reduced. This changed when shrinking of the clayey mud led to better percolation and oxidation, followed by contamination of groundwater in underlying sandy layers. Shrinking was advanced by trees planted for recultivation.

2.2.3 Sorption of anionic pollutants

The fixation of anions was a wellknown problem in fertilization. Until

now we are lacking a good and precise method for phosphorus fertilizing calculations. On the other hand agricultural fertilization on organic soils was charged with highly eutrication in natural surface waters. The German Soil Society ruled criterias and recommendations (Wohlrab, 1985) for land using and soil management in water protection areas. In this connection the problem of excessive liquid manure application was involved too. Mass animal production with hens, chickens, pigs and dairy cattle led to liquid manure fertilization with extremely high nitrate application in maize grown for silage. This is done without regarding soil quality and depth of groundwater level. Contrary to very strong specific phosphate sorption and resulting low mobility in mineral soils is nitrate only adsorbed in an unspecific way. Nitrate is therefore highly available and easily washed out from the soil.

With high liquid manure application pollution of ground- and surface waters are programmed. But even in thick loess covers a regeneration of groundwater and a connected translocation of nitrate from fertilization under the german climatic condition is observed. Because of lower percolation it needs some years to reach the groundwater level (Voss, 1985).

Still unanswered is the question about the conditions and the rate of gaseous nitrogen loss in greater depth by microbial denitrification. Experiments with piping natural gas to introduce self cleaning of nitrate contaminated percolates are carried out in the lower Rhine area.

2.2.4 Use of pesticides and soil organisms

As a special indicator for soil injuries the activity of soil organisms is mentioned. Soil fertility is therefore often equated with intensive life in soils. Regardless of the impossibility to give a generally accepted definition of soil fertility, all soils with high natural productivity are intensively animated.

In emotional public discussions the meaning is expressed again and again, modern agricultural practices with high fertilizer and pesticide input led to dead and devastated soils. According to Ottow (1985) a large information-deficit despite of many publications has to be recognized. Above all an integrated ecological evaluation is missed. The reasons

are:

- Soil organisms (microbes and larger animals) are in reaction with a complicated ecological system. Injurious effects can be accumulated or compensated. It is extremely difficult to evaluate only one factor.
- There are many kinds of organisms with numerous species and subspecies. Isolation, identification and determination of themselves and their metabolism is complicated by many analytical problems
- Due to changes in climate, vegetation and land using the activity of soil organisms varied even without any pollution to a great extent
- Mostly it is impossible to evaluate gradual differences in soil organism activity, especially the short-term, reversible influences. Using of soils has to be considered definitely
- The statement, decreasing activity of soil organisms is disadvantageous at all; an increase is favourable at any time, can't be accepted
- To take into consideration, but difficult to judge is the bio-accumulation in the foodchain. Toxic effects may appear in chainlinks which are not studied.

Most of the pesticides (herbicides, fungicides, insecticides, acaricides, nematicides etc.) are sorbed at polarized or dissociated cationic or anionic groups. Dissociation is often related to pH and to the content of humified organic matter. Again the sorption is governed by specific conditions and general interpretations are impossible.

Despite of short-term effects (less than 60 days) irreversible damages to microbes or animals are the exception. Due to slow decomposition of pesticides and metabolites a changing in pH or higher salt-concentration in soil solution by fertilization can cause mobilization. Dangerous is the concentration in organisms by uptake with food.

2.2.5 Radionuclides

Since the Tschernobyl-accident the risk of soil contamination with radionuclides is remembered to the public. Dominant longterm pollutants in the soils are Cs 137 and Cs 134. Sorption is comparable with potassium and sodium. Despite of relatively high radionuclide pollution all Cs was fixed in the upper 5 cm, only in sandy soils it migrated down to 25 cm

depth (GRS, 1987). Estimated transfer-factors in different soils are vague. In competition with potassium in intensively fertilized soils the plant uptake is low.

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GROUND-WATER QUALITY - U.S.A.

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ABSTRACT

A trace of the history of scientific achievement and legislation in the U.S.A. indicates great progress has been and is being made to solve ground-water quality problems. It also indicates there is still a long way to go.

1. INTRODUCTION

We have come a long way since the days when water-borne diseases such as cholera and typhoid were common deadly killers. To appreciate what vast progress has been made toward safer drinking water, it helps to take a backward glance.

The United States has long depended on ground water for many uses, but the primary use has been as a source of drinking water. Over 90 percent of the nation's public water supplies obtain their source water from ground water (Lappenbusch, 1984). Additionally, 97 percent of the water needs for domestic use in rural areas is served by ground-water resources (Solley et al., 1983).

National reliance on ground water has increased dramatically over the past 20 years, and during the past 10 years ground-water use has increased almost 30 percent (Solley et al., 1983). It is anticipated that the nation's reliance on ground water will continue to increase as demand for water increases in the future.

Concomitant with our reliance on ground water has come the need to protect our ground-water resources from contamination. Although

contamination due to man has occurred for centuries, only in the past few years has the nation become aware of the dangers of ground-water contamination and of the many ways in which ground water can become contaminated. Moreover, in recent decades, the diversity of potential pollutants produced and used by man has increased dramatically. Since 1974, the Congress of the United States has been making an attempt to protect the nation's ground-water resources through legislation. The Safe Drinking Water Act (SDWA) (Public Law 93-523) mandated the establishment of drinking water standards to protect the public health, established the underground injection control (UIC) program to protect underground sources of drinking water from subsurface injection of wastes through wells, and established the Sole-Source Aquifer program. The Resources Conservation and Recovery Act (RCRA) (Public Law 94-580), passed in October 1976 and amended in November 1982, is the legislation which controls the management and disposal of solid and hazardous waste in such a manner that ground water will not be contaminated. The amended Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) (Public Law 92-516) as first passed in October 1972 and amended in 1975 and 1978, allows EPA to prohibit or mitigate ground-water contamination by pesticides by denying registrations, by modifying application methods, and through cancellations and suspensions of pesticides registrations. FIFRA also explicitly requires EPA to monitor environmental pollution. The Toxic Substances Control Act (TSCA) (Public Law 94-469), signed into law in October 1976, has no direct impact on ground-water protection but has the potential to be used as a mechanism in ground-water protection because the Act provides EPA with the power to regulate the use and manufacture of specific chemicals, some of which may pose ground-water contamination potential. The Surface Mining Control and Reclamation Act (SMCRA) of 1977 is the legislation which controls environmental impacts resulting from all mining activities. By establishing standards for these facilities, ground water may once again be protected. Finally, the Comprehensive Emergency Response Compensation and Liability Act (CERCLA) also known as "Superfund" provides a mechanism for the cleanup of ground water which has been contaminated by abandoned hazardous waste sites. A more complete discussion of these acts and their provisions which relate to

ground water is given by Lehr, et al. (1984). This host of legislative measures has sought to help prevent the pollution of ground water in the future and to help mitigate some of the problems which have been created in the past.

Prevention practices in the future must ensure against ground-water contamination. It is now important that we use planning and management tools to help recognize the places where certain activities pose high risks.

2. EPA DRINKING WATER ACT

The theory of the EPA Safe Drinking Water Act is simple and in two parts. First, EPA is to establish national standards for drinking water quality. These standards are numerical criteria for each contaminant that may be found in drinking water supply and that has or may have an adverse effect on health. The EPA standard is the maximum concentration levels (MCL) of the contaminant allowable.

The second part is that water suppliers, the operators of the 60,000 public water systems in the U.S.A., will monitor the quality of the water delivered to consumers and treat that water if necessary to assure that the concentration of each contaminant remains below the acceptable levels established by EPA.

On June 19, 1986, the President signed into law a new drinking water program which passed both houses of the Congress by overwhelming margins, but only after three long years of study. The 1986 Amendments go beyond the simple two-part program of the original law and include a series of protection strategies:

- Standard-Setting
- Monitoring for Unregulated Contaminants
- Treatment and Protection
- Technical Assistance

In the 1970's, national environmental concern focused mainly on natural resources and pollutants that could be seen or smelled. Surface water and air quality, specific types of contaminants such as pesticides, or

obvious sources of contamination such as uncontrolled hazardous waste sites, were of primary concern. Unfortunately, ground water is hidden from view and few understood how seriously this resource can be contaminated.

In the 1980's, ground-water contamination became a major environmental issue. The attention of agencies at State and Federal levels of government, as well as that of industry and environmentalists focused on this vital resource. As contamination has appeared in well waters the public has expressed growing concern about the health implications and inappropriate disposal of chemicals. They demanded expanded protection of the resource.

Scientists can now measure specific organic chemicals at the parts-per-billion or -trillion levels. As new health studies are completed and as we learn more about various sources of ground-water contamination, our capacity to deal with this problem increases. Scientists and engineers have also learned more about how contaminants move in the subsurface -- which ones bind to soils and which ones pass through to the water table are now identifying technologies to prevent, control, and clean up ground-water contamination.

Ground-water protection is a complex and difficult issue. It will require sustained effort at all levels of government over before this resource will be adequately protected. Within this context, EPA developed its Ground-water Protection Strategy.

2. EPA'S GROUND-WATER PROTECTION STRATEGY

The EPA Strategy includes four major components that address critical needs. They are:

- Short-term build-up of institutions at the State level;
- Assessing the problems that may exist from unaddressed sources of contamination--in particular, leaking storage tanks, surface impoundments, and landfills;
- Issuing guidelines for EPA decisions affecting ground-water protection and cleanup; and
- Strengthening EPA's organization for ground-water management at the

Headquarters and Regional levels, and strengthening EPA's cooperation with Federal and State agencies.

3. SYSTEMS TO EVALUATE GROUND WATER - DRASTIC

Within the last 20 years the need to expand existing systems or create new systems to address ground-water quality has become evident. Many different systems have been developed to address site selection for waste disposal facilities such as sanitary landfills or liquid waste ponds. Among these, the LeGrand System (LeGrand, 1983) and the modified version used by the EPA in the Surface Impoundment Assessment (SIA) are probably the most well known. The LeGrand system uses numerical weighting to evaluate ground-water pollution potential from a given waste disposal site. By evaluating the site through a series of four stages, a description of the hydrogeology of the site, the relative aquifer sensitivity combined with the contaminant severity, the natural pollution potential presented at that site, and the engineering modifications which might change that potential are all evaluated.

The LeGrand system presupposes only a limited technical knowledge but encourages the user to become familiar with the concepts presented in the manual so that skilled judgements can be made in the subjective portion of the system. The similarities between sites are emphasized and the uniqueness of each site is downplayed.

The EPA methodology (U.S. EPA, 1983) uses the basic LeGrand System to define the hydrogeologic framework, but modifies the system to place emphasis on establishing a monitoring priority for the facility. Once the hydrogeologic characteristics have been rated, a table is used to define the monitoring priority. This priority may be adjusted by the rater using prescribed techniques. Once again only a limited technical knowledge is presupposed.

Other systems have been designed to tailor the results to more specific purposes. Thornthwaite and Mather (1957) and Fenn et al. (1975) developed water-balance methods to predict the leachate generation at solid waste disposal sites. This approach is based on the premise that

by knowing the amount of infiltration into the landfill and the design of the cell, the leachate quantity for the landfill can be determined. The system is intended as a tool to be used by engineers in the early design phase of a facility.

Gibb et al. (1983) devised a rating scheme to establish priorities for existing waste disposal sites with respect to their threat to human health by ground water. Via ranking the site through four factors, (1) health risk of the waste and handling mode, (2) population at risk, (3) proximity to wells or aquifers, and (4) susceptibility of aquifers, a number that ranges from --100 was used to display the relative risk. The system was used in a specific 2-county assessment by technically qualified individuals.

Another rating scheme, developed by the Michigan Department of Natural Resources (1983), is designed to rank large numbers of sites in terms of risk of environmental contamination. By evaluating the five categories: (1) release potential, (2) environmental exposure, (3) targets, (4) chemical hazard, and (5) existing exposure, the user obtains a number ranging from 0 to 2000 points which evaluates the relative hazard of that site with respect to other sites in Michigan.

Seller and Canter (1980) evaluated seven empirical methods to determine their usefulness in predicting the ground-water pollution effects of a waste disposal facility at a particular site. The methods they reviewed included rating schemes, a decision tree approach, a matrix and a criteria-listing method. They determined that each method took into account the natural conditions and facility design and construction, but that each method was best applied to the specific situation for which it was designed.

This brief review of selected existing systems reveals that there are a number of methods that can be applied to site-specific situations or to evaluation of the pollution potential of existing sites. However, a planning tool is need for use before the site-specific methods are employed. The system must (1) function as a management tool, (2) be simple and easy-to-use, (3) utilize available information, and (4) be able to be used by individuals with diverse backgrounds and levels of expertise. This document contains a system which attempts to meet

these needs and to provide the planning tool necessary before site-specific evaluations.

Inherent in each hydrogeologic setting are the physical characteristics which affect the ground-water pollution potential. A wide range of technical positions was considered regarding the relative importance of the many physical characteristics that affect pollution potential. Factors including aquifer chemistry, temperature, transmissivity, tortuosity, gaseous phase transport, and others were evaluated. The availability of mappable data has also been considered. As a result of this evaluation, the most important mappable factors that control the ground-water pollution potential were determined to be:

- D - Depth to water
- R - (Net) Recharge
- A - Aquifer Media
- S - Soil Media
- T - Topography (Slope)
- I - Impact of the Vadose Zone
- C - Conductivity (Hydraulic) of the Aquifer

DRASTIC: A Description of the Factors. While this list is not all inclusive, these factors, in combination with a basic requirement to assess the general pollution potential of each hydrogeologic setting, must be evaluated. The DRASTIC factors represent measurable parameters for which data are generally available from a variety of sources.

In August 1984, the EPA released the EPA Ground-Water Protection Strategy. Among other things, the strategy commits EPA to assisting states in building the institutional capability they need to protect their ground water. This report is part of that effort. It presents information EPA compiled from available sources on the basic elements of ground-water programs and activities in the fifty states and selected territories. It is not a comprehensive summary of all state ground-water programs.

EPA uses DRASTIC for program development purposes, and will make it available to the states to help them exchange information and ideas on approaches for addressing common ground-water problems.

4. GROUND-WATER MONITORING STRATEGY

The Ground-Water Monitoring Strategy provides a cross-Agency analysis of the need for and use of ground-water monitoring data. Within this approach, individual program monitoring strategies focus on their program's specific needs while the Ground-Water Monitoring Strategy focuses on the interrelationships between programs and the overall direction of the Agency's ground-water monitoring effort. As the blueprint, or framework, for EPA's ground-water monitoring decisions and activities, the strategy is designed to:

- Be broad in scope and not address specific details of any program monitoring requirement.
- Focus on a five-year horizon for implementation, with both short-term and long-term action items.
- Recognize that the job is complex and that EPA and others are interested in considering what constitutes an appropriate overall ground-water monitoring program.
- Provide a balance in the strategy implementation plan between general action items and a detailed work plan.
- Focus on solutions to the ground-water monitoring problems identified in the Office of Technology Assessment (OTA) report Protecting the Nation's Ground Water from Contamination and other reports, and not restate their analyses.

The Ground-Water Monitoring Strategy focuses attention and resources on improving the fundamental activities of ground-water monitoring. For this reason, the strategy stresses the need for improving the quality and management of ground-water data collected and analyzed by or on behalf of EPA programs. The strategy concentrates on upgrading existing Agency activities and filling the gaps between these activities. Such an effort requires the identification of data users, uses, and accessibility. This is the first attempt by the Agency to do this on a comprehensive scale for an environmental issue.

Ground-water monitoring is viewed as a continued activity ranging from defining background conditions, to defining the performance of the waste treatment and storage facilities, to defining the success of EPA

programs in protecting the ground-water resource. The Ground-Water Monitoring Strategy addresses this range of activities through seven monitoring objectives, each of which is summarized below. Ground-water monitoring research is not identified as a separate monitoring objective, because it was addressed by the Science Advisory Board through a committee on ground-water research. EPA recognizes that research is an integral component of monitoring activity and is important to the development of more effective monitoring programs.

- Objective 1: Characterize the Nation's Ground-Water Resources
- Objective 2: Identify New Contamination Problems
- Objective 3: Assess Known Problems to Support Regulatory Development and Standard Setting and Respond to Site-Specific Problems
- Objective 4: Assure Compliance with Regulations
- Objective 5: Evaluate Program Effectiveness
- Objective 6: Improve Data Quality
- Objective 7: Develop Ground-Water Data Management System

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IMPLEMENTATION OF A SOIL PROTECTION POLICY
IN THE NETHERLANDS

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ABSTRACT

In The Netherlands the introduction of the Soil Protection Act in 1987 marks the transition from a period of developing legislation and strategies for a soil protection policy, to a period of implementation of this policy. The Dutch soil protection policy is embedded in a general environmental policy, characterized by an integrated approach. In this paper the basic philosophy and the outlines of the soil protection policy are discussed, with a short review of the policy objectives, being effect-oriented and source-oriented. The objectives of the effect-oriented policy are aimed at the preservation of a good soil quality. One of the key-issues is the formulation of reference standards for a good soil quality in quantitative terms. Source-oriented policy distinguishes between local sources and diffuse sources. Local sources have to meet the criteria of isolation, monitoring and control, for diffuse sources a link is made between the application of substances and the preservation of a good soil quality. As an example a short description is given of the Dutch regulation on manuring.

Finally, some attention is paid to the management tools of monitoring, modelling and mapping and to research with respect to the implementation of the soil protection policy in The Netherlands.

1. INTRODUCTION

The capability of man to exploit soil and groundwater to his benefit, is one of the major factors in the development of society. Until the 20th century, this was done almost in harmony with the properties and dynamics of nature. However, the explosive socio-economic and technical developments in this century have led to a serious assault on the quality of soil and groundwater. Today, all over the world, one is encountering a variety of problems: physical, chemical and biological degradation of soils, soil erosion, overdrawn aquifers, salt water intrusion and groundwater contamination. Fortunately, there is not only a growing scientific understanding of the nature of the problems, but also a growing (social) awareness of the seriousness of these problems. In many countries a consensus exists that high priority must be given to the development and implementation of policies and strategies aiming at the protection of soil and groundwater and the sustainable development of these natural resources. Also international organizations like the European Communities, the OECD and the U.N. Economic Commission for Europe are occupying themselves with this important environmental issue.

It is obvious that in a densely populated and highly industrialized country like The Netherlands man-induced stresses on soil and groundwater are manifold and of special significance for the environmental quality of every km² throughout the country. In January 1987 the Soil Protection Act came into force, which provides the legal basis for an integral protection of soil quality. Soil in this respect being defined as including the groundwater, gases and soil organisms. This event marks the transition from a period of developing legislation and strategies for a soil protection policy, to a period of implementation of this policy. A major effort will be put into

activities to prevent (further) deterioration of soil quality.

2. THE NEED FOR A SOIL PROTECTION POLICY

Many activities hold a potential threat for soil and groundwater pollution. Hence, it is not surprising that cases of pollution are being reported for quite some time. At first, these were seemingly only local pollutions, caused by point sources like waste disposals, and accidental spills of chemicals, and of minor importance for the state of the subsurface environment at regional or national scale.

However, in the 1970's it became gradually clear that soil and groundwater were treated rather carelessly in The Netherlands, as in many other countries. Numerous human activities appeared to have significant and large scale effects on the groundwater quality, in spite of the natural protection provided by physical, chemical and biological properties of soil and groundwater. The discovery of some serious cases of soil pollution in urban areas at the end of the 1970's, led to a nation wide inventory of suspect sites of soil and groundwater pollution. The result was a long list of several thousands of sites, polluted by mainly industrial sources. At present, there is a large operation in progress to investigate and to clean-up these polluted sites, with a yearly budget of about Dfl. 200 million. It is expected that until the year 2000 some 5 milliard kg of polluted soil has to be cleaned, in situ or after excavation, at an estimated total cost of Dfl. 3 milliard (Eikelboom and Von Meijenfëldt, 1985).

Included in this operation are also groundwater abstraction and purification in about 50% of the cases involved.

Another serious impact on soil and groundwater results from the intensification of agriculture. The use of fertilizers, pesticides, sewage sludge and animal waste produces a substantial deterioration of soil and groundwater quality. Several groundwater pumping stations in agricultural areas are threatened by high levels of nitrate, potassium, heavy metals and organic micropollutants.

At present special attention is paid to the nitrate problem. In 1980 the number of pumping stations exceeding the EC-guide level for drinking water of 5.6 mg N/l was 6. By the year 2000 it is expected that this number will have increased to some dozens, if no restrictions in agricultural practices would become operative. The EC-maximum permissible level of 11.3 mg N/l has been reached in 1985 in two pumping stations. In several private wells concentrations have been observed of more than 20 mg N/l. Nitrate problems in The Netherlands have been discussed at some length by several authors, e.g. Scheltinga (1985). Several models are being developed to predict future nitrate concentrations in groundwater in relation to different manuring practice scenarios (e.g. Van Drecht, 1987). High application rates of manure may eventually cause phosphate leaching. In The Netherlands, the capacity of the soil to adsorb phosphate is already exhausted at several locations (Breeuwsma and Schoumans, 1987). The vulnerability of groundwater to the leaching of yet another group of agrochemicals, the pesticides, has been pointed out very illustratively by Loch (1987).

Another actual issue is the harmful impact on the environment of acid deposition caused mainly by industry, traffic and agriculture. A major research program on this important phenomenon has started in The Netherlands in 1983. Emphasis lays on the effects on terrestrial ecosystems, woods and cultural-historical monuments. Attention is also paid to the consequences of acid deposition for the groundwater quality, and consequently for the water supply. On the basis of preliminary results, Zweegman and Van Duijvenbooden (1986) concluded that acid deposition is of direct relevance for circa 30 pumping stations situated in sandy areas with low acid buffering capacity. For these pumping stations the concentrations of sulphate, nitrate, and aluminium and some other metals, are likely to increase significantly at some time in the future.

The need for the protection of groundwater as an essential resource for the water supply in the Netherlands was already expressed in the late 1950's and more generally endorsed in the 1960's. During the late

1960's and the early 1970's a basic concept of protection zones, with restrictions for land use and other activities, was introduced by the former National Institute for Water Supply, inspired by work in this field in the Federal Republic of Germany. Further elaboration of this concept led to the introduction in 1975 of protection zones with dimensions based on travel times of groundwater towards the pumping wells. At that time it was argued quite rightly, that this concept is only second best, as the protection of the whole catchment area would be better, but not feasible in the Dutch hydrological and socio-economical situation without further pertinent legislation (Van Waegeningh, 1985).

As in many other countries, several aspects of soil and groundwater protection are covered by a number of legal and other regulatory instruments on national, provincial and municipal level. This fragmentation made developing and implementing a coherent soil and groundwater protection policy a difficult task. Therefore, in the early seventies an initiative for a Soil Protection Act as an integrating framework was taken. However, because of the complex nature of the problems it took years of consultation and negotiation before a Soil Protection Bill could be presented to Parliament by the Dutch Government. In January 1987 the Soil Protection Act became operative. This act now provides the structural basis and the necessary administrative instruments for the implementation of the soil protection policy already developed in recent years, and for further policy development. It should be noted here that, anticipating on this act, already in 1983 a Soil Clean-up Interim Act became operative for the regulation of soil clean-up operations.

3. SOIL PROTECTION POLICY

Soil protection policy in the Netherlands is embedded in a general environmental policy, characterized by an integrated approach. Measures taken to maintain the desired quality of one part of the environment, air, water or soil, should not lead to a shifting of the

problems to another compartment. An example of such problem-shifting is the problem of sewage sludge. The purification of waste water leads to large quantities of sewage sludge which contain the contaminants in a concentrated form. This sludge has to be disposed of somewhere, and part of it is used on agricultural land, thereby spreading the contaminants throughout the soil compartment.

Characteristic for the Dutch environmental policy is the "guest in one's own house" philosophy: man has the right to organize his environment according to his views and to enjoy it, but he has also the duty to carry it over in a good condition to future generations. To this end a so-called two track environmental policy is being developed: an effect-oriented and a source-oriented policy. The effect-oriented policy defines the objectives which are to be pursued with respect to the quality of the environment in The Netherlands as a whole or in certain parts, and the tasks for target groups, such as industry and agriculture, implied by those objectives. In addition, a source-oriented policy is necessary, indicating the manner and the pace in which the behaviour of target groups will be adjusted, with respect to the environmental quality objectives and tasks formulated in the framework of the effect-oriented policy. The priorities defined for following these two tracks are formulated in a yearly Environmental Program.

Generally described, the overall objective of the effect-oriented policy is to maintain an environmental quality such that the health and well-being of people and the preservation of animals, plants, materials and modes of use are ensured. In soil protection policy this goal has been translated into the task of preserving the properties of the soil which are of importance for its various possible functions, the so-called multi-functionality concept. The Netherlands is a densely populated country where the soil has many functions, which exist close to each other or even above each other. Land use is frequently changing and human activities may often lead to irreversible changes in soil structure and chemical composition. The strategy of preserving the multi-functionality of the soil is aimed at

"keeping all options open" for future generations. A change in use of the soil after some time must remain possible. A soil of good quality may then be defined as follows: it poses no harm to any use by human beings, plants and animals, it can function without restriction in natural cycles, e.g. the hydrological cycle, the nitrogen cycle and the carbon cycle, and it does not contaminate other parts of the environment.

From a scientific point of view, "multi-functionality" is a complex, abstract concept. A complete and unambiguous description of a multi-functional soil in terms of measurable chemical, physical and biological characteristics may be a long and arduous task. But the development of a soil protection policy does not fully depend on the availability of such a complete description. It may primarily be focused on those human activities with irreversible effects on the structure and composition of the soil, that might endanger any use of the soil by human beings, plants and animals. Examples are pollution of the soil with heavy metals, several organic chemicals and nitrates in groundwater.

An important step in defining good soil quality in quantitative terms is the formulation of reference standards. In 1986 the Ministry of Environment has published a discussion note on provisional reference values for certain parameters, taking into account the heterogeneity of the soil environment. This note is aimed at stimulating discussion in the scientific community and, at a later stage, in political circles. For some major pollutants, such as nitrate and phosphate, provisional values are already operative, indicating the desired quality of groundwater, based on the EC-directive on the quality of drinking water.

As for the source-oriented-policy, a division is made into local or point sources and diffuse or non-point sources.

For local sources only remotely a link with soil quality is made, as the approach for those sources is "isolation": they have to meet the so-called ICM-criteria (isolation, control, monitoring). Priority is laid on development and implementation of criteria for the construction of new storage or dumping sites. In order to be able to

standardize technical provisions for different materials and different soils, general and source-specific standards for the acceptable risk levels of a possible failure of such provisions are being developed. A research program to obtain the necessary methodology is in progress, mainly concentrating on storage facilities for chemical fluids and mineral oil, and on risk analysis with respect to (facilities on) industrial premises. For the discharge of liquid and solid wastes, underground storage tanks for liquid fuels and the use of waste and other materials for construction purposes, a more detailed specification of the ICM-criteria is now in preparation.

Diffuse sources have to meet other criteria. One of the policy objectives is to define a link, mathematical or otherwise, between the application of substances and the preservation of a good soil quality. For long term preservation of soil quality an acceptable equilibrium between input and output of substances must be reached, which may be only possible with non-accumulating or non-persistent substances, degraded in a natural way, or substances removed by crops. Most heavy metals and many organic pollutants which do not meet these requirements are placed on a "black list" of substances that should no be allowed to enter the soil, based on the EC-Guideline on Groundwater Protection. This list forms one of the bases for the selection of priority substances. For these substances so-called criteria-documents are being prepared, which contain the present knowledge on emissions, risks, behaviour in air, water and soil, effects on man, animals, plants and ecosystems, financial and technical aspects of emission reduction and monitoring strategies. These documents provide the scientific basis for measures with regard to emissions to soil, air and water.

The Soil Protection Act distinguishes two levels of protection: the general protection level and a specific protection level. Both protection levels differ only in the height of the acceptable risk-level for soil pollution caused by certain activities.

The general protection level is formed by regulatory measures to be

set by the national government. These rules concern the regulation of activities that may lead to pollution or impairment of the soil and the formulation of soil quality standards.

In addition to this general protection level, a specific protection level must be effectuated in special areas, the so-called soil protection areas and groundwater protection areas. In areas for which a specific protection level is indicated, potential harmful activities are not tolerable or additional preventive measures are necessary: the acceptable risk level of soil pollution is lower in these areas.

Soil protection areas are areas of particular value where the chemical, physical and biological properties of the soil are not or only to a slight extent adversely affected by human activities. The provinces are obliged to initiate an inventory on the presence of such areas in their territory. The national government may provide guidelines to define such areas. Furthermore, provincial authorities are obliged to draw up, before 1989, a plan for protection of the quality of the groundwater in their province indicating areas that require specific protection in view of the drinking water supply, the groundwater protection areas. They shall also provide regulations to realise this specific protection level.

So, 15 years after the introduction of the concept of protection zones, finally a sound legal basis for the implementation of this concept has been obtained.

4 REGULATION OF MANURING

As an example of the approach to diffuse sources, the regulation on manuring of agricultural land is discussed.

The Netherlands has about 5 million cows, grazing on grassland, 13 million pigs and 85 million of poultry, fed mainly on imported feed. This has led to animal waste surplusses measured in millions of tons that have to be disposed of. These surplusses lead to leaching of nitrate and phosphate to groundwater and other water reservoirs. The evaporation of ammonia from manure is considered to contribute for

about 30% to acid rain and its effects.

At the end of 1984 the Interim Act Restriction Swine- and Poultry Farms was adopted. This law forbade the operation of new swine and poultry farms and, in the districts with the most intensive animal husbandry, even the extension of existing farms for a two year period. In the other parts of the country only limited extensions were permitted. The Fertilizer and Manure Act of January 1987, regulating many aspects of the manure problem, e.g. the quality of manure to be applied, replaced this Interim Act. The regulation of manure application is based on the Soil Protection Act. For the regulations on manuring, as for other aspects in soil protection relevant to agriculture, a close cooperation exists between the Minister of Environment and the Minister of Agriculture. Regulation involves the quantity of manure to be used in relation to type and composition and to use of the soil, the manner of application and the circumstances and location for application. A decree based on the Soil Protection Act came into force May 1987.

The approach of the manure problem is divided into 3 phases of 5 years each. For practical reasons the regulation is largely based on the phosphate content of the manure: ultimately, no more phosphate in the form of animal manure should be given than is necessary for the desired crop yield. When the phosphate level in the soil is sufficient a dose equal to the amount withdrawn by crops can suffice. Table 1 shows the reduction in manure application foreseen in this regulation.

Table 1 Regulation of manure application

	Maximum of manure to be applied per hectare (kg P ₂ O ₅)			
	1987-1991	1991-1995	1995-2000	2000-
crops	125	125	125	final standard
maize	350	250	175	
grassland	250	200	175	

In 2000 the final standard should be reached. The exact value of this final standard remains to be defined (about 125 kg P₂O₅ per hectare). Of course this will lead to a parallel reduction of the nitrate load. A levy on surpluses will provide the means for provisions on handling, marketing and in the future possibly exporting of the manure products. In close cooperation between government and the agricultural sector research is going on to establish the best way to handle the large mass of surpluses in an environmentally and economically sound way.

The incentive for these source-oriented measures forms the intended quality for phosphate and nitrogen compounds in groundwater as mentioned before. Provisional values for these compounds have been formulated in the Environmental Program 1986-1990. Purification of groundwater is seen only as a possible temporary measure: the emphasis must lie on prevention. Environmental monitoring will show the effectiveness of the measures foreseen.

5 RESEARCH NEEDS AND MANAGEMENT TOOLS

Already a fair knowledge exists of the properties of the subsurface environment and the sources and behaviour of pollutants in soil and groundwater. Together with the present insight into the environmental impacts and into the health aspects, a sufficient basis exists for the implementation of a soil protection policy. Nevertheless much research will still be needed. Especially with respect to ecological aspects, the natural regeneration potential of soils, risk-analysis and remedial action in case of pollution. In The Netherlands, soil protection research has become a priority area of Dutch science policy. In addition to existing research programs, in May 1986 a coordinated soil research program of the Ministers of Science, Environment, Agriculture and Water Management came into being. It covers a total extra budget of Dfl. 56 million for a period of 4 years. Major topics are basic research, mainly on soil ecology, effects of substances on soil functions and technology development

both for prevention and clean-up operations.

Research in the field of soil and groundwater protection often requires a multi-disciplinary approach. This may include a wide range of scientific disciplines like groundwater hydrology, geology, pedology, geochemistry, environmental chemistry, biology, human toxicology, ecotoxicology, mathematical physics and operations research. The different ways of thinking and the varying working methods challenge to cross boundaries and to level barriers between disciplines. This challenge will undoubtedly be taken up and one may expect further valuable results of the scientific co-operation in the field of soil research.

There are at least three important tools developed by soil scientists and groundwater hydrologists for use in soil and groundwater protection management: monitoring, modelling and mapping. These 3 M's are essential for an adequate implementation of soil protection policies.

The first tool for soil and groundwater protection management is monitoring. To provide an insight into the gradual changes in groundwater quality over the years, a national monitoring network has been completed some years ago in The Netherlands, in addition to the monitoring of the groundwater pumping stations. More information regarding the network and some recent results are given by Van Duijvenbooden (1987). Complementarily, it is felt necessary to set up inter-related regional monitoring networks as well as local networks aiming at groundwater protection areas. To this end concerted action by national and regional authorities and water supply companies is important. Furthermore, this year a start will be made with a monitoring program for soil quality.

As to the groundwater protection areas, one may say that a "long-standing" experience with the calculation of the dimensions of protection zones is available. Several computer models have been developed for the calculation of groundwater flow patterns and travel times. These models have proved to be very useful tools. However, the development of simulation models for migration and distribution of contaminants in real world subsurface systems is still in its

infancy. A lot of research efforts and funds have already been put in the development of advection-dispersion models for non-reactive solutes, as well as in the development of models which include geochemical and biochemical processes. The achievements thus far illustrate that much research in the laboratory and in the field remains to be done, before practical and reliable models for management purposes are available. One of the problems to overcome is to get enough and sufficiently diverse data to feed models in order to allow for realistic simulations of solute transport. Special attention should be paid, in the coming years, to the significance of measurements and descriptions on microscopic or macroscopic scale for parameters such as concentrations, adsorption properties, equilibrium constants and dispersivity, in a megascopic model environment. It is obvious that the reliability problems, arising from uncertainties in model input, are much greater than the corresponding problems in groundwater flow models aiming at the simulation of hydraulic heads and groundwater fluxes.

A third management tool in soil and groundwater protection is vulnerability mapping, which may be useful in the process of planning. Today, the vulnerability of soil and groundwater is well known. However, on short term a zero option with respect to emissions of pollutants is neither feasible nor practical. So, a differentiation in terms of higher vulnerability - higher protection - lower risks may have to be accepted. That leaves the question how to define and how to handle vulnerability in the context of soil and groundwater protection policies and strategies. The answers are not easy to give, as this involves a complex mixture of physical, chemical and biological properties that are of relevance for the different functions of soil and groundwater which are to be protected.

Vulnerability maps as management tool could be defined as a geographical representation of information which is relevant for specific management or policy decisions to be made in the context of environmental policy or physical planning. These maps include information on the polluting sources, emissions and their probability of occurrence, objects to protect, groundwater protection areas,

environmental properties to be effected and the actual vulnerability assessment. These maps could be used for instance:

- to set priorities in policy development and implementation;
- to develop and implement areal differentiated protection policies;
- to select sites for certain activities;
- and to take protective or mitigating measures.

In several countries there is already some experience in vulnerability mapping of aquifers. In The Netherlands too, there are already some interesting results which are helpful in the development of a definite and systematic procedure. A study of the vulnerability of the groundwater in The Netherlands has been prepared as a contribution to the groundwater resources study of the Commission of the European Communities (CEC, to be published). Furthermore, the National Institute of Public Health and Environmental Hygiene, in co-operation with the Soil Survey Institute and the Geological Survey, has recently compiled a set of vulnerability maps (Breeuwsma and Van Duijvenbooden, 1987). A next step may be the compilation of more detailed vulnerability maps for groundwater protection areas. This will include further research into the spatial variability of the parameters describing the relevant properties of the subsurface.

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BACTERIA IN THE SATURATED ZONE OF THE SOIL

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ABSTRACT

The saturated zone of the Dutch soil contains a large number of mainly facultative anaerobic bacteria. Since a large number of bacteria is present in the saturated zone the capacity for biodegradation of xenobiotic compounds in this environment can not be excluded beforehand but must be a subject of further research.

1. INTRODUCTION

The subsoil is often considered very vulnerable to pollution since no microbial activity is assumed in that environment. The classical method of diluting soil samples and growing bacteria on agar plates revealed low numbers of microorganisms.

The use of fluorescence microscopy on stained soil bacteria showed large numbers of bacteria to be present in aquifers both in the U.S.A. and Germany. While in top soils the number of bacteria varies between 10^8 and 10^{10} bacteria per gram dry soil, the number of bacteria in sandy aquifers in the U.S.A. was reported by Wilson and McNabb (1983), and by Balkwill and Ghiorse (1985) to be 10^6 - 10^7 bacteria per gram. Most subsoil bacteria are small cocci which are attached to soil particles. In Holland most of the groundwater is anaerobic and therefore one might expect an anaerobic microflora to be present in the subsoil. This poster describes a novel sampling method for the characterization and enumeration of subsoil bacteria and shows some preliminary results obtained with this method.

2. ASEPTIC AND ANAEROBIC SAMPLING OF SUBSOIL BACTERIA

A hole was dug into the ground using Edelman augers and a sample was taken below the water table using a piston sampler. The piston sampler was taken above the ground and a sterile stainless steel tube was pushed into the sample in order to take an aseptic subsample. The tube was closed again with a cotton wool plug and stored in an ice box filled with cotton wool and a bit of liquid nitrogen. Since the tubes are stored on top of the cotton wool they are continuously flushed with cold nitrogen without being frozen. In this manner both a low temperature and a low oxygen tension were maintained. In the laboratory the tubes are put in the airlock of an anaerobic chamber and evacuated and gassed three times. A part of the sample was used for the determination of the number of colony forming units on rich and nutrient poor media. Another part was used for direct microscopical counts of the bacteria stained with fluorescein isothiocyanate.

3. RESULTS

Table 1 shows the results of the viable counts of soil bacteria on diluted nutrient broth which gave the highest counts of all the media we tested. The plates were incubated for several weeks at 15 degrees celcius.

TABLE 1 VIABLE COUNTS OF SUBSURFACE BACTERIA

date	location	soil	pH (H2O)	c.f.u./g dry soil
090186	Scheveningen	sand		10^5
150186	Leidschendam	clay		$2 \cdot 10^7$
120286	Katwijk	sand	8	$6 \cdot 10^4$
120286	Katwijk surface	sand		10^8
040686	Bilthoven	sand	6	$2 \cdot 10^7$
180686	Bilthoven	sand	5.5	$6 \cdot 10^4$
180686	Bilthoven	sand	5.5	10^6
130886	Bilthoven	sand	6.5	$3 \cdot 10^4$
160986	Bilthoven	sand	6	$2 \cdot 10^5$
				$2 \cdot 10^5$ anaerobic

Note that the subsurface sample from Katwijk contains only 0.03% of the number of viable counts of the surface sample. This shows that the contamination of the subsurface sample by the surface soil is much less than 0.03% .

From the last sample from Bilthoven, bacteria were extracted, diluted, and grown under strict anaerobic conditions. In the anaerobic glove box the colonies on nutrient poor media were so small that they could not be counted. At a rich medium $2 \cdot 10^5$ colony forming units per gram dry soil were counted. Replica plating showed that the bacteria isolated in the glove box could grow in air whereas the aerobic bacteria could grow in the glove box. Hence the majority of viable bacteria are facultative anaerobes in this sample of the vadose zone from a sandy soil.

4. DISCUSSION

The number of viable counts is much lower than the number of direct counts under the fluorescence microscope. For example $1.6 \cdot 10^8$ bacteria per gram were counted from the last sample from Bilthoven. The visible bacteria were very small cocci, which are predominant in soil but can not be grown at reasonable rates in the laboratory.

The biomass per gram soil is much lower in the saturated zone than in the upper soil. However the saturated zone is much thicker and is not plagued by droughts or frost. Hence this zone may perform an important task in the biodegradation of xenobiotic compounds.

5. ACKNOWLEDGEMENTS

This research was supported by the Dutch Ministry of Housing, Physical Planning and Environment.

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TOXICITY AND BIOACCUMULATION OF CHLORINATED
PHENOLS IN EARTHWORMS

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ABSTRACT

The toxicity and bioaccumulation of five chlorinated phenols in two earthworm species were determined in two sandy soils having a different organic matter content, and compared with adsorption data. Toxicity and bioaccumulation of these compounds were generally higher when adsorption onto soil was lower. Toxicity data obtained with both earthworm species showed a good correlation, whereby the "compost species" Eisenia fetida andrei appeared to be more sensitive than the soil-inhabiting species Lumbricus rubellus. When toxicity and bioaccumulation data were recalculated to concentrations in soil solution using the adsorption data, both toxicity and bioaccumulation appeared to increase with increasing lipophilicity.

INTRODUCTION

The toxicity and bioaccumulation of chemicals in soil organisms is expected to be dependent on the bioavailability in soil, which is a function of the physico-chemical properties of the chemical and of soil properties. Adsorption has a great influence on bioavailability (Böttger, 1976). For organic chemicals adsorption is correlated with lipophilicity (expressed as the octanol/water partition coefficient P_{oct}) of the chemicals and the organic matter content of the soil (Brown and Flagg, 1981).

The purpose of this study was to establish relationships between toxicity and bioaccumulation of chemicals in earthworms on the one hand and adsorption onto soil and lipophilicity on the other. This paper

describes some preliminary results.

MATERIALS AND METHODS

Table 1 shows the pK_a and $\log P_{oct}$ values of the chlorinated phenols used in this study. Unfortunately two different isomers of tetrachlorophenol were used: the 2,3,4,6-isomer in the adsorption experiments and the 2,3,4,5-isomer in the toxicity and bioaccumulation experiments.

Table 1: pK_a and $\log P_{oct}$ values of chlorinated phenols

	chlorophenol					
	3-	3,4-	2,4,5-	2,3,4,5-	2,3,4,6-	penta-
pK_a	9.37	8.62	6.72	5.64	5.22	4.74
$\log P_{oct}$	2.5	3.2	3.9	4.5	4.4	5.0

The soils used were Holten, having 6.1 % organic matter and pH-KCl 5.6, and Kooyenburg with 3.7 % organic matter and pH-KCl 4.8.

The earthworm ("compost") species Eisenia fetida andrei was grown in the laboratory on horse manure. The "wild" species Lumbricus rubellus was collected from the field. Adult earthworms with a well-developed clitellum were used.

Chemicals were mixed homogeneously through the soils, and soils were moistened to a water content of 16 % (w/w). Glass jars were filled with c. 0.5 kg dry weight of soil. Jars contained 10 worms each in case of E. fetida andrei, and 5 worms each in case of L. rubellus, and were incubated at the optimal temperature for each species, i.e. 23 and 15 °C, respectively. In each test five concentrations and a control were evaluated. Per concentration 30 earthworms were used. LC_{50} values based on 14 days mortality data were calculated using a logit model.

To determine bioaccumulation, samples of soil and earthworms of a non-lethal concentration were taken on days 0 and 14 and analysed.

Adsorption onto soil was determined by shaking aqueous solutions of chlorinated phenols with soil. After centrifugation supernatants were analysed. Adsorption coefficients were calculated using the Freundlich

equation.

RESULTS AND DISCUSSION

Table 2 shows the Freundlich adsorption coefficients K ; $1/n$ values were between 0.77 and 0.85. From this table it is obvious that for mono-, di- and trichlorophenol differences in adsorption between the two soils reflect the difference in organic matter content. For tetra- and pentachlorophenol adsorption seems to be influenced by soil pH too, probably because their pK_a values are as low as the pH values of the soils used.

Table 2: Adsorption coefficients $K(\text{dm}^3.\text{kg}^{-1})$ for five chlorinated phenols in soils Holten and Kooyenburg

soils	K ($\text{dm}^3.\text{kg}^{-1}$) for chlorophenol				
	3-	3,4-	2,4,5-	2,3,4,6-	penta-
Holten	12	30	78	95	125
Kooyenburg	6	15	43	85	120

It appears that toxicity in terms of LC_{50} values is mostly higher in the soil with the lowest organic matter content (Table 3).

Table 3: LC_{50} values for the toxicity of chlorinated phenols to earthworms in two soils

chlorophenol	LC_{50} ($\text{mg}.\text{kg}^{-1}$ dry soil) for species in soil			
	<u>E. fetida andrei</u>		<u>L. rubellus</u>	
	Kooyenburg	Holten	Kooyenburg	Holten
3-	>56 <100	>100 <180	150	296
3,4-	>100 <180	>180 <320	303	486
2,4,5-	52	90	201	290
2,3,4,5-	116	176	514	828
penta-	86	143	1094	883

LC_{50} values are correlated with adsorption. Recalculation of the LC_{50}

values from Table 3 to concentrations in soil solution using the adsorption coefficients of Table 2 results in nearly the same LC_{50} values (in $\mu\text{mol.l}^{-1}$) for both soils.

In all tests E. fetida andrei appears to be the most sensitive species, although this may be partly due to the difference in experimental temperature. The difference between the two species seems to increase with increasing lipophilicity of the test substances. There is, however, a good correlation between the results obtained with both species ($r = 0.951$ with $\log LC_{50}$ in $\mu\text{mol.l}^{-1}$).

There is also a fairly good correlation between toxicity ($\log LC_{50}$ in $\mu\text{mol.l}^{-1}$) and $\log P_{\text{oct}}$ ($r = -0.943$ for E. fetida andrei, and $r = -0.850$ for L. rubellus).

To calculate bioconcentration factors (BCF) for the accumulation of chlorinated phenols in earthworms, average soil concentrations for the total 14 days exposure period were calculated assuming that soil concentrations decline following first-order kinetics and using the results of the 0 and 14 days soil analysis. Table 4 shows BCF values for E. fetida andrei, as the ratios of concentrations in earthworms (dry weight) to concentrations both in soil and in soil solution (calculated using the adsorption coefficients of Table 2). Log BCF values based on concentrations in soil solution showed a correlation with $\log P_{\text{oct}}$ ($r = 0.853$).

Table 4: *Bioaccumulation of chlorinated phenols in E. fetida andrei*

chlorophenol	BCF as $C_{\text{worm}}/C_{\text{soil}}$		BCF as $C_{\text{worm}}/C_{\text{soil solution}}$	
	Kooyenburg	Holten	Kooyenburg	Holten
3-	1.1	1.3	7.1	16.2
3,4-	1.8	0.8	27.0	24.4
2,4,5-	1.5	0.4	64.0	33.7
2,3,4,5-	0.5	0.4	40.7	35.9
penta-	5.3	3.1	633.6	391.1

From this study it can be concluded that toxicity and bioaccumulation of chlorinated phenols in earthworms is dependent on adsorption onto soil and correlated with lipophilicity ($\log P_{\text{oct}}$).

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USE OF SOIL ORGANISMS IN EXPERIMENTS ON VULNERABILITY OF SOIL
TO POLLUTANTS

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ABSTRACT

A pilot study was initiated to explore the possibilities of joint long-term physical, chemical and biological experiments in soil columns of 110 cm height on the behaviour and effects of organic pollutants. The effects of 4 aliphatics and 1,4-dichlorobenzene on these soils inhabiting Rotifera, Nematoda and Enchytraeidae are discussed.

INTRODUCTION

Vulnerability of ecosystems to pollutants depends on many factors. Single-species tests are of limited value, because they do not give information on population interactions and ecosystem processes. This can be illustrated by the influence of nematode-bacterial interactions on degradation of chemicals. Free-living nematods appear to play an important role on decomposition by grazing on bacteria. They can stimulate microbial metabolism and thus increase the decomposition rate. On the other hand the nematodes can reduce the bacterial population and thereby inhibit degradation of pollutants (Woombs and Laybourn, 1986). Other information on species-species interaction and the influence of pollutants on such interactions are very scarce, but essential to understand possible effects of pollutants on ecosystems. Therefore, in addition to several other types of information, suitable test systems on the ecosystem level are needed. Large soil columns, used for long-term studies on the behaviour of pollutants in soil (Loch et al., 1986), provide also laboratory microcosms for studying population dynamics under controlled conditions. Percolation experiments on the behaviour of 1,4-dichlorobenzene and a combination of chloroform, 1,1,1-trichloro-

ethane, trichloroethylene and tetrachloroethylene provided an excellent opportunity to start a pilot study to explore the advantages and disadvantages of these long-term exposure systems under controlled conditions. This communication describes the results of such experiments on the microfauna and the usefulness of such columns.

MATERIALS AND METHODS

Percolation experiments were done in stainless steel cylinders of 110 cm length and 20 cm inner diameter, with a water table at 100 cm depth. The columns were equipped with a drainage system and sprinkled during 9 months with artificial rain supplied with 250 $\mu\text{g}/\text{dm}^3$ for 1,4-dichlorobenzene or 100 $\mu\text{g}/\text{dm}^3$ for each chlorinated aliphatic. Experimental and soil column designs were described by Loch et al. (1986) and Lagas et al. (1986). The percolation water was never anaerobic.

The columns were packed by natural soils, from Kootwijk (podzolic sand), Holten (eerd soil) or Teckop (peat soil), The Netherlands. Some characteristics of the soils are presented in table 1.

Table 1. *Physical and chemical characteristics for soil material in the columns (partly after Loch et al., 1986).*

soil type	depth cm	available water %	dry bulk density ³ g/cm	porosity %	org. matter %	lutum %	pH (KCl)	CEC meq./100 g
podzol	0-30	11	1.6	45	1.5	2.4	4.1	1.4
	30-60	9	1.6	37	0.5	-	4.4	0.8
	60-100	11	1.8	38	0.7	0.9	4.4	-
eerd soil	0-30	29	1.8	49	7.0	5.2	4.5	8.5
	30-60	25	1.6	48	7.4	-	3.7	7.6
peat soil	0-30	29	1.3	75	20	-	5.1	39
	30-60	46	0.9	87	61	-	4.5	70
	60-100	48	0.9	82	97	-	3.6	39

The soils were dug out in the field in layers of 10 cm and were placed in the same order in the cylinders. After 9 months percolation was terminated and the columns were broken down in layers of 5 or 10 cm.

No material was available from the start of the percolation experiments. So the results have a comparative value.

For sampling Nematoda and other mesofauna each layer was extracted according to Oostenbrink (1960). All animals were enumerated under a stereomicroscope.

RESULTS AND DISCUSSION

After terminating 9 months percolation experiments, there were 5 faunal groups that survived these conditions: Rotifera, Nematoda, Enchytraeidae, Tardigrada and Acari. The results are summarized in figure 1. The numbers of the Tardigrada and Acari were of minor interest and are not shown. The depth distribution pattern of the organisms in the columns is similar in natural profiles: most organisms were found in the top layer of 20 cm. Nematoda were the only group found in high numbers in all soil types. Enchytraeidae were not present in eerd soil and peat soil, while Rotifera inhabited mainly eerd soil. There appeared to be a clear difference between the effects of the pollutants tested: the columns rained with 4 aliphatics showed lesser faunal densities than those rained with 1,4-dichlorobenzene. This result is consistent with the observation of Loch et al. (1986) that 1,4-dichlorobenzene shows a stronger degradation rate than the 4 aliphatics. Because of lack of data on the start of the experiments, no definite conclusions on the effect of the pollutants tested can be drawn. However, the results of this pilot-study indicate that such system could provide essential information on the effects of pollutants on the functioning of ecosystems.

ACKNOWLEDGEMENT

The authors are grateful to Dr J.P.G. Loch, Drs P. Lagas and S. van den Berg for their helpfull suggestions as well as for providing us with data, and to Mrs. J. Aker for technical assistance.

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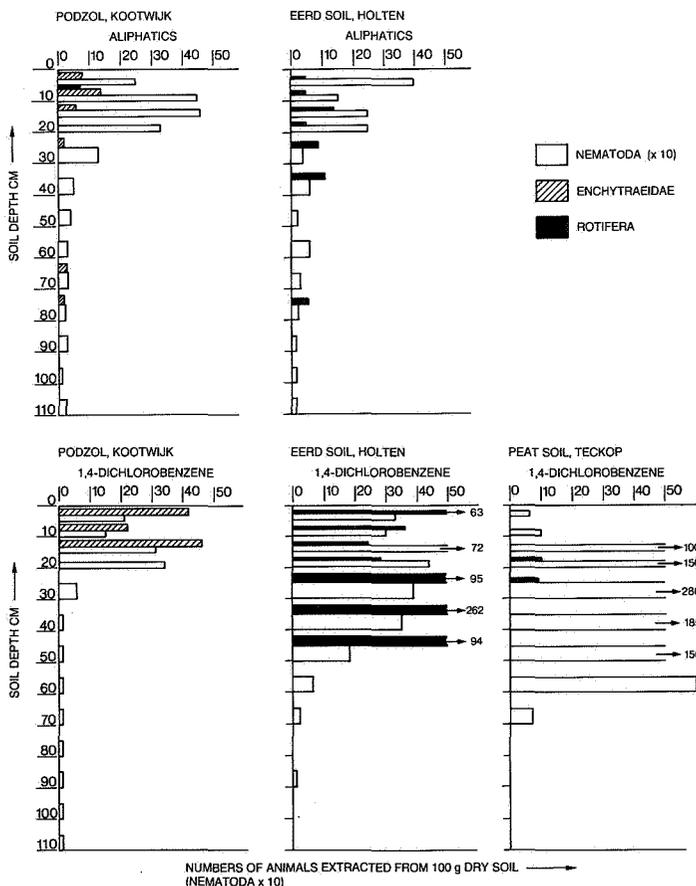


FIGURE 1. VERTICAL DISTRIBUTION OF NEMATODA, ENCHYTRAEIDAE AND ROTIFERA IN SOIL COLUMNS FILLED WITH PODZOL, EERD SOIL OR PEAT SOIL AND SPRINKLED WITH ALIPHATICS OR 1,4-DICHLOROBENZENE

**TOPIC 2: MONITORING STRATEGIES FOR THE QUALITY OF
SOIL AND GROUNDWATER**

GROUNDWATER QUALITY MONITORING - STRATEGY, OBJECTIVES
PROGRAMMES AND METHODS

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ABSTRACT

The groundwater quality monitoring is a complex process which provides data and information for the development, protection and management of groundwater. The long-term planning, strategy and policy for national and regional groundwater resources is based on the analysis and implementation of data obtained from the relevant monitoring programme. The basic objectives of monitoring are to determine the physical, chemical and biological parameters of groundwater systems, identify the time and space effects of natural processes and human activities on the groundwater, and to forecast long-term trends in the groundwater quality variations. Groundwater monitoring programme, systems and methods are evaluated with regard to the monitoring strategy and objectives.

1. INTRODUCTION

Monitoring activities play an important role in the planning, development, protection and management of groundwater resources. In general terms, by monitoring we understand the continuous, standardized measurement and observation of the environment - UNESCO/WHO (1978). Meyer (1973) defined monitoring of groundwater quality as a scientifically designed programme of continuing surveillance, including direct sampling and remote quality measurements, inventory of existing and potential causes of change, and analysis and predicting of the nature of future quality changes. The groundwater quality monitoring methodology was analogously formulated by Tinlin and Everett (1978), Ward (1979), Everett (1983) and EPA (1985).

Additional definitions of monitoring were expressed by various authors in the "Water Quality Bulletin" journal (1985), three issues of which were devoted exclusively to water quality monitoring.

To summarize, groundwater quality monitoring can be understood to be a continuous, methodologically and technically standardized programme of observations and measurements of selected components and variables of a hydrogeological system and pollution sources, with the following objectives:

- to collect, process and analyze background data on water quality as a baseline for evaluating the current state and for forecasting the changes and trends of the hydrogeological system quality due to natural processes and anthropogeneous impacts in space and time;
- to provide information for the planning, decision-making, implementation of control and legislative measures and regulations, and groundwater quality management and policy in view of regional interests and national priorities.

The groundwater quality monitoring activity should not be separated from the monitoring network of the hydrogeological system's quantitative components. The integrated design of a groundwater quality monitoring programme with surface water, precipitation, evaporation and soil monitoring networks is usually desirable, because there exist interrelations and immediate and/or retarded influences between the above mentioned components.

So far, groundwater quality monitoring has not been a regular, but rather an exceptional part of environmental monitoring programmes. In most cases, only heterogeneous and fragmented data are available, while compact data sets on groundwater quality on a national or regional scale are scarce.

The groundwater quality monitoring process comprises the following action steps:

- monitoring strategy;
- monitoring objectives;
- monitoring programme;
- monitoring system and methodology.

2. GROUNDWATER QUALITY MONITORING STRATEGY

The principal criteria affecting the groundwater quality monitoring strategy include:

- monitoring objectives;
- importance of groundwater resources for regional or national development;
- financial means available;
- economic and social aspects;
- type and extent of environmental problems;
- constraints on monitoring;
- benefits derived from monitoring activities;
- national political priorities and regional interests;
- international cooperation.

The different properties of a hydrogeological system in comparison with surface water should be considered when establishing the monitoring strategy.

Groundwater is rarely contaminated sooner than surface water. The response of an aquifer system to natural and anthropogenic impacts is usually not immediate but delayed. If a monitoring system exists this delay time can be used effectively for groundwater quality protection. Through monitoring, the contaminant can be identified when still in the unsaturated zone, rehabilitation and remedial measures can be initiated, and aquifer contamination prevented. The monitoring activity also leads to a timely detection of the contaminant in the saturated zone, which accelerates its isolation, the clean-up processes and removal techniques. The time and space effects of the contamination on the hydrogeological system are thus substantially limited. Groundwater quality monitoring supports the groundwater protection strategy. It is considered to be one of the most effective methods of groundwater preventive protection and of groundwater pollution problems anticipation.

3. GROUNDWATER QUALITY MONITORING OBJECTIVES

The decisive role in a groundwater quality monitoring strategy is played by the objectives of monitoring. Due to the different interests and needs of individual users, their determination is complicated.

The following objectives of groundwater quality monitoring are especially emphasized:

- to identify the physical, chemical and biological properties of the groundwater system;
- to define groundwater quality in view of its use for water supplies and other purposes;
- to forecast long-term trends in the groundwater quality variation;
- to identify the time and space effects of natural processes and human impacts on the hydrogeological system;
- to define the degree and risk of the hydrogeological system's vulnerability;
- to identify the existing and potential sources of pollution and the degree of their impact to water potability;
- to assess the existing and potential sources of contamination - their kind, extent and hazard;
- to define measures to be adopted to prevent groundwater contamination or those to restore the quality of groundwater which has already been polluted;
- to determine priorities amongst water resources and other natural resources;
- to improve groundwater protection management.

4. GROUNDWATER QUALITY MONITORING PROGRAMME

The groundwater quality monitoring programme depends strongly on the extent of the territory to be monitored, the monitoring period and objectives. It is emphasized that groundwater quality monitoring is related mainly, but not only, with the observation of human impacts on the hydrogeological system. The monitoring of natural processes impacts on the groundwater quality is also an important part of the monitoring activities.

Monitoring programmes can be local, regional, national (state) and international.

4.1 The international groundwater quality programme

This programme has been operating within the Global Environmental Monitoring System (GEMS) since 1974. One of the objectives of GEMS water programme is a water quality monitoring as a basis for the "assessment of the incidence and long-term trends of water pollution by selected persistent and hazardous substances", Meybeck (1985). The GEMS groundwater monitoring network has been, so far, less developed than the surface water network. Only exceptionally have monitored aquifers continental extent like the surface water streams. The variations in groundwater quality as obtained from GEMS monitoring stations have a merely regional rather than international representativity. This also holds for pollution sources which are, except for certain limited areas on our planet (acid rains effects) defined as point or non-point, and which affect the groundwater and aquifers locally or regionally only.

To increase the representativity of groundwater monitoring stations included in the GEMS requires priority observations in aquifers developed on the territory of two or more countries (for instance, the Nubian sandstone aquifer in Africa, the Cretaceous aquifer in Central Europe, Ogallala aquifer in USA, etc). In these regions increasing competition for water, and conflicts related to consequences of overpumping and depletion of aquifers and/or groundwater pollution can be anticipated. Monitoring activities can help to solve such international problem. The main task of the International Groundwater Quality Monitoring Programme is to be, in coordination with national monitoring programmes and using a uniform methodology and techniques of observation and sampling, helpful in the study of the hydrogeological system. This support national and international water policies in the management and control of aquifers in frontier zones. For reasons listed above, a transnational coordination of the GEMS groundwater quality monitoring programme is being stressed.

4.2 State - national groundwater quality monitoring programme

State and national groundwater quality monitoring programmes have been operating so far in a limited number of countries only. This is a difference when compared with surface water networks and networks of aquifer quantitative parameters, which have been in operation on the national level for many years.

National groundwater quality monitoring programmes, as an integral part of other national environmental programmes, are multi-objective. They are intended for collecting information on the natural background level, the current state and long-term trends of groundwater quality variations over the state territory as a baseline for a national policy of groundwater protection.

The benefits deriving from long-term data obtained from national monitoring networks for the economic and social development of society have been recognized. A national groundwater quality monitoring programme is methodologically, organizationally and administratively coordinated and controlled by the same water or environmental agency as the other national water monitoring programmes. A national monitoring network comprises baseline and trend stations (classification by the GEMS system). Impact stations are not a common part of national monitoring networks whose design is not directly connected to pollution sources, to well fields of water supplies, etc. At selected so called pilot stations, some variables are monitored continually. The stations of a groundwater quality monitoring network need not be, and often are not, identical with those for the monitoring of groundwater quantitative parameters.

4.3 Regional groundwater quality monitoring programme

Regional (also municipal, districts, provincial) groundwater quality monitoring programmes are multi-objective and interrelated with regional water-monitoring and environmental programmes. A regional monitoring programme should be flexible and able to serve several purposes.

The objective of a regional groundwater quality monitoring programme is to acquire statistically significant sets of data on the groundwater quality for the establishment of regional groundwater protection plans. Accurate and representative data are especially desirable for:

- collecting information on the state and quality changes of the hydrogeological system in a given region;
- protecting the recharge, vulnerable and discharge areas of aquifers;
- protecting public water supply systems;
- anticipating regional groundwater pollution problems;
- identifying non-point pollution sources and threats having a regional effect on the quality of groundwater resources;
- determining the regional extent of groundwater deterioration and contamination, and their consequences on the quality of the hydrogeological system;
- proposing changes in the operation and control of water management projects in a given region;
- assessing of regional economic, social and ecological priorities;
- decision-making concerning the control, regulatory actions and creation of a regional policy framework in groundwater quality protection.

The trend stations are dominant in the design of regional groundwater quality monitoring networks, while impact stations and, exceptionally, baseline stations supplement the monitoring network. The baseline stations connect the regional and national groundwater quality monitoring networks.

Correctly applied monitoring information helps the regional decision and policy makers to interrelate the regional and national water protection plans and policies.

4.4 Local groundwater quality monitoring programme

Local groundwater quality monitoring programmes have alarm functions and are usually closely related with pollution sources and groundwater abstraction sites. Groundwater quality site specific monitoring help to:

- anticipate effect of point sources on the groundwater quality (warning monitoring networks);
- identify the pollutant under the ground and determine methods for its removal;
- carry out the clean-up processes;
- assess the influence of local water management projects on the hydrogeological system.

The unsaturated zone's permeability and thickness, the aquifer's vulnerability and its hydraulic behaviour and geometry, groundwater flow direction, the type of contamination (accidental or hidden spills of wastes, leakages from landfills or septic tanks, etc), the contaminant's properties and its fate, mobility and transport - all these should be known before designing a local groundwater quality monitoring programme. The recognition of effects on public and private drinking water supplies (e.g. aquifer depletion, groundwater contamination), irrigation return flow's effects on groundwater quality, groundwater salinization as a consequence of irrigation or overexploitation in coastal areas, etc., requires design of local monitoring networks. Local groundwater quality monitoring programmes are separated from other monitoring programmes. They usually operate temporarily and require a great density of sampling stations and a high sampling frequency of selected variables depending on the kind of existing and/or potential contaminants. An immediate redesign of the monitoring network based on contamination control is frequent. Easy access to the data bank and a fast procedure for record and data retrieval are highly desirable in local monitoring programmes.

The impact stations (by GEMS classification) of a local monitoring network serve for conjunctive measurements of quantitative as well as qualitative parameters. For monitoring the contaminant plume movement in the unsaturated zone, special screened boreholes supplement the monitoring network.

Monitoring boreholes are usually situated close to the pollution source and are often temporarily used for pollutant and polluted water removal. The continuous monitoring of certain variables is frequent and needed. Remote sensing methods, such as aerial photography, geobotany and geophysical measurements are being successfully used for local monitoring of the contaminant plume movement in an aquifer or for monitoring other phenomena sensitive to this methods.

5. GROUNDWATER QUALITY MONITORING SYSTEM AND METHODOLOGY

Different methods for the design of monitoring networks, and for data acquisition are used, depending on the objectives of monitoring. A simplified monitoring system is shown in the following diagram:

Delimitation of monitored area

Determination of hydro-
geological system's
characteristics

Identification of existing
and potential pollution
sources

Location of monitoring stations,
establishment of monitoring networks,
operational management

Data acquisition

Data transmission, processing and storage

Data retrieval and analysis

Data utilization for decision-making

Technical, administrative and legislative
implementation of protective measures

Steps and methods of groundwater quality systems were described by Tinlin and Everett (1978), Ward (1979), Everett (1983), EPA (1985), Van Duijvenbooden (1986), Vrba (1986) and others.

6. CONCLUSIONS

A groundwater quality monitoring programme is usually integrated or coordinated with other hydrological monitoring networks and interrelated with atmospheric, soil and other ecological monitoring programmes. Depending on the monitoring objectives, the integration of groundwater quality monitoring networks is not always needed. Independent and separate local and site specific detection monitoring programmes also satisfy many of the monitoring objectives. The conjunctive design of monitoring networks and multiple use of monitoring stations are recommended, primarily for financial reasons, but not always can they be applied. The data produced by monitoring activities serve for the long-term planning, strategy and policies of water resources, but also for immediate decision-making and control in groundwater protection and conservation or quality restoration. Only analyzed and applied monitoring data are beneficial for economic and social development. Groundwater quality monitoring is considered to be one of the important activities in groundwater preventive protection. It ranks among the technically most complicated and financially most demanding monitoring programmes of the hydrological cycle components. That is why the cost and benefits of information are always carefully compared and evaluated. The monitoring budget includes the input costs on the network design and the costs on the operational management of the monitoring system. The latter is, especially in regional and national networks with long-term activities, costly, and usually does not show immediate effectiveness or financial returns. On the other hand, the financial return of the expenditures on site specific monitoring programmes is generally quick, because the possible producers of contamination need the data, to anticipate or reduce the environmental problems.

At the time of economic depressions and financial constraints, the government authorities are increasing pressure for modification and reduction of the activities of national and regional monitoring programmes. Cost benefit studies considering the increasing value of monitoring data and information with time are desirable. Investment into the preventive protection of national groundwater resources, the monitoring activity included, usually without immediate financial returns, require a morally mature society and far-thinking governmental mechanisms.

The water sciences' task is to introduce and develop new methods for the design, operation and evaluation of monitoring programmes. This will help to decision an policy makers and water project managers. Representative data and information on the state-of-the-art and trends in the groundwater quality variations will support the selection of the optimum variants of the construction, operation and management of water projects.

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GROUNDWATER QUALITY MONITORING NETWORKS:
DESIGN AND RESULTS

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1. ABSTRACT

A proper design of monitoring networks requires well defined objectives and a lot of information on the area to be monitored. The establishment of the Dutch national groundwater quality network was finished in 1985. It consists of 370 measuring points. The main criteria for site selection were type and use of soil, and the hydrogeological situation. The network shows a severe human impact on the quality of groundwater: heavy impacts of agriculture on groundwater and a severe, still increasing acidification of groundwater. Besides, even in "natural" areas organic pollutants, like chlorinated hydrocarbons, toluene and xylene, can often be found in the groundwater.

2. INTRODUCTION

This paper deals with the design of groundwater quality monitoring networks. It will be illustrated on the basis of the Dutch national groundwater quality monitoring network. Some results will be presented. Attention will be given to the Dutch integrated networks on the quality of air, precipitation, soil and groundwater as well as the design of provincial networks connected with the national network. Finally some possible new developments will be indicated. More information on the design of networks can be found in (1, 2, 3).

3. DESIGN OF NETWORKS

The objectives of a proposed network and the area under consideration are always the starting point of the design of networks. Quality of groundwater is strongly related to hydrogeological conditions, type of soil and soil use. For this reason the first step in design of a groundwater quality monitoring network will be collection and interpretation of relevant data available in the area to be monitored. In this way it will be possible to distinguish several systems in the area with specific combinations of hydrogeology (seepage, infiltration, protective covering layers) type of soil and soil use. When necessary additional field research has to be carried out.

In general the establishment of a monitoring network is an expensive affair. For this reason it is often necessary to establish priorities. These priorities are mostly given to facts as vulnerability of groundwater to pollutants, intensity and nature of human activities, quality of groundwater and use of groundwater. Handling in this way most attention will be given to vulnerable areas with a lot of human activities and with groundwater important for water supply.

Expenditure can be reduced even more by optimum use of already existing monitoring points in the area. Mostly these points were drilled for other reasons, like groundwater level measurements. Owing to this, most of these points do not fulfill the requirements of a monitoring point for quality measurements. Particularly, when also organic and inorganic micropollutants have to be monitored, special attention is needed for a well done drilling, avoiding the intake of aquifer strange material via drillmud water or devices in the borehole and disturbance of subsoil. Furthermore a detailed description of the structure of the subsoil is needed. Most existing boreholes do not meet these requirements.

Sometimes, however, it is possible to establish a monitoring point for several networks. Combination will be possible for e.g.

- quality and quantity networks;
- local, regional, provincial and national networks.

Choice of parameters is strongly dependent on the nature of polluting sources and mobility, persistency, environmental and health aspects of the pollutants related to the situation in the areas to be monitored. In

this scope information has to be collected on type and nature of pollutants in the area and their behaviour in the subsoil.

In practice network density for the areas to be monitored is related to requirements of accuracy, which are amongst other things based on a political decision-making. Eventually a maximum and minimum desirable network density can be calculated or estimated. In this respect, in spite of the availability of statistical techniques that can be applied, an adequate technique to determine the optimal network density is not available.

Selection of measuring points depends on the type of network. In case of local networks these points have to be placed in the area possibly influenced by the polluted site (excluding some reference wells). In case of national or provincial networks primarily directed to diffuse sources of pollution, local polluting sources have to be avoided. In that case it will be of importance that the recharge area over the whole depth of the monitoring point is homogeneous with respect to hydrogeological situation, type of soil and soil use. Sometimes it will be possible to use the monitoring points for other purposes, e.g. safeguarding groundwater pumping stations, by some shifting in the location of monitoring points. Networks for safeguarding groundwater pumping stations require, after inventory of (potential) local and diffuse sources of pollution is made, a well-chosen location downstream of these polluting sources.

For the establishment of the optimum frequency of measurement no adequate techniques are available. In this respect there is also a relation to network density. In the first place frequency is related to groundwater velocity. So in the Netherlands with an average groundwater velocity of about 30m/year in general, a more frequent sampling than once or twice a year is not useful. Furthermore the risk of contamination plays an important role.

Other important factors for network design are:

- structure of monitoring points (e.g. location, number and length of well screens);
- way of sampling;
- quality control;
- data handling.

More information on these subjects is given in (3).

4. THE DUTCH NATIONAL GROUNDWATER QUALITY MONITORING NETWORK, DESIGN ASPECTS

In practice several types of monitoring networks can be distinguished, namely international, national, regional or provincial and local networks (3). An example of a national network is the Dutch national groundwater quality monitoring network. The network has been established during the period 1978-1984. The objectives of the network are:

- to make an inventory of the present quality in relation to soil use, type of soil and hydrogeological conditions;
- to distinguish long term changes in quality;
- to provide data for quality control and groundwater management;
- to indicate the extent of human influence on groundwater quality.

The network includes 370 monitoring points (1 per 100 km²) divided over the whole country with special emphasis on areas of importance for drinking water supply. Well screens are situated at about 10, 15 and 25 m-ls. The frequency of sampling is once a year. The basic programme of analysis consists of 19 parameters. Besides on ad hoc basis a lot of other parameters are analysed for special selections of monitoring points. For interpretation and presentation of data several computer programmes are developed. Total costs of establishment were Hfl. 7.000 per monitoring point, exclusive the necessary manpower of about 14 manyears for the establishment of the whole network. No already existing wells were used, partly due to the desired uniformity of monitoring points, partly because of the desired quality of the wells. All boreholes were drilled with the cable-tool drilling system.

Main criteria for site selection were:

- type of soil;
- land use;
- hydrogeological conditions.

For most important combinations enough monitoring points were selected to insure the availability of applicable mean values of most parameters and the possibility of trend analysis.

Secondary criteria for site selection were:

- geological conditions (due to the used sampling system no very deep

- groundwater levels; no very thick poor permeable covering layers);
- location of groundwater pumping stations;
 - property of the site;
 - accessibility of the site;
 - no influence of local pollution sources.

At least the wellscreen at 25m-ls is situated in the upper aquifer. Location of the wellscreen at about 10m-ls is a compromise between the desire for early measurement of pollution and to avoid very frequent sampling due to large quality variations in the very undeep groundwater. Also chosen length of wellscreen is related to this variability in combination with the possibility of short-circuit flow when using long well screens (1). The principle of the monitoring points is given in figure 1.

For Dutch conditions the system chosen made it possible to restrict frequency of sampling to once a year. This frequency is only concerned to the basic programme of analysis (table 1). Choice of these parameters is based on the nature of the network, which is directed to diffuse sources of pollution like air pollution and agricultural use of soil.

Fig. 1 Principle of the monitoring points of the Dutch national groundwater quality monitoring network

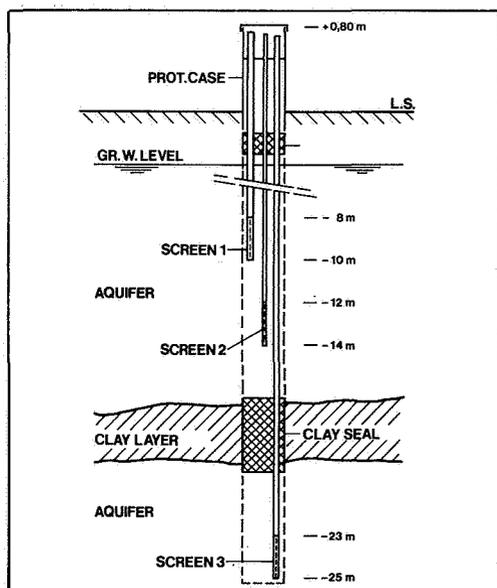


Table 1. Basic programme of analysis of the Dutch groundwater

Electr. conductivity	EC
Acidity	pH
Sodium	Na ⁺
Potassium	K ⁺
Magnesium	Mg ⁺⁺
Calcium	Ca ⁺⁺
Ammonium	NH ₄ ⁺
Bicarbonate	HCO ₃ ⁻
Chloride	Cl ⁻
Nitrate	NO ₃ ⁻
Sulfate	SO ₄ ²⁻
Total Phosphate	t.P.
Total Organic Carbon	TOC
Aluminium	Al
Arsene	As
Nickel	Ni
Zinc	Zn

Presentation of data occurs on different levels:

- individual presentation of data;
- yearly presentation of data on provincial level;
- presentation of statistical prepared data (relation with e.g. type of soil and land use, correlation and relation between parameters);
- mapping (graphical plot).

5. FIRST RESULTS OF THE NETWORK

First results of the network showed the close relationship between groundwater quality and type of soil and, especially in case of sandy soils, also the land use. This can be illustrated with tables 2 and 3. In these tables groundwater quality in the areas distinguished are related to groundwater quality in non-developed sandy regions. All average concentrations for the several parameters are divided by the concentration in the non-developed sandy soils.

Table 2. Relation between type of soil and groundwater quality at 10m-ls
(Cl⁻ < 200 mg/l)

parameter	sand natural	sand	peat low	clay river	clay sea
K ⁺	1	3.8	1.8	2.6	9.6
NH ₄ ⁺	1	4.8	15.3	8	35
NO ₃ ⁻	1	4.0	0.1	0.8	0.1
SO ₄ ²⁻	1	1.9	0.4	1.5	1.1
total P	1	3.0	6.0	6.0	17
Zn	1	1.6	0.4	0.4	0.4
As	1	1.7	1.0	4.0	1.0

All concentrations divided by the concentrations in natural sandy soils

Table 2 made clear that soil characteristics are of utmost importance for groundwater quality. In anaerobic areas relatively low concentrations on oxidized elements als NO₃⁻, SO₄²⁻ can be found, combined with high NH₄⁺-concentrations. The genesis of sea clay is reflected in K⁺, P and NH₄⁺-context. The absorption capacity of clay and peat is reflected in the concentration of heavy metals like Zn. Table 2 also indicates the effects of human activities in sandy regions. These are further indicated in table 3.

Table 3. Relation between land use and groundwater quality below sandy soils at 10 m-1s ($\text{Cl}^- < 200 \text{ mg/l}$)

parameter	natural areas	pasture land	arable land	urban areas
K^+	1	3.2	5.7	7.9
NO_3^-	1	1.1	12.7	4.9
Cl^-	1	2.5	3.1	4.3
NH_4^+	1	3.5	9.5	7
SO_4^{2-}	1	2.0	2.5	2.0
total P	1	3	6	6
Zn	1	2.2	2.0	1.0
Ni	1	1.1	1.9	0.9
As	1	1.9	2.2	1.4

All concentrations divided by the concentrations in natural sandy soils

At this moment especially NO_3^- and K^+ are of importance, due to the fact that in large areas in the Netherlands drinking water standards for these parameters (50 mg NO_3^- /l or 11.3 mg N/l and 12 mg K^+ /l) are exceeded.

At the moment 20% of all monitoring points in sandy regions at 10m-1s show an exceeding the drinking water standards for K^+ and NO_3^- . The average K^+ concentration below arable land is now 13 mg/l. Monitoring points in the sandy regions exceeding the K^+ standard are given in fig. 2. For NO_3^- the same holds true for figure 3. Table 4 shows mean nitrate concentrations for several areas and depths in 1981 and 1985. The table shows slowly increasing NO_3^- concentrations. Especially below arable land the groundwater is totally unsuitable for drinking water purposes. Figure 4 shows trends in nitrate for one of the monitoring points.

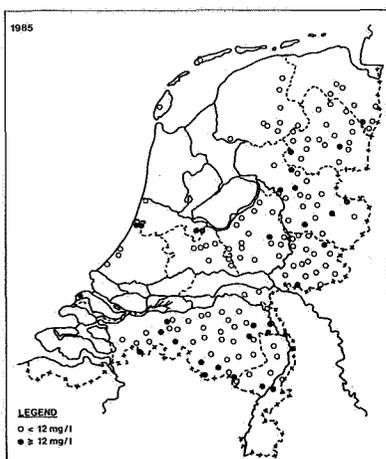


Fig. 2 Monitoring points of the Dutch groundwater quality monitoring network exceeding the drinking water standard for K^+

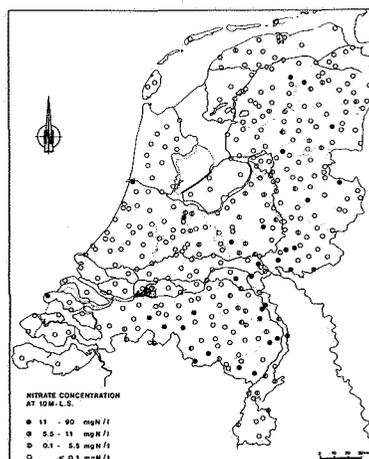


Fig. 3 Monitoring points of the Dutch groundwater quality monitoring network exceeding the drinking water standard for NO_3^-

Table 4. Average nitrate concentrations below sandy soils in mgN-1 (Cl⁻ < 200 mg/l)

	10 m-ls		25 m-ls	
	1981	1985	1981	1985
arable land	19	24	3,9	4,7
pasture land	1,7	3,2	0,4	0,7
natural areas	1,5	1,8	0,5	0,9

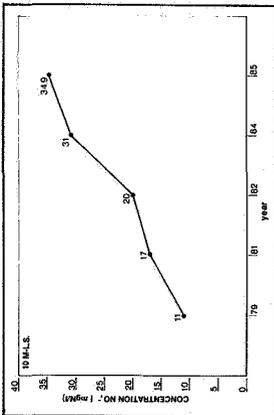


Fig. 4 National groundwater quality monitoring network trend nitrate concentration point 16

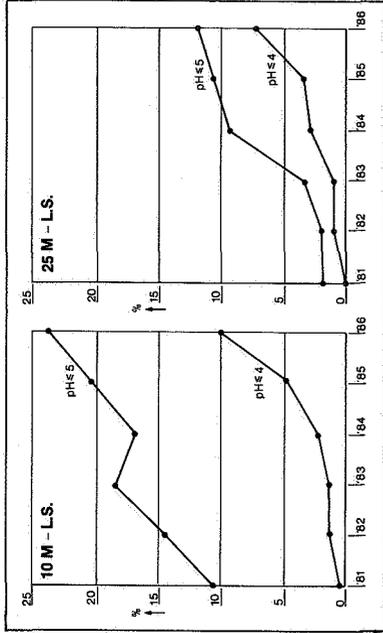


Fig. 5 Percentage of monitoring points of the Dutch groundwater quality monitoring network situated in sandy soils with pH ≤ 5 respectively ≤ 4 (210 monitoring points)

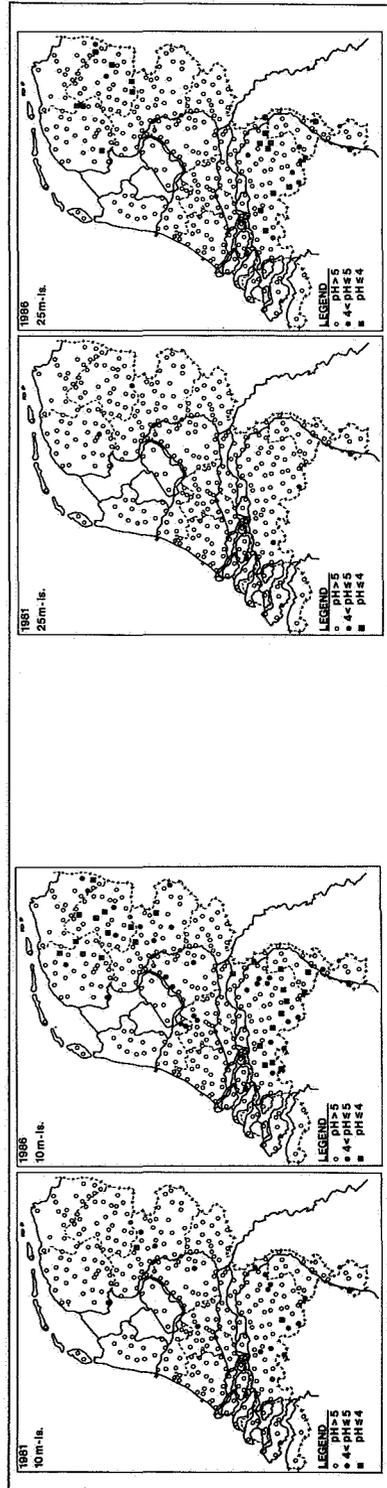


Fig. 6 Monitoring points of the Dutch national groundwater quality monitoring network with pH-values below 5 and 4

Of special concern are the still growing areas in The Netherlands with very low pH-values in the groundwaters. This trend is indicated in figure 5. At the moment about 10% of all monitoring points in the sandy regions are showing at 10m-ls a pH-value below 4. At 25m-ls this is 7.4%. The division of monitoring points with pH-values below 5 and 4 over the country is given in figure 6. These figures indicate that most acidificated regions can be found in the north-east and south of the country. These low pH-values are often accompanied by very high Al-concentrations in the groundwater. Concentrations are found of 10 and even more till 34 mg/l. Thus probably causing many problems in surface water and the drinking water supply. As shown by Arends et al. (8) mobility of many other inorganic micropollutants can also change.

Acidification of groundwater is not only found below sandy developed natural areas, but also in sandy agricultural regions. In fact most monitoring points with low pH-values are found in agricultural areas. Furthermore there is not only a strong correlation between lowering pH-values and increasing SO_4^{2-} -concentrations, but also with Na^+ and Cl^- thus indicating effects of agricultural use of soils.

Last year attention was also given to the possible presence of organic micropollutants in the groundwater. For this reason 40 monitoring points were selected, sampled and analysed on 15 phenols, 14 organic chloropesticides, 7 pcb's, 16 pah's, 20 chlorinated hydrocarbons and 6 volatile organic hydrocarbons. Only chlorinated and volatile organic hydrocarbons were detected in relatively high concentrations. Not only below urban regions but also in non-developed areas and agricultural regions these components could be found. Also bankfiltration by branches of the river Rhine could clearly be indicated in this way. Especially dichlorethene and tetrachloroethylene could be found widely spread in the groundwater; the same holds true for toluene and xylenes. Some quantitative information is given in table 5.

Polyaromatic hydrocarbons were generally found in concentrations from $< 0,01 - 0.05 \mu \text{g/l}$. All other micropollutants analysed were below detection limit.

Concerning the Dutch groundwaters it can be concluded that quality is far worse than expected. Many times the quality does not meet the

drinking water standards. In this respect land use is of great influence.

Table 5. Organic micropollutants ($\mu\text{g/l}$) found above detection limit in groundwater at 10 m-ls
Based on 40 monitoring points of the Dutch groundwater quality monitoring network

	pasture land 9 mon.points	arable land 6 mon.points	natural areas 6 mon.points	urban areas 13 mon.points	bank filtration 4 mon.points	det. limit
influenced mon. points	5	6	5	11	4	
benzene				2.9		0.5
toluene	1.0	1.8	0.5-0.6	0.6-1.6-6		0.5
ethylbenzene		0.6		0.1		0.5
xylenes	0.6	3.2	0.6	3.3-10		0.5
trichloroethene				0.5-1.8-20		0.1
tetrachloroethene	0.2		6-9	0.3-1.1-1.9-5500	0.2-0.2-2.0	0.1
chloroform	0.4	0.1-0.2	0.7	0.3-0.7	0.6	0.1
tetra				0.3		0.1
1,1,1 trichloroethane				0.1		0.1
1,1,2 trichloroethane				0.7		0.1
1,3 dichloropropane		0.7		0.2-0.5		0.1
1,2,3 trichloropropane		1.6-9				0.1
dichlorobenzenes					0.2-0.3-0.3	0.1
1,2 dichloroethane	0.2-0.4	0.5-0.5	0.3-0.6	0.1-0.2-0.2-0.3- 0.3-0.6	0.5-0.9-1.4- 1.8-3.0	0.1
mesitylene				2.6		0.5
alpha methylstyrene				2.0		0.5

6. FURTHER DEVELOPMENTS

Further developments in The Netherlands are expansion of the national groundwater quality monitoring network with some monitoring points in the deeper groundwater, the establishment of an integrated network directed to vegetation, air, precipitation, soil and groundwater and the establishment of provincial networks. Furthermore attention will be given to new sampling techniques.

The integrated network consists of 17 monitoring stations (see figure 7). These stations exist of a selection of monitoring points of the national networks for air and groundwater, the 13 monitoring points of

the national rain quality network and 40 locations of the national soil quality network under preparation. This soil quality monitoring network is directed to the 10 most important combinations of land use and type of soil. Of every combination 4 areas are selected in the vicinity of the monitoring stations of the integrated network. These 40 locations will be monitored every 2 years at 2 levels of depth. For every location and depth mixed samples will be analysed on heavy metals, pesticides and pcb's. Every mixed sample will consist of about 40 samples. First sampling and analyses will take place in the second part of 1987.

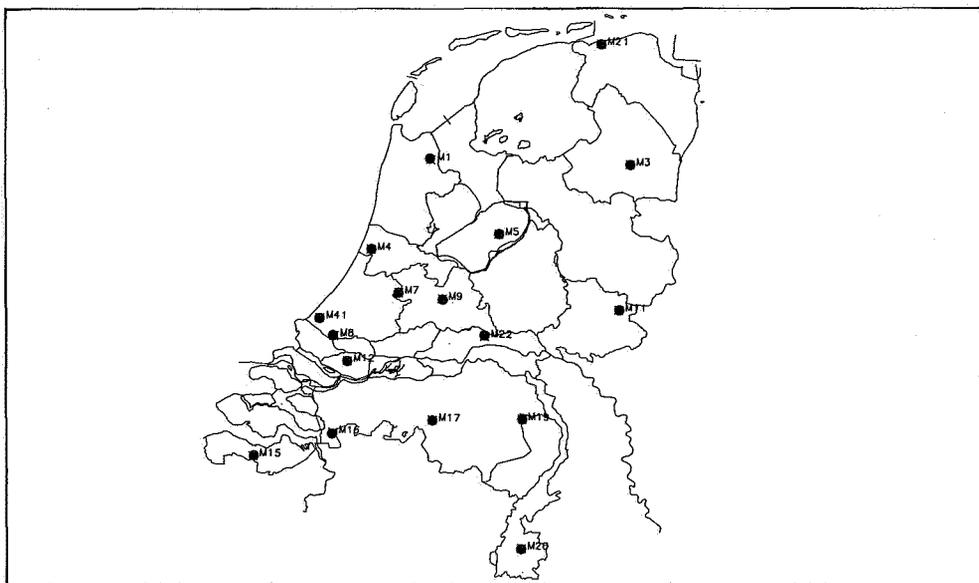


Fig. 7 Locations of the Dutch integrated network

Also a first step has been made in the development of provincial networks in the Netherlands. Basically these networks have the same objectives as the national networks. In future it will be possible that all provincial networks together form a new national groundwater quality monitoring network, with the original 370 monitoring points as key-points. Especially interesting are the developments in the province of Gelderland. With the 60 monitoring points of the national network as key points a provincial network is designed. Starting point in the design has been the necessity to get the same reliability when interpreting the data in the sandy soils of the province as in the sandy soils in the whole country. This could be approached with the help of statistical techniques (6).

Future developments in the Netherlands will be the drawing up of monitoring strategies in the recharge areas and protection zones around groundwater pumping stations. In this scope inventory of local and diffuse sources of pollution in these areas are of importance. Local monitoring networks are widely spread in the country around local polluting sources. In the scope of this paper these networks will not be taken into consideration separately.

In general, sampling procedures do not get the attention given to analysis. In many cases that reduces the value of the results of analysis considerably. Besides, sampling is a very time consuming occupation. For this reason it is necessary to give a lot of attention to the development of standardized sampling procedures and the development of new, simple and quick sampling techniques. In this scope recent developments in Israel, based on the dialysis membrane technique, can be of importance (7).

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THE QUALITY OF GROUNDWATER ABSTRACTED BY THE WATERWORKS
IN THE NETHERLANDS

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ABSTRACT

The abstracted water of all the wellfields of the waterworks in the Netherlands has been analyzed for the presence of purgable organic compounds by means of purge and trap GC/MS. Volatile organics were only considered present if their concentration exceeded 0,1 µg/l. In this research a total of 33 organics has been identified, many of them only once.

The results of this inventory have been evaluated with respect to the geohydrological situation of the wellfield. In total five different geohydrological situations have been distinguished: the upper aquifer, deeper aquifers, bankfiltrate, artificially recharged surface water and limestone aquifers. Large differences in groundwaterquality were observed.

The purgable organics present had quite different origins, i.e. naturally occurring compounds, products from disinfection, pollutants and intermediates of (bio)transformation from pollutants.

1. INTRODUCTION

In the Netherlands 99,9 % of the population is connected to the public watersupply. About 70 % of the drinking water is prepared from groundwater. These numbers already indicate the importance of the quality of groundwater for the public watersupply. For this reason the abstracted groundwater in all the wellfields of the waterworks has been analyzed for the presence of purgable organics. This information is also relevant to the government, as the abstracted groundwater is more or less representative of the quality of a large body of groundwater. To gain insight into the vulnerability of wellfields, the results of these analyses have been evaluated with regard to the geohydrological situation.

The results described in this contribution have been reported elsewhere in more detail (Veenendaal et al, 1986).

2. GROUNDWATERABSTRACTION

The greater part of the Netherlands consists to a great depth of unconsolidated sediments. These sediments are built up of aquifers, consisting of rather fine grained sands, and aquitards, more or less permeable layers consisting of clay, loam or peat. In the Netherlands groundwater is abstracted at about 250 wellfields for the public water supply. An "average" wellfield abstracts about $3 \cdot 10^6 \text{ m}^3/\text{y}$ and consists of 12 to 15 wells. The abstracted water is discharged into a raw water line which conveys the water to a treatment plant. In the treatment plant iron, manganese and ammonium are removed by aeration followed by filtration. There are only a few wellfields where the abstracted groundwater can be distributed as drinking water without any treatment. With respect to geohydrology it is possible to distinguish several systems: 1. abstraction from the uppermost aquifer (A); 2. abstraction from a deeper aquifer covered by an aquitard (B); 3. abstraction near the major rivers of a mixture consisting of groundwater and infiltrated surface water (C). The modal residence time of the infiltrated surface water varies between 0,5 to more than 10 year (Stuyfzand, 1985);

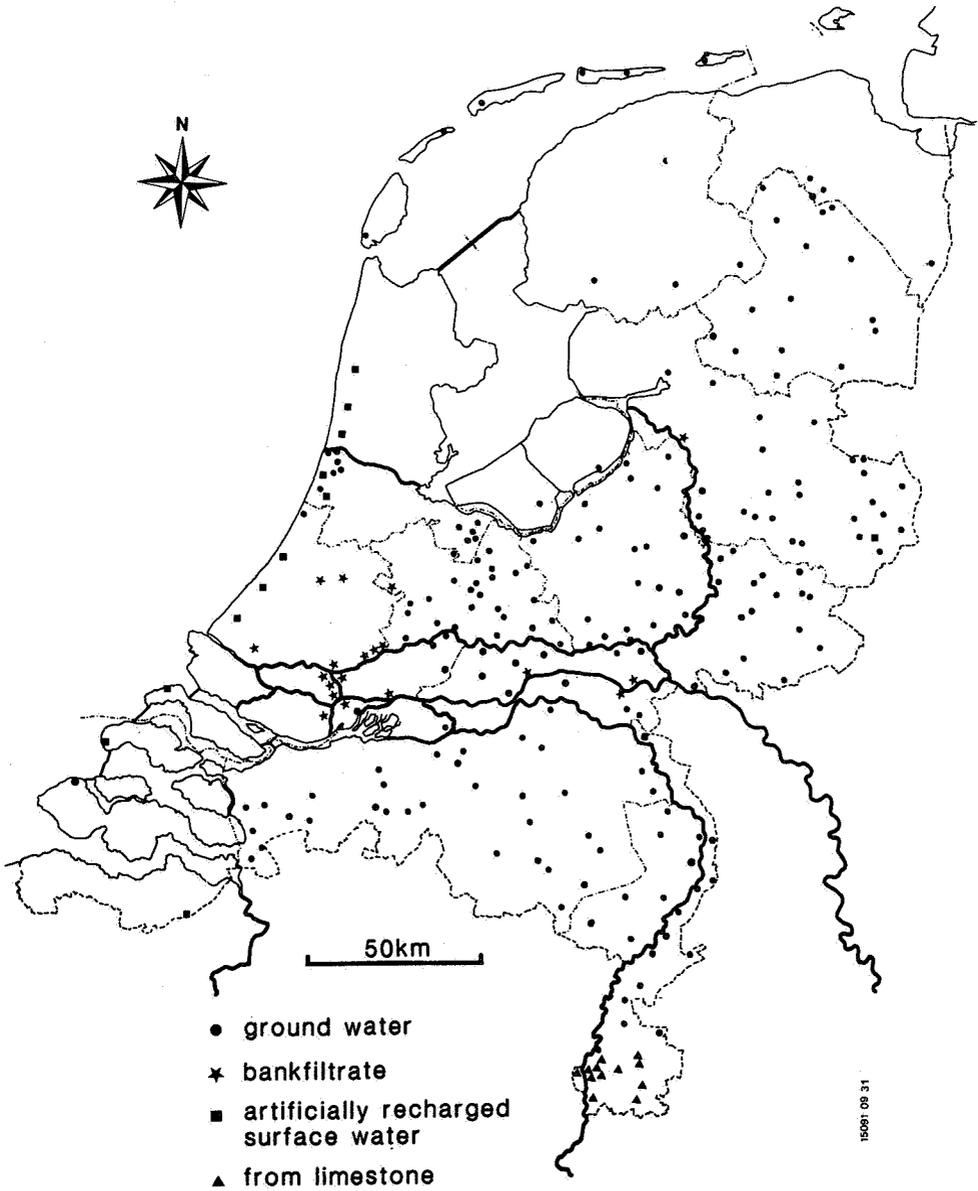


Figure 1: Location of the wellfields, exploited by the waterworks in the Netherlands. The symbol denotes the type of the wellfield.

4. abstraction of groundwater consisting for the greater part of artificially recharged surface water (D). This practice is particularly employed in the dune area near the coast. The modal residence time of the artificially recharged surface water is about 2 months (Stuyfzand, 1986); and 5. abstraction from limestone (K). The location of the wellfields is presented in Figure 1. At several wellfields more than one aquifer is exploited, most often by different wells, but sometimes by one well. This situation is demonstrated more explicitly in Figure 2.

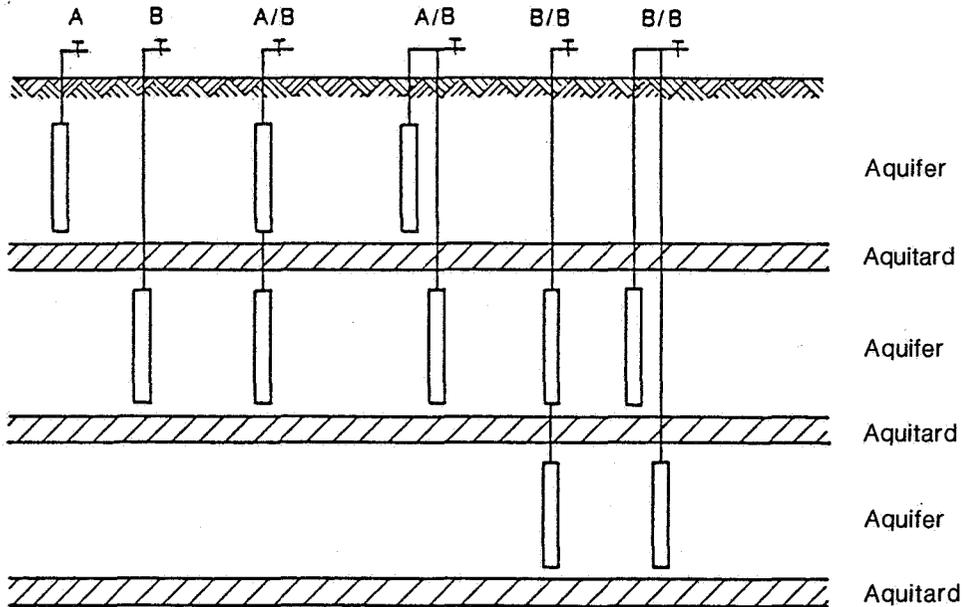


Figure 2: Subdivision of the wellfields exploiting unconsolidated aquifers. If the sampled water originates from one aquifer, the wellfield is symbolized by one capital; if more aquifers are involved two capitals have been used.

The wellfields abstracting from unconsolidated aquifers have been further subdivided based upon the resistance (coefficient of leakage, c) of the aquitard on top of the aquifer. This subdivision is summarized in Table 1.

Table 1: Geohydrological classification of wellfields abstracting from unconsolidated aquifers, covered by a less permeable layer

Resistance of less permeable layer (days)	Abstraction from shallow deeper aquifer aquifer		Explanation
$c < 250$	A1	B1	less permeable layer is not present or presents hardly any protection
$250 \leq c < 2.500$	A2	B2	less permeable layer includes probably weak spots
$2.500 \leq c < 10.000$	A3	B3	less permeable layer may contain weak spots
$c \geq 10.000$	A4	B4	less permeable layer is considered impermeable

From Table 1 it may be deduced that the distinction between A and B is not always clear. A sequence consisting of alternating thin aquifers and aquitards may also be considered as a complex aquitard.

In cases where the wellfield could not be classified as one geohydrological situation the following rule was applied; first the situations C, D and K were set aside, and then A/B and B/B situations were classified according to the more vulnerable situation, eg. A1/B4 as A1.

3. SAMPLING

Each wellfield was sampled once. All samples have been taken from the raw water line just before the treatment plant. The sampling has been done with the utmost care to prevent escape or introduction of purgable organics. Each sample was taken from a smoothly free flowing tap into a bottle, which was allowed to flow over for a few minutes. Moreover,

escape is minimized as most wells are equipped with a submersible pump. Usually not all wells of a wellfield are in simultaneous production. This means that the sample is a composite of the wells connected to that raw water line operating on the moment of sampling. Water is supplied to a wellfield by its recharge area, and each well of that wellfield is supplied by its own part of that recharge area. This may result in not detecting the presence of a pollutant if the contaminated well is not producing during the sampling.

At some wellfields the presence of pollutants is known. During this research, however, the pollutant was not present in the abstracted water, because the water abstracted by the polluted wells is diverted from the supply and is after treatment either flushed to surface water or recharged again. Also interceptor wells may be sunk between the source of the pollution and the production well involved, followed by the same procedure.

At some wellfields several, up to 14, raw water lines convey the abstracted water to the treatment plant. In this case a sample was taken at each line; in the laboratory up to three samples were randomly composited.

At several wellfields which exploit more than one aquifer, it was possible to sample each aquifer separately. In such cases, the wellfield was considered as consisting of two wellfields. At some wellfields clusters of wells are separated by some distance. If permitted by sampling conditions these clusters were considered as separate wellfields. All these considerations led to a total of 305 samples from 243 wellfields.

4. CHEMICAL ANALYSIS

The analysis of the purgable organic compounds has been carried out by purge and trap GC/MS. In this technique volatile lipophilic compounds are purged from the sample at 95 °C and trapped on Tenax. A condenser (10 °C) is placed between the purge vessel and the Tenax to remove the watervapor. Thereafter the components are analyzed with gas chromatography/mass spectrometry. In this way lipophilic compounds with

a boiling point between about 30 and 160 °C can be identified and quantified. The compounds that can be analyzed in this way, are summarized in Table 2.

Table 2: Summary of compounds that can be analyzed by purge and trap GC/MS.

- aliphatic hydrocarbons with 5 to 12 C atoms
- aromatic hydrocarbons, like
 - monoaromatics: benzene to C5-benzene
 - diaromatics: naphtalene to C2-naphtalene
 - indane, indene
- aliphatic ketones, ethers, alcohols with 4 to 6 C atoms
- ethyl- and propylacetate, methyl- and ethylbenzoate
- aromatic oxygen compounds, like
 - benzaldehyde and C3-C4 phenols
- aromatic halogenated compounds, like
 - mono-, di- and trichlorobenzenes and -toluenes
- aliphatic halogenated compounds like
 - di-, tri-, and tetrahalogenated methanes, -ethanes, -propanes, -ethenes and -propenes
- chlorinated ethyl- and (iso)propylether
- terpenoids like
 - di-isopropene structures
- sulphur compounds, like
 - CH₃SCH₃ to C₃H₇S₄C₃H₇ thio-ethers
 - C₂ to C₄ mercaptans

From Table 2 it is clear that very volatile compounds like chloroethene (vinylchloride), bromomethane (methylbromide) and chloromethane (methylchloride) cannot be analyzed in this way.

Of the identified compounds only the concentrations exceeding 0,1 µg/l have been reported. Compounds identified and quantified between limit of detection and this concentration have been reported as less than 0,1 µg/l.

The precision of the purge and trap GC/MS method depends upon the concentration, boiling point and polarity of the compound, but varies between 20 and 50 %. The absolute amount of compounds present below the limit of analysis (0,1 µg/l) amounts to 25 to 50 ng. Regarding these very small amounts their presence in the groundwater was not considered proven by only one analysis. Presence of these low concentrations can only be confirmed by repeated sampling.

5. RESULTS

The results of the chemical analyses of the purgable organics are summarized in Table 3. In total 33 volatile organic compounds with concentrations exceeding 0,1 µg/l have been identified, many of them only once.

The identified organics may originate from very different sources. Terpene may have a natural origin (Lalonde, 1984) and tetrahydrothiophene is a marker gas added to natural gas before distribution.

Schwarzenbach et al (1986) describe the formation of volatile sulphur compounds from volatile halogenated alkanes under anaerobic conditions in the presence of hydrogen sulfide. They, however, do not describe the formation of dimethylsulfide.

During chlorination trihalomethanes may be produced. The presence of these compounds, like bromodichloromethane, may be considered as an artifact resulting from the disinfection of a well with chlorine shortly before sampling. However, the presence of trichloromethane (chloroform) was known in the abstracted water of several wellfields before the start of the inventory, and its presence should be considered as a pollution. Chloroform was also found at unexpected locations. Some of these wellfields were resampled but analysis did not confirm its presence. As a consequence the results of this research have to be evaluated carefully with regard to chloroform and the other trihalomethanes.

Table 3: Summary of the number of samples exceeding 0,1 µg/l of the denoted purgable organic, subdivided with regard to geohydrological situation (-: not present)

Type of wellfield	upper aquifer				lower aquifer								total
	A1	A2	A3	A4	B1	B2	B3	B4	C*	D**	K***		
Number of samples	113	25	4	2	21	25	30	20	20	20	25	305	
Benzene	4	2	-	-	-	-	1	-	3	-	-	10	
Toluene	2	2	1	-	-	3	3	1	1	-	1	14	
Ethylbenzene	1	-	-	-	1	-	-	-	-	-	1	3	
Dimethylbenzene	11	2	-	-	2	4	-	1	4	1	6	31	
Dichloroethene	2	-	-	-	1	-	-	-	13	-	-	16	
Trichloroethene	15	2	-	-	3	4	-	4	6	2	4	40	
Tetrachloroethene	2	-	-	-	1	-	-	-	1	-	-	4	
1,2-Dichloroethane	4	-	-	-	1	-	-	-	11	-	-	16	
1,1,1-Trichloroethane	1	-	-	-	1	-	-	-	-	-	-	2	
1,1,2-Trichloroethane	-	-	-	-	1	-	-	-	-	-	-	1	
1,2-Dichloropropane	3	-	-	-	-	-	-	-	2	2	-	7	
Trichloromethane	15	-	-	-	1	-	1	2	1	-	3	23	
Bis(chloro(iso)propyl)ether	-	-	-	-	-	-	-	-	15	-	-	15	
Methyldioxolane	1	-	-	-	-	-	-	-	5	-	-	6	
Methylethyldioxolane	-	-	-	-	-	-	-	-	3	-	-	3	
Diisopropylether	-	-	-	-	-	-	-	-	4	-	-	4	
Dichlorobenzene	-	-	-	-	-	-	-	-	8	-	-	8	
Bromodichloromethane	-	-	-	-	-	-	-	-	-	-	1	1	
Chlorodibromomethane	-	-	-	-	-	-	-	-	-	-	1	1	
Tribromomethane	-	-	-	-	-	-	-	-	-	-	1	1	
Aldehyde C8-C10	1	-	-	-	-	-	-	-	-	-	-	1	
Terpene C10H16	-	-	-	-	-	-	3	-	-	-	-	3	
Tetrahydrothiophene	1	-	-	-	-	-	-	-	-	-	-	1	
Dimethylsulphide	1	-	-	-	-	-	-	-	-	-	-	1	
1,2,3-Trichloropropane	1	-	-	-	-	-	-	-	-	-	-	1	
N-undekane	1	-	-	-	-	-	-	-	-	-	-	1	
Pentylbenzene	1	-	-	-	-	-	-	-	-	-	-	1	
Methylpentanon	1	-	-	-	-	-	-	-	-	-	-	1	
Dipropoxyethane	-	1	-	-	-	-	-	-	-	-	-	1	
Tetrahydropyrane	-	-	-	-	-	-	-	-	2	-	-	2	
C10H20 isomeres	-	-	-	-	-	-	-	-	-	-	1	1	
Tetrachloromethane	1	-	-	-	-	-	-	-	-	-	-	1	
Paraldehyde	-	-	-	-	-	-	-	-	1	-	-	1	

*C mixture of groundwater and bankfiltrate

**D artificial recharge of surface water in the dunes

***K limestone

6. DISCUSSION

From Table 3 it is apparent that only 7 compounds occurred more than 10 times, i.e. trichloroethene 10x, dimethylbenzenes (xylenes) 31x, trichloromethane (chloroform) 23x, dichloroethene 16x, 1,2-dichloroethane 16x, bis(chloro(iso)propyl)ether 15x and toluene 14x. Table 3 also shows the highest frequency of the presence of purgable compounds in wellfields abstracting (partly) bankfiltrate. Several purgable compounds are only present in bankfiltrate, but not in all samples. During recent years the quality of surface water has improved, perhaps explaining their absence in some wellfields. Compared to bankfiltrate the waterquality of the wellfields in the dune area, where surface water has been recharged, is very good. This phenomenon may be ascribed to several causes. During periods of very poor quality of surface water the intake is closed. Moreover the surface water is aerated in the initial stage of infiltration and, as already mentioned, the quality of the surface water has improved during recent years. The wellfields C and D are mainly recharged by surface water, the wellfields A, B and K are recharged directly by precipitation. In order to compare their quality, the frequency of occurrence of the purgable organics present 5 times or more, is summarized in Table 4. In this table the wellfields have been grouped according to degree of natural protection: wellfields with less natural protection, i.e. A1, B1 and A2, the wellfields with more natural protection, i.e. B2, A3, B3, A4 and B4 and limestone wellfields.

From Table 4 it is clear that toluene is under represented in the wellfields with less natural protection, but the other compounds are normally or over represented. In the wellfields with more natural protection all compounds are normally or under represented, with the exception of toluene. Assuming that the load of pollution around the wellfields is comparable, this difference in occurrence of toluene on the one hand and benzene and xylenes on the other is remarkable. The difference in natural protection is confirmed by comparing the ratios of the occurrence of type of wellfield and the presence of the various pollutants: except for toluene this ratio is always less for more protected wellfields.

Table 4: Frequency distribution of the purgable organic compounds, 5 times or more present, over the wellfield situations recharged by precipitation (-: not present).

Type of well-field	Number of well-fields	Fraction of the well-fields	Fraction of the indicated purgable organics present in the various wellfield situations					
			benzene	toluene	xylenes	tri-chloro-ethene	1,2-di-chloro-ethane	tri-chloro-methane
Total number	265		7	13	26	32	5	22
A1+B1+A2 B2+A3+B3+	159	0,60	0,86	0,31	0,58	0,63	1,0	0,73
A4+B4	81	0,31	0,14	0,62	0,19	0,25	-	0,14
K	25	0,09	-	0,08	0,23	0,13	-	0,14

There are various reports that describe the (bio)transformation of volatile organic compounds, eg the transformation of tetrachloroethene to trichloroethene to dichloroethenes to chloroethene and chloroethane (Barrio-Lage et al 1986). Bouwer and McCarty (1983) describe the almost complete oxidation to carbondioxide of trichloromethane, tetrachloromethane, 1,1,1-dichloroethane, 1,1,2,2-tetrachloroethane and tetrachloroethene and other compounds under methanogenic conditions. The situation with regard to the limestone wellfields is more complicated. The total number of wellfields is considerably smaller than the two situations distinguished with respect to natural protection and at least in one case disinfection products have been identified (see Table 3). However only xylenes seem to be over represented. The evaluation of these results with respect to groundwaterquality for the waterworks is complicated. There are clearly differences in natural protection against purgable organic compounds between the distinguished situations of wellfields, but these differences in natural protection seem not identical, not even within the group of purgable organic compounds. Moreover groundwater abstracted at wellfields with less natural protection will be younger than at more protected wellfields. It may be that these purgable organics have not yet reached the wellfield; but a more or less longer traveltime may not be confused with vulnerability. The same reasoning holds for the time that will elapse

before the effect of corrective actions will become visible. Vulnerability has only a meaning in conjunction with mobility and persistence, that means that longer traveling times coincide with greater possibilities for (bio)degradation to harmless natural compounds.

7. CONCLUSIONS

In total 33 purgable organic compounds have been identified and quantified. The origin of these compounds may be very different: natural compounds, intermediates of (bio)transformation, disinfection products and pollutants.

Vulnerability is not simply related to geologic structure. It may refer to the time necessary for a pollutant to reach a wellfield. However from this inventory it becomes clear that all volatile organic compounds do not behave identically. Vulnerability has only a meaning if a pollutant during its movement to a wellfield is (bio)transformed to natural compounds.

This investigation does not necessarily result in a complete inventory. It was known that at several wellfields measures have been taken to divert pollutants. Moreover there is an, admittedly small, chance that pollutants have not been detected because at the moment of sampling the wells abstracting polluted water were not in production.

ACKNOWLEDGEMENT

The research described in this paper was carried out in accordance with the research program of the Netherlands Waterworks' testing and research institute KIWA Ltd, as appointed by the Netherlands Waterworks Association, VEWIN. The research was funded by the Department of Public Housing, Physical Planning and Environment.

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COMBINED USE OF A NEW NEUTRON AND GAMMA-GAMMA PROBE FOR
MONITORING THE WATERMOVEMENT WITHIN CONTAMINATED SOILS

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ABSTRACT

The advantage of the neutron probe for measuring the soil moisture is its simple application, the disadvantage is the great effort of the calibration. Therefore a new calibration method, the differences method, was developed when the neutron probe was used on a testing area within a three layer waste site covering system. This method is fast and does not need any soil sample for calibration. It is based on the concept of determination of the wet density differences between two measurements with the gamma density probe. The measured wet density difference equals the difference in volumetric water content and results the gradient of the calibration line by simultaneously measuring of the neutron probe count rate. Hence, for each sphere of importance an own calibration is determined which takes in account all soil characteristics like inhomogenities, boundaries of the bed or variation of bulk density. The used RAYMESS gamma-gamma probe is newly developed and specially furnished for the combination with the WALLINGFORD neutron probe. The influence of photon absorber (Z_{eq} -effect) on the count rate is eliminated by certain setting of the detector response, the Z/A-correction for water is taken in consideration.

1. INTRODUCTION

The use of the Neutron moisture probe is a common method to determine the water content of the soil. When monitoring the change in water content during a certain time period, the water movement within soils, like covering systems of contaminated sites, is easy to control.

During a research project concerning the effectiveness of soil covering systems, a new and easy method for the calibration of the neutron moisture probe has been developed and applied successfully. This method is described in the following paper.

2. THE USE OF THE NEUTRON MOISTURE PROBE

The neutron probe method for measurement of soil water content is a widely used technique because it is fast and non-destructive. A great difficulty is to obtain the correlation between the relative count rate and the volumetric water content of the soil.

In the simplest case a calibration recommended by the producer or some intermediate compromise can be used (USER'S HANDBOOK). These straight line equations give only a rough estimation of the water content. For measurements where a higher accuracy is necessary, calibration is usually performed in the field by taking undisturbed core samples. A number of these samples should be obtained over the seasonal range of the water change.

The calibration can also be done by taking disturbed soil samples in a soil of known bulk density. The bulk density can be determined from the wet density measured with a gamma density probe.

3. THE USE OF THE GAMMA DENSITY PROBE

The use of a gamma density probe requires also the determination of a calibration curve. Contrary to the common opinion there is not just one calibration curve. The count rate depends on the nature of the soil. Mainly the following factor occur, which affect the response of the probe: scattering of photons by collision, energy decrease (COMPTON-effect) and photoelectric absorption (Z_{eq} -effect after CZUBEK 1966).

These three effects superpose additively, considering the count rate, in the decreasing part of the calibration curve (see Figure 1).

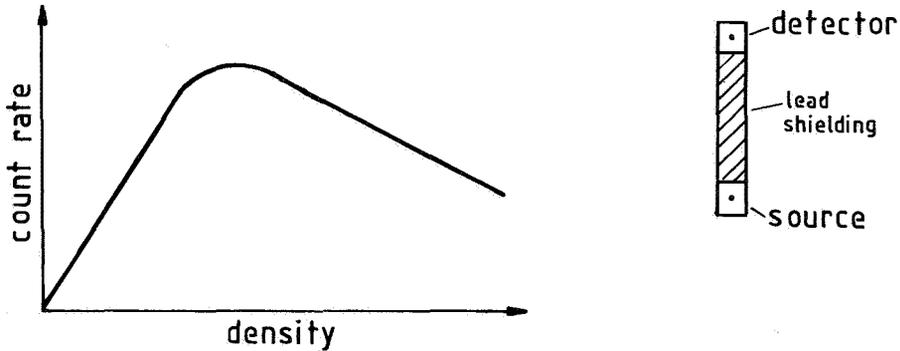


Figure 1. Principle calibration curve by given detector-source geometry

As shown by CHRISTENSEN (1974) the response of the probe depends on the presence of strong photon absorbers in the soil (for example lime). This could also be proved in the preliminary tests in loess sand mixtures in the testfield.

Since the effect of the photoelectric absorption occurs mainly with low detection energies, it can be erased by reducing the detector response. This fact was considered by the development of the RAYTEST probe. Moreover the gamma density probe is especially furnished for the combination with the WALLINGFORD IH II neutron probe. It can be used with the rate-scaler of the neutron probe by simple exchange of the probe tube.

4. CALIBRATION BY THE DIFFERENCES METHOD

A gravimetric field calibration is an expensive and time consuming procedure, since altogether 8 different soil mixtures are used on the testfield. Therefore a new calibration method, the differences method, was developed when the neutron probe was used within a three layer waste site covering system. The method is based on the concept of the

determination of wet density differences between two measurements with the gamma density probe. The measured wet density difference equals the gradient of the calibration line by measuring of the neutron probe count rate simultaneously (see Figure 2).

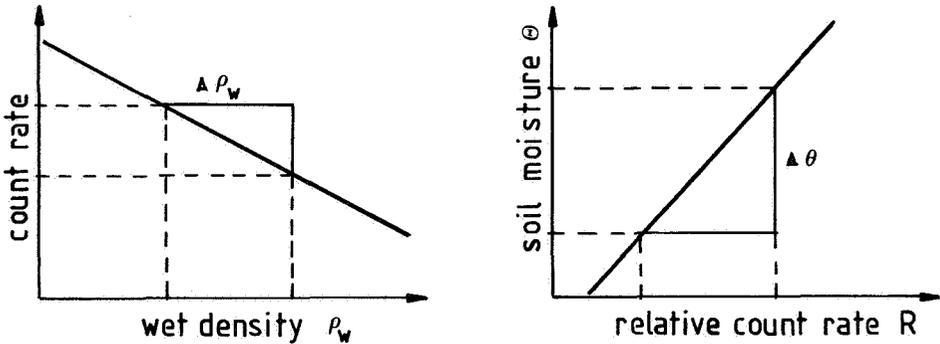


Figure 2. Relationship between wet density difference and moisture difference

This may be expressed as follows

$$\Delta \theta = \left| \rho_{w2} - \rho_{w1} \right| \times 1.113 \quad (1)$$

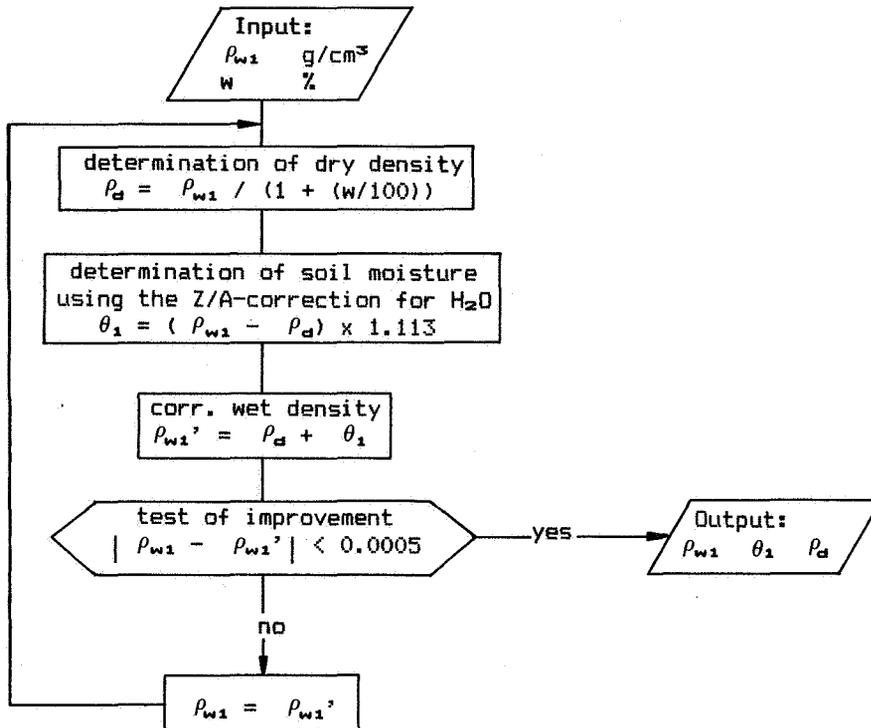
where $\Delta \theta$ is the difference in volumetric water content, ρ_{w1} and ρ_{w2} are the wet densities measured at two different times and 1.113 is the correction factor for water (Z/A-correction). This correction must be applied, because the relation between the electron and mass densities of water, which equals the Z/A-ratio, does not have the usual value of 0.499, but 0.555.

The count rate of the neutron probe, R , is linearly related to the volumetric water content. Therefore the gradient of the line, m , can be calculated

$$m = \Delta \theta / \left| R_2 - R_1 \right| \quad (2)$$

when R_1 and R_2 are the relative count rates measured in field. With the gradient of the calibration line the change in water content

between successive time intervals can be monitored. If, however, the absolute value of the volumetric water content is necessary, the intercept, c , on the y axis of the calibration line can be calculated by the following iteration:



where w is the water content per gram of the oven-dry soil, which was determined by taking disturbed soil samples of every counting depth, when drilling the bore-hole for the access tube with the hand auger. The result of the iteration is the dry density ρ_d , the wet density ρ_{w1} and volumetric water content θ_1 for the first measurement of neutron probe count rate. The gradient and intercept of the line will then be calculated by the results of a second measurement (see equation 1 and 2):

$$c = \theta_1 / (m \times R_1) \quad (3)$$

It is the advantage of the differences method, that the calibration considers automatically all inhomogeneities of the soil even though they are unknown (for example: differences of the bulk density, clay lenses,

boundaries of the layers. The inhomogenities mainly affect the gradient of the calibration line.

5. APPLICATION OF THE DIFFERENCES METHOD

This new method has been applied to several types of soil covering systems. The aim of our efforts was to evaluate the amount of seepage water through a cover consisting of three layers, 1.5 m soil cover, 0.5 m compacted clay and 0.3 m sand filter (HÖTZL & WOHNLICH 1985). Especially the influence of several soils used as vegetative support layer should be tested.

The ability of each soil is tested during a period of 2 years by modeling the soil water balance (WOHNLICH 1987). This model requires accurate values of the volumetric water content as one input parameter. Figure 3 shows that a considerable deviation occurs with the soil moisture if different calibration methods are used.

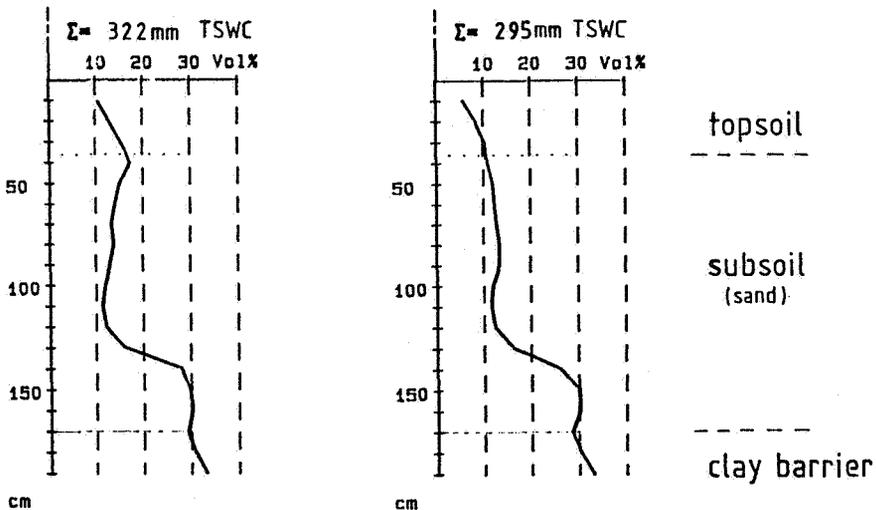


Figure 3. Comparison of two calibration methods (see text)

The left profile has been determined by the differences method. Especially at the boundaries of the layers a better resolution can be read.

The right profile was determined by the adoption of the WALLINGFORD calibration lines and shows a smoother curve. At the boundaries of subsoil to subsoil and subsoil to the clay barrier this method results in completely different values. This effects a deviation up to 10% of the total soil water content (TSWC).

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EVALUATION AND DESIGN OF COMBINED NETWORKS
FOR GROUNDWATER POLLUTION MONITORING

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ABSTRACT

A methodology for designing a combined groundwater pollution monitoring network considering both monitoring accuracy and cost is presented. The monitoring scheme consists of a combination of surface geoelectrical measurements and monitoring wells. Geophysical interpretation, geostatistics, and multicriterion decision making are used to estimate the prediction error for a given monitoring scheme and to select the cost-effective monitoring design. This selection is performed by a trade-off analysis using composite programming considering the cost of monitoring and the prediction accuracy criteria for selected locations within the plume.

1. INTRODUCTION

The purpose of this paper is to present a methodology for designing a groundwater pollution monitoring network considering both monitoring accuracy and cost. The monitoring scheme consists of a combination of surface geoelectrical measurements and traditional monitoring wells. Methods of geophysical interpretation, geostatistics, and multicriterion decision making are used to estimate the prediction error for a given monitoring scheme and to select the cost-effective monitoring design.

Surface electrical measurements cannot completely substitute for monitoring wells and as a consequence, pollution predictions based on surface geoelectrics alone are generally not possible and in any case would be very uncertain. This paper aims at quantifying this uncertainty and finding the "best" observational schemes which we propose would be a proper combination of direct and geophysical measurements.

2. SURFACE GEOELECTRICS TO MAP GROUNDWATER POLLUTION

Electrical methods respond directly to the resistivity or conductance of ground water which can in many cases be directly related to the degree of ground water pollution (Fried, 1975, Todd, 1980). Since both the soil material and the saturating fluid influence aquifer resistivity, it is convenient to characterize soil electrical properties by their formation factor defined as

$$FF = \rho_s / \rho_w \quad (1)$$

where ρ_s is the resistivity of the saturated soil-water mixture, and ρ_w is the water resistivity. Formation factor can in turn be related to soil porosity n using Archie's Law

$$FF = n^{-m} \quad (2)$$

where m is a constant - about 1.5 for sands. When the soil contains significant amounts of clay, the relation between formation factor and porosity at high water resistivities includes a dependence on matrix resistivity. In pollution studies, the resistivity of the water will generally be low enough to allow Equation 2 to be used.

Since soil properties exhibit spatial variability (both stochastic and deterministic), formation factor cannot be constant even under constant aquifer geometric conditions. As a consequence, we use Equation 1 to calculate ρ_w from electrically measured ρ_s and statistically known FF in the form

$$\frac{\rho_w}{\sim} = \frac{\rho_s}{\sim} / \frac{FF}{\sim} \quad (3)$$

where \sim means random variable.

Thus, the prediction error for water resistivity is influenced by both the uncertainties in aquifer resistivity and formation factor.

The illustrative example, based on the study by Kelly (1976), has a relatively simple geology which can be represented by a three-layer geoelectrical model - topsoil, unsaturated zone, saturated zone. Variations are assumed to be due mainly to variations in the resistivity of the third layer. Saturated zone resistivities are determined from profiling data using a calculated relationship between apparent resistivity (profiling resistivity) and layer resistivity for the three layer model representing site conditions (Kelly, 1976).

In the example, several combinations of field data are considered: average specific conductances (SC) at a relatively small number of regularly spaced monitoring wells, aquifer resistivities estimated from profiling measurements at the well locations, aquifer resistivities determined at a relatively large number of locations from profiling measurements, locations include well locations, and additional measurements at irregularly located points.

3. SPATIAL ANALYSIS OF POLLUTION PLUMES

Pollutant movement in aquifers is governed mainly by advection and dispersion-diffusion (Fried, 1975). These processes are controlled mainly by the distribution of aquifer hydraulic properties which generally exhibit geostatistical properties (Neuman, 1983; de Marsily, 1984), that is, they can be assumed to have a deterministic component (drift), and a spatially correlated stochastic component. As a consequence, the distribution of specific conductance in a plume will also exhibit geostatistical properties: the deterministic component is assumed to correspond to the governing advection - dispersion - diffusion process, while the stochastic component, corresponds to a spatially correlated noise term.

The geostatistical analysis starts with the fitting of a trend surface to the available data points. However, this fitting should not be a least-square fitting since then the residuals cannot be considered to be spatially correlated. In the example we used a linear function of distance from the pollution source.

In the next step residuals from the trend are statistically analyzed.

Figure 1 shows the histogram for resistivity corresponding to 87 resistivity measurements.

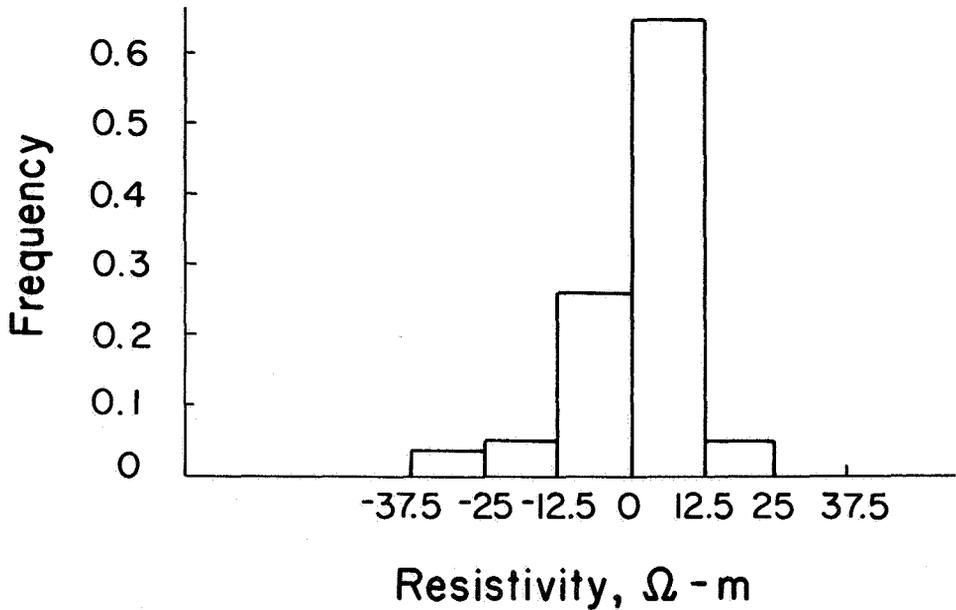


Figure 1. *Histogram of residual resistivity*

Variograms are used to study the spatial correlation of the observations, Figure 2 shows the variogram for residual resistivity.

The variograms are used with kriging techniques to construct the contour map of specific conductances characterizing the extent and intensity of pollution. As an example, Figure 3 shows the contour map estimated from 87 resistivity measurements.

For the maps, the error is characterized by the estimation standard deviation which is calculated by geostatistics. An important part of the analysis is the calculation of errors for all possible measurement

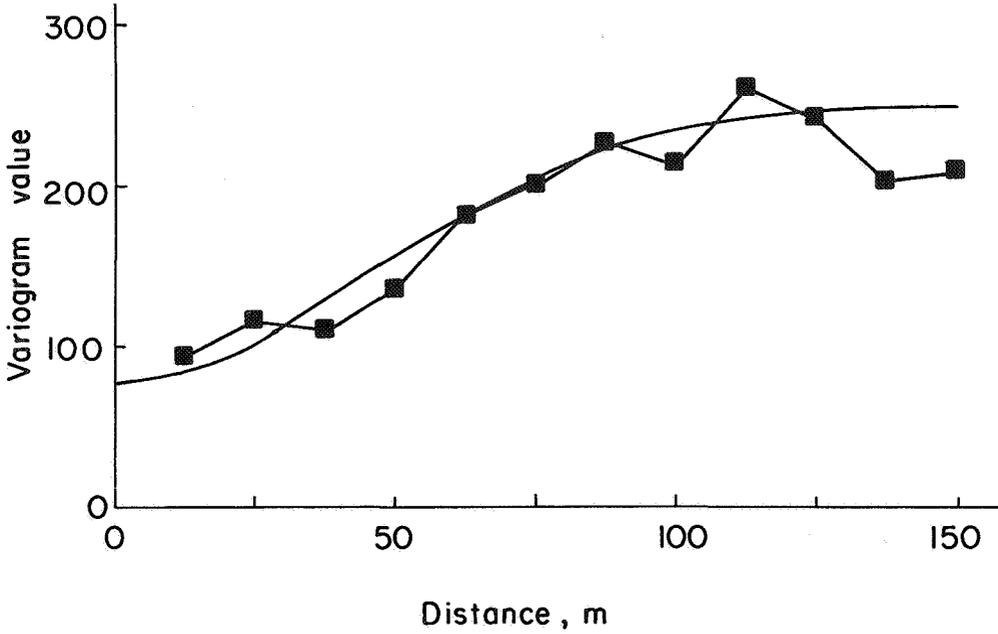


Figure 2. Gaussian residual variogram of resistivity

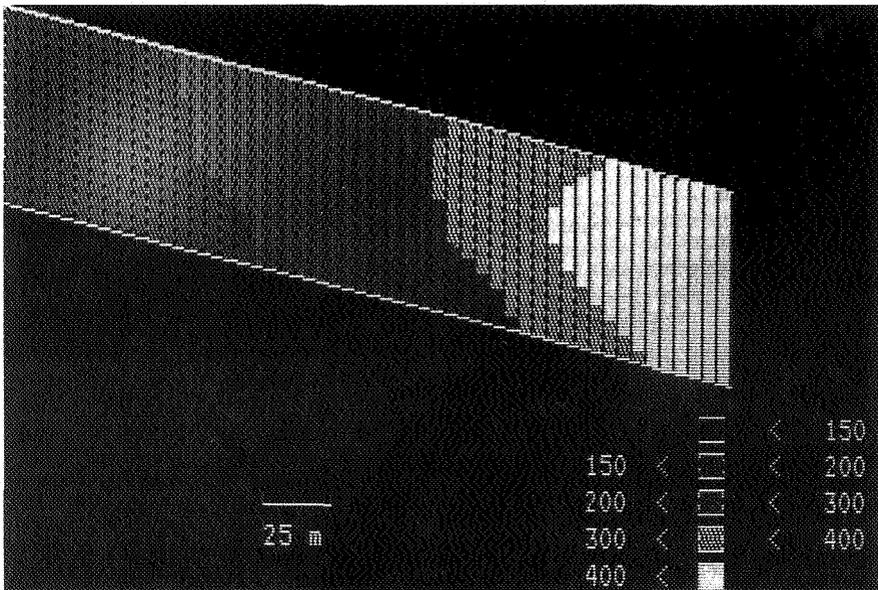


Figure 3. Map of groundwater specific conductance based on 87 resistivity measurements

combinations (Bardossy et al., 1986, Kelly et al., 1986). Figure 4 is the error map for 87 resistivity measurements.

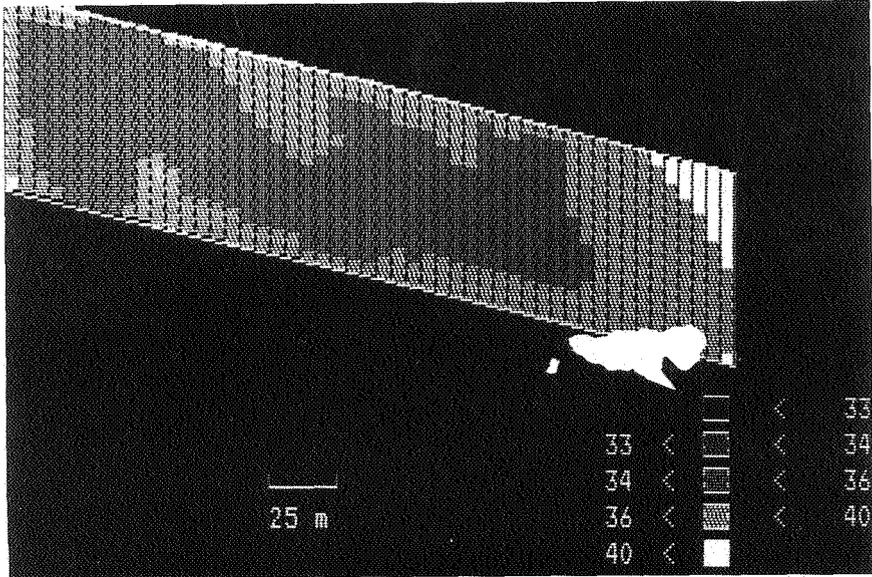


Figure 4. Error map for specific conductances defined from 87 resistivity measurements

4. MONITORING NETWORK DESIGN

Monitoring network design as a Multicriterion Decision Making (MCDM) problem considers the following interrelated factors: 1) observational effort (cost, time, instrumentation); 2) relative importance of the parameters to be measured; 3) the different geostatistical properties of the parameters, 4) estimation error criteria for the various parameters, and 5) loss or disutility function related to uncertain information. The two sets of objectives are 1) to minimize the criteria related to estimation error and 2) to minimize the criteria related to the observation effort with due regard to their relative importance and geostatistical properties. These are conflicting sets of objectives. The geostatistical methodology outlined in the previous section makes it possible to determine those areas where additional measurements

(monitoring well and geophysical) would be necessary to improve prediction accuracy. In fact, an error map (Figure 4) indicates such areas, in this example the estimation error is higher where the gradient of specific conductance is higher, that is, close to the pollution source. In addition to this evaluation technique a mathematical programming method is proposed. Here the question to be addressed is to find the "best" combination of the available types of measurements.

The observation network can be represented by three decision variables:

T - the area covered by one station, that is the reciprocal of station density,

a - the average distance between two stations, measured along the network orientation,

ϕ - the azimuth of the network orientation

In the simplest case two networks are defined: a monitoring well network and a geoelectric network. The accuracy of plume prediction can be characterized by a set of estimation variances for SC. The simplest case is to consider an average estimation variance while the most complicated one is to consider the entire areal distribution. Certainly, there will be locations, within a plume where a higher prediction accuracy is needed. It is assumed that a number K of estimation variances are selected to characterize the plume. For any k , $k=1, \dots, K$, the variance is a function of the decision variables: $T_1, T_2, a_1, a_2, \phi_1, \phi_2$. Thus one set of objectives refers to

$$\min_{k=1, \dots, K} \sigma_k(T_1, T_2, a_1, a_2, \phi_1, \phi_2) \quad (6)$$

where I is the number of locations where the prediction error criteria is considered.

The second set of objectives refers to the minimization of the observational effort characterized, here as a typical example, by a composite criterion, the cost of the two networks, which increases with the density of stations T_1^{-1} , T_2^{-1} . One thus seeks to consider as the second set of objectives:

$$\max T = t_1^{-1} \cdot T + t_2^{-1} \cdot T \quad (7)$$

where t_1^{-1} and t_2^{-1} are the unit costs.

For calculation of the estimation variances a geostatistical model can be developed as shown for a single type and error free observation network in Bogardi et al. (1985).

For the selection of the best networks (T_1 and T_2) a compromise is sought which is the closest by some distance measure, or metric, to the ideal one. To this end, the trade-off relationship between the cost of measurements and the corresponding average estimation standard deviation is shown in Figure 5.

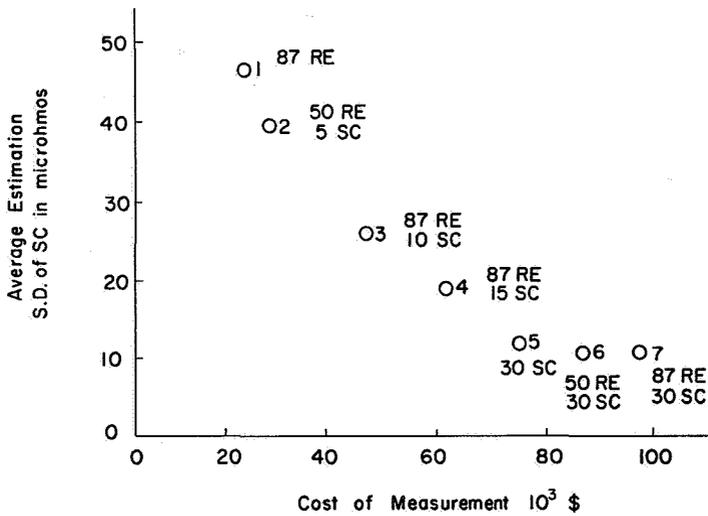


Figure 5. Trade off between the cost of measurement and the average estimation standard deviation for a plume

For this example, the unit cost of resistivity measurements is taken as \$260 and the unit cost for monitoring wells is \$2500.

The trade-off between measurement cost and estimation error (Figure 5) indicates that not much can be gained in terms of prediction accuracy beyond data combination 5 but the cost would be much higher. Also, it can be concluded that if the importance of measurement cost and plume prediction accuracy is about the same, the "best" observational scheme would be 3 or 4. The programming method outlined makes it possible to analyze a much larger set of measurement schemes and to consider an areally distributed prediction error criteria instead of the average one used to illustrate the principles of the proposed method.

5. CONCLUSIONS

A methodology has been outlined for design of cost-effective monitoring networks for groundwater contamination.

From this paper the following conclusions can be drawn:

1. Results of groundwater pollution monitoring from surface geoelectrics and monitoring wells can be combined using geostatistics.
2. In addition to predicting the degree of pollution, the prediction error, characterized by the estimation standard deviation, can be calculated for any possible measurement combination.
3. Cost-effective monitoring schemes can be identified considering the cost of monitoring, and prediction error at selected locations within a plume.

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INVESTIGATION AND EVALUATION OF THE GROUNDWATER
CONTAMINATION POTENTIAL OF WASTE DISPOSAL SITES

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ABSTRACT

Waste deposits constitute a potential hazard to groundwater. Owing to the great number of known sites a methodological concept for the detection and separation of problematic sites from the multitude of suspected ones is needed. Groundwaters up- and down-gradient of 35 abandoned and presently operated waste disposal sites were thoroughly analyzed and results subjected to comprehensive statistical treatment. Findings were used to develop and test the investigation scheme. In this hierarchically structured scheme by a first - low cost - step the presence of leachate in groundwater can be detected and its nature can be roughly qualified. Then at given conditions more detailed analytical procedures are to be employed until the information gathered allows an assessment of the waste impact on groundwater of an investigated site. The scheme proved to be satisfactory for a wide range of abandoned and presently operated waste disposal sites. Of 35 investigated sites 9 showed no considerable groundwater impact, contamination in 10 cases was considerable, in 9 cases serious and in 7 very serious.

1. INTRODUCTION

Until the passing of the Federal Waste Disposal Act in 1972 an estimated 30.000-50.000 abandoned waste disposal sites had been in use in the Federal Republic of Germany. About most of these and many others presently operated there are no sufficient records concerning the nature of the disposed wastes, especially whether hazardous materials were deposited. Considering the hazard potential of these sites the groundwater contami-

nation potential is the most important effect. In some cases gaseous emissions (vinyl chloride), dusts and smoke of fires or direct contact on the site (workers, playing children) must be taken into account. However, the latter risks are fairly easily recognized and remedial action is no greater problem.

The groundwater contamination potential can be subdivided into the acute leachate resulting in a plume in the groundwater and a latent potential (possible barrel corrosion) which only in a few cases - i.e. where knowledge about content and locality of barrels can be gained - will be of practical interest.

Besides possible 'normal' groundwater contaminations caused by household and construction refuses serious groundwater pollutions e.g. by chemical wastes probably exist in numerous cases.

Since in the FRG groundwater is the main source of drinking water (>70%) strategies are sought which allow to identify and to monitor the influence of hazardous waste deposits on groundwater and give sufficient informations for risk assessment and remedial action plans.

2. DEVELOPMENT AND STRUCTURE OF THE METHOD

Within a pilot projekt involving abandoned and presently operated waste disposal sites in a selected area in Northern Germany with pleistocene sediments, the Institute for Water-, Soil- and Air-Hygiene of the Federal Health Office has developed a hierarchically structured method for systematic recording of problematic sites involving groundwater hazards (Table 1). This method is composed of several investigational steps: Preliminary investigation, screening (first analytic step), analysis of problematic substances (second analytic step), detailed examinations (third analytic step) and evaluation of findings (Kerndorff et al., 1985; Arneth et al., 1986).

At the stage of preliminary investigation, available documentation must be evaluated and the hydrogeological situation of the site be established. In view of the subsequent hydrochemical examinations, there should be a search for data on a possible disposal of special wastes from defined types of production, above all by local industries. In addition to analysis by general criteria, it is recommended to perform a specific

Table 1. Method for investigation and separation groundwater-endangering waste sites

Pre-investigation	-collection, evaluation and interpretation of existing data of a site (incl. targets) -registration and characterization of the hydrogeological situation			
Screening (1. analysis step)	inorganic Boron Sulfate ↓ household construction refuse waste	organic AOX GC-fingerprints ↓ chemical wastes x-containing x-free (x=halogen)		
Analysis of problematic substances (2. analysis step)	Group 1 (Group D, EC)	inorganic 1. priority: As, Cd, Cr, Ni, Pb, Cu 2. priority: Be, Hg, Sb, Se, V... (targets)	organic halogen containing group 1 Dichloromethane Trichloromethane Tetrachloromethane 1,1,1-Trichloroethane Trichloroethene Tetrachloroethene	halogen free group 1 Benzene Toluene Ethylbenzene Xylene Isopropylbenzene
	Group 2 (Group C, EC)	1. priority: Cu, Zn, Fe, Mn, NO ₃ , NH ₄ , TOC 2. priority: NO ₂ , F, Co, Ba, Ag... (targets)	group 2 1,1-Dichloroethane 1,2-Dichloroethane 1,1-Dichloroethene Tribromomethane Chlorodibromomethane Chlorobenzene	group 2 Di-n-butylphthalate Diethylphthalate Bis(2-ethylhexyl)phthalate Naphthalene 2-Methylphenol
Detailed investigations (3. analysis step)	e.g. additional and auxiliary analyses (GC-MS, HPLC...) biotests (Microtox), sediment investigations (organic, inorganic) more intensive hydrogeological investigations...			
Hygienic evaluation assessment of contamination	- abundance and concentration of serious hygienic or toxic substances - effective areas, hazard potential/risk decision			

search for substances being characteristic of these wastes (target substances).

Owing to the variety of possible contaminants, there is a principal need for a hierarchic analytic system, commencing with the proof of a hydraulic contact between the deposit and the groundwater and in the event of positivity, enabling a stepwise delimitation of possibly present problematic substances.

The presence of groundwater contamination may be demonstrated by screening using boron and sulfate as inorganic and AOX (adsorbable organic halogen compounds) and GC-(gaschromatographic-)fingerprints as organic parameters. At the same time it is possible to establish a first principal characterization of contamination as being due to the influences of domestic refuse (boron), construction waste (sulfate) and/or organo-chemical wastes (AOX, GC-fingerprint).

Where screening has been positive, an examination for problematic substances (analysis of problematic substances) becomes necessary. Such examination should include the most important - statistically confirmed - inorganic and organic substances. Among inorganic substances, these are

toxic and/or undesirable ones as listed in the EC Directive (European Communities, 1980) and/or German Drinking Water Regulation (BMJFG, 1986), among the organic ones specific substances demonstrated to occur frequently in the groundwater downstream of disposal sites and proved to be of environmental relevance.

It is the purpose of the second analytic step to separate problematic sites. Only these should be subjected to the third analytic step comprising more intensive examinations so that after a detailed evaluation the necessity of remedial actions can be established where this is indicated.

In the absence of special criteria for the assessment of groundwaters, their contaminations are estimated by the presence and the concentration of hygienically hazardous substances, e.g. by comparison with the limit values given in legislation on drinking water, taking into account the prevailing situation with regard to the utilization of such waters.

3. APPLICATION OF THE METHOD AND RESULTS

3.1 Characteristics of sites investigated

35 sites in pleistocene and non-pleistocene unconsolidated sediments and in solid rock aquifers in the Federal Republic of Germany and Berlin (West) were studied. Volume and composition of the wastes showed a very wide range of variation including construction waste, domestic refuse as well as large tips of mixed wastes, even including special industrial wastes. The method described was used to evaluate the contamination situation at the individual sites. At the sites examined partially extreme contents of inorganic and/or organic contaminants have been found strongly influencing the groundwater.

3.2 Characterization of the effects of leachates from waste disposal sites on the groundwater constituents

The substances which have penetrated into groundwater dissolved in leachates produce considerable changes in the composition of groundwater

Table 2. Statistical parameters of constituents from uncontaminated and contaminated groundwaters

		uncontaminated					contaminated by waste disposal sites					mean contaminated mean uncontaminated mean value of cont. factor
		min	mean	max	std.-dev.	n	min	mean	max	std.-dev.	n	
temperature	°C	9.3	10.6	14.2	1.1	18	8.7	11.7	17.2	1.8	90	1.1
Eh-value	—	15	180	350	123	13	-8	177	490	97	66	1.0
pH-value	—	5.5	6.7	7.4	0.5	18	4.2	6.8	8.9	0.6	90	0.8
conductivity	µS/cm	83	506	740	176	18	227	1900	30000	3790	90	3.8
HCO ₃	mg/l	203	214	227	12.1	3	145	439	2260	356	42	2.1
SO ₄	mg/l	12.1	72.5	138.5	38.6	18	0.8	223	1630	303	90	3.1
Cl	mg/l	3.2	27.3	63.1	16.2	18	14.7	243	3680	504	90	8.9
NO ₃	mg/l	< 0.5	6.6	31.4	11.5	18	< 0.5	173	11500	1242	90	26.2
NO ₂	mg/l	< 0.2	< 0.2	1.3	0.3	17	< 0.2	0.4	7.4	1.2	72	> 1.8
F	mg/l	< 0.1	< 0.1	0.12	0.64	3	< 0.1	0.26	0.73	0.2	42	> 2.6
Br	mg/l	< 1	< 1	< 1	—	15	< 1	< 1	5	0.7	46	1.0
PO ₄	mg/l	< 0.5	< 0.5	< 0.5	—	17	< 0.5	1.7	75	9.7	68	> 3.4
CN	µg/l	<10	<10	<10	—	2	<10	<10	20	4.0	27	1.0
K	mg/l	0.6	1.0	1.2	0.3	3	0.7	27	330	65	40	27.0
Na	mg/l	< 5	9.6	21	6.4	18	< 5	140	1520	246	90	14.6
Ca	mg/l	< 5	90	138	32	18	22	185	840	151	90	2.1
Mg	mg/l	< 2	8.1	21	5.4	18	< 2	36	252	22	90	4.4
NH ₄	mg/l	0.12	0.19	0.25	0.09	2	< 0.05	11.8	155	32	27	62.1
Fe	µg/l	546	6990	24200	7835	17	<10	10400	172000	23600	81	1.5
Mn	µg/l	19	498	1350	481	18	<10	2020	24700	3750	89	4.1
Sr	µg/l	<40	147	430	104	18	<40	465	6350	745	90	3.2
As	µg/l	< 2	3.2	25	6.3	17	< 2	109	1930	360	70	34.1
Pb	µg/l	< 2	3.4	27	7.3	17	< 2	17	336	55	76	5.0
Cd	µg/l	< 0.2	< 0.2	0.6	0.14	16	< 0.2	1.3	19	3.6	74	> 6.5
Ni	µg/l	< 5	9.4	16	5.6	17	< 5	28	330	49	89	3.0
Zn	µg/l	10	36	95	24	17	<10	170	2620	417	82	4.7
Cu	µg/l	< 5	5.8	43	10.9	18	< 5	27	373	64	90	4.7
Cr	µg/l	< 5	< 5	8.0	2.5	18	< 5	25	1710	180	90	> 5.0
B	µg/l	<20	<20	27	11.5	18	<20	1270	31200	4420	90	>63.5
TOC	mg/l	1.3	1.7	2.1	0.4	3	1.1	13.3	71	19	42	7.8
AOX	µg/l	<10	<10	<10	—	18	<10	270	5360	808	88	>27.0
ECD area	—	8.4	29.5	58.5	13.7	17	3.8	99	873	170	67	3.4
ECD number of peaks	—	4	6.5	10	1.7	17	2	7.1	24	4.4	67	1.1
FID area	—	0.7	2.5	10.0	2.7	15	0	13.6	210	33.5	61	5.4
FID number of	—	1	1.4	3	0.7	13	0	3.7	16	4.0	44	2.6
Trichloroethene	µg/l	< 1	< 1	1.6	0.4	18	< 1	22	850	108	88	>22.0
Tetrachloroethene	µg/l	< 1	< 1	4.7	1.1	18	< 1	2.8	170	18	88	> 2.8
sum volatiles	µg/l	< 1	< 1	4.7	1.2	18	< 1	25	1025	124	88	>25.0

constituents. The level of the (mean) contamination factor (CF), i.e. the relationship of the mean values of the influenced and uninfluenced groundwater can be considered as a measure of the influence exerted by a substance (Table 2).

In 82% of the parameters studied, contamination factors of >2 indicate a specific influence exerted on groundwater by the deposited wastes. From the number of inorganic parameters, above all, boron, ammonium, arsenic, potassium and nitrate have shown extreme contamination factors while among the organic ones, these were the purely anthropogenic contaminants AOX, total volatiles and trichloroethene.

3.3 Evaluation of the groundwater contamination

When comparing the mean values of unaffected groundwaters with the maxi-

imum acceptable concentration (MAC) and guide levels (GL) of the EC Directive (Table 3) relating to the quality of water intended for human consumption, it is seen that these groundwaters are of drinking water quality, apart from relatively high geogenic iron and manganese contents (>EC-MAC) and values for conductivity, sulfate and chloride above the EC-GL.

Table 3. Mean values of uncontaminated and by waste sites contaminated groundwater samples in comparison with European Community guide levels (GL), maximum acceptable concentrations (MAC) and German drinking water thresholds

	mean uncontaminated	mean contaminated	EC-GL	EC-MAC	GDW Th ⁴⁾ (10/86)
temp. °C	10.6	11.7	12	25	25
Eh- value -	+180	+177	-	-	-
pH- value -	6.7	6.8	6.5-8.5	-	6.5-9.5
condu. µS/cm	506	1900	400	-	2000
HCO ₃ mg/l	214	439	-	-	-
SO ₄ mg/l	73	223	25	250	240
Cl mg/l	27	243	25	-	-
NO ₃ mg/l	6.6	● 173	25	50	50
NO ₂ mg/l	< 0.2	● 0.4	-	0.1	0.1
F mg/l	< 0.1	0.26	-	8-12°C: 1.5 25-30°C: 0.7	1.5
Br mg/l	< 1	< 1	-	-	-
PO ₄ mg/l	< 0.5	1.7	P ₂ O ₅ : 1.4	5.0	-
CN µg/l	<10	<10	-	50	50
K mg/l	1.0	● 27	10	12	12
Na mg/l	9.6	140	20	175	150
Ca mg/l	90	185	100	-	-
Mg mg/l	8.1	36	30	50	50
NH ₄ mg/l	0.19	● 11.8	0.05	0.5	0.5
Fe µg/l	● 6990	● 10400	50	200	200
Mn µg/l	● 498	● 2020	20	50	50
Sr µg/l	147	465	-	-	-
As µg/l	3.2	● 109	-	50	40
Pb µg/l	3.4	17	-	50	40
Cd µg/l	< 0.2	1.3	-	5	5
Ni µg/l	9.4	28	-	50	50
Zn µg/l	36	170	100	-	-
Cu µg/l	5.8	27	100	-	-
Cr µg/l	< 5	25	-	50	50
B µg/l	<20	1270	1000	-	-
TOC mg/l	1.7	● 13.3	2	5	5 ¹⁾
AOX µg/l	<10	270	-	-	-
Tr1 µg/l	< 1	22	1	-	-
Per µg/l	< 1	2.8	1	-	25 ²⁾
Σ v ³⁾ µg/l	< 1	25	-	-	-

● exceeding of EC-MAC
 □ exceeding of EC-GL

1) COD (KMnO₄)
 2) Trichloroethene(Tr1)+Tetrachloroethene(Per)+1,1,1-Trichloroethane+Methylenchloride
 3) volatiles (2) + Carbontetrachloride +Chloroform+ Bromochloromethane
 4) German Drinking Water Threshold

In affected groundwater, however, values exceeding the EC-MAC and/or GL were found for numerous parameters. Most prominent were ammonium (mean 24xMAC; >MAC 70%, <MAC 30%), nitrite (mean 3.6xMAC; >MAC 11%, <MAC 89%), nitrate (mean 3.5xMAC; >MAC 12%, <MAC 88%), TOC (mean 2.7xMAC; >MAC 57%,

<MAC 43%), potassium (mean 2.3xMAC; >MAC 33%, <MAC 67%), arsenic (mean 2xMAC; >MAC 20%, <MAC 80%). Guide levels were surpassed for trichloroethene (mean 22xGL; >GL 46%, <GL 54%), chloride (mean 10xGL; >GL 94%, <GL 6%), sulfate (mean 9xGL; >GL 93%, <GL 7%), sodium (mean 7xGL; >GL 73%, <GL 27%), conductivity (mean 4.8xGL; >GL 96%, <GL 4%), tetrachloroethene (mean 2.8xGL; >GL 38%, <GL 62%), calcium (mean 1.9xGL; >GL 68%, <GL 32%), zinc (mean 1.7xGL; >GL 17%, <GL 83%), boron (mean 1.3xGL; >GL 13%, <GL 87%) and magnesium (mean 1.2xGL; >GL 34%, <GL 66%).

When looking into maximum concentrations found in the affected Groundwaters, even considerably higher levels in excess of MAC or GL may be found in individual cases. Such extremes were present, above all, for arsenic (39times) and chromium (34times).

For most organic compounds, there are no legal limit values permitting an evaluation of the contaminations found. As a consequence, such compounds could not be evaluated in the present study.

Furthermore, no GL and MAC for the assessment of groundwater contaminations exist. In a recent research program financed by the Federal Ministry of Research and Technology 'reference values' based on statistical and toxicological data shall be elaborated to provide a standardized and more objective risk assessment.

3.4 Statistical evaluation of data

Quite comprehensive data to characterize the effects of disposal sites on groundwater were developed and evaluated statistically. These examinations including even substances which were not directly needed for the separation of problematic sites permitted the elaboration of valid statements for broad fields.

With the aim to analyse and evaluate the huge data set a special databank based on the databank management system SIR (Scientific Information Retrieval) was developed. Utilized statistical techniques had been frequency distributions, correlations, factor analyses, discriminant analyses and cluster analyses (Schleyer et al., this volume). Frequency distributions show the possible spectrum of contamination for special parameters from which objective reference values may derive. An example is given by the comparison of frequency distributions of the screening pa-

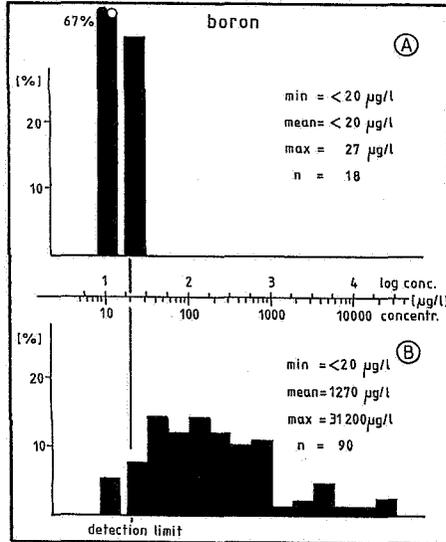


Figure 1. Frequency distributions of boron concentrations in groundwaters, uncontaminated (A) and contaminated by waste sites (B)

parameter boron in uncontaminated and contaminated groundwaters (Figure 1). It shows an almost ideal case in which the distributions slightly overlap so that values of influenced groundwaters clearly can be separated from not affected ones. Correlation coefficients between various contaminants show clear and chemically plausible relations between main constituents of the waste deposits and groundwater contamination:

- domestic wastes: HCO_3 , Cl, Mg, B, NH_4 , K, TOC, Na, Fe, Mn
- construction waste: Ca, Sr, SO_4

On this basis key parameters for the investigation scheme have been selected.

Factor analysis of downstream groundwater pollutants of the 35 investigated waste sites reveal several factors in which the respective most typical components carry highest loadings:

- household refuse factor (1): Na 0.91, Cl 0.81, conductivity 0.80, B 0.67, temperature 0.65, the factor loading for AOX 0.56 indicates that household refuses mostly contain substances produced by the chemical industry
- construction waste factor (4): SO_4 0.85, Sr 0.68, Ca 0.62
- factors which are supposed the result from chemical waste components: Factor for volatile solvents (2): Trichloroethene 0.95, tetrachloro-

ethene 0.61, sum of volatiles 0.99.

Factors for heavy metals: (3) Fe 0.79, Mn 0.76 and (5) Pb 0.65, Cd 0.84. Discriminant and cluster analysis had been in use to verify these findings or to recognize more complex connections between parameters investigated (Schleyer et al., this volume).

3.5 Recognition of groundwater-endangering problematic sites

Positive screening findings for 33 of the 35 sites examined revealed influences on groundwater emanating from these sites. At the 33 sites affecting groundwater, onward examinations for problematic substances were performed. Judging by present knowledge, the organic and inorganic substances studied within the second analytic step are the most frequently occurring and most important ones in groundwaters contaminated by waste disposal sites. It is thus become possible to estimate the degree of the groundwater hazard and to recognize problematic sites by taking account of these substances (Brill et al., 1986).

As a result of the examinations performed, 7 (20%) of the 35 sites examined proved to be problematic ones which exerted an extreme influence on groundwater and which might ask for sanitation measures to be considered after further more detailed investigations. These include two sites above solid rock (sandstone) aquifers demonstrating that the method which had been developed is not confined to areas of unconsolidated sediments if there is a geochemical similarity of substrates. With one exception, the disposal sites estimated as problematical exhibited very high concentrations of both inorganic and organic substances posing hazards. In almost all cases the acceptable maximum levels for drinking water were surpassed for several toxic elements. In addition, the content of volatile halogen containing substances was above a cumulative concentration of 25 $\mu\text{g}/\text{l}$. There are also extreme AOX levels ($>300 \mu\text{g}/\text{l}$) and in four cases substances free of halogen being of documented hygienic and toxicological relevance were detected.

In groundwaters downstream of another 9 sites (25%), either one toxic inorganic parameter exceeded the EC-MAC or there was a heavy organic groundwater pollution with AOX levels of $>300 \mu\text{g}/\text{l}$, total volatiles $>25\mu\text{g}/\text{l}$, or a presence of compounds free of halogen so that the ground-

water had to be rated as 'heavily influenced' (Brill et al., 1986). 10 (30%) of the sites examined significantly influence the groundwater. Both, screening and analysis for problematic substances demonstrated, by a comparison of upstream and downstream samples, that the groundwater had been thoroughly contaminated. However, the MAC of substances involving great environmental hazards (toxic inorganic substances, organic problem substances) were not surpassed. 9 (25%) of the sites examined were considered as not hazardous for groundwater for the time being. They include both, sites downstream of which, neither at short nor at larger distances, influences could not be traced as well as disposal sites which did influence the groundwater (positive screening) but did not contain problematic substances or significant amounts of these. In the case of the sites recognized as extremely contaminated further characterization of the contamination will be necessary to evaluate the necessity of sanitation measures. For this characterization, detailed investigations would be necessary (third analytic step) followed by an assessment of the entire locality as an additional step. For the evaluation of a problematic site and an estimation of a risk involved for man and/or environment, not only data about concentrations should be considered but also data about the total abundance of contaminants. In case of utilization of contaminated groundwater negative effects (at this place) must be taken into consideration.

4. CONCLUSIONS

The results of the investigations involving abandoned and presently operated waste disposal sites in pleistocene and non-pleistocene unconsolidated sediments as well as in aquifers in solid rock with a geochemical background similar to that of the unconsolidated sediments have shown that the method proposed can be applied on a broad scale. The findings of the first and second analytic steps will permit a classification of influences on groundwaters and thus permit an identification of problematic abandoned and presently operating waste sites.

ACKNOWLEDGEMENTS

These investigations were supported by the BMFT (Federal Ministry for Research and Technology) and the UBA (Federal Agency for Environment, Grant No. 1430233). Supplementary funds for this research program were provided by the SenStadtUm (Environmental Agency of the Senate of West-Berlin). The authors are particularly grateful to many agencies in the Federal Republic of Germany, which gave permissions for groundwater sampling and technical assistance. Special thanks are expressed to many colleagues and friends in our institute for making analyses and for helpful discussions.

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STRATEGIES FOR GROUNDWATER MONITORING IN DENMARK

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ABSTRACT

Denmark has recently recognized the need for a more organized monitoring of groundwater quantity and quality. This recognition is the result of a growing awareness of threats especially to groundwater quality. These threats result from, among other things, agricultural activities and pollution from point sources such as old landfills.

In the past year, Denmark has begun establishing a groundwater monitoring system composed of so-called monitoring stations grouped into at least three different networks. The quality demands with respect to the execution of borings and the taking and chemical analysis of water samples depend on the network the boring in question belongs to as well as on the intended use of the performed analysis.

Stringent quality requirements will apply to monitoring stations in the first-order network which is intended to be a national reference network. The monitoring stations in the first-order network will be established in areas consisting of geologically and hydrologically representative basins where it is possible to describe both vertical and horizontal changes in groundwater quality with time.

The purpose of the second-order network is to follow changes in the quantity and quality of regionally important groundwater reservoirs which can be used for drinking water. The second-order network will

therefore consist of selected borings at water abstraction plants and analysis of water samples will focus on the most important drinking water quality parameters.

No general description of the monitoring stations in the third-order network can be given as this network will be established to monitor specific human activities such as future landfill sites.

INTRODUCTION

Water supply in Denmark is based almost exclusively on groundwater. Until a few years ago, it was believed that drinking water would always remain as clear, clean and cool as it was in our grandparents day. Unfortunately, this is not the case. Today, groundwater is threatened by both diffuse and point sources of pollution. This can undoubtedly cause great difficulties in the attempts to provide adequate high-quality drinking water in the future.

One of the greatest threats to the quality of groundwater in an agricultural country such as Denmark comes from nitrate contamination due to the use of large quantities of manure in certain parts of the country. Another threat results from the use of certain ecotoxins while quantities of manure and nitrogen fertilizers may also be responsible for a recently recognized drop in the pH of groundwater in some parts of the Country. Other threats to the quality of groundwater include pollution from point sources such as old landfills, old chemical waste dumps and localities formerly used by heavily polluting industries.

The debate on groundwater quality and its variations began in the late 1970s. The debate resulted in the preparation of a proposal for a national "groundwater level and quality monitoring program" by a working group appointed by the National Agency of Environmental Protection.

In the 1981 and 1982 oxygen depletion in various parts of Kattegat and the little Belt was reported and the serious threats to groundwater and surface water quality due in particular to the input of nitrogen and phosphorous salts was recognised.

Against this background, numerous studies have been carried out which illustrate in more detail the connection between the environmental quality of groundwater and surface water on the hand and the addition of nitrogen, phosphorus and organic matter on the other.

One of the more important of these studies is The NPO Report from 1984 which focuses on "the input of nitrogen, phosphorus and organic matter to groundwater fresh water and marine surface water. Effects of this input. Recommendations for remedial measures".

The NPO Report as well as reports such as "Nitrate in Drinking Water and Groundwater in Denmark" from October 1983 show (figure 1), that there are serious threats to groundwater quality and thereby to the quality of drinking water in Denmark.

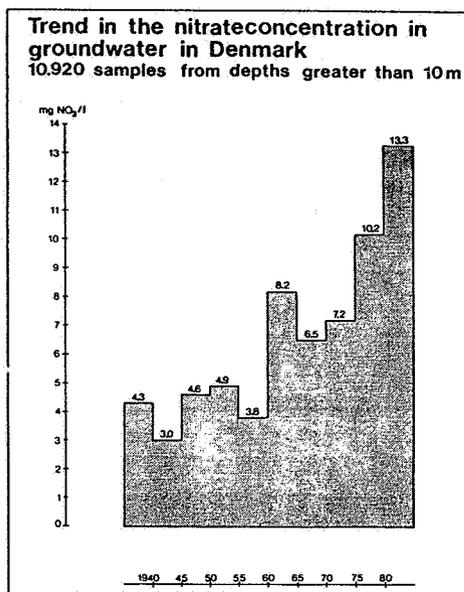


Figure 1. From the NPO-rapport.

As a result of the NPO Report, the Parliament launched a special research project in the spring of 1985 to further investigate the possibility of applying remedial measures as well as the environmental effect of such measures. The project is to be carried out over a period of five years and will cost approximately 50 million Danish crowns.

In the autumn of 1986, the discovery that oxygen depletion in the deeper parts of the open Kattegat had killed invertebrates led to a heated debate in the Danish Parliament. The debate resulted in a Parliament decision which requires that the total Danish discharge of nutrients to surface and groundwater be reduced by 50% for nitrogen and 80% for phosphorus within three years.

The implementation of the NPO research program as well as the Parliament decision of November 1986 require that the quality of groundwater and surface water be monitored.

This paper discusses only the groundwater monitoring system.

THE GROUNDWATER MONITORING SYSTEM

In its report from 1985, the working group appointed by the National Agency of Environmental Protection defined groundwater monitoring as "observation and evaluation of temporal variations in groundwater level and groundwater quality within a delimited groundwater reservoir. The aim of groundwater monitoring is, thus, to predict changes caused by natural and/or human activities".

Due to the various purposes of and requirements for monitoring, the working group proposed that the following three networks composed of so-called monitoring stations be set up:

- a first-order, or reference network of borings selected or established to provide general knowledge on groundwater quality and to be used for both practical and scientific purposes;

- a second-order network of borings from waterworks (including time series of drinking water data) to record changes significant for water planning in the broadest sense of the word, both at the national and at the regional level;
- a third-order network of borings selected or established to fulfill specific local monitoring requirements, such as the recording of the water quality near waste disposal sites or other possible pollution sources and the surveillance of water table levels and water quality in reservoirs which are significant to the local environment.

Rather than constituting isolated networks, these borings form an integrated system in which the sampling, analysis requirements and handling of data may however, differ.

To the extent it is found possible, the three networks will be composed of existing borings. However, the borings in the first-order network in particular may involve special quality and siting requirements which cannot be satisfied by existing borings. Moreover, the third-order network requires per definition that a number of special control borings be established.

FIRST-ORDER NETWORK

Due to its function as a reference network, the borings of the first-order network must fulfill certain requirements. For example, there must be information as to the location of the boring relative to all known pollution sources as well as to the geology of the area so that the location of the filter and the abstraction depth are well-defined.

The monitoring stations in the first-order network will be established in areas that represent various geological and hydrogeological conditions. The geological conditions are considered to be more important since Denmark's hydrology is relatively uniform with respect to rainfall and evaporation. (Rainfall in Denmark varies between 500 and 850 mm per year while evaporation varies between 350 and 400 mm per year).

The most important geological factors for groundwater recharge are variations in the quaternary geology, which can be very complex and difficult to describe, and the deeper geological formations that actually constitute the groundwater reservoirs. There, deep formations composed of miocene sand deposits and chalk deposits from Danien and Senon period are especially of interest. A possible geographic distribution of monitoring stations with respect to the prequaternary geology is shown in figure 2.

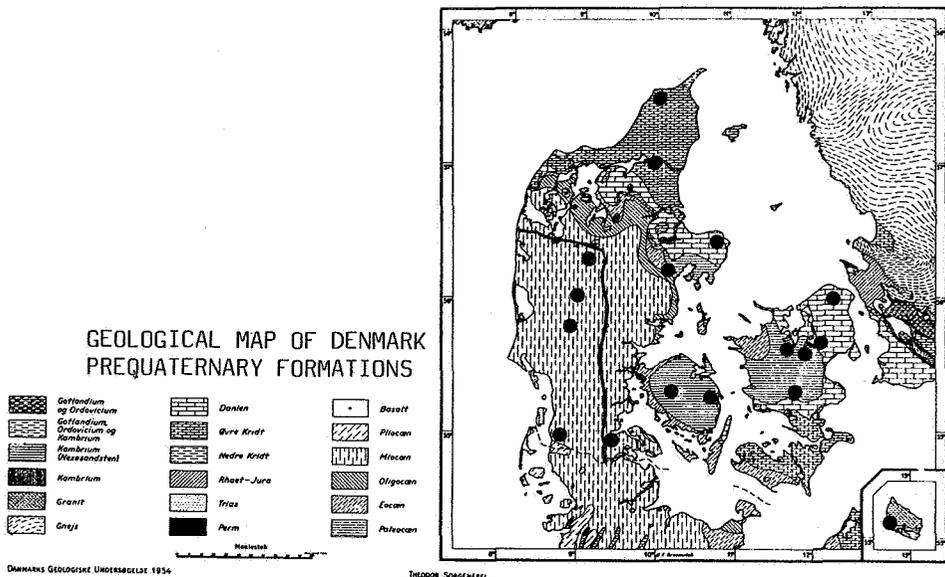


Figure 2. From "vandforsyningsplanlægning 1. del".

A need for approximately 150 borings at the 18-20 monitoring areas included in the first-order network is expected. At each location 2-3 borings with 2-3 sample depths in the primary reservoir must be chosen or executed. A corresponding number of borings must be established to any secondary reservoirs. The borings will be evenly distributed between the groundwater divide and the major outlet (a watercourse or waterwork) as shown in figure 3. Water samples from all sampling points

will be analyzed regularly 2-6 times per year.

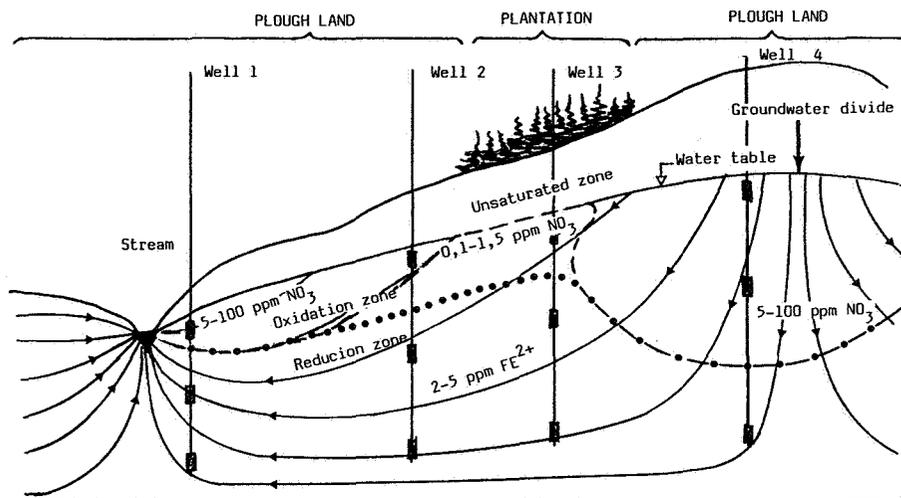


Figure 3. Schematic section showing water quality and land use in "theoretical" monitoring area. Modified from "Prøvetagningsteknik"

The analysis parameters for water samples taken from stations in the first-order network will include heavy metals and organic micropollutants. Sampling guidelines will be developed to help prevent contamination during sample collection and transport. Special measures regarding the materials and substances used in the construction of borings will also be required.

The first-order network should make it possible to qualitatively describe vertical and horizontal changes of groundwater quality with time and perhaps, in the future, to predict changes in groundwater quality outside the monitoring areas.

SECOND-ORDER NETWORK

The second-order network, which serves to record changes which significantly influence the regional water supply, has its strength in the relatively large number of monitoring stations. Less attention is given to the "scientifically" correct location and design. A limited number of drinking water analyses will be accepted, especially from waterworks that do not carry out extensive water treatment. It is estimated

that in order to obtain sufficient surveillance of the groundwater reservoirs currently in use, about 100-200 stations in every region (amtskommune) are required, approximately 1500 stations in all.

THIRD-ORDER

The need for third-order monitoring stations cannot be defined in detail since stations in this network are to observe the impact of specific human activities. Therefore, the number of stations and the extent and nature of sample analysis depend totally on the activity in question.

It is likely, however, that the third-order network will include a large number of stations. A minimum of 3-8 groundwater control borings are typically required in connection with establishing new sanitary landfills and even more borings can be required for the investigation of chemical waste sites. Furthermore, all the drinking water analyses from Denmark's approximately 4000 waterworks might be included.

Design requirements for borings in the third-order network may vary depending on the use of the boring the requirements may be less strict when observing the impact of intensive animal husbandry and more strict when investigating chemical waste sites since this monitoring must be adapted to the analysis of micropollutants.

CHEMICAL ANALYSIS PROGRAM

The number and type of analysis parameters examined at each station depends on the network involved and on the "problem" substances known to influence the water quality.

Chemical analysis will be especially extensive in the first-order network as this network will provide a general knowledge of background levels of various substances in groundwater. Based on the results of these analysis, it should eventually be possible to minimize the extent of analysis and maximize security in connection with the second and third-order networks.

Almost all parameters - including trace elements - in the EEC directive on "the quality of water intended for human consumption" will be covered by water sample analyses in the first-order network. Furthermore, determinations of organic substances or substance groups in groundwater will be carried out in an attempt to establish the background level in Danish groundwater.

The analysis of organic substances will include non-volatile organic carbon (NPOX), volatile organic carbon (POX), adsorbable organic halogen (AOX), volatile organic halogen (VOX) and a selection of aromatic hydrocarbons, halogenated aliphatic hydrocarbons, phenols including chlorophenols, pesticides and anionic and non-ionic active detergents.

Among specific substances which may be selected are trichloroethylene, cresol, zyleneol, tri- and tetrachlorophenols and pesticides such as Dichloroprop, Aldicarb and Carbofuran. A pesticide may be selected in view of the quantity which is utilized, its toxicity, persistence or mobility.

The analysis program for the second-order network will be restricted to the important quality parameters for drinking water. If necessary, special analyses can be carried out. It is not possible to give a general description of the analysis program for the third-order network. However, the number of parameters will be restricted to a minimum.

THE GOVERNMENTS PLAN OF ACTION

As a consequence of the Parliaments discussion and decision of November, 1986 to reduce the discharges of nutrients to groundwater and surface water, the government presented a plan of action in January, 1987 to deal in particular with the discharge of nitrogen and phosphorus from municipalities, industry and agriculture.

The plan states the measures to be taken to reduce nitrogen discharges by 50% and phosphorus discharges by 80%. It also estimates the effect

of this reduction as well as the costs involved. The plan sets a time limit of three years regardless of the difficulties which might be involved in reaching the goal.

To determine whether the intended reduction is met, it will be necessary to create a more effective monitoring system than the one described in this paper. This system must include a combination of data collection and mathematical models based on a running control of the various segments of the water cycle.

This expanded system should be capable of identifying the contribution of various sources of pollution (the atmosphere, agricultural activities, water treatment plants, individual industrial discharges, fish farming in streams and the sea) as well as giving an overall picture of the nutrient load and its ecological consequence for groundwater, streams, lakes and the sea. Measurements of the quality of near-surface groundwater reservoirs, springs and drain systems under various agricultural conditions must be taken regularly in order to establish the connection between changes in agricultural activities and groundwater quality.

SELECTING AND FINDING THE MONITORING SYSTEM

The selection of monitoring stations, analysis frequency and parameters for the groundwater monitoring system will be made in cooperation between regional authorities and the National Agency of Environmental Protection, assisted by the Ministry of Agriculture and the various institutions that are to be responsible for the data storage, processing and transmission.

These institutions will furthermore be responsible for the development of mathematical models and reporting the results in a manner usable to the institutions responsible for political decisionmaking.

STRATEGIES FOR SOIL SAMPLING FROM A STATISTICAL POINT OF VIEW

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ABSTRACT

Strategies for soil sampling are closely related to the questions one would like to answer. Here attention will be focussed on a network for monitoring soil quality. In addition to the monitoring networks we have in Holland for the quality of air, rainwater, groundwater and surface water, the installation of a monitoring network for soil quality is being seriously considered. Questions one would like to answer using such a network are e.g.: Does diffusive pollution lead to detectable accumulation of specific contaminants in the soil and, if so, can trends be quantified for each specific contaminant in each of a number of different types of burden and composition of the soil? In order to get effective possibilities for interpreting network data, it is essential to get quantitative information about two components of spatial variation on each of the time points at which observations were made, i.e. (a) the degree in which a measured variable varies within a test-area (called an 'observation point') and (b) the degree in which a measured variable varies between observation points 'equally' burdened and composed. These two components of variation define the natural scales for measuring differences in observed values. For the statistical analysis of the data obtained from the network, methods from the Analysis of Variance and Regression will be appropriate. In a pilot study concerning the monitoring network, data were obtained from four observation points. A number of simple statistical operations and conclusions appropriate to these data are presented.

1. INTRODUCTION

Strategies for soil sampling are closely related to the questions one would like to answer. Here attention will be focussed on a monitoring network for soil quality.

In the Netherlands there have been monitoring networks for air quality, groundwater quality, rainwater quality and the quality of surface water for many years. A monitoring network for the quality of soil, which is the missing link in this chain, has not been established yet. Such a monitoring network should, among other things, be aimed at the quantification of the changes in time of the pollutant contents of the soil in dependence on soil type, soil use and immission density. For many years, the realization of such a monitoring network has been retarded in the opinion that it would be impossible to discern the level of diffusive pollution of the soil due to the noise level in soil material caused by spatial variability. Eventually, it was decided to study the noise in soil material prior to making more final decisions about the realization of a soil monitoring network. As a result of this study, we can state that the first opinion was largely caused by the prevailing unfamiliarity with the handling of noise, as I intend to show shortly. To that end, we will give a short outline of the relevant pilot study as carried out by the Dutch Institute of Soil Fertility and the data resulting from it. And in line with this, we will present some simple statistical techniques with which we will draw some conclusions.

2. DATA ACQUISITION

On four selected locations, the contents of the elements As, Cd, Cu, Hg, Pb and Zn were established by (1) selecting an area of 25*25 m² on each location, (2) taking, from each of the four areas, 8 mixed samples each consisting of 40 random pitches covering the area (and thus

representative for the area considered), (3) homogenizing the mixed samples and establishing the contents of the six elements in each mixed sample.

Thus, for each of the 4 areas and each of the 6 elements one obtains 8 independent observations of the contents. The information obtained on an element (for instance on lead) can be symbolized as follows:

location I $Pb_{I,1}$, $Pb_{I,2}$,..... , $Pb_{I,8}$
 location II $Pb_{II,1}$, $Pb_{II,2}$,..... , $Pb_{II,8}$
 location III ...
 location IV $Pb_{IV,1}$, $Pb_{IV,2}$,..... , $Pb_{IV,8}$.

The variation present in such a set of 8 observations yields a measure for the variation within an area considered.

For the interpretation of the data, it is of relevance to note that the 4 selected locations differed widely in soil composition and/or soil use, as is roughly indicated by

location I : clay, tree nursery
 location II : clay, arable land
 location III: sand, grassland
 location IV : sand, arable land.

As an illustration, the contents of Cd and Zn are given in the following tables.

Table 1. Cd content (mg/kg dry weight)

Location	Observation								$\bar{x} =$	$s =$
	1	2	3	4	5	6	7	8	mean of obs.	stand.dev.of obs.
I	.56	.51	.48	.50	.63	.57	.52	.51	.53	.049
II	.36	.37	.27	.30	.23	.39	.36	.33	.32	.057
III	.18	.22	.20	.16	.16	.16	.14	.15	.17	.027
IV	.09	.13	.14	.14	.12	.19	.22	.15	.15	.044

Table 2. Zn content (mg/kg dry weight)

Location	Observation								$\bar{x} =$	$s =$
	1	2	3	4	5	6	7	8	mean of obs.	stand.dev.of obs.
I	84	86	82	84	81	82	80	81	82.5	2.00
II	98	95	87	85	95	93	95	91	92.5	4.44
III	24	28	27	25	25	25	21	24	24.6	2.12
IV	23	23	23	24	24	23	24	23	23.2	0.55

3. STATISTICAL ANALYSIS

3.1. Questions

Now we will try to give some simple answers to some elementary questions, more specifically:

If we, annually, load the soil with sewage sludge plus fertilizer or just fertilizer in the maximum amounts applying in the Netherlands and the corresponding net immission of the elements mentioned before taking into account removal by harvesting and leaching, to be more specific:

If we use the next table for the net annual immission of the mentioned elements into the soil,

Table 3. L = net annual immission into the soil

L(mg/kg dry weight):	As	Cd	Cu	Hg	Pb	Zn
grassland with						
(a) sew. sludge + fert.		.025	1.29			5.12
(b) fertilizer		.011	.29			1.81

arable land with

(a) sew. sludge + fert.	.010	.0076	.40	.0068	.40	1.54
(b) fertilizer		.0021	.003	.0002	.0069	.22

QUESTION (A):

How many mixed samples do we have to take from an area now and after x years in order to be able to detect, for that location, a significant increase in the content of an element considered (i.e. an increase that is significant with respect to the noise level present in the soil material)?

question (a) in short: How large should the sample size n be?

QUESTION (B):

For a fixed number of mixed samples n :

After how many years do we have to repeat an initial sampling in order to be able to detect a significant increase of the element considered on the sampled location?

question (b) in short: How long is the waiting time p in years?

QUESTION (C):

For a fixed sample size n on each of k locations:

After how many years do we have to repeat an initial sampling in order to be able to detect an overall increase of the element considered on the set of k locations?

3.2. Methods

As said before, we will just look for simple answers to these first questions. To that end, we will make a number of simplifying assumptions which were not tested on their validity.

assumption (i): A sample from a location, symbolized by x_1, x_2, \dots, x_n (in the example $n=8$), can be considered to be an independent sample from a Normal distribution $N(\mu, \sigma)$. Thus, for instance, the parameter μ can be estimated by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (1)$$

and the parameter σ can be estimated by

$$s = \left[\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \right]^{\frac{1}{2}}. \quad (2)$$

assumption (ii): The variance σ^2 on a location is constant in time.

Then, it follows from elementary statistics that

If we look at two independent samples taken from some location on two different time points t_1 and t_2 ($t_1 < t_2$) and symbolized by

$$\begin{array}{l} x_1, x_2, \dots, x_n \text{ on } t_1 \\ y_1, y_2, \dots, y_n \text{ on } t_2 \end{array}$$

and focus on their respective sample means

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad \text{and} \quad \bar{y} = \frac{1}{n} \sum_{i=1}^n y_i,$$

then we can state the following properties for their difference

$$\bar{z} = \bar{y} - \bar{x}$$

- 1) $\text{Var}(\bar{z}) = \text{Var}(\bar{y} - \bar{x}) = \text{Var}(\bar{y}) + \text{Var}(\bar{x}) = 2 \sigma^2/n$.
- 2) \bar{z} is Normally distributed.
- 3) and, if the mean level of the content has not changed in time:

$$E(\bar{z}) = 0 \quad (E = \text{'expectation'}).$$

Now, a realization of \bar{z} based on two samples does not contradict $E(\bar{z})=0$ if this realization differs just a little from zero, since such a difference is a consequence of the variation of \bar{z} according to 1).

A realization of \bar{z} only indicates a significantly increased content (level of significance α) if

$$\bar{z} > T(n-1, \alpha) \frac{s \sqrt{2}}{\sqrt{n}}, \quad (3)$$

where

$T(n-1, \alpha)$ is the upper α point of Student's t-distribution with $n-1$ degrees of freedom (see tables for T-values) and s is the standard deviation in a sample as defined before by Equation (2).

If one is to detect a significant increase after x years on the basis of an annual net immission L as given in Table 3, the following relation must be true:

$$xL > T(n-1, \alpha) \frac{\sqrt{2}}{\sqrt{n}} s \quad (4)$$

and so

$$n > \frac{T^2(n-1, \alpha) 2s^2}{x^2 L^2} . \quad (5)$$

Relation (5) yields an answer to question (a).

Similarly, an answer to question (b), about the number of years p one has to wait before taking a second sample of some fixed sample size n in order to detect a significantly increased content on the basis of the net annual immission L , is given by

$$pL > T(n-1, \alpha) \frac{\sqrt{2}}{\sqrt{n}} s$$

or

$$p > \frac{T(n-1, \alpha) s \sqrt{2}}{L \sqrt{n}} . \quad (6)$$

A simple answer to question (c) about overall accumulation is easily constructed since:

if $\bar{z}_1 = \bar{y}_1 - \bar{x}_1 = N(0, \frac{\sqrt{2}}{\sqrt{n}} \sigma_1)$ on location 1,

$\bar{z}_2 = N(0, \frac{\sqrt{2}}{\sqrt{n}} \sigma_2)$ on location 2, ..., $\bar{z}_k = N(0, \frac{\sqrt{2}}{\sqrt{n}} \sigma_k)$ on location k,

(mark: different variances on different locations are allowed!)

then

$$\frac{1}{k} \sum_{j=1}^k \bar{z}_j = N(0, \frac{\sqrt{2}}{k\sqrt{n}} \left[\sum_{j=1}^k \sigma_j^2 \right]^{\frac{1}{2}})$$

and so, analogous to relation (4), a significant overall increase of content on the basis of the net annual immission is found if

$$p \cdot \frac{1}{k} \sum_{j=1}^k L_i > T(k(n-1), \alpha) \frac{\sqrt{2}}{k\sqrt{n}} \left[\sum_{j=1}^k s_j^2 \right]^{\frac{1}{2}} \quad (7)$$

or

$$p > \frac{T(k(n-1), \alpha) \frac{\sqrt{2}}{k\sqrt{n}} \left[\sum_{j=1}^k s_j^2 \right]^{\frac{1}{2}}}{\frac{1}{k} \sum_{j=1}^k L_i} \quad (8)$$

Relation (8) yields an answer to question (c).

3.3. Results

Application of the just-mentioned methods to the data from the 4 locations gives the following results.

On grassland, accumulation of Cd, Cu and Zn is

- (a) easy* to detect on each location after 2, 1 and 1 year respectively, if there is a heavy load on the land,
- (b) easy* to detect on each location after 5, 5 and 2 years respectively, if there is a light load.

(*'easy' = sample size $n < 10$)

On arable land, accumulation of As, Cd, Cu, Hg, Pb and Zn is

- (a) easy* to detect on each location after 100, 10, 5, 1, 5 and 2 years respectively, if there is a heavy load,
- (b) detectable with some effort ($25 < n < 40$) after ?, 10, 250, 10, 250 and 10 years respectively, if there is a light load.

Consequently, of the elements considered only the accumulation of As and (if there is a light load) Cu and Pb is hard to detect per location. However, for these elements there are good possibilities to detect an overall accumulation on all locations of a monitoring system or on smaller subsets consisting of similar locations. For instance, if one has 40 lightly burdened locations of arable land to one's disposal, then, according to relation (8), overall accumulation of Pb is detectable with one repeated sample (sample size $n=25$ per location) after only 20 years instead of the 250 years one would have to wait to detect accumulation on each separate location if $n=25$.

4. CONCLUSIONS

On the basis of the available data and the statistical results, there are good perspectives for the establishment of a monitoring network for soil quality since, on the one hand, the noise level against which accumulation has to be detected is far from discouraging and, on the other hand, it should be noted that the statistical analysis which was carried out was only very elementary and far from optimal, which means that the data from a monitoring system could be analyzed much more powerfully leading to conclusions which would be much more refined.

Particularly, methods from the Analysis of Variance and Regression are much more appropriate for the analysis of the data from monitoring systems. Thus, for instance, the accumulation of a pollution in time (a so-called trend) can be detected and described much more effectively by methods from Regression Analysis fitting small samples taken periodically (e.g. every two years) from a location. The Analysis of Variance and Regression also give much better possibilities for the analysis of the wealth of information available on the different locations and different time points, not only as far as the mean levels are concerned but also with respect to the variance properties and their interrelations.

Based on the positive results of this pilot study, the realization of a monitoring network for soil quality consisting of 40 locations is being seriously considered. On each location of this network, 4 independent mixed samples will be taken from each of two sampling depths every two years. For each of the mixed samples, the contents of the elements mentioned before and the contents of some organic compounds will be measured. The observations from one location will give information about a first component of variation, that is: the variance within a location. In order to enable an efficient statistical analysis and the possibility of generalizing conclusions, it is essential that the monitoring network gives information about a second component of variation as well, that is: the variation between similar locations. To that end, the forty locations will be chosen in such a way that if a combination of soil type, soil use and immission density is represented in the network, this particular combination will be represented by 4 locations of the network. In the selection of the locations, 4 types of soil, 4 types of soil use and 2 immission densities will be distinguished and, as a consequence, of the $4 \cdot 4 \cdot 2 = 32$ theoretical combinations only 10 combinations can be represented in the small-scale monitoring network, due to the wish for 4 time-repetition in order to get sufficient information about the second component of variation, that is: the variation between similar locations.

MONITORING GROUNDWATERS BY SURFACE GEOELECTRICAL
METHODS IN HETEROGENEOUS AQUIFERS

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ABSTRACT

The use of stable geoelectrical networks in monitoring the migration of some types of contaminants contributes not only new knowledge of the processes of their transfer, but also represents substantial savings in hydrogeophysical survey expenses. The principal methodological problems are formulated as related to the basic types of hydrogeological and the corresponding models used to determine the detectability of contamination in heterogeneous aquifers by geoelectrical methods. The separate stages of migration of contaminants in these aquifers are defined in relation to the geoelectrical properties of the aquifers. It is also indicated how surface geoelectrical monitoring methods may, in particular cases, provide important information about the dynamics of contaminant transfer in heterogeneous aquifers.

1. INTRODUCTION

The current increasing interest in the analysis of the dynamics of migration processes and especially in their detectability in connection with soil and groundwater vulnerability to pollutants by means of monitoring networks, however, can be seen in recent publications, as well as in the papers presented at this conference (Kelly et al., 1987). The geoelectrical monitoring systems, which enable at least the main stages of the process of contaminant migration in heterogeneous aquifers to be monitored, may play an important part in objectivizing hydrogeological prognostication computations and especially in optimizing protective measures taken against the consequences of polluting groundwaters.

2. HYDROGEOLOGICAL ASPECTS

We shall analyse two basic types of heterogeneous aquifers characterized by double permeability: a two-layer percolation aquifer (Figure 1) and a percolation-fracture aquifer (Figure 2) in which, apart from the percolation matrix of the aquifer, also fractures come to bear. If the permeability of the matrix is close to zero, the percolation-fracture aquifer becomes a limiting case, i.e. a fracture aquifer (single-permeability aquifer).

There is so far no sufficiently universal mathematical expression for contaminant transfer in either type of heterogeneous aquifer. However, essentially one can distinguish between four basic stages of contaminant transfer:

The *first stage* represents the condition of the unaffected aquifer before contamination. In the *second stage* (model with infinite capacity), convective diffusive motion occurs in the more permeable phase of the system, as well as partial migration to the less permeable phases (layers, blocks) due to molecular diffusion (D_b). In the *third stage* (model with concentrated capacity), the contaminant penetrates (diffuses) completely into the more permeable phase and into a large volume of the less permeable phase. In the *fourth stage* (model with the asymptotic solution), both phases of the aquifer are in fact filled with the contaminant, and diffusion into the less permeable phase has no effect on the transfer dynamics of the contaminant.

In the limiting type of the heterogeneous, single-permeability, fracture aquifer, in which the matrix phase of the aquifer is impermeable, only convective diffusive motion along the fractures takes place without change in the properties of the blocks, and the first stage of contaminant transfer immediately develops into the fourth.

3. GEOELECTRICAL ASPECTS

The geoelectrical model of migration processes is based on the assumption that the contaminant affects the geoelectrical properties of ground waters and, consequently, also of the separate phases of the heterogeneous aquifer. This effect depends primarily on the type of the hetero-

geneous aquifer and on the developmental stage of the contamination. To be able to assess the detectability and possible application of surface geoelectrical methods, it is necessary to analyse the integral effect of the geoelectrical properties of the aquifer phases on the nature of the geoelectrical field observed on the Earth's surface.

The geoelectrical model of the *two-layer aquifer* can be schematized as a double-permeability aquifer. We have assumed (Figure 1) that the upper layer (phase) is less permeable. The layer over- and underlying the aquifer are considered impermeable. Eight models are shown, characterized by different resistivities ρ and thicknesses m of both the contaminated and uncontaminated layers.

The results of the modelling indicate that the parameters of these layers in various stages can be determined by the usual interpretation procedures, provided the investigated medium can be considered one-dimensional (1-D) (Johansen 1977, Mašková and Mazáč 1985). This condition is satisfied, if the thickness of the layer overlying the aquifer $m_1 \leq L/6$, where L is the minimum dimension of the geoelectric layer in the horizontal direction. Under favourable circumstances, these procedures can be used to construct the function $\rho_{01,02}^{(I)-(IV)} = f(t)$ (or $m_{01,02}^{(I)-(IV)}$), and to distinguish between the separate stages of the migration process.

Under less favourable circumstances, which are most common, the migration stages can be identified by means of the monitored apparent resistivities $\rho_a^{(I)-(IV)} = f(t)$ (Figure 1). If the medium has to be considered as 2-D or 3-D, the interpretation becomes quite complicated, although it is theoretically possible (Hohman 1982).

The geoelectrical model of the *percolation-fracture aquifer* has a block structure and can also be characterized as a double-permeability aquifer. The blocks, schematically cube-shaped, create a less permeable phase as compared with the permeable three fracture systems perpendicular to one another. The layer over- and underlying the aquifer are also considered impermeable.

Figure 2 again shows 8 models characterized by different resistivities ρ and thicknesses m of the elements making up the model under the assumption that the relative width of the fracture k in one direction is $k = 0.05$.

The results of the modelling indicate that geoelectrical measurements cannot be used to determine the dimensions of these aquifer elements

quantitatively. The aquifer will be reflected in the VES curves as a layer of resistivity ρ_0 , whose value can be determined from Nechaj's relation (Militzer et al. 1978) for the first and fourth stages. No formulae are as yet available for calculating ρ_0 in the second and third stages:

$$1/\rho_0^{(I)} = 2k/3\rho_{02} = (3 - 2k)/\rho_{01}(3 - k) \dots \text{for the first stage,}$$

$$1/\rho_0^{(IV)} = 2k/3\rho_{02} + (3 - 2k)/\rho_{01}(3 - k) \dots \text{for the fourth stage.}$$

What is important, however, is that the interpreted resistivities ρ_0 can be used to construct the function $\rho_0^{(I)-(IV)} = f(t)$ and to determine qualitatively the separate stages of the migration process on the corresponding curve. In the less favourable case, in which the resistivity of the aquifer ρ_0 cannot be interpreted, the apparent resistivities at characteristic points, $\rho_a^{(I)-(IV)} = f(t)$, can be used to determine the migration stages (Figure 2).

4. CONCLUSION

Designing and operating hydrogeological monitoring systems in a number of cases requires monitoring surface geoelectrical fields. Geoelectrical monitoring in stable, electrode, surface networks in a complex with parametric logging measurements in support and monitoring boreholes in the process of monitoring the contamination of shallow heterogeneous aquifers also enables important data to be obtained on the migration process. To distinguish between the separate stages of contamination, one can use to an advantage the functional dependences of the variations of resistivity ρ_0 or apparent resistivity ρ_a with time. This will provide the data for more accurate prognostic calculations of contamination as well as for taking the appropriate technical measures to protect groundwaters from contamination.

The reliability of the qualitative and quantitative analysis of VES curves is improved significantly if the results of hydrochemical monitoring observations and results of geoelectrical logging methods can be used simultaneously. This provides for a better choice of the formulae

valid for the separate stages of contamination, as well as of the formulae used for the prognostic calculation of groundwater contamination.

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FIGURE CAPTIONS

Figure 1. *Two-layer percolation aquifer*

a) Hydrogeological 1-D model

- 1 - impermeable layers over- and underlying the two-phase aquifer;
 2 - earth surface; 3 - less permeable phase; 4 - permeable phase;
 5 - contaminated parts of aquifer; 6 - effect of molecular diffusion D_b ; 7 - direction of convective motion N_f ; 8 - VES site.

b) Geoelectrical 1-D model

c) Stages of contamination I, II, III and IV

d) Parameters of geoelectrical models analysed

- ρ , m - resistivities and thicknesses of the geoelectrical layers for stage (II) (III) of the migration process; ρ_{01} , m_{01} (ρ_{02} , m_{02}) - parameters of the first (second) phase of the aquifer; the parameters of the contaminated aquifer are marked with superscript +.

e) ρ_a [ohm.m] = $f(\frac{1}{2}AB$ [m]) for different stages of contamination pro-

cesses, $\frac{1}{2}AB$ for the optimum differences in ρ_a is marked with a vertical arrow.

- f) ρ_a [ohm.m] as a function of contamination stages I to IV for 8 geo-electrical models (A, B, $\alpha - \delta$) shown in Figure 1d.

Figure 2. *Percolation-fracture aquifer*

- a) Hydrogeological 3-D model
- b) Detailed diagram (cross-section) of the various stages of the contamination process (I - IV). 1 - impermeable layers over- and underlying the aquifer; 2 - earth surface; 3 - fractures; 4 - less permeable phase; 5 - effect of molecular diffusion D_b ; 6 - direction of convective motion N_f ; 7 - contaminated parts of the aquifer; 8 - VES site; 9 - boundary between contaminated and uncontaminated parts in the first phase of the aquifer.
- c) Stages of contamination I, II, III and IV
- d) Geoelectrical parameters of the aquifer
 k - relative width of fractures; ρ_{01} (ρ_{02}) - resistivity of the first (second phase of the aquifer; parameters of the contaminated aquifer are marked with superscript +; 1 - contaminated parts of the aquifer.
- e) Equivalent 1-D geoelectrical model of the 3-D hydrogeological model shown in Figure 2a.
 ρ, m - resistivities and thicknesses of the geoelectrical layers; $\rho_0^{(I)-(IV)}$, m_0 - equivalent parameters of the aquifer for various stages of contamination I - IV.
- f) Parameters of geoelectrical layers
 $\rho_0^{(I,IV)}$, $m_0 = \text{const.} = 10 \text{ m}$ - parameters of the equivalent aquifer in stages I and IV of the contamination process; resistivity $\rho_0^{(I,IV)}$ was calculated from Nechaj's relation where k is the relative width of the fractures in all 3 directions; the meaning of ρ_{01}^+ , ρ_{01}^+ , ρ_{02}^+ , ρ_{02}^+ is shown in Figure 2d; A - models with limited resistivities of the aquifer phases; B - model in which ρ_{01} (the first phase impermeable) and the model represents a fracture aquifer; $\alpha - \delta$ - parameters of the layer over- and underlying the aquifer.
- g) ρ_a [ohm.m] for $\frac{1}{2}AB$ $m_1 = 6.2$ as a function of the various stages of contamination for 8 geoelectrical models shown in Figures 2e,f.

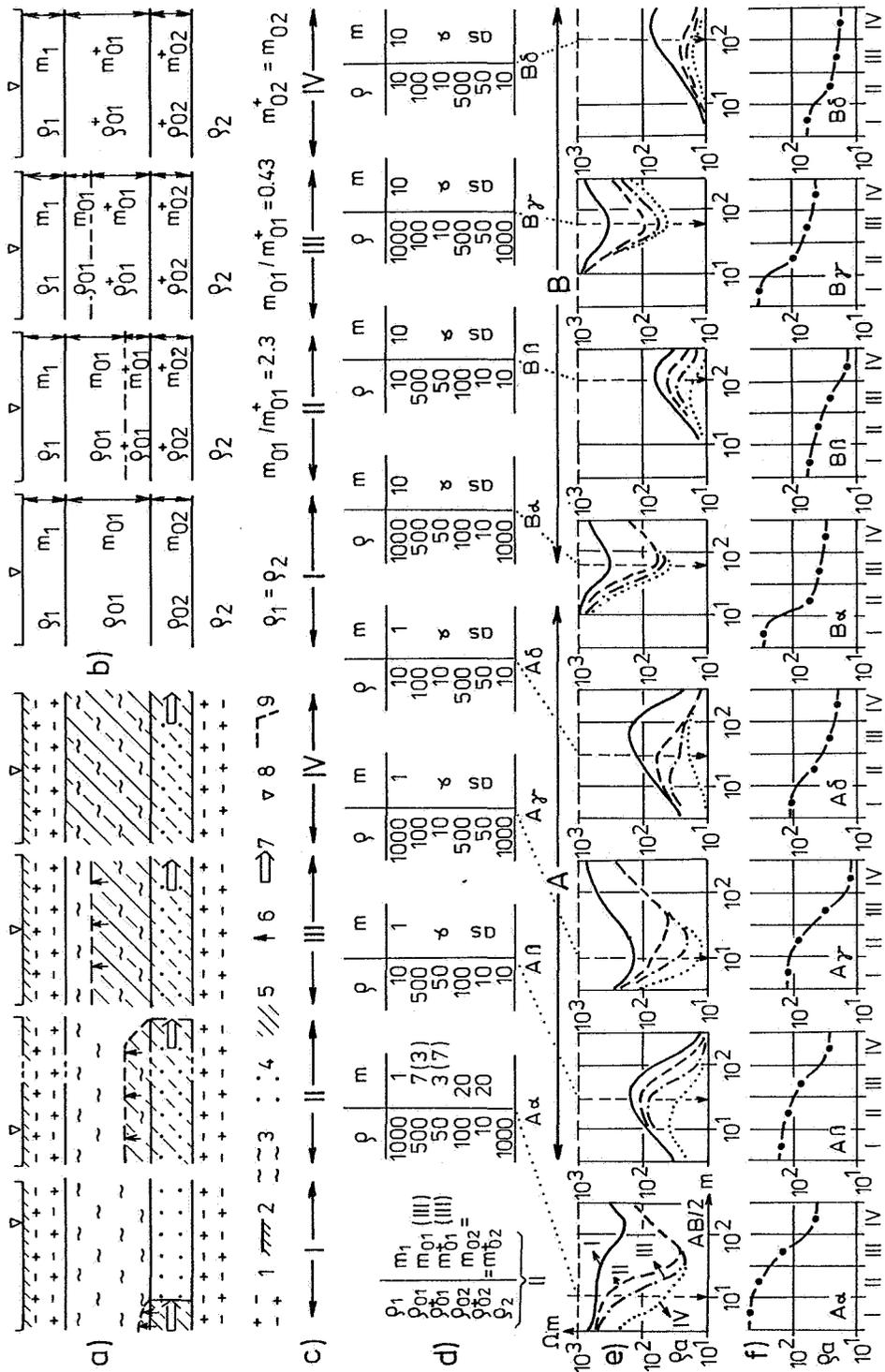
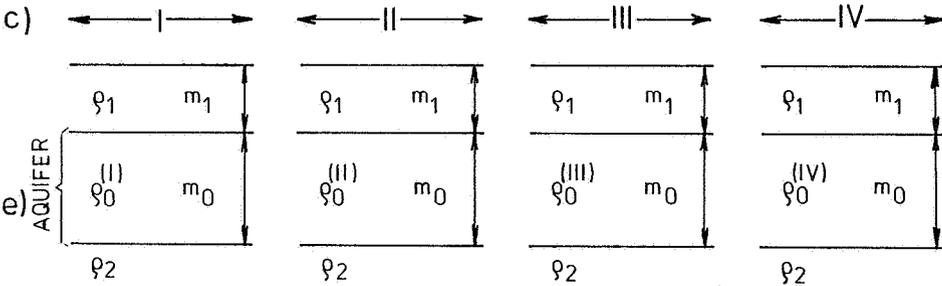
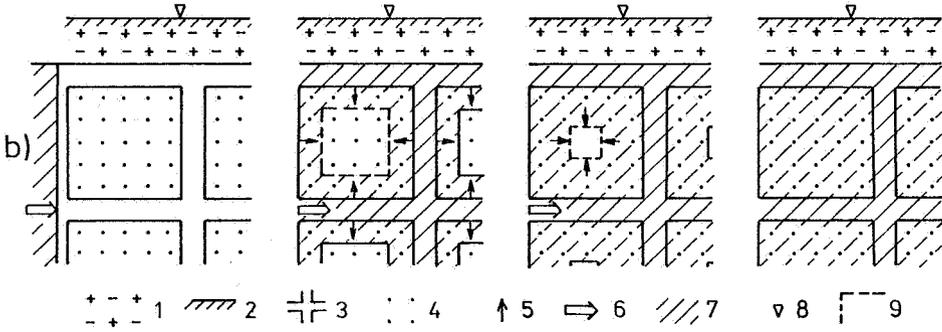
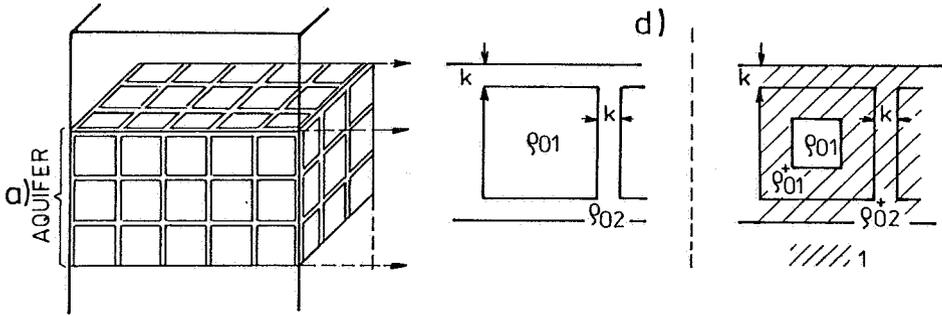


Figure 1



f) $\left. \begin{matrix} \rho_{01} = 1000 \Omega m ; \rho_{02} = 100 \Omega m \\ \rho_{01}^* = 100 \Omega m ; \rho_{02}^* = 10 \Omega m \end{matrix} \right\} \text{is}$ $\left. \begin{matrix} \rho_0^{(I)} = 760 \Omega m ; m_0 = 10 m \\ \rho_0^{(IV)} = 76 \Omega m ; m_0 = 10 m \end{matrix} \right\} A$

$\left. \begin{matrix} \rho_{01} \rightarrow \infty ; \rho_{02} = 100 \Omega m \\ \rho_{01} \rightarrow \infty ; \rho_{02}^* = 10 \Omega m \end{matrix} \right\} \text{is}$ $\left. \begin{matrix} \rho_0^{(I)} = 3000 \Omega m ; m_0 = 10 m \\ \rho_0^{(IV)} = 300 \Omega m ; m_0 = 10 m \end{matrix} \right\} B$

$\left. \begin{matrix} \rho_1 = \rho_2 = 5000 \Omega m \\ m_1 = 1 m \end{matrix} \right\} \alpha$ $\left. \begin{matrix} \rho_1 = \rho_2 = 5000 \Omega m \\ m_1 = 10 m \end{matrix} \right\} \beta$ $\left. \begin{matrix} \rho_1 = \rho_2 = 50 \Omega m \\ m_1 = 1 m \end{matrix} \right\} \gamma$ $\left. \begin{matrix} \rho_1 = \rho_2 = 50 \Omega m \\ m_1 = 10 m \end{matrix} \right\} \delta$

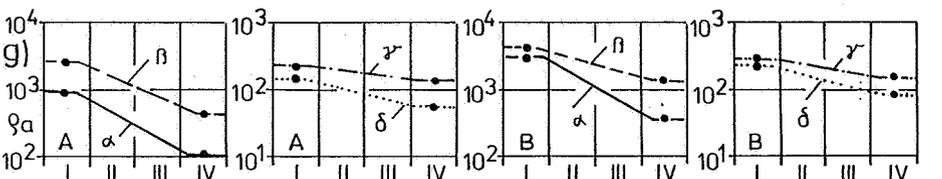


Figure 2

NITRATE IN SHALLOW GROUNDWATER: RECONNAISSANCE OF SATURATED
SOIL AT SELECTED FARMS

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ABSTRACT

A review is given of the research methods applied at the investigation of the saturated soil at a project aiming at the study of the effects of high nitrogen gifts on nitrate contents in groundwater. At the scale of a farm geo-electrical and electromagnetical surface measurements, suction core drillings and sedimentological study of the cores, installation of screens at small intervals have been applied up to now. The nitrate contents observed lead to the conclusion that soil properties such as indicated by the sedimentological analysis are of great importance to explain the large variation.

1. INTRODUCTION

Within a larger project aiming at the research of nitrogen contents in groundwater and small surface water of The Netherlands, ten special farms have been selected for a detailed investigation. The farmers keep an account of fertilizer and manure distribution to their lands so that the input of nitrogen is reasonably well known. Part of the investigations concern the saturated soil with the emphasis on shallow layers. Different techniques have been applied to study the sub-surface, the direction and the intensity of groundwater flow and the composition of shallow groundwater. Results obtained by now are:

- geo-electrical observations executed with an ABEM Terrameter and cables at the Barker arrangement yield Wenner arrays; the interpretation shows the general structure of the soil to a depth of about 100 m. Electromagnetical readings are done with a Geonics EM-31 at a regular pattern to map changes in the electrical conductivity of the upper 10 metres of the soil;

- suction corer drilling by hand has been executed to a depth of about 7 m. The lacquer peels of the cores were analysed sedimentologically;
- observation screens have been installed at 1 m intervals at the boreholes. A sampling and analysing round with regard to nitrate has been executed. A more detailed program will follow.

At the following stage much attention will be given to the horizontal flow (by level observations) and the vertical flow (tritium profiles) of the saturated groundwater. From the present results can be deduced that differences in landscape, water depth, recharge and sedimentology of the shallow soil, give outspoken variations in the nitrate content of the groundwater. A case where sedimentology is important is the Wanroij farm.

2. LANDSCAPE AND HYDROGEOLOGICAL SITUATION OF THE WANROIJ FARM

The investigated farm at Wanroij, in the northeastern part of the province of North Brabant, is situated in the valley of the river Meuse (Figure 1). The valley is bordered by the Peel horst at the southwest and the ice pushed hills of Nijmegen in the north. In the middle a somewhat higher area of fossil river banks lies as an island between the present river bed and a subrecent gully, now an area characterized by "broek" (= marsh) names. The farm is located in that broek lands. The subsurface contains sandy sediments of Pleistocene and upper Tertiary age, at a depth of 50 m underlain by thick Tertiary claylayers. The general direction of groundwater flow is to the northeast. In the non cultivated situation upward seepage occurred but nowadays deep ditches catch the seepage water and drain the former marsh. In between the ditches the upper groundwater is recharged by local precipitation. The general direction of groundwater flow is in the lengthwise direction of the farm. De deep ditch dug at the south-east border of the parcellation may cause a local deviation.

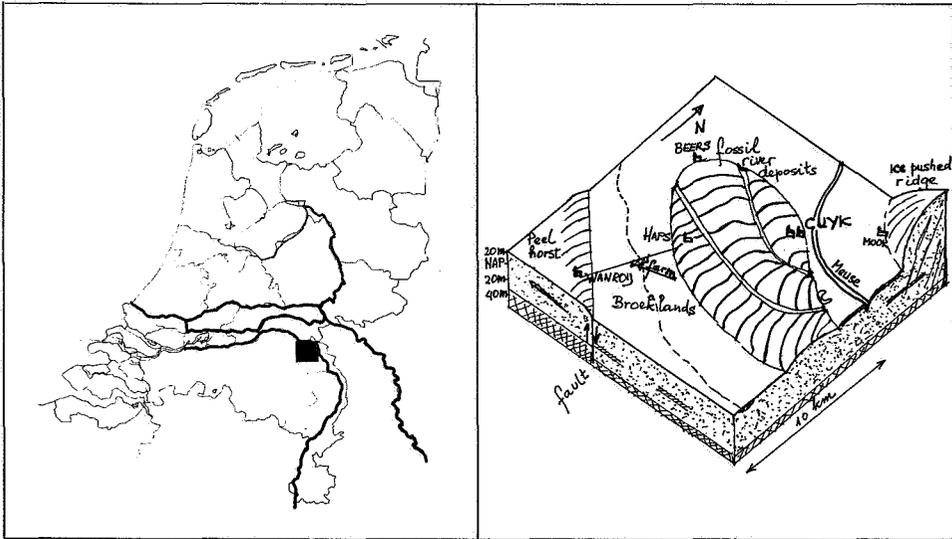


Figure 1. *Situation, landscape and subsurface*

3. GEOFYSICAL INVESTIGATIONS

At the farm three geo-electrical spreads have been laid. Interpretation results in a sandy soil to a depth of 50 m, where the top of the Tertiary claylayers is situated. At a depth of about 12 m the sand becomes more coarse and maybe the groundwater more conductive. A meaningful difference is that in spread g-e 2 an unsaturated loam layer of 0.5 m thick is interpreted at the top, which lacks in the other spreads. A spatial image of the loamy layers can be derived from the electromagnetical readings (Figure 2). Generally, where the EM-values are in between 7 and 8 mS/m the thickness will be about 0.5 m and where they are higher than 8 mS/m about 1 m. The exception is a zone along the road and the farm where higher EM-values are caused by a more severe pollution leading to a higher conductivity of groundwater. The pattern of EM-values can be seen as the expression of an abandoned river system later filled in with finer sediments.

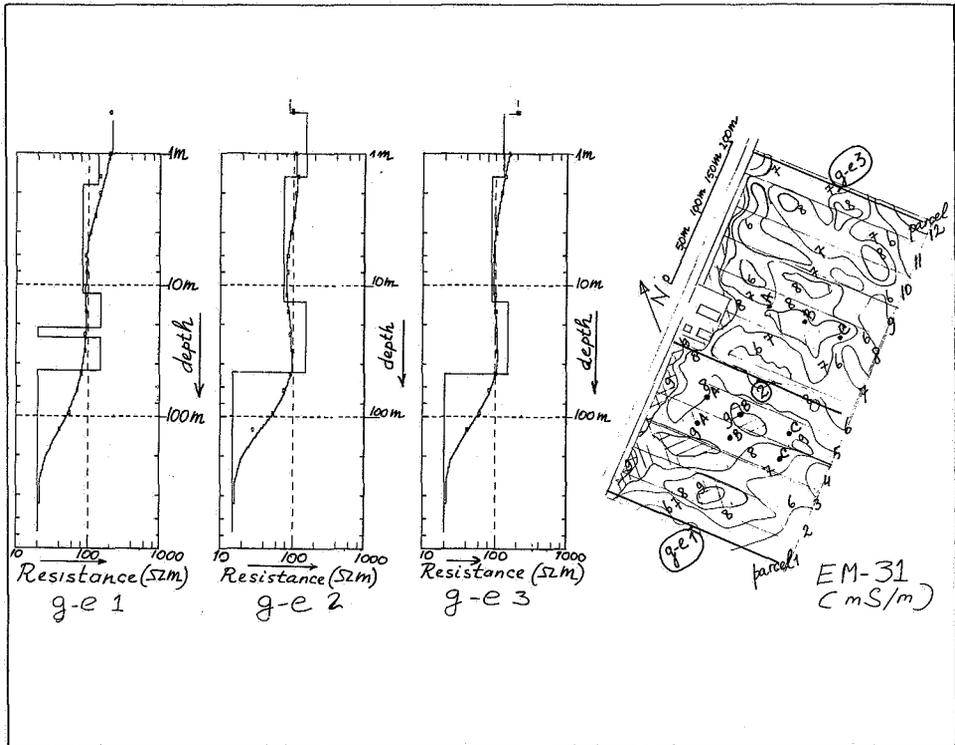


Figure 2. Results of the geophysical investigations

4. LACQUER PEELS AND SEDIMENTOLOGICAL ANALYSIS

At the farm ten drillings have been made; the cores of eight borings have been cut and lacquered. The lacquer peels have been analysed sedimentologically. The results corroborate the geophysical interpretation. The soil has been deposited by a braided river system abandoned subrecently.

During deposition of the saturated zone (which only has been analysed) the river was present all the time at the location of the farm. Mostly the main gully ran through parcels 4 and 5 following the pattern of the EM-values of Figure 2. In the lacquer peels of boring 4A three main sequences of river activity can be distinguished (Figure 3), the upper one still indicating river bed sedimentation at the top. The top sediments of boreholes 8A and 8B indicate more quiet deposition (even bedding) outside the main river bed. The abandoned gully system has

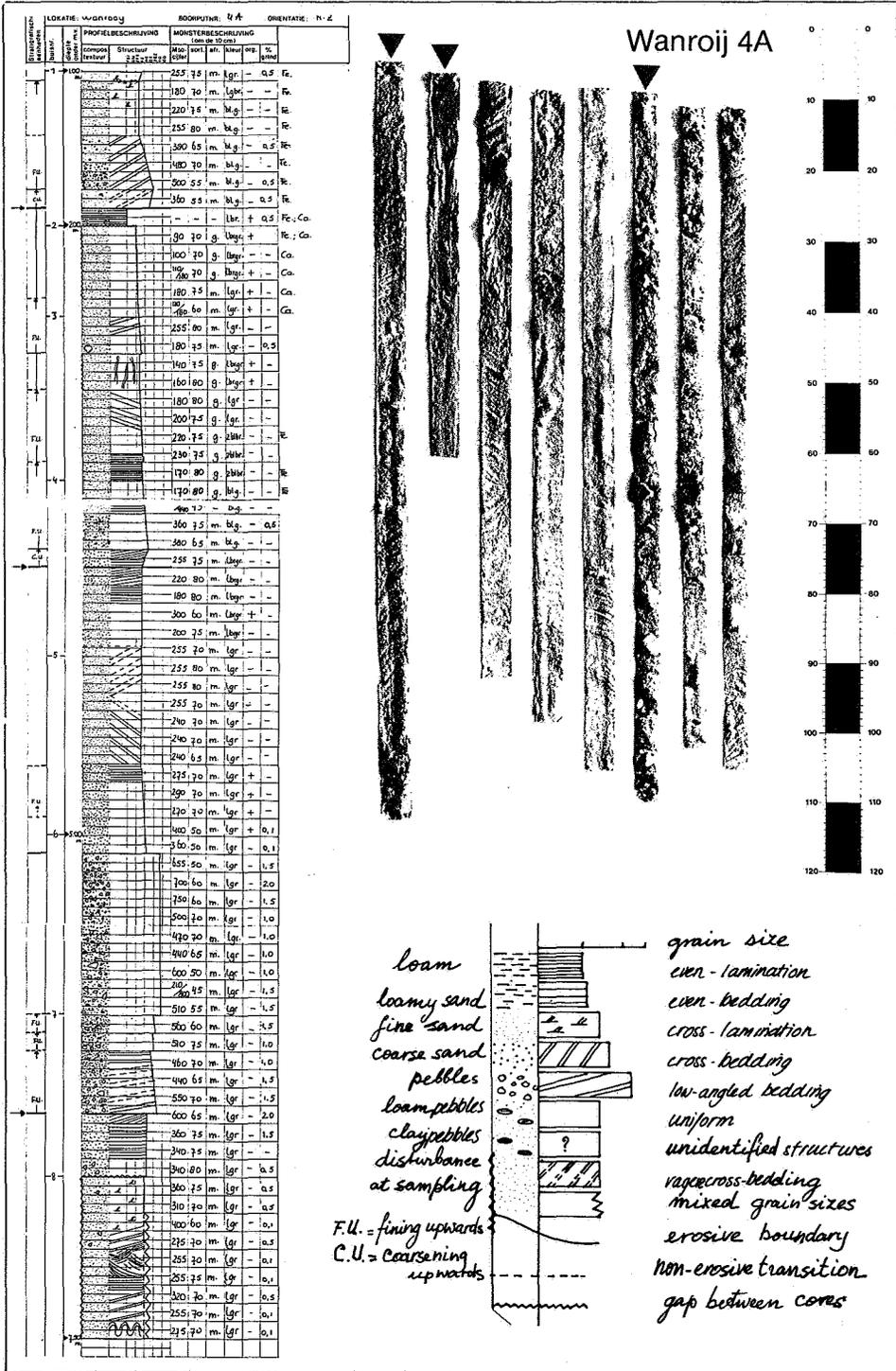


Figure 3. Lacquer peel and sedimentological analysis of boring 4A

afterwards been filled in with finer sediments, which therefore have its greatest thickness at parcels 4 and 5.

5. FIRST RESULTS OF NITRATE SAMPLING

Nitrate contents have been investigated at nine boreholes in parcels 4, 5 and 8. Variations (Figure 4) are large. The largest values of more than 100 mgN/l have been found at the upper screens in borehole 8A. The location of this hole, presumably downstream of the farm buildings, makes it likely that a point source pollution derived from the farm yard has influence. In the other boreholes the values vary between 0 and 55 mgN/l. The maximum values have to be related to the nitrogen gifts which over the past six years were on the average 800 kgN/ha. At an estimated groundwater recharge of 0.2 m/year the gift comes down to an input of 400 mgN/l. Hence, an immission to saturated groundwater of maximum 15% of the gift at surface would occur. This is slightly less than could be expected at a fully sandy soil and a minimum depth of groundwater of about 1.50 m (Figure 2). In considering the variations per borehole, it seems that they roughly can be related to the soil conditions at the recharge area. These recharge areas follow from a southwest to northeast flow at an estimated rate of 30 m/year and a downward percolation of about 0.5 m/year. High nitrate contents relate to a sandy soil and low contents to more loamy components in the soil of the recharge area. Although further studies are needed, it can already be concluded that the shallow soil conditions may have a large impact on the nitrate contents of groundwater. The sedimentological analysis is of great help in a better understanding of the soil conditions.

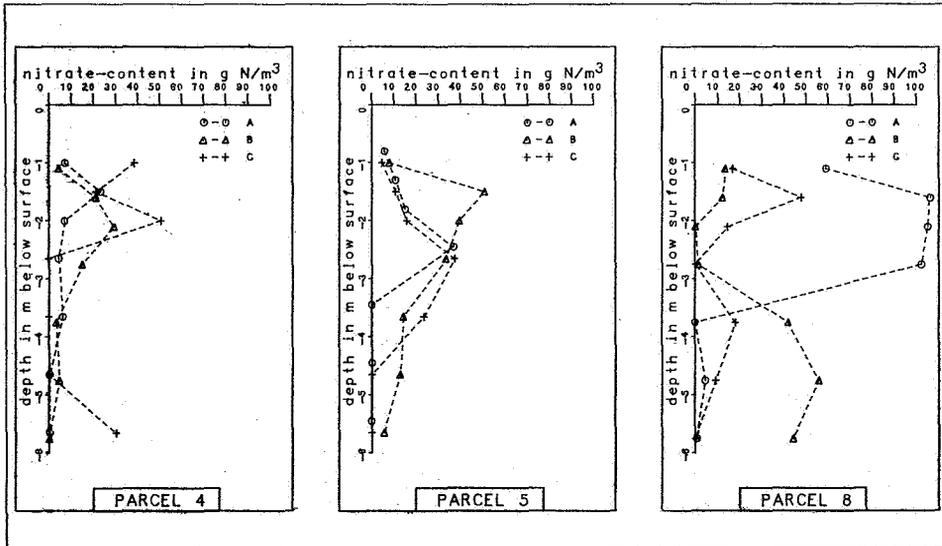


Figure 4. First results of the nitrate sampling

A SIR DATABASE FOR CONTAMINATED SITES -
STATISTICAL DATA EVALUATION AS A TOOL FOR
GROUNDWATER CONTAMINATION ASSESSMENT

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ABSTRACT

A database scheme for contaminated sites based on the databank system SIR is presented. The multivariate statistical evaluation of the data derived from more than 1000 groundwater analyses of samples upstream and downstream of 35 waste sites in the Federal Republic of Germany shows a significant impact on groundwaters clearly subdividable into three main waste types, these are household waste, construction waste and 'chemical waste'. Thus, the indication of an impact of these waste types to groundwaters is feasible by screening using the parameters boron, sulphate, AOX and GC-fingerprints.

1. INTRODUCTION

Within the last years a continuous agglomeration of data from contaminated sites can be observed. This is due to an increasing number of investigated localities and the fast development of modern multicomponent analytical techniques. Databank systems make it possible to handle and manage this mass of data. The electronic data storage enables a rapid retrieval of selected data groups, its comparison, graphic presentation and different statistical evaluations.

2. THE DATABANK

Investigations of contaminated sites result in hierarchically structured data sets (Figure 1). They can be arranged into five groups (Table 1):

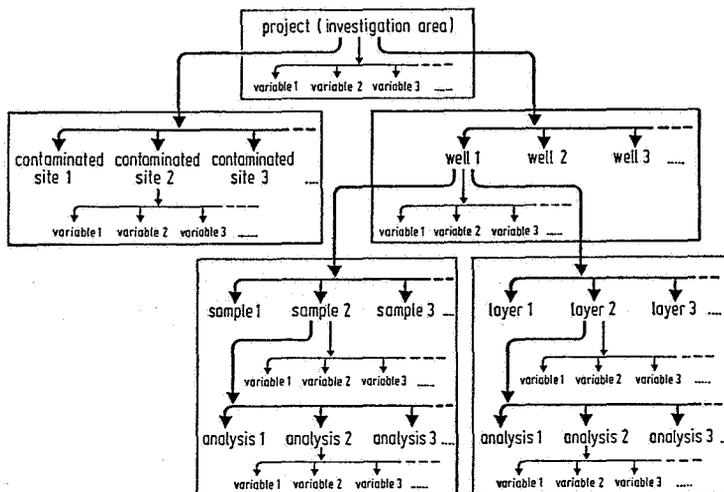


Figure 1. Hierarchical structure of data based on investigations of contaminated sites

- General data of (an) investigation area(s)
- Data of (a) contaminated site(s)
- Data of (groundwater) observation wells
- Geological, hydrogeological and geochemical data
- Data of (ground) water samples

Due to the hierarchical structured data sets and the capability to combine both, hierarchies and network structures, the databank management system SIR (Scientific Information Retrieval) (Robinson et al., 1980) can be recognized as very suitable for this purpose.

A databank scheme was developed including 33 'record-types' with 250 variables (Table 1). The 'case id', a variable for identifying different cases, is called 'project'. Any investigation area, each with one or more contaminated sites, represents one value for this variable. The detailed description of the databank scheme is given elsewhere (Kerndorff et al., 1985; Arneth et al., 1986).

3. STATISTICAL DATA EVALUATION

The databank allows a relatively easy preparation of different data matrices for statistical analysis. Processing follows by well known stati-

Table 1. Structure of data and database

structure of data			structure of databank		
data group	data sub group	kind of data	rec-type number	number of variables	some examples for variables
general data		general data of (an) investigation area(s)	1	8	begin/end of investigations
		literature about the project(s)	2	11	author, titel, pages
		coordinates of the surrounding line(s)	3	4	x/y-coordinates, height
		coordinates of objects (i.e.: river, lake)	4	6	name of object, x/y-coordinates
		meteorological data	5	5	precipitation, temperature
data of contaminated sites		general data	6	11	name of site, begin of deposition
		data about waste type(s)	7	2	waste type, quantity
		coordinates of the surrounding line(s)	8	4	x/y-coordinates, height
data of (groundwater) observation wells	installation data	general data	9	15	kind of well, year of construction
		coordinates	10	3	x/y-coordinates, height
geological and geochemical data	sedimentological data	data about the filter(s)	11	7	number of filter, material
		data about the pipe	12	5	length, diameter, material
		general data	13	5	number, name, depth, thickness
	inorganic geochemical data	grain size data	14	3	grain size, quantity
		other sedimentological data	15	6	porosity, permeability
		common cations	16	21	K, Na, Ca, Pb, Cd
	extraordinary cations	extraordinary cations	17	3	name, quantity
		common anions	18	10	SO ₄ , Cl, HCO ₃
		extraordinary anions	19	3	name, quantity
	radiochemical data	radionuclides	20	3	name, quantity
		organic group parameters	21	12	AOX, TOC
		most common organic substances (volatiles)	22	9	trichloroethene, tetrachloroethene
		other organic substances	23	4	name, quantity
data of (ground) water samples	inorganic chemical data	in situ parameters	24	17	date, temperature, colour
		common cations	25	22	K, Na, Ca, Pb, Cd
		extraordinary cations	26	3	name, quantity
		common anions	27	11	HCO ₃ , Cl, SO ₄
		extraordinary anions	28	3	name, quantity
	organic chemical data	radionuclides	29	3	name, quantity
		organic group parameters	30	14	AOX, TOC, TON, TOS
		most common organic substances (volatiles)	31	9	trichloroethene, tetrachloroethene
		other organic substances	32	4	name, quantity
		microbiological data	33	4	name of bacterium, number of colonies

tical software, i.e. SPSS (Statistical Package for Social Sciences) (Schubö & Uehlinger, 1986) or Clustan (Wishard, 1984). For example, data matrices of exclusively contaminated or uncontaminated groundwaters can be produced as well as data matrices of groundwaters from discharge or recharge areas. Furthermore, special data matrices of groundwaters being influenced mainly by one waste type can be prepared. Using multivariate statistical methods different kinds of relations among groundwater samples, groundwater constituents and waste types can be elaborated.

3.1 Factor analysis

Important results were gathered from factor analysis which show a more or less specific influence of emissions from the three main waste types into groundwaters, these are household waste, construction waste and chemical waste (Table 2). Factor 1, including about one third of the total variance, is interpreted as the influence of household waste. Here, temperature, conductivity, chloride, sodium, boron and AOX yield factor scores >0.5. AOX in this factor demonstrates the presence of halogen organic compounds in contaminated groundwaters of this type, indicating that 'pure' household refuses are rarely deposited. Factors 2 and 5 show the influence of industrial waste which often has high contents of volatiles or heavy metals, respectively. Factor 4, with high scores for calcium, sulphate and strontium is typical for construction waste.

Table 2. *Factor analysis of groundwater constituents (90 samples downstream of 31 waste sites in unconsolidated sediments)*

	factor 1	factor 2	factor 3	factor 4	factor 5	communality	
eigenvalue	7.1	2.9	2.3	2.1	1.6		
per cent of variance	36.5	14.9	12.1	10.7	8.1		
temperature	0.651					0.604	
pH value						0.605	
conductivity	0.803					0.976	
SO ₄				0.846		0.744	
Cl	0.812					0.899	
NO ₃						0.677	
Na	0.913					0.919	
Cu				0.618		0.922	
Mg						0.849	
Fe			0.793			0.736	
Mn			0.763			0.686	
Sr				0.680		0.743	
As						0.467	
Pb					0.649	0.877	
Cd					0.842	0.787	
Ni						0.718	
Zn						0.643	
Cu						0.856	
Cr						0.610	
B	0.672					0.638	
AOX	0.558					0.756	
ECD (area)						0.501	
FID (area)						0.763	
trichloroethene		0.951				0.940	
tetrachloroethene		0.609				0.601	
volatiles (sum)		0.987				1.001	

3.2 Discriminant analysis

Utilizing discriminant analysis contaminated and uncontaminated groundwater samples as well as groundwater samples contaminated by different

waste types are clearly subdividable. 54 samples from an investigation area in Berlin (West) were, based on their chemical composition, pre-classed into 3 groups, these are 'uncontaminated', 'contaminated mainly by household refuses' and 'contaminated mainly by construction waste'. Discriminant analysis confirms 98.1% of the preclassified cases to be in the right group. Only one sample of the second group received a higher probability to be in group one.

3.3 Cluster analysis

Cluster analysis relates groundwater samples or groundwater constituents in a more complex manner considering qualitatively and quantitatively effects. Resulting clusters most frequently combine groundwater samples having similar contamination patterns which can be explained by similarities of leachate compositions and/or (hydro)geochemical conditions around a waste site. However, also complex dendrograms are produced which often prove to be difficult to interpret.

3.4 Frequency distributions

Based on the multivariate statistical evaluation screening parameters typical for distinct waste types could be elaborated (Kerndorff et al., this volume). These are boron for household waste, sulphate for con-

Table 3. *Interim reference values for screening parameters*

	boron ($\mu\text{g/l}$)	sulfate (mg/l)	AOX ($\mu\text{g/l}$)	sum of peak area of GC-fingerprints ECD FID	
geogene background	< 20	< 70	< 10	< 30	< 5
contaminated	> 50	> 150	> 10	> 60	> 10
heavily contaminated	> 1000	> 500	> 300	> 200	> 50

struction waste and AOX as well as GC-fingerprints for organic 'chemical waste'. Frequency distributions were made to elucidate the range of measured concentrations. Founded upon the comparison of frequency distributions and statistical parameters of contaminated with uncontaminated groundwater samples interim reference values for different types and

intensities of groundwater contaminations caused by waste deposits have been elaborated (Table 3).

4. CONCLUSIONS

Consequent data collection and storage of data derived from contaminated sites and their environs is a valuable procedure which creates the pre-conditions for a better and faster handling of further projects. The quality of statistical evaluations and their results increases with the number of cases. Frequency distributions of sufficient analytical data from groundwaters show the level of geogene background and the range of possible contaminations. In combination with toxicological data they possibly may provide a basis for elaborating reference and threshold values.

Furthermore, each contaminated site stored in a database has a distinct pattern formed by the values of its variables. Typical, well known contaminated sites may be compared statistically with those of less investigated ones and in this way the degree of conformity could be quantified using multivariate techniques, providing a better and more objective groundwater contamination and risk assessment.

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THE MONITORING OF HYDROLOGICAL, HYDROGEOLOGICAL AND
HYDROCHEMICAL PARAMETERS OF SUPERFICIAL AND UNDER-
GROUND WATERS IN APULIA (SOUTHERN ITALY)

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ABSTRACT

Apulia is a Karstic coastal region: while it is almost without superficial water resources, it houses a huge mass of ground water which is being heavily pumped for domestic, industrial and agricultural uses. In order to be able to monitor supplies, outflows and pollution, observation networks have been set up and are now in operation. As a result of thorough region-wide hydrogeological investigations, these networks are being extended and integrated.

TEXT

Apulia is a coastal region: its geological basement is a mesozoic carbonate formation with varying degrees of fracturing and Karstism. The formation crops out in three hydrogeological units i.s., the Gargano, Murgia and Salento. Instead, throughout the "Tavoliere", the carbonate formation lies at a considerable depth below field level and is covered by a very thick post-cretaceous formation.

In the Gargano, Murgia and Salento hydrogeological units, a basic feature is the huge mass of ground water housed inside the carbonate formation. Conversely, in the Tavoliere, large amounts of ground water flow inside the plio-pleistocenic formation.

The region is almost without superficial water resources.

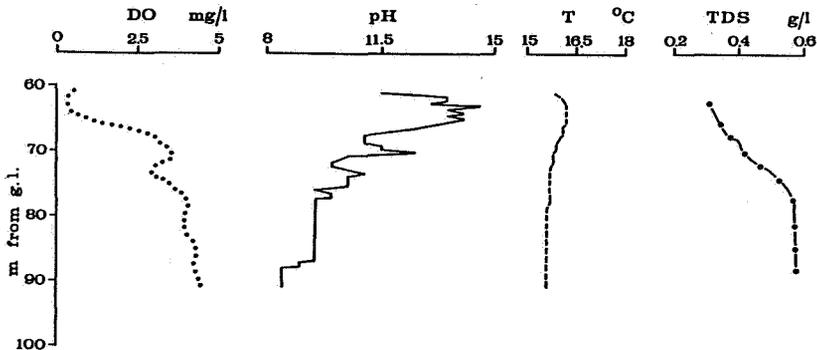
Water supplies for domestic, industrial and agricultural uses are obtained from the above mentioned aquifers as well as from outside the region; however, given the growing demand for water from the various sectors, ground water is being heavily drawn upon and this practice is steadily

expanding. It is therefore of paramount importance to be aware of the parameters describing the processes by which ground water is fed to, or flows through, the aquifer and is discharged from it, as well as the chemical and physical properties of the waters.

Apulia ground waters are currently undergoing saline pollution, especially in the more coastal areas where they are heavily pumped essentially for irrigation purposes, as well as pollution caused by civil, agricultural and industrial activities.

At present, extended ad hoc networks are in operation to monitor the rate of ground water rejuvenation as well as the amount and evolution of pollution over time. The following parameters are considered: weather and climate (rainfall, air temperature and atmospheric pressure); regime of main water streams in the region; piezometric heads of ground water as measured by continuous surveye through a thick network of specially equipped wells; sea levels, representing the ground water base level; vertical distribution of temperature and salinity along the water columns of observation wells namely, wells sunk into the sea water underlying the fresh ground water mass.

To test water quality, survey campaigns have already been launched using the wells of the water gauging and recording network, the network monitoring saline intrusion and any other available wells. To this effect, the essential characteristic ions indicating pollution are determined such as: NH_4 , NO_3 , NO_2 , MBAS, DO and pH; wherever possible, logs are also taken for the latter parameters from the water columns in the wells as in the following figure.



Investigations have shown that: a) 50% of the rainfall in the autumn-winter semester, or about 200 mm, is supplied to the aquifer; b) piezome-

tric head fluctuation in the Murgia inland areas are in the order of a few meters; c) the fluctuations recorded in a large coastal belt extending over 15 km inlandwards are remarkably different from those that are not "affected", i.s. are free from the fluctuations induced by the sea and atmospheric pressure. Amplitudes are about 40% less in the average and may occasionally be over 60% less, that is, considerably less than the recorded excursions of between 20 and 110 cm. Another finding is that the hydrological divide line in the Salentine peninsula may be shifting several kilometers due to the different levels of the Adriatic and the Ionian seas.

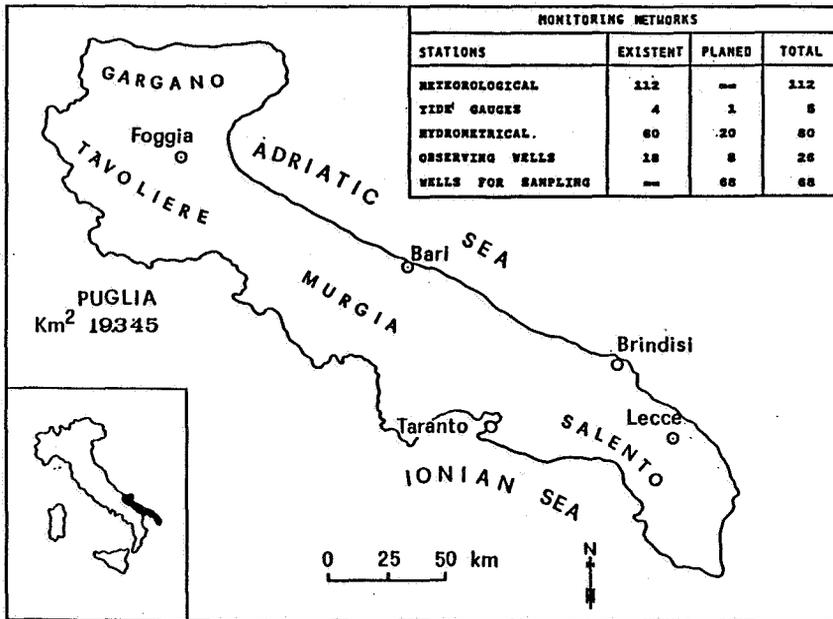
The analysis of data obtained from logs in the observation wells shows that the interfaces undergoes significant changes with time, both in terms of position and thickness - a fact that is essentially connected to the impoverishment suffered by ground water as a result of pumping. The study had identified areas in which saline contamination is especially severe and is present as far away as several kilometers inland from the coast. Also human pollution has been found to be quite widespread; locally, such type of pollution is further enhanced by such contributing factors as intensive human activities and the aquifer's own peculiar hydrogeological properties (high transmissivity, preferential underground drainage areas, etc., etc.).

Based on these findings, and because it appears necessary to monitor the described phenomena more extensively and in greater detail, steps have been taken to expand the monitoring network and to set up a survey network for the main parameters describing biological and chemical pollution.

The map represents the overall number of points making up the monitoring network, including those already in operation and those now being organized or just only in the planning stage.

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MONITORING OF GROUNDWATER QUALITY IN STEAD OF
REMEDIAL ACTIONS IN RELATION TO SOME DISPOSAL SITES

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ABSTRACT

The necessity of closing down groundwater pumping stations due to the presence of pollutants in groundwater is a common feature of today's society urging a continuous effort to monitor groundwater quality. The vulnerability of soil and groundwater with respect to their multifunctional character is illustrated by the numerous pollution-sites discovered the last couple of years in The Netherlands.

Given the current known volumes of contaminated soils and groundwater, removal of the pollution is for various reasons (momentarily) unnecessary or unacceptable. Postponing remedial actions may demand monitoring strategies, whether or not in combination with partial remedial actions. Monitoring systems with respect to groundwater pollution have to be set up. Design-criteria for monitoring systems have to be developed.

Based on general criteria and illustrated by two case-studies, conclusions can be drawn up on the general set up of a monitoring network.

1. INTRODUCTION

Either as a result of local or diffuse sources of contamination groundwater pumping stations in the Netherlands, have been closed down or are threatened with it. Deterioration of the quality of groundwater is acknowledged and formal regulations are in varying stages of development, aiming to reduce or at least to induce a stand-still of the contamination of groundwater.

Historically speaking an analogy with the contamination of the surfacewater can be made from the point of view of drinkingwater supply.

The use of surfacewater as drinkingwater, being hampered by contamination, gave rise to several options namely removal of the sources of pollution, purification of the surface water to drinkingwater quality or turning to another source of supply. Along those lines solutions have been sought.

Generally speaking the long term policies are aimed at removal of the sources of pollution. However considerable efforts are involved, to restore the multifunctionality. Direct approach for the availability of drinkingwater has been sought by treatment of surface water for use as drinkingwater. In combination with monitoring the waterquality, this approach gives way to investigate the environmental impacts and to develop an adequate policy.

The same parallel in a different context can be drawn in cases of design of remedial actions with respect to groundwater contamination.

The general policy is to remove contaminants if necessary from the point of environmental pollution control. Given the current known volumes of contaminated soils and groundwater in the Netherlands, removal may for various reasons being momentarily unnecessary or unacceptable (finances, degree of (potential) contamination, risks assessments etc.).

Given the acceptance of the presence of polluted groundwater and the implicit limitations on its multifunctionality, a comparison with the short term policy on surfacewater-approach can be made.

The pollution being accepted for the moment, awaiting long term clean-up actions, criteria and standards have developed to 'determine' the waterquality and the usefulness for various purposes. This in combination with the set up of waterquality monitoring programmes.

Therefore the expertise developed by monitoring programmes aimed at surfacewater control also applies for groundwater monitoring.

2. MONITORING STRATEGIES FOR LOCAL GROUNDWATER CONTAMINATION

This paper deals with monitoring of groundwater quality in relation to local soil contamination sites. However the local characteristics are part of regional patterns determined by regional (primary) monitoring systems. Groundwater quality is determined by processes such as weathering, atmospheric deposits, "industrial and urban activities" (fertilizers, manure, leakage of chemicals during industrial handling, defect sewage systems), dumpsites etc. This implies diffusive or local impacts on the waterquality to be taken into account during site investigations and the development of a local (secondary) monitoring system.

Since monitoring local groundwater contamination may tend to location-dependent solutions an effort should be made to avoid ad-hoc design criteria.

A clear definition of monitoring objectives and the monitoring programme is the first step in the design process, as shown in figure 1.

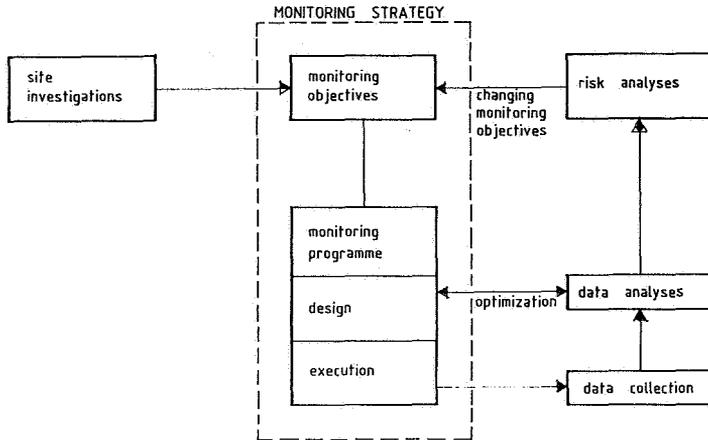


Figure 1: Cycle of monitoring activities

In general, the monitoring strategy consists of monitoring objectives and a monitoring programme.

As a part of the monitoring programme, data will be collected, resulting in an analysis and evaluation of this data, followed by a risk analysis. In some cases, this will lead to a change of the monitoring objectives, and correspondingly the monitoring programme. At that stage, the monitoring-cycle has been walked through. The optimization of the monitoring activities takes place by evaluation of the programme design and the results of the data analysis.

In the following sections, some parts of the monitoring cycle will be dealt with.

3. SITE-INVESTIGATIONS

Prerequisites for the design of a monitoring strategy is knowledge of the site and pollution characteristics, provided by a site-investigation. This investigation has to deliver at least the following information:

- Geohydrological situation : aquifers (confined, semi-confined or phreatic);
- : direction of groundwater flow (horizontal and vertical);
- : groundwater velocity (horizontal and vertical);
- Geochemical situation : geochemical and microbial processes in ground and groundwater;
- : pollutant mobility;
- Characterization of quality and quantity of pollutants : size and boundaries of the polluted area (horizontal and vertical);
- Regional background : threshold-values.

The aim of the site investigation is to determine the physical and chemical characteristics of the site in order to enable detection of changes in composition and also to indicate pollution migration.

The purpose is not to obtain information concerning the quantitative aspects. Collection of such data can only be provided by a long term intensive data collection through the installation of a large number of detection points on behalf of such monitoring programme. Otherwise no statistically significant measurements of the mass-balances can be obtained.

4. MONITORING STRATEGY

4.1 Monitoring objectives

The selection of the monitoring objectives depends highly on the results of the site investigations, the evaluation of the risk of further spreading of the pollution and the (im)possibilities to remove the contamination. In this way some different objectives can be distinguished:

1. monitoring, to collect more information on the long term environmental impact of a disposal site. In fact, this kind of monitor, is an extension of the site investigations;
2. monitoring, to verify the effectiveness of a clean-up of a contaminated location;
3. monitoring, to check changes in the environmental impacts as a result of changing boundary conditions, which may increase the need of an urgent clean-up. For instance, changing geohydrological circumstances, landuse, etc.

4.2 Monitoring programme

When the monitoring objective has clearly be defined, a programme can be designed and executed, consisting of:

- size of monitoring area;
- maximum monitoring depth;
- sampling technique;
- sampling locations;
- sampling frequency;
- parameters to analyse;
- additional monitoring techniques, for example geophysical surveys.

The monitoring programme must be set up in such a way that it can be used both during and after the execution of remedial actions and the design must therefore be integrated in the overall-design of that remedial actions.

However, the objective of a monitoring system can be changed, depending of the half-term results.

6. APPLICATION

The design of a monitoring strategy, as described in the preceeding sections, can be illustrated by two different cases in which the authors were recently involved. The cases deal with contamination sites under varying circumstances with respect to their geohydrological situation, source of pollution, as well as the urgency for clean up measures.

6.1 Site-investigations

At location A, a coal to factory had intensily polluted its surroundings, resulting in both ground- and groundwater pollution. The geohydrological situation consists of an aquifer of 40 m thickness, covered by Holocene to players of 1 - 10 meter of clay and peat.

The contamination has been subject to diffuse spreading over the direct surrounding of the factory. This surroundings consists partly of residential areas. Along the vertical, the pollution has partly migrated downward to the aquifer, were the groundwater flow is influenced by several groundwater extractions. From the site-investigations it was concluded that the migrated contamination was a severe risk for the surrounding inhabitants and that remedial actions had to be taken. From technical and financial point of view a total removal was impossible, so a partial removal is planned in combination with measures to stop further migration of the contamination.

Location B consists of a very large domestic waste disposal site. The geohydrological situation consists of one aquifer with a thickness of appr. 130 m. The upper 20 meter of the aquifer consists of loamy fine sand (with at 1 meter depth a loam layer), further downward the sand is more coarser. In spite of the high permeability of this sand, the average groundwater velocity is rather low. This is caused by the low hydraulic gradient. The landuse in the surrounding of this waste disposal site is agricultural.

The percolation from this waste disposal site has migrated into the aquifer for many years. Recently, measures are taken to reduce this migration. No indication is available that the contamination forms a severe threat to the surroundings. Nevertheless, the process of (slow) migration is followed by a monitoring network.

The two cases - which are described - are schematized in figure 2.

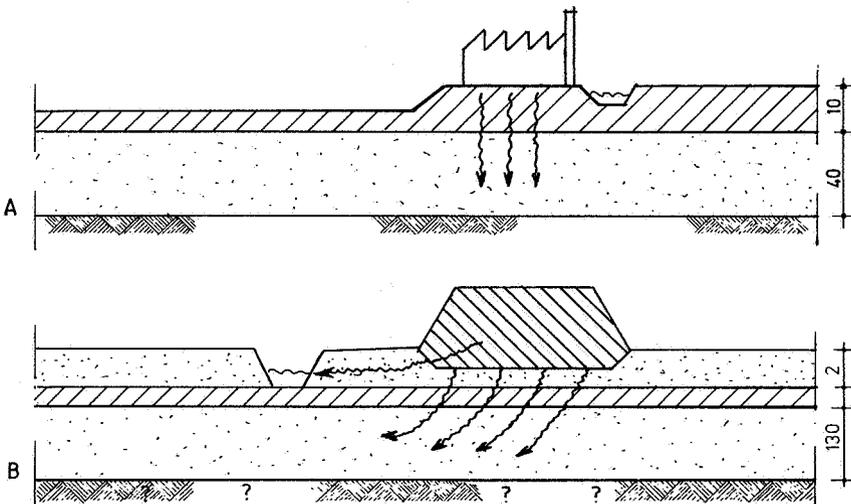


Figure 2: Schematization of the two investigated cases

6.2 Monitoring strategy

According to figure 1, the monitoring strategy consists in the first place of the definition of the monitoring objectives, followed by the design and execution of the monitoring programme. Those elements will be described for the two cases in the following subsections.

6.2.1 Objectives

For case A, where partial remedial actions are planned, the monitoring objectives are (see objectives 1 and 2 in section 4):

- to collect more information on the long term environmental impact;
- to verify the effectiveness of the clean-up action.

For case B (a disposal site still in use where further extension is programmed), the monitoring objective is to check changes in the groundwater quality, see objective 3 (section 4). This monitoring objective is part of the management of a large-scale waste disposal site, resulting from formal regulations concerning waste disposal under controlled circumstances.

6.2.2 Design and execution

Case A

For this case, the design of the monitoring programme is integrated in the overall-design of the clean-up actions. The collection of data to describe the complex geohydrological situation was at the same time used as basic design for the monitoring network.

The optimization of this network will take place after the implementation of the remedial actions.

The network comprises mainly of series of observation wells, situated according to local pollution characteristics and the geohydrological constraints.

Special attention is given to the adaption of the sampling frequency on the change on groundwater velocities induced to the execution of the remedial actions.

Case B

In case B the monitoring activities are focussed on the optimization of an existing network. Due to the continuing migration of percolation into the underground, the original monitoring network had to be re-designed. This case illustrates the optimization process between data analysis and design of monitoring programme; see figure 1.

Due to the fact that the waterbearing layers are rather deep, geophysical techniques (geoelectrical and geothermal surveys) are applied as basic for the optimal selection of observation wells.

These geophysical surveys are supplementary to the standard monitoring activities and are regularly repeated.

7. EVALUATION

The application of a monitoring strategy may avoid ad-hoc design criteria for the monitoring of local groundwater quality.

A tool for the development of a monitoring strategy is the cycle of monitoring activities, as schematized in figure 1.

A clear definition of the monitoring objectives should always be the first step of the monitoring strategy.

However, the results of the monitoring network on a local scale should be evaluated, taken into account the relation with the larger-scale ("primary") network.

An important issue of the monitory cycle is the optimization between data analysis and monitoring programme. In cases of local contamination sites optimization is hampered by lack of long term data collection.

Taken into account the increasing numbers of monitored contamination sites, in the future the emphasis can be laid on the above mentioned optimization, resulting in improved designs of monitoring programmes.

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TOPIC 3: VULNERABILITY MAPPING

MAPPING TO ASSESS GROUNDWATER VULNERABILITY TO POLLUTION

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ABSTRACT

Groundwater vulnerability to pollution may be defined as the sensitivity of its quality to anthropogenic activities which may prove detrimental to the present and/or intended usage-value of the resource. Vulnerability assessment aims at providing preliminary information and criteria for decision-making concerning management of water resources and land-use as related to groundwater quality control. A clear determination of the decisions and of the requisite information are therefore essential for an effective assessment of vulnerability. Vulnerability mapping is the technique of quantifying the assessment of vulnerability and displaying it in a fashion which makes it useful and convenient for actual application in the decision-making process. This paper identifies a minimal set of key parameters representing physical quantities which are critical for the assessment of vulnerability of groundwater to surficial sources of pollution. The background data required for evaluating these parameters are determined and the mode of displaying them is presented.

INTRODUCTION

Groundwater is gaining increasing attention as a source of water supply owing to its relatively low susceptibility to pollution in comparison to surface water and due to its relatively large storage capacity. However, long-term over-exploitation and uncontrolled land-use cause deterioration of the quality of this resource and decline in its exploitable yield. This, combined with simultaneous growth in demand for water, results in an ever-increasing gap between available supply and demand. Any postponement in properly addressing this problem reduces the scope of feasible solutions and the time for implementation, whilst increasing the required funds to that end.

Due to the time lag between contamination at the ground surface and its occurrence in the groundwater, even regions still enjoying satisfactory groundwater quality must be concerned with the consequences of land-use on the soil and water. A rational, well-planned and implemented groundwater quality management programme should therefore be prepared in the earliest stages of regional development.

The decisions involved in a groundwater quality management programme include decisions taken within the agency responsible for managing the groundwater system and decisions made externally to this system but over which the agency ought to exercise significant influence. Information required to make these decisions includes demand for water in each quality category, sources of supply, quality trends under present or anticipated patterns of operation both of the aquifer and its surroundings, and the resultant economic impact, all subject to prescribed goals, standards, and measures of effectiveness. Vulnerability assessment represents an important preliminary tool in decision-making pertaining to the management of groundwater quality.

DEFINITIONS

"Groundwater quality" is the set of values of physical, chemical, and/or biological parameters of the groundwater as related to chosen standards for a given category of use;

"Usage-value" of a given water quality for a particular category of use is the worth of a unit volume of water of that quality for a user in that category;

"Pollution" of groundwater is the addition to the water of a substance which has the potential to alter the quality of the water so as to lessen its usage-value;

"Vulnerability" of groundwater to pollution is the sensitivity of its quality to anthropogenic activities causing pollution;

"Vulnerability mapping" is the technique of assessing and displaying the vulnerability of groundwater as a function of location and time.

OBJECTIVES OF VULNERABILITY ASSESSMENT

Vulnerability assessment aims at providing preliminary information and criteria for decision-making in the following areas:

- designation of land-use and management of water resources in the context of regional planning as related to groundwater quality control;
- legislation, including zoning, regarding land-use alteration and practices in the context of protecting groundwater quality;
- siting and operation of facilities for waste disposal, treatment, and reuse;
- selection and timing of pollution abatement activities;
- design and management of groundwater quality monitoring networks;
- allocation of costs related to groundwater pollution.

Vulnerability assessment ought to be a periodically updated activity on the basis of new knowledge and data.

CRITERIA OF EFFECTIVENESS OF VULNERABILITY ASSESSMENT

The effectiveness of vulnerability assessment may be evaluated on the basis of the following criteria:

- relevance to the decision-making process, viz., the extent to which information contained in the vulnerability assessment can be used and is indeed critical for this process;
- the reliability or level of confidence which may be ascribed to the information provided;
- the extent to which information communicated in the vulnerability assessment is presented clearly, simply, and conveniently, and involves the minimum of essential parameters;
- actual implementation of the information provided by the vulnerability assessment in control of groundwater quality by the decision-making authorities and those who might have influence upon them;
- adaptability, viz., applicability to various users, as well as the ease of extrapolating the information from one site to another within the system, and/or updating it in the course of time.

PARAMETERS OF VULNERABILITY ASSESSMENT

The change in the quality of a groundwater body is affected by five basic factors. These include net influx of constituents in the water through lateral boundaries, direct supply to or withdrawal from the groundwater, reactions undergone by constituents within the domain occupied by the groundwater, and supply of constituents from above the groundwater via the unsaturated zone or from below the groundwater body. Of these factors, vulnerability assessment, as approached in this paper, deals only with the effect of sources from above the groundwater body, and specifically with anthropogenic sources on the ground surface. Loss to a consumer of groundwater in any given category of use due to an increase in concentration of a particular substance in the groundwater may be expressed by:

$$\Delta L = \frac{\Delta L}{\Delta C} \times \frac{\Delta C}{J_s} \times \frac{J_s}{\Delta a} \times \Delta a, \quad (1)$$

where ΔL = loss increment;

ΔC = increment in the concentration of the substance in the groundwater;

J_s = efflux of mass of the substance at the ground surface as a result of a given anthropogenic activity;

Δa = a measure of the increment of that anthropogenic activity.

By definition, vulnerability should be expressed in terms of $\Delta C/\Delta a$, or change in concentration of a given substance per unit increment in a given anthropogenic activity. However, since the same substance may be contributed by different pollution sources and for the purpose of adaptability of the information provided by the vulnerability assessment to various users, we have preferred to split the expression of vulnerability into two parts, viz., $\Delta C/J_s$, which is independent of a particular source of pollution and any particular category of use, and $J_s/\Delta a$, which is specific for each particular source. In this paper we refer only to $\Delta C/J_s$, namely the anticipated change in concentration of a given substance in the groundwater per unit efflux of mass of the substance to the ground surface. As a possible manner of arriving at this information, let us consider an element of a groundwater body

which has a horizontal extent of a unit area, is exposed to its surroundings only at the top, and extends from the top of the saturated zone down to the effective mixing depth of the pollutant once it enters the groundwater from above. The change in the concentration of the substance in the groundwater body in the course of time is given by the equation:

$$Bn \frac{dC}{dt} = J_s - F, \quad (2)$$

where B = thickness of the mixing zone;

n = the porosity of the aquifer in this zone;

and F = the rate of loss per unit area of the substance en route from the ground surface to the groundwater.

For the sake of simplicity, we assume $J_s - F$ is a constant. Assuming further that the substance was released to the ground surface at $t = 0$ and is transported through the unsaturated zone primarily by advection, and denoting the travel time of the pollutant substance by T , we can write the condition:

$$C(T) = C_0, \quad (3)$$

where C_0 = the concentration of the substance in the groundwater just preceding arrival of the pollutant from the surface.

Given those two relations, we obtain the change in the concentration of the pollutant substance in the groundwater as:

$$\Delta C = C(t) - C_0 = \frac{J_s - F}{Bn} (t - T), \text{ with } t - T \geq 0, \text{ hence,}$$

$$\frac{\Delta C}{J_s} = \left(1 - \frac{F}{J_s}\right) \times \frac{t - T}{Bn} \quad (4)$$

We have thus arrived at a set of four parameters which determine the expression $\Delta C/j_s$, these being:

T = travel time of the pollutant substance from the surface of the ground to the groundwater;

t = time elapsed since initial application of the pollutant substance to the ground surface;

B_n = mixing volume of the pollutant substance in the groundwater body per unit area, and

F/J_s = fraction of mass of the pollutant lost en route from the ground surface to the groundwater.

For a conservative, inert pollutant, $F/J_s = 0$, which yields the maximum vulnerability of groundwater in a given area to pollution from a given substance.

TYPES OF DATA REQUIRED FOR ASSESSMENT OF VULNERABILITY

In this section we consider some of the types of data needed to estimate the four parameters identified as relevant to the assessment of vulnerability.

Travel time (T)

The unsaturated zone is usually composed of a sequence of N lithologically differentiable, homogeneous layers. The travel time of a pollutant through a given layer is:

$$\Delta T = \frac{L}{V}, \quad (5)$$

where L = the thickness of the layer, and

V = the magnitude of the average downward velocity of the pollutant through the layer.

Total travel time through the unsaturated zone is given by:

$$T = \sum_{i=1}^N (\Delta T)_i = \sum_{i=1}^N \left(\frac{L}{V} \right)_i. \quad (6)$$

The velocity of the pollutant can be estimated by using models at three different levels of accuracy:

- the "piston-flow" model, which assumes that the pollutant moves at the average velocity of the water, i.e.,

$$v = \frac{q}{\theta_e}, \quad \Delta T = \frac{L \theta_e}{q} \quad (7)$$

where q = the vertical specific discharge of the water, and

θ_e = the effective moisture content of the layer.

The specific discharge itself is given by:

$$q = \begin{cases} q^{(\theta_e) \max} & - \text{ for } q^{(\theta_e) \max} < \alpha R \\ \alpha R & - \text{ for } q^{(\theta_e) \max} \geq \alpha R \end{cases} \quad (8a)$$

$$(8b)$$

$$\text{where } q^{(\theta_e) \max} = \frac{k_v(\theta_e)}{\phi} g(h_c/L+1). \quad (9)$$

Here, k_v and h_c are the permeability and the increment in capillary head along the layer, respectively (Polubarinova-Kochina, 1952), ϕ is the kinematic viscosity of the liquid phase, whilst αR is intensity of vertical supply of water to the layer. Thus, a mean travel time based upon the piston-flow model and equation 8b is given by:

$$T = \frac{1}{\alpha \bar{R}} \sum_{i=1}^N \theta_i L_i \quad (10)$$

where \bar{R} = a mean annual intensity of inflow of water (e.g., from rain)

and α = the fraction reaching the groundwater.

- the "advection-dispersion" model (Bear, 1979), which assumes that the pollutant is advected at the average velocity of the water, and dispersed owing to the fluctuation of the velocities of the individual water particles. It can be shown that, in this case, the travel time of a pollutant front is:

$$\Delta T \approx \frac{\theta_e}{q} L - 16 a_L \sqrt{1 + \frac{L}{8 a_L} - 1}, \quad (11)$$

where a_L is the longitudinal dispersivity of the pollutant at the given moisture content.

- the "pollutant-specific velocity" model, which assumes that the pollutant moves with its own velocity, which may differ with that of the carrier; e.g., in the presence of anion exclusion, the velocity of an anion may exceed that of the water (Gvirtzman et al, 1986).

So far we have assumed a conservative, ideal, and inert pollutant. If retardation of the pollutant occurs due to interaction with its surroundings (e.g., adsorption, plant-root uptake, complexation, precipitation, filtration, etc.), possibly accompanied by decay owing to biological, chemical, or radioactive processes, the specific discharge, q , ought to be replaced by q/R_d , where R_d is a retardation factor (Jackson et al, 1980). In this case, therefore, the two most significant types of data involved are the characteristics of the soil layer and of the pollutant concerned. For instance, in the case of adsorption, the retardation factor may be expressed as:

$$R_d = 1 + \frac{\rho_b}{\theta} K_d, \quad (12)$$

where ρ_b = the bulk density of the adsorbent, whilst

K_d = the distribution coefficient between the sorbed and the dissolved part of the pollutant.

For an already existing pollution source one can obtain a better estimate of the actual travel time by use of historical data regarding rate of supply of water and pollutant to the unsaturated zone, as well as the lithologic profile of the unsaturated zone and the concentration profile of the pollutant in that zone (Gvirtzman et al, 1986).

Time since application of pollutant at the ground surface (t)

This parameter is required for estimating the quantity $t - T$, which is the time since arrival of the pollutant at the groundwater (in case $t > T$), or for estimating $T - t$, which is the time remaining before the pollutant will arrive at the groundwater (in case $t < T$).

Mixing volume of the groundwater body per unit area (B_n)

The effective mixing depth is generally smaller than the total thickness of the saturated zone, and can, for practical purposes, be estimated by the depth of penetration of operating wells into the saturated zone and/or by the actual vertical concentration profile of the specific pollutant in that zone (Ronen et al, 1986).

Fraction of pollutant mass lost en route from ground surface to groundwater (F/J_s)

An estimate of F/J_s can be obtained from field experiments combined with mathematical models of the processes involved for each particular pollutant. The types of data required for estimating F/J_s are determined by the mathematical models employed in describing the relevant process. Examples of such data are the concentration of the pollutant and its distribution coefficient in the case of adsorption, the cation exchange capacity of the soil (in its relation to the type and content of clay and organic matter in the soil), the decay constant in the case of a biological pollutant, constants of chemical reactions, etc. It should, in conclusion, be noted that the multitude of factors involved in the transport and transformation of a pollutant percolating with leaching water from the ground surface down to the groundwater makes it difficult to predict concentrations and times of arrival at a high level of accuracy. Data acquired as a result of in situ field measurements combined with adequate mathematical models of processes involved can serve as optimal means of making such forecasts at a desired level of accuracy. However, in practice, only a limited number of sites exist where actual case studies based upon historic data pertinent to the source of water and pollutant may be undertaken. Therefore, and given the fact that decisions must be made in places where such studies cannot be or have not been undertaken, one is forced to make inferences from observed to unobserved sites, thus requiring a model for such a transfer of information. Such a model should be based upon relationships between characteristics which are common to the observed and the unobserved sites. It should also include an estimate of expected error owing to the neglect of certain factors. We are at a state where we have to compromise between the multitude of factors and mechanisms pertinent to the processes of

interest to be included in the model, the amount and kind of data available, and our capability of providing estimates within given time and budget limits.

MAPPING VULNERABILITY

Vulnerability mapping in the context of this paper should provide the decision-maker with answers to the following questions:

- what is the vulnerability of the groundwater to supply of a pollutant from a surficial source?
- what is the travel time of a pollutant from source to groundwater?
- what is the anticipated time of arrival of a pollutant from an already existing source? and
- to what depth might the groundwater body be contaminated by the pollutant?

The answers to these questions are provided by the quantities $\Delta C/J_s$ for $T-t=1$ (which is equivalent to $\Delta C/\Delta M$, where M is pollutant mass supplied to the ground surface per unit area), T , $t-T$, and B , respectively.

The final product of vulnerability mapping should therefore be a presentation of the quantities referred to above for each pollutant which might have an impact upon any of the relevant categories of water use. For ease of implementation the information ought to be presented in terms of averages (or distribution parameters) over areal cells possessing hydrogeologic and administrative homogeneity.

A map can communicate this information to a decision-maker with maximum clarity. At the same time, this information as well as all the relevant background data, such as those listed in the previous section, must be stored in a computerized data bank, in order to facilitate both access by various users and updating. Thus, a set of maps can be prepared for specific pollutants (including one for an ideal, inert, conservative pollutant such as Cl^-), each stipulating numerically for each areal cell the quantities $\Delta C/\Delta M$, T , $t-T$, B , and C , where C is the present concentration of the pollutant in the groundwater.

CONCLUSIONS AND RECOMMENDATIONS

Vulnerability assessment can serve as an effective preliminary tool for the policy and operational levels of decision-making concerning groundwater quality management.

Vulnerability assessment should be based upon a clear determination of the decisions relevant to groundwater management, the types of information required for such decision-making, and the necessary process and background data for providing this information.

Vulnerability assessment should be expressed in quantitative terms, which can be used for decision-making regarding land- and water-use.

Vulnerability assessment is an important aid in evaluating economic losses caused by pollution of groundwater vis-a-vis economic benefits of land-use alterations; a cost/benefit analysis including these losses should result in specific land- and water use recommendations.

Vulnerability assessment as defined here accounts only for the contribution of surficial anthropogenic sources, which represents only one component in the mass balance of the pollutant in the groundwater.

In situ field data are essential for reducing uncertainty as regards the values of particular parameters of vulnerability assessment, specifically those which are pertinent to transport and transformation of pollutants in the soil and the underlying unsaturated zone.

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MAPPING OF GROUNDWATER VULNERABILITY TO POLLUTANTS
IN THE NETHERLANDS

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ABSTRACT

The mapping of groundwater vulnerability to pollutants started in the 1960s. It was primarily based on hydrological characteristics, such as the thickness and extent of poorly permeable layers overlying the aquifer. The pollutants considered were mainly of bacterial origin, and protection was realized by designating sufficiently large protection zones around pumping stations tapping groundwater.

Today environmental pollution is so widespread that a different approach is required which quantifies biochemical and chemical processes as well as physical processes. In the Netherlands, this has led to a systematic survey of soil characteristics relevant to the behaviour of percolating pollutants. The characteristics of the unsaturated and saturated zones overlying the aquifer have been mapped at a scale of 1 : 400 000 for the entire country. The information was obtained from existing data in archives and reports and from soil and geological maps. The unsaturated zone was studied by Stiboka and the saturated zone by RIVM and the Geological Survey. The characteristics mapped were: thickness, carbonate, clay, organic matter, cation exchange capacity and travel time of percolating water. The two latter soil properties were obtained from soil data by "transfer functions". The maps can be used to delineate areas susceptible to the leaching of various substances, for example, nitrate, heavy metals and organic pollutants. The quantitative information on the maps allows them to be used in the modelling of groundwater quality.

In future studies the net effect of soil composition on groundwater vulnerability could be shown by a more integrated approach. However,

groundwater protection policies not only require integration of the effects of soil factors but also those of non-soil factors such as climate, land use and type and input of pollutants. Digitized geographical information systems are now being developed for these factors. The combination of these systems with process-based leaching models and areally distributed parameters will significantly improve vulnerability mapping in the future and, hopefully, contribute to a more environmentally sound use of land resources.

1. INTRODUCTION

In the past, prime attention was paid to the pollution of groundwater by pathogenic bacteria, and protection measures were addressed to preventing this type of pollution. The situation today is very different because of the huge increase in the use and emission of numerous chemicals. This has prompted studies of the vulnerability of the groundwater to chemical pollutants in all industrial countries. Until recently, most studies were concerned with the hydrogeological conditions in the subsoil. Initially, these studies mainly focussed on the physical processes affecting the transport of solutes in the saturated zone. However, it became increasingly clear that pollutants are also affected by chemical and biological processes and substantially influenced by the topsoil (unsaturated zone). The soil factors controlling the physical, chemical and biological processes vary with depth and location. These variations can be shown on maps and used to identify areas according to their vulnerability to pollution. Integrating information on soils with other information (for example, land use/vegetation and input of pollutants) and using models of water quality allows groundwater vulnerability to be expressed quantitatively. This paper primarily discusses the recent mapping of soil characteristics on a national scale and some new developments in groundwater vulnerability assessment as developed in the Netherlands.

2. GROUNDWATER PROTECTION IN THE PAST

The ancient Mediterranean civilizations were already acquainted with the vulnerability of soil and groundwater to pollutants as shown by ancient documents regulating protection of water wells against pollution. At the end of the 19th century it became clear that pathogenic bacteria were a particularly dangerous pollutant in well waters. In the first part of the 20th century research on the vulnerability of groundwater was directed to the pollution caused by these organisms. Much attention was given to the protection of public water supply against bacterial pollution, especially in Germany. This resulted in bacteriological protection zones being designated around groundwater pumping stations, based on the groundwater in the aquifer having a residence time of about 50 days. This residence time is still widely used all over the world.

The industrial revival after World War II led to increased pollution of groundwater by chemical substances. At first, concern was directed to oil pollution. Vulnerability was defined in terms of distance from the source of pollution. Based on this principle, a chemical protection zone of 2 km around groundwater pumping stations has long been common in Germany. However the presence, thickness and nature of poorly permeable layers overlying the aquifer also need to be taken into account. This is certainly true for Dutch guidelines on the protection of public water supply wells, which are based on the residence time of pollutants in the aquifer (Van Waegeningh, 1981).

Since the 1960s, serious attention has been given to mapping the vulnerability of groundwater in its own right. This mapping was primarily based on several hydrogeological conditions e.g. the thickness, nature and extent of poorly permeable layers overlying the aquifer. The interpretation of these maps was very subjective. Based on these principles, maps were compiled in several countries, including W. Germany, France and Czechoslovakia. Further efforts were directed to defining the vulnerability of groundwater to specific types of pollutants. Danish research (Villumsen et al., 1981), focussing on physical and physico-chemical soil characteristics, namely permeability, thickness, reduction and sorption capacity, deserves mention in this respect.

3. RECENT MAPPING OF VULNERABILITY CHARACTERISTICS

In the Netherlands, maps showing information on soil characteristics relevant to groundwater vulnerability were first compiled in 1984. The main objective of the project was to produce maps that could be used to characterize the vulnerability of the upper aquifers. The layers overlying the aquifer were defined as clayey, peaty or finely-grained sandy layers with a relatively low transmissivity ($kD < 250 \text{ m}^2/\text{day}$).

Sometimes, thin, more or less coarse sandy layers are incorporated in these layers (e.g. $kD > 50\text{-}150 \text{ m}^2/\text{day}$). These layers are considered to be part of the overlying layers. The aquifer is defined as more or less coarse sand with a permeability of $kD > 250 \text{ m}^2/\text{day}$. The soil data were collected for the soil layer overlying the aquifer ("cover layer"). The data for the unsaturated zone of the cover layer were collected from soil maps (mainly the 1 : 200 000 map) and soil data bases and the data for the saturated zone from geological maps and reports and from hydro-geological investigations. The unsaturated zone was studied by STIBOKA and the saturated zone by RIVM in collaboration with the Geological Survey.

The type of data surveyed in this study had to be (i) relevant to the vulnerability of groundwater to pollution and (ii) available over large areas. This led to the following choice:

- thickness of the cover layer
- thickness of the unsaturated zone
- carbonate
- clay
- organic matter
- cation exchange capacity (CEC)
- travel time of water

The latter five soil characteristics were mapped for each zone. Therefore the results are relevant to both the vulnerability of the shallow groundwater (at the phreatic level) and the groundwater in the upper aquifer. The thickness of the unsaturated zone was defined by the mean lowest water table, as presented on the soil map. Each mapping unit was defined by a profile representative in terms of type, thickness and composition of the soil layers (horizons). The cation exchange capacity and

the travel time of water were derived from these data as described by Breeuwsma et al., (1986). Soil properties (and land qualities) may be related to soil survey data that can be measured, e.g. clay content, or ascertained in the field, e.g. soil horizon and soil type. These relations were called "transfer functions" in a recent paper by Bouma et al. (1986). In this study we related the CEC to the clay and organic matter contents. The travel time of water in the unsaturated zone was derived from physical characteristics of the soil horizons, after horizons with similar soil-physical properties had been grouped together (Wösten et al., 1986). The delineations of the classes on the maps of the unsaturated zone were derived from the 1 : 200 000 soil map. The delineations on the maps of the saturated zone were established using geological maps of different scales, from 1 : 600 000 to 1 : 50 000. The maps for this zone are less detailed than those for the unsaturated zone, because less information is available on the subsoil. The maps were recently published at a scale of 1 : 400 000 (Van Duijvenbooden and Breeuwsma, 1987). They show classes defined in a quantitative way. Data on clay, organic matter and CEC were expressed per unit area to facilitate their use as parameters in water quality models. The CEC map of the saturated zone of the cover layer illustrates the type of information obtained (Fig. 1). Five CEC classes were defined and expressed in megamol (+) per ha. The white areas indicate regions without a water saturated cover layer (in the central and southern parts of the country) or an aquifer (eastern part). The data should be combined with those for the unsaturated zone of the cover layer to obtain information for the total cover layer. Quantitative applications are not yet available. However, the possible applications include:

- (i) using the CEC and travel-time maps to ascertain the transport of certain heavy metals and nutrients
- (ii) using the organic matter map to ascertain the transport of copper and organic micro-pollutants and
- (iii) using the map of the thickness of the unsaturated zone to ascertain the leaching of nitrate

It should be emphasized, however, that the maps can only be used for a general orientation on a large scale. The high degree of generalization does not allow applications in local studies.

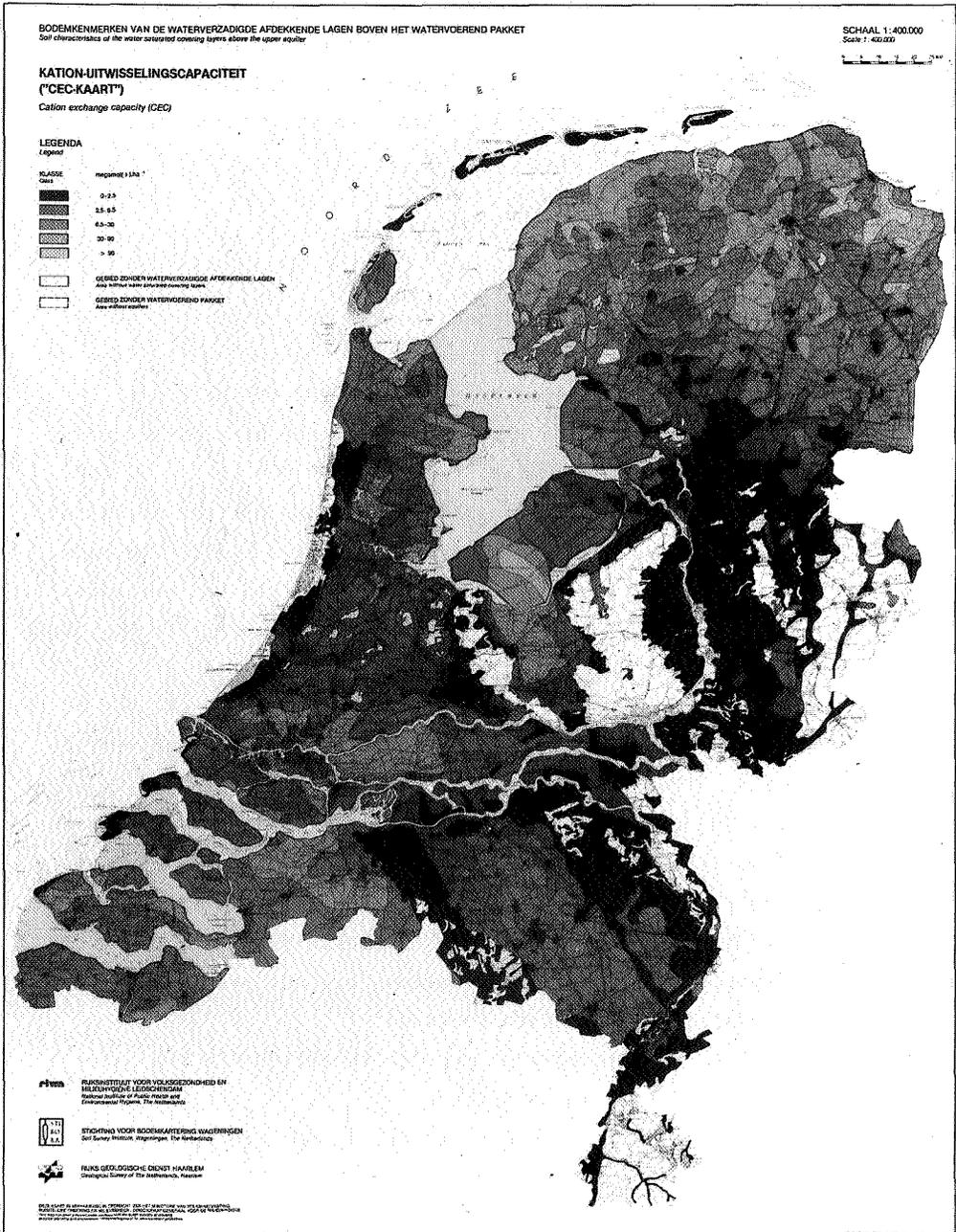


Fig. 1. Map, scale 1 : 400 000, of the cation exchange capacity (CEC) of the water saturated zone in the soil covering the upper aquifer in the Netherlands.

4. RECENT DEVELOPMENTS AND NEW PERSPECTIVES

Groundwater protection increasingly requires quantitative information on the effects of abatement strategies, because of their important environmental, economic and social impact. To what extent should the emission of pollutants be reduced to meet, for example, the standards for drinking water, groundwater and surface water? How can soil and water management help to reduce or prevent the leaching of pollutants from agricultural soils? How can soil maps be used to trace vulnerable areas that need special protection measures? Many of these questions have to be answered at least partially, on a national or regional scale. A more quantitative approach on a regional scale requires an appropriate integration of (i) geographical information and (ii) water quality models (Fig. 2).

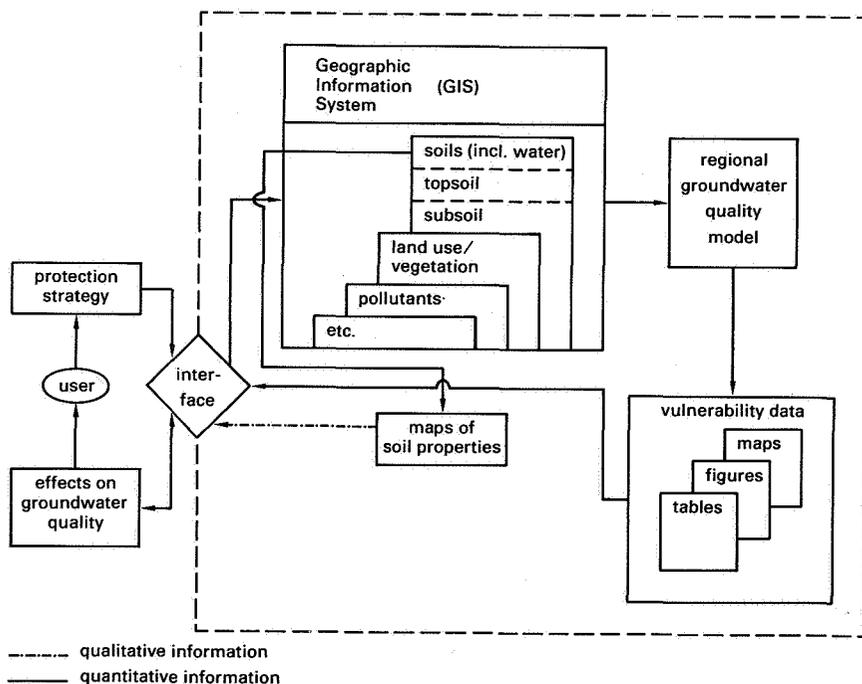


Fig. 2. Conceptual diagram of a groundwater vulnerability assessment system.

Geographical Information Systems

Computerized Geographical Information Systems (GIS) can be very helpful in rapidly providing systematic information. Use of GIS as a part of a groundwater vulnerability assessment system requires digital data bases on soils, land use/vegetation, input of pollutants, geology, hydrology, etc. In the Netherlands, we currently have a digitized soil map at a scale of 1 : 250 000 for the entire country and at a scale of 1 : 50 000 for about 85% of the area. In addition to this, a Soil Information System has been developed, in which information on characteristics measured in the field is stored for each boring, together with analytical data on selected profiles (Bregt et al., 1986). The system is operational and the input of data is still in progress. Thus, soil information is becoming increasingly available in a readily accessible way. The soil information system can be linked to an interactive graphics system to derive interpretive maps from the soil map (Fig. 3).

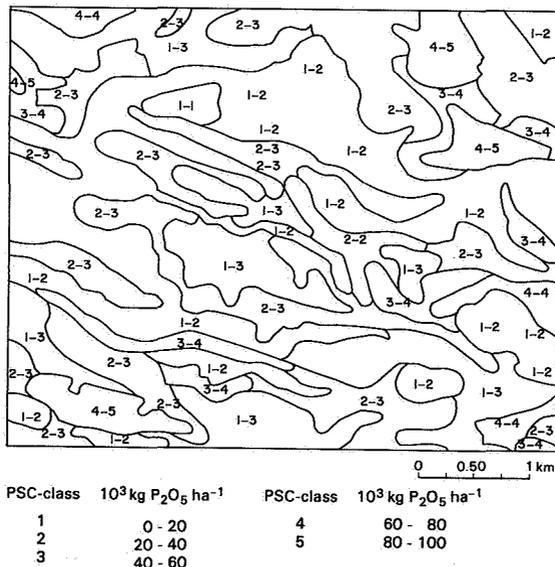


Fig. 3. Polygon map of the phosphate sorption capacity (PSC) of the unsaturated zone as derived from the soil map using an interactive graphics system. (The number denote the PSC class at the mean highest and lowest water levels, respectively).

The digital soil data base can also be used to construct grid maps (Fig. 4). The above-mentioned developments also occur in the mapping of geological and hydrogeological data. The grid maps are very helpful when data bases with different spatial boundaries have to be combined.

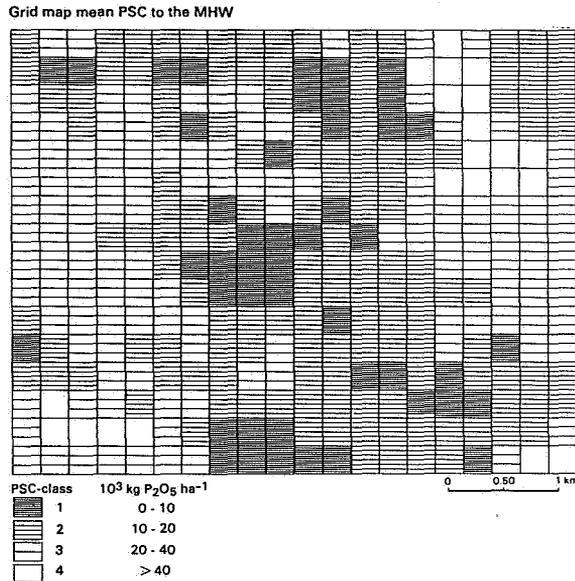


Fig. 4. Grid map of the phosphate sorption capacity to the mean highest water table (same area as in Fig. 3).

For example, the integrated effects of soils, land use and fertilization may be calculated for each pixel using digitized data bases and then generalized to the cell information presented on the map. This procedure is currently being applied to a pilot study of phosphate leaching from soils in areas with intensive livestock farming. The digital soil data are derived from the 1 : 50 000 soil map using a grid of 100 m x 100 m. The data on land use are collected for the same grid using a digitized data base derived from remote sensing images of the Landsat Thematic Mapper (Schoumans et al., 1987). The data on manure production will be determined for larger areas of, e.g., 4 km x 4 km, and distributed over different crops. These data are meant for tracing vulnerable soils in small areas using the 1 : 50 000 soil map. Studies in larger areas, for example 10 000 - 100 000 ha, do not always require the detailed de-

termination of soils and actual land use described above. In this case combinations of soil type and land use can be estimated by less detailed sampling procedures (Breeuwsma and Schoumans, 1987) or by assuming a constant relation between soil type (incl. the water regime) and land use (Van Drecht, 1986). To integrate GIS in a groundwater vulnerability assessment system, as depicted in Fig. 2, will often require the data to be transformed into parameters that can be used in water quality models. The development of "transfer functions" as defined above for soil data thus greatly stimulates the potential use of GIS.

Water Quality models (unsaturated zone)

Combining water quality models with GIS has certain implications on the modelling approach. First, model parameters do not have to be lumped over a given area because their spatial distribution is known. Second, the limited availability of spatially-distributed data usually precludes a detailed description of the processes. Simplification ("aggregation") of processes is needed to reduce the number of model parameters that can be obtained from GIS.

Furthermore, a prerequisite for rapidly assessing vulnerability on a large scale is the use of model parameters that can be related to available soil survey data. This can be illustrated with regional leaching models, defined here as models predicting the leaching from the unsaturated zone of the soil to the groundwater on a regional scale, using soil-survey oriented and spatially-distributed parameters. Three such models developed at the Netherlands Soil Survey Institute are:

- (i) a regional phosphate transport model (REPTRAM) (Breeuwsma and Schoumans, 1987)
- (ii) a regional nitrate leaching model (RENLEM) (de Vries et al., 1987)
- (iii) a regional soil acidification model (RESAM) (de Vries, 1987)

The above models use a simplified deterministic description of the processes. Each set of input data leads to a uniquely defined outcome. A different approach using stochastic models to allow for spatial variability of solute transport has been discussed by Addiscott and Wagenet (1985). This approach may be applied when studying the leaching from a

given area. However, it cannot be used to identify spatial variations in vulnerability within the area as described in this paper.

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APPLICABILITY OF VULNERABILITY MAPS

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ABSTRACT

A number of aspects related to the vulnerability maps is discussed: the vulnerability concept, mapping purposes, possible users and applicability of vulnerability maps.

Problems associated with general-type vulnerability mapping: large scale maps, universal pollutant and universal pollution scenario, are discussed.

An alternative approach to vulnerability assessment - specific vulnerability mapping for limited areas, specific pollutant and pre-defined pollution scenario - is suggested.

A simplification of the vulnerability concept is proposed in order to make vulnerability maps more objective and by this more comparable. An extension of the vulnerability concept to the rest of the hydrogeological cycle: lakes, rivers and the sea is proposed.

Some recommendations regarding future activities are given.

1. INTRODUCTION

The awareness about environmental pollution is a quite recent phenomenon and our ability to deal with this problem is rather limited. In search for tools to deal with pollution of groundwater the concept - "vulnerability of groundwater" - has been introduced. Due to the emotional meaning of the word vulnerability, everybody understands, that "vulnerable aquifers" should be protected, on the other hand, not

everybody would accept that "less vulnerable aquifers" should be allowed to be polluted, particularly if "less vulnerable" means polluted after 20 years instead of 1 year. It is known, that in a lot of cases there are no technical means to eliminate the on-going pollution. Furthermore it is obvious that new sources of pollution are being planned and established - hopefully under better controlled conditions. How does the vulnerability concept fit in this situation? Should the vulnerability maps be used to evaluate the effects of the pollution from the past, should these maps be used to plan the future or should they be used for both purposes? It is not always clear which situation is considered under preparation of the vulnerability maps. An answer to this question is essential for discussion of applicability of these maps.

2. EXISTING VULNERABILITY MAPS

During the last decade a number of groundwater vulnerability maps have been produced: BRGM (1975) in France, Aust et al. (1982) in Germany, Villumsen et al (1982) in Denmark and Fried (1987) for ECE countries.

It is not the purpose of this paper to discuss in details the contents of the individual maps but rather to discuss the principles and usefulness of the mapping approach.

All the maps are similar, as the mapped area is divided into "more" and "less" vulnerable categories.

The procedures and choice of the key parameters, leading to the comparable final statement, are however different and therefore it is impossible to compare these maps directly.

The information combined into the final categorization takes into account the processes affecting pollutants and the protective properties of the soils above the aquifer, like sorption, filtering, decomposition, hydraulic conductivity etc., with regard to a "general" pollutant.

Most of the information combined into the final vulnerability categorization is of course relevant, but it is questionable whether vulnerability should depend on the pollutants travel time to the aquifer.

2.1 Protective properties of the soils

Human activities introduce constant flow of harmful substances into the geosphere. Some of these substances end up in the aquifers, while other are removed on the way down to or within the aquifer.

An evaluation of the protective properties of soils is the most important task for vulnerability assessment. Our knowledge about this subject is limited and there is an urgent need for research effort in this field.

One major problem occurs when these protective properties have to be included in the vulnerability categorization: how to express "recoverable" (or permanent) property and "deplecable" property in a comparable way? For example a biological activity can protect an aquifer indefinitely by decomposing harmful pollutant (permanent protective property), while in other situation the protective property is being used up during cleansing processes (deplecable property).

2.2 Percolation time

For some vulnerability maps the travel time of the pollutant from the source to the aquifer plays an important role. Shorter travel time is made equivalent to higher vulnerability and longer travel time results in lower vulnerability.

Except for the situations where removal of the pollutant is dependent on time, the vulnerability should be the same for aquifers polluted after one, twenty or hundred years. The time scale appropriate for the environmental considerations should not differentiate between such short periods. For comparison it can be mentioned, that in connection with establishment of radioactive waste repositories risk analysis has been performed for periods ranging from 10.000 to 1 million years

- time scale regarded applicable for environmental considerations. From such a point of view percolation time should be removed from vulnerability concept.

2.3 Aquifer chemistry

There is a tendency to assign lower vulnerability to aquifer, where water quality is poor.

However, the water quality should not play any role in evaluation of the vulnerability of an aquifer for three reasons: the vulnerability concept becomes more complicated and less objective and within the environmental time scale the water quality may change.

2.4 Other information

Beside cleansing properties of soils and percolation time mentioned above, there is a number of parameters and conditions taken into account in vulnerability mapping: type of geological formation, thickness of the geological layers, depth to aquifer, infiltration distribution, land use, transmissivity and porosity, chemistry and composition, groundwater withdrawal and distribution etc. Combining all these parameters and conditions into one meaningful number or class is indeed a subjective task and the final product - the vulnerability map - is a highly composite one and may be interpreted differently by different users, in spite of the fact, that the map is non-interpretible. This certainly limits the usefulness of the map.

3. VULNERABILITY MAPPING, PURPOSE

Dealing with groundwater pollution is a multidisciplinary task and specialists from different fields have to be involved. Hydrogeologists, chemical engineers, geologists and financing authorities have to cooperate for a common goal: prevent and reduce deterioration of

the groundwater resources.

If vulnerability maps were meant to provide decision makers with a tool eliminating the need for a multidisciplinary cooperation, the purpose of the mapping is not fulfilled, particularly if site selection for polluting activities is considered.

In the authors' opinion it is not possible to prepare a one-parameter map which alone can be used for analysis of variety of situations, where the groundwater resources may be threatened.

A general vulnerability mapping for a whole country, an universal pollutant and an universal type of pollution scenario is unlikely to be successful.

Example: A waste disposal site may relatively safely be chosen on location where protective properties of the soil are sufficient to neutralize the amount of pollutant disposed. Therefore an aquifer on this location should be regarded as less vulnerable.

If instead, another type of polluting activity is planned on the same location and continuous input of pollutant is expected, the protective properties of soils would not be sufficient and the aquifer should then be regarded as more vulnerable, an entirely different result for similar situations.

If the pollution scenario is specified, and the boundary of the area are defined, a relative vulnerability within this area and for this particular scenario can be defined. With other words: for a well-defined situation it can be useful to define relative vulnerability, while general vulnerability mapping would be misleading.

4. POTENTIAL USERS OF VULNERABILITY MAPS

Most of the vulnerability maps are prepared in large scales 1:500.000 or more. Some authors indicate that maps in smaller scales requires much more detailed information than is available, and it is pointed out that the information on the maps is not detailed enough for local use and that the maps can only be used for planning purposes in large scale: regional, national and even international. The potential users

may therefore be politicians, and governmental and regional health authorities. Furthermore authorities related to water-supply management and groundwater protection could be potential users, direct or via professional consultants. However, general vulnerability maps, especially in scale 1:500.000 can only be used for illustrative purposes and not for planning purposes as their information are not valid generally.

5. APPLICABILITY OF VULNERABILITY MAPS

As mentioned before, it is not quite clear if vulnerability maps are prepared for evaluation of consequences of past and present pollution situations or for the future planning regarding site selection for polluting activities.

5.1 Past and present situations

Vulnerability maps together with maps showing location and type of polluting activities could be used to point-out the locations, where investigations should start first. Unfortunately, the usual scale of the maps is not appropriate for this task. The existing pollution situations should be used to verify the vulnerability map.

However, as soon as an investigation of a site is started, the specialists will use the basic parameter maps: head distribution, permeability, thickness etc., rather than the vulnerability map.

The applicability of vulnerability maps is furthermore reduced by the fact, that the decision about initiating an investigation will primarily depend on knowledge about the pollution source and/or pollution indicators in the aquifer rather than an estimate of vulnerability.

5.2 Future situations

Vulnerability maps are most likely ment as a tool for an optimal distribution of the future pollution sources.

It is unlikely that the final decision about these locations could be based on a 1:500.000 vulnerability map alone; site specific investigation, or analysis, must be done. The question is: would not some of the single parameter maps do the same job? The answer is yes. The specialists would always prefer thematic maps rather than a map containing a subjective, composite parameter which originates from general considerations valid for a larger area, rather than for the site they look at.

5.3 Conclusion

Aplicability of general-type, ready made vulnerability maps valid for all geological, hydrogeological and hydrochemical situations, not considering pollutant type and pollution scenario is very limited. That kind of maps can not be used for the final decisions instead of the basic single-parameter maps. If variation of the pollutant travel time within the order of magnitude few years is regarded as relevant in vulnerability mapping, the maps are directly dangerous as a planning tool.

The main factors reducing applicability of the general-type vulnerability maps are:

- incorporation of percolation time
- subjective nature
- composite character of the vulnerability concept.

6. VULNERABILITY ASSESMENT, ALTERNATIVE APPROACH

The major disadvantages of the present vulnerability mapping are:

1. The vulnerability are influenced by percolation times within a time frame inconsistent with environmental considerations.
2. The vulnerability categorization is made without taking into account the type of pollutant and type of source.
3. The vulnerability concept is subjective and not comparable.
4. The vulnerability concept is too complicated and debatable - how to combine so many different properties into one single term?

Therefore it should be recommended that:

1. The percolation time is taken out from the vulnerability concept, at least if the time is shorter than let us say 10.000 years?
2. General vulnerability mapping is replaced by vulnerability mapping for a specific pollutant and for a specific pollution scenario and within a limited area.
3. Some standards are introduced in order to make vulnerability maps comparable.
4. The vulnerability concept is simplified and made dependent on two parameters only: cleansing capacity of the soils and "restoration capability" of the aquifer.

6.1 Removal of percolation time

As mentioned before, the pollution risk should not be considered within time periods irrelevant for environmental considerations. Percolation time is of course one of the most important parameters when the movement of pollutant is considered and as such it should be expressed on a single parameter maps. But in principle, the aquifer is equally vulnerable if pollutants travel time is one year or one hundred years. In few situations a short percolation time may theoretically increase vulnerability if the cleansing capacity of soils can not be fully utilized due to the short travel time of the pollutant. For a typical situation, where the percolation time is of the order of magnitude several years, the time factor is without importance.

6.2 Specific vulnerability mapping

It is unrealistic to believe, that within foreseeable future it will be possible to eliminate sources of pollution. The opposite will be the case: new sources will be added. If this is the case it is important to be able to point out the locations where the pollution results in a minimum of damage. Usually, the choice will have to be made within limited area or few areas and the characteristics of the source will be relatively well known.

A lot of conflicting interests may be involved and the decision-makers have to make the final choice. The decision-makers would not be able to evaluate the variety of technical information and may ask the specialist to do it. And under these, relatively well-defined conditions, the specialist should come with a relative evaluation of vulnerability in relation to the specific pollutant and within the possible areas.

The main difference in this approach, as compared to the general vulnerability mapping, is that the specific vulnerability mapping is done after the pollution scenario is known and more proper weighting of the conflicting interests can be made; for example the most valuable groundwater resources of the community, even if well-protected, can be excluded beforehand from the vulnerability evaluation-task.

6.3 Standardization

If the vulnerability categories are obtained by weighting many different and practically incomparable parameters, it is hopeless to try to introduce any standards. However, if the vulnerability concept is simplified, as suggested below, it should be possible to define some standards or references which would make vulnerability mapping more objective and comparable from map to map. Such a standardization could be introduced if the cleansing capacity of a soil was expressed as mass of pollutant removed per unit volume of the soil.

6.4 A simplified vulnerability concept

The vulnerability concept should be simplified to a parameter taking into account the cleansing capacity of the soil and "restoration capability" of the aquifer.

As mentioned above, there could be two processes preventing pollutant from entering the aquifer: for example, a continuous process decomposing the pollutant into harmless component indefinitely (i.e. reduction of nitrate in the root zone) and a process which results in depletion of the cleansing capacity of the geological material (i.e. reduction of nitrate in the layers below the root zone).

If the vulnerability mapping is done for a specific pollutant and for a known pollution scenario, the relative cleansing capacity of the soil, within the area considered, can be established.

The "restoration capability" of an aquifer can be defined in terms of average residence time of the water within the aquifer (the volume of the water contained in the aquifer divided by the rate of recharge: $m^3/(m^3/year)$). A thin aquifer with a high influx will have a short residence time and a high "restoration capability".

It can be argued, that aquifers with short residence time in some cases are less vulnerable than aquifers having long residence time as the pollutant will be removed by natural processes within shorter time.

A question arise how to weight the cleansing capacity in relation to restoration capability?

7. VULNERABILITY OF THE AQUATIC ENVIRONMENT

Above the vulnerability of the aquifers, or the groundwater has been discussed, but it could be relevant to extent the vulnerability concept to other components of the hydrological cycle: rivers, lakes and the sea.

If the vulnerability concept has to be used for planning purposes, a broader perspective than the vulnerability of the aquifers is needed. It is often so, that if a pollutant is not allowed to pollute

the groundwater, it may pollute a surface water body.

If the approach to vulnerability proposed in this paper is used, the estimation of vulnerability of lakes, rivers and the sea is straight forward. In many respects it would be easier to determine cleansing capacity and residence time for lakes, rivers and sea than it is the case for groundwater reservoirs.

8. CONCLUSIONS AND RECOMMENDATIONS

The applicability of the existing vulnerability maps is severely limited because of:

- lack of consistent and widely accepted definition of vulnerability,
- complexity of the vulnerability concept,
- general, rather than case-specific information displayed by the maps referring to universal pollutant and universal pollution scenario,
- the scale of the map is often incompatible with the scale of the vulnerability-related problems,
- the time concept is inappropriate for environmental considerations.

Therefore it is recommended that:

1. A consistent set of definitions and possibly standards, preferably worked out through an international cooperative effort, is established.
2. Production of thematic maps as a base for preparation of specific vulnerability maps and risk evaluation is encouraged.
3. Vulnerability maps are produced for specified situations only.
4. Estimation of vulnerability is extended to the rest of the hydrological cycle.

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MAPPING THE VULNERABILITY OF GROUNDWATER TO
POLLUTION FROM AGRICULTURAL PRACTICE,
PARTICULARLY WITH RESPECT TO NITRATE

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ABSTRACT

In recent years groundwater supplies from British aquifers have shown rising levels of nitrate and in some districts the EEC's maximum acceptable concentration for drinking water has been exceeded. A major source of pollution is agricultural fertilizer, which passes through the soil into underlying aquifers. Careful land management, in vulnerable areas, can limit the amounts of nitrates reaching the groundwater but first the vulnerable areas must be identified. The Soil Survey of England and Wales (SSEW) and the British Geological Survey (BGS) have designed a scheme which uses detailed information on soil and geology to place each land unit into one of four vulnerability classes. A pilot study was undertaken for the Severn Trent Water Authority (STWA), to investigate the vulnerability of the Staffordshire Triassic sandstone aquifer to nitrate pollution. A quantitative assessment of potential losses was also made for all extensive soil types on the aquifer using a leaching model. Field experiments funded by Imperial Chemical Industries (ICI) monitored nitrate losses from a wide range of agroclimatic conditions. Vulnerability maps and accompanying reports will aid management decisions in the water and agricultural industries particularly relating to conservation issues.

1. INTRODUCTION

Nitrate levels in water supplies from the main British aquifers, chalk, limestone and Triassic sandstone, have in some districts exceeded,

either continuously or intermittently, the EEC's maximum admissible concentration of 50 mg l^{-1} of nitrate in potable water. There has been a dramatic increase in fertilizer use since the war and, in 1985, 1.58 million tonnes of inorganic nitrogen and 1.0 million tonnes of organic nitrogen from animal manures and slurries were used. Leaching losses of fertilizer can be very high and 20-50% of original applications is common, depending on crop, soil type, climate and agricultural practice (Burns and Greenwood 1982). Nitrogen losses from soils are also attributable to the leaching of mineralized nitrate from organic residues either from previous cropping policy or ploughed-in grassland. Many shallow grassland soils over chalk and limestone have been ploughed, and nitrogen losses can be as high as $200 \text{ kg ha}^{-1} \text{ year}^{-1}$ due to the mineralization of organic matter and subsequent leaching. Pollution of water supplies will continue for many years due to the time lag (in nitrogen transport) associated with the transmission of water through the unsaturated zone (Foster and Young 1980).

Environmental, economic and medical considerations have led to an urgent need to reduce the potential contamination of aquifers so that water quality in the long-term can be safeguarded. Laurence Gould Consultants (1985) concluded that sweeping controls on agricultural practice would not be appropriate, and current U.K. policy (Department of the Environment 1986) proposes selective local control and changes in land use as options to protect future water quality. These proposals require a detailed knowledge of the distribution and properties of soils and rocks to identify the parts of aquifers and specific boreholes which are vulnerable to pollution.

In July 1986 STWA invited a joint proposal from SSEW and BGS to produce, as a pilot study, a map of groundwater vulnerability for an area around Stafford in the western Midlands. Groundwater nitrate levels already exceed or are close to the EEC maximum at a few borehole sites in the area. Several others indicate a rising trend which may necessitate expensive and unaesthetic treatment to water supplies in the future. The alternative option of selectively restricting land use practices is currently under active investigation for these and other boreholes in the STWA region.

2. SOIL ASSESSMENT

Mineral nitrate is readily soluble in water and consequently its movement within the soil profile is closely associated with the soil water regime. The mechanisms of water movement in soils are complex but water is retained as both mobile and immobile phases (Addiscott 1977). Mobile water can be displaced by infiltrating rainfall and is held in the larger pores usually at soil moisture suctions below field capacity (0.05 bar). Water held within soil aggregates or peds at suctions above 2.0 bar is considered to be immobile. The relative volumes of mobile and immobile water depend on soil texture, organic matter content and soil structure. Sandy, porous arable soils such as the Newport series retain little water above 2.0 bar suction and therefore contain small amounts of immobile water. Vertical water movement through these soils is almost entirely by displacement and soil nitrate is readily flushed to depth. In contrast the Salop series, a dense, fine textured soil, retains a large amount of water at suctions greater than 2 bars and hence contains much more immobile water than Newport soils. The amount of nitrate lost from Salop soils is controlled by both the molecular diffusion between the mobile and immobile phases and by bypass flow through fissures.

The SSEW has accumulated over the last 40 years extensive data on soil properties and their distribution which are stored in the Land Information System (LandIS). The soil physical properties which influence nitrate leaching were accessed for each soil type. Topsoil and subsoil texture and organic carbon content were chosen as indicators of soil water retention. Porosity data were taken to represent soil permeability and Wetness Classes (Ragg et al. 1984) gave an indication of soil water regime and the influence of drainage treatments. Soil profile depth and lithology of the underlying substrate, if encountered within 1.2 metres, were the remaining properties considered in the assessment. A score was assigned to each each of these parameters for individual soil types and, by adding each parameter score, an overall risk rating or leaching class was given. Four leaching classes, ranging from extreme to low are used (Table 1) and these represent physically distinct groups of soils.

Table 1. *Leaching Classes and their Characteristics*

Score	Rating	Class	Soil Characteristics
21 - 30	Extreme	1	Deep permeable sandy soils, some affected by fluctuating groundwater in winter; shallow loamy and sandy soils over sandstone. 1.0-2.5% organic carbon ¹ .
16 - 20	High	2	Deep permeable light loamy soils. 1.5-2.5% organic carbon ¹ .
11 - 15	Moderate	3	Deep moderately permeable medium loamy soils; moderately permeable, medium loamy soils with dense slowly permeable subsoils. 2.0-4.0% organic carbon ¹ .
0 - 10	Low	4	Slowly permeable loamy, loamy over clayey or clayey soils; deep moderately permeable loamy alluvial soils. 2.0-4.0% organic carbon ¹ .

¹ Relates to arable soils

The SSEW leaching classification is based on soil properties and characteristics which are measured and observed by experienced soil scientists. In addition, the scheme has been tested against data collected during a field monitoring programme for ICI and on data contained in recently published scientific papers (Burns and Greenwood 1982, Barraclough et al. 1983, Haigh and White 1986). The leaching categories are broad, do not include agroclimatic considerations and are designed only to provide an idea of relative susceptibility. However, the soil information can also be put into a leaching model designed to quantify potential nitrate losses (Addiscott 1977). The model was run using 10 year average meteorological data from weather stations in the

Stafford area. Soils were assumed to be at field capacity on 1st November for the southern part of the district and 1st October for the wetter north. The model assumes 100 kg of nitrate-nitrogen is distributed down the soil profile at the start and allowed to leach from the base at a depth appropriate to the soil type. Leaching classes correspond well with the total nitrate loss predicted by the model. Soils in the extreme class showed significant nitrate leaching losses within one month of the soil moisture deficit being replenished and losses are virtually complete after three months. Leaching losses from the low class are slower and part of the original nitrate input remains in the soil profile. Soils occurring in both climatic areas have larger losses in the wetter north emphasising the importance of climate in the estimation of nitrate leaching. Nitrate losses for contrasting soil types monitored over the leaching period 1985-1986 are significantly different (Figure 1). Total losses from the Cuckney soil series ($91 \text{ kg ha}^{-1} \text{ yr}^{-1}$) were attributed to spring mineralization of the potato crop residue and subsequent leaching losses. There was little change in the nitrate content of the deep subsoil of the Salop series and the of $44 \text{ kg ha}^{-1} \text{ yr}^{-1}$ losses were probably by lateral flow through macro-pores and mole drainage channels at 60 cm depth.

3. AQUIFER ASSESSMENT

Geological records, ranging from field sheets to borehole logs, held by BGS were researched and collated to produce a map of aquifer distribution. Three types of aquifer were identified by the degree of protection afforded to the aquifer by drift or bedrock cover (Table 2). Well and borehole records provided thicknesses of materials above the aquifer and geological field sheets and Memoirs were invaluable in establishing the inter-relationships of the drift deposits and their lithology. Hydrogeologists from STWA were able to provide further, more detailed, observations for specific locations.

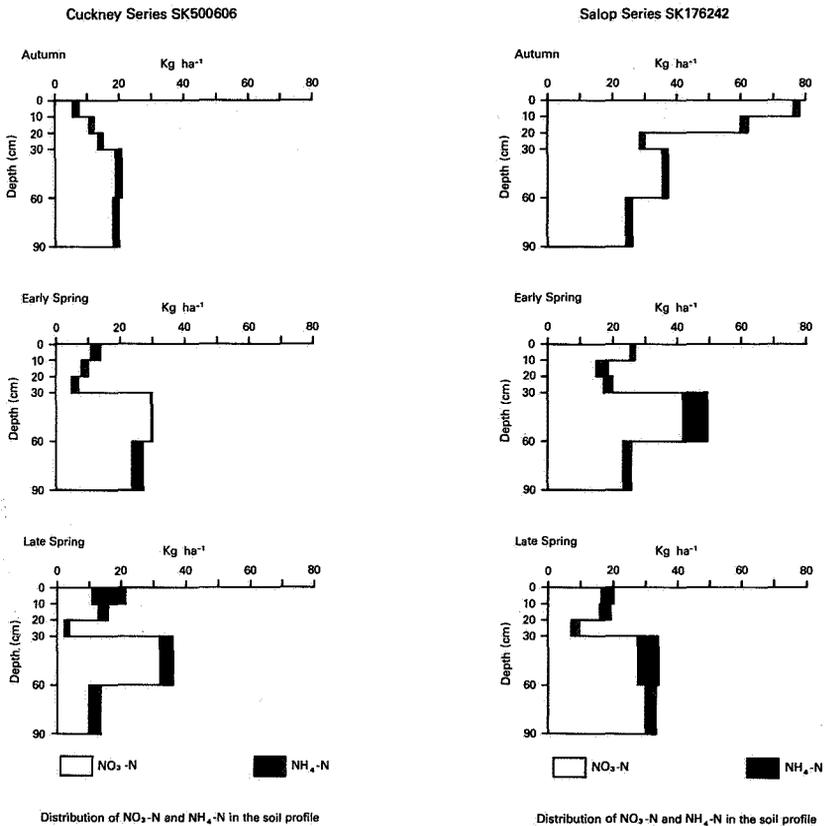


Figure 1. Nitrate and ammonium-nitrogen distributions in two soil profiles

Table 2. *Aquifer Classification*

Aquifer Type	Aquifer Characteristics
1	aquifer outcrop without drift cover or with cover of permeable drift (sands and gravels).
2	aquifer outcrop covered by less permeable drift (thin lacustrine clays, peat), or by thin and/or patchy boulder clay.
3	aquifer outcrop covered by impermeable drift (boulder clay), or by impermeable bedrock cover (Mercia Mudstone Group), or no aquifer present.

4. COMBINED VULNERABILITY ASSESSMENT

Groundwater vulnerability categories were determined using a matrix which combined the assessments of leaching class and aquifer classification (Table 3). The maps derived from the soil and geological assessments were overlain and all the land overlying the aquifer was allocated a vulnerability category.

Table 3. *Groundwater Vulnerability Categories*

Aquifer Classification (Type)	Soil Leaching Classification (Class)			
	1	2	3	4
1	Extreme	High	Moderate	Low
2	High	Moderate	Low	Low
3	Low	Low	Low	Low

Notes

Extreme	Type 1 aquifer with shallow or sandy very permeable soils.
High	Type 1 aquifer with moderately deep or deep permeable loamy and/or peaty soils <u>OR</u> type 2 aquifer with shallow or sandy very permeable soils.
Moderate	Type 1 aquifer with moderately permeable loamy over clayey and some clayey soils <u>OR</u> type 2 aquifer with deep or moderately deep permeable loamy soils.
Low	Type 1 aquifer with slowly permeable loamy or clayey soils <u>OR</u> type 2 aquifer with moderately permeable loamy over clayey and some clayey soils <u>OR</u> type 3 aquifer with any soils.

5. THE STAFFORD PILOT STUDY

The national 1:250,000 scale soil map of England and Wales (Ragg *et al.* 1984) indicates twenty-two soil associations occurring in the study area and represent a broad cross-section of the soils of the western Midlands.

The Sherwood Sandstone Group is the only aquifer of primary importance in the district, and reaches a maximum thickness of more than 300 m. The dominant rock type is sandstone, sometimes pebbly and occasionally conglomeritic. However, this formation is not wholly homogeneous, horizons of mudstone and siltstone providing in some areas relatively impermeable layers within the sandstones. Borehole yields are generally good, ranging from $1,500 \text{ m}^3\text{d}^{-1}$ to $15,000 \text{ m}^3\text{d}^{-1}$ with an average of around $5,000 \text{ m}^3\text{d}^{-1}$. The limit on yields depends largely on the degree of cementation within the sandstone. Within the area of the pilot study map up to $17,000,000 \text{ m}^3$ is supplied annually from 38 public supply boreholes.

The overlaying of soil properties onto the initial geological screen significantly refined the vulnerability assessment. The type 1 aquifer, though predominantly extremely vulnerable includes appreciable amounts of low and moderate vulnerability caused by impermeable subsoils developed in thin spreads of boulder clay. Similarly the type 2 aquifer also contains a small proportion of land with low vulnerability.

6. LIMITATIONS AND OTHER USES

The vulnerability categories are based on an appraisal of soil and geological characteristics and were checked against results from a limited set of field measurements. Replicate field experiments in different climatic regions and with a range of crops are currently under way to improve predictions of the quantitative aspects of nitrate leaching from agricultural land. The results from such experiments can also be used to improve the predictive ability of the more sophisticated leaching models.

While a 1:100,000 scale map cannot provide a vulnerability assessment at the field level it indicates the local variation of vulnerability above

the Sherwood Sandstone. Interpretations for a specific location, for example a protection zone around a public water supply borehole, require detailed investigations in order to advise on management at the field scale.

This system of predicting the vulnerability of aquifers to pollution is strictly designed for the leaching of nitrate through soils and rocks to groundwater. The behaviour of other substances such as agrochemicals, and simple anions such as sulphate and chloride, may differ significantly as a result of their particular absorption coefficients within soil or rock and also their solubility and mobility. It is probably safe to say that aquifers shown as having low vulnerability to nitrate are also protected from these other pollutants. The converse however is not necessarily true but those soils and rocks which are judged to be permeable to nitrate are probably also at risk from the more soluble agrochemicals, particularly those having a slow rate of decay.

ACKNOWLEDGEMENTS

The authors wish to thank STWA and ICI for their permission to publish this material, T.M. Addiscott and G.J. Bland for providing the predictions of nitrate leaching and A.J. Thomasson who edited the text.

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POLLUTION RISK TO PUBLIC SUPPLY BOREHOLES
IN THE YORKSHIRE WATER AUTHORITY AREA

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ABSTRACT

All Ninety five public supply borehole sites in the Yorkshire Water Authority area (14000 Km²) were examined for potential pollution risk. A one kilometre radius zone around each site was examined for potential risk from municipal, agricultural, industrial and environmental sources (motorways, railways and streams). From a desk study, borehole sites were classified on an overall risk assessment into three categories based primarily on bacteriological history and disinfection equipment available on site; the assumption being that public sources met other water quality standards. Fifty five boreholes were placed into Category I, the highest risk category, though with further study and limited fieldwork the numbers of boreholes in this category were reduced. Twenty nine boreholes were classed as Category II, a lower risk, and further investigation work was recommended. Eleven boreholes were in Category III, showing no obvious risk to groundwater supplies. Hydrogeological investigation was undertaken to find the source of bacteriological pollution. Disinfection equipment at each site was critically appraised and recommendations for its updating, at certain sites, were made. After further study the three risk categories were increased to five to take account of sites where risk had to be accepted owing to the importance of the source after adequate and acceptable disinfection or treatment facilities had been provided.

INTRODUCTION

In July, 1980, two public supply boreholes at Bramham in Yorkshire were polluted by surcharge of the sewers by a nearby stream. The sewers

leaked and the polluted water was drawn by the public supply boreholes whose disinfection system had failed. Following from this pollution incident, a comprehensive study of all the Authority's public supply boreholes was instituted to find the potential sources of pollution and reduce the risk of a recurrence of the incident.

ASSESSMENT OF POLLUTION RISK

A one kilometre radius around each public supply source was examined for potential pollution risk from environmental, municipal, industrial and agricultural sources. Information on borehole logs along with construction details and their annual licensed abstractions were obtained. A summary sheet was prepared for each groundwater abstraction site (Table 1). These sheets contained the above-mentioned information and also the type of disinfection equipment, bacteriological and some chemical water quality data. Finally, the category and degree of risk were assessed from this data.

CLASSIFICATION OF SOURCES INTO RISK CATEGORIES

Considerable weight was given to the presence or absence of coliform bacteria in the raw and/or treated water during the previous three years and of the sophistication and reliability of the disinfection equipment provided. It was primarily on these criteria that each borehole site was placed within an overall decreasing risk category of I, II or III.

Category I was used where there was any notable record of bacterial pollution, Category II was adopted when either occasional bacterial pollution had occurred or when surface activities in the locality indicated a risk, and Category III where there was no obvious risk. Hydrogeological investigation was undertaken to find the source of bacteriological pollution. It became evident that groundwater could not be guaranteed to be and to remain totally free from risk of pollution. If boreholes were to be continued to be used as sources for public supply a risk had to be accepted just as it is for surface water sources.

Therefore, the three categories were extended as follows :-

Category IA This denoted a site which appeared to be of high risk. An investigation was required to define the risk or where capital works (e.g. super chlorination) or monitoring procedures were required.

Category IB This was a site of high defined risk which had been accepted and appropriate works, monitoring and other procedures undertaken. For example, where full chemical treatment or super chlorination was provided.

Category IIA A lower degree of risk was assumed than Category IA site but further investigation was required to confirm the assumption or where defined capital works or monitoring procedures were required to cater for a low to moderate risk.

Category IIB A low defined risk was identified and appropriate steps taken to safeguard the supply.

Category III This category remained as No Obvious Risk either because there was no record of bacteriological pollution in raw water, or the borehole was only part of a supply system which received full treatment.

A more sophisticated aquifer protection policy for Yorkshire is now being prepared. Specific protection zones around public supply sources have been drawn to take account of the aquifer characteristics, thickness of the unsaturated zone and to allow 100 days for the pollutants to be diluted and degraded before reaching an abstraction point. Within these protection zones sources of pollution would be carefully monitored.

ACKNOWLEDGEMENTS

The author wishes to thank Yorkshire Water for permission to publish this paper. Thanks are also due to J.C.C. Paul, formerly of Yorkshire Water, for assisting in this study.

SITE NAME : KELDGATE (2 BOREHOLES)

GRID REFERENCE	TA 027 330
LAND USAGE (1km radius) ON SITE	Arable and urban Concrete base, run-off to a soakaway ditch.
ROAD	Trunk Road 600m west - A164 Minor Roads 100m south and 400m north and east.
RAILWAY	None
MOTORWAY	None
WATERCOURSE(S)	Road drainage soakaway 100m south Sewage work effluent. Soakaway 1km north. Artesian Pond 1km east.
SEWERS	None
WATER AUTHORITY SEWAGE WORKS	Skidby 1.3km NW
PRIVATE SEWAGE WORKS AND SOAKAWAY SYSTEMS	Roof drainage to soakaways Hospital 700m south Cemetery 450m east Chlorination contact tank 400m north
INDUSTRIAL PREMISES	Disused chalk pits Arable farms to the north and west Marginal chlorination with direct delivery into nearby service reservoir giving longer contact time.
TIPS	1977-80 Coliform/E.coli. counts occur often after heavy rainfall: 20/20 typical (0.2) Minimum
AGRICULTURAL PREMISES	1977-78 5.5 Treated (T)
STERILISATION	1978-79 6.3 T
BACTERIOLOGICAL HISTORY	1979-80
RESIDUAL CHLORINE	
NO ₃ ⁻ mg l ⁻¹ (Max. values)	1977-80
Cl ⁻ mg l ⁻¹ (Max. values)	1977-78
Fe Total mg l ⁻¹ (Max. values)	1978-79 0.01 T
	1979-80
CATEGORY AND DEGREE OF RISK	
ROAD/RAIL ACCIDENT	Significant to High
SEWAGE (DIRECT OR VIA STREAMS)	High
INDUSTRIAL PREMISES	None
TIPPING	None
AGRICULTURAL (INCLUDING FERTILISERS)	Significant
OVERALL RISK	IA
COMMENTS	Source of E.coli. to be investigated.

TABLE I

EXAMPLES OF GROUNDWATER POLLUTION AND
VULNERABILITY IN THE PO VALLEY (ITALY)

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ABSTRACT

The hydrogeological characteristics of the Po Valley (Northern Italy), where a vast alluvial aquifer characterised by good transmissivity is present, are described in the poster. In this area some of the most urbanised areas of Italy and the largest industrial and cattle-raising complexes are concentrated. During the past decades groundwater pollution of various origin was registered; some of these cases are here described which conditioned the drinking water supply in some areas. In relation to this situation and to those registered in other parts of the Italian peninsula, the Department of Civil Defense, through the National Council of Research (CNR), started a research programme in 1986 finalised to the drawing of aquifer vulnerability maps, to be used as a model for the forecast and the prevention of emergency situations.

1. INTRODUCTION AND HYDROGEOLOGICAL SITUATION

The Po Valley is the largest plain in Italy (56,000 Km²) and among the main ones in Europe. It is made up of Quaternary alluvial deposits of the River Po and its tributaries and is bordered to the north and to the west by the Alpine range, to the south by the Apennine range and to the east by the Adriatic sea. The average thickness of the alluvial deposits,

constituted by loose sediments with varying particle-size from gravels to clays, is about 200 metres. They form an aquifer which, on a regional scale, is characterised by an evenly extended nappe of the confined type in the axial and coastal part of the plain and unconfined in the mountain-foot area. The underground hydric supplies have always represented one of the main factors of development and wealth of all the plain, satisfying, up to the present, the needs of one of the most intensely urbanised and industrialised zones of Italy (e.g. Milan and its outskirts), also characterised by a specialized and intensive agriculture, to which cattle and pig farming is associated. From a hydrogeological point of view, always on a regional scale, at least the first 100 metres of thickness of the aquifer constitute nearly everywhere a variously subdivided monostratum layer, with good hydraulic conductivity ($10^{-5} < K < 10^{-2} \text{ ms}^{-1}$), recharged by the effective infiltrations of surficial waters, mainly in the high valley zones, at the foot of the hills (roughly between 200 and 30 metres above sea level). Especially in the southern part of the plain the watercourses flowing from the Apennines are mostly infiltrating. Instead in the plain at the foot of the Alps the feed factors are represented, apart from rainfalls, by irriguous waters derived from the rivers through canals. The surficial water infiltration is also favoured by conditions of non saturation of the mean, induced by intense pumping of groundwater which lowered the aquifer up to 30 metres (Milan area). The hydrogeological situation and the high intensity of the productive activities, often characterised by untreated waste in the soil and water-courses, have caused widespread and localised pollution, favoured by the aquifer vulnerability conditions.

2. CASE HISTORIES

During the past decades the aquifer pollution cases have occurred more

and more frequently, causing sometimes the closedown of public water systems. Naturally such pollutions have taken place where the aquifer outcrops (fluvial and fluvio-glacial deposits with coarser particle-size) or where it is hydraulically connected with infiltrating water-courses. Among the various examples we can remember:

Casale Monferrato (Piedmont, 1986): some illegally drilled wells dispersed a range of liquid and semi-solid toxic wastes in the subsoil (mainly phenols and other aromatic compounds) just upstream of the feeding walls of the local aqueduct which served over 20,000 inhabitants and the supply had to be interrupted for about two months. The site upgrading was carried out with the construction of a hydraulic barrier, the removal of the polluted soil and the simultaneous drilling of new wells.

Milan, its hinterland and Mantua (Lombardy, 1975/1985): the high industrial concentration in a territory which is among the most transmissive of the whole Po Valley, with aquifer outcropping, has favoured the dispersion in the subsoil of chlorinated solvents and chromium compounds in an area a few square kilometres wide. Moreover, in all the province of Mantua high concentrations of nitrates are present. The considerable thickness of the monostratum aquifer has dispersed the pollutants up to over 100 metres in depth, with the closedown of wells used for public and private water supply purposes. In particular, in Porto Mantovano, a village situated along the River Mincio north of Mantua, vast pollution was due to the dispersion in the soil of trichloroethylene and other chlorinated solvents, which polluted a 2 Km² wide area with pollutant concentration values over 2 mg/l in the aquifer waters, with peaks up to 19 mg/l in some wells less than 50 metres deep. In a limited area, just around the vertical line of the dispersion points, the pollution reached a depth of about 100 metres, scattering according to the well-know diffusional model for this kind of compounds.

Modena, Bologna, Rimini (Emilia Romagna, 1970/1986): high concentrations

of nitrates have been found in the groundwaters, even beyond 100 mg/l, due to the subsoil dispersion of chemical fertilisers and farming sewage. In particular in the area of Modena, the high density of gravel quarries represents a hazard of aquifer contamination together with the dispersion of nitrogen rich waters from the drainage network. Instead the water-courses, thanks to the low nitrogen content of their waters at least in low water hydraulic regimen, develop a delimiting action. Bergamo and Mantua (Lombardy, 1986): high concentration of atrazine and simazine, chemical products used as herbicides in some crops such as maize, even over 20 times the limit fixed for drinking waters (0,1 µg/l) by the EEC, have been found. The dispersion takes place from the farming land and from some well localised points.

3. RESEARCH PROGRAMME: THE AQUIFER VULNERABILITY ASSESSMENT

The researches that will be developed within the limits of the programme have as a main goal the study of the effective and potential pollution phenomena of the underground hydric bodies, through a reliable forecasting system in space and time in order to:

- give a cognitive base on every territorial situation;
- give an instrument of quick assessment of the pollution potential of any effective or potential agent;
- assess the opportunity of installing monitoring systems suitable for a rapid and efficient detection in order to plan the prevention interventions and safeguard the populations subject to short and middle-term impact hazards.

The studies, carried out in suitably selected sample-areas, will allow the setting up of the formation methodologies of the base documents (aquifer vulnerability maps), and of the accessory ones in order to give to the State central and local institutions, appointed for the protec-

tion and defence of the environment, valuable instruments of evaluation, to be applied on an extensive scale.

At this stage it is possible to individuate the following phases and articulations of the research programme:

- a. selection of some sample-areas with high exploitation of underground waters where conditions of aquifer effective and/or potential vulnerability exist. It will be necessary to select a wide enough range of different hydrogeological situations in order to obtain the most possible representative survey of the territory and of the climatic conditions of the different areas of the country.
- b. a complete hydrogeological study in order to identify the geometric, hydrodynamic and geochemical characteristics of the hydrogeological systems, the manners of formation of the underground hydric resources, the interception points of the aquifers and/or water-supply systems, the finalised quality of the resources.
- c. identification of the sources and causes (effective and/or potential) of concentrated and widespread pollution and related types and quantities of pollutants, in order to define the impact load.
- d. quick assessment of the pollution potential, considering the aquifer/water/pollutant interaction phenomena which take place underground (dilution, absorption, oxidation, etc...), of the aquifer characteristics (permeability, diffusion coefficient, gradient, etc...) and of the evolutionary characteristics of the process (depth of the saturation zone, distance between active and passive hazard subjects, etc...).
- e. drafting of aquifer vulnerability maps, containing in a clear and not equivocal form all the above listed data, accurately selected and translated in terms of modern thematic cartography.
- f. localisation of the protection areas.
- g. localisation of the hazard passive subject points to be monitored and related alarm system.

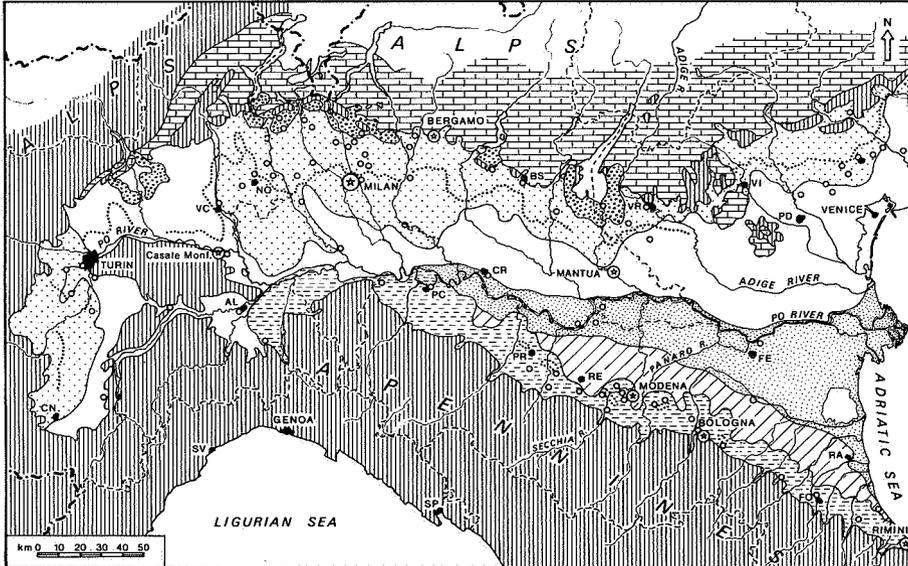
h. study of the lowering and mitigation methods of the effects of a pollution in progress.

The legend of the aquifer vulnerability maps comprises the following elements:

1. characteristics of the aquifers;
2. real and potential sources of pollution;
3. preventive and/or reducing factors of pollution;
4. pollution in progress;
5. main points subjects to pollution.

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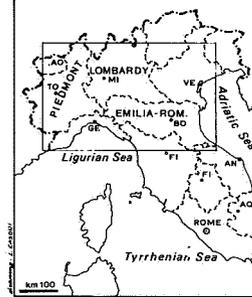
(Fig. 1) HYDROGEOLOGICAL SCHEME OF THE PO VALLEY

AQUIFER SUBSTRATUM (OUTCROPPING AT THE MARGIN OF THE PLAIN: ALPS AND APENNINES):

- Formations with high and middle permeability (mainly limestones).
- Formations with low to very low permeability.

AQUIFER OF THE PLAIN:

- Moraine deposits (varying permeability).
- Fluvio-glacial and fluvial deposits (mainly gravels) of the Alpine-foot high plain with high transmissivity; mostly outcropping aquifer with unconfined nappe.
- Fluvial deposits (and fluvio-glacial in the western sector: Piedmont) of the Alpine-foot low plain with middle transmissivity; variable confining conditions.
- Fluvial deposits of the Apennine-foot high plain, outcropping middle-transmissivity aquifer with unconfined nappe in the apical and intermediate part of the alluvial fans, with impervious covers and confined nappe in the frontal part of the alluvial fans.
- Fluvial deposits of the Apennine-foot low plain with next to nought transmissivity.
- Pollution case histories.
- Fluvial deposits (mainly sands alternating silts and clays) of the River Po low plain; middle transmissivity aquifer with confined nappe due to mostly continuous silt-clay covers.
- "Fontanili" springs.
- Principal pumping stations for aqueducts.



VULNERABILITY MAPPING IN FLANDERS, BELGIUM

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ABSTRACT

The groundwater vulnerability is determined by static as well as dynamic factors. However, the vulnerability map of the Flemish Region of Belgium is based on a number of static factors only. Taking this into account, the vulnerability map is defined as a map expressing the degree of risk for contamination of the groundwater in the upper aquifer by contaminants entering the soil from the surface. The present map provide the user with a general picture in view of a regional planning. For the evaluation of actions causing a potential hazard of contamination, the map serves as a directive for investigations in this matter. In the future, this map can be used as a basis for more detailed maps including dynamic factors.

1. INTRODUCTION

Groundwater is a precious resource. Once contaminated, it is difficult, perhaps impossible, for the waterquality to be restored. The risk for contamination depends on a number of factors, jointly determining the groundwater vulnerability. In depth knowledge of the vulnerability is of prime importance for its protection. A map represents a reference for a good management of groundwater reserves.

On that account a decision has been taken by the Community Minister for Environment, J. Lenssens, for a vulnerability map to be compiled, this on a scale of 1/100.000, for each province. The vulnerability map for Antwerpen and Oost Vlaanderen is compiled and drawn by Prof. Dr.

W. De Breuck (State University of Ghent), for Vlaams-Brabant and West-Vlaanderen by Prof. Dr. W. Loy (Catholic University of Louvain) and for Limburg by Prof. Dr. T. Van Autenboer University of Limburg). Several workshops under the leadership of the Administration of Physical Planning and Environment resulted in the formulation of the definitions and in the agreements about the method of mapcompilation.

2. DEFINITION

The aquifer is regarded as a saturated zone of the formation, being of sufficiently acceptable thickness and extent, so as to be an economically justified watersupply source. In this respect, a minimum supply of, at least, $4 \text{ m}^3/\text{hr}$ was set.

The groundwater vulnerability is determined by static as well as dynamic factors.

These are :

- the extent and type of the aquifers and the covering layers
- the hydraulic parameters, particularly the kind and degree of permeability
- the groundwater condition in natural and artificial circumstances
- the interaction of neighbouring formations
- the kind and the degree of contamination

However, the vulnerability map of the Flemish Region is based on static factors, compiled from currently available data, in order to provide the user with a general picture at short notice.

A formulation for the definition of this map could be as follows : it is a map expressing the degree of risk of contamination of the groundwater in the upper aquifer by contaminants entering the soil from the surface, taking into account static parameters only.

3. METHOD

3.1 General scheme

The procedure is presented schematically (Figure 1). Topographic maps on a scale of 1/25.000 were used as a reference.

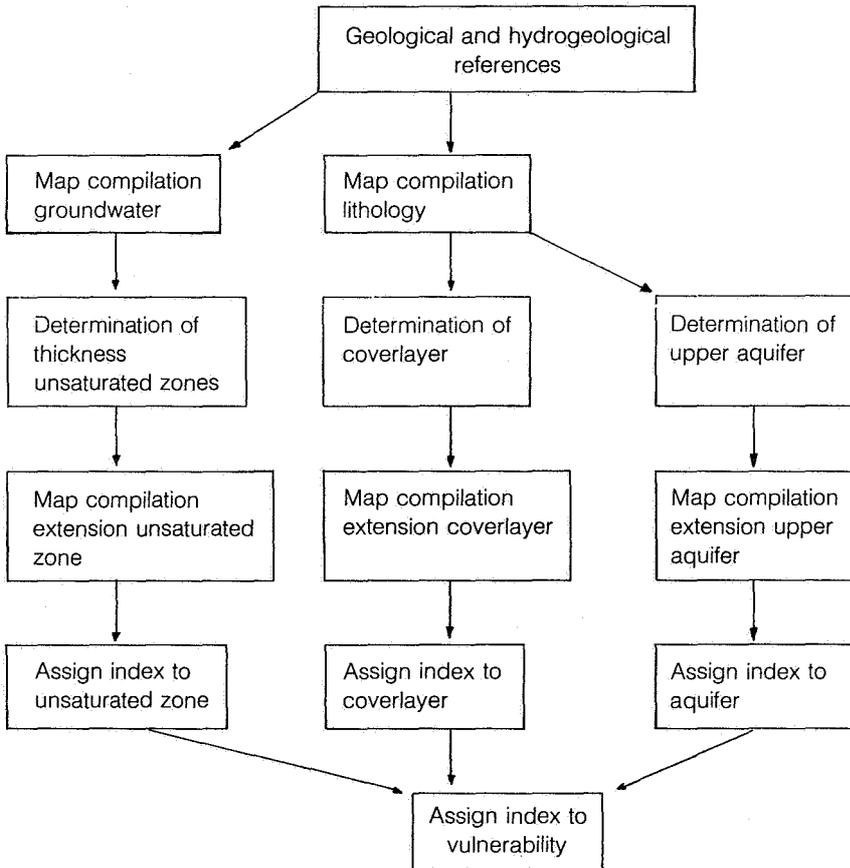


Figure 1. Procedure of compilation of the vulnerability map

3.2 The vulnerability scale

3.2.1 Factors determining the vulnerability scale

3.2.1.1 The aquifer

Determining factors for a classification of the aquifers are, the type of the formation, the permeability and the behaviour of contaminants in the aquifer.

The aquifers are classified in four groups :

- A. chalk, limestone, sandstone, marl
- B. gravel
- C. sand
- D. loam sand, argillaceous sand

3.2.1.2 The coverlayer

The coverlayer is that layer on top of the aquifer. The thickness of this cover, taking into account excavations for construction activities, canals, etc., should be at least 5 meters in order to offer sufficient protection. In case the thickness is less than 5 meters, the coverlayer is regarded as non existent. A formation composed of sand, is not regarded as a protective cover.

Determining factors for a classification of the coverlayers are the type of formation, the thickness and the hydraulic resistance.

A distinction is made between :

- a. no cover (less than 5 m and/or sandy)
- b. a loamy cover
- c. a clayey cover

3.2.1.3 The unsaturated zone

The characteristic of the unsaturated zone is relevant only in case of absence of a coverlayer. The determining factor for a classification is the thickness.

One distinguishes :

- 1. a thickness of 10 m or less
- 2. a thickness of more than 10 m

3.2.2 Classification

The vulnerability scale is subdivided into five classes. A specific class is the result of the combination of all factors on which the

vulnerability scale was based. A value of 1 to 5 will be assigned to each of them.

Table 1. *Classification of the vulnerability scale*

Aquifer	Cover			
	a		b	c
	a ₁	a ₂		
A	1	2	3	4
B	1	2	3	4
C	2	3	4	5
D	4	4	5	5

Legend :

1. extremely vulnerable
2. highly vulnerable
3. vulnerable
4. moderately vulnerable
5. little vulnerable

4. THE LOCAL SITUATION

Supplementary to the vulnerability map and explanatory brochure deals with the real physical situation of the province under consideration. The following items are discussed. Subsequently, relief and hydrography geology and hydrogeology and in particular, the vulnerability map. On the other hand a warning is mentioned on the vulnerability map saying that the map should always be used together with its explanatory brochure.

5. THE OBJECTIVE

The objective of the present map, compiled from currently available data, is to provide the user with a general picture in view of a regional planning.

First and foremost the vulnerability map will be used by the municipal and provincial government in order to permit activities causing a potential hazard of contamination. Nevertheless, regulations for groundwater protection will always require further local investigation.

6. NEW DEVELOPMENTS

Next to the static factors, also dynamic factors are influencing the vulnerability. On that account, and for the province of Vlaams-Brabant, the compilation of a second map, additional to the currently available vulnerability map, is under investigation. This map, compiled by Prof. dr. F. De Smedt (Free University of Brussels), will provide the user with local flow patterns, eventually expressing a higher or lower class of vulnerability.

In the future further investigation in sensitivity of the groundwater-quality to specific chemical parameters in some regions in Flanders will be worked out. Detailed maps dealing with these problems will be compiled.

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CLASSIFICATION OF GROUNDWATER PUMPING STATIONS IN THE UTRECHTSE
HEUVELRUG AREA

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ABSTRACT

The Utrechtse Heuvelrug is a sandy infiltration area (an ice-pushed ridge) in the central part of The Netherlands.

The vulnerability of the existing groundwater pumping stations is rather high with respect to pollution of different origin. This is caused by the absence of covering (semi-)confining layers, the occurrence of numerous spots of contamination and the poor capacity of the subsoil with respect to adsorption and degradation.

A regional-scale groundwater study has been carried out in this region, including original groundwater quality and influences of point and non-point sources of pollution.

Furthermore, path lines and travel times have been calculated of the groundwater, flowing to the existing pumping stations. Knowing the recharge areas around the pumping sites, it was possible to develop a classification system, including the risk of pollution based on the following criteria:

- effectiveness of the existing situation with respect to groundwater protection (with subcriteria: accuracy of computed recharge areas and quality of existing monitoring network);
- danger of pollution of soil and groundwater within the recharge area;
- existing contamination (type, extension);
- effect-reducing capacity of the subsoil (adsorption and degradation capacity).

The method is discussed and results are presented, followed by recommendations.

INTRODUCTION

In The Netherlands, groundwater is a very important source for water supply. It is available in considerable quantities, due to favourable hydrological conditions. However, the possibilities for exploitation are limited, due to the influence of withdrawal of groundwater on agriculture, infrastructure, and the natural environment. Furthermore, in several parts of the country human activities cause deterioration of the groundwater quality and consequently restrict the possibilities of exploitation too. Therefore, management of groundwater resources must be based on knowledge of the consequences for the interests involved and on insight into the various factors influencing the groundwater quality.

In the Utrechtse Heuvelrug area, in the central part of the Netherlands, recently a regional-scale groundwater study has been carried out with abovementioned characteristics. The main objective of this study concerned the proper allocation of groundwater resources for public water supply, taking into account on one hand the impact of withdrawal of groundwater on different waterrelated interests and on the other hand (possible) effects from (potential) sources of pollution on groundwater quality. The outline of the project is depicted in Figure 1.

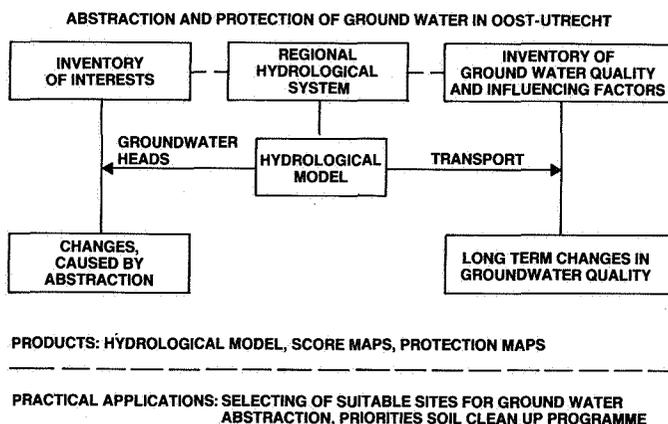


Figure 1. Outline of the Oost-Utrecht Project

A specific objective of the study was the systematic evaluation of the risks of pollution of the groundwater pumping sites in the area, by putting together on one hand information on path lines and travel times of the groundwater which is flowing to the well fields and on the other hand data on groundwater quality and on (potential) sources of pollution. Based on these categories of information it was possible to develop a classification system including the risk of pollution of the existing pumping stations.

THE PROJECT AREA

The Utrechtse Heuvelrug is a sandy infiltration area. The ice-pushed ridges in this area originate from the glacial period of the Saalian. A hydrogeological cross-section of the area is given in Figure 2.

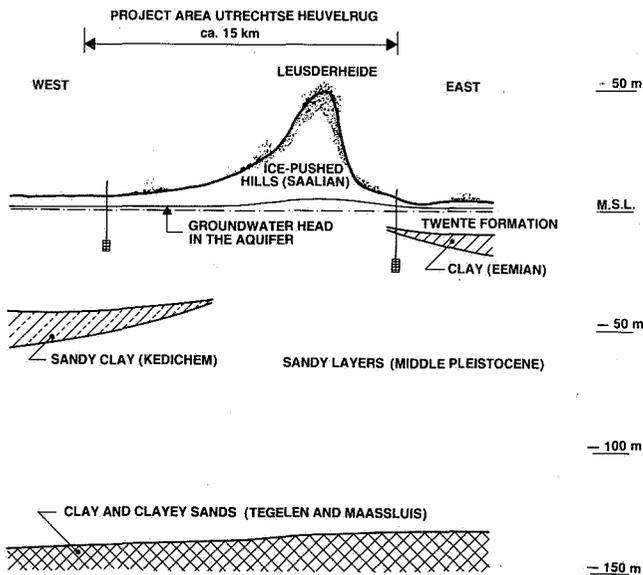


Figure 2 Hydrogeological cross section.

In large parts of the Utrechtse Heuvelrug, the groundwater does not have its natural composition any more, but is being influenced by human activities. Contamination of soil and groundwater has already caused

some trouble in this area with respect to groundwater withdrawal for water supply.

This concerns mainly contamination by chlorinated hydrocarbons.

Table 1 is giving an illustration of these problems.

Sum of detected concentrations($\mu\text{g}/\text{l}$)	number of wells
not detectable	13
0.1 - 1	1
1 - 2	8
2 - 10	8
10 - 100	13
100 - 200	3
	3
	49 (total number of investigated wells)

Table 1 Average concentration (average sum of concentrations of five chlorinated hydrocarbons) in industrial wells which appeared to be contaminated after sampling twice.

Furthermore, it has been concluded that the vulnerability of the existing groundwater pumping stations for public water supply is rather high with respect to pollution of different origin. This is caused by the absence of protective covering (semi-confining) layers, the existence of numerous sources of contamination and the poor capacity of the subsoil with respect to adsorption and degradation of different types of contaminants.

CRITERIA, USED FOR CLASSIFICATION

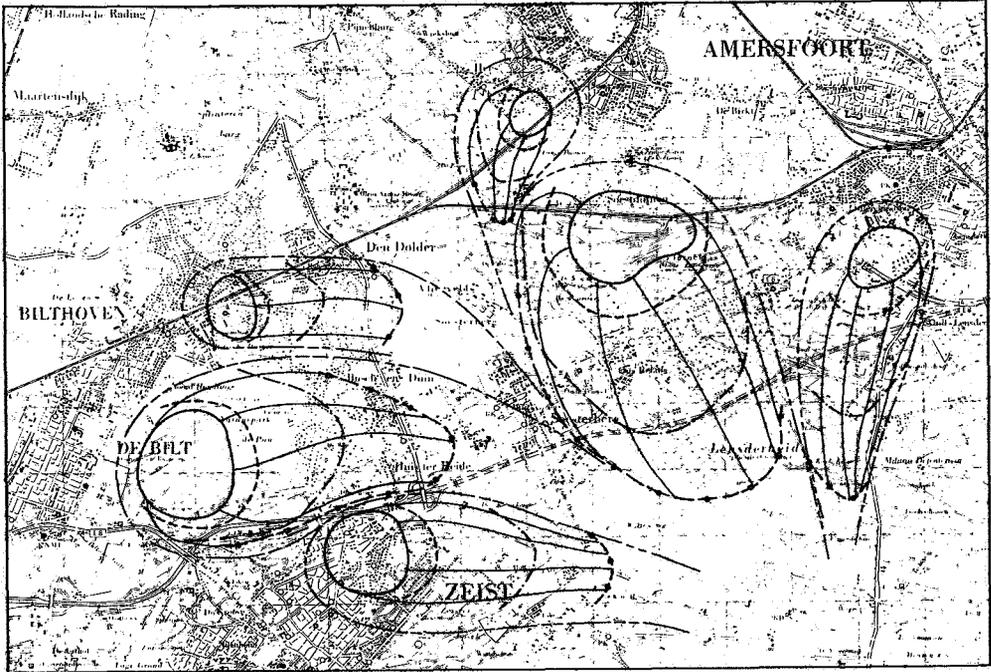
The risk of pollution of the existing groundwater pumping sites has been evaluated, based on the following criteria:

1. Effectiveness of the existing situation with respect to groundwater protection, with subcriteria:

- * accuracy of calculated recharge areas around the pumping sites;
- * density of existing monitoring networks.

2. Danger of pollution of soil and groundwater within the recharge areas around the groundwater pumping sites. The existence of potential sources of pollution of different character is taken into account, such as roads, railways, density populated and industrialized areas.
3. Existing (known) sites of contamination of soil and groundwater within the recharge areas, such as waste disposal sites, contaminated sites of different industries. Type and extent of contamination have been taken into account.
4. Effect-reducing capacity of the subsoil (adsorption and degradation capacity). This factor depends not only on the type of soil but also on the properties of the contaminants.

ad.1 Some of the calculated recharge areas around the pumping stations are depicted in Figure 3. They have been obtained by joining together the results of analytical calculations of the path lines close around the well fields and results of regional scale flow path calculations based on a numerical approach using measured groundwater head observations (Van den Akker 1982, Van den Akker et al.1987, Heij et al. 1985). For the regional flow path calculations, interpolation of groundwater heads is necessary. Accuracy of the calculation results is depending strongly on the availability of data on groundwater heads (density of observation network). Also the interpolation method which is applied has its influence on accuracy. In this case, Kriging interpolation has been used, giving good estimates of the groundwater head.



Legend: line of equal travel time of 10 years —————
 line of equal travel time of 25 years - - - - -
 line of equal travel time of 100 years - · - · - · -
 line of equal travel time of 200 years - ◊ - ◊ - ◊ -
 boundary of recharge area. - - - - -

Figure 3 Path lines and travel times of groundwater flowing to the pumping sites

The density of the existing network with respect to monitoring of the groundwater quality differs from pumping site to pumping site. The denser the network, the smaller the chance of unnoticed passing of contaminated groundwater (under the condition that the observation wells have been located taking into account the pattern of groundwater flow). For the rest it must be noticed here, that most observation wells around pumping sites are not originally installed to play a role in groundwater quality monitoring, but primary for measurement of groundwater heads.

weights of criteria

variant 1	1	1	1	1
variant 2	2	5	4	3

criteria

pumping site + criterion	Effectiveness of existing protection	Risk of pollution	Existing sites of contamination	Effect reducing capacity	variant 1		variant 2	
					overall score	order	overall score	order
Beerschoten(shallow abstraction)	1	2	3	4	10	5	36	7
Bilthoven	4	3	3	4	14	3	47	4
Bunnik	3	4	3	2	12	4	44	5
Doorn	4	3	4	5	16	1	54	2
Driebergen	4	2	2	4	12	4	38	6
Soest	4	2	1	3	10	5	31	8
Soestduinen	2	4	4	4	14	3	52	3
Zeist	2	5	5	4	16	1	61	1
Amersfoort Berg	4	4	3	4	15	2	52	3

scores of pumping sites

overall scores
= $\sum(\text{score} \times \text{criterion-weight})$

Table 2 Classification of pumping sites with respect to risk of contamination.

Sensitivity analysis produced no significant change in order, so a stable classification with respect to risk of pollution has been obtained. This has led to the following conclusions:

- Zeist and Doorn are relative high-risk groundwater abstraction sites, with as a main cause existing and potential contamination of soil and groundwater.
- Next pumping sites with respect to risk of pollution are Amersfoort Berg and Soestduinen and, in less measure, Bilthoven.
- Bunnik has a medium score.
- Driebergen is a rather safe pumping site, because of (practically spoken) absence of threats and no contamination of importance in the recharge area.
- The safest pumping sites are Soest and Beerschoten, because there are no threats of any importance within their recharge areas.

ad.4 With respect to this criterion, only the hydrogeological situation has been taken into account, in combination with the depth of abstraction. The leading thought behind this concept is, that the locally existing semi pervious layers have some potential as to adsorption and degradation because of containing organic material. The depth of abstraction has its influence on travel times of the groundwater (from the ground surface), thus being also a measure with respect to potential protection.

CLASSIFICATION OF PUMPING SITES

The classification does not have an absolute character, because this method has been developed and applied in the studied area. There is no reference available in other parts of the country.

Existing water treatment facilities have not been taken into account, so this classification is based on the expected quality of the groundwater which is flowing to the pumping sites.

To each pumping site a score per criterion has been attached. This score has been scaled from 5 (contribution to risk is high) to 1 (low contribution).

Doing so, for each criterion a column with scores of every pumping site has been obtained. After this, weighing of criteria has been carried out. Weights have been given, scaled from 5 (very important) to 0. Finally, overall-scores have been obtained by multiplying (for each pumping site) the score per criterion and the weight per criterion and adding these products, thus ranking the pumping sites. In Table 2 the results of two variants are listed:

- all criteria have equal weights (variant 1);
- criteria 2 and 3 (danger of pollution and known sites of contamination) have highest weights, with a gradual difference (variant 2).

Table 3 Recommended protective measures and actions per pumping site

Pumping site	Recommended measures and actions
Doorn	remove, or supply by other pumping sites
Zeist	<ul style="list-style-type: none"> - investigation of possibilities of deeper abstraction - extension of monitoring networks (groundwater head and -quality) and better fixation of recharge area - investigation of sewerage systems (possible leakage) and defence terrains - extension of water treatment facilities
Amersfoort (Berg)	<ul style="list-style-type: none"> - investigation of sewerage systems - extension of monitoring networks (groundwater head and -quality) and better fixation of recharge area - investigation of defence terrains - investigation of waste disposal site
Soestduinen	<ul style="list-style-type: none"> - (possible) installation of interception wells - investigation of defence terrains
Bilthoven	<ul style="list-style-type: none"> - investigation of sewerage systems - extension of networks (groundwater head and -quality) and better fixation of recharge area
Bunnik	<ul style="list-style-type: none"> - investigation of waste dump - investigation of monitoring networks (groundwater head and -quality) and better fixation of recharge area - investigation of extent and hydraulic resistance of covering claylayer
Driebergen	<ul style="list-style-type: none"> - investigation of sewerage systems - extension of monitoring networks (groundwater head and -quality) and better fixation of recharge area
Beerschoten (shallow abstraction)	<ul style="list-style-type: none"> - investigation of former waste disposal site
Soest	<ul style="list-style-type: none"> - extension of monitoring networks (groundwater head and -quality) and better fixation of recharge area

POSSIBLE PROTECTIVE MEASURES

Possible protective measures for pumping sites with high to moderate risk to pollution are:

- installation/extension of water treatment facilities;
- installation of interception wells;
- making use of the effect-reducing capacity of the subsoil (for instance by abstraction on a deeper level);
- more accurate calculation of the recharge area, around the pumping site (based on extension of observation facilities concerning groundwater head);
- regular monitoring of groundwater quality in the flow direction;
- tracing (and elimination) of (potential) sources of contamination, in recharge areas;

In Table 3 the measures are listed, which have been recommended to take within the considered recharge areas.

ACKNOWLEDGEMENTS

The project was carried out under contract with the Ministry of Housing, Physical Planning and Environment (Directorate-General for Environmental Protection) and in close co-operation with the Provincial Waterboard of Utrecht, the water supply company "Waterleidingbedrijf Midden-Nederland", the water supply company of the city of Amersfoort and the Inspectorate for the Environment of Utrecht.

Many thanks are due to M.J.H. Pastoors and H. Snelting of RIVM for their co-operation and for carrying out the necessary calculations.

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ASSESSING AQUIFER SENSITIVITY TO ACID DEPOSITION

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ABSTRACT

A logical extension of current scientific study of surface water and soil acidification due to airborne deposition is to ask whether groundwater quality might be affected by this same deposition. Historical records of groundwater quality are scarce. However, recent monitoring of groundwater chemistry has uncovered changes occurring in some shallow, non-calcareous, sandy aquifers. At the International Institute for Applied System Analysis (IIASA), a methodology has been developed for evaluating the sensitivity of European aquifers to the deposition of acidifying compounds. This paper presents maps of aquifer sensitivity and risk resulting from the application of this methodology on a European regional scale.

IMPACT OF ACID DEPOSITION ON AQUIFER SYSTEMS

Cation exchange and mineral weathering are the primary transformation processes that contribute to the neutralization of acid deposition by the release of base cations and the formation of bicarbonate ions. Weathering rates of different minerals under natural conditions are not well established. However, the weathering rates of carbonate rocks appear to be fast enough to counteract the present levels of acid deposition, while the weathering rates of many silicate minerals are too low (von Brömssen, 1986).

The expected impact of acid deposition on groundwater is not necessarily a decrease in the pH value but an increase in the content of leached base cations and sulphate, possibly accompanied by a decrease in bicar-

bonate. Such an evolution of groundwater chemistry has been documented e.g. by Jacks et al. (1984) in parts of Sweden, by Soveri (1985) in Finland and by Wieting (1986) in the FRG.

Ideally, assessing the impact of acid deposition on aquifer systems would involve a quantitative prediction of the temporal development of chemical concentrations in the groundwater. Although the biogeochemical neutralizing processes in soils and aquifers are qualitatively well known, quantitative estimates of elemental transport, release, and accumulation are not available on a regional scale. In addition, seasonal and regional variations in European hydrology are complex, requiring substantial computational resources to model. For these reasons, a qualitative approach was chosen, in which the aquifer sensitivity is evaluated by assessing the neutralizing capability of the soil/aquifer system.

SENSITIVITY INDICATORS

In the IIASA methodology, the neutralization capability is assessed on the basis of soil depth, texture and base cation content, the size and the mineral composition of the aquifer, and the annual amount of water potentially available for recharge. The indicators were chosen to reflect the geochemical processes involved in neutralizing acid deposition. The choice of these indicators was influenced by sensitivity studies by Jacks et al. (1984), Aust (1983) and Edmunds and Kinniburgh (1986) and by the availability of regional data. There are few sources of data that are consistent over large areas, yet detailed enough for this purpose. Soil depth, texture, and base cation content were compiled from the FAO Soil Map of the World (1974). Aquifer size and mineral composition were taken from the Int. Hydrogeological Map of Europe which is currently being compiled.

The efficiency of neutralization by cation exchange in the soil depends upon the exchanging surface available and the residence time of the matric water. These factors have been included in an indicator called soil-water contact, the value of which is determined on the basis of soil depth and texture. Soil texture is divided into 5 classes, ranging from coarse to fine. Soil depths are classified as either shallow or

deep (less than or greater than 0.5 m). The total neutralizing capability of the soil is evaluated from the soil-water contact and the content of base cations in the top 0.5 m of the soil. The base cation content has been calculated from data on cation exchange capacity and percentage of base saturation for 80 European soil types. The division of these soils into 6 classes is based primarily upon this measure, although in some cases soil pH or the occurrence of carbonate minerals was considered.

The neutralizing capability of the aquifer depends on the residence time of the groundwater and on the weatherability of the minerals in the aquifer. Groundwater residence time depends on the recharge rate and the size of the aquifer. Rather than create a comprehensive hydrological model of Europe, potential annual recharge, defined as annual precipitation minus calculated annual evapotranspiration, has been chosen as a surrogate variable. The potential annual recharge is divided into 3 classes (0-100 mm, 100-400 mm, 400- mm).

The International Hydrogeological Map of Europe defines 4 productivity classes based on permeability and aquifer size. For the purpose of assessing aquifer sensitivity, highly productive aquifers were assumed to possess long residence times because of their sizes and depths. Low or nonproductive aquifers were assigned shorter times since groundwater moves primarily through fractures in many of these aquifers. These considerations were used to classify European aquifers into 4 size categories ranging from extensive to small. Aquifers have also been classified into 4 mineral composition categories according to their mineral weathering rates, ranging from acid silicate to carbonate rocks.

METHOD OF SENSITIVITY ASSESSMENT

The neutralizing capability is estimated by a stepwise evaluation of the combined neutralizing effect of a pair of sensitivity indicators. The neutralization capabilities of the aquifer and the overlying soil are estimated in separate branches of the assessment procedure. In each step the combined neutralizing capability of two factors is evaluated using two-dimensional combination tables. This process is illustrated in Figure 1. The combination tables are constructed to reflect the current

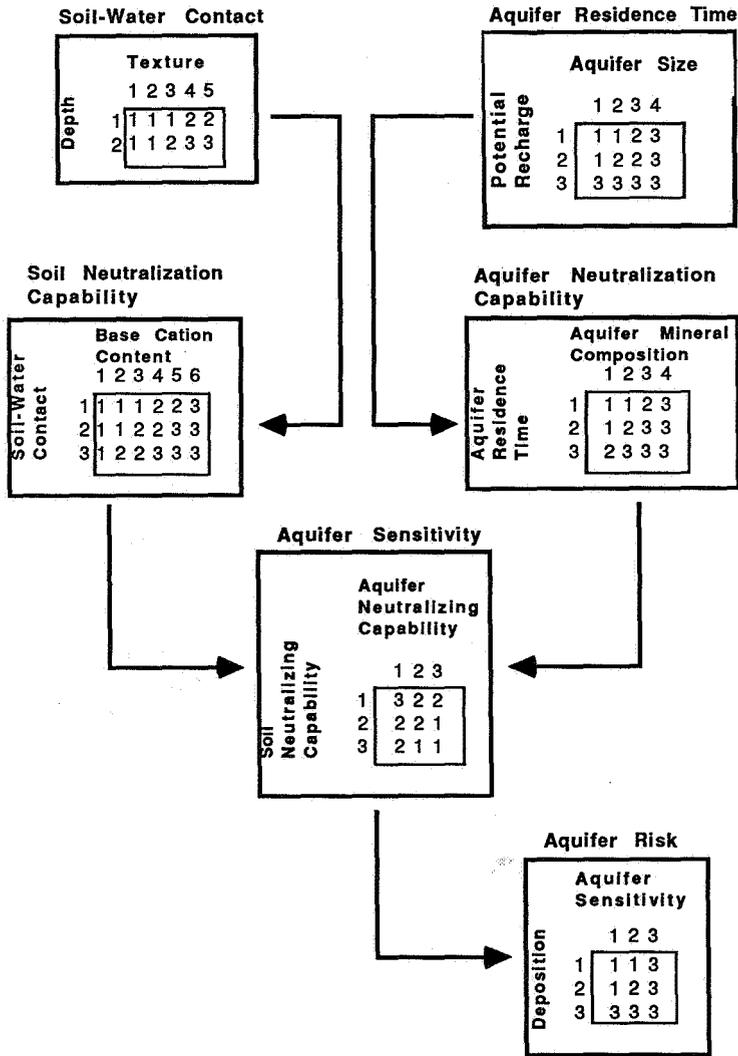


Figure 1. *Combination procedure*

knowledge of the impact of neutralizing mechanisms in soils and aquifers. This procedure has the advantage of being more transparent than an additive algorithm with non-linear weighting coefficients. The resultant sensitivity and risk are divided into three classes (1 stands for low and 3 for high sensitivity or risk).

In the computer implementation of this methodology, Europe is subdivided by a grid system with individual cells of 1.0 degree longitude by 0.5 degree latitude, in accordance with the IIASA RAINS model (Alcamo et al.

1985). Data for each of the 1844 grid cells is passed through the combinational assessment procedure and assigned a sensitivity class. An example of the resulting map is shown in Figure 2. This map is based on the indicator data for the dominant (largest area) soil type and aquifer in each grid cell. It contains 528 grid cells of Class 1 (low), 815 cells of Class 2 (medium), and 501 cells of Class 3 (high) sensitivity. Most of the aquifers categorized as highly sensitive are situated in the Nordic countries. Other regions of high sensitivity include e.g. Scotland, Brittany, North-western Spain and Bohemia.

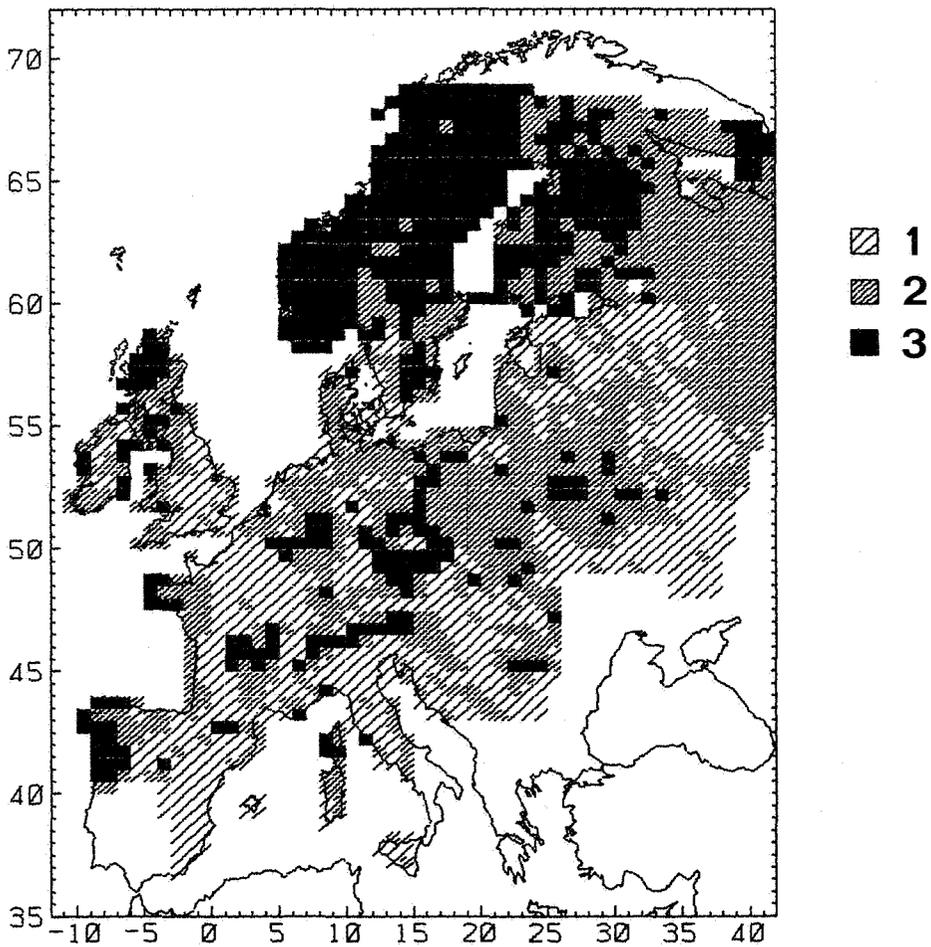


Figure 2. *Aquifer sensitivity to acidification*

RISK OF GROUNDWATER ACIDIFICATION

The process can be carried one step further to assess aquifer risk, a combination of aquifer sensitivity and acid deposition. An example of a risk map is shown in Figure 3. This map results from combining the sensitivity map in Figure 2 with the 1980 sulphur deposition pattern as calculated by Alcamo et al. (1985). The deposition has been divided into 3 classes for this purpose (0-1, 1-5, and 5- g/m²/yr). Using this classification, most of Europe receives medium deposition.

The majority of the aquifers at risk lie in central Europe, the Nordic countries, Great Britain and Northern Italy. The results have not been validated by comparison with field data, since such data are scarce.

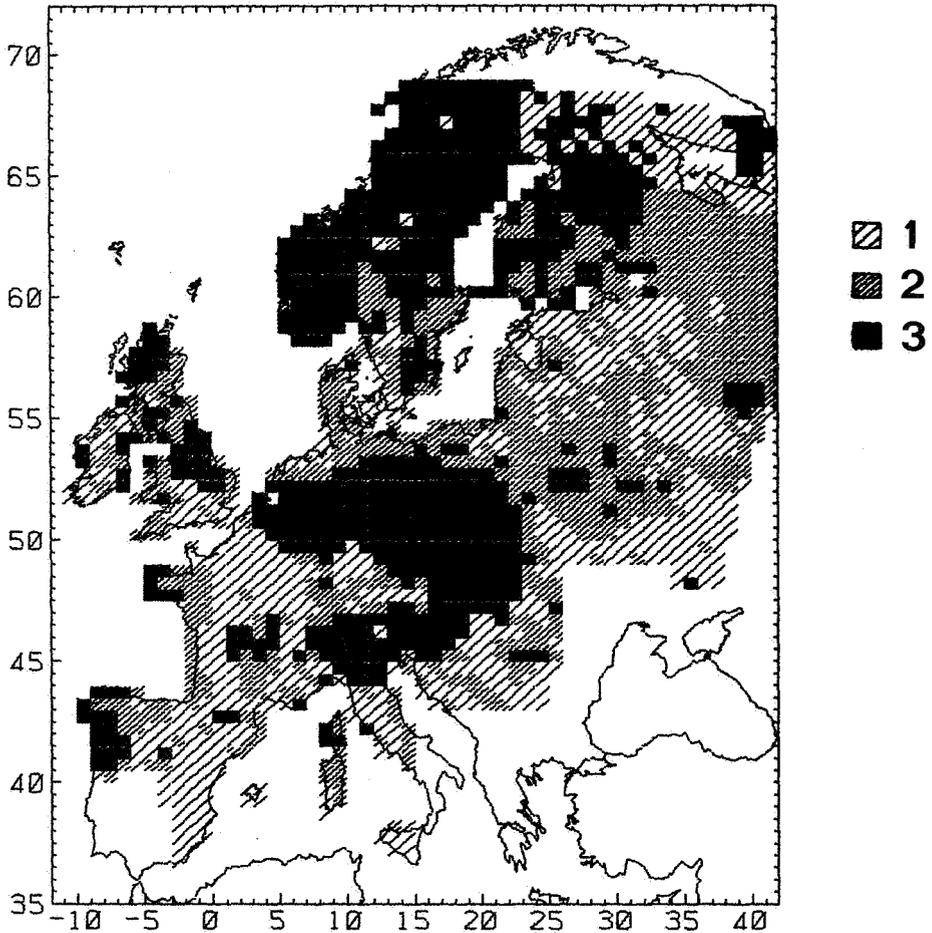


Figure 3. Risk of aquifer acidification

Pointwise observations (Jacks et al. 1984, Soveri 1985, Wieting 1986) do not contradict the result, but perhaps it could be argued that the impact of high deposition has been overestimated in this example. In the future, the acid input will be represented by the sum of deposition over time rather than the deposition pattern of a single year.

UNCERTAINTY

Examination of the screening methodology and output variations under different input conditions suggests three sources of uncertainty. The first source is, of course, the input data. Not all of the data are quantifiable in a straightforward way. The estimates of aquifer sizes from productivity classes and the use of potential recharge instead of actual recharge are cases in point. It may also be noted that, because of lack of data, no attempt has been made to incorporate the neutralization of the water as it flows between the soil zone and the aquifer represented on the maps.

The second source of uncertainty is a data resolution problem associated with the regional scale. The deposition grid cells are larger than some essential map features. Additionally, because data were taken from different sources, they are not related spatially within the grid cell. One way to deal with this problem is to use the dominant soil type and aquifer in each grid and ignore the rest of the data. This is the approach used in creating Figures 2 and 3. Another approach is to calculate an areally weighted average of the soil and aquifer characteristics in the grid cell. This approach gives a result similar to what is presented here.

The third source of uncertainty is the parameters used and the choices made in the combinational tables. Test runs show that the model is relatively insensitive to reasonable changes in all the tables except the sensitivity and risk tables. In the upcoming year, research efforts will focus on exploring these uncertainties and developing confidence that the results of this methodology are a fair representation of reality.

SUMMARY

This paper has presented a European-scale methodology for estimating the sensitivity of aquifers and the associated risk that geochemical changes may occur as a result of acid deposition. Example maps prepared using this methodology are also presented. Although this approach cannot be said to predict future geochemical changes, it can be used as a screening tool to locate those aquifers which are liable to experience changes first. Research on the uncertainties involved in the methodology continues, as well as on the validation of the results.

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THE PHYSICAL AND CHEMICAL PROCESSES IN THE UNSATURATED ZONE,
THE VULNERABILITY PROJECT 2

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ABSTRACT

Physical and chemical processes in the unsaturated zone in different geological deposits were investigated to select some factors important to the ground water vulnerability. Different hydrogeological parameters such as field capacity, porosity, unsaturated conductivity were compared to the chemical kinetics of the solid-interstitial water interface. It is then possible to estimate some of the important reactions responsible to the changes in water quality during percolation through the unsaturated zone to the ground water. Special emphasize was paid to nitrate reduction and to phosphate retention capacity in different geological deposits. It was found that microbiological nitrate reduction was accessible in all depths down to about 40 m.b.s. of three profiles investigated. Decomposable organic matter appears to be the limiting factor for the reduction capacity. Indications of nitrate reduction were obtained from soil gas analyses. Phosphate retention capacity is highly dependent on the geological material and the maximum sorption capacity could be calculated from percolation experiments.

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INTRODUCTION

It is known that the properties of the unsaturated zone and the processes within it govern the recharge to ground water. The unsaturated zone determines the vulnerability of the aquifer to surface pollution. The individual processes, physical, chemical, and biological, are mostly known qualitatively. However, the quantitative aspect of processes and their mutual dependence of various geological, chemical, and hydrogeological conditions are not too well known. A holistic approach to solve the problems on transport and transformation of contaminating compounds to the ground water has not yet been carried out.

The main purpose of the project was to study the hydraulic and chemical processes in the unsaturated zone under different geological and/or hydrological conditions.

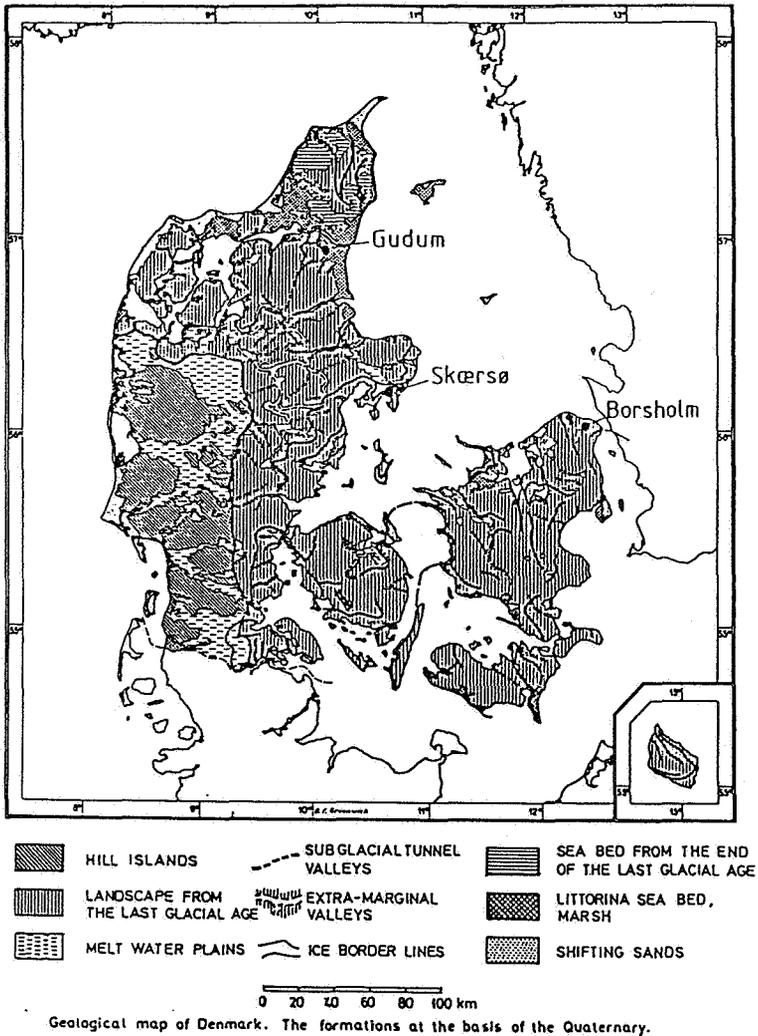
At three test sites in Denmark wells were performed and cores and bulk samples of the penetrated formations were taken for laboratory analyses and experiments.

In the laboratory sediments, interstitial water, formation gas, ground water, and rain water samples were analysed. Experimental work in the laboratory were performed on sediment samples to determine bulk-process kinetics, to measure nitrate and sulphate reuction and to differentiate between biochemical and chemical reduction processes in sediments. This paper only intent to review the vulnerability projects and to present some results from the experimental part.

METHODS AND PRINCIPLES

The procedure for site selection has already been described by Jacobsen et al., 1986. The field stations are placed in three different parts of Denmark with different geology, Fig. 1. & 2.

Gudum field station is situated in a sandy/clayey till over a limestone bed, which forms the aquifer. The geological formation rises from the surrounding raised littorina sea-floor as an island up to 67 meters m.s.l. No surface runoff systems are present. The station altitude is 42 meters a.s.l.



VULNERABILITY TESTSITES

Fig. 1. Geological map of Denmark.

Skærsø field station is placed on a push moraine deposit 24 meters a.s.l. The aquifer is situated in silty sand 15.3 meters below surface. No surface runoff system are present.

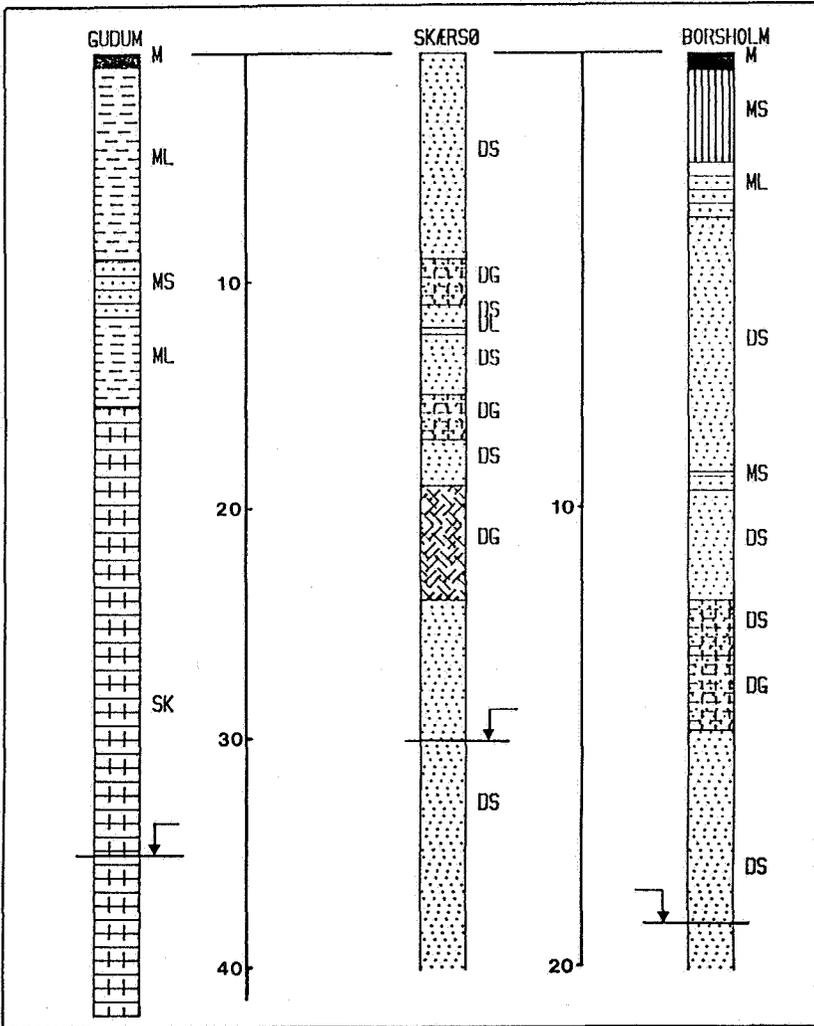


Fig. 2. Geological profiles.

M: Mull, ML: galcial clay, MS: glacial sand, MG: glacial gravel, DS: diluvial sand, DG: diluvial gravel, DL: diluvial clay, SK: senonian chalk.

Borsholm field station is situated in a sandy till area where clay layer is rather abundant as local "plates". The main aquifer is connected to the silty sand 18 meters below surface. No surface runoff systems are detected nearby the station, but minor pot holes are present within 200 meters.

The soil samples taken out during the drilling should serve several purposes and consequently they had to be treated very carefully in the field.

The mixed material collected with the 6" auger bit, was geologically described just after the sampling, and the placed plastic bags. Sub-samples for determination of soil water content and chemistry were transferred into several 50 ml plastic jars and sealed. All bags were vacuum sealed immediatly afterwards and cooled.

Soil cores, 4" in diameter 50 cm long, were screw-capped after demounted from the corer and vacuum packed in plastic bags and cooled.

The interstitial water was separated from the soil samples by suspending a pre-weighted sample of approximately 60 g of frozen soil in 50 ml denaturated demineralized water for 5 minutes in a closed polypropylene flask, and then centrifugated in 15 minutes at 1200 g. The supernatant was then sipped off through a 1.7 micron filter.

The sedimented soil was after drying at 105°C weighted in order to determine the original water content.

The reduction capacity (REC) of a soil sample was estimated by modified chemical oxygen demand method (Standard Methods, 1978). The cation exchange capacity (CEC) of a soil sample was determined at fixed pH = 8.20 using the Na-acetate/NH₄-acetate procedure with ethanol wash.

Chemical analyses on the water samples were carried out using standard analytical method, Jacobsen, 1986. Following elements were measured:

pH, Alkalinity, Ca, Mg, Fe, Mn, K, Na, Cl, F, NO₃, NO₂, PO₄, SO₄, NH₄, Cd, Cu, Pb.

The lithological analyses were performed by Well record laboratory at DGU according to the national standard. The granulometric analyses were performed using wet sieving technique following the national standard:

Unsaturated hydraulic conductivity were estimated by triplicate measurements of percolation through undesturbed soil columns, Todd, 1959.

Specific density, porosity, and bulk density was determined gravimetrically.

RESULTS

Two of the field stations are placed in farmland. The one in Gudum is applied with rather high amounts of fertilizer and with normal rotation of crops. The other one in Borsholm is placed on grassland, where fertilizer has not been used for 15 years, and is used only for grassing and hay harvest.

The third field station i Skærso is placed on a windcut deforested area which was given up as farmland 60 years ago, and since has been covered with moorland and later on with spruce forest.

In the Gudum profile cation exchange capacity, CEC, reflects the lithology. In the till CEC varies between 5 and 16 meq/100 g DW, but in the upper limestone it is lower than 5 meq/100 g DW. CEC is normally related to the clay fraction, which agrees with the measured fraction, clay-silt.

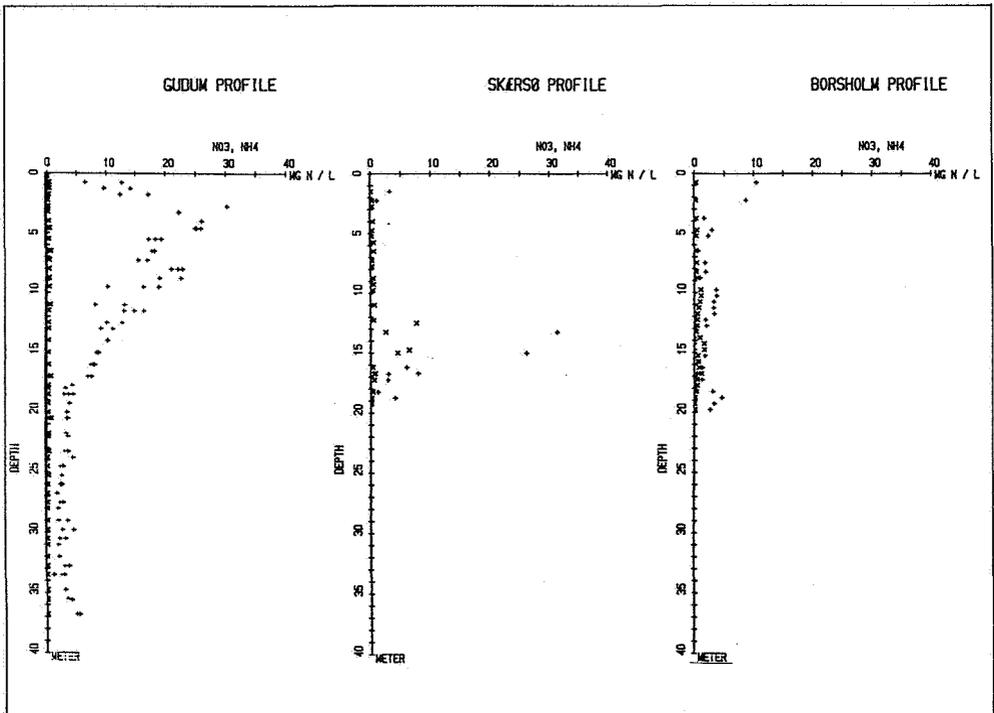


Fig. 3. Nitrate and ammonia profiles. +: nitrate, x: ammonia.

Reduction capacity, REC, is very high in the upper 5 meters of till, probably related to the higher amount of organic matter and other reduced compound leached from the root zone. In the limestone REC is less than 1 mg O₂/g DW.

The nitrogen compounds, NO₃, NO₂, and NH₄, in the interstitial water reflects the intensive agricultural use of the area and the subsoils ability to reduce the nitrate, Fig. 3. Concentrations up to 30 mg N/l in the upper 5 meters of the profile indicate the leaching of nitrate from the root zone during the winter period. From 5 meters below surface and down to about 20 meters a steady decrease in nitrate is found. Below 20 meters the nitrate concentration is lower than 5 mg N/l, only increasing in the ground water to about 9 mg N/l.

At Skærsø station cation exchange capacity, CEC, reflects the lack of clay mineral and is therefore low, 2-8 meq/100 g DW, Fig. 4. In the part of the profile just below the clay layer the highest values are found. Reduction capacity, REC, is high in 1.5 meter, about 2.2 mg O₂/g DW, probably related to the higher amount of organic matter and some other reduced compounds leached from the root zone. All other analyses show values less than 1 mg O₂/g DW.

The nitrogen compounds, NO₃, NO₂, and NH₄, reflects the lack of agricultural use of the area and the low atmospheric input in relation to consumption of the vegetation, Fig. 3. Concentrations less than 1 mg N/l of all compounds are found in the profile. However, in 13-16 meters depth detectable amounts of NH₄, NO₂, and NO₃, indicate an event which has released a considerable part of the soil fixed nitrogen. It is believed that the storm cut in 1977 must be the release factor. Below 18 meters the nitrate concentration is less than 1 mg N/l, and does not increase in the ground water.

The cation exchange capacity, CEC, in the profile from Borsholm reflects the lack of clay minerals below 3 meters and is therefore low, 2-10 meq/100 g DW. In the gravel part of the profile the highest values are found. The exchangeable Ca, Mg, and K cover around 50 to 60% of the CEC in the profile. Most dominant below 3 meters depth is Ca, whereas above 3 meters some free capacity seems to be present.

Reduction capacity, REC, is low in the total profile, about 1-3 mg O₂/g DW. In the gravel layer very high values are found, up to 30 mg O₂/g DW, probably related to the higher amount of organic matter and some other reduced compounds deriving from the Jurassic slate.

The nitrogen compounds, NO₃, NO₂, and NH₄, reflects the lack of use of fertilisers on the area and the low atmospheric input in relation to consumption of the vegetation, Fig. 3. Concentrations less than 2 mg N/l of all compounds are found in the profile. However, in the upper 3 meters detectable amounts of NO₃ were present, 10 mg N/l.

Experiments

In the present subproject two types of experiments were carried out. The experiments aimed to give a preliminary knowledge about the anion reaction in the subsoils, and with special emphasize on nitrogen compounds. The first type of experiment was batch reactor test with soil samples in 500 ml bottles filled with 400 ml water of different chemical composition. The soil-water mixture was suspended by air flushing, either with atmospheric air or with high grade nitrogen gas.

The other type of experiment was percolation test with undisturbed columns kept in darkness at 10°C and without changing the natural water content, e.g. at field capacity level.

The difference between the two types of experiment should indicate the difference between non-transport limited and transport controlled reaction.

The batch experiments were set up in an order of different driving parameters, testing each element's share of the total reaction.

Three samples were selected for this purpose:

- Sample No. 12A, from Gudum, 7.25 meters b.s., silty clay
- Sample No. 124, from Skærsø, 18.25 meters b.s., fine sand
- Sample No. 224, from Borsholm, 16.25 meters b.s., gravel with Jurassic fragments.

Each sample was tested in batch reactors under oxic and anoxic conditions, with and without glucose addition and in the case of anoxic condition, with and without Fe^{++} addition, Fig. 4 and Table 1.

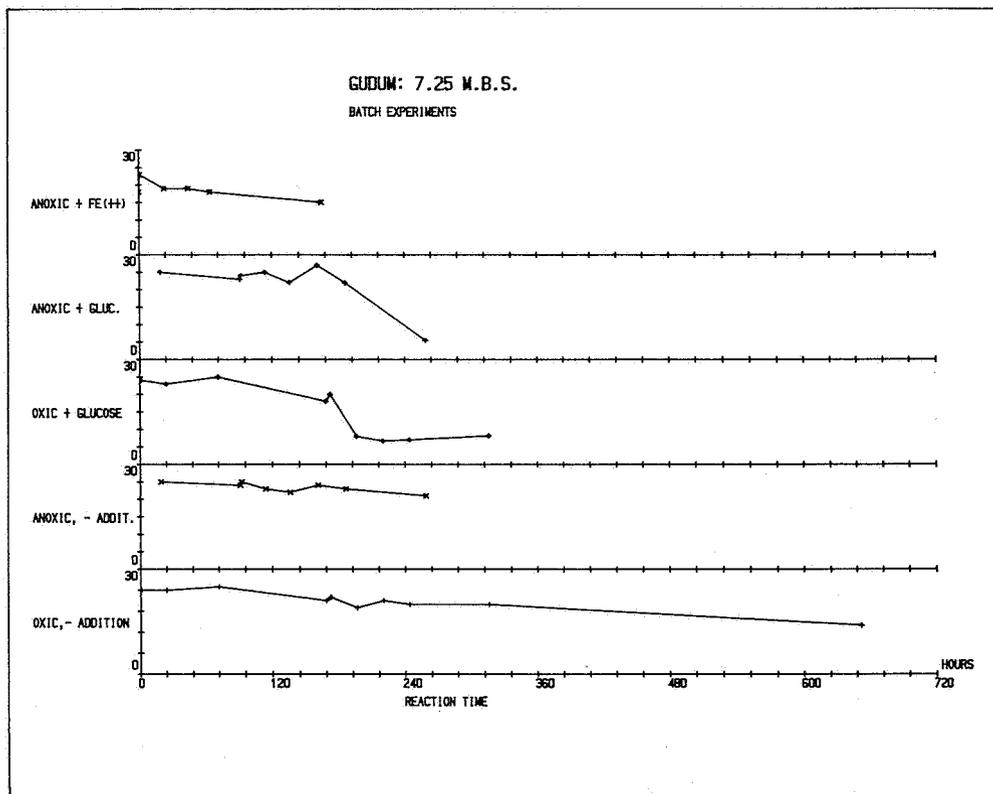


Fig. 4. Batch experiments with nitrate reduction. Nitrate in mg/l.

In spite of some uncertainty in the interpretation of the experimental results there are quite identical trends in the reduction rates depending on the external conditions.

In the experiments with high and low initial NO_3 concentration there is a linear relation between concentration and nitrate reduction rate.

Table 1. The estimated nitrate reduction rates in mg NO₃/l day.

Experimental conditions	Location and soil type		
	Gudum Silty clay	Skærsø fine sand	Borsholm gravel
OXIC:			
no addition	0.4	0.33	0.3
+ glucose	6.5	6.0	10
ANOXIC:			
no addition	0.4	3.3	2.7
+ glucose	5.3	7.3	20
+ Fe ⁺⁺	1.1	1.4	0.6
+ glucose & Fe ⁺⁺	10	11	10

volume: 400 ml, soil weight: 10 g DW

initial NO₃ concentration: 25 mg/l

temperature: 22°C.

Without addition of glucose nitrate reduces very slowly and mainly in the start of the experimental run. At high concentration (50 mg NO₃/l) less than 1 mg/l was reduced.

With addition of glucose the reduction of nitrate was found much higher. At high initial concentration 50-60 mg NO₃/l were reduced and at low concentration 9-10 mg/l.

Measurements from percolation experiments gave information of transport limited reactions in the unsaturated soil. The main process besides the chemical reaction includes advective transport on the mineral surfaces and diffusion of molecules in dead end pores, e.g. immobile water. As diffusion is a slow process 10^{-5} - 10^{-6} cm²/sec, steady state conditions in the eluate may be obtained after quite a long time. However, by extrapolating the phosphate concentration curve it is possible to calculate the phosphate sorption capacity, PSC. This value is highly depending on the origin of the geological deposit. In the Gudum clay the

PSC is 10-20 mg P/g DW, whereas in the Skærsø sand PSC is less than 0.01 mg P/g DW.

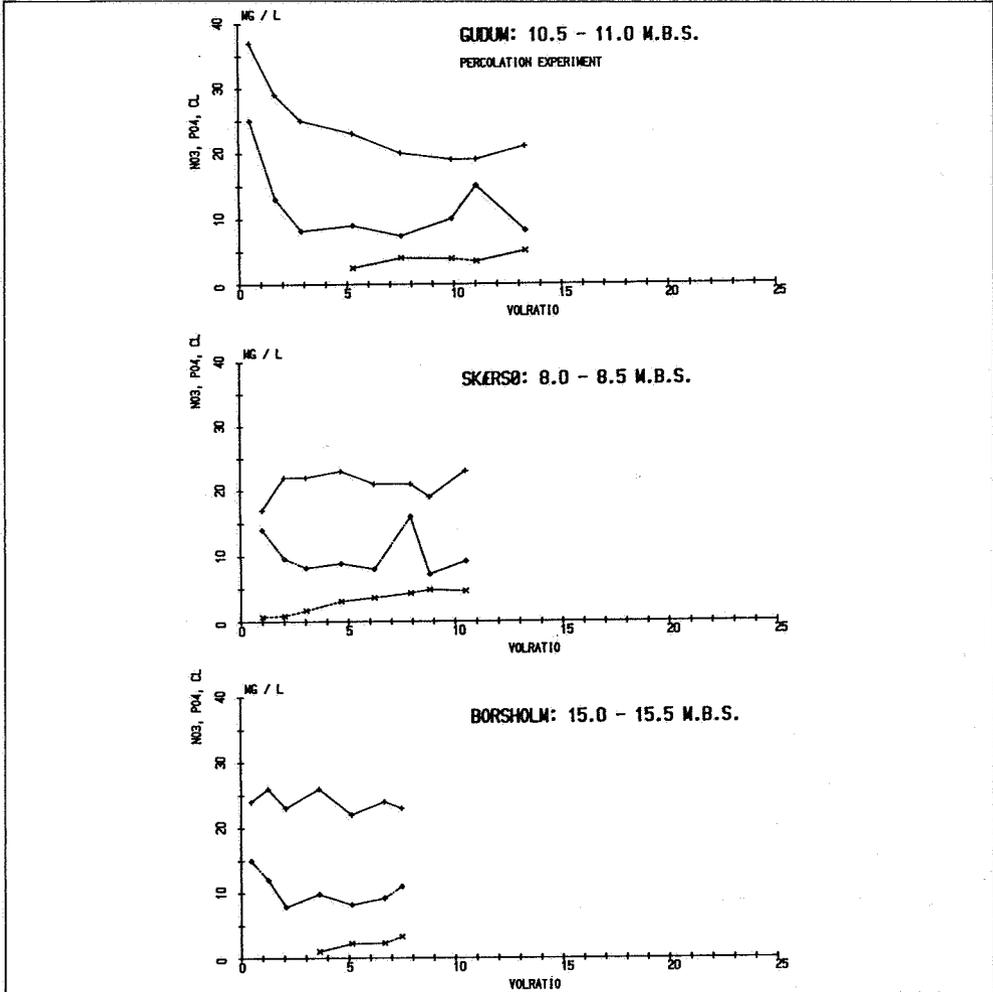


Fig. 5. Percolation experiments. Inlet concentration +: NO₃: 25 mg/l, x: PO₄: 10 mg/l, <: Cl 20 mg/l.

Nitrate reduction, in present experiments without glucose addition, is generally low, near to the detection limit corresponding to 0.02 mg NO₃/l day, Fig. 5.

Sulphate reduction has not been observed during this investigation, and is not believed to occur in the oxic unsaturated zone.

FINAL REMARKS

The measurements from the three profiles have given a valuable information of the interstitial concentration of different cat- and anions. Anion concentrations are mostly depending on bio-geochemical reaction in the water-solids interface, and of the soil gas composition. Nitrate reduction by microorganisms occurs all through the profiles, only depending of available reductants, as Fe^{++} or organic matter. This is supported by soil gas analyses, showing amount of N_2O in all samples. Lind, 1986. Kristiansen, 1986, and Kölle & Schreeck, 1982, have shown that iron may play an important role in the saturated zone according to nitrate reduction, but in the unsaturated zone it has not yet been detected.

In depths greater than 2-3 meters no detectable phosphate (0.1 mg/l) was present, and free phosphate sorption capacity varies depending on the lithology.

All profiles showed that oxic conditions were present from top soil to ground water level. The soil gas analyses showed a composition quite similar to the atmosphere with small elevations of CH_4 , CO_2 , and N_2 , whereas O_2 never falls below 15%, Lind, 1986. In the deep root zone anoxic condition may occur temporarily.

The batch experiments have very clearly shown that a basic nitrate reduction capacity is present in all depths independent of lithology. However, an increase in nitrate reduction activity of 10-20 times by addition of easy accessible organic matter, e.g. glucose, shows that a very high potential biological reduction capacity is present in all investigated samples.

Addition of reduced iron, Fe^{++} , seems not implicit to increase the reduction capacity. Anoxic condition may in some samples elevate the reduction activity, but not unambiguously. In case of presence of both Fe^{++} and easily decomposable organic matter, e.g. glucose, very high nitrate reduction rates are obtained.

Phosphate may generally be sorbed by Fe^{+++} containing and clay minerals. Some samples showed that the capacity may be used by an extended load.

Investigation by Lind, 1976 a & b, indicated that chemical reduction of nitrate may be the major mechanism to remove nitrate from soil solution, but present investigation has shown the presence of micro-organisms responsible for denitrification. However, organic sources must be present.

Consequently, future study might treat the subsoil microbiology for a quantification of the forcing parameters for biological and abiotic reaction systems.

A more intensive study of unsaturated flow may be of value to predict the unsaturated zone's ability to protect the ground water against excessive amount of nutrients.

By dividing the reaction system in the unsaturated zone in simple sub-models it will be possible to evolve large scale models for planning the land-use effects on ground water quality.

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THE VULNERABILITY OF THE QUALITY OF THE SOIL AND GROUNDWATER TO
CIVIL ENGINEERING ACTIVITIES

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ABSTRACT

It is well known that the use of chemicals is an important item of an environmental impact assessment. However, also civil engineering works such as roads, dykes, bridges, canals etc. can have a major impact on the quality of soils and groundwater. This is especially the case where there are large multiple demands and constraints on limited land areas such as is commonly the case in Western Europe, Coastal Asia and areas of the United States.

The nature of the environmental impact of civil engineering activities can be classified into four divisions:

- a. Aspects of changing the groundwater flow regime;
- b. Damage to the natural barriers in the soil;
- c. Pollution dispersion by civil engineering structures;
- d. The infrastructure itself as a threat to groundwater quality.

In relation to the vulnerability mapping of soil and groundwater it is of great importance to evaluate past and future civil engineering activities as one of the items which influences the environment.

1. INTRODUCTION

Conventional environmental theory recognizes the multifunctional nature of the ground and groundwater system and that these demands are more often competitive than complimentary. This is especially the case in urban centers of high population density and industrial activity such as commonly occur on the delta plains of large rivers. Rijnmond in the Netherlands, Bangkok, New Orleans, and Calcutta are but some of the more well documented examples.

As a result of the combination of high water tables, weak soils and intense usage one of the characteristics of these zones is the difficulty associated with even the simplest civil engineering activity. The difficulties are usually overcome by allowing the construction to interact with large and often deep volumes of the soil such as in deep piling, excavated roads, deep drainage etc. These activities can change the natural characteristics of the soil and consequently have a correspondingly major impact on the environmental parameters of the soils.

A further complication in assessing the overall environmental impact of the constructional activity on the soil is that there are often significant pockets of pollution already present from past discharges. These can be displaced, mobilized and otherwise dispersed to cause problems in hitherto clean soils.

In what follows, an overview will be given of four main problem areas encountered by the designer. These are changes in the groundwater flow regimes, changes in the value of natural barriers in the soil, mobilization of pollutants and creation of new potential point sources.

2. ENVIRONMENTAL IMPACT OF CIVIL ENGINEERING ACTIVITIES

A number of aspects of civil engineering activities is dealt with in the following paragraphs:

- a. Aspects of changing the groundwater flow regime;

of brackish water more or less throughout a fresh water polder if no countermeasures were taken.

The second groundwater zoning of interest is one of high or low redox status. In Indonesia studies were made as to the effect of permanent drainage for a petrochemical complex. It was shown that the measures would cause a shift in the redox fronts in such a way that significant acidification of the soil profile would occur resulting in major corrosion problems in the facility footings.

In both the above cases computer simulations of the groundwater movement and quality lead to alternative proposals where the unacceptable problems were avoided.

2.2 Damage to the natural barriers in the soil

Delta areas are of sedimentary origin and highly layered in soil structure. Clay and peat layers, often at depth, form a barrier (although imperfect) to the transport of contaminants from polluted upper soil strata to deeper and unpolluted ones which can be a major aquifer in the area.

Civil engineering measures such as piling and deep vertical drainage can seriously damage these layers and make connecting pathways between strata. Furthermore this damage occurs at the most sensitive places, i.e. underneath factories, storage areas and roads. This is illustrated in figure 2.

Some combinations of civil techniques and land use are especially dangerous. Well known examples are piles with broad footings, vertical drains or band drains connecting tank parks with the deeper ground layers, deep cuttings backfilled with permeable sands etc. In these cases the engineering design criteria are exactly contrary to those arising from environmental risk analysis considerations.

- b. Damage to the natural barriers in the soil;
- c. Pollution dispersion by civil engineering structures;
- d. The infrastructure itself as a threat to groundwater quality.

2.1 Aspects of changing the groundwater flow regime

Notwithstanding its often marginal quality, the groundwater in these regions is heavily exploited for industrial, agricultural and even consumptional purposes. Any activity that threaten further this quality will have very significant impacts on its use.

On the other hand, construction usually demands at least temporary, and more often than not permanent changes in the groundwater levels and thus flow directions and velocities. This leads to significant displacements in the boundaries between regions of low and better quality groundwater. Examples are illustrated in figure 1.

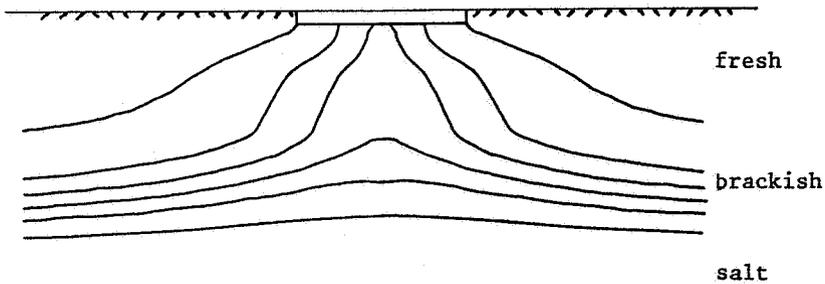


Figure 1. Upconing of brackish water as a consequence of dewatering a roadcutting

- Firstly, the proximity of the sea is invariably associated with system of salt water - fresh water interfaces.

In the Netherlands it has been shown that the continuous dewatering of a proposed roadcutting would lead to the dispersion

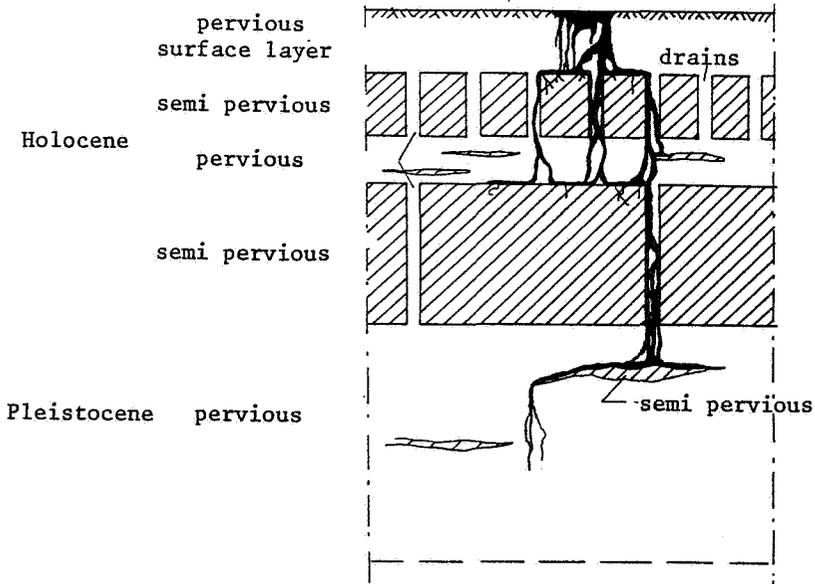


Figure 2. Consequences of deep vertical drains to the transport of contaminants more dense than groundwater

A particularly interesting case was one where vertical sand drains were installed under a tank mound inside the bunt wall, to control and accelerate its settlement. These drains were taken down to the deep aquifer to maximalize their effect. The tank was subsequently filled with a toxic organic liquid, more dense than groundwater. If this tank should leak, then hundreds of tons of toxic liquid will be dumped into the bottom of a deep and valuable aquifer where the chances of effective recovery are small.

2.3 Pollution dispersion by civil engineering structures

The highly industrialized delta areas under consideration have a long history of leaks and other discharges into the ground, not all of which

have been properly charted and evaluated. Counter measures, usually involving groundwater manipulation have been started locally at several sites.

Changes either in the background geohydrology or, as mentioned above, in the configuration of natural barriers in the soil can lead to a wider dispersion of the pollutant. This is illustrated in fig. 3.

- Of particular concern are changes in the gradient of the water table upon which hydrocarbon layers are floating. Two effects can be identified:

- Firstly the hydrocarbons follow a falling water table, but not completely, roughly between 10 and 20% of the oil is left. This oil then becomes immobile and is not flushed as the water table rises again.

However, it continues to leach into the groundwater thereby degrading it.

- Secondly the hydrocarbons can flow along the sloping groundwater table away from its original source usually in the direction of the drains and pumps where serious explosion risks will be created. In any case the area over which leaching down into the groundwater can occur will be significantly increased.

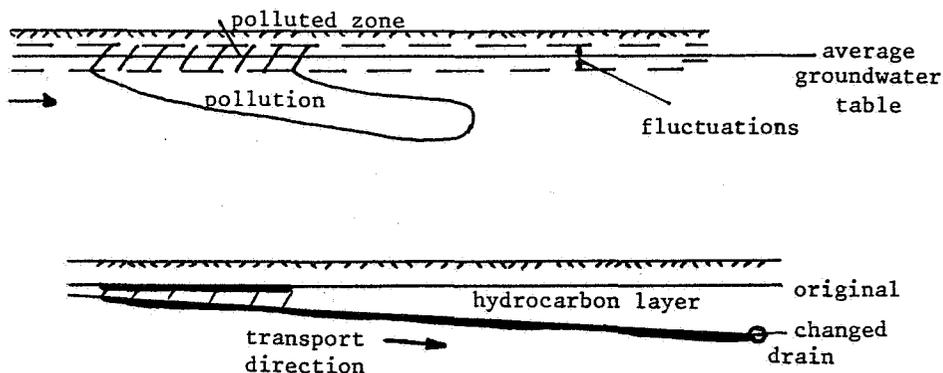


Figure 3. Wide dispersion of pollutants due to the change in background geohydrology

Land reclamation near the coast where the groundwater is saline, leads to fresh water lenses being formed. This water can then be seriously polluted by the activity on the reclaimed land. Fortunately the salt-fresh interface can act as a barrier to the convective transport of pollutant to the clean salt groundwater. However, measures such as dewatering and reinfiltration as part of the building program can seriously disturb this situation and lead to widespread pollution problems.

2.4 The infrastructure itself as a threat to groundwater quality

This threat can take two forms.

Firstly the materials used in the construction can give an emission of environmentally undesirable substances. This is an especially pertinent problem in areas where natural bulk construction material is scarce and bulk wastes are used in stead. Examples include blastfurnace slag, phosphoric acid gypsum and fly ash from both domestic waste incinerators and coal fired power stations illustrated in figure 4.

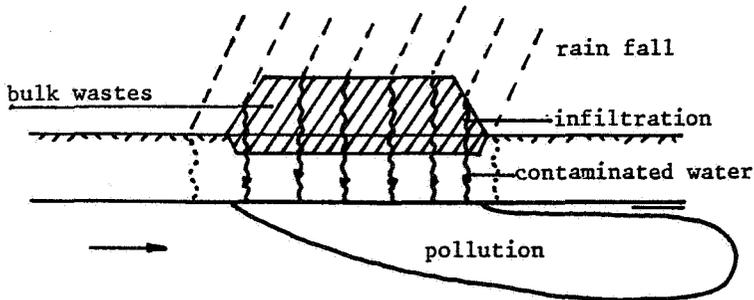


Figure 4. Consequences of the infrastructure to groundwater quality

Secondly the use of the construction and the construction program itself usually involves the transport or presence of hazardous substances. These can be released into the soil and cause an additional hazard. In the extreme this can lead to changes in land (mis)use that can no longer be properly supervised by the relevant authorities.

3. CONCLUSIONS

The intense and continuing use of the scarce land resources in the highly built-up and industrialized deltas will lead to a deterioration of the environmental quality of the ground and associated groundwater system. In that sense they are vulnerable. Because of the large impact of civil engineering construction methods on the system, this vulnerability will increase rather than remain constant or even decrease in time.

Commonly both the natural characteristics of the soil and the use of chemicals are the main items of an environmental impact assessment. As civil engineering activities can change these natural characteristics of a soil which is mostly already polluted to some extent, relating factors have to be taken into account in defining soil vulnerability criteria for economically key areas.

MOTION OF POLLUTANTS IN THE GROUNDWATER AS FACTOR OF
THEIR VULNERABILITY

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ABSTRACT

In the conditions of the flow in the porous environment with a frequent groundwater level pulsing the variability factor of the groundwater flow presents itself as a very significant, yet scarcely accepted vulnerability factor.

INTRODUCTION

It appears, that vulnerability of groundwater from the point of view of their utilization as drinking water is determined not only by vertical penetrating of pollutants through soil cover but also by their diluting or cumulating in water-bearing layer. By another words, territory vulnerable from the point of view of intensity and speed of pollutant penetrating on the level of groundwater ought not to be in reality declared to be threaten one, if there can be calculated with intensive pollutant dilution within it. the same is valid also vice versa. Cumulating, respectively eliminating of pollutant contents within the frame of water-bearing layer depend mainly on conditions of groundwater flowing.

The following example will demonstrate the influence effected by the permanently changing direction of the groundwater flow upon the reduction or possibly complete discontinuation of the contaminating activity. At the same time it will be shown how to define this factor also within the scope of a large area.

MECHANISM OF THE CONTAMINATION ELIMINATION

The importance of the groundwater flow variability factor for the contamination elimination is shown in fig. 1. When the direction of the groundwater flow does not change significantly (Fig. 1 a) a concentric symmetric conic cloud formation occurs, i.e. traces of the groundwater contamination can be observed. As soon as the change of the groundwater flow direction take place (Fig. 1 b) the processes of dispersion start to present themselves at the both poles of the shifting trajectory vector. On its frontal side the concentration of the pollutant just being dispersed is gradually established. In other words the fast enough change in the flow direction will secure that the dispersion practically does not take up the form as it would be originally expected (Fig. 1 a). Nevertheless at the trajectory backside, on the other hand, higher rate of the pollutant dispersion can be noted. Supply of the "fresh" - not contaminated water into this area affects upon their further dilution. Thus once the change in the flow direction takes place the cloud of the contaminated waters gets over into a relatively "clean" zone. This kind of over-washing prevents the accumulation of pollutants in the water-bearing horizon. The more frequent flow changes and higher the rate of the flow the more positive will be the effects of the variability factor upon the contamination elimination.

MATHEMATICAL FORMULATION OF THE PROBLEM

The used solution is derived from the groundwater flow direction specification based on the interpolation of the groundwater level values obtained through measurements in the observation points. The observation period took 7 days. In calculation as such it was proceeded from the assumption that the trajectory of the particle in this time limit according to the Law of Darcy can be approximated. The flow direction was determined by the first-order derivatives of the interpolation function (1) along the "x" axis and by relations (2) and (3) along the "y" axis. The groundwater level gradient was

expressed by relation (4). For the calculation of the derivatives there was used an auxiliary square element. In its vertexes the groundwater levels were expressed by the aforesaid interpolation.

$$H_{x,y} = \frac{\sum_{i=1}^n h_i \cdot q_i}{\sum_{i=1}^n q_i} \quad (1) \quad ; \quad H_x = \frac{H_1 + H_4 - H_2 - H_3}{4 \cdot a} \quad (2)$$

$$H_y = \frac{H_1 + H_2 - H_3 - H_4}{4 \cdot a} \quad (3) \quad ; \quad I = \left(H_x^2 + H_y^2 \right)^{\frac{1}{2}} \quad (4)$$

where : $H_{x,y}$ is the interpolated groundwater level of the point examined with x,y coordinates

H_x, H_y is the 1st derivatives of changes in hydraulic gradient

h_i, q_i groundwater level measured at the i -observation centre with coordinates x_i, y_i ; coefficient of distance

I gradient of groundwater level

a half length of side of auxiliary square element

H_1, H_2, H_3, H_4 interpolated groundwater level of the point examined with coordinates :

$$H_1(x-a, y-a), H_2(x+a, y-a), H_3(x+a, y+a), H_4(x-a, y+a)$$

In optional points of the studied environment the variability of the groundwater flow was evaluated by means of distance dispersion of the points, two vectors following one another. Isolines of the dispersion of this value calculated for one complete hydrologic period are then defined within the whole studied area by zones which are characteristic by their variability of the groundwater flow.

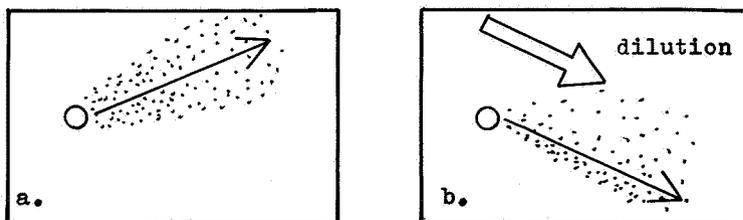
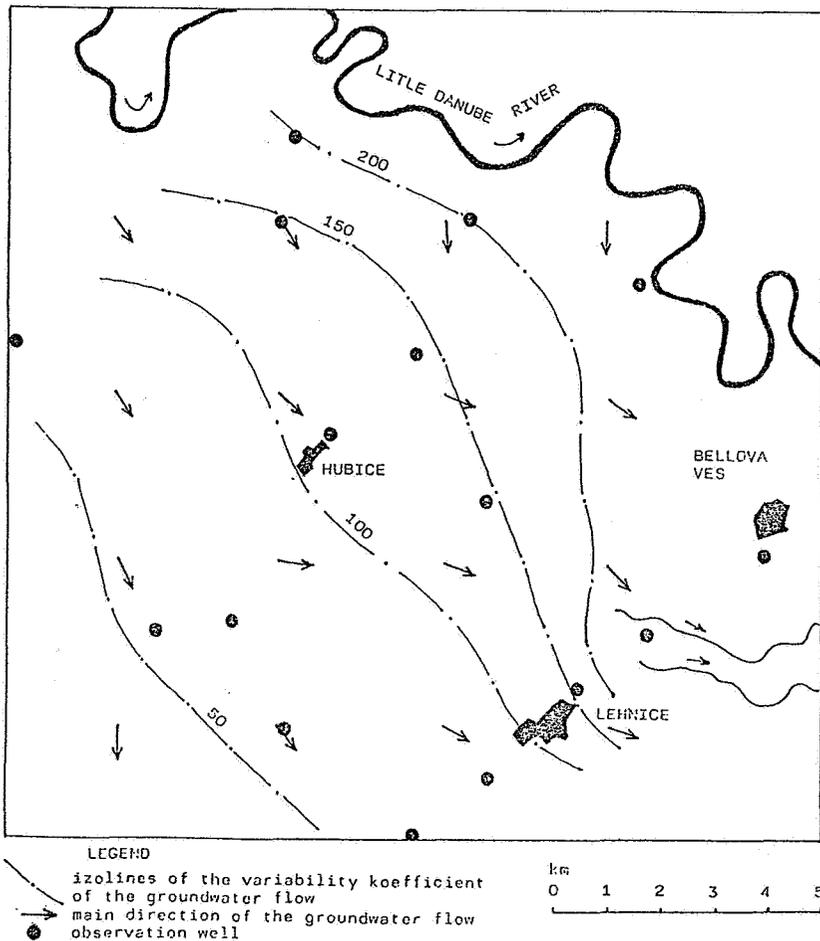


Figure 1. Dilution of the contaminant plume by groundwater flow change

EVALUATION RESULTS

The evaluation of the groundwater flow variability was carried out under conditions of vast alluviums of the Danube river which stretch over the southeast of the town Bratislava. The geographic unit (approx. 1 600 km²) formed by these alluviums is called "Žitný ostrov". The depth of the sandy gravel deposits ranges from 8-10 to 250-300m. In the observed part of the territory there is an important source of groundwater pollution, i.e. a black cattle - farm (not far from the Hubice village). In the groundwater flow direction in approx. 7 km distance there is a big water resource (Lehnice village). In spite of the fact that this resource has been functioning already

Figure 2. Zoning of the groundwater flow variability



for some years, quality of its waters has not been yet attacked. It is worth while mentioning that the pollution from the farm has not been noted even in the observing sites located approx. 0,5 - 1 km in the groundwater flow direction from this pollution source (table 1).

Table 1. Changes of the pollutants concentration in the groundwater

pollutant	concentration (mg.l ⁻¹)	
	source pollution	700 m off
K	45,9	2,8
NH ₄	6,0	0,05
SO ₄	82,3	34,2
NO ₃	220,1	22,5

Besides the values of filtration coefficient and values of effective porosity also the data on water-table fluctuation from 16 observing within the period from 1981 - 1985 were used as basic input data. By means of the mentioned mathematical procedure the isolines of the coefficient of the distance variation of the one-week groundwater flow trajectories end points were specified in the given part of the territory (Fig. 2).

The pollution source is located in the area with relatively high groundwater flow dispersion, a fact which partially explains the ascertained pollutants degradation. It can be said that the existence of this high variability is caused by the infiltration of waters from the river Small Danube as well as by natural outflows between the localities Dunajská Streda and Bellova Ves.

From the point of view of the groundwater vulnerability it can be presumed that in the area characterized by an even higher flow variability values even more intensive processes of pollutants degradation can be considered. Vice versa it will be necessary to pay more attention to an area with lower flow variability from the point of view of the possible pollution impact.

HYDROCHEMICAL DEFORMATION AT DIFFERENT OCCURRENCES
AND ENDANGERING OF GROUNDWATER IN LOWER SILESIA,
SW POLAND

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ABSTRACT

The water resources of Lower Silesia are sufficient for the necessities of this region. The groundwater is the most important part of the water supply (2 mln m³/day). About 80 % of the groundwaters occur up to the depth of 100 m. These reservoirs are susceptible to pollutions. In this paper the authors give examples in which the degree of contamination can be termed as the deformation of primary chemical composition of water. In the mountainous part of the Sudetes, increased concentrations of SO₄, HCO₃ and Ca are observed, as well as lowered pH values (4-5.5). In agricultural and rural areas the most common pollutants are NO₃, NO₂, K, Hg, Cu and pesticides. Catastrophic degenerations occur around towns and industrial centres where the TDS values and sulphate contents increase several times and contaminations with phenol, detergents, Pb, and Cd are noted. A very burdensome source of pollution are degraded waters of the rivers. The authors present their own proposal concerning the strategic activities on the nation-wide scale, which are indispensable to prevent natural, unpolluted groundwaters for the future generations. In Lower Silesia it is necessary to proceed immediately with liquidation of polluting sources in areas rich in groundwater. In the current economic conditions, there is no possibilities to extinguish all the sources of pollution and to protect actively all groundwater reservoirs. It is postulated to create protected zones of potable water in the areas of main reservoirs, which cover 25 % of the whole area of Lower Silesia. Within these zones, "factories" of clear water and water

preserves could be formed, all this for the water which is indispensable for living.

1. INTRODUCTION

Groundwaters are the main source of the water supply in SW Poland. In the most area shown on the map (Figure 1) the groundwater resources were sufficient for the water intakes. The process of groundwater pollution has been increasing considerably for many years. In many cases the contamination is so intense that it can be referred to as a deformation of the primary chemical composition of the groundwater. Frequently, the utilization of water is impossible due to its high degree of transformation. That is why the identification of the contamination processes is of great importance in practise. The recognition of the origin and course of the changes in water quality will make possible their spatial localization (mapping). This will allow to decide where the degrading processes must be stopped and the groundwater should be protected, and where the protection might be gives up and the water supplying source changed. The problem of recognition of hydrochemical deformations, discussed in this paper, is the first research stage which will be followed by hydrochemical mapping for various purposes: water protection and management, and land use planning. Such hydrogeological studies should afford new proposals, and solutions for the water management in the area. The important point of this management must be the active protection of groundwater resources.

2. REGIONAL CHARACTERISTICS OF GROUNDWATER RESOURCES

The area of SW Poland shown in Figure 1 (about 27 000 km²) is a natural geographic region (Lower Silesia). The flat Silesian Lowland and undulated foreland are abutted on to the mountainous terrain of the Sudetes. The Sudetes are composed of several crystalline massifs separated by intramountainous basins filled up with sedimentary rocks. A part of the crystalline area is located within the foreland and it forms a lowered

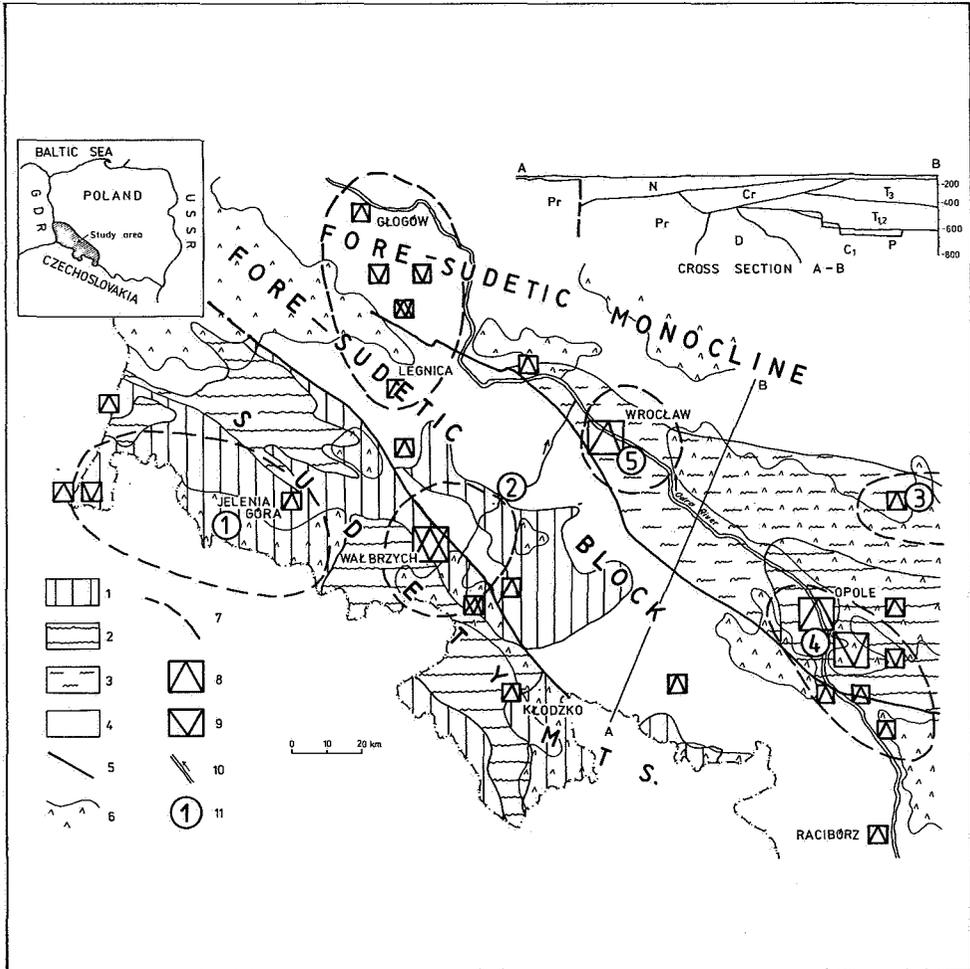


Figure 1. Sketch map showing groundwater reservoirs in SW Poland and their endangering. Main types of aquifers: 1 - aquifers in fractured rocks of crystalline massifs, 2 - sedimentary intramontainous basins, 3 - water bearing structures of the Fore-Sudetic monocline isolated from the surface by Cenozoic deposits, 4 - water bearing horizons in unconsolidated limnic and glacial deposits, 5 - main tectonic boundaries of hydrogeologic units. Endangering of groundwaters: 6 - forest, 7 - areas of ecological endangering, 8 - main areas of urbanization endangering, 9 - areas of mining endangering, 10 - polluted river, 11 - example of deformations in groundwater (Figure 2 - 6)

block covered with unconsolidated Cenozoic deposits. To the north, the Fore-Sudetic block abuts on to the monocline which consist of Carboniferous, Permian and Triassic rock series (Figure 1). Five main aquifer types have been distinguished in SW Poland:

1. fissure-water reservoirs in crystalline rocks mantled with water bearing weathering waste in the mountain area,
2. groundwater aquifers in the sedimentary basins of the intramountainous depressions,
3. fissure-porous aquifers in a deep part of the Permian-Mesozoic Fore-Sudetic monocline,
4. fissure-karst aquifers of the Opole part of the monocline,
5. porous-water bearing aquifers in Cenozoic deposits, especially in Quaternary buried valleys.

The most productive water reservoirs are found in the fourth and fifth groups of the aquifers. In spite of their smaller capacities, the other types are very important for the urban and rural water supply.

3. SOURCES OF POLLUTION

In SW Poland the sources of groundwater pollution are strongly diversified as far as their types, range of action and concentration of pollutants are concerned. Regarding the problem of water protection on a regional scale, the main criterion of the classification of pollution sources are the spatial type of contamination focus and the range of its influence. Among the regional types of the sources one can distinguish between those of industrial and the others of agricultural provenance. The differentiated influence of both the types depends not only on the distance from a focus of emission but also on many complex factors, particularly on the vulnerability of water-bearing structures to contaminations. Polluting processes modify the original hydrochemical background, which is understood as a characteristic range of contents of determined constituents. When these regional factors are put with local contaminations connected with rivers, transportation, urbanization, rural settlements and mining constructions (Figure 1), then we obtain a complex mosaic of hydrochemical zones. All these anthropogenic agents are imposed

on migration of natural (geogenic) hydrochemical fronts which sometimes are induced by changes in water circulation caused by human activities. Regional-scale sources of pollution result from common occurrences of contaminating centres. The basic source of the air pollution in SW Poland are electric power-stations in which the amount of coal equal to 20 mln tons per year is burnt. The other regional factor of the atmospheric pollution are common hearths of individual buildings in an average quantity about $10/\text{km}^2$. Both the sources burn a huge amount of coal-over 700 tons/ km^2 every year. The second most important regional pollutants are fertilization and manuring, the latter particularly usual in small individual farms, as well as use of chemical means of plant protection. The Polish indices of fertilization reach the value of 180 kg NPK/hectare. Also the influence of urban and rural-settlement areas has become a regional-scale factor. Such terrains including roads, have an area equal to 10 % of the whole region.

4. EXAMPLES OF HYDROCHEMICAL DEFORMATIONS

Out of several tens of the study objects, the authors wish to present a few representative examples of hydrochemical deformation. The examples illustrate regional changes rather than local ones, because the liquidation of the formem will be more complex.

The first problem to be discussed is connected with transformation of composition of ultrafresh waters in the crystalline massifs under the influence of acid rain. The winds from SW and W carry huge amounts of SO_2 from the territories of Czechoslovakia, GDR, and other countries of Western Europe (Figure 2). These amounts are complemented by local industry, power engineering, and heat-generation plants. In 1985 the emission of SO_2 in most endangered voivodeship reached a value of 45 tons/ km^2 . The rains in the Western Sudetes often have the pH index equal to 3-4. Such rains totally devastate the Sudetic forest as well as chemically deform shallow groundwaters. In a few representative river basins, the authors ascertained an increase of groundwater mineralization, higher concentration of SO_4 , HCO_3 , NO_3 , Ca, Na, and changes in pH values. In the western part of the Karkonosze ridge the mean pH value of the groundwater is equal 5.2. The groundwaters in the highest sector of that ridge

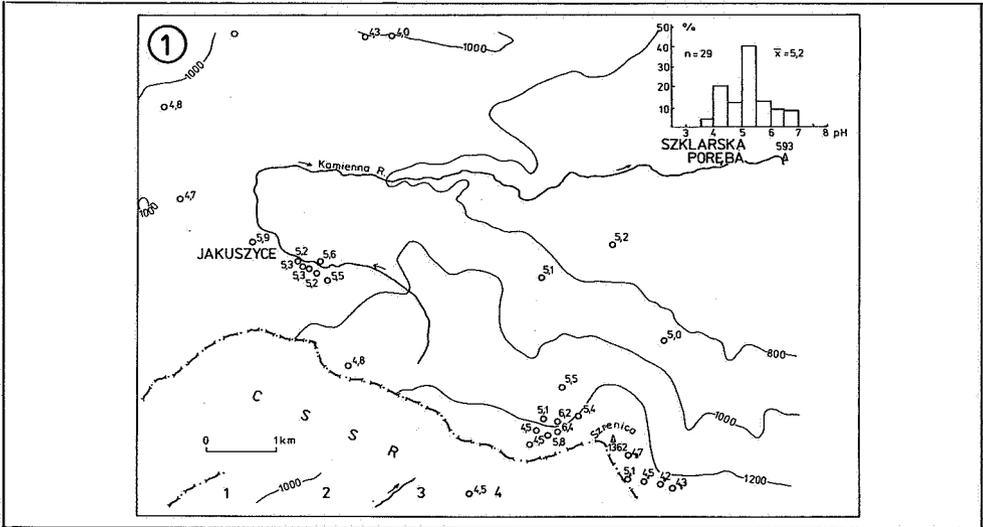


Figure 2. Hydrogen ion exponent (pH) values in groundwaters of the granitic massif of Karkonosze. 1 - state boundary, 2 - contours lines, 3 - main river, 4 - pH values at observation points.

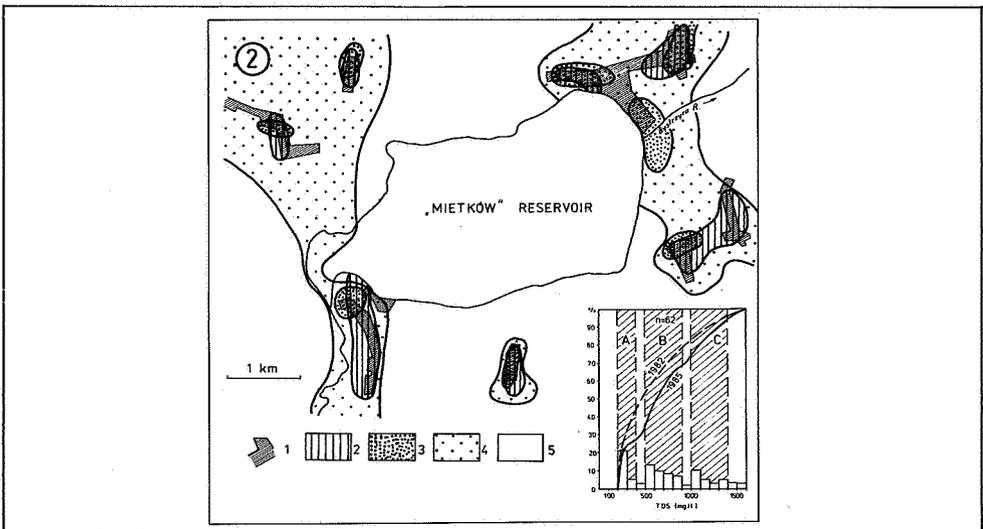


Figure 3. Groundwater pollution produced by agricultural activity and rural urbanization in the area of the storage reservoir of Mietków. 1 - rural urbanization areas, 2 - zones polluted with nitrates ($>10 \text{ mg NNO}_3/\text{l}$); zones of TDS values: 3 - >1000 , 4 - $500-1000$, 5 - $<500 \text{ mg/l}$. Histogram of TDS values for 1982 and cumulative curves for 1982 and 1985.

have this index near 4.0 (Figure 2). The water in such crystalline massifs generally are not isolated from the atmosphere and also easily join the deeply penetrating waters. This is a real endangering for the rich mineral water resources in the Sudetes.

An example of the area influenced by multifactoral groundwater pollution is the vicinity of the storage reservoir of Mietków (Figure 3). The shallow groundwaters, in the Cenozoic deposits, are affected by large-scale contaminations connected with industrial emissions into the atmosphere. The commonly observed concentrations of phenols up to 0.9 mg/l in these waters are indicators of this type of pollution. Agricultural activity in this area is also endangering for the groundwater. These regional polluting factors, occurring over the whole area, are imposed by mosaic zones associated with villages. The natural hydrochemical background of TDS is equal to 200-400 mg/l (Figure 3). Within the zones of rural urbanization the recent background of TDS ranges from 500 to 900 mg/l, while around individual farms it reaches a value of 1000-1400 mg/l. The process of water degradation in rural areas makes rapid progress as illustrated by the cumulative curve of TDS for the period 1982-1985 (Figure 3). This type of water pollution, in rural areas, despite of its limited extent, is a serious endangering for the groundwaters and makes difficulties in water supply for villages (90 % of farm use shallow wells). In the area of Mietków, 90 % of dug wells have undrinkable water. In 80 % of them the main pollutants are phenols (in 80 % of wells), TDS and Mn (50-60 %), Hg, pesticides, SO_4 , NO_3 , Zn and hardness (20-30 %) and finally Fe, Cd and Pb (in 10-20 % of wells).

Within urban areas the groundwater environment is strongly changed. A small industrial town in the eastern part of the study area is an illustrative example (Figure 4). Near the town, located in a flat alluvial valley, steel works dumps are disposed on the ground surface. The concentrations of main constituents in the water of the first, and most important, water-bearing horizon have increased many times since 1947. The natural background of TDS primarily ranged from 100 to 200 mg/l. Nowadays, the TDS values has reached 400-800 mg/l. This deformation of water composition is limited to the urban area and almost completely disappears in the forests surrounding the town. The high TDS values results mainly from higher contents of SO_4 , Cl, Ca and K. In villa districts, lacking

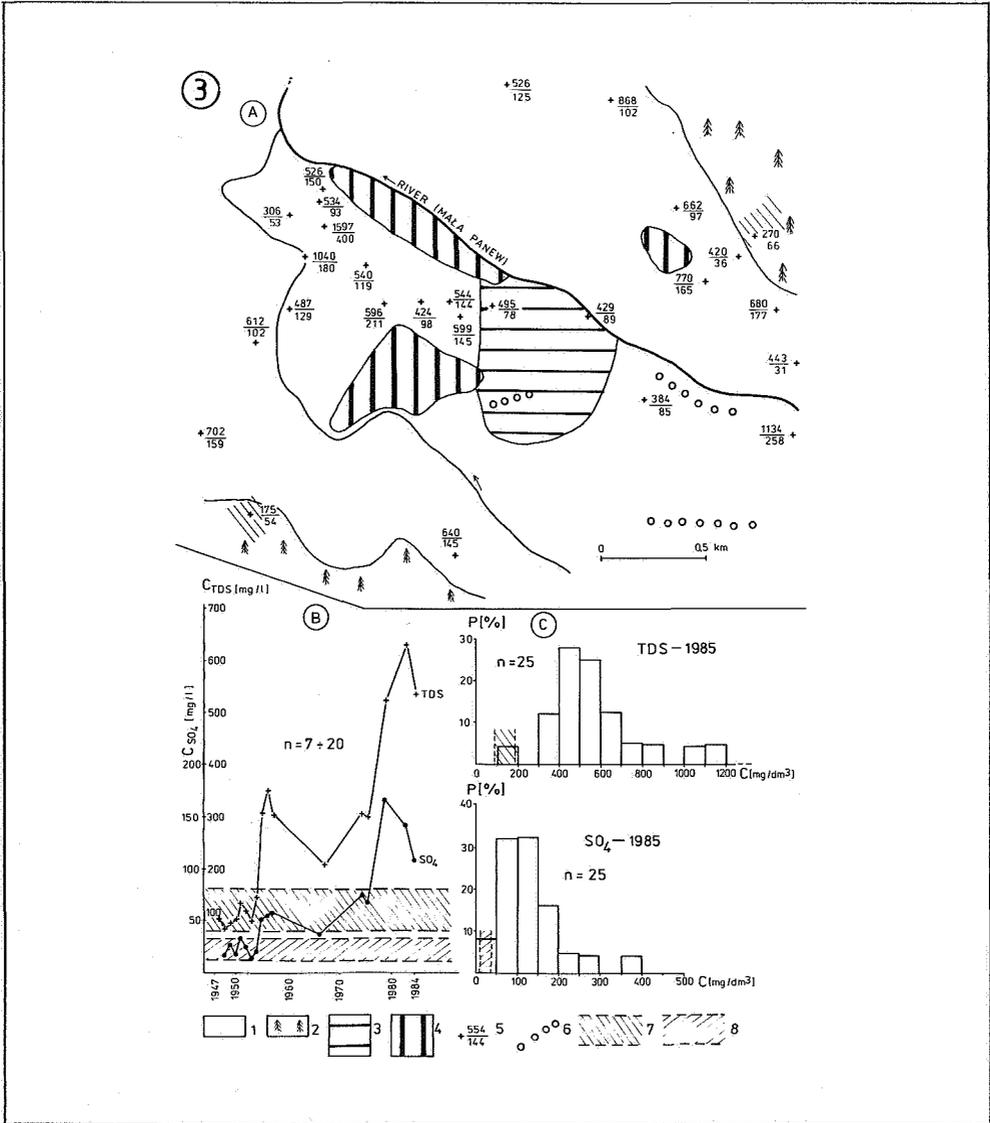
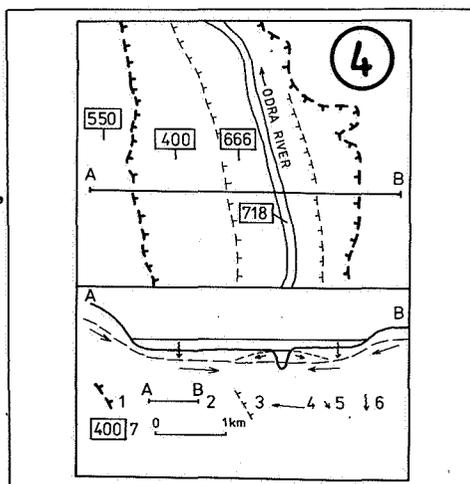


Figure 4. Example of hydrochemical deformations in industrial town-area. A. Sketch of main management elements. 1 - urbanized area, 2 - forests, 3 - industrial area, 4 - waste-product dumps, 5 - observation points (numerator = TDS, denominator = sulphates, in mg/l), 6 - water catchments, 7 - TDS values approximating natural values (mg/l), 8 - SO_4 concentrations approximating natural values (mg/l). B. Changes in TDS and SO_4 concentrations and their natural background in 1947-1984. C. Histograms of TDS and SO_4 for the recent pollution.

a sewage system, especially dangerous is the expansion of nitrogen compounds and stable detergents. A mosaic distribution of contaminations including phenol, Zn, Cr and Pb, is characteristic of such an industrial area. Nearly 50 % of this area have unpotable water containing high amounts of the above mentioned pollutants.

The Odra is the main river in SW Poland. It carries contaminations from the Ostrava coal basin, Upper Silesian industrial district, and from other town in Poland. This linear source of pollution influenced the quality of groundwaters in the valley (Figure 5). The contamination of groundwaters occurs predominantly due to inundation of the valley by flood waters. In spite of clearly draining character of the river, during the high water the pollutants from the river infiltrate the alluvium.

Figure 5. *Example of water pollution in the Odra river valley.*
 1 - valley edge, 2 - cross-section line, 3 - extent of strongly polluted water, 4 - main drainage directions of the river, 5 - high water infiltration of the river water into alluvium, 6 - infiltration of flood waters, 7 - TDS values (mg/l)



These zone of extremally polluted groundwaters in the Odra valley south of Opole, forms a belt, up to several hundred metres wide, at both sides of the river. The same type of pollution is observed along the whole 300 km long Lower Silesian sector of the Odra river and this disqualifies the valley, very rich in groundwater, as possible source of potable water. In a few thousands of places in SW Poland there is local endangering of quality of groundwaters which comes from industrial dumps, waste disposal

and other objects. In some places the pollution sources are situated very disadvantageously in relation to groundwater intakes. Figure 6 shows an example of the influence of a metallurgical plant, producing Fe-Cr alloy, on a nearby large infiltration water catchment. The Cr concentration in the porous water of the waste products equals 0.5-2.0 mg/l.

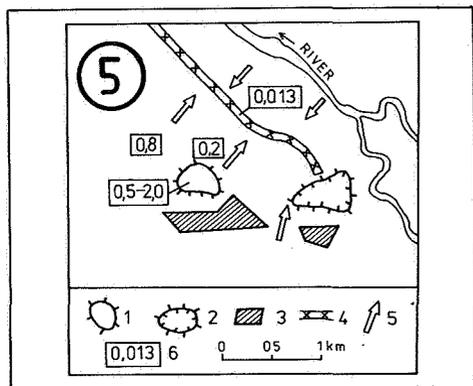


Figure 6. Example of local endangering of infiltration intakes by industrial plant. 1 - dumps of metalurgic plant, 2 - decanter, 3 - industrial areas, 4 - infiltration intake line, 5 - main directions of water runoff, 6 - Cr concentrations in mg/l

In the surrounding area the concentrations of that metal reach the following values: 0.8 mg/l - in shallow groundwater within the zone influenced by wind transport of pollutants, 0.2 mg/l - around the dump, and up to 0.013 mg/l at the water intake.

5. SUMMARY AND RESEARCH DIRECTION

Nowadays, the groundwater pollution is a very important industrial and social problem a barrier in the development of the region. The degradation of groundwater quality has followed the phenomena which led to an ecologic catastrophe in rivers and lakes. The deformations are multifactoral and of various range and this implies the observed spatial mosaic and time fluctuation in waters' chemical compositions. In the research program of the strategy of protection of main groundwater reservoirs, attempts are undertaken to determine the degree of water pollution over the whole area of Poland. The contamination of the first groundwater aquifer in Lower Silesia is general. These waters (up to depth of 20 m at villages and towns) in considerable part are inadequate when compared with the norms for the potable water. This type of pollution is particularly com-

mon in the areas characterized by low groundwater runoff ($0.5-1.5 \text{ l/skm}^2$). Outside the cities and rural urbanization, deformations of water quality are not so significant and have respect only to specific substances. The ultrafresh waters of the mountainous crystalline massifs are an exception. The natural TDS value of these waters usually is lower ($30-50 \text{ mg/l}$) than the mineralization of the acid rain ($30-80 \text{ mg/l}$). That is why these water display deformations in pH values and SO_4 contents. The deeper water-bearing horizons are contaminated only locally. The pollutants are phenol, nitrates, pesticides and other organic matter. Certain regionally polluted zones reach the depth of 300 m. This is the case of the fissure-karst reservoirs, in the areas of catchments with intense water drawing. The task of research groups is to estimate the depth of pollution penetration in main types of water bearing structures. This can be achieved by wide-scale chemical and isotopic sampling.

6. STRATEGY OF GROUNDWATER PROTECTION IN LOWER SILESIA

The liquidation, or at least alleviation, of the noxiousness of the sources of groundwater pollution, is a pressing task of the local administration. Certain attempts are being made using administrative regulations, to stop generation of new sources of pollution in the areas having rich groundwater resources. Big waste disposals are being controlled. Illegal disposal sites successively are being closed, as well as those sanitary emissions, which influence the groundwater quality (e.g. leaky individual septic tanks) are going into liquidation. The execution of these tasks requires more efficient, than so far activities of the local administration and pro-ecological changes in consciousness of the most part of the society.

The initiated mapping aims to define protected areas which will cover the main groundwater reservoirs. These terrains will include intake areas of the most important groundwater reservoirs and, supposedly, they will reach about 25 % of the whole region area. The authors suggest to create water supply system basins having regulations strongly limiting the management of the areas (all human activities should be subordinated to the water management). In the most valuable terrains, special "preserves

of clear water" (having the status of protected landscape areas) ought to be created. A practical aspect of all these measures is that the water exploitation will be concentrated and intensified within the areas which can be actively protected and affectively controled. The intensification of groundwater exploitation should be achieved by more extense making use of river runoff, artificial infiltration, and formation of barriers protecting from percolation of pollutants. In several places in SW Poland there are appropriate conditions for construction of "factories" producing natural, clear potable water from reservoirs of discharge ranging from 300 to 500 thousand m^3 /day. This could resolve the problem of water supply in large urban agglomerations. More difficult are the problems connected with the replacement of thousands of shallow farm wells by water pipe systems drawing clear water from behind the zones of pollution within a village.

AN OUTLINE OF A METHOD TO ASSESS THE
RISK CAUSED BY SOIL POLLUTING ACCIDENTS
TO DAMAGE DRINKING WATER PRODUCTION

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ABSTRACT

Each activity in the recharge area of a drinking water production site may lead to an accident and therefore to the presence of a certain range of pollutants in the soil and in the groundwater. The effect of a pollutant at the production site is defined as the ratio between the concentration in the groundwater and the concentration allowed in the drinking water. The probability of occurrence of the concentration in the groundwater is, amongst others, dependent on the probability of occurrence of the accident at the activity site. The risk of a pollutant to the production site is then expressed by the product of the effect and the probability of occurrence of the pollutant.

In this paper (an outline of) a calculation method is presented based upon manipulations with the relation between the effect and the probability of occurrence. The method can handle different types of activities in the recharge area each apart as well as all together. One of the results of the method, is a single valued risk parameter which provides comparison of the risks to the production site caused by different activities in the recharge area.

INTRODUCTION

The protection of a drinkingwater production site (using groundwater) in the Netherlands is mainly carried out by the Provincial Governments. At the moment the safety of the site is guaranteed by using a combination

of prohibition orders and dispensations. However, in the decision making concerning the allowability of activities (new or existing) in the protection area of the site, there is a need for a calculation method in which the risks caused by all types of activities (Figure 1) can be treated in an objective way (lit. 3).

DESCRIPTION OF THE METHOD

An activity in the intake area of a drinking water production site (using groundwater) may lead to an accident. Different types of activities may lead to different types of accidents (Figure 1). Also in general even one type of activity may lead to different (types of) accidents (compare chemical industries). Observe one pollutant coming from different types of accidents at a single activity. A certain magnitude (M) of this pollutant entering the groundwater can be related to a single probability (P) of occurrence. Different magnitudes occur with different probabilities and therefore a one to one P-M relation can be derived (Figure 2).

The magnitude of pollutant entering the groundwater will be used to calculate the maximum concentration of this pollutant in the groundwater. Division by the concentration allowed in drinking water "normalizes" this maximum concentration to a dimensionless parameter expressing the effect to the production site. Then a one to one relation is found between this effect (E) and its probability (P) of occurrence.

As mentioned before, the P-E relation can be derived from the P-M relation. For many cases this latter relation can be found in literature (1,2). In some cases research has to be carried out into this relation. So far, all cases mentioned are of the type of point-sources (drilling, gasoline tank, etc., Figure 1). In many cases the activities are of the type of line-sources (pipelines, Figure 1) or of area-sources (waste sites, Figure 1). Then the P-E relation is specified with respect to a unit length or unit area. In these cases we calculate the P-E relation in the situation in which at least one accident occurs in the relevant length (e.g. the length of a pipeline in the recharge area) of the

line-source, or in the relevant area of the area-source respectively. In this way any type of activity can be handled in the calculation method.

During the flow along the path between the activity (accident) site and the production site, the concentrations of pollutants will decrease as a result of retardation, degradation, etc. Also the extreme concentration levels will be lowered due to spreading out of the pollution by dispersion, diffusion, etc. These influences on the effect of the pollutants also occur with certain possibilities. Besides, due to chemical reactions, new pollutants may be developed in the flow path. In the method these new pollutants are thought to come from the accident itself. Again here the worst case situation must be considered. So processes decreasing the risk must be certain if taken into account. If processes increasing the risk are probable, then they must be taken into account.

In this way we are able to derive P-E relations near the production site of all pollutants (in)directly coming from the accident either by theoretical calculation (from simple analytical assessment to comprehensive numerical computations) or by measurement in situ. The schema of this part of the method is presented in Figure 3.

As shown in Figure 3 the different P-E relations calculated near the production site form the basis of decision making. In order to assess the risks due to combinations of different types of pollutant and/or of different activities some summation rules have to be developed.

We assume a certain concentration of pollutant (with a probability of occurrence) to come from an accident with the same probability of occurrence. Near the site of the accident this will be a rather good approximation. Because all processes in the flow path (Figure 3) are dependent on the presence of the pollutant, this assumption will also hold approximatively near the production site. So the occurrences of effects of all pollutants coming from one accident are dependent occurrences. The effect (dimensionless value) per pollutant can be seen as a "normalized effect" (made independent of the type of pollution). Then we may add the normalized effect values of all pollutants with the same probability of occurrence in order to derive the total effect

belonging to the accident with this probability of occurrence (Figure 4). In this way a new P-E relation can be calculated, in which E expresses the total effect on the production site of accidents at the production site.

A same kind of analysis as above leads to a summation rule of P-E curves over all activities (Figure 5). We assume independency of occurrence of accidents at different activities. Then the summation over different activities per pollutant is carried out per "normalized effect", so over the (independent) probabilities of occurrence.

Each P-E relation of Figure 6 gives an insight into the risks to the production site caused by (a combination of) pollutants coming from (a combination of) activities. The value of the risk to the production site caused by a single effect value (see Figure 2) and its probability of occurrence in any P-E relation can be defined by (lit. 5):

$$\text{Risk}(i) = \text{Effect}(i) * \text{Probability-of-occurrence}(i)$$

Then each P-E relation leads to a risk to the production site of which the value is defined by the summation (or integration) over all these single risk values:

$$\text{Risk to site} = \text{Sum} [\text{Risk}(i)]$$

and because

$$\text{Sum} [\text{Risk}(i)] = \text{Sum} [P(i) * E(i)] = E (= \text{average effect})$$

we have derived a parameter value of the risk to the production site expressed in this P-E relation. Taking into account the meaning of each P-E relation of Figure 6, single valued decision parameters can be calculated expressing

- the risk of one pollutant coming from one activity
- the risk of more pollutants coming from one activity and
- the risk of one pollutant coming from more activities.

The risk caused by more pollutants coming from more activities can be estimated by the maximum value of either the sum over all the results of summation over one activity or of the sum over all the results of summation over one pollutant.

CONCLUSIONS AND RECOMMENDATIONS

- A theoretical description is presented of a calculation method which results into single-valued decision parameters concerning the allowability of activities and/or pollutants in the recharge area of a drinking water production site.
- The most important decision parameters is the parameter expressing the risk of several pollutants coming from several activities. This parameter may also express the allowability of all pollutants coming from all activities to the production site. Therefore it may be seen as a decision parameter to the presence of the production site itself.
- The concentration of pollutant allowed in drinking water needs attention with respect to its use in this method.
- After calculation of decision parameters, in many cases a factor may be found expressing the minimum current safety of drinking water production sites.

ACKNOWLEDGEMENT

The author wishes to thank drs. J.W. Stellingwerff of the department of Public Works of the Province of South-Holland in The Hague for his cooperation during the initial state of the research.

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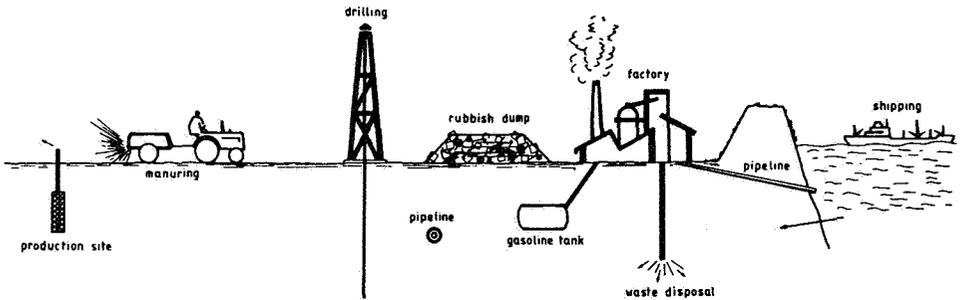


Figure 1 : Different types of activitier in the recharge area of a drinking water production site.

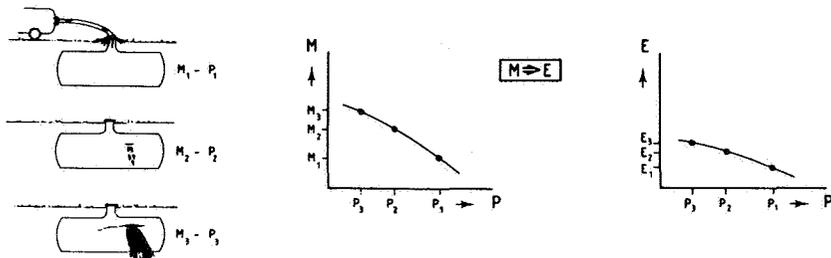


Figure 2 : Demination of P-M and P-E curves . (relation)

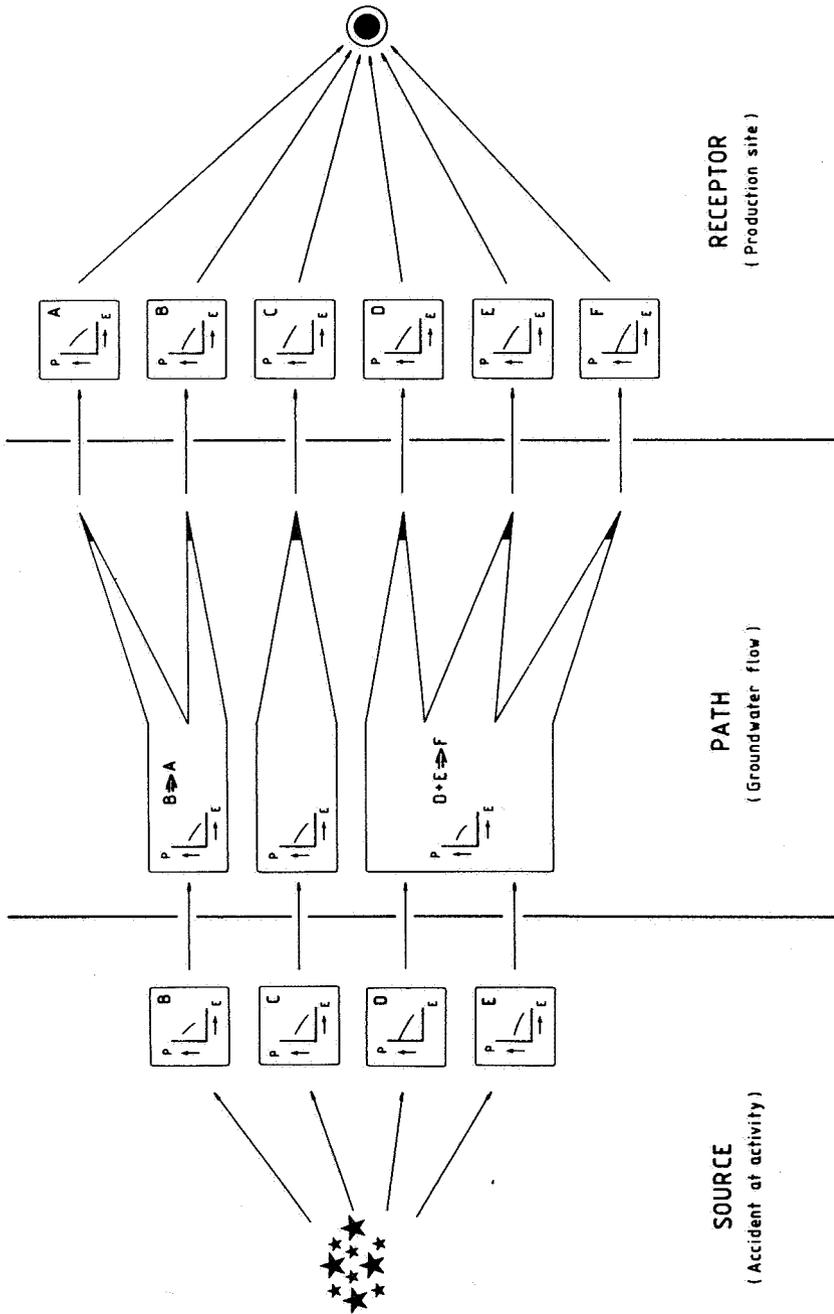


Figure 3 : Schema of P-E calculations.

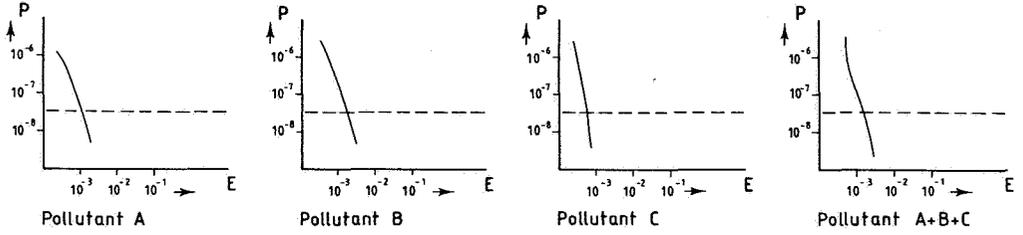


Figure 4 : Summation of P-E curves of pollutants coming from one activity.

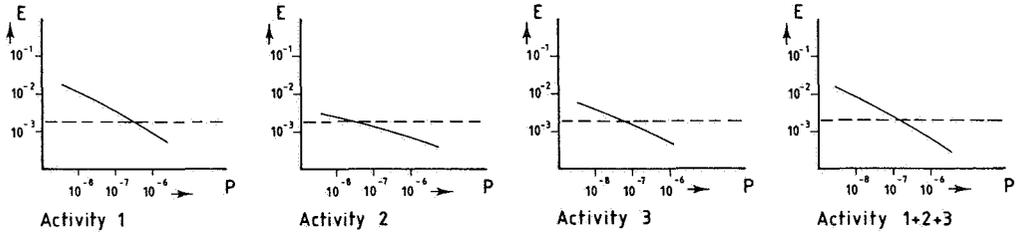


Figure 5 : Summation of P-E curves of one pollutant coming from different activities.

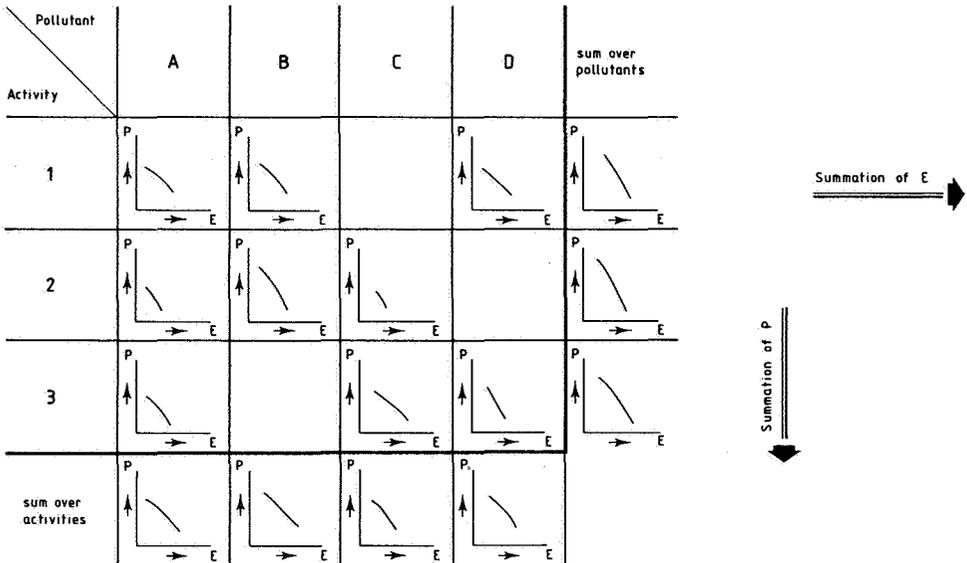


Figure 6 : Summation of P-E curves.

THE LIMITATIONS OF CLAY AND PEAT SOILS AS BARRIERS TO THE SPREAD
OF INORGANIC POLLUTANTS TO DEEPER AQUIFERS

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ABSTRACT

The efficiency of clay and peat layers in the unsaturated zone as barriers to point leakages of contaminants is considered. It is shown that these efficiencies can be estimated by simple calculation and that in many practical situations they will be considerably less than 100%.

1. INTRODUCTION

One of the characteristics of urban and industrialised environments is the large number of potential point sources of pollutants. Examples include factories, transport networks, sewers and many others quite apart from hazardous waste dumps. Naturally occurring soil barriers or artificially constructed ones, such as clay and peat layers are often relied upon in the unsaturated zone to prevent any leakage or leachate from reaching deeper aquifers. Both hydraulic and adsorption factors play a role but for leaking barriers and especially for heavy metals, the latter is the more important.

The case of a point source above an impermeable clay lens will be considered. Leakage will sustain a perched groundwater mound on the lens and the contaminants will move across it to the first discontinuity and down to the deeper aquifer, (see fig.1). As the pollutant convects along the lens, some will diffuse into the clay and be adsorbed there whilst the remainder will flow off at the discontinuity. The calculation of the pick-up efficiency and the water quality at the discontinuity are the objects of this study.

2. THEORETICAL

Consider the situation sketched in fig. 2. where a continuous leak (Q) of water has formed a mound of thickness (h) on a thick impermeable lens of length (L).

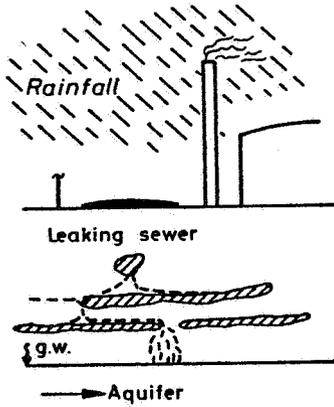


Fig.1

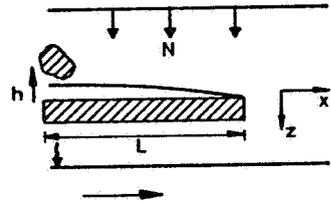


Fig.2

For $h \ll L$ then:-

$$h^2 = \frac{N}{K} (L^2 - x^2) + \frac{2Q}{K} (L - x) \dots\dots\dots \textcircled{1}$$

And the concentration in the water is: -

$$\frac{C}{C_0} = \operatorname{erfc} \left[\frac{x \sqrt{R_c D / v \bar{h} \theta_s} + (z - \bar{h}) \sqrt{R_c / D_c}}{2\sqrt{t - x R_s / \bar{v}}} \right] \dots\dots\dots \textcircled{2}$$

whereas in the clay lens it is: -

$$\frac{C}{C_0} = \operatorname{erfc} \left[\frac{x}{2\bar{h} \theta_s} \sqrt{\frac{D R_c}{(t - x R_s / \bar{v})}} \right] \dots\dots\dots \textcircled{3}$$

where (D) is the molecular diffusion coefficient of the contaminant in the clay, (\bar{v}) the mean actual velocity in the mound, (\bar{h}) the mean mound thickness and where (R_c) and (R_s) are the retardation adsorption factors in the clay and sand.

3. RESULTS AND DISCUSSION

In order to illustrate the usefulness of the above relationship calculations have been made for the simple scenario where a factory sewer is leaking water containing 1 ppm Cd^{2+} at a rate of $10 \text{ m}^3/\text{m}\cdot\text{year}$. The netto infiltration is 50 mm/year, the sand permeability 3150 m/year and the sand retardation factor is taken as 2.5.

The porewater concentration in the mound and in the lens are shown in table 1. for the case of $L=10\text{m}$, $t=10$ years and $R_c=1500$.

Table 1 Concentration profile - ppm Cd^{2+}

x-m	depth - m					
0.00	0.01	0.02	0.03	0.04	0.05	
0.00	1.000	0.507	0.184	0.046	0.008	0.001
1.00	0.919	0.444	0.152	0.036	0.006	0.001
2.00	0.839	0.385	0.125	0.028	0.004	0.000
3.00	0.761	0.332	0.102	0.021	0.003	0.000
4.00	0.684	0.283	0.082	0.016	0.002	0.000
5.00	0.611	0.240	0.065	0.012	0.002	0.000
6.00	0.541	0.201	0.052	0.009	0.001	0.000
7.00	0.476	0.167	0.041	0.007	0.001	0.000
8.00	0.415	0.138	0.031	0.005	0.000	0.000
9.00	0.358	0.112	0.024	0.003	0.000	0.000
10.00	0.307	0.091	0.018	0.002	0.000	0.000

As can be seen the actual penetration depth of the contaminant front in the clay is quite small and in the order of 20 mm. This penetration depth increases as the adsorption factors diminish but for the case considered here the assumption that the clay lens is infinitely thick is justified. The development of the cadmium concentration at the end of the lens is shown in fig. 3. for the first 100 years and this behaviour of fast breakthrough and long tailing is characteristic of these systems.

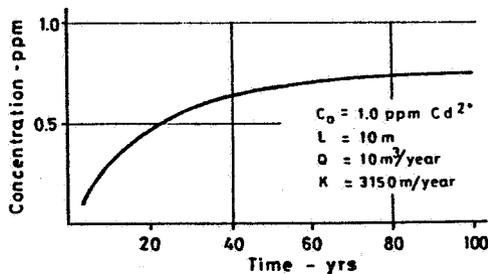


Fig. 3 Break through curve

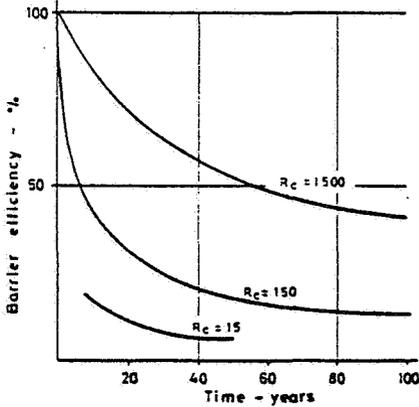


Fig. 4 Efficiency vs Time

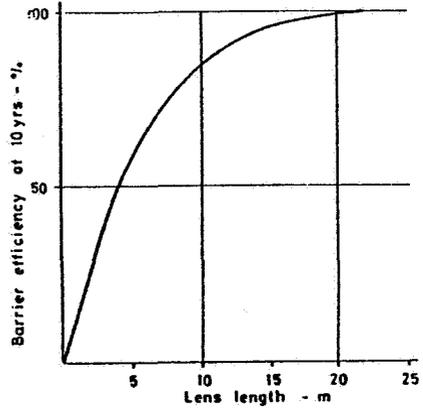


Fig. 5 Length vs Barrier Efficiency

The barrier efficiency can be defined by:

$$\eta = \frac{100}{QTC_0} \cdot \int_0^T QC dt \quad \dots\dots\dots (4)$$

and in these terms the dependance of that efficiency on system parameters such as the clay adsorption factor and the time from the start of the leak is illustrated in fig. 4. where it can be seen that the barrier function falls off rapidly after the first few years.

In practical terms it is important to know how extensive a barrier strata has to be to meet a given duty. For the case considered here this is shown in fig. 5. for a 10 year period.

The plot shows, for example, that if the time to respond and correct a leakage is taken as 10 years, then the lens will have to be whole for at least 15 meters from the leak to hold back 95% of the leaking cadmium. Alternatively, a monitoring position at 25 m from the sewer will in no case detect a leak within the first 10 years after inception.

4. CONCLUSIONS

The simple relationships presented here can be used to estimate the expected adsorption barrier efficiencies of natural and artificial clay lenses. These efficiencies can be less than generally expected and this will impact on the design and monitoring strategies of these systems.

MAPPING THE VULNERABILITY OF GROUNDWATER TO POLLUTION. SOME
LESSONS FROM EXPERIENCE IN FRANCE

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ABSTRACT

The mapping of groundwater vulnerability to pollution risks, initially conceived as a means of representing a general condition, can convey only a limited amount of static, numerical information on the factors in natural protection of groundwater against potential attack. Now, however, an advance on this is available through computer graphics, which make it possible to adapt the analysis of the multiple factors concerned in vulnerability to a variety of criteria, and thus to visualize information that is more critical for decision-making.

The idea of describing by means of maps the various degrees of vulnerability of groundwater to pollutants as a function of hydrogeological conditions was originally conceived in France (J. Margat, 1968, M. Albinet, J. Margat, 1970) in an effort to create general awareness. At a time of growing concern for the preservation of the quality of groundwater threatened by pollutants, the aim was to show that their "natural protection" varied according to location and to identify the areas where protection measures were most needed. The visualization provided by maps proved to be an effective way of delivering the message to a fairly large audience of decision-makers and implementers.

This map was based on the simple principle that various steady state and non-steady state spatial variables characterising hydrogeological conditions and commonly already described on general hydrogeological maps such as: average depth of the free water-table, permeability of surficial sedimentary cover, connection between aquifer and surface water and the average velocity of groundwater flow governing the

persistance of regional accidental pollution, must be important factors in vulnerability. The causes of pollution considered were mainly surface, chronic or temporary, localised or diffuse, and undifferentiated. The interpretation of hydrogeological conditions in terms of vulnerability was qualitative and intuitive, and relied on no quantified analysis of different processes of pollutant migration from surface to groundwater and therefore gave only indications and orders of magnitude.

Following a 1:1,000,000 scale map of the whole France completed in 1970, various regional maps at medium scale (1:250,000, 1:200,000), which were sometimes included in Departmental and Regional atlases, had the same purpose and the same features. The transition to larger scale maps (1:50,000, 1:25,000) in some regions was accompanied by greater ambition. To the more detailed description of assumed fundamental factors in vulnerability were added inventoried potential causes of contamination (fixed sites: "classified risk establishment", waste dumps, transport routes, potential accident locations) and sites and zones most requiring protection, in particular areas of potable water catchworks with information enabling quantitative evaluation of the damage that would result from a potential pollutant. This includes in particular the location of the catchment structures indicating the amount of water extracted and the distribution of consumption giving the directions and average rate of flow of the surrounding subsurface aquifers. If they exist, the sanitary zones of protection for potable water wells are indicated.

The vulnerability map consists of three superimposed maps enabling simultaneous reading of factors of varied origin and nature equally represented according to different criteria. In such a representation only well-defined cases characterized by an accumulation of criteria can be immediately identified. An example can be made of a catchment zone located in a very vulnerable area which is the sole source of water supply for several communities.

Given the limitations of an analysis of the above-mentioned factors in the natural protection of groundwater against different types of

pollution, the limited decisional scope of a map based on factors is coherence, firstly because vulnerability depends not only on stable factors, but also on variable states of the ground and groundwater and especially of the fact that it is closely related to the way which the pollution originates, to the extent and duration of pollutant actions and to the nature of pollutants, and also because the pollution itself is related to various norms of usage (M.F. Parascandola, 1980). The aim of providing information enabling evaluation and decision-making in order to assess the dangers and to plan future protection measures can only be partially fulfilled by classical simple mapping.

The vulnerability maps completed to date have therefore been mainly orientation documents necessary for impact and safety studies and for their contribution to land-use zoning.

Progress in computer graphics coupled to cartographic databases, possibly with systems for interpolating scattered data, is opening up new perspectives in the synthetic visualization of the spatial variations of an object, both multiparametric and relative to multiple criteria, such as the vulnerability of groundwater to pollution. Demultiplied and optional mapping has become possible enabling easy updating of the data entered and the adaptation of responses to specific interrogations.

At first the images produced will still be maps of ordinal classification combining however the various factors classified according to a graduated scale and possibly weighted according to the desired objective, therefore offering a wide range of possible variations and representing an instrument well suited to analyses of sensitivity.

As the quantitative analytical relations between the fundamental factors and the responses of the environment to different forms of pollution become better established, it will be possible to establish zonings based on selected threshold values and specific to the identified pollution.

Thus using selected data replying to pre-established criteria, it will be possible to create images of relative vulnerability of the environment to specific types of pollution and also its ability to withstand various pressures or on the other hand, constraints required for its conservation according to economic criteria approved by both the water development and management authorities.

It is planned that the new map of groundwater vulnerability to pollution will be developed along these lines.

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ASSESSING THE SUSCEPTIBILITY OF GROUND WATER
SUPPLIES TO NON POINT-SOURCE AGRICULTURAL
CONTAMINATION IN SOUTHERN ONTARIO

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ABSTRACT

The susceptibility of ground water supplies to contamination by agricultural crop chemicals was assessed for an intensely cultivated part of southern Ontario (27,000 km²). The study was based on water well data and geologic, hydrogeologic and soil survey maps and reports. Four hydrogeologic zones were identified according to similar conditions within 10 m of ground surface. These zones were (i) fine-grained soils (silt and clay), (ii) granular soils (sand and gravel), (iii) near-surface bedrock, and (iv) mixed or variable soils. Zones (ii) and (iii) were considered susceptible due to high permeabilities resulting in potentially rapid infiltration of contaminants. The hydrogeologic zones were further classified according to the soil organic matter content. Soils with high organic matter contents exhibit increased sorption of organic chemicals and therefore retard the migration of organic contaminants. Fifteen percent of the study area was identified with low organic matter content. The availability of alternative deeper ground water sources was also assessed for the susceptible hydrogeologic zones. Ultimately, twelve percent of the study lands were wholly dependent on shallow ground water supplies. This study concludes that these vulnerable areas should be protected by the careful handling and application of agricultural chemicals.

1. INTRODUCTION

The susceptibility of ground water supplies to contamination by agri-

cultural crop chemicals was assessed for an intensively cultivated part (27,000 km²) of southern Ontario, Canada (Figure 1).



Figure 1. *Location of study area*

In order to assess the potential for non point-source (i.e., diffuse) contamination of ground water, a description of the physical setting and a fundamental understanding of the geology and hydrogeology was needed. Technical judgement was applied to assess the potential for the migration of agricultural chemicals into the subsurface. Water well data, and maps and reports of the study area for geology, hydrogeology, and soil were used to identify regions where the application of agricultural chemicals could pose a contaminant threat to ground water supplies.

Three resource maps were prepared describing: (a) susceptibility of near-surface materials (permeability), (b) organic matter content of the soils, and (c) areas where deeper or alternative ground water supplies were not available. These maps were then used to prepare a derived map showing the areas where ground water supplies would be highly vulnerable to contamination from the application of agricultural chemicals on farm lands. A description of the resource maps and their preparation follows.

2. RESOURCE MAPS

2.1 Susceptibility of near-surface materials

The susceptibility of the materials found at surface was assessed from published geologic and physiographic sources for southern Ontario (Chapman and Putnam, 1984; Gartner Lee Associates Limited, 1982).

Some published water well information was also consulted (Ontario Ministry of the Environment, 1974 to 1983) to provide an indication of subsurface conditions where data were sparse. These published data were used to divide the study area into general categories of ground water susceptibility to contamination from surface sources. Susceptible areas were identified as:

- surface materials comprised of high permeability overburden sands and gravels, or
- bedrock exposed at/or within 10 m of ground surface.

The above-mentioned surface conditions would be most conducive to non point-source entry of agricultural chemicals into ground water (Figure 2). These materials generally have a poor attenuation capacity and

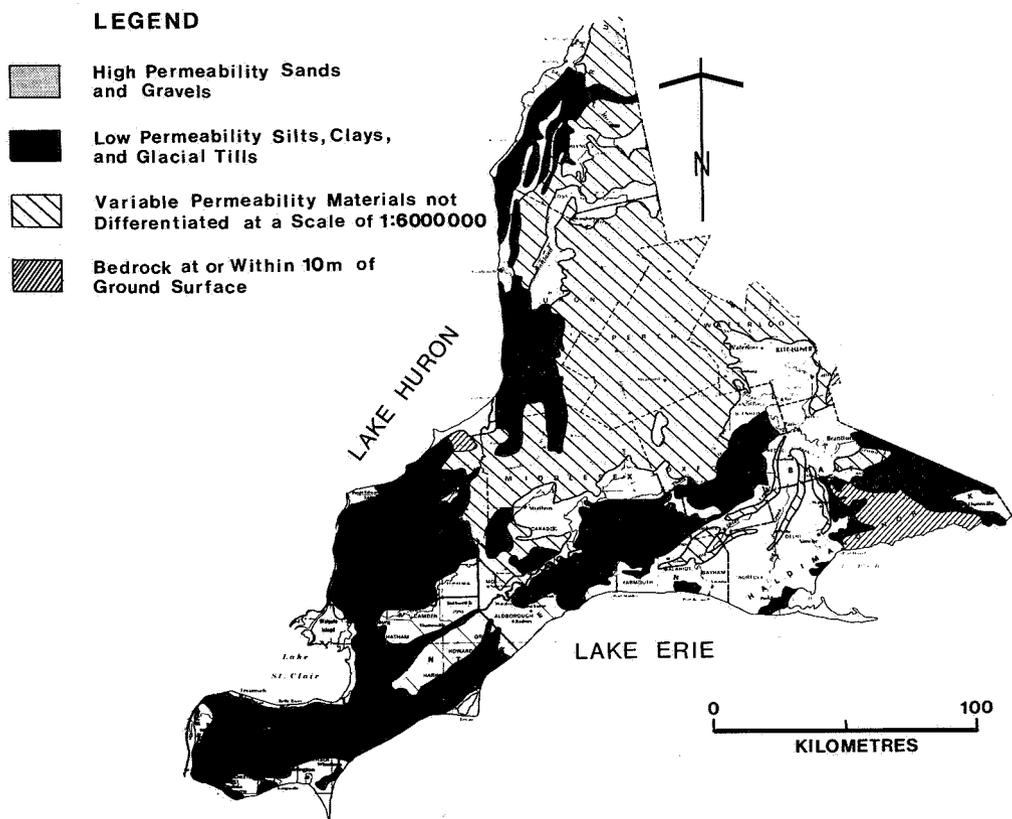


Figure 2. *Susceptibility of near surface materials*

chemicals are likely to migrate further than in low permeability materials. The total area comprised of high permeability surface materials is about 8,350 km² or about 31% of the study area.

The permeability of fractured rocks found in southern Ontario is highly variable and unpredictable. As a result, removal of chemicals is difficult to remediate once the chemicals reach the bedrock. Furthermore, the attenuation capacity of the bedrock from sorption mechanisms is generally small because the surface area of the fracture openings is usually small compared to the total volume of the rock. The total area comprised of bedrock within 10 m of the ground surface is 1,820 km² or about 7% of the study area.

Areas of low susceptibility were defined as regions comprised of low permeability overburden materials at surface that are likely to extend more than 10 m in depth. These low permeability materials are usually comprised of fine-grained deposits such as clays, silts and glacial tills that have a large surface area; and thus there is a large capacity to attenuate chemicals, generally by sorption. Based on these properties, movement of agricultural chemicals in this category of soil materials is likely to be contained within a short distance from their point of entry.

A fourth category of varying susceptibility included those areas where the surface materials are comprised of a mixture of the above mentioned soil types that cannot be differentiated at a map scale of 1:600,000. These are areas of variable stratigraphy representing a variety of hydrogeological conditions. For example, significant, local water-bearing surficial sands separated by low permeability till ridges and till plains are included in this category. Detailed, site-specific studies would be required to differentiate the smaller areal extent of these units. For the purposes of this study these areas were considered to have a low susceptibility.

2.2 Organic matter content of soils

Organic matter in soils is derived from decomposed original plant tissue and affects the sorptive properties of soil. The large surface area and sorption capacity of the organic matter in the soils is much greater

than that provided by the soil particles themselves. In general, soils with a high organic matter content will inhibit migration of an organic chemical more than soils with a relatively low organic matter content. The main factors that affect the amount of organic matter in soils include:

- soil texture
- drainage
- slope
- tillage and farm management practices
- vegetative cover
- lime content

The organic matter content map (Figure 3) was compiled using a preliminary soils landscape data base provided by Agriculture Canada (Acton and Harkes, in preparation).

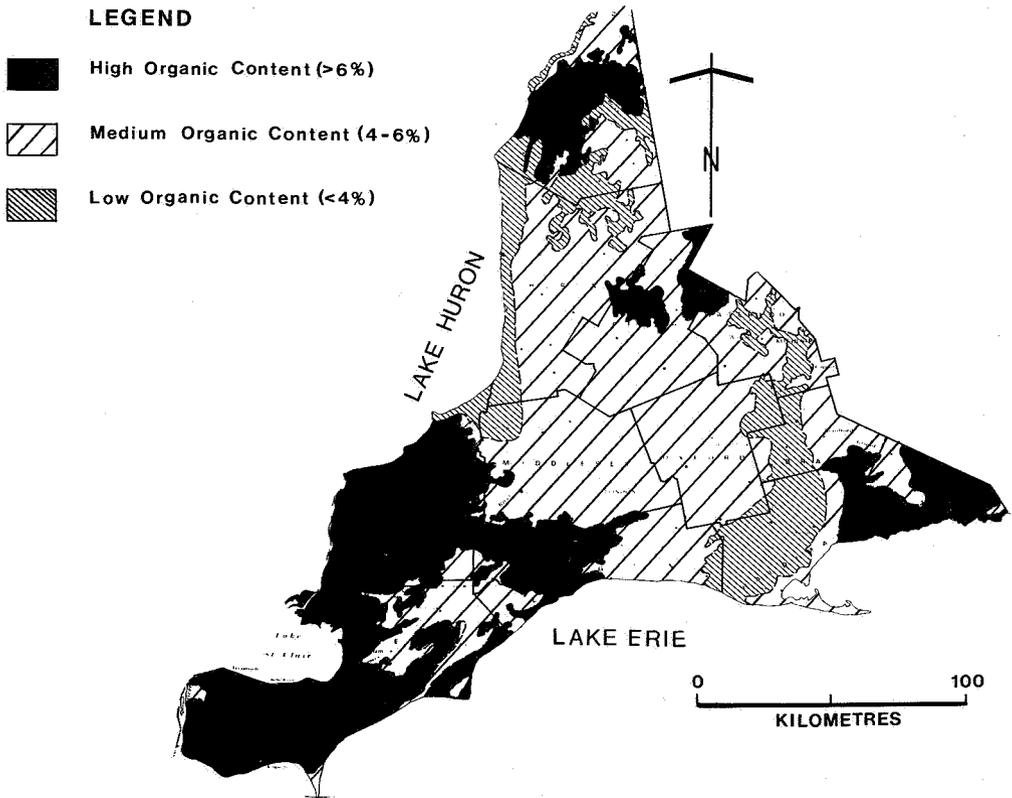


Figure 3. *Organic matter content of soils*

The data consist of a series of small, contiguous map areas, referred to as soil polygons, which depict soil landscapes (Agriculture Canada, 1986). The soil landscapes in the soil polygons consist of major soil properties such as soil development, soil texture, parent material, surface form and slope gradient. For this ground water susceptibility study, three parameters; slope, drainage, and soil texture were chosen to qualitatively infer the organic matter content of the soil in each soil polygon. The resulting map (Figure 3) shows the relative organic matter contents of <4%, 4 - 6% and >6% which were calibrated by reference to actual organic matter data that were available for specific areas (Canada Department of Agriculture, 1936 to 1984). The total area of surface soils having less than 4% of organic matter content is about 4,150 km² or about 15% of the study area.

2.3 Alternate ground water supplies

Ground water supplies in southern Ontario are located in a variety of hydrogeological regimes. Those most susceptible to the entry of non point-source chemicals are located in near-surface granular materials. Aquifers located at depth in either the overburden or bedrock are often confined or semi-confined and are thus, less likely to contain chemicals from either point and non-point sources. The alternate ground water supplies map (Figure 4) was compiled from the Ground Water Probability map series published by the Ontario Ministry of the Environment (1972 to 1985). The intent of this map is to identify areas where alternate sources of ground water are available at depth in the subsurface. As well, this map identifies areas where insufficient yields were available from deeper geologic formations. These areas would require more difficult remediation, if the presence of agricultural chemicals in the ground water were to occur. The total area where deeper ground water supplies are not available is 3,175 km² or about 12% of the study area.

3. VULNERABLE AREAS

Soil areas with <4% organic matter content (Figure 3), and areas where

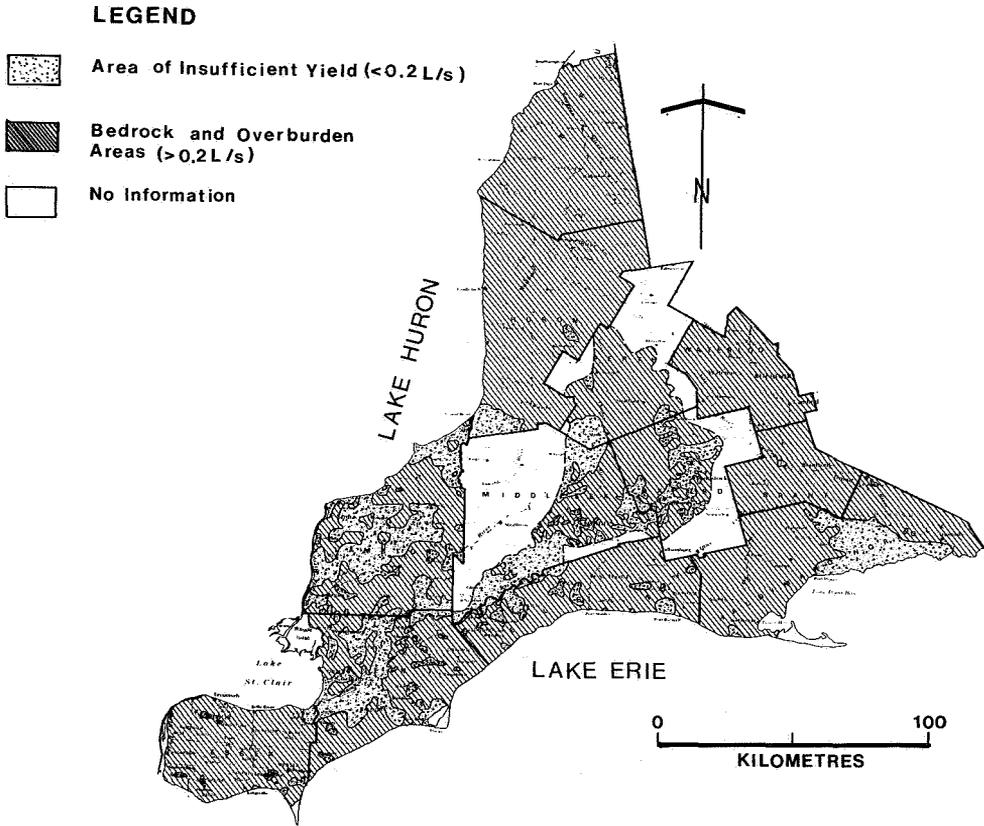


Figure 4. *Alternate ground water supplies*

deeper alternate ground water supplies are not available (Figure 4) were superimposed on the susceptible areas shown on Figure 2. The underlying assumption was that permeable soils with a high organic matter would have a greater sorption capacity to attenuate agricultural chemicals than permeable soils with a lesser organic content. The lack of a deeper ground water supply would also be critical if the shallow ground water system or bedrock became contaminated. The resulting derived map (Figure 5) indicates the total vulnerable area is about 500 km² or less than 2% of the study area.

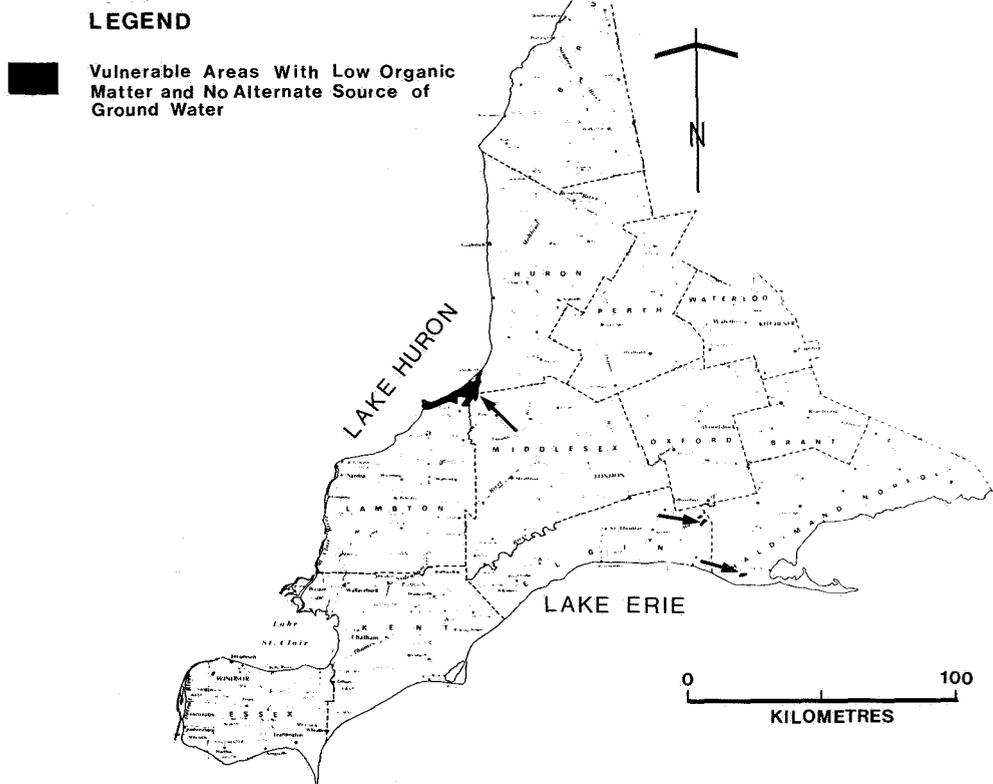


Figure 5. *Vulnerable areas to agricultural chemicals*

4. CONCLUSIONS

Office based studies can rapidly and economically provide geo-data maps for assessment of man's activities. The methodology outlined in this paper of using existing data banks to assess large areas of land for the potential of non point-source contamination proved useful. It is important to remember that studies of this nature require field confirmation to calibrate the data, particularly in areas of uncertainty.

For the 27,000 km² agricultural study area in southern Ontario we provide the following four main conclusions:

- (i) 38% of the study area is susceptible to non point-source contamination from agricultural chemicals
- (ii) 15% of the susceptible areas have an organic content of less than

- 4% and would provide minimum attenuation of agricultural chemicals
- (iii) 12% of the susceptible areas are estimated to have no deeper alternative sources of ground water available as a water supply
 - (iv) less than 2% of the susceptible areas is vulnerable to contamination from agricultural chemicals. These areas should be protected by the careful handling and application of agricultural chemicals

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THE USE OF GEOSTATISTICAL METHODS WITHIN THE
FRAMEWORK OF THE DUTCH SOIL SANITATION OPERATION

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ABSTRACT

Geostatistical techniques, such as kriging, local trend surface analysis, splines and weighted moving average, commonly used in geology and soil science, provide useful tools for estimating the distribution of any given property over an area. In this paper the use of geostatistical interpolation techniques for mapping soil pollution is evaluated, using an investigation in the surroundings of Eijsden (Limburg). The area surrounding this little village in the southernmost part of the Netherlands is contaminated by atmospheric and fluvial deposition of zinc, barium and lead. The patterns of contamination could not be discerned and evaluated until geostatistical tools were used.

1. INTRODUCTION

During the last 5 years several hundreds of millions of guilders have been paid for soil sanitation and soil sanitation survey in the Netherlands. The minister of Housing, Physical Planning and Environment has estimated that the national contribution to the soil sanitation operation in the period 1987-1997 will be two billion guilders at least. More than half of this amount, some 1250 million Dfl, has been allocated to the provincial soil sanitation programs.

The soil sanitation program of the province of Limburg has cost about 30 million Dfl in the period 1981-1987. Two thirds of this amount is used for five large soil clean-up operations; the rest is used for research. During this period, approximately 235 investigations have been carried out on more than 100 sites. Most of these investigations have been

carried out on former industrial areas and in the surroundings of waste disposal sites (Table 1).

Table 1. *Number of soil pollution surveys commissioned by the provincial authorities in Limburg in the period 1981-1986*

description of contaminated site	annual number of investigations					
	1981	1982	1983	1984	1985	1986
waste disposal site - domestic	1	4	7	15	17	6
- industrial			3	1	6	11
- carwrecks			1	1	7	17
(former) industrial site	2	16	15	34	21	29
floodplain			1	1	1	1
others (atmospheric deposition)			1	2	2	2

At such locations the soil pollution can easily be located and mapped by organoleptic observations and chemical analyses. Generally speaking, these kind of sites are characterized by sharp boundaries between polluted and unpolluted spots. Consequently, changes in pollution level occur in steps. In these situations geostatistical interpolation techniques, such as kriging, local trend surface analysis, splines and weighted moving averages, are not appropriate because they rely on assumptions of gradual change and an underlying spatial dependence of the variable under consideration. The appropriate technique for mapping the extent of soil pollution on former industrial sites is that of the choropleth map, where discrete, isotropic units can be characterized in terms of central tendency. Often the arithmetic mean and the standard deviation are calculated, but these figures only give a representation when the variable of interest is more or less normally distributed, a demand which is not always met. For this reason it is better to characterize the rate of pollution by percentile values or by the frequency of exceeding certain norm values.

Geostatistical interpolation techniques are most suitable in situations where the variable under consideration changes continuously. This occurs when pollution is not caused by direct anthropogenic input, but by

processes such as flooding with polluted surface water, or by atmospheric deposition.

Since 1981 several investigations have been carried out in Limburg on sites where soil pollution was caused by one of these processes. In two of these investigations use has been made of geostatistical interpolation techniques. This paper presents the results of one of these studies, that of heavy metal pollution in the surroundings of Eijsden.

2. SOIL POLLUTION IN EIJSDEN

The soil in the surroundings of Eijsden has been polluted with heavy metals in several ways. Apart from the diffuse inputs through atmospheric deposition and the use of metal containing fertilizers, three site specific sources of heavy metals may be distinguished. The first one is a factory that manufactures pigments from barium sulphate and zinc sulphide for the paint industry. This factory has been located in the municipality of Eijsden since 1870. Earlier this century, large quantities of Ba, Zn and Pb containing particles were emitted to the atmosphere. In 1974, the annual emission from the factory chimney was estimated as: zinc 64 tons, barium 210 tons and lead 94 tons. In 1975 the emission stopped almost completely as a result of changes in the production process. Most of the emitted particles were deposited within a radius of 3 km around the factory.

The second site specific source of heavy metal pollution is formed by roads sealed with zinc oxide cinders, which are a waste product of the pigment industry. Between 1870 and 1975 approximately 250,000 tons of these cinders were produced. The total length of cinder-sealed roads is about 100 km. Because the cinders contain a high concentration of Zn, Ba, Cd, Pb and As the soil near these roads may be seriously polluted. The third site specific source of heavy metals is the river Meuse. A part of the area of investigation is located in the floodplain of this river. As a result of waste disposal by mines and metallurgic industries in the Belgian part of the catchment, the river muds are severely contaminated with heavy metals. The sedimentation of these muds has

caused a considerable increase in the heavy metal concentrations of the topsoils in the floodplain area (Rang and others, 1986).

3. EXPERIMENTAL METHODS

Soil samples were collected from allotments and from vegetable gardens only, because pollution of these areas is considered to be the most important threat to public health. An additional advantage of this choice of sampling sites is the improvement of the homogeneity of the data set. Previous investigations showed significant differences in heavy metal concentrations of the topsoil between arable land, vegetable gardens and pastures, due to differences in soil tillage and landuse. All sample sites are located within a radius of 3 km around the pigment factory in Eijsden. Because it is assumed that short distance variation is greater in the surroundings of cinder roads than in areas that are polluted by diffuse sources only, no samples were taken within a distance of 50 m from such roads. At distances greater than 50 m the influence is assumed to be negligible.

In total 62 samples of the topsoils were taken. Each sample formed a composite of about 15 sub-samples, which were taken from the top 20 cm of the soil over an area of about 50 m².

All soil samples were dried for 24 h at 60° Celsius and crushed in a mortar. Two grams of this material were boiled gently with 20 ml 30% HNO₃ for 2 h. The extract was then separated from the sediment by centrifugation and brought to 40 ml with distilled water. The concentrations of Ba, Zn and Pb in the extract were determined by inductive coupled plasma photometry (ICP).

4. GEOSTATISTICAL METHODS

The spatial correlation structures of heavy metal concentrations were estimated by calculating the semivariances. Semivariance is a concept from the regionalized variable theory. This theory rests on the recognition that the spatial variation of any geological, soil or hydrological property, known as a "regionalized variable", is too

irregular to be modelled by a smooth mathematical function, but can be described better by a stochastic surface. The spatial variation is assumed to be the sum of a structural component, a random, spatially correlated component and a random noise, or residual term (Burrough, 1986).

The semivariance is a measure of the degree of spatial dependence between samples along a specific support or sampling network. A plot of the semivariance against h , the distance between the sampling points, is known as a semivariogram. If assumed that samples are spaced along straight lines with a sampling interval of Δ , the semivariance can be expressed as:

$$\hat{\gamma}(h) = \frac{1}{2n} \sum_{i=1}^n \{Z(x_i) - Z(x_i + h)\}^2$$

Difficulties arise when transects are sampled at irregular intervals. This can be overcome by choosing a set of lags $h(i)$ at arbitrary but constant interval d . All pairs of observations that are separated by a lag that falls in the range $h(i) \pm d$ are then used to estimate the average semivariance, at a recalculated, average lag $h(i)$ (Davis, 1986; Burrough, 1986).

In general, a few simple features contribute to the form of a semivariogram. The semivariance at zero lag must be zero. In practice the extrapolated semivariogram usually intercepts the ordinate at a positive value known as the "nugget variance". The nugget variance may arise from measurement error, discrete random variation and spatially dependent variation occurring over distances much smaller than the sampling interval (Oliver and Webster, 1986). In most instances it is found that the semivariance increases to a maximum value at which it levels out. This maximum value is known as "the sill" and is of the same magnitude as the variance of the variable. The lag at which the sill is reached is known as the range, beyond which no spatial dependence is present anymore. In some cases, the increase of the semivariance appears to have no limit: the soil properties have no finite variance. Less commonly, a semivariogram has a remarked reversal of slope after reaching its maximum, suggesting some degree of regular repetition in the variable. These two types of semivariograms are mainly found when a regional trend is present. Regional trends can be accounted for by first fitting a global polynomial trend surface to the data. This surface can

then be said to represent the "deterministic" component of the spatial variation. Subtracting the estimated values for the trends from the original data values yields a set of residuals, which can then be analyzed further using the semivariogram.

A structural component that appears as a global trend, can be modelled easily by a polynomial surface fitted by least squares through the data points. It is assumed that the spatial coordinates X, Y are the independent variables, and that Z, the property of interest, is the dependent variable. This means that an observation is thought to be in part a function of the location. In many circumstances Z is not a linear function of X but varies in a more complicated way. In these situations quadratic or still-higher-order polynomials can be used (Burrough, 1986).

5. RESULTS AND DISCUSSION

5.1. Measures of central tendency

Before geostatistical interpolation techniques were used, the data set was described in terms of central tendency. In Table 2 some measures of central tendency are given for areas within a specific distance from the emission point.

Table 2. *Measures of central tendency of the concentration of three heavy metals in the topsoil (mg/kg).*

metal	distance	mean	median	standard dev.	skewness	bckgrnd
Zn	0-1 km	1556	950	1529	-1.2	
	1-2 km	499	296	649	-0.9	(45-110)
	2-3 km	314	217	239	-1.2	
Ba	0-1 km	739	399	964	-1.4	
	1-2 km	184	152	109	-0.9	(20-40)
	2-3 km	130	111	43	-1.3	
Pb	0-1 km	196	109	284	-0.9	
	1-2 km	73	42	87	-1.1	(22-41)
	2-3 km	44	44	15	0	

The clear decrease of concentration with distance from the source of pollution, namely the chimney of the pigment factory, suggests that atmospheric deposition is the dominant process. This is supported by the product-moment correlations between concentration and distance, which for Zn, Ba and Pb are -0.52, -0.48 and -0.38 respectively.

Table 2 also shows that lead concentrations are the least affected by the factory, and that within 3 km, "background" levels are reached. So, further spatial analyses concentrated on zinc and barium.

5.2. Semivariance

The Figures 1a and b display the semivariograms for the concentrations of zinc and barium in the topsoil. The semivariogram of zinc shows a scatter of points, but there is a strong suggestion of an increase of semivariance with distance up to approximately 1.5 km, followed by a decrease. That for barium is similar but even clearer. These results fit in clearly with a symmetric pattern of deposition around a central emission point.

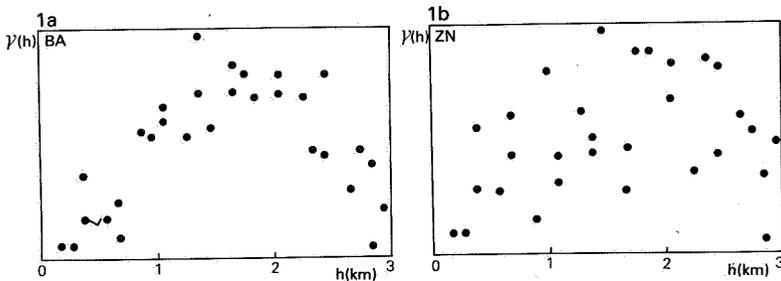


Figure 1. *The semivariograms for the concentrations of barium and zinc*

Given the presence of clear trends around the emission point, the data were detrended by using global polynomials (Table 3). The R-value is the "goodness of fit", which reflects the proportion of total variation "explained" by the polynomial. The F-value reflects the level of statistical significance. All estimated surfaces gave significant results, so a second F-test (Davis, 1986) was performed to examine the significance of increasing the order of the trend surface. For both metals, increasing the order of the surface from 2 to 3 did not result

in a significant improvement, so the data sets were detrended using second order polynomials.

Table 3. *The results of the global trend surface analysis ($\alpha = 0.05$)*

metal	significance of regression				significance of increasing degree			
	degree	R	F-calc.	sign.	degree	F-calc.	F-crit.	sign.
zinc	1	0.22	5.67	y	1-2	4.14	2.84	y
	2	0.42	5.30	y	2-3	0.89	2.61	n
	3	0.50	3.58	y	3-4	1.51	2.45	n
	4	0.61	3.02	y				
barium	1	0.21	5.09	y	1-2	6.10	2.84	y
	2	0.47	6.50	y	2-3	1.50	2.61	n
	3	0.56	4.48	y	3-4	3.44	2.45	y
	4	0.73	5.21	y				

Semivariograms were calculated for the residuals of zinc and barium (figure 2a and b). That for zinc shows only pure nugget variance, or totally random variaton. The residuals are the sum of a random, spatial correlated term and a random noise, or error term, so it may be concluded that the latter is dominant over the first. This may be caused by the fact that all spatial correlation occurs within the minimum sampling interval, or that the spatial variation over the study area is not homogeneous. For this reason, the spatial pattern of zinc can be described adequately by the second order trend surface plus a random noise component.

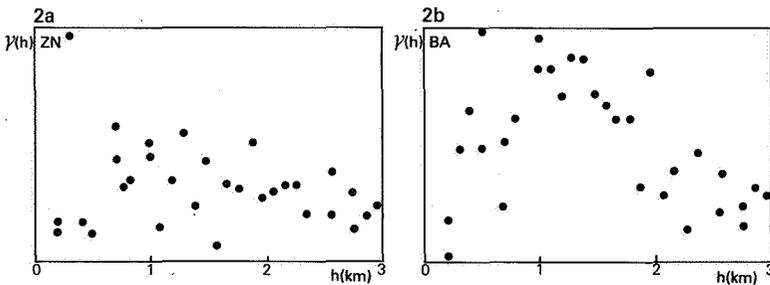


Figure 2. *The semivariogram for the residuals of zinc and barium*

The semivariogram of the residuals for barium shows a similar pattern to that of the original data. This suggests that there are other components of spatial variation present, but because of the number and density of the samples, these components cannot be accurately identified. This lack of data effectively meant that optimal interpolation techniques, such as kriging, could not be used.

5.3. Local trend surface analysis

In order to portray the variation of zinc and barium as faithfully as possible over the area, it was decided to make use of another local interpolation technique. The chosen technique is local trend surface analysis, because this technique is part of the geostatistical package PC-geostat, developed by the State University of Utrecht and is available for use on small desktop computers.

Local trend surface analysis is similar in principle to global trend surface analysis, with the important exception that the polynomial fitting and interpolation occurs within a local area, or "window". This window is systematically moved over the sample area in such a way as to achieve the best local fit. Experience has shown that this technique can give a reasonable representation of spatial variation in complex areas. The size of the window has to be selected by trial and error, but in any case its maximum dimension should be less than the range of the semivariogram of the data.

Figures 3 and 4 show the results of the interpolation. The map of barium concentrations, obtained using a second order local trend, appears to coincide with the intuitively expected distribution: the highest level of pollution coincides with the emission point and in the south-west the concentration decreases more rapidly with distance than in the north-east. This matches the expected effect of the prevailing winds. For zinc, the estimated pattern east of the emission point is similar to that from barium, but differs considerably in the west. The reason is the deposition of heavy metal polluted sediments in the floodplain of the Meuse in the western part of the study area.

Although the interpolated maps give a good overview of the distribution of the pollution, the user of these maps must be aware of a number of

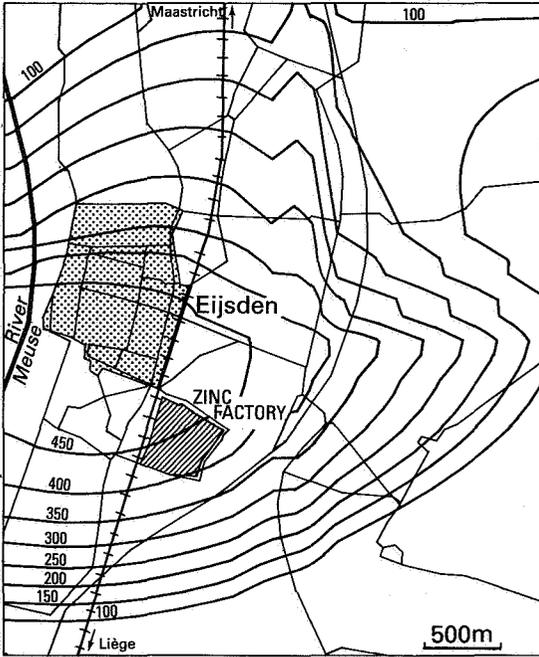


Figure 3. Interpolation map of barium concentrations in the topsoil

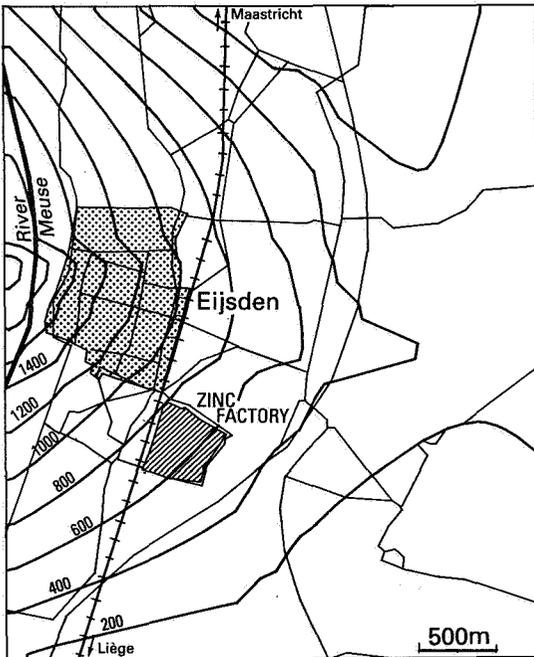


Figure 4. Interpolation map of zinc concentrations in the topsoil

important limitations governing their use. First, the results apply only to allotments and vegetable gardens. Second, the maps do not give the actual concentration of heavy metals, but an estimate thereof.

6. CONCLUSIONS

Geostatistical techniques require careful sampling, a proper choice of locations and a sufficient sampling density. Unless sufficient, good data are available, no technique can give optimal estimates of the levels of soil pollution. Within the Dutch soil sanitation program, it is unlikely that this demand will be met, because of the economical constraints.

Because large trends were present, the main features of the spatial variation over the study area could be mapped using local trend surface analysis.

The resulting maps give a good indication of the general distribution of the pollution, but of themselves are insufficient for determining exactly which parcels of land match environmental health norms. However, the maps form an excellent basis for preparing a program of detailed sampling.

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IDENTIFYING REGIONAL DIFFERENCES IN GROUNDWATER QUALITY IN
A DENSELY POPULATED LOESS REGION

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ABSTRACT

Using modern geostatistical techniques, data on groundwater quality, derived from existing wells and springs, may be of a considerable assistance in planning a regional groundwater monitoring network. This is illustrated using an investigation of the groundwater quality in two contrasting geohydrological regions in the hilly loess-covered area of South Limburg (the Netherlands).

1. INTRODUCTION

In the Netherlands, it is planned to design groundwater quality monitoring systems for each province in the near future to ascertain the regional variation and the temporal trend in the quality of both the phreatic and the deeper groundwater. However, the drinking water supply has been centralized and the phreatic groundwater is no longer a major source of drinking water. Nevertheless, it is extremely important to monitor the phreatic groundwater, because it is an indicator of expected long-term trends in the heavily exploited, deeper groundwater bodies. If the phreatic groundwater is severely polluted over large areas, the future of the deeper groundwater is rather bleak. Another important function of the phreatic groundwater is to supply water to streams and wetlands. The deterioration of the quality of this water will eventually lead to a degradation of the aquatic and groundwater-dependent ecosystems.

In the loess covered hill country of South Limburg, the phreatic groundwater is still the major source of drinking water for over 600.000

people. Therefore, in this region it is extremely important to monitor the phreatic groundwater. Furthermore, the monitoring of the phreatic groundwater benefits the management of water resources.

The density of the monitoring network depends on the variability of the parameters under investigation. In an intensively used and densely populated area the spatial variability of the phreatic groundwater will probably be high, making it necessary to set up an extensive sampling program. In general, a sampling program is a compromise between accuracy and economy. In most regions of the Netherlands the phreatic groundwater is within hand-auger reach, making it possible to sample this groundwater extensively before setting up a monitoring network. In contrast to the lowlands of the Netherlands, the water table in the hill country of South Limburg is found at depths of up to 40 metres below the surface. Only in the valleys does it locally reach the surface in springs and seepage areas. Consequently, a large part of the research budget goes towards installing observation wells. It is therefore sound economics to incorporate the existing observation and pumping wells and the hundreds of natural springs into the groundwater monitoring network. A disadvantage is that these wells and springs are not uniformly distributed in space and thus if there is a trend, or the observations correlate spatially, the data set obtained is not geographically representative of the groundwater in the geohydrological unit under consideration. In that case, the water quality cannot be characterized in terms of central tendency.

However, when there is no trend and the spatial autocorrelation is stationary at the scale of investigation, it may be possible to describe regional groundwater quality solely from existing sampling points. In this paper, two questions will be briefly discussed, in relation to an investigation of the groundwater quality in two contrasting geohydrological regions in South Limburg. These questions are:

1. Is it possible to use data on water quality of springs and wells to obtain a better understanding of the spatial variation in groundwater quality?
2. Is it possible to use existing groundwater sampling sites, such as springs and wells, in a groundwater monitoring programme?

2. GROUNDWATER POLLUTION IN SOUTH LIMBURG

In the unconfined aquifers of South Limburg levels of nitrate, sulphate and chloride are rising. Locally, the phreatic groundwater is no longer suitable for the drinking water supply. Diffuse sources of pollutants, such as the increasing application of mineral fertilizers and manure, and the atmospheric deposition of nitrogen and sulphur species are mainly responsible for this degradation of the groundwater. In a few geohydrological units the groundwater is strongly influenced by point sources of pollution, such as dumps of colliery spoil or of domestic and industrial wastes (Schouten and others, 1986, Rang and Schouten, 1987-1).

3. GEOHYDROLOGICAL REGIONS

A number of geohydrological units can be distinguished in South Limburg on the basis of the hydrological isolation resulting from relief and fault systems (Figure 1).

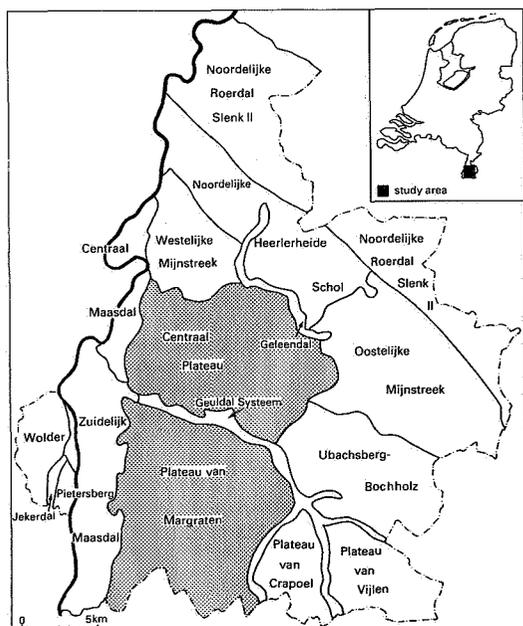


Figure 1. Geohydrological regions in South Limburg

Two important geohydrological units with different retention times were selected, so that the problem of the design of a water quality monitoring system could be investigated in detail: the Centraal Plateau, an area which supplies springs of high ecological value, and the Margraten Plateau, an area which is of high importance for the domestic water supply in the region. The relevant pedological and hydrogeological properties are more or less homogeneous within a unit. In both regions, a mantle of several metres of loess overlies Quaternary gravel. The geology of the Centraal Plateau differs from that of the Margraten Plateau by the presence of a mantle of Tertiary sands and clays. The clays form an aquiclude and little or no percolation water reaches the underlying confined limestone aquifer. The unconfined aquifer is formed by sandy Tertiary deposits and has a relatively short retention time of 20 to 30 years at maximum.

On the Margraten Plateau the limestone aquifer is unconfined and has an estimated maximum groundwater retention time of approximately 80 years (Rang and Schouten, 1987-2). The difference in retention time is considered to be the main cause of the contrast in pollution level between these two geohydrological units. Aquifers with short retention times and high groundwater flow velocities react to changes more quickly than aquifers with long retention times and low flow velocities.

4. SAMPLING STRATEGY

Data on groundwater quality in South Limburg are available from both wells and natural springs. The wells have been drilled for private and public water supply, and also near waste disposal or soil sanitation sites, for control purposes. In observation wells the water is mainly derived from a specific depth, using a short filter. In pumping wells the filter is mostly very long and groundwater is derived from various depths. The water table near pumping stations is lowered (the cone of depression), this may cause groundwater to seep from deeper layers, thus changing groundwater quality. A possible cause for variation in quality between two wells in the same region is stratification of the groundwater in a region. If the filters are situated at different

depths, vertical differences in water quality can easily be assumed to be regional differences.

Springs form a natural contact of the groundwater with the surface. Therefore, water in springs and seepage areas is considered to be more representative of the groundwater in a geohydrological unit than water derived from pumping or observation wells. The continuous flow of water induces a regular mixing of the groundwater. For this reason, the water quality of springs hardly changes from season to season and from year to year.

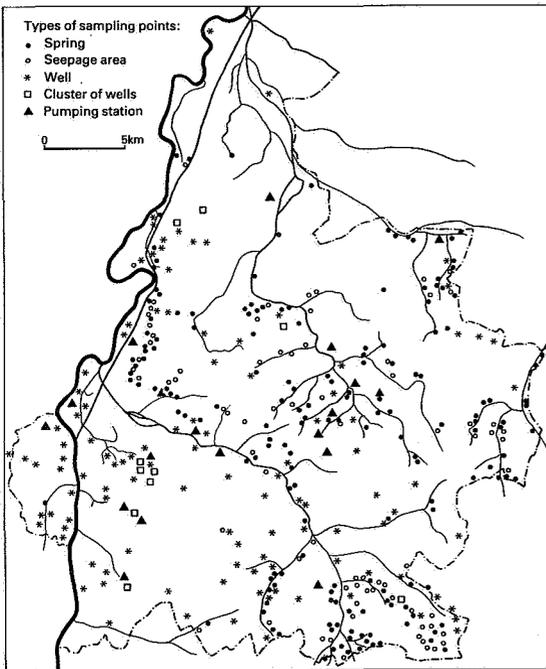


Figure 2. *Sampling points of the phreatic groundwater*

In 1982 a programme was started to inventarize and sample natural springs in South Limburg. In the period 1982–1986 the water from many hundreds of natural springs was sampled and analysed (Figure 2). Unfortunately, springs are not uniformly distributed in space, but are clustered along the foot of the plateaus and on the steep slopes. It was therefore decided to use both spring waters and wells in the same data set, to obtain a more uniform distribution, and to use this data set in the spatial analysis of groundwater quality. To prevent possible long

term trends in groundwater quality influencing the results, data of only one year (1984) were used.

A secondary groundwater monitoring network is set up to obtain a better insight into the regional variations in groundwater quality; therefore, observations in the immediate vicinity of point sources of pollution, such as waste dumps, must be eliminated. Furthermore, the short range variability in the vicinity of these locations is much larger than in the area with only diffuse sources. The effects of point sources of pollution can be established separately, from a tertiary groundwater quality network.

5. GEOSTATISTICAL METHODS

The sophisticated geostatistical techniques available to tackle the problems of the spatial distribution of sampling sites will now be described. In order to ascertain the spatial correlation structure the semivariances of the concentration of the parameters under investigation were calculated. Semivariance is a concept from the regionalized variable theory. This theory is based on the recognition that the spatial variation in any geological, soil or hydrological property (i.e. in any "regionalized variable") is too irregular to be modelled by a smooth mathematical function, but can be described better by a stochastic surface. The spatial variation is assumed to be the sum of a structural component, a random, spatially correlated component and a random noise, or residual term (Burrough, 1986).

5.1. Global trend surface analysis

The simplest way to calculate the structural component is to model the trend by polynomial regression. The idea is to use the least squares method to fit a polynomial surface through the data points. It is assumed that the spatial coordinates X , Y are the independent variables, and that Z , the property of interest, is the dependent variable. This means that an observation is thought to be in part a function of the location. In many circumstances, Z is not a linear function of X but may

vary in a more complicated way. In these situations, quadratic or still-higher-order polynomials can be used (Burrough, 1986).

5.2. Semivariance

The semivariance is a measure of the degree of spatial dependence between samples along a specific set of sampling points. A plot of the semivariance against h , the distance between the sampling points, is known as a semivariogram. If it is assumed that samples are spaced along straight lines with a sampling interval of δ , the semivariance can be expressed as:

$$\hat{\gamma}(h) = \frac{1}{2n} \sum_{i=1}^n \{Z(x_i) - Z(x_i + h)\}^2$$

Difficulties arise when transects have been sampled at irregular intervals. This can be overcome by choosing a set of lags $h(i)$ at an arbitrary but constant interval d . All pairs of observations that are separated by a lag that falls in the range $h(i) \pm d$ are then used to estimate the average semivariance, at a recalculated, average lag $h(i)$ (Davis, 1986; Burrough, 1986).

If we calculate the semivariances for different values of h , we can plot the results in the form of a semivariogram, which is analogous to a correlogram. The greater the distance between the points the less closely related to each other the points being compared will be. At a certain distance, the points being compared are so far apart that they are not related to each other and their squared differences become equal in magnitude to the variance around the average value. The semivariogram no longer increases and it levels out (the sill).

5.3. Kriging

After a semivariogram has been constructed, a mathematical model is fitted through the calculated semivariances. The fitted semivariogram model is used in an optimal interpolation technique called kriging (Davis, 1986; Burrough, 1986). The kriging estimates are in fact statistically predicted values. The advantage of the technique is not

only the accuracy of the interpolation, but also the possibility of constructing a kriging variance map, which tells us something of the reliability of the interpolation.

6. RESULTS

6.1. Comparison of water quality in springs and wells

In order to investigate if samples taken from springs and wells are comparable, statistical analysis was carried out. Mann-Whitney tests were used to test whether observed differences in average concentrations were statistically significant at a 0.05 level of significance. In only one case, the difference in average concentration between wells and springs was found to be significant (Table 1). Chloride concentrations in wells on the Margraten Plateau were found to be significantly higher than the chloride concentrations in springs issuing from that plateau. The explanation for this exceptional behaviour is the heavy withdrawal of groundwater from deep wells by the public pumping stations, which may result in a local upwelling of saline water from the underlying Paleozoic formations.

Table 1. *Comparison between the average composition of water samples obtained from wells and from natural springs (in mg/l)*

geohydrolog. unit	sampling point	n	NO ₃ -N		SO ₄		Cl	
			mean	s.d.	mean	s.d.	mean	s.d.
Centraal Plateau	springs	208	15	8.4	74	28	42	35
	wells	14	21	24	72	36	87	166
Margraten Plateau	springs	30	7.2	2.9	29	36	15	23
	wells	30	8.4	9.9	30	51	41	34

The variance of concentrations in spring water is generally smaller than the variance in the concentration in groundwater derived from wells in the same area. This is the result of the natural mixing process in the aquifer immediately upstream of springs.

6.2. Regional trends

If a clear surface trend is present in a geohydrological unit, measures of central tendency such as the mean, median and variation are inappropriate to characterize water quality. This is especially the case when the sampling points are not uniformly distributed in space. In such units the design of a representative sampling network has to be directed by the trend surface.

With exception of chloride, in either of the hydrogeological units no significant trend surfaces could be established. The chloride concentrations on the Margraten Plateau showed to be the only exception, with a significant 2nd-order trend surface. This trend surface explained about 35% of the observed variance and showed an increase in chloride concentration southwestwards. The explanation for this phenomenon is the presence of relatively shallow saline formation water in the south western part of the Margraten Plateau. However, trend surfaces that explain less than 40% of the total variance may be ignored in further analysis.

6.3. Semivariance

Figures 3a-f show the semivariograms of nitrate, sulphate and chloride for both units. For all but one parameter the semivariogram represents pure random scatter (nugget). This may be because all spatial correlation occurs within the minimum sampling interval, or because the noise term dominates the spatially correlated component.

The nitrate concentrations in the Centraal Plateau show a significant spatial dependency at sampling distances from 1 to 5 km (Figure 3a). Since the sampling points are strongly clustered, the measures of central tendency of the available data set are not geographically representative for the nitrate concentration in this unit. Therefore, the spatial distribution of the nitrate concentrations was investigated in more detail.

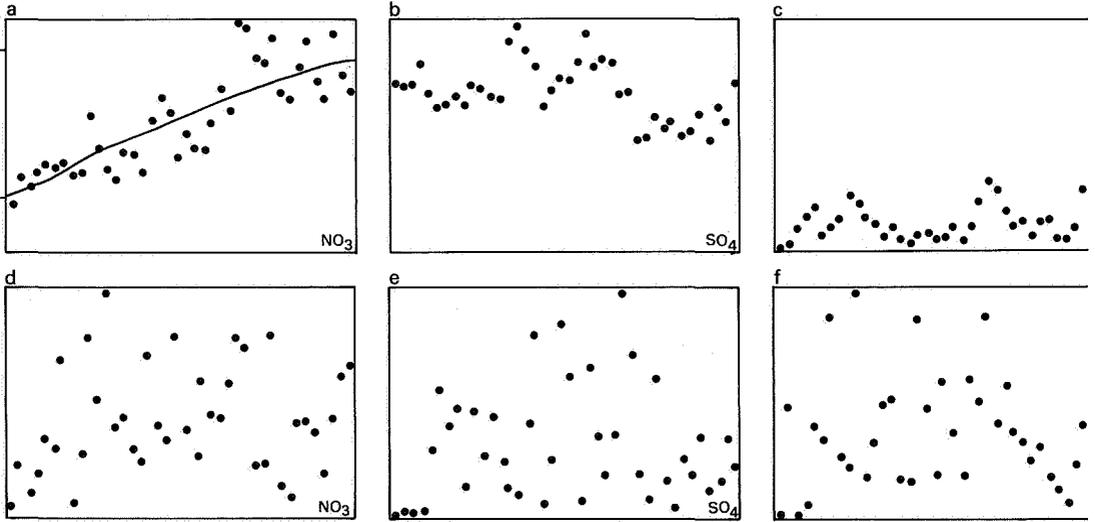


Figure 3. The semivariograms of nitrate, sulphate and chloride for the Centraal Plateau (a-c) and the Margraten Plateau (d-f)

6.4. Kriging

A mathematical function was fitted through the experimental values of the semivariance of nitrate. The parameters derived from this model were used in the optimal interpolation technique of point kriging. The result of the interpolation is represented graphically (Figure 4). On this map, an area with very high nitrate concentrations can be observed in the southern part of the Centraal Plateau. These high concentrations coincide with an area of short groundwater retention times.

Furthermore, several areas with low nitrate concentrations are present on the map. Two of these areas, one in the north east and one in the south west corner of the map, coincide with regional waste dumps. It is remarkable that even after all the samples taken in the immediate vicinity of these dumps had been removed from the data set, the effect of these dumps on water quality is still noticeable. The process of denitrification of the groundwater in and near domestic waste dumps seems to have a large effect upon the surrounding groundwater. The map of the kriging variance (Figure 4) shows maximum variances in the

central part of the Centraal Plateau, this is probably because of a lack of samples.

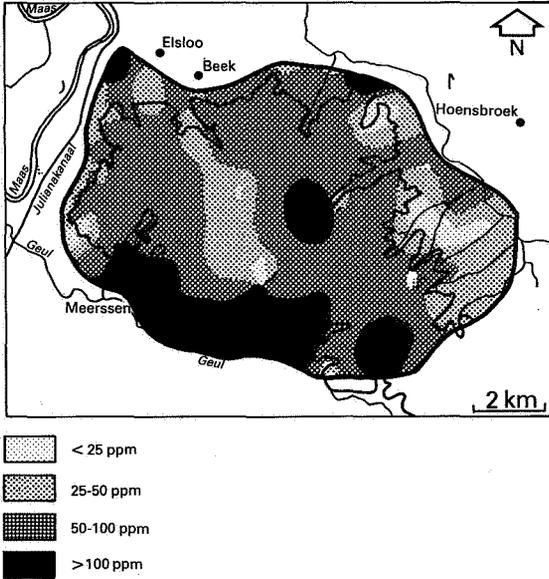


Figure 4. Point kriging interpolation map

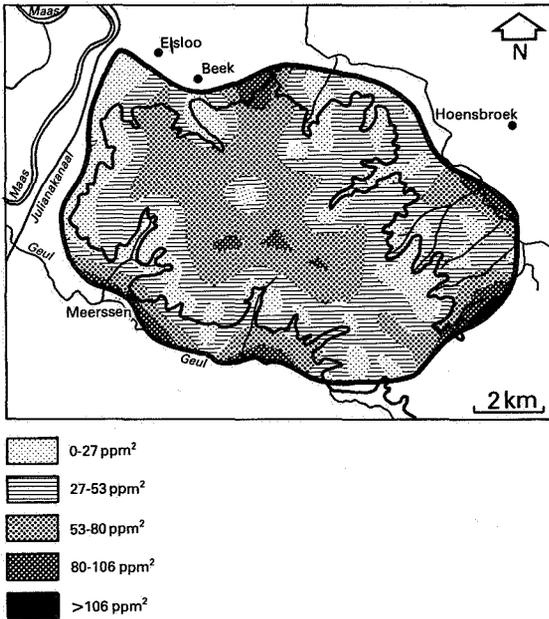


Figure 5. Map of the kriging variance

7. CONCLUSIONS

The use of data on water quality from springs and existing wells may contribute to the design of groundwater monitoring networks.

In most cases there is no significant trend in the concentrations of the water quality parameters of interest. It is therefore possible to describe the groundwater quality in terms of central tendency, using data from springs and existing wells.

In the Centraal Plateau, the nitrate concentrations show a clear local trend, because of the presence of waste dumps and possibly because of geological differences. When designing a monitoring network in such inhomogenous units, this trend should be taken into account.

Our investigation clearly shows the importance of geostatistically analysing existing data on groundwater quality before setting up a monitoring network. Such an analysis should ensure that the best possible monitoring programme is obtained for the money available.

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SOME REMARKS ON THE CONCEPT OF VULNERABILITY MAPS

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ABSTRACT

Cartographic methods are the most illustrative form of the graphical expression of data and information on the anthropogenic stress and natural effects on a hydrogeological system. Groundwater vulnerability and protection maps are used for the depicting of the groundwater system's response to man's impact. The different concepts of the two types of map are emphasized.

1. INTRODUCTION

Disregarding special-purpose maps (for instance those related to groundwater pollution accidents, hydrochemical maps, maps based on aerial or space remote sensing methods, etc.), hydrogeological maps and groundwater vulnerability and protection maps are the most common form for the graphical expression of data and information on a hydrogeological system at the regional and national scales.

The production of hydrogeological maps has a long tradition. The methodological principles of the construction of hydrogeological maps and their graphic design have been developed and unified thanks to a wide-ranging international co-operation under the sponsorship of UNESCO. The maps produced in accordance with the International Legend for Hydrogeological Maps (1983) are internationally understood, and are helpful to scientists and environmental specialists as well as to regional or national planners, managers and decision-makers responsible for water policies. According to UNESCO, the purpose of hydrogeological maps is to enable various areas to be distinguished according to their hydrological character in relation to the geology (1983).

Hydrogeological maps are usually interrelated with maps of other components of the hydrological cycle, geological maps and various types of environmental maps.

Groundwater vulnerability and protection maps began to be produced in some European countries (e.g. France, Czechoslovakia) and in the USA in the early 1970s. The methodology of these maps' construction, graphical design and symbols has not yet been internationally co-ordinated or standardized. Even within a single country groundwater vulnerability and protection maps are constructed using different methods. The maps are not comparable on the worldwide scale, and their international understanding is low. This is why a co-ordinated effort should be made to standardize the methodological principles, construction and classification of these maps under the sponsorship of an international organization.

2. CONCEPT OF VULNERABILITY MAPS

Groundwater vulnerability maps can only be constructed for those regions for which the geometry and hydraulic behaviour of the unsaturated zone and the aquifer/aquiclude system, natural and artificial boundary conditions, parameters of groundwater flow and recharge/discharge ratio are known. It is recommended to base the groundwater vulnerability maps on hydrogeological maps.

The concept of groundwater vulnerability maps has not yet been unambiguously defined. Some specialists do not differentiate between groundwater protection maps and vulnerability maps. However, the two types of map have different objectives, and therefore the concepts and methods of their construction cannot be identical. Vulnerability and protection are not synonymous, but different terms. The extent of a hydrogeological system's protection and its pollution (existing and potential) depend on the degree of its vulnerability.

By vulnerability of a hydrogeological system is understood the ability of this system to cope with external, both natural and anthropogenic, impacts which affect its state and character in time and space.

The natural influences - geological, climatic, hydrological - affecting the hydrological system are, except for unpredictable catastrophic events, permanent, they change cyclically, and the intensity of their action is of a planetary extent. The result of these influences is a state of dynamic stability of the hydrogeological system, which also involves the level of its vulnerability - its natural component.

When evaluating a hydrogeological system's vulnerability, the decisive role is played by its properties, especially:

- permeability, reaction and retardation ability and the thickness of the unsaturated zone, including the soil layer;
- extent of the groundwater level fluctuation throughout the annual hydrological cycle;
- properties of the aquifer and its type (phreatic, artesian);
- complexity of the aquifer system (single or multiaquifer system).

Cartographic methods serve for the depicting of a hydrogeological system's vulnerability in groundwater vulnerability maps. The parameters which are most frequently used in the construction of such maps are listed in Table 1.

Anthropogenic impacts - industry, agriculture, urbanization, transport, mining, etc. - do not effect the hydrogeological system continuously. Their intensity changes rapidly with time, and they are spatially limited. Anthropogenic impacts are generally destructive for the hydrogeological system, and there are efforts to eliminate them. Thus they constitute an unnatural part of the hydrogeological system. They are displayed in groundwater protection maps, pollution maps, risk (hazard) maps, etc.

Hydrogeological and vulnerability maps depict the natural parameters of a groundwater system. The groundwater protection, pollution and hazard maps supplement the set of hydro-ecological maps. However, since the anthropogenic impacts on the groundwater system change rapidly, the protection, pollution and hazard maps should be continually updated. This is why they are printed using simple, inexpensive techniques. The digital interpretation of aerial photographs can be a suitable form especially for synoptic maps. For large-scale maps, transparent sheets placed over vulnerability of hydrogeological maps are very practical.

3. DISCUSSION

The basic material for discussing the main parameters of vulnerability is the vulnerability map of the Czech Cretaceous Basin at a scale of 1 : 100,000.

- The soil parameter values are derived from a soil map and laboratory and field measurements. On the basis of statistical analysis, soils having k_f greater than $2.3 \cdot 10^{-5} \text{ m} \cdot \text{s}^{-1}$ are considered highly permeable, those with k_f from $2.3 \cdot 10^{-5}$ to $5.7 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$ medium permeable, and soils with k_f lower than $5.7 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1}$ have a low permeability. On farmland, these parameters can be affected by agricultural activities. The soil plays the decisive role for the degree of a hydrogeological system's vulnerability.
- The groundwater level under surface and its fluctuation are important criteria for groundwater system protection. In general, an aquifer's vulnerability declines with the depth of its level. The risk of vulnerability is also lower for confined aquifers. Large fluctuations of the water table throughout the annual hydrological cycle lead to accelerated leaching of contaminants from the upper layers of the unsaturated zone, thereby increasing aquifer vulnerability;
- The pollution risk is the greatest for the first aquifer. For deeper aquifers, particularly when they are covered by regionally developed, impermeable layers, the degree of vulnerability is lower;
- An aquifer's ability to transform, degrade and propagate contamination is expressed in relation with its permeability and the physico-chemical characteristics.

The set of the above vulnerability parameters applied to a hydrogeological basis and considering anthropogeneous impacts constitutes an important part of the maps of the Czech Cretaceous Basin.

4. CONCLUSIONS

The difference is emphasized between the concepts of vulnerability maps and groundwater protection and other types of map depicting anthropogenic impacts on the hydrogeological system. By vulnerability is understood natural characteristics of the hydrogeological system, usually invariable on the human scale.

On the other hand, groundwater protection and pollution maps display phenomena which are, on the human scale, short-term and considerably variable. The concept of vulnerability maps is being discussed on the basis of the map of the Czech Cretaceous Basin.

An internationally recognized legend and uniform concepts and methodologies for vulnerability maps are essential for their international understanding.

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Table: Main parameters expressed in vulnerability map

Parameters	Significance expressed by a score of points	Cartographical representation	Based on
soil permeability ($m \cdot s^{-1}$)	> $2,3 \cdot 10^{-5}$ $2,3 \cdot 10^{-5} - 5,7 \cdot 10^{-6}$ < $5,7 \cdot 10^{-6}$	simplified symbol	soil map, laboratory and field analyses
unsaturated zone thickness (m)	0 - 5 5 - 20 > 20 overflow	isolinie	hydrogeological map, observations
groundwater level fluctuation throughout annual hydrologic cycle (m)	> 4 0 - 4 0 - 2	numerical figure	groundwater level monitoring
aquifer transmissivity ($m^2 \cdot day^{-1}$)	> 10^{-3} $10^{-3} - 10^{-4}$ < 10^{-4}	colour	hydraulic tests
hydrogeological system vulnerability	high middle low	ornament	soil permeability, unsaturated zone thickness, groundwater level fluctuation, transmissivity, geological and hydrogeological properties and geometry of aquifer system

GROUNDWATER VULNERABILITY TO POLLUTANTS MAP OF THE LOW
LLOBREGAT VALLEY (BARCELONA, SPAIN). WORK METHOD AND
EVOLUTION STUDY OF THE GRAVEL-PIT EXPLOITATIONS

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ABSTRACT

In the alluvial aquifer of the Low Valley Llobregat River a global study of groundwater pollution was realized to know the quality of groundwater in this area.

This study was elaborated with looking to the usefulness of the vulnerability map to land planning. This poster-contribution explains the work method followed in the elaboration of the map, specially the criteria of vulnerability's classification of materials and other related concepts drawn in the map.

A greater part of the anormal contents in heavy metals detected seems to be related with industrial wastes refilling old gravel-pits. Their historical evolution was mapped, by studying seriated aerial photographs.

1. INTRODUCTION

A vulnerability to pollution map of the Low Valley Llobregat River has been realized in order to evaluate the groundwater pollution risk by human activities.

The relation between old gravel-pits filled with industrial wastes and localized pollutions induced us to carry out a specific mapping of the spatial localization and time evolution of such exploitations.

The studied area is included in the Low Llobregat district, mainly when the fluvial valley crosses the Litoral Range. The low valley of the Llobregat River is a long and narrow tectonic valley filled with pliocene and quaternary sediments. On the coast the delta is connected to the plain where Barcelona is built.

2. WORK METHODOLOGY FOR THE ELABORATION OF THE GROUNDWATER VULNERABILITY MAP

To classify the soil according to different ranks of vulnerability to pollution we have taken the outcropping lithology and the capacity of the non-saturated zone to neutralize, retain and delay the pollutants impact to groundwater.

Following this criteria four types had been characterized:

Very Vulnerable , including phreatic alluvial aquifers and mesozoic limestones with secondary permeability by jointing or karstification.

Vulnerable , including the breaches and quaternary caliches, the pliocene conglomerates poorly cemented with clay matrix.

Locally vulnerable , for the conglomerates and Buntsandstein's sandstones the conglomerates and sandstones of miocene age and the granites.

Not much vulnerable , for the Keuper's marls, the Middle Muschelkalk clays and gypsum, the Miocene red clays and the Paleozoic slates and schists.

Moreover, information concerned to pollution, like water supply wells, actual gravel-pits, leaved gravel-pits filled with solid wastes, induced recharge by ploughing the bottom of the river, waste water sewage, among others have also been included.

3. EVOLUTION'S STUDY OF THE GRAVEL PITS EXPLOITATIONS

The alluvial plain and delta has suffered a long history of gravels exploitations with a remarkable incidence on groundwater quality.

Until 1960 only some edges, the meandres and beaches were exploited moderately, but later because of the great demografic growth of the area, an important increase of request produced an intense and incontrolled exploitation to supply building industries.

During last years several and evident groundwater pollution events related with the leaved gravel-pits refilled with wastes has been detected.

The pollution is produced by the water level rise and the rain infiltration that causes a progresive leach of the waste and consequently the continue introduction of pollutants to groundwater.

Field mapping, many inquiries and mainly the study of aerial photographs series from to 1965 allow us to establish the problem dimension since the surface affected by leaved gravel-pits on the Llobregat low valley is $1.7 \times 10^6 \text{ m}^2$ and $3.3 \times 10^6 \text{ m}^2$ on the delta.

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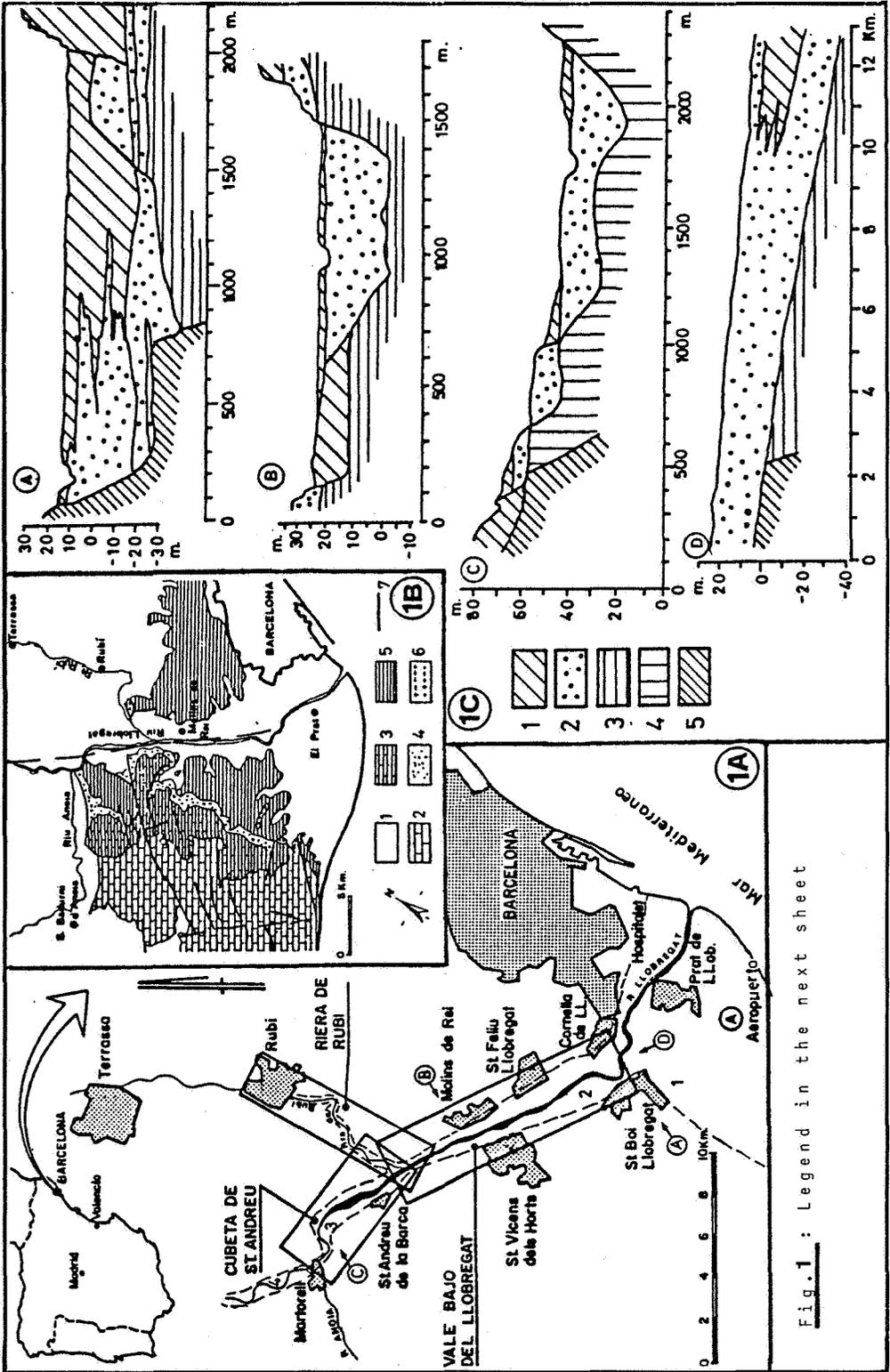
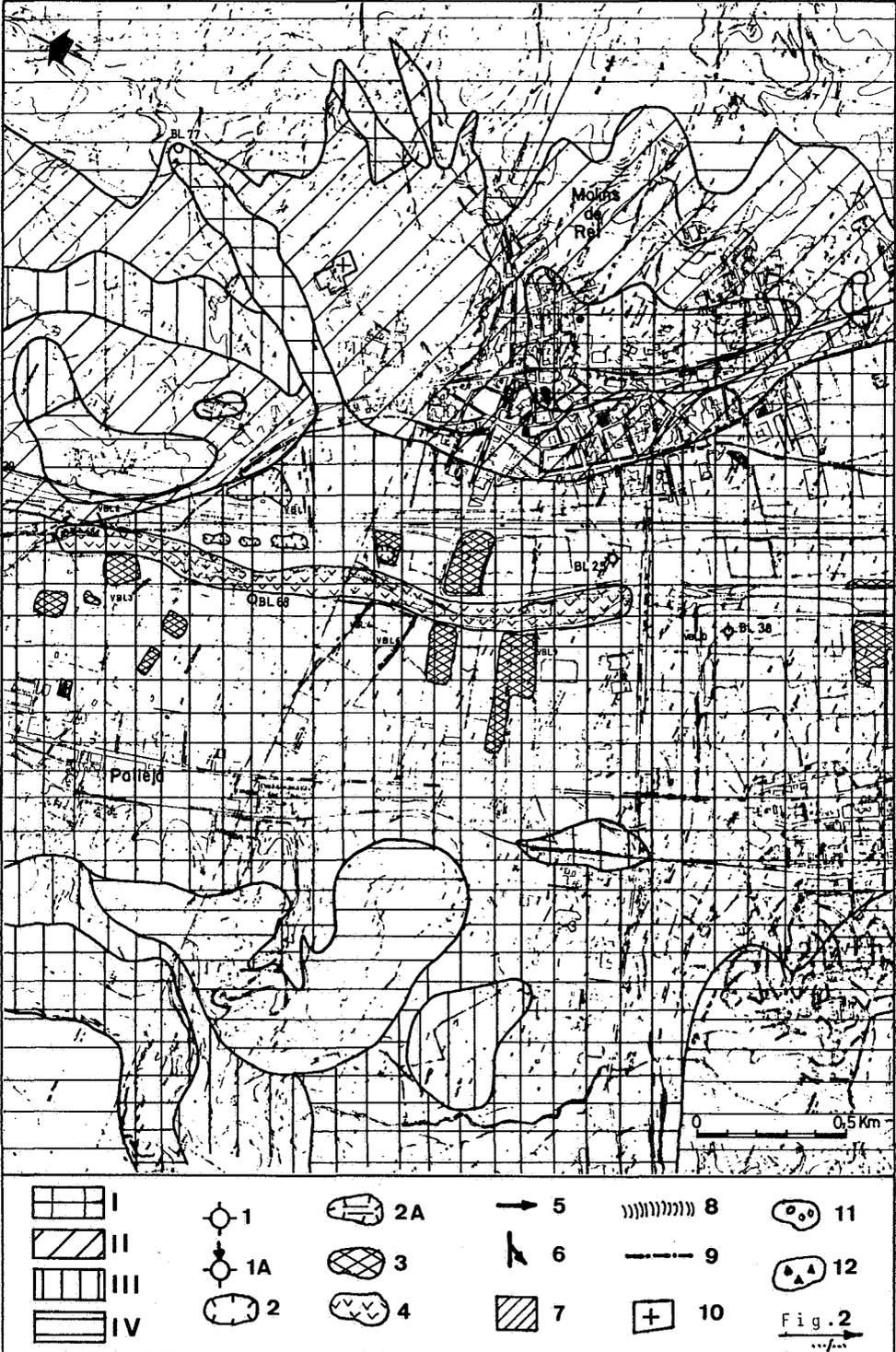


Fig. 1 : Legend in the next sheet



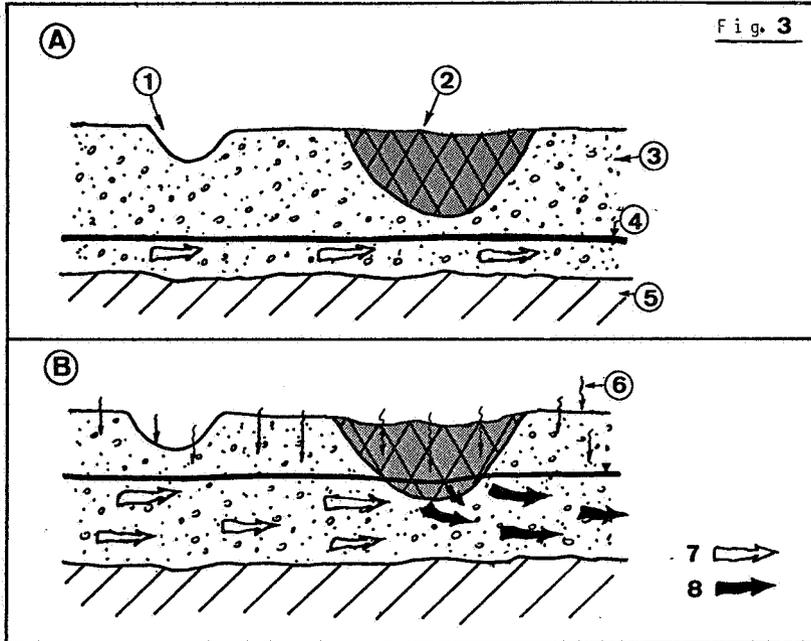


Fig. 3: Groundwater pollution process evolution due to phreatic level rise affecting an old gravel extraction refilled with wastes.
 A: Low phreatic level stadium; B: High phreatic level stadium, 1. Functional gravel exploitation 2. Exploitation refilled with wastes, 3. Gravel and sand aquifer, 4. Phreatic level, 5. Impermeable basement, 6. Rain infiltration, 7. Groundwater flow, 8. Polluted water flow.

- Fig. 1: 1a: Studied zone situation map. Lines indicate the aquifer arising extension. Hydrogeological units: 1. Llobregat delta; 2. Low valley alluvial aquifer; 3. St. Andreu basin; 4. Abrera basin.
- 1b: Low Llobregat geological scheme. 1: Tertiary Quaternary; 2. Jurassic Cretaceous; 3. Triassic; limestones; 4. Triassic sandstones; 5. Paleozoic; 6. Granite; 7. Fault.
- 1c: Schematic geological sections. A: St. Boi-Cornella; B: Molins de Rei; C: St. Andreu basin; D: Longitudinal along low valley. Materials: 1. Clays and silts (Quaternary); 2. Sands and gravels aquifer (Quaternary); 3. Clays (Pliocene); 4. Sandstones and clays (Miocene); 5. Slates and schists (Paleozoic).

Fig. 2: Vulnerability Map (Detail)

- I. Very vulnerable; II. Vulnerable; III. Locally vulnerable; IV. Not much vulnerable; 1. Supply wells; 2. Gravel-pits exploitations; 2a. Swamped gravel pit exploitations; 3. Refilled gravel-pit exploitations; 4. Induced recharge zone by bottom river ploughing; 5. Waste water sludges; 6. Flow derivations; 7. Water treatment plant; 8. Very polluted superficial flow; 9. Channels dredging; 10. Cemeteries

SPECIFIC PROBLEMS OF GROUNDWATER PROTECTION IN ALPINE AREAS OF
WEST CARPATHIANS MTS

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ABSTRACT

High mountains occupy only 1 percent (515 sq.km) of the Slovak territory. They are economically interesting because they represent significant groundwater intake areas. They are mostly protected landscape areas or parts of national parks, so water protection has specific feature there. Point contamination sources (recreation and tourist centres) are dispersed and mostly cause bacterial contamination, in some places also partial eutrophication of lakes. Regional contamination sources act by means of acid- and contaminated precipitation. They affect hydrobiology of brooks and mountain lakes. There is a serious problem concerning extremely intensive soil erosion in high mountains, affecting negatively the water quality and protection. The erosion is partly due to antropogenic influence. Mapping of groundwater vulnerability to contamination included categorization of the geologic basement, hydrogeologic properties of rocks and soil types.

1. INTRODUCTION

The most part of the Slovak territory is occupied by the West Carpathians characterized as a complicated mountain system with a classical nappe structure resulting from the extensive alpinotype folding. Paleozoic granitoids and crystalline schists form cores overlain by schistose sandstone and carbonate Mesozoic lithofacies. These are unconformably overlain by Inner Carpathian Paleogene sediments and Neogene sediments of inner depressions. The internal margin of the West Carpathians is bordered by a neovolcanic garland. It is reflected in very complicated hydrogeologic conditions of the

region, in the formation regime and accumulation of groundwater in individual formations.

The high mountains represent a typical landscape macrocomponent in Slovakia by their peaks projecting markedly above the top forest line and surpassing the absolute altitude 1.500 m. They occupy about 1 percent (515 sq.km) of the Slovak territory, but together with the adjacent mid-highlands areas (800 to 1.500 m a.s.l., 6.350 sq.km, about 14 percent of the Slovak territory) they represent an economically significant complex, because besides exceptional nature and attractive scenery (interesting for tourism and recreation) they represent important intake areas of groundwater. The areas are paid a great attention during regional hydrogeological research of the Slovak territory because of specific problems concerning groundwater protection in relation to other regions. The typical phenomena are most conspicuous in the Vysoké Tatry (High Tatra) Mts. with the highest peak of ČSSR - the Gerlach peak (2.655 m).

2. GROUNDWATER PROTECTION IN ALPINE AREAS

The problem of groundwater protection in alpine environment may be approached from the views of quantity and quality. In our paper we mainly deal with qualitative water protection, discussing the example of the Vysoké Tatry Mts. With respect to quality protection of groundwater in alpine environments two aspects should be considered:

- contamination sources;
- protective function of soil cover and selfpurifying ability of rock environment.

2.1 Contamination sources

Distinguished are local (point) and regional contamination sources. Local contamination sources effects in alpine environments are less intense, being dispersed to quite a great extent. Most significant are recreation centres, tourist centres, and motorism. These cause mostly bacterial contamination of surface- and groundwater (Table 1) and in some places (e.g. Popradské pleso lake) also partial eutrophisation of

lakes (Straskrabová 1986). Their negative effects are interesting because contaminated surface flow waters in mountain parts of valleys infiltrate into groundwaters.

Owing to intensive traffic the areas near roads are mostly contaminated by lead compounds.

Regional contamination sources are particularly significant, although less conspicuous. Regional water contamination is done by the atmosphere and precipitation infiltrating into groundwater through vegetation and soil cover. Acid precipitation on crystalline rock basement causes soil cover degradation and destroys vegetation. Lake acidification has negative biologic effects. Examples of chemical composition of snow from the Vysoké Tatry Mts. are in Table 2. In the alpine environment the precipitation can transport quite a large portion of salts (even more than 50% in crystalline areas). It is serious mainly for antropogenic components causing natural water acidification (SO_4 , NO_3). These phenomena are extremely important because they control the changes in the character of geochemical and biochemical processes in the water-soil-rock system. Degradation of the soil- and vegetation cover results in decreasing groundwater quality.

Table 1. *Partial results of chemical and bacteriological analyses of water samples (High Tatra region)*

Loc.	m a.s.l.	TDS	NO_3 mg/l	SO_4	Bacteria		
					M	P	C
M		15	3.0	3.7	8	6	0
1 J	2025	24	1.8	3.7	2	18	0
A		25	2.6	4.5	4	92	0
M		20	3.5	5.8	16	36	0
2 J	1945	24	2.2	4.1	30	48	0
A		26	2.4	4.9	2	6	50
S		26	2.4	3.3	2	28	0

Loc.	m a.s.l.	TDS	NO ₃ mg/l	SO ₄	Bacteria		
					M	P	C
M		25	2.7	4.9	38	18	380
3 J	1494	25	1.8	4.1	32	148	2400
A		23	2.1	3.7	2	24	76
S		20	1.7	3.7	10	114	80
M		22	2.8	4.1	12	24	80
4 J	895	25	2.1	4.9	14	186	2400
A		116	5.9	23.0	312	500	2400
S		30	2.6	4.9	6	2	2400

Explanatory notes:

M= 26.-29.5.1985

J= 18.-22.7.1985

A= 10.-13.8.1985

S= 25.-26.9.1985

Bacteriological analyses performed by OHS Poprad.

Localization: 1: Velká studňá dolina valley, spring; 2: Run-off from Hincove pleso lake; 3: Run-off from Popradské pleso lake; 4: Tatranská Lesná-Studený potok creek.

Table 2. Chemical composition of snowpack in High Tatra area

Locality (m a.s.l.)	P	pH	TDS	NH ₄ mg/l	NO ₃	SO ₄
Tatranská	X	4.57	14.69	0.59	1.55	4.36
Lomnica	SD	0.77	7.17	0.37	1.14	2.29
(900)	Min.	3.90	4.86	0.16	0.00	1.80
n= 10	Max.	6.45	24.56	1.39	3.40	9.20
Skalnaté	X	4.44	10.25	0.40	1.32	3.15
pleso	SD	0.45	4.32	0.35	1.03	0.96
(1751)	Min.	3.90	5.55	0.00	0.00	1.85
n= 10	Max.	5.40	18.34	1.24	3.15	4.86

Locality (m a.s.l.)	P	pH	TDS	NH ₄ mg/l	NO ₃	SO ₄
Lomnický	X	4.70	13.04	0.37	0.68	2.45
stít	SD	0.78	11.98	0.31	0.73	1.52
(2632)	Min.	3.80	4.96	0.07	0.00	0.41
n= 9	Max.	6.45	43.72	1.06	0.29	4.94

After K. Vrana et al (1987, in press).

2.2 Protective function of soil cover and selfpurifying ability of rock environment

The geologic structure of the region belongs among primary components of natural environment. The core of the Vysoké Tatry Mts. consists of crystalline complexes truncated on the south by an extensive disturbance zone - the Subtatran fault. The contact of the core with the Inner-Carpathian Paleogene sediments of the Podtatranská kotlina basin. On the north the crystalline complexes are bordered with a broad belt of sediments of the mantle series- and Krížna nappe Mesozoic. Valleys and the southern foreland of the Tatra Mts. are filled with a thick layer (in places more than 400 m) of glacigenic, glacifluvial and polygenetic Pleistocene-Holocene sediments with variable grain-size and hydraulic conductivity 10^{-7} to 10 m/s. In the area studied are diverse soil types, subtypes and varieties owing to heterogeneous geologic structure, variable geomorphologic dissection, diverse climatic conditions, a.o. The largest area is occupied by brown soils concentrated on upland levels of the region. On weathering material of silicate rocks the soils display a deeper soil horizon 30-60 cm. Acid and podzolic brown soils with a coarser skelet, strong acid soil reaction (pH below 4.5) comprise about 8% humus. They are usually developed on glacifluvial sediments. On carbonate rocks and debris are developed rendzinas. Beneath the humus horizon (10-40 cm, 15% humus) is frequently weathered carbonate rock with loam admixture and high CaCO₃ content, and neutral to alkaline reaction (Linkeš 1980). On higher relief elements on silicate rocks

podzols occur among litosols. They are extremely permeable, show markedly acid soil reaction (pH about 3), their maximum sorption capacity in a humus horizon is high (20 to 45 meq./100 g). In the iluvial horizon the sorbtion capacity ranges to 50 meq./100 g. In the top parts above forest line are rankers and litosols. They usually only show indications of a humus horizon. The skelet content surpasses 75%.

Rock reefs in the highest levels are partly devoid of soil cover.

3. CONCLUSIONS

The complex analysis of most important factors shows that in the alpine environment the total selfpurifying and filtrating abilities of most rock complexes is low (Hanzel et al., 1984), increasing characteristically from the Mesozoic fissure-karst carbonates through pore glacialic sediments to crystalline fissure rocks, pore glacialfluvial sediments up to fissure-pore Paleogene sandstones. From the view of practical solution of the problems concerning groundwater protection it is important that rock aquifers most sensible to antropogenic contamination owing to their morphologic position, display higher selfpurifying and/or filtrating abilities and thus a certain natural equilibrium. The only exception is represented by pore water of glacialic sediments, and in some places by fissure-karst waters of Mesozoic carbonates. This fact should be considered during technogenic activity in natural environment of the Vysoké Tatry Mts. In alpine mountains of Slovakia a serious problem is extremely intensive soil erosion resulting in reduced overlying protective layer with negative influence upon water protection and its quality. The average denudation of the surface by combined destroying relief-forming processes above the top forest line in the Slovak mountains ranges up to 0.26 mm per year (Midriak, 1985). A large part of the erosion is due to antropogenic influence.

For the mapping of groundwater vulnerability to contamination in alpine environments it is necessary to categorize the geologic basement, hydrogeologic properties of rocks and soil types.

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USING SOIL MAPS TO PREDICT NITRATE LEACHING WITH A
REGIONAL TRANSPORT MODEL

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ABSTRACT

At the Netherlands Soil Survey Institute, a process-oriented simulation model is being developed to predict the vulnerability of groundwater for nitrate pollution. The model will be used to analyse the impact of nitrogen application on a regional scale. It utilizes relatively simple descriptions for all relevant nitrogen transfer reactions like volatilization, mineralization, nitrification, plant uptake and denitrification. The nitrogen load consists of atmospheric deposition, fertilizer, organic manure and crop residues. The methodology of model application is illustrated by predicting nitrate concentrations at the phreatic surface for each combination of soil type and land use in a pilot area. Information on soil type, hydrological conditions and land use was derived from the soil map and the topographical map of the pilot area. The results, grouped in four nitrate concentration classes, are presented on a map of vulnerability to nitrate pollution.

1. INTRODUCTION

High applications of animal manure in agriculture cause severe nitrate pollution of groundwater aquifers in the central, southern and eastern parts of the Netherlands. In order to assist decision-makers to evaluate strategies for controlling manure production, a simulation model for predicting nitrate leaching on a large regional scale is being developed at the Netherlands Soil Survey Institute. Models relating nitrate concentration in groundwater to nitrogen application rates are either based on empirical relationships for various combinations of

land use, soil type and water table (Hoeijmakers, 1986) or on mechanistic descriptions of the nitrogen transfer processes (Berghuijs-Van Dijk et al., 1985). A fundamental criticism of empirical models is that they lack a scientific understanding of the system being described. The complex multi-parameter mechanistic models generally lack input data. Consequently, at the Netherlands Soil Survey Institute we have approached the problem of estimating large-scale water quality response to nitrogen application by developing a relatively simple, yet process-oriented model, called RENLEM (Regional Nitrate Leaching Model). Special attention is paid to achieving a level of generalization for process description that meets the need for data on a regional scale. The final model will be used to predict the quantitative impact of various manure and fertilizer application scenarios on nitrate leaching for characteristic combinations of soil type and land use. In this paper, we illustrate the use of soil maps and associated soil survey information to predict nitrate leaching by using a preliminary version of RENLEM.

2. MODEL STRUCTURE

The model represents all nitrogen transfer processes considered to be important in describing the nitrate leaching behaviour of a soil system. The processes incorporated are: volatilization of NH_3 , mineralization, nitrification, denitrification and plant uptake. Biological fixation and nitrogen/solid-phase interactions are ignored. Nitrogen input is divided into atmospheric deposition, fertilizer, organic manure application and crop residues. An overview of the different processes accounted for in the model is given in Figure 1.

The vertical variability of the soil system is represented by two soil layers: a root zone whose thickness depends on land use, and a subsoil limited by the mean lowest water level (MLW). All nitrogen transformations are assumed to occur in the root zone.

The time step used in the model is six months; that is a summer period from April through September or a winter period from October through March.

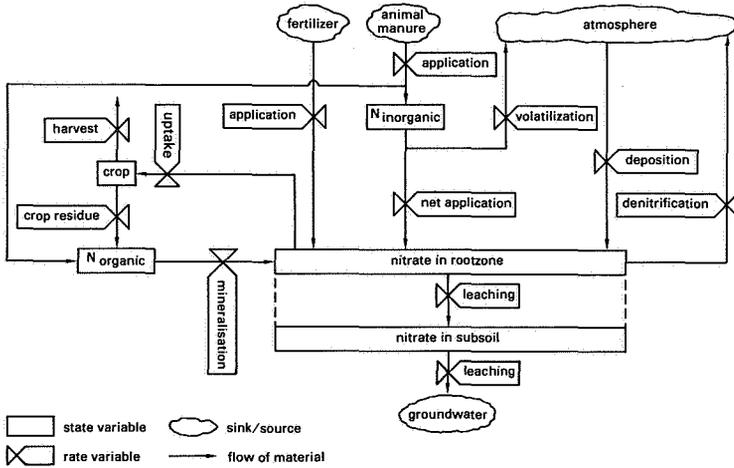


Figure 1. A simplified relation diagram of the regional nitrate leaching model RENLEM

The balance of inorganic and organic nitrogen in the root zone (in $\text{g}\cdot\text{m}^{-2}$) can be derived from Figure 1 and is defined by:

$$\Delta N_{is} = N_a + N_f + N_i + N_m - N_v - N_u - N_d - N_l \quad (1)$$

$$\Delta N_{os} = N_o + N_c - N_m \quad (2)$$

where

ΔN_{is} and ΔN_{os} = change in soil inorganic and organic nitrogen

N_i and N_o = inorganic and organic nitrogen applied in animal manure

N_a = atmospheric deposition N_v = volatilization

N_f = fertilizer application N_u = uptake

N_c = crop-residue input N_d = denitrification

N_m = mineralization N_l = leaching

The following assumptions are made:

- the soil organic nitrogen content scarcely changes from year to year. The annual application of organic nitrogen from animal manure (including dung from grazing cattle) and crop residues thus equals the annual mineralization. The amount of nitrogen mineralized in a

time step is calculated as a fraction of this input. The mineralization fraction f_m depends on the time period, the kind of organic nitrogen and the time of application;

- nitrification is completed within the time step considered;
- volatilization of ammonia is a fraction of the input of mineral nitrogen in animal manure. The volatilization fraction f_v is a function of land use and mode of application;
- uptake of nitrogen by the crop is limited to the summer period and equals a standard requirement;
- denitrification is a fraction of the net nitrogen input to the soil system. The denitrification fraction f_d is reduced by factors that depend on the mean highest water table (MHW) and the soil type.
- The nitrate concentration is calculated with the convection - dispersion equation, assuming negligible diffusion/dispersion and perfect mixing in each soil layer.
- Leaching of nitrate is calculated by multiplying the nitrate concentration with the water flux.

3. DATA REQUIREMENTS

The data required by the model can be summarized as follows:

- Inputs: Nitrogen fluxes: $N_a, N_f, N_i, N_o, N_c, N_u$;
Water flux : F_w ;
- Variables: Initial nitrate concentration per soil layer: $cNO_3(i, t=0)$;
- Parameters: Fractions : f_m, f_v, f_d ;
Land characteristics : MHW, MLW, soil type, land use;
Soil characteristics per layer: T, θ .

Figures for atmospheric deposition, fertilizer use, input of nitrogen from animal sources, distribution of nitrogen in residues and harvested parts of crops, and the nitrogen requirement of a crop are all gathered from relevant literature (e.g. Lammers et al., 1983). The initial concentration of nitrate in each soil layer is assumed to be negligible, because the model reaches equilibrium with nitrogen inputs in a relatively short time period (about 10 years).

4. MODEL APPLICATION

The pilot area chosen to illustrate the methodology of model application on a regional scale is situated in the central part of the Netherlands. It consists of two morphologically different areas: an area in the north with pronounced relief (ice-pushed ridge), and a flat river region. Information on soil types and land use was derived from the 1 : 50 000 soil and topographical maps:

- the ice-pushed ridge (sandy soils) is mainly forest-covered and has some maize fields and heathlands on its edges;
- the river region (predominantly clayey soils) mainly consists of grasslands with some deciduous woodland.

A representative soil profile from each mapping unit was used to derive soil characteristics to be used in simulating nitrate transport.

In order to calculate the concentration of nitrate at the phreatic surface, the following assumptions were made:

- the total annual application of nitrogen amounts to $490 \text{ kg} \cdot \text{ha}^{-1}$;
- the annual application of manure consists only of cattle slurry and is about $64 \text{ tons} \cdot \text{ha}^{-1}$ ($280 \text{ kgN} \cdot \text{ha}^{-1}$) on grassland and about $94 \text{ tons} \cdot \text{ha}^{-1}$ ($415 \text{ kgN} \cdot \text{ha}^{-1}$) on maize;
- the annual nitrogen application in fertilizers is $210 \text{ kg} \cdot \text{ha}^{-1}$ on grassland and $75 \text{ kg} \cdot \text{ha}^{-1}$ on maize;
- the annual atmospheric deposition of nitrogen is $50 \text{ kg} \cdot \text{ha}^{-1}$ independent of land use.

The calculated nitrate concentrations were grouped into four classes: $0\text{-}25 \text{ mg} \cdot \text{l}^{-1}$ (target value), $25\text{-}50 \text{ mg} \cdot \text{l}^{-1}$ (the European Community standard for drinking water); $50\text{-}100 \text{ mg} \cdot \text{l}^{-1}$ (WHO norm); and above $100 \text{ mg} \cdot \text{l}^{-1}$. The results of the model calculations are shown in Figure 3.

The map shows the sandy soils on the ice-pushed ridge to be very sensitive to nitrate leaching. In this area, the nitrogen load from atmospheric deposition on forest results in high nitrate concentrations at the phreatic surface. Very high concentrations occur below the maize fields, because of large applications of animal manure in spring.

Accordingly, the total nitrogen load exceeds the requirement of maize by about $350 \text{ kg} \cdot \text{ha}^{-1}$, of which 17-53% is leached to the groundwater.

The nitrate leaching depends on the depth of the water table; this

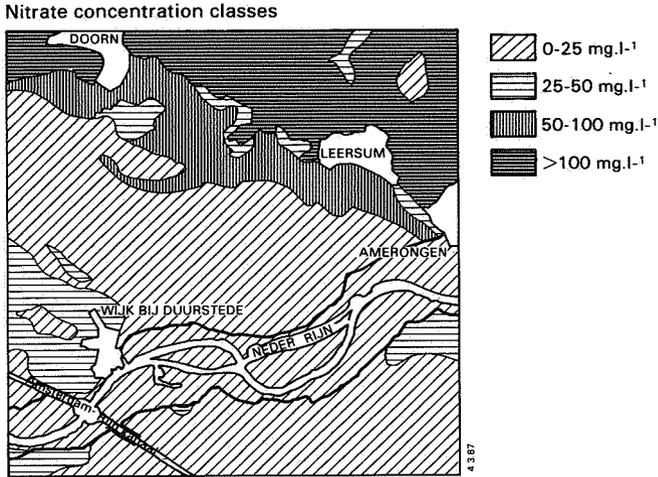


Figure 3. *Map of the nitrate concentration classes at the phreatic surface*

considerably influences the denitrification. Accordingly, the poorly drained sandy soils at the foot of the ice-pushed ridge have a greater denitrification than the deeply drained sandy soils, and therefore have a lower nitrate concentration at the phreatic surface.

In the clayey river area, the nitrate concentration is mostly below the target value of 25 mg.l^{-1} . Only the river bank soils having a depth to the water table greater than 1.10 m show a nitrate concentration above the EC standard for drinking water of 50 mg.l^{-1} . No differences in nitrate concentration classes were found between different land uses (grassland and deciduous woodland) within one soil type in this area. A conclusion at this stage of model development is that the order of magnitude of the calculated nitrate concentration is consistent with available data (Hoeks, 1986; Steenvoorden and Oosterom, 1977). However, denitrification is described simply in this pilot version of RENLEM. Accordingly, factors such as texture, pH and organic matter, which are known to influence denitrification, were not explicitly taken into account. In the final version, denitrification will be described as a first-order process, but research first has to be done to ascertain the precise impact of these factors (including the interactions between them) on the denitrification rate constant. By then, the model will

also be validated.

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VULNERABILITY OF MAJOR GROUNDWATER RESOURCES
IN CYPRUS TO CONTAMINATION FROM THE SURFACE

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ABSTRACT

The most important aquifers of Cyprus, which are exploited for large-scale water supply schemes, are situated in the semi-arid parts of the country and are generally not or only incompletely covered by layers with low permeability. Under the climatic conditions of the region, hazards of movement of pollutants with infiltrating water have to be expected, in particular, in areas where a high hydraulic loading is produced over extended periods by surface water flow, irrigation or artificial infiltration. An efficient protection of water supply wells against degradable contaminations can be achieved through the establishment of protection zones according to guidelines commonly followed in European countries, but the introduction of modern agricultural techniques, urban and industrial developments and waste disposal practices in Cyprus cause hazards of groundwater contamination through nitrates and persistent organic chemicals. A protection of the aquifers exploited for water supplies against far-reaching contaminations may be achieved, to a certain extent, through a regional protection policy. The conception for such a regional approach, based on the definition of the major hazards of contamination and a mapping of the aquifer vulnerability, is discussed in the paper.

1. INTRODUCTION

The island of Cyprus is situated in the eastern Mediterranean region, which is, in general dominated by semi-arid climate conditions. Cyprus

extends over 9250 km². About 30 % of the island is covered by the Troodos Mountain Range, which rises to elevations of nearly 2000 m. The climate in the mountain area is relatively humid with an average annual precipitation between 600 and 1200 mm, and semi-arid in the coastal and inland plains where average rainfall is around 400 mm to < 300 mm/year. The precipitation is concentrated to the period between November and April, practically no rainfall occurs from June to September.

Because of the rather arid conditions in wide parts of Cyprus, the natural groundwater salinity is elevated in many aquifers. Groundwater resources with adequate quality for domestic supply or irrigation are therefore limited, but constitute, on the other hand, a vital resource for the economic life of the country.

The groundwater quality of various aquifers has been adversely affected by intensive groundwater exploitation, which caused intrusion of salt water in coastal areas or an uprising of deeper brackish groundwater in some parts of the inland plains. Man-made groundwater contamination from the surface apparently did not create wide-spread problems until recently. In the past decade, Cyprus experienced a period of rapid economic development with significant growth of urban areas and touristic centres, establishment of numerous small-scale industrial enterprises and an intensification of irrigation agriculture where water for irrigation is available.

These developments created a number of environmental problems and, in particular, various hazards to the quality of groundwater resources. It was therefore necessary to identify the vulnerability of the major aquifers, exploited for domestic supply, to contaminations from the surface. An approach to a preliminary appraisal of the aquifer vulnerability is discussed in this paper for the region between Nicosia, Larnaca and Limassol.

2. MAJOR GROUNDWATER RESOURCES USED FOR DOMESTIC SUPPLY IN THE REGION BETWEEN NICOSIA, LARNACA AND LIMASSOL

The Troodos Massif comprises an ophiolite complex with plutonic and volcanic rock formations which constitute, to some part, fissured aquifers

with generally low productivity. The elevated regions of the Troodos Massif receive relatively high amounts of precipitation, but they don't comprise extensive aquifers which could store or yield sufficient water quantities for large-scale water supply schemes.

The Troodos Massif is surrounded by sedimentary formations, forming the "Circum Troodos Sedimentary Belt", which comprises various interstitial and fissured aquifers with moderate to high productivity. A substantial percentage of recharge of these aquifers is produced by infiltration of surface water from streams originating in the higher parts of the Troodos Mountains.

The most important groundwater resources with adequate quality for domestic supply in the Nicosia - Larnaca - Limassol region (Figure 1) are constituted by sand and gravel aquifers in the western part of the central plain of Cyprus (Mesaoria) and in river valleys in the northeastern, southeastern and southern surroundings of the Troodos Mountain Massif (valleys of the Yiallias, Tremithos, Yermasoyia and Garyllis Rivers). Aquifers with moderate productivity, which are exploited for domestic supply, comprise sand and gravel aquifers in parts of the central plain and fissured aquifers in limited areas of the Troodos Massif (diabase and volcanics in the Stavrovouni area, the Arakapas Fault Belt and the Pyrgos-Parekklisha area) and in the southeastern and southern Troodos foothills (mainly Lefkara Chalk Formation in the area between Klavdhia and Skarinou).

All these aquifers exploited for domestic supply are comprised in out-cropping geological formations, which generally contain marly or clayey intercalations. The aquifers are phreatic or semi-confined. Groundwater from deeper confined aquifers cannot be used for domestic supplies because of elevated Cl or SO₄ concentrations. The groundwater levels in the exploited aquifers are situated at depths between 5 m and several tens of metres below land surface.

3. AQUIFER VULNERABILITY AND CONTAMINATION HAZARDS

Under the climatic conditions of the plain and hill areas of Cyprus, where the most important aquifers are located, direct recharge from

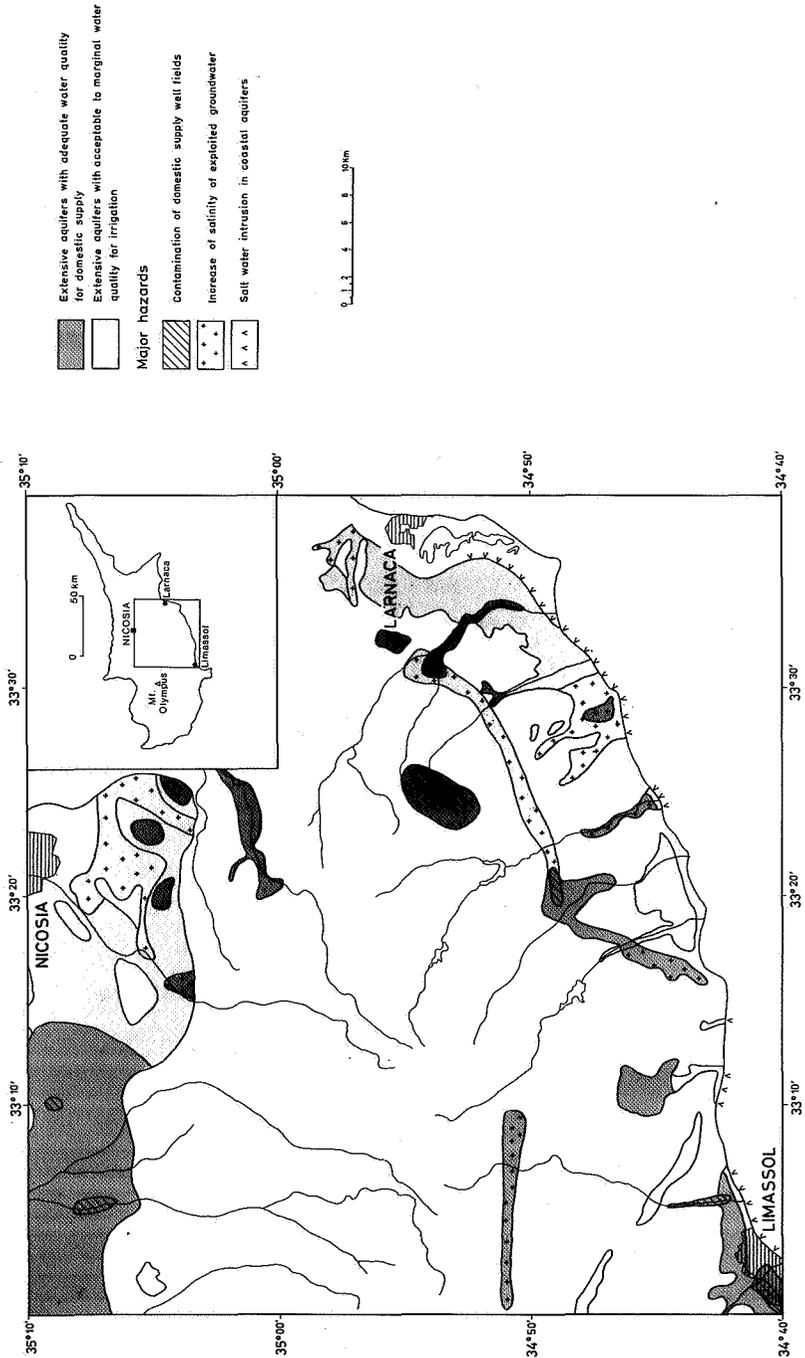


Figure 1. Major groundwater resources and hazards to groundwater quality in the Nicosia - Larnaca - Limassol region

rainfall is very limited. Major hazards of groundwater contamination from polluted infiltrating water are therefore restricted to areas where the groundwater recharge is elevated by natural or man-made reasons. It can be assumed that groundwater recharge is concentrated to areas where an elevated hydraulic loading is created over longer periods by standing or running surface water or by artificial infiltration of water. Such areas comprise in Cyprus in particular

- natural recharge areas where surface flow of streams from the mountain areas crosses the major aquifers in the plain and hill areas,
- irrigation areas,
- areas where domestic or other sewage waters infiltrate.

Potential sources of groundwater contamination in Cyprus are in particular

- unsewered sanitation of settlements,
- industrial wastes,
- intensive agriculture with increased use of fertilizers, herbicides and pesticides.

In the natural recharge areas at the foot of the Troodos Mountains, infiltrating surface water may - at certain periods - be contaminated from residues of agricultural chemicals, in particular pesticides applied in vineyards, or locally from sewage of villages situated upstream in the catchment area. A study of possible surface water contamination in streams of the Troodos Mountains has been initiated by the Geological Survey Department with a particular view to water quality hazards in surface water reservoirs used for domestic supply, but also to groundwater contamination hazards.

In areas with intensive irrigation, fertilizers and soluble residues of pesticides are transported directly with infiltrating irrigation water. Irrigation practices have changed from traditional furrow or flood irrigation to more advanced water-saving techniques like drip-irrigation or mini-sprinkler irrigation in most areas of Cyprus. No specific information on mass transport processes of infiltrating irrigation water under these conditions is available for Cyprus, so far.

Preliminary studies of the groundwater quality and contamination hazards were made in various parts of the Nicosia - Limassol region. In the Akrotiri area west of Limassol, where citrus and table grape planta-

tions are irrigated, locally high nitrate concentrations and traces of DDT and phosphor esters were found in the groundwater (Charalambides 1987). Water levels in this area are situated at around 3 - 10 m below land surface.

In the Peristerona Valley, situated in a rural area in the central plain west of Nicosia, a near-surface sand and gravel aquifer ("Western Mesaoria Upper Aquifer") is exploited through numerous wells for the domestic supply of Nicosia and of surrounding villages as well as for irrigation. Agricultural activities include in particular citrus orchards and stock farming. Dynamic water levels of the groundwater are situated at depths between 5 and > 50 m below land surface. Moderate increases of nitrate concentrations were recorded in some of the production wells during the past few years and the results of stable isotope and tritium analyses show that contaminants can reach the presently exploited aquifer with infiltrating water within a few years.

In areas where sewage waters are infiltrated into the underground, the infiltrating water is often highly contaminated by organic or anorganic pollutants. Disposal of domestic sewage is generally made in towns and villages of Cyprus through absorption pits. A central sewerage system exists for parts of Nicosia town and is in the stage of planning for Limassol and Larnaca. A study of the groundwater quality in the urban area of Nicosia showed a significant relationship between density and duration of habitation and groundwater contamination indicated by elevated concentrations of nitrate and boron (Hahn et al., 1986). Waste waters of industrial enterprises in Cyprus are commonly disposed into open pits or unused boreholes. Though Cyprus is not a highly industrialized country, the practices of industrial waste disposal may create locally severe problems of groundwater contamination. A study of the effects of industrial waste disposal on the groundwater quality has been initiated by the Geological Survey Department, but no representative results are available, so far.

4. NECESSARY MEASURES FOR GROUNDWATER PROTECTION AGAINST CONTAMINATION

For an efficient protection of groundwater resources in Cyprus, two main objectives must be considered:

- Protection of domestic supply wells against degradable contaminants.
- Protection of wells and of aquifers, which are or will be exploited for domestic supply at present or in the future, against non-degradable or persistent contaminants.

A protection of wells against degradable contaminants can, in general, be achieved by an adequate well design and the establishment of protection zones according to guidelines commonly followed in European countries.

To protect the exploited aquifers against persistent contaminations, protection measures in a wider area of the catchment will be required. The catchment areas of the major aquifers and well fields in the Nicosia - Larnaca - Limassol region cover wide parts of the eastern Troodos Mountains. A schematic application of protection measures, e.g. restrictions of agricultural activities in these extended catchments, would not be practicable. A more pragmatic approach should be based on existing hazards of water contamination and the local vulnerability of the water resources.

5. ASSESSMENT OF THE VULNERABILITY OF THE MAJOR GROUNDWATER RESOURCES

A pre-requisite for the development of an efficient water protection policy is the mapping of the vulnerability of the aquifers exploited for domestic supply and the definition of existing hazards of persistent water contamination.

According to a preliminary conception, the following features will be considered in the mapping:

- location of major aquifers and well fields used for domestic supply,
- location of recharge areas,
- type of aquifer, aquifer permeability, thickness and nature of the unsaturated zone,

- location of settlements, industrial areas, irrigation areas, agricultural areas with elevated application of chemicals (e.g. vineyards),
- location of surface water storage reservoirs.

The mapping will produce a relatively simple schematic basis for the planning of water protection measures. At the present stage of knowledge, a more differentiated approach may, however, not be appropriate. To obtain a more adequate basis for the definition of specific water protection measures, it will be necessary to improve the knowledge on transport processes of contaminants under the natural conditions of Cyprus and under various agricultural and waste disposal practices.

ACKNOWLEDGEMENTS

This paper summarizes the results of discussions with various Cypriot and German scientists, in particular Messrs. S. Afrodisis, Dr. A. Charalambides, Dr. M. Geyh, Dr. J. Hahn, Dr. D. Ploethner and G. Schmidt. The contributions of these scientists are greatly acknowledged, as well as the support of the investigations in Cyprus by Dr. G. Constantinou, Director of the Geological Survey Department.

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SUBSTANCE AND WATER BALANCE OF THE GROUNDWATER
CATCHMENT AREA UPPER OKER VALLEY, LOWER SAXONY

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1. INTRODUCTION

Increased nitrate problems in groundwater have been reported in the FRG as well as in other regions of central Europe. In southeast Lower Saxony mainly small public water works (serving less than 10.000 inhabitants), which are situated in the rural areas and have aquifers lower than 50 m, have nitrate problems. It is expected that in future these problems will get worse. In the upper Oker valley, between Braunschweig and the northern edge of the Harz mountains, there are huge groundwater reserves of a still good quality. These reserves are used by several water works. The largest of the works, the water work Börßum, has at present a delivery of 25 Mio cbm per year, serving about 300.000 inhabitants and also delivering process water for a steel work. In its groundwater catchment area like in many other catchment areas in Europe there exists a competition between different kinds of land use which are potable water supply, agriculture, gravel pits, settlements, and in this case sugar industry. Additionally, the soils and flowing waters are contaminated by heavy metals which have been mined for in the Harz mountains for centuries. The nitrate content in the raw water of the water work Börßum increased steadily in the past and has now reached the level of 25 mg/l nitrate. At the beginning of 1986 a case

study was started to carry out a survey of this regionally important water work and to use this as a model for a large aquifer in quarter-ary sediments with a multiple use of the catchment area.

2. QUESTIONS AND METHODS OF RESEARCH

The objectives of this study are to examine to what degree the different kinds of land use influence the water quality and, respectively, to examine how the water quality can be kept on the present high level. The following questions are still to be answered in the course of testing:

- (a) Definition of the catchment area and its geological situation; water contributors from the edge of the Harz mountains; water contributors out of the mesozoic layer below sedimentary rock.
- (b) Relation between groundwater and the flowing waters Oker, Ecker, Ilse, Warne (bank filtrates).
- (c) Possible salinisation processes caused by an increased water delivery, influence of saliferous strata.
- (d) Impact of groundwater recharge with water out of the river Ilse on the discharge and quality of the groundwater
- (e) Influence of arable land use, settlement and industry.
- (f) Impact of gravel pits.
- (g) Influence of heavy metal sedimentation in the flood areas of the Oker, transported in bank filtrates and groundwater discharge.
- (h) Kind of biological and chemical metabolisms in parts of the catchment.
- (i) Effect of the above mentioned processes on the substance and water balance.

Our research aims at a sectional balancing of the water and substance fluctuation in the catchment area. According to this approach we installed observation equipment (Figure). The chemical programme constantly records all important anions and cations of the solution and the most important heavy metals. Organic trace substances like chlorinated hydrocarbons are recorded only periodically.

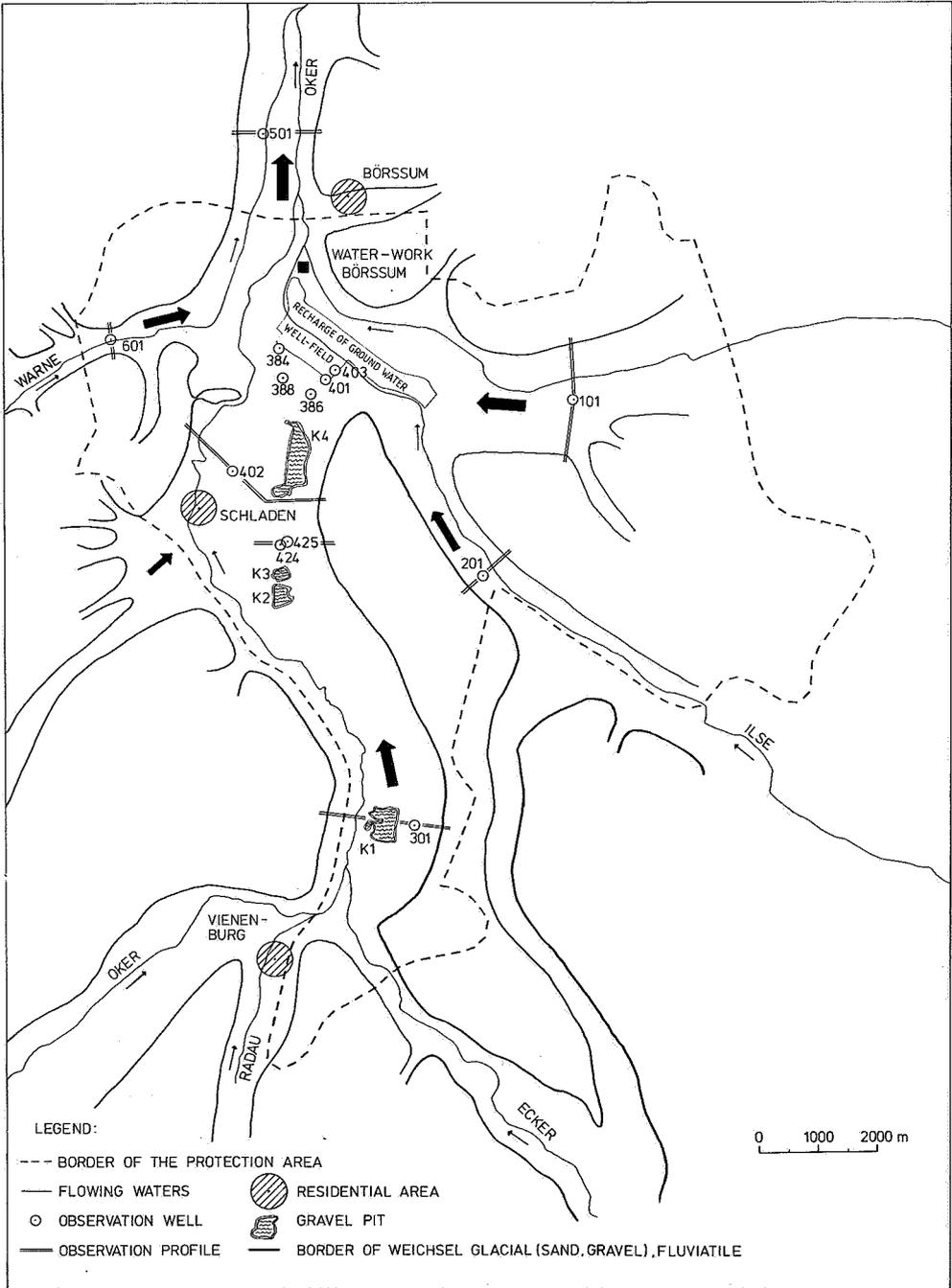


Figure: Protection zone water work Børssum

3. SOME FIRST RESULTS

According to our present knowledge the size of the catchment area is 140 km², that of the protection area 87 km². The area is mainly built of mesozoic rocks, which are covered by quarternary sands and gravel. The prequarternary sediments consist of limestone and marl which belong to the uppercretaceous. The pleistocene sediment cover consists of fluviatile sands and gravel (mainly weichselglacial). The fluviatile deposits have a surprisingly high thickness (Warne valley 57 m, Großes Bruch valley 54 m and Oker valley under the well field more than 60 m).

The main groundwater fluxes are indicated by black arrows in the figure. To our knowledge the larger amount of groundwater flux follows the Oker valley and flows directly into the well field of the water work. The first results of measurement indicate the expected distinct influences of the gravel pits on the groundwater flow, and the infiltration of the river Ecker/Eckergraben into the groundwater and that of the river Oker between the village Schladen and the well field of the water work.

The table shows some chemical data of the groundwater observation wells and gravel pits. As far as possible we tried to sample at different depths. The situation in the Oker valley can be described as follows: At the observation well 301 the groundwater shows concentrations of oxygen and nitrate near to zero. The groundwater flow is aereated by the gravel pits K2, K3, K4 (gravel winning and oxygen diffusion) so that we can measure high nitrate and oxygen values downstream the gravel pits in the wells 424, 386 and 401. The solution in the water at the observation points 301, K2, K3, 424, K4, 386, 401 is of a similar content. Today we can observe a stabilized stratification with the metalimnion between 12 and 15 m in the gravel pit K4. In the other pits gravel is still being produced. The groundwater which flows parallel to the gravel pit K4 has still reduced conditions, (Table). Apparently, the flowing solution has not yet been affected by the gravel pits. The solution content increases in the direction of the well field.

Well or gravel pit no.	depth of sampling (m)	pH	conductivity $\mu\text{S}/\text{cm}$	O ₂ mg/l	NO ₃ mg/l	Cl mg/l	SO ₄ mg/l	Pb $\mu\text{g}/\text{l}$
301	8	6.6	834	0.2	1.0	62	230	1.6
	14	6.6	843	0.2	1.1	63	230	0.9
K 2	0	8.1	567	9.8	27.5	70	130	5.9
K 3	0	8.1	632	10.1	28.8	81	150	5.6
424	6	6.8	706	9.5	30.6	81	150	6.3
	13	6.9	700	9.3	28.8	80	150	1.0
K 4	0	8.1	656	10.0	29.2	86	160	4.1
	10	8.3	667	9.1	29.7	84	160	4.0
	20	7.5	676	4.0	31.0	84	160	5.3
386	8	6.9	753	2.9	33.7	85	160	3.0
	31	7.1	745	4.8	32.9	84	160	1.1
401	8	7.0	740	5.4	30.6	86	170	2.5
	38	7.1	738	5.3	28.4	85	160	
402	5	6.2	844	0.0	5.3	77	270	2.1
	16	6.2	853	0.0	5.3	73	270	3.3
384	9	6.9	1127	0.4	2.0	90	190	1.2
	45	6.9	1138	0.6	0.7	90	170	0.7
601	4	7.2	2250	3.1	33.7	400	220	2.0
	31	7.2	3660	3.2	29.2	790	410	0.2
101	4	6.9	2390	0.0	0.04	93	990	2.6
	50	6.9	2360	0.1	0.04	94	980	2.5

Table: Chemical data of groundwater and gravel pits,
observation Sept./Okt. 1986

In the side-valleys we have found the following situation:

The groundwater in the valley Großes Bruch (well 101) and also in the Warne valley (well 601) shows high salt contents which increase with depth. The solution content is to a large degree influenced by a local succession of formations and to a lesser degree by the land use. Furthermore the water of well 601 indicates the influence of a salt dome situated near by.

The concentrations of heavy metals, measured at all observation points, are below the limits for potable water. But in the gravel pits the concentrations of e. g. lead are in most of the observed cases higher than in the groundwater, (Table). This is probably influenced by an atmospheric input and by the erosion of contaminated soils and gravel pit banks.

A first inventory of our study shows

- (a) that we will probably find different mechanisms of nitrate reduction (heterotrophic and autotrophic denitrification ?).
- (b) that the gravel pits work like aerators and that they influence the chemical property of the groundwater to a considerable degree.
- (c) a clear contribution of agricultural land use to groundwater load
- (c) in one valley a clear influence of a salt dome

We hope that further geological, chemical and microbiological investigations, which will be carried out in the near future, will give us more information about the groundwater situation of this catchment area.

ACKNOWLEDGMENTS

The authors wish to thank the Umweltbundesamt/FRG for the financial assistance.

**TOPIC 4: VULNERABILITY IN RELATION TO SUBSURFACE
BEHAVIOUR OF INORGANIC POLLUTANTS**

VULNERABILITY IN RELATION TO PHYSICO-CHEMICAL COMPOUND BEHAVIOUR, AND SPATIALLY VARIABLE SOIL PROPERTIES

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INTRODUCTION

Soil quality assessment should be based on the relation between composition and functioning of soil (VTCB, 1986). When conditions are imposed on the soil causing changes in its composition, one or more functions may be affected adversely. Whereas the nature of the perturbation determines which soil function is the first to be affected, both the perturbation rate and soil vulnerability control how fast soil quality deteriorates. Here vulnerability is defined as the lack of (buffer) capacity to counter changes, i.e. to return to approximately the original situation within a short-relaxation time.

The scope of this contribution is to relate in general terms the vulnerability with behaviour of contaminants. For comprehensiveness, processes and trends are given emphasis rather than exhaustive treatment of some of the many nutrient elements involved. Vulnerability is illustrated mainly with reference to transport and uptake by plants. In view of the importance of, and recent emphasis given to, soil heterogeneity (spatial variability) this topic is also given some consideration.

PHYSICO-CHEMICAL INTERPRETATION OF VULNERABILITY

Within the context of soil pollution, the increase of contaminant inflow is generally the kind of perturbation of interest. The interaction of the soil-groundwater system with its surroundings (e.g. immission, emission) inevitably involves the boundaries of the system. For the soil system these are chosen as the interfaces with 1. the atmosphere, 2. the saturated groundwater zone (i.e. freatic level), and 3. the interface with living organisms (i.e. skin, root

surface). For the groundwater system such a demarcation is less easy to give, but for the scope and the emphasis in this paper it suffices to define groundwater as the zone receiving percolation water. Perturbation of the balance in the soil system by an increase of (inorganic) contaminant inflow generally implies that the distributions of inorganic solutes over the soil phases (gaseous, liquid, solid) are changed. A new equilibrium will be attained by a shift in the distributions which is often such that effects of the perturbation are attenuated. Both the capacity to attenuate continuing perturbations and the relaxation time to reach a new equilibrium control the overall response of the system and hence control soil vulnerability in a physico-chemical sense. This interpretation is applicable to both the soil and the groundwater system. Processes affecting the distribution of solutes over the various soil phases, thus controlling vulnerability, are the interaction processes (ad)sorption and desorption, chemical precipitation and dissolution, complexation and (biological) decomposition. These processes influence and are influenced by phenomena controlling the mobility. Due to the key position of the concentrations in solution with respect to speciation, transport and bio-availability (De Haan and Van Riemsdijk, 1986) the solution concentration is often the starting point for the evaluation of contaminant behaviour. In the following sections we will indicate how differences in the nature of the contaminant and the composition of soil influence the effect of contamination.

INTERACTION PROCESSES

One of the processes often studied is adsorption (and to a lesser degree desorption) on which an exhaustive literature exists. Adsorption is usually described by relating the concentration in the equilibrium solution to the concentration associated with the (charged) solid-solution interface. Models used for the description of adsorption phenomena vary from relatively simple equations (e.g. linear, Freundlich, Langmuir), that consider only one solute, to (multicomponent) exchange relations and involved electrochemical models. Model choice depends on practical and theoretical considerations such as sophistication, system knowledge, accuracy, and complications due to solute specific and soil specific properties. For macronutrients a change in the distribution over the soil phases influences the distributions of other solutes

requiring descriptions with exchange or electrochemical models (Bolt and Van Riemsdijk, 1982), whereas for micronutrients a constant background electrolyte is often assumed for which simple monocomponent models may suffice. Application of electrochemical models based on detailed mechanistic visualizations of the solid-solution interface (continuity of mass and potential) is usually limited to pure minerals due to model complexity and detailed input required. However, accuracy and versatility (effects of e.g. pH, ionic strength) are high (Sigg and Stumm, 1981). Applying such models to phosphate adsorption on goethite Van Riemsdijk and Van Der Zee (1986) showed the relatively small pH-dependence in the acid pH-range: Fig. 1.

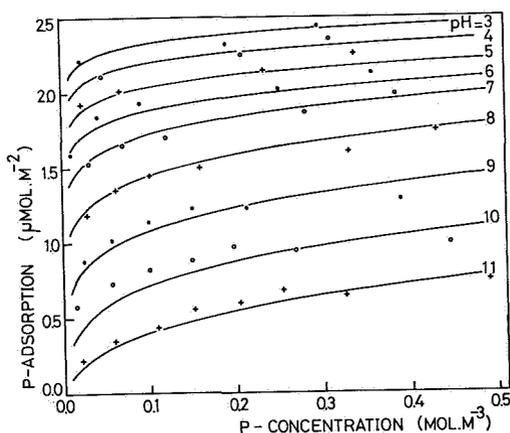


Figure 1: Adsorption isotherms calculated with the one-pK Basic Stern model for phosphate adsorption on Goethite. Experimental data of Bowden et al (1980).

This supported the validity of the approximation often made to neglect this effect in the case of small pH-variations (Van Der Zee et al., 1986). If specific properties of soil material or solute are not taken into account applicability of models may be very limited. Thus exchange-reactions are often described with semi-empirical equations such as the Gapon equation.

Besides that this relation is valid only for part of the complete range of exchange, the Gapon constant (K_G) is not really a constant (Bruggenwert and Kamphorst, 1982). Heterogeneity of e.g. the clay mineral surface may cause

different interaction phenomena. Thus for K-exchange against Ca at illitic clays three types of interaction with each a particular, apparent K_G may occur: (1) very specific $K_{G \rightarrow \infty}$ intra lattice diffusion, (2) preferential ($K_G \approx 100-200$) edge or edge-interlattice adsorption, and (3) planar side exchange ($K_G \approx 0,5$) (Bolt et al, 1963) Similar trends were found for NH_4^+ -adsorption (Bruggenwert and Kamphorst, 1982). The effect of soil mineral heterogeneity for oxides was discussed recently by Van Riemsdijk et al., (1986).

At relevant concentrations in solution microelements adsorb predominantly onto reactive surfaces with a high specificity for these components. Then relatively simple adsorption equations lead to an accurate description in the case of a constant background electrolyte (Harmsen, 1977; Chardon, 1984). If, however, experimental results for different conditions of e.g. pH, electrolyte composition, etc. are to be combined in a unified description adaptations of the adsorption equations are necessary. For the description of Cd-adsorption (Christensen, 1980; Chardon, 1984) or Cu-adsorption (based on findings from Lexmond, 1980) for particular conditions an explicit relation between adsorbed amount (q) and concentration (c) may be derived: $q = k^* oc^a c_H^b c^n$ where for Cd: $a=1$, $b=-0.5$ and $n=0.85$, and for Cu: $a=1$, $b=-0.5$ and $n=0.5$. This extended Freundlich equation thus explicitly incorporates the effects of organic carbon content (oc) and pH. Clearly metal complexation and a change in other variables (redox potential) may affect the values of the constants.

Other speciation processes may significantly influence adsorption and complicate parameter assessment apart from the mentioned effect of heterogeneity of soil (e.g. % oc) and of soil solution (e.g. pH). For phosphate the precipitation of metal phosphates may obscure the adsorption phenomena and complicate the assessment of adsorption constants (Van Der Zee and Van Riemsdijk, 1986). At the same time the nature of precipitation-dissolution kinetics causes considerable hysteresis in the sorption-desorption curves. It depends on activities in the solution and the solubilities of solid compounds whether precipitation or dissolution prevails. With numerical models such as MINEQL (Westall et al, 1976) and GEOCHEM (Mattigod and Sposito, 1979) the equilibrium composition of a solution as well as the precipitates or minerals controlling this equilibrium may be assessed. Such models require a good description of the components and species present, and of equilibrium constants, and initial composition (De Haan and Van Riemsdijk, 1986). In many

cases the assumption of chemical equilibrium may not be valid due to slow chemical kinetics or (diffusion controlled) physical kinetics. Thus the mineral dissolution rate may affect e.g. the rate of soil acidification due to natural causes and due to enhanced atmospheric deposition of SO_2 , NO_x , and NH_3 (Van Grinsven et al., 1986). An example of diffusion controlled precipitation is described with the unreacted shrinking core model (Lu, 1963). This model is applicable to e.g. pyrite (FeS_2) or chalcopyrite (CuFeS_2) oxidation in mine waste, which is relevant in this context because of the resulting acid production and heavy metal mobilization (Braun et al., 1974). The same model was used by Van Der Zee and Van Riemsdijk (1986c) to describe the slow reaction of phosphate with metal oxide particles of spherical geometry. Precipitation-dissolution phenomena (e.g. for calcium carbonate and evaporites like gypsum) are also of importance in salt affected soils. The calcium concentration may be controlled by different solid phases as well as by specific effects (e.g. presence of Mg) and non-specific effects (ionic strength) of salt concentration (Doner and Pratt, 1969). Complexation reactions and ion pair formation may cause an increase of solubility and of the dissolved solute fraction. Thus solubilities in seawater (calcite: 1 eq.m^{-3} ; gypsum: 108 eq.m^{-3}), with an ionic strength comparable with severely salt affected soils, are larger than in distilled water (calcite: 0.1 eq.m^{-3} ; gypsum : 30 eq.m^{-3}). When gypsum is applied in particular form, its dissolution is often kinetically controlled. This is important in view of the reclamation of salt affected soils (Swartzendruber and Barber, 1965).

RELATION BETWEEN VULNERABILITY AND PSYCHICO-CHEMICAL PROCESSES

The vulnerability of soil and groundwater to adverse effects due to the inflow of contaminants depends among others on the mobility of the contaminants in soil. Usually vulnerability decreases as mobility decreases. The fraction immobilized by sorption, precipitation, etc, may be expressed in terms of the distribution ratio, r_d , which is the immobilized amount divided by the dissolved amount, per unit volume soil. By means of batch experiments the (range of) values of r_d may be assessed and used to evaluate compound mobility. However several reasons may exist why r_d -values derived from batch experiments may not be appropriate to assess mobility in the field. One of

these reasons is non-uniformity of soil such that part of the soil is bypassed by the percolating fluid. Examples are flow around aggregates or through cracks and macropores (Skopp and Warrick, 1974; Van Genuchten et al., 1985). Due to bypass the mobility of contaminants may be significantly higher than as estimated on the basis of batch experiments. A related phenomenon (at least with respect to displacement) is the kinetically controlled retention. Slow kinetics also imply bypass of part of the reaction capacity on time scales that are short with respect to the time required to reach pseudo-equilibrium and will lead to the same effects on displacement as physical flow bypass. Besides an enhanced mobility another effect may be the evolution of a non-symmetrical concentration profile. This phenomenon is also observed for solutes adsorbing according to a non-linear isotherm, such as Cd or Cu.

The other speciation processes (e.g. complexation) may have a pronounced effect on contaminant transport. Where precipitation may regulate the maximum concentration in the system, complexation with organic or inorganic ligands may cause an increase or decrease in the total dissolved contaminant (Harmsen and Bolt, 1982; Chardon, 1984). The effect of slow precipitation kinetics on transport was considered by e.g. Van Der Zee and Van Riemsdijk (1986a) who found concentrations of phosphate in the effluent of rapidly percolated columns, that exceeded phosphate solubility. Due to the short mean residence time of phosphate in the column precipitation was not able to reduce the concentration to the equilibrium concentration.

Another component converted slowly during its presence in soil is nitrate. This component is not very reactive in soil but may be denitrified into N_2 or N_2O in anaerobic layers containing e.g. organic matter or sulfides. The conversion apparently is rather slow with respect to the flow velocities and nitrate loads relevant to areas where large quantities of animal manure slurry are being disposed of. Thus in some parts of the Netherlands nitrate has reached even the deeper groundwater. As a consequence of the prolonged contamination with nitrate it may take a long time before groundwater quality will improve again in those regions. In the same context of animal manure slurry disposal the potential long term deterioration by phosphate of soil percolation water quality is of interest. Since saturation of soil with phosphate occurred at a concentration of a few $\text{mol P}\cdot\text{m}^{-3}$ during 10-20 years and as leaching will occur predominantly at concentrations a few hundred times smaller after disposal is

stopped it becomes clear that the removal of accumulated P may require long times. In view of the small concentration in which P causes surface water eutrophication ($0.001 - 0.003 \text{ mol.m}^{-3}$) it is of interest to assess how long it takes to decrease the concentration to such values by natural leaching processes.

Whereas leaching of contaminants constitutes a hazard to ground water quality it is beneficial to soil quality as it implies the removal of contaminants from this zone. Assuming that contaminant uptake by plants is controlled by the concentration in solution and taking leaching losses into account, contaminant accumulation may be calculated. Generally the information for such a contaminant balance of the soil system is only partly available. For some heavy metals data necessary to estimate immission, leaching and removal due to plant uptake were critically reviewed for the Dutch situation by Ferdinandus (1987). Referring to this work for details we can give an illustration of some trends for a specific compound (cadmium) and situation. For a field (sandy soil, 4% organic matter, pH-KCl 5) receiving Cd from atmospheric deposition and as present in commercial fertilizer the immission rate is approximately, $A = 9 \times 10^{-4} \text{ g.m}^{-2}.\text{y}^{-1}$. Assuming that Cd adsorbs according to a non-linear Freundlich isotherm ($q = kc^n$ with q in g.kg^{-1} and c in g.m^{-3}) reasonable values of k and n are 0.02 and 0.5, respectively, estimated from results of Chardon (1984) for Cd-adsorption in the presence of excess Zn ($\text{Zn/Cd} = 100$, by mass). For a bulk density of 1400 kg.m^{-3} and net infiltration rate of 0.3 m.y^{-1} the leaching losses are given by $L = b_1 x^2 \text{ (g.m}^{-2}.\text{y}^{-1})$ where $b_1 = 3.8 \times 10^{-4}$ and x is the Cd-content in g.m^{-3} . Removal by the crop (barley grain) is calculated using the data of Van Luit (1984). Assuming for simplicity that uptake (U) is also proportional to x^2 , we find $U = b_2 x^2 \text{ (g.m}^{-2}.\text{y}^{-1})$ where $b_2 = 0.16 \times 10^{-4}$ for a harvest of $5000 \text{ kg grain.ha}^{-1}.\text{y}^{-1}$. The accumulation rate is given by $dx/dt = A - B x^2$ with $B = b_1 + b_2$, which may be integrated to yield the Cd-content in soil, x (Figure 2, curves I). At pseudo-steady state ($dx/dt = 0$) the long term equilibrium is given by $x_E = (A/B)^{1/2}$ which equals 1.51 g.m^{-3} or 1.08 mg.kg^{-1} for the situation studied. This value is considered high as it implies a leached concentration of 2.85 ug.L^{-1} which may be compared to the advised maximum of 2.5 ug.L^{-1} allowed in surface water. The content in barley grain (0.07 mg.kg^{-1}) is sufficiently below the maximum of 0.15 mg.kg^{-1} allowed. These calculations were performed for a layer thickness of 1 m. If only a fraction of this thickness (e.g. ploughed layer

of 0.2 m) is to be considered then the times of Figure 2 should be multiplied with this fraction too. The results of this type of calculation gives an indication of Cd-contents that would be in equilibrium with the current immission and Cd-removal. In the following section some complications are discussed.

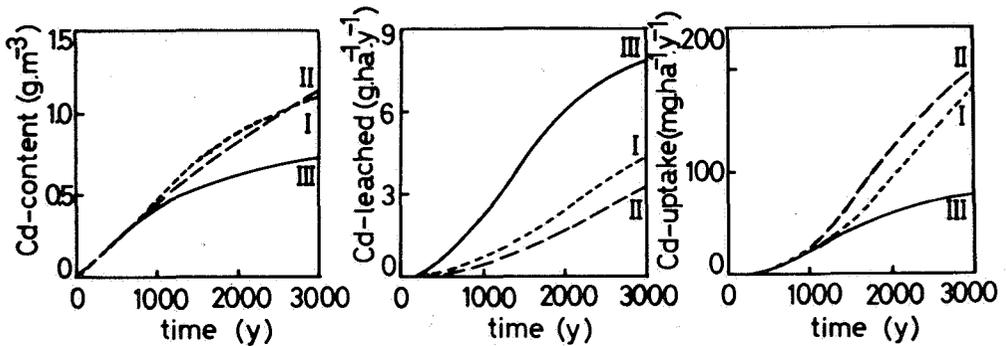


Figure 2: Cadmium content in soil (x), leaching rate of cadmium (L) and cadmium removal rate in barley grain (U) as a function of time.

I: Reference case, II: case with percolation water flux of 0.2 m.y^{-1} , and III: case with adsorption constant $k = 0.01$ (see text)

VULNERABILITY AND HETEROGENEITY

The intrinsic heterogeneity of soil composition was mentioned in the previous sections. It was indicated for transport that small scale heterogeneity (aggregates) may have a profound effect. Nielsen et al., (1973) reported that waterflow may differ considerably with place. During the past decade a fast increasing literature was devoted to the spatial variability of hydraulic soil properties, to scaling theory, and to development or implementation of statistical tools and theories (e.g. the theory of regionalized variables) in order to describe such variability.

Based on the concept of spatially variable flow parameters which are lognormally distributed Dagan and Bresler in a series of papers (reviewed in Bresler et al., 1984) treated the effect on transport of non-reactive solutes. For such solutes transport is controlled largely by the waterflow velocity. Dagan

and Bresler showed that variability in the horizontal plane may be far more important than variability within one column, such as giving rise to pore scale dispersion. The concept of stochastic modelling was also adopted by Van Der Zee and Van Riemsdijk (1986) so as to describe the field averaged displacement of phosphate. For their field, which exhibited spatial differences in the phosphate sorption capacity and in the cumulative disposed quantity of P (present in animal manure) they showed that it is important to consider such differences.

The same reasoning holds not only for transport but for uptake by plants and for accumulation as well. The speciation processes regulate compound mobility and therefore the fractions leached, accumulated and removed by plants. As the immission rate, the soil and the soil solution composition that control mobility, may be spatially variable properties also accumulation, leaching and plant uptake will vary as a function of place. Thus depending on the spatial variable properties (e.g. Freundlich-k, infiltration rate, immission etc.) the accumulating amount may be locally larger or smaller than on average. In Figure 2 the curves are shown for the Cd-content in the reference case (I), the case where the net infiltration rate is 0.2 m.y^{-1} (II) and the case where k is only 0.01 (III). Assuming that for the region considered such differences may occur, e.g. as a consequence of differences in soil type, a large difference in x_E , in leaching, and in uptake by plants will result.

In the study of soil and groundwater pollution spatial variability has only recently been introduced as an aspect of importance. Inasfar as mobility is a main characteristic that influences the effect of pollution and this mobility depends on spatially variable process intensities, it is clear that vulnerability is itself a stochastic property. This realization gives a new dimension to theoretical as well as experimental work required to assess vulnerability.

ACKNOWLEDGEMENT: The first author appreciated helpful discussions with H.N.M. Ferdinandus.

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INFLUENCE OF ACIDIFICATION ON THE CONCENTRATION OF LESS
COMMON TRACE ELEMENTS IN DUTCH GROUNDWATER

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ABSTRACT

Thirty six rare trace elements were measured in groundwater at 31 locations in the Netherlands. Especially in sandy soils with a low pH, relatively high values of some metals are found, while concentrations of trace anionic species like As are decreasing.

1. INTRODUCTION

Knowledge of background levels of trace elements in groundwater is important as a reference in pollution events and in the assessment of groundwater acidification.

Little information is available on a number of less common elements in Dutch groundwater. This relates to their background concentrations, the variation in concentration and the dependence of element concentrations on soil type and groundwater pH.

In this work less common elements in Dutch groundwater have been analyzed in relation to soil type. Concentrations are presented as a function of pH, which gives an indication of the consequences of acidification, especially in sandy soils. Elements measured are: Ag, Al, As, Ba, Br, Cl, Co, Cr, Cs, Eu, Hf, Hg, J, Mn, Mo, Ni, Rb, Sb, Sc, Se, Sr, Th, U, V, W, Zn and at some locations: Au, Ce, La, Lu, Nd, Sm, Sn, Ta, Tb, Yb.

2. SAMPLING AND ANALYSIS

Sampling stations were selected from the national groundwater quality network of the National Institute of Public Health and Environmental Hygiene [1], figure 1.

At 31 location samples were taken at 10 m and 25 m depth using a vacuum pump system in order to minimize contamination [2]. A small sample was used for on-site pH-measurements. Analysis of trace elements requires special precautions to avoid contamination from sampling materials or particulate suspended matter. Immediately after collection the sample is filtered under nitrogen through a 0.45 μm membrane-filter using a full-teflon filtration apparatus [3], and subsequently acidified with HNO_3 to pH 2.

In comparison with common practise to collect unfiltered samples the difference in final results is obvious. For La, for example, the concentration in groundwater ususally is less than 100 ppt. The concentration in clay is about 45 ppm [4]. Assuming that per liter 5 mg of suspended particulate matter is dissolved by acidification to pH=2, this would lead to an incorrect dissolved concentration of 225 ppb La. Other elements showing a similar behaviour are Ce, Co, Eu, Hf, Lu, Sc, Sm, Ta, Ti and Th.

In our laboratory, neutron activation analysis was used after a pre-concentration procedure, which has been applied in the determination of trace elements in sea water [5-8].

3. RESULTS

Average values of the measured elements are listed in table 1, divided into three pH-ranges and two sampling depths. In this table no distinction is made according to soil type.

Average pH-values in groundwater of three soil types clay, sand and peat are given in tabel 2. Especially under sandy soils a fairly wide pH-range has been observed. Low pH-values are measured under sand in the south of the Netherlands (pH = 3.8) in an area sensitive to soil and groundwater acidification.

In table 3, the concentrations of some important elements are given according to soil type and pH. As there is only a limited amount of samples in each group, the values show a great variation.

The effect of increasing acidification of groundwater on the concentrations of less common elements in groundwater can be deduced from figures 2-5. Europium is an example of an element which is dissolved in acidic groundwater. Other elements behaving similarly are Co, Ni, Cr^{III}, Zn, Sc and lanthanides. According to the results for Zn and Ni based on sampling of all 370 measuring points of the national groundwater quality network, highest concentrations and variations can be found in groundwater under sandy soils. Probably this is caused by wide pH ranges in and low cation exchange capacity of sandy soils. Aluminium shows a minimum in dissolved concentration at pH ~ 5.5, which is in agreement with the minimum solubility of Al phases at this pH [9]. Extremely high Al-concentrations can be found around a pH-value of about 4.

Many trace oxy-anions like As, Mo or W show decreasing concentrations with increasing acidification. In this scope also the redox can be of importance, for example the reduced form As^{III} is more soluble. The As concentration may increase in reducing environments [10], particularly in deeper groundwater.

Element correlation studies have shown a striking correlation of vanadium with total organic carbon. An explanation might be found in the combustion of oil, as oil ash may contain considerable amounts of vanadium (~ 5%) [11]. According to Pacyna [12] the atmospheric deposition of vanadium through oil firing is considerable.

Moreover, relatively high V concentrations (up to 100 ppb) have been observed in rainwater, particularly in the more industrialized western part of the Netherlands [13]. The mobility of the oxyanion vanadium in soil is higher than that of trace metals, like Cu and Zn, which carry a greater potential for further dispersion into deeper groundwater. We did not measure sufficient locations to completely exclude dependence of vanadium concentration on soil type. Here further research is needed. Solubility relations are found for Ba and SO₄, for Sr and CO₃ and for U and CO₃. High concentrations of the cation are only possible in water with low concentrations of the anion.

4. CONCLUSIONS

The limited number of data can already give an indication of the consequences of increasing acidification of groundwater in the province of North Brabant and Drenthe, as described in the contribution of W. van Duijvenbooden [14]. It shows that the concentrations of heavy metals like Zn, Co and Ni and also Al will increase with decreasing pH, while anions like Mo or As will decrease in concentration. As a result, an essential anionic trace element like Mo, might not be available in necessary concentrations for plants, leading to plant damage. More research is needed on the influence of acidification on trace element concentrations in groundwater in different soil types. On the other hand very high Al-concentrations may cause troubles in case of drainage of groundwater to surface waters.

Information on the chemical form of trace elements in groundwater is important for a correct description of the behaviour of trace pollutants. Speciation techniques are available, but speciation has to be done in the field immediately after sample collection which requires the use of field laboratories. In this respect more information on the redox state of the sampled groundwater is required.

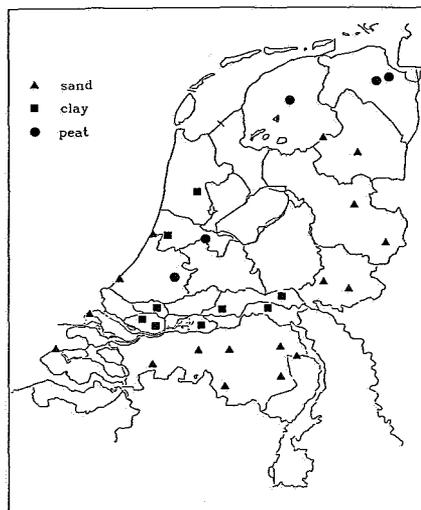


Figure 1: Sampling stations for groundwater on different soil types.

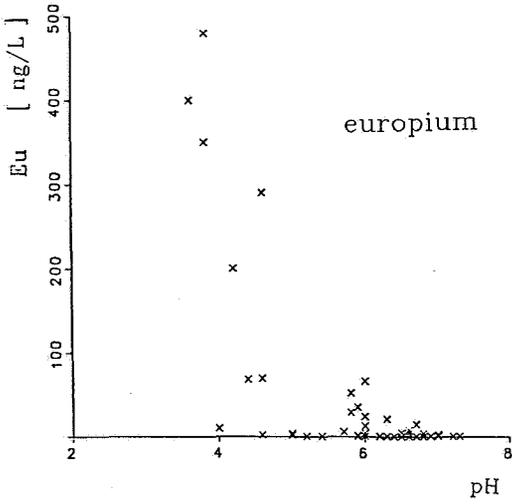


Figure 2: Europium concentrations in groundwater

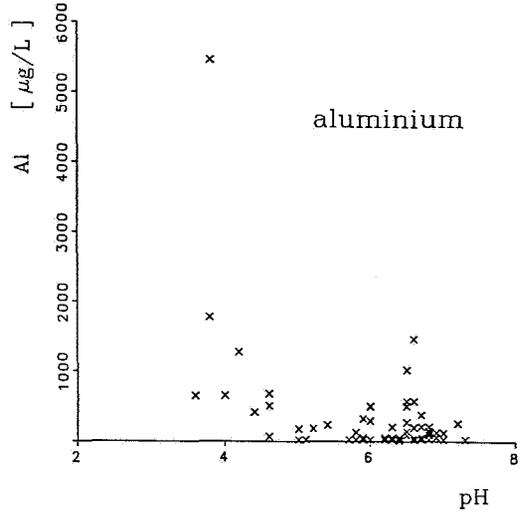


Figure 3: Aluminium concentrations in groundwater

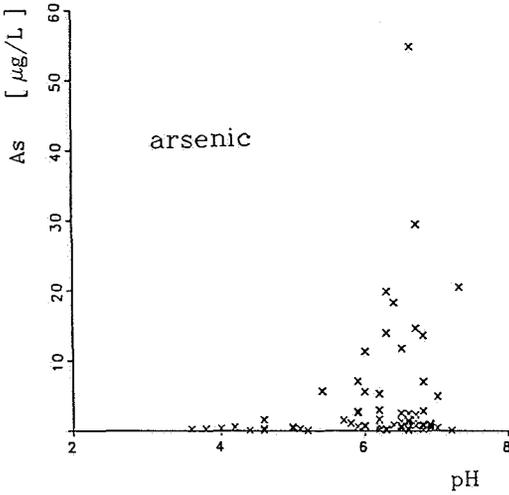


Figure 4: Arsenic concentrations in groundwater

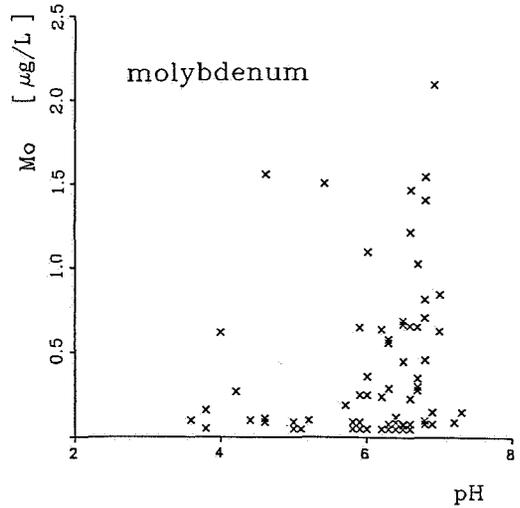


Figure 5: Molybdenum concentrations in groundwater

Table 1. Average concentration of Dutch groundwater in ppb for three pH-ranges and two depths (10 m and 25 m).

Element	pH 3,6-5		pH 5-6		pH 6-7		range
	10 m	25 m	10 m	25 m	10 m	25 m	
Al	1834	410	70	206	69	290	<20-5460
As	0.31	0.43	2.0	0.9	3.0	4.6	<0.01-55
Co	4.9	4.4	0.3	0.21	0.16	0.15	0.01-19.3
Cr ^{IV}	0.55	0.53	0.7	0.61	0.65	0.83	0.03-9.76
Eu	0.21	0.138	0.016	0.021	0.004	0.005	<0.005-4
Hg	0.026	0.014	0.02	0.019	0.018	0.019	0.01-0.05
La	max91	max105	max2.1	<0.1	<0.1	<0.1	<0.1-105
Mn	300	197	436	510	440	430	5-2060
Mo	0.23	0.34	0.14	0.14	0.44	0.47	<0.05-2.1
Ni	16.9	2.4	2.9	0.9	2.9	1.2	0.2-36.7
Sb	0.32	0.04	0.05	0.031	0.06	0.042	<0.02-1.33
Sc	0.15	0.25	0.087	0.069	0.031	0.052	0.05-0.84
Se	0.014	0.011	0.034	0.009	0.012	0.008	<0.005-0.179
Sr	609	365	800	970	870	1549	80-6050
U	0.43	0.29	0.16	0.02	0.11	0.04	<0.01-1.3
V	0.76	0.57	1.2	0.72	0.84	0.83	0.06-3.44
W	0.019	0.035	0.5	0.08	0.18	0.22	<0.015-3.64
Zn	102	53	85	7	23	4.1	<1-440

Table 2. pH in Dutch groundwater for different soil types.

soil type	clay	sand	peat
mean pH	6.4	5.7	6.1
standard deviation	0.3	1.2	0.3
number of samples	9	17	5

Table 3. Average concentrations of selected elements (ppb) for different soil types at 10 m depth.

pH-range	clay		sand			peat	
	5-6	>6-7	<5	5-6	>6-7	5-6	>6
Al	<50	38	2300	<20	41	200	113
As	6.2	3.2	0.3	0.66	3.15	0.87	2.7
Co	0.27	0.16	6.20	0.29	0.15	0.40	0.16
Eu	0.013	0.006	0.260	0.004	0.003	0.032	0.007
Mo	<0.05	0.46	0.27	0.10	0.59	0.35	<0.05

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VULNERABILITY OF GROUNDWATERS TO METAL
MICROPOLLUTANTS : ARE SOILS AND SUBSOILS
GEOCHEMICAL BARRIERS ?

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ABSTRACT

The ability of micropollutants to migrate or to be retained, when migrating through soils and subsoils, is related (i) to their dissolved speciation (complexation, hydrolysis), which depends on the water composition in major anions and cations, (ii) to the mechanisms responsible for mass transfers between the liquid and the solid phases. These theoretical aspects will be illustrated by results obtained from laboratory work performed with mercury. The pollutant mobility is often retarded by temporary trapping on the solid phases (surface complexation). However the delay can be minimal depending on the composition of the liquid phase (complexing agent Cl^- , pH). Moreover changes in the water phase composition can remobilize mercury sorbed on clay particles or oxides/hydroxides by scavenging (effect of peptization of clay minerals or of NaClO injection). These observations will be used to discuss the existence of a risk of migration of metal micropollutants towards aquifers.

INTRODUCTION

How fast and how far do micropollutants migrate through soils and subsoils ? Of special significance is the fate of toxic chemicals leached downwards through soil horizons from surface disposal sites or transported through bottom and bank sediments from a polluted

river towards an alluvial aquifer (Figure 1).

The accidental discharge of organic and inorganic micropollutants in the Rhine river in Basel, Switzerland, in November 1986 gives us a recent example of massive river pollution. What is the rate of spreading of these compounds from the river to the Rhenish aquifer? Are the sediments located at the river/aquifer interface an efficient geochemical barrier?

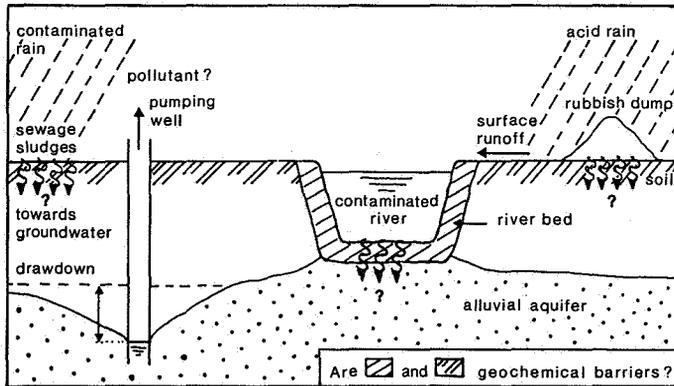


Figure 1. Diagram of possible ways for pollutants towards an alluvial aquifer

Three complementary approaches can provide an understanding of the behaviour of micropollutants : laboratory experiments, field work (experimental investigations or observations of real situations) and mathematical modelling.

The present paper will first review the various physico-chemical mechanisms which are capable of governing the migration through and the retention of metal micropollutants in soils and subsoils. In a second part these concepts will be illustrated by our own laboratory experimental results on mercury.

1. A GENERAL OVERVIEW OF MECHANISMS CONTROLLING THE MIGRATION/RETENTION OF MICROPOLLUTANTS

The biogeochemical processes governing the migration of metal micropollutants through porous media are not fundamentally different from those controlling major metals (Na, K, Ca, Mg). However, being present

in very small quantities, trace metals are easily influenced by major dissolved anions and cations of the aqueous phase (Bourg, 1984). The soils and subsoils can be subdivided into three major components: air, water and the porous solid medium. We will restrict our own discussion to reactions in, and exchanges between the two latter phases.

1.1 Water

Water is an ambivalent medium : it is both a physical support and a solvent. As physical support, water is the vector of the transport of dissolved chemical compounds, and of particulate substances or colloids (solid transport). As solvent, water is the medium of chemical reactions in which pollutants can undergo chemical reactions thus modifying their toxicity or transport characteristics.

1.1.1 Complexation reactions

In the presence of dissolved complexing agents (inorganic coordinat-tes : halides, OH^- , SO_4^{2-} , S^{2-} , NH_3 , PO_4^{3-} , CO_3^{2-} , ... or organic coordinat-tes : fulvic or humic acids...), complexes are formed which are more or less stable depending on the trace metal ion. These complexes can be cationic, anionic or neutral according to concentrations of the elements involved in the reaction.

Let us point out here that the anions listed above are all conjugated bases of acids. They are thus capable of accepting protons, the extent of their protonation being, of course, dependent of the solution pH. The anions most subject to this effect in the pH range of natural waters are CO_3^{2-} , PO_4^{3-} and organic ligands. Complexes of different strengths and charge can thus be formed with the various protonated or unprotonated forms of these anions.

1.1.2 Oxido-reduction reactions

The most important redox reactions take place in the upper part of soils and at the interface between rivers and alluvial aquifers but

they can also occur in any other aquifer with sufficient biological activity. Rain and river water are usually oxidizing but biological respiration can, as the water moves underground, deplete the dissolved oxygen. The ambient conditions are thus favourable to the occurrence of reduction reactions, sometimes extensive enough to produce H_2S (Bize et al., 1981).

These redox reactions most often do not directly involve metal micro-pollutants (with the exception of Cr, As, Se and Hg) but they do influence their solubility and thus their mobility (Bourg, 1987). Some important side reactions are the reduction of sulfate in sulfide, of Fe (III) in Fe (II) and of Mn (IV) in Mn (II).

1.2 The porous medium

The porous medium (soil or subsoil) is often considered as a geochemical barrier, i.e. as a support able to stop the migration of elements by physico-chemical mechanisms. Indeed the global surface charge of the solid is negative, while free metal compounds are cationic. The involved mechanisms call out the solid phase and the liquid phase : they are then heterogeneous.

1.2.1 Precipitation/dissolution

When the solution is saturated with respect to a mineral, precipitation occurs, i.e. a new solid is formed. This notion of precipitation/dissolution is independant of fixation or fixation sites. Precipitation is a faster mechanism than dissolution, but kinetic laws are still ill-known (Schweich and Sardin, 1986).

1.2.2 Uptake/release

Several concepts can explain the fixation or release of a metal micro-pollutant (James et al., 1975). We will present two current cases. The first one is ionic exchange. For metals, it is mainly cationic exchange (A^{Z+} and B^{W+}) according to the reaction (Bolt, 1982) :

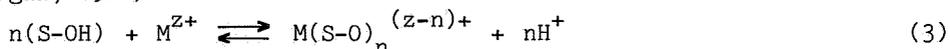


associated with the preservation of electroneutrality in the solid phase, expressed by the relation :

$$N_E = z\bar{A}^{Z+} + w\bar{B}^{W+} \quad (2)$$

in which the bar denotes the surface species and N_E the exchange capacity of the solid.

The second concept is surface complexation. Surface sites (S-OH) play the role of a ligand and the adsorption of metal (M^{Z+}) is assimilated to a surface coordination reaction, $n = 1$ or 2 , (Stumm and Morgan, 1981) :



These reactions are not always instantaneous because of rate-limiting steps in reaction processes (Stumm, 1986). The surface complexation model can be considered as a particular case of ionic exchange where exchanged cations are M^{Z+} and H^+ , H^+ being used as a reference cation. The success of the surface complexation model comes from its accountability of the strong pH dependence of adsorption and of surface charge. Surface sites are then considered as ionizable and comparable with weak acids depending on environmental conditions (Stumm and Morgan, 1981). The main surface sites or cation exchangers are clays, oxides/hydroxides and organic matter.

1.2.3 Scavenging associated with flocculation/peptization

Colloid particles or clays -which show surface sites able to fix micropollutants- are mobile depending on the physico-chemical characteristics of the medium (Bourg, 1984). These particles may be mechanically retained, the porous matrix being considered as a filter. Their mobility is also dependent on the electrostatic charges of the solid surface and on the content in major elements of the solution. Then, clays flocculate in the presence of Na^+ , while the disappearance of this element -i.e. a decrease in ionic strength- leads to a peptization of clays which disperse in the porous medium scavenged by the percolating fluid.

On the other hand, some solids can dissolve, depending on environmental conditions, thus releasing then adsorbed or coprecipitated micropollutants. This is the case of Fe and Mn oxides/hydroxides which

are dissolved at low pH and/or under reducing conditions (Jenne, 1968).

From this short survey it follows that before any experiment or modeling, it is important to determine the preponderant mechanisms allowing to describe the behaviour of a metal micropollutant. In this purpose, it is necessary to know (i) not only the chemical species in the solution (according to the complexation, the redox reactions and the potential precipitation of micropollutants), (ii) but also the geochemical properties of the porous matrix in order to propound hypotheses or descriptive/predicting models.

Only experiments or computations allow to confirm the hypotheses, until a limit appears which makes the conceptualization go forward.

2. APPLICATION TO MERCURY

2.1 Materials and methods

Experiments were performed using monodimensional model systems of the column type. Altuglas columns were filled with 690 g of natural quartz sand (99 % quartz, 1 % feldspars, 1 ‰ clay minerals and traces of oxides/hydroxides of Fe and Mn). The effective pore volume (V_p) was 0,140 - 145 l. The mercury solutions were composed of a mercury (II) salt (chloride or nitrate) dissolved in distilled water, a sodium (NaCl or NaNO_3) or an acid (HCl or HNO_3) to give a total Hg concentration (C_0) of about 0,5 $\mu\text{mol/l}$. The dissolved Hg speciation was calculated with a computer model using thermodynamic constants collected in the literature (Behra, 1987).

The solutions were percolated through the sand columns at a mean pore velocity of 7,5 to $8,5 \cdot 10^{-5}$ m/s. Before each experiment, the sand-aqueous solution system was equilibrated by running a mercury free solution through the column until the pH and conductivity are identical at the inlet and at the outlet of the column. The mercury (II) solutions was then injected.

The total mercury concentration (C) in the eluted fluid was followed as a function of time, by analysing the collected liquids with flame-

less atomic absorption (cold vapor), immediately after sampling.

2.2 Results

To illustrate the theoretical aspects of migration/retention of metal micropollutants through/on a porous medium, we will describe results obtained from laboratory experiments performed with mercury.

2.2.1 Ligand-mercury complexation in solution

Two sodium salts were used : NaCl (with HgCl_2) and NaNO_3 (with $\text{Hg}(\text{NO}_3)_2$). Cl^- forms strong complexes with Hg^{2+} , while NO_3^- cannot. Without Cl^- , complexes between Hg^{2+} and OH^- are formed (hydrolysis). When NaCl or NaNO_3 concentration is 10^{-2} M, the most abundant species is a neutral complex : HgCl_2 or $\text{Hg}(\text{OH})_2$ (Table 1).

Table 1. The three major species of mercury¹ in different experiments

Experimental conditions					
NaCl 1M	HCl 10^{-2} M	HNO_3 10^{-2} M	NaCl 10^{-2} M	NaNO_3 10^{-2} M	NaNO_3 1M
HgCl_4^{2-} 79	HgCl_2 93	Hg^{2+} 95	HgCl_2 91	$\text{Hg}(\text{OH})_2$ 100	$\text{Hg}(\text{OH})_2$ 100
HgCl_3^- 19	HgCl_3^- 7	HgOH^+ 3	HgCl_3^- 7	HgOH^+ 0,2	HgOH^+ 0,2
HgCl_2 2	HgCl_4^{2-} 0,2	HgNO_3^+ 1	HgOHCl 2	Hg^{2+} ($2 \cdot 10^{-3}$)	Hg^{2+} ($3 \cdot 10^{-3}$)

1 Values (C_o % ; $C_o = 0,5 \mu\text{mol/l}$) are determined using a speciation computer model (Behra, 1987)

The results shown in figure 2 clearly demonstrate that Cl^- influences the behaviour of mercury by increasing its rate of transfer through the porous medium.

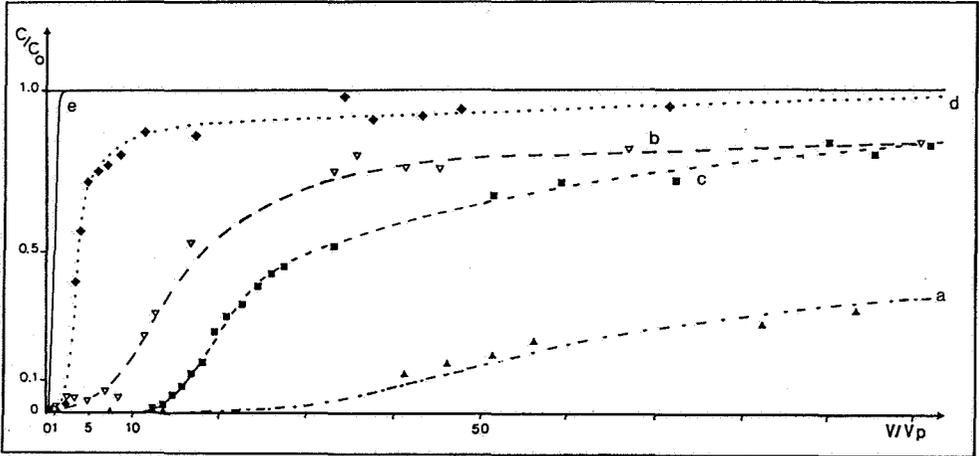


Figure 2. Breakthrough curves in response to injection of mercury solutions through a porous medium : effects of Cl^- and H^+
 (a) \blacktriangle NaNO_3 10^{-2} or (b) ∇ HNO_3 10^{-2} , $\text{Hg}(\text{NO}_3)_2$ 5.10^{-7} M ;
 (c) \blacksquare NaCl 10^{-2} M or (d) \blacklozenge HCl 10^{-2} M, HgCl_2 5.10^{-7} M ;
 (e) - curve of a tracer.

An increase in NaNO_3 concentration until 1 M (in presence of $\text{Hg}(\text{NO}_3)_2$) does not modify the breakthrough curve when with the same concentration of NaCl (in presence of HgCl_2) mercury nearly behaves like a tracer (Behra et al., 1986). With the nitrate electrolyte, the major species is again $\text{Hg}(\text{OH})_2$; with the chloride electrolyte, it is the anionic form HgCl_4^{2-} (Table 1).

So the variation in Cl^- concentration has some consequence on mercury (II) mobility.

2.2.2 Fixation of mercury on the solid phase

May a precipitation of mercury occur ? The results from speciation modelling show that, considering the value of the solubility product of $\text{Hg}(\text{OH})_2$, Hg^{2+} and OH^- cannot precipitate. The concentrations of these two species are always too low.

Is it an ion exchange or a surface complexation ? We have previously shown that Na^+ did not play a significant role in the Hg uptake. Breakthrough curves are the same for Na^+ 0, 10^{-2} and 1 M (Behra et

al., 1986). If there is any competition between Na^+ and Hg^{2+} for adsorption, it must therefore be extremely weak.

If surface complexation occurs, an increase in H^+ concentration must cause a decrease in retention. Two experiments performed at $\text{pH} = 2$ using either HCl (in the presence of HgCl_2) or HNO_3 (in the presence of $\text{Hg}(\text{NO}_3)_2$) show that mercury is less retained than in experiments performed with $\text{NaCl } 10^{-2} \text{ M}$ or $\text{NaNO}_3 10^{-2} \text{ M}$ (Figure 2). The major mercury species in the solution are respectively HgCl_2 and Hg^{2+} (Table 1).

The decrease in mercury uptake under acidic conditions can be explained by the fact that an increase in proton concentration should displace reaction (3) towards the left.

2.2.3 Scavenging

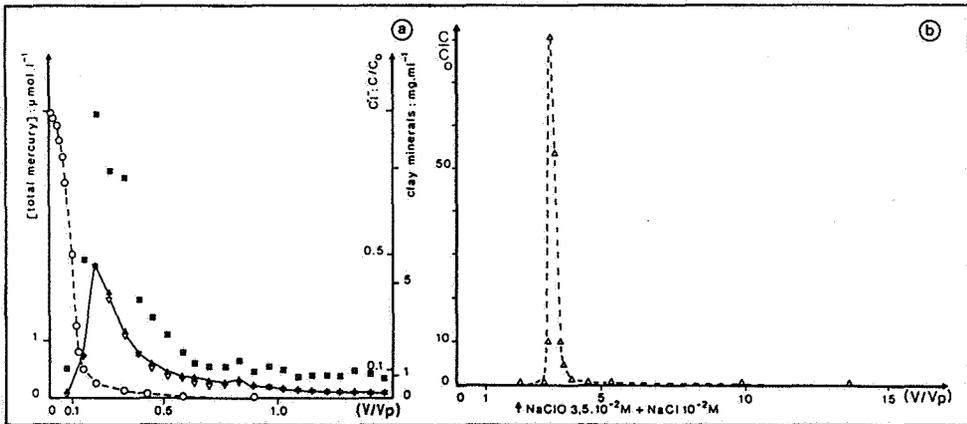


Figure 3. Scavenging of mercury from a contaminated porous medium (from Behra, 1986)

a Mercury associated with peptized clay particles : \circ represents the decrease in Cl^- as an indicator of peptization ; \blacksquare mass of clays released ; \blacktriangle total eluted mercury ; ∇ eluted mercury associated with clays

b Mercury associated with colloids released by NaClO

Several experiments show the role of small or colloid particles in transport/fixation of mercury (Behra, 1986). Two cases are descri-

bed in figure 3. At first, the porous medium is saturated in mercury, i.e. $C/Co = 1$; then, a salt solution without mercury is injected until $C/Co = 0$. After this step the mercury mass balance is deficient : mercury is trapped on the porous matrix. Figure 3a shows the transport of mercury associated with clays when they are peptized. Figure 3b illustrates the role played by surface coatings (oxides/hydroxides of Fe, Al and Mn) which are scoured by an injection of sodium hypochlorite ($NaClO$). When surface coatings are removed out previous to a mercury injection, the retention is very weak (Behra, 1986 ; Behra et al., 1986).

CONCLUSION

The migration of a metal micropollutant -such as mercury- through a water-saturated porous medium depends strongly on the chemical composition of the liquid phase. Increasing concentrations of ligands and protons will accelerate the metal transfer. For example chloride can keep the metal in solution by forming dissolved complexes. Protons inhibit metal adsorption by competing for surface coordination. An exchange model taking into account the speciation of the elements present in the column is then essential to progress with understanding and predicting the propagation of a pollutant such as mercury.

Can soils and subsoils be considered as geochemical barriers ? The answer depends on the metal and environmental conditions. Indeed we shown that a local variation in physico-chemical properties of the substratum (pH, oxidoreduction, concentration of ligands) can be the origin of a migration.

ACKNOWLEDGEMENTS

We thank M. Sardin and D. Schweich (ENSIC, Nancy), P. Muntzer and L. Zilliox (IMF Strasbourg) for valuable suggestions. This work is supported by the Interdisciplinarian Environment Research Programme of CNRS (PIREN) and by the programme EGO7 on "Micropollutants in Groundwater" of the French National Geological Survey. Many thanks

to Elisabeth Jamet for editing the English of the text and Catherine Helmeringer for typing the manuscript.

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IN-SITU ESTIMATIONS OF PROTECTIVE PROPERTIES OF
THE SATURATED ZONE TO GROUNDWATER CONTAMINATION

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ABSTRACT

The chemical removal from the groundwater in the saturated zone is measured. A submersible pump, placed in a withdrawal well, circulates the natural groundwater through a tube to the surface, into an injection well and back through the saturated zone. At the surface chemicals and a tracer are added continuously into the tube. After sampling and analyzing the withdrawn groundwater, the rate of chemical removal in a unit soil volume, is calculated.

1. INTRODUCTION

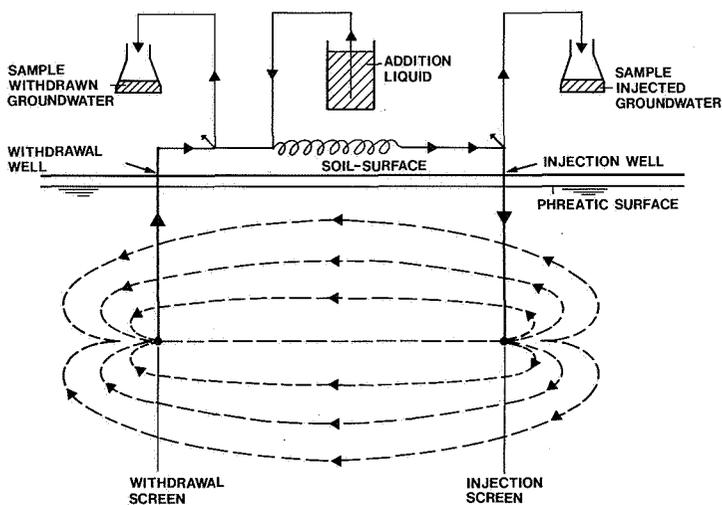
Agricultural or other chemicals can leach into the saturated zone. To predict the groundwater quality, the removal of the chemicals from the groundwater must be known. The applicability of laboratory studies to field studies are often in doubt. Interpretation of field studies can be difficult because of spatial variability. Therefore *in-situ* experiments provide additional knowledge. A special method and three applications are presented. The studied volume of soil is undisturbed and the natural groundwater is used. Differences in the water transmissivity of the soil are not important for the calculations. Also dispersion effects are expected to be unimportant because there is a travel time distribution.

2 METHOD AND MATERIALS

2.1 Introduction

Two bore holes penetrating into the saturated zone are equipped with screens (figure 1). A submersible pump, placed in the withdrawal well, circulates the natural groundwater through a tube to the surface and into the injection well. The groundwater travels in the saturated zone through paths differing in volume. The wells are situated parallel with the hydraulic gradient. The groundwater is withdrawn downstream and injected upstream. In this way most of the injected groundwater is recovered. The circulation rate is constant and so are the travel paths. The groundwater is circulated until differences in the groundwater quality have smoothed out. Then dissolved chemicals, mixed with a tracer, are added continuously into the tube at the surface. The groundwater in the tube is sampled before and after the addition point. The travel time distributions and volumes of the travel paths are calculated. These are needed for the calculation of the rate of chemical removal in a unit soil volume.

Figure 1: Scheme of the experimental set-up



2.2 Travel time distribution

Assume the timespan of the experiment to be divided in n periods and:

$C_{tw}(i)$	mean tracer concentration in the withdrawn groundwater, during period i , $1 \leq i \leq n$	[dimension= $M \cdot L^{-3}$]
C_{ta}	background tracer concentration in the groundwater	[$M \cdot L^{-3}$]
$C_{ti}(i)$	mean tracer concentration in the injected water, during period i , $1 \leq i \leq n$	[$M \cdot L^{-3}$]
$a(i)$	fraction of the injected groundwater during period 1 that is withdrawn during period i , $1 \leq i \leq n$	[1]
j, i	ranknumbers	[1]
n	largest ranknumber	[1]

The tracer is added continuously with a constant rate q into the tube at the surface. Therefore the relation between $C_{ti}(i)$ and $C_{tw}(i)$ is:

$$C_{ti}(i) = C_{tw}(i) + C_{t1} \cdot q / Q, \quad 1 \leq i \leq n$$

C_{t1}	tracer concentration in the added liquid	[$M \cdot L^{-3}$]
q	amount of liquid added each period	[M^3]
Q	amount of groundwater withdrawn and infiltrated each period	[M^3]

Note that Q and q are kept constant and $q \ll Q$.

The tracer concentration injected during the first period arrives during the first period through the smallest travel path (number 1) into the withdrawal well. The relation between the mean injected and withdrawn concentration during the first period is:

$$C_{tw}(1) = a(1) \cdot C_{ti}(1)$$

The withdrawn tracer concentration during the second period equals:

$$C_{tw}(2) = a(1)*C_{ti}(2)+a(2)*C_{ti}(1)$$

In general we can write:

$$C_{tw}(j)-C_{ta} = \sum_{i=1}^j \{a(i)*C_{ti}(j-i+1)\}, \quad 1 \leq j \leq n \quad (1)$$

2.3 Volume of travel paths

The total volume $V(j)$ of all travel paths 1 to j equals the sum of volumes of groundwater injected into these paths just before the injected tracer arrives into the withdrawal well.

$$V(j) = \sum_{i=1}^j \{(i-1)*a(i)\} * Q \quad [L^3] \quad (2)$$

2.4 Chemical removal from the groundwater

Assume the background concentrations to be zero. The fraction chemical removed in the saturated zone is the difference between the fraction withdrawn of the tracer in the saturated zone and the fraction withdrawn of the chemical in the saturated zone. The amount chemical removed is the fraction chemical removed times the injected amount of chemical. Because the volumes of the travel paths are known (equation 2), the cumulative amount $X(j)$ of chemical removed per unit volume of soil after period j , can be calculated assuming the porosity p to be known.

$$X(j) = p * C_{cl} * \sum_{i=1}^j \{C_{to}(i)/C_{td} - C_{cw}(i)/C_{cl}\} * \sum_{i=1}^j \{(i-1)*a(i)\}^{-1} \quad (3)$$

$C_{cw}(i)$ chemical concentration in the withdrawn groundwater during period i , $1 \leq i \leq n$

$[M*L^{-3}]$

C_{cl} chemical concentration in the added liquid

$[M*L^{-3}]$

2.5 First order kinetics

The effect of first order kinetics removal is substituted in equation 1, giving equation 4. A homogeneous reactive soil is assumed.

$$C_{cw}(j) = \sum_{i=1}^j \{a(i) * C_{ci}(j-i+1) * e^{(-i*K)}\}, \quad 1 \leq j \leq n \quad [M * L^{-3}] \quad (4)$$

$C_{ci}(i)$ chemical concentration injected during period i , $1 \leq i \leq n$

K first order rate constant [1]

2.6 Linear equilibrium removal

In the case of linear equilibrium removal, a constant fraction R of the total amount of chemical is in the liquid phase of the soil. An injected chemical concentration arrives R times later than a tracer concentration. Therefore the chemical concentration increase in the withdrawn groundwater is R times slower than the tracers.

2.7 Linear equilibrium and first order removal

The effect of linear equilibrium removal can be fitted best in the beginning of the experiment because non-equilibrium effects are less. Then the difference between the fitted and measured curve is described with first order removal kinetics (equation 4). Iteration gives a good fit.

3 APPLICATION

3.1 Purpose

The method described here has been applied three times. Experiments a and b were performed in groundwater not influenced by agriculture. The purpose was to show the effects of leaching of agrochemicals. The injected concentrations resemble the groundwater quality in a root zone heavily dressed with manure but with a lower nitrate concentration so that even a small removal is measured.

Experiment c was done in a layer where nitrate removal was expected.

3.2 Performance

During experiment a and b groundwater samples were taken at intervals. During experiment c samples were taken continuously with a membrane pump. The circulation rate was always controlled continuously. The dilution was checked by taking samples before and after addition. Table 1 gives specifications for the different experiments.

Table 1: Experimental conditions

Experiment:	a	b	c
groundwater table(m)	3	3	0.5
screen-bore	2"	2"	2"
screen depth (m)	5	6	3.5
screen length(m)	0.1	0.1	0.3
screen distance (m)	1	1	2
circulation rate(m^3h^{-1})	0.025	0.019	0.015
addition rate (m^3h^{-1})	0.00025	0.0002	0.00005
timespan (h)	92	92	450

concentrations in the added liquid ($kg \cdot m^{-3}$):

chloride	12.4	12.4	20
phosphorous (PO_4)	30	28	0
nitrate (NO_3)	10	10	2
kalium	50	50	5.6
natrium	10	10	13

3.3 Results

The concentrations in figure 2a, 2b and 2c, are made dimensionless by abstracting the background and dividing by the addition. The fraction chemical removed is represented by the area between the tracer (chloride) and chemical curves.

fig. 2a fig. 2b fig. 2c
 Dimensionless concentrations in the withdrawn groundwater

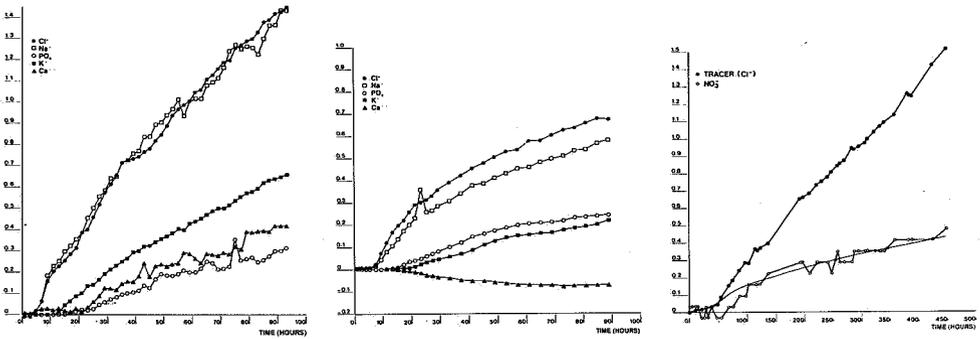


Figure 3 shows the cumulative travel time distribution as a function of time, calculated with equation 1 .

fig. 3a fig. 3b fig. 3c
 Cumulative travelttime distribution in time

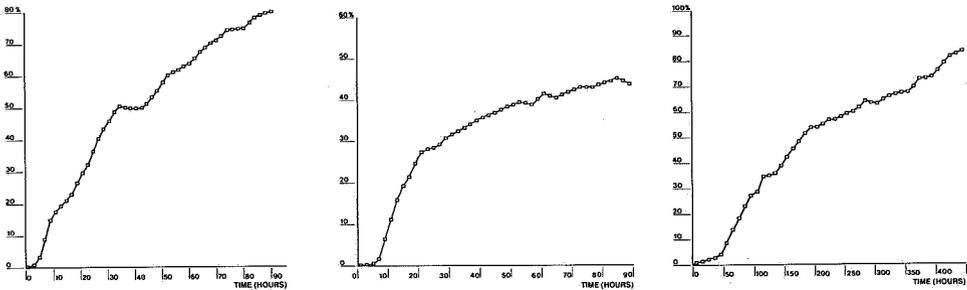


Table 2 mentions the amounts chemical removed at the end of the experiments, calculated with equation 3.

Table 2: Amounts chemical removed ($g \cdot m^{-3}$)

Experiment:	a	b	c
phosphorous (PO_4)	546	440	
nitrate (NO_3)	0	43	3.6
kalium	31	73	
calcium	34	130	
natrium	0	18	

Besides the chemicals removal other quality changes in the groundwater can be measured. During experiments a and b the pH in the withdrawn groundwater decreased although the pH of the added liquid was higher than the pH of the groundwater. Acidification of deeper groundwater can be explained by leaching of agrochemicals.

3.4 Interpretation

In both experiments a and b the phosphorous and kalium removal is about 5000 and 500 kg respectively, calculated for a hectare and a layer of 1 meter. The nitrate removal in experiment b was not reliable because of the high background concentration and its variations.

The unmarked line in figure 2b is calculated with $K= 0.025\text{h}^{-1}$ and $R= 3$ according to paragraph 2.7 and describes the phosphorous removal. The nitrate removal in experiment c is $700\text{ kg}\cdot\text{a}^{-1}$, calculated for a hectare and a layer of 1 meter. The nitrate removal in time of experiment c is fitted with $K= 0.01\text{ h}^{-1}$ only (unmarked line in figure 2c).

First order rate constants and linear equilibrium constants fitted to these experiments, are not reliable for concentrations other than measured. Also the chemical removal is in general not only dependent on its own concentration and the soil but also on all other chemicals and their concentrations.

4 CONCLUSIONS

The chemical removal from the groundwater in the saturated zone, is measured *in-situ* in a simple way. The amounts of removed K, PO_4 and NO_3 are $500\text{ g}\cdot\text{m}^{-3}$, $50\text{ g}\cdot\text{m}^{-3}$ and $70\text{ g}\cdot\text{m}^{-3}\cdot\text{a}^{-1}$ respectively. Also the removal can be described with first order kinetic and linear equilibrium processes. The effects of complex chemical transformations *in-situ* can be shown.

ECONOMIC MEASURES AGAINST LEACHING LOSSES OF NITROGEN

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ABSTRACT

In Sweden payments of wheat and barley are based on protein contents in the grain. While yields and protein contents rise to a maximum level with increased fertilizing, the N-leaching is unlimited. Increasing fertilization of cereal crops leads to increased N-leaching to the surface water and groundwater. Leaching will decrease if the protein bonus is abolished, if the price of nitrogen is increased and if the grain price is decreased.

1. INTRODUCTION

In Sweden quality bonus payments have been introduced for wheat and barley based on the protein content in the grain. Since the protein content increases with increased inputs of nitrogen fertilizers, at least to a certain limit, this encourages increased fertilization. And this is an expressed aim since the protein content in wheat is sometimes too low for the baking methods used on an industrial scale. The standard levels are 11 % protein for wheat and 12 % for barley. Each percentage point above these levels gives a 4.5 % price increase for spring wheat, 3 % for winter wheat and 1.2 % for barley. Protein contents below the standard level result in price deductions.

2. MATERIAL AND METHODS

The experimental design has been described by Brink & Lindén (1980) and Bergström & Brink (1986). It consists of six well-operating, separate

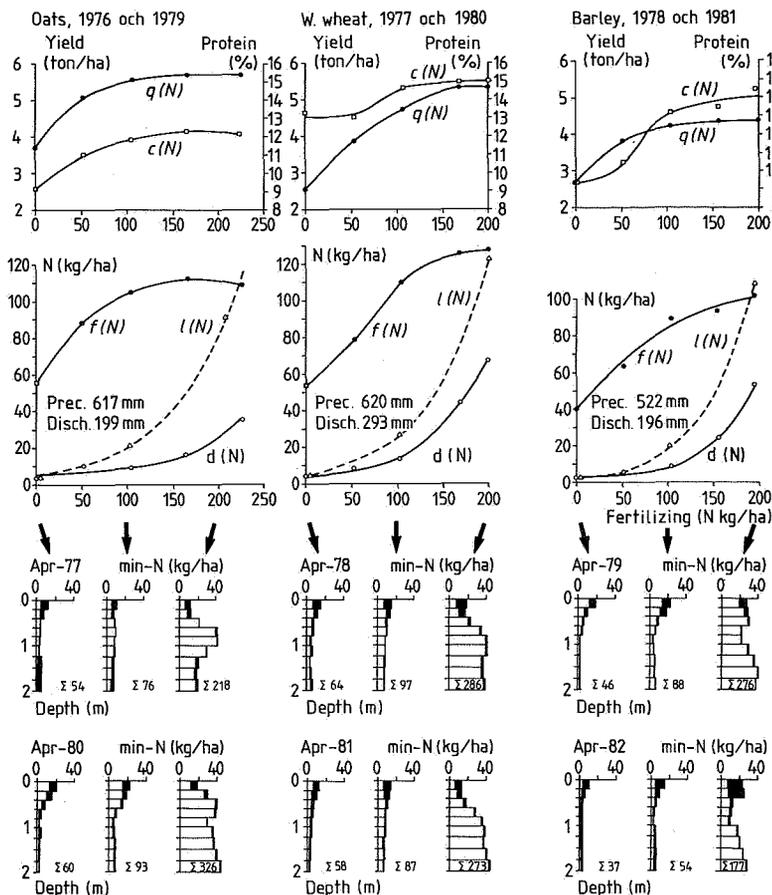


Figure 1. $q(N)$ = yield, $c(N)$ = protein in the grain, $f(N)$ = harvested protein, $d(N)$ = leaching with drainage water, $l(N)$ = $d(N)$ + leaching to horizons below 1 m depth. Means of two ecohydrological years (July-June). Mineral N in soil

plots with tiled drainage, each plot being 0.40 ha. The water discharge from each plot is continuously measured.

The topsoil is a moderately humus-rich heavy sedimentary clay. The subsoil is heavy clay down to 0.5 m and very heavy clay deeper down.

The amount of mineral N in the soil was determined each autumn and spring down to a depth of 2 m according to the procedure described by Lindén (1977). On two occasions the depth was extended to 3 and 4.5 m.

The crop rotation from 1976 was oats, winter wheat and barley. Since 1975 the nitrogen rate was nominally N0, N50, N100, N150 and N200 kg/ha

annually. Commercial fertilizer was used throughout.

3. RESULTS AND DISCUSSION

3.1 Fertilization, harvest and leaching

The top row of diagrams in Figure 1 shows how the yield and the protein content increased considerably at low N-rates and levelled out at high rates. The extra yield became minimal after 70-80 N kg/ha for oats and barley and after about 140 kg/ha for winter wheat. The amount of extra protein obtained was largest up to the 100 kg/ha rate of nitrogen in all three cases and thereafter insignificant.

In the centre row of diagrams we find the harvested N in the grain and the leached amount to the surface water and groundwater. At rates where the yield increased strongly the leaching was small but increased drastically when the yield increase fell or was completely absent.

The lower part of Figure 1 shows how the mineral nitrogen became accumulated and moved from the soil surface down to a depth of 2 m. The variations at the fertilization levels of N0 and N100 were relatively small but were considerable at N200. From the time before the fertilization started to be differentiated in 1975 until December 1981 large quantities of mineral N had migrated below the 1 m depth, as can be seen from the following table (values in kg/ha):

Time	Layer (m)	N0	N100	N200
Dec-74	0-1	25	30	55
Dec-81	0-3	31	120	432
Increase per year	1-3	1	11	54

The annual increase of mineral N within 1-3 m depth divided similarly over the three crops gives the dashed leaching curves in the figure.

If the amount of N taken up in the grain is summed together with the losses to the surface water and groundwater there is a deficit of 0-60 kg/ha. The deficit is covered at least partly through atmospheric deposits (10-20 kg/ha) and nitrogen fixation, which probably amounts to maximum 30 kg/ha. Since the harvest residues were incorporated into the

Table 1. *Coefficients in the equations (1), (2), and (3)*

Coeff.	Oats	W. wheat	Barley	Coeff.	Oats	W. wheat	Barley
Q_0	37.08	25.55	26.25	Q_2	$-2.04 \cdot 10^{-3}$	$-6.86 \cdot 10^{-4}$	$-2.00 \cdot 10^{-3}$
Q_1	0.352	0.277	0.311	Q_3	$3.84 \cdot 10^{-6}$	0	$4.36 \cdot 10^{-6}$
C_0	5.2	13.0	9.2	k	0.011	0.025	0.019
C_{200}	12.3	15.0	14.0	Ni	-45.0	70.0	52.0
L_0	3.912	4.338	4.791	L_2	$9.21 \cdot 10^{-5}$	$-1.12 \cdot 10^{-3}$	$-2.56 \cdot 10^{-3}$
L_1	0.105	0.144	0.174	L_3	$6.33 \cdot 10^{-6}$	$1.68 \cdot 10^{-5}$	$2.09 \cdot 10^{-3}$

soil, the nitrogen in them can be omitted from the balance sheet. Denitrification, immobilization and mineralization at different rates further complicate the picture.

The curves in the figure can be described very well with the following functions of the fertilizer N kg/ha:

$$q = q(N) = Q_0 + Q_1 N + Q_2 N^2 + Q_3 N^3, \quad (1)$$

$$c = c(N) = C_0 + (C_{200} - C_0) / (1 + 10^{k(Ni - N)})^2, \quad (2)$$

$$l = l(N) = L_0 + L_1 N + L_2 N^2 + L_3 N^3, \quad (3)$$

$$f = f(N) = 0.16q(N) \cdot c(N), \quad (4)$$

where q kg/ha is the grain yield, c % is the protein content in the grain, l kg/ha is the leaching, f the amount of harvested nitrogen in the grain, and where 0.16 is the relationship between N-content and protein content. Q , L and k are all constants, C_0 kg/ha is the protein concentration at $N = 0$, and C_{200} at $N = 200$ kg/ha. Ni is the N-value for the inflexion point of an S-shaped curve. All coefficients in (1), (2) and (3) are shown in Table 1.

3.2 Environmental and economic aspects

From environmental aspects the fertilizer rates above 100 N kg/ha are hardly justified. The extra yield became increasingly smaller and the additional yield of protein remained the same, whereas leaching increased strongly. However, this may appear different from the business economics angle.

The term biological optimum is used in production-biological situations to describe the point where an increased input of, for instance, N-fertilizer no longer gives any extra yield. From the ecological viewpoint it is reasonable to also include the nitrogen which disappears into the air and, foremost, to the water, where small amounts occasionally may have positive effects but where large amounts will be disastrous. If we limit ourselves to the leached amount we can obtain an optimum fertilizer level from the derivative of the difference between (4) and (3):

$$f'(N) - l'(N) = 0. \quad (5)$$

At this point the N-leaching grows as rapidly as the N-yield and subsequently faster. We can call the point an *ecobiological optimum*.

As a background to an economic calculation it is possible to start from (1), (2) and (3). Income minus the sum of the fertilizer cost and the environmental costs will be:

$$F(N) = q(N) \cdot p(1 + (c(N) - b) \cdot r) - (N + m \cdot l(N)) \cdot s, \quad (6)$$

where p is the price per harvest unit at b % protein content, r % is the price bonus for each percentage point above b %, s is the cost of the nitrogen and m is an environmental factor. The environmental costs must in some way depend on the leached amount of N . In the simplest case m can be assumed to be constant. The derivative

$$F'(N) = 0 \quad (7)$$

gives the *business economic optimum*, when $m = 0$ and an *environmental economic optimum*, when $m > 0$.

3.3 Optimum curves

Optimum fertilizer levels in Figure 2a are found from (5) and those in Figure 2b and c from (6).

By placing a cost on the environment the optimum fertilization level and income will decrease but, in return, one may avoid for instance the

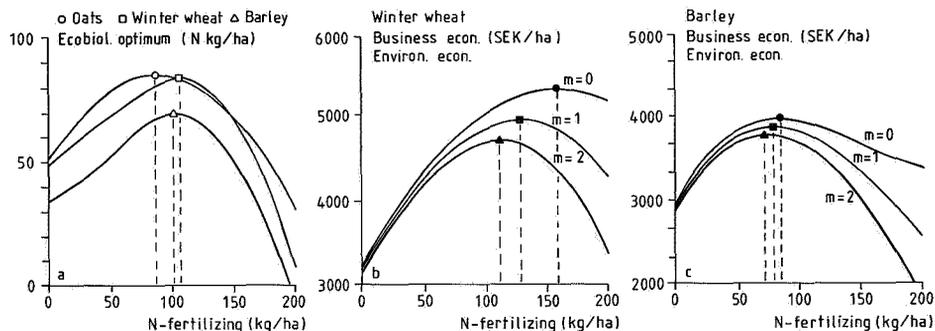


Figure 2. Ecobiological, business economic ($m = 0$), and environmental-economic optima ($m > 0$). Wheat: $p = 1260$ SEK/ton, $b = 11$ %. Barley: $p = 1130$ SEK/ton, $b = 12$ %, $r = 1.2$ %. Wheat and barley: $s = 7.60$ SEK/kg

costs for poor water in wells and those involved when cleaning ditches of vegetation. The environmental economic optimum coincides with the ecobiological optimum when $m = 2$ for winter wheat and is much lower for all three m concerning barley.

3.4 Economic measures

We now proceed and inquire how the price bonus r for protein shifts the optima. The curves in Figure 3 are found from (6) and (7).

The largest effect is obtained for barley with the largest range in protein content. For wheat, the optima were on the upper part of the protein content curves, which means that the content is not so distinctive. The largest spaces between the curves concern wheat. These depend on the yield, which increased strongly over almost the entire fertilization scale as opposed to the yield curves for barley.

By removing the price bonus for protein the leaching would decrease. We now limit ourselves to winter wheat and again start from (6) and (7) where we allow the N-cost s to be independent and the N-fertilization N be the dependent variable. If m is given the values 0, 1 and 2 we get the curves in Figure 4a showing optimal fertilizer level and corresponding losses at different nitrogen costs. Figure 4b shows fertilizer levels at a 3 % price bonus for protein as well as the losses.

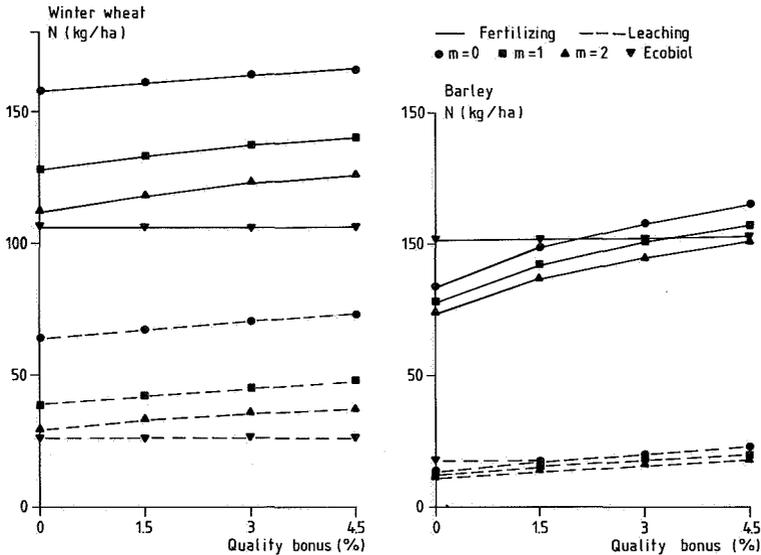


Figure 3. Optimum fertilizer levels and leaching as functions of the bonus payment for protein contents in winter wheat and barley. p , b , s the same as in Figure 2

Increasing nitrogen cost gives decreased fertilization levels and decreased leaching. The method is utilized by Swedish authorities who have introduced a 25 % duty on commercial fertilizer included in the price given above. The effect of this on the leaching is limited. A two-fold increase in the N-price would, on the other hand, reduce the losses by half. The method is general and easy to handle.

Fertilization can also be controlled using the environmental factor m . With rising values the N-losses decrease owing to decreasing N input. When $m = 1$, i.e., the same price placed on fertilized and leached N, the losses decrease to nearly half in comparison with the losses at the business economic optimum ($m = 0$) and an N-price of 7.60 SEK/kg. The method is difficult to manoeuvre in practice, but is theoretically interesting since the environmental costs are introduced at source.

Decreased price of grain also has a depressing effect on the optimal fertilizer level as well as on leaching (Figure 4c and d). It should be mentioned that the wheat price on the world market is only one-third of the domestic price in Sweden!

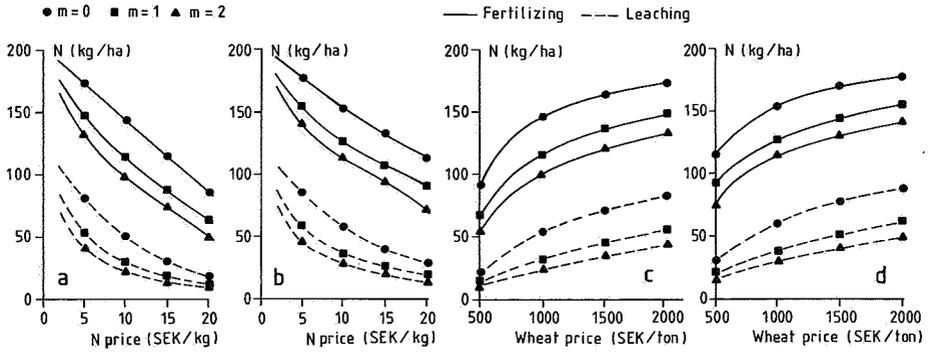


Figure 4. Optimum fertilizer levels and leaching as functions of N price and wheat price. Business ($m = 0$) and environmental ($m > 0$) economics. (a) and (c) 0 % bonus. (b) and (d) 3 % bonus

ACKNOWLEDGEMENTS

Warm thanks to Dr. Börje Lindén for valuable contributions of data on soil nitrogen, and to Mr. Gunnar Torstensson for valuable assistance with data processing.

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FAST RELEASE OF SALINITY AFTER A FLOOD IN THE LLOBREGAT VALLEY
(CATALONIA, SPAIN)

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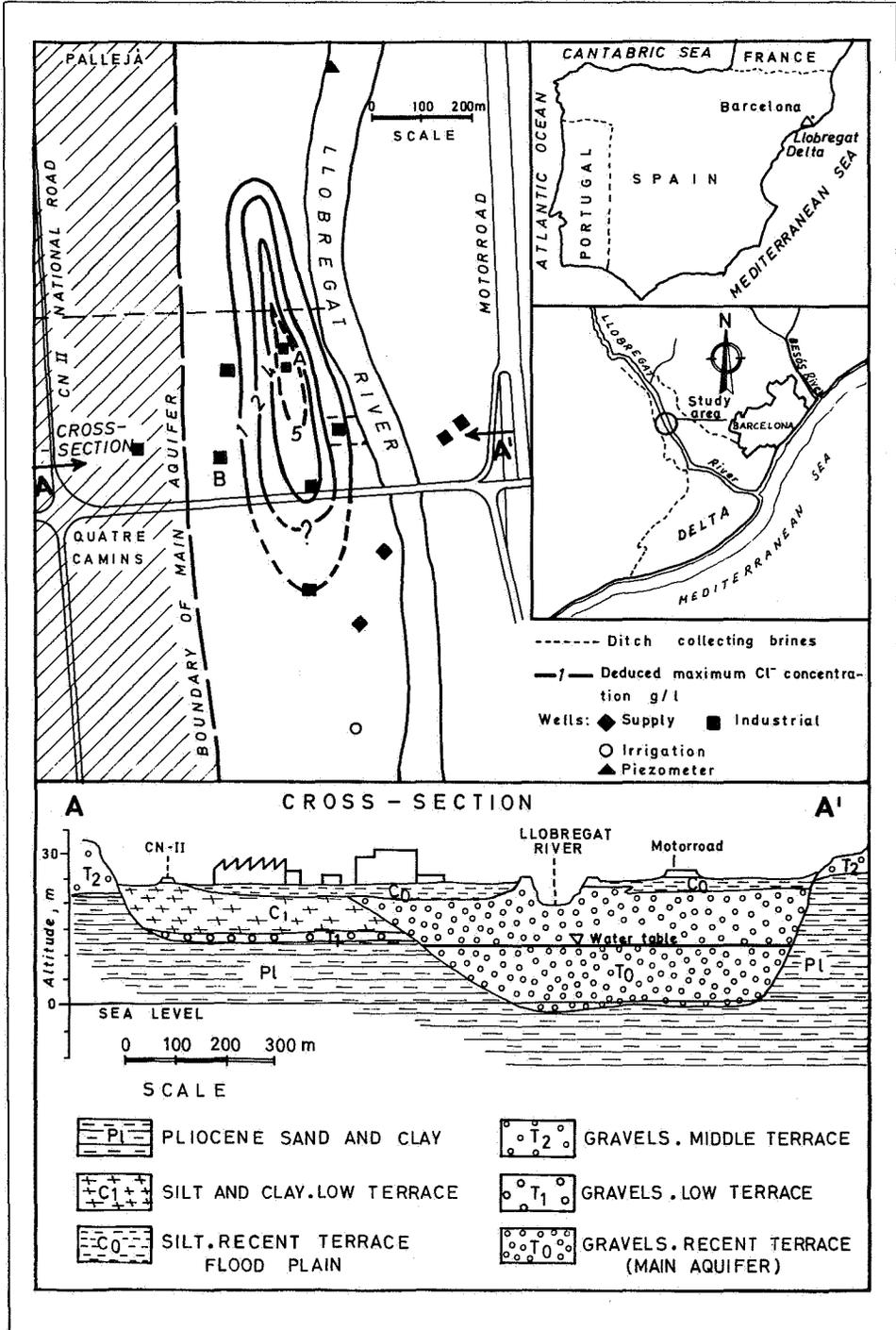
ABSTRACT

The uncontrolled disposal of brines from water softening industrial plants is not only a source of continuous salt pollution to the alluvial aquifer of the Lower Llobregat valley, but also the origin of intense point salinizations after a river flood, when brines stored in the unsaturated zone during downward transit are rapidly incorporated into the saturated zone. This occurs as a result of a sudden increase in the water table elevation combined with increased river percolation through the unsaturated zone. Serious short-term problems may arise. Br^- and K^+ contents indicate the origin of the salt.

1. INTRODUCTION

The Lower Llobregat valley is a rather deep, wide trench back-filled by fluvial terraces of gravel and coarse sand with minor interlayering of silty materials. There is a widespread cover of eolic loess at the sides and arable soil on the lower reaches (Figure 1). The area is close to the South-Eastern boundary of Barcelona Metropolitan Area, in Catalonia (NE corner of the Iberian Peninsula). The flat area of the valley combines irrigated agriculture with several important urban and industrial settlements.

Figure 1. General situation, inferred maximum salinization problem and representative cross-section



Geohydrologically the area is part of the Llobregat delta complex and is close to the main area of aquifer recharge through river water infiltration. Figure 1 shows a simplified cross-section of the valley (Custodio et al., 1983; Llamas and Molist, 1967). The lower terrace has a permeability of between 300 and 500 m/day (3 to $5 \cdot 10^{-3}$ m.s⁻¹), and a specific yield of about 0.2 (MOP 1966; PHPO 1985).

The water table is permanently several metres under the river bed due to the intensive groundwater abstractions downstream. River infiltration near the area under study is through unsaturated materials. Mean water table slope along the river is about 0.0035. This means a down-valley physical water velocity of about 5 to 8 m/day. Thus, mean groundwater transit-time is typically less than one year. In the main groundwater flow system water is chemically quite homogeneous.

2. WATER QUALITY SITUATION

The Llobregat river water is rather saline due to brine disposal upstream in an area of salt mines exploiting potassium (potash) minerals (Custodio and Queralt, 1981). This produces a water high in chloride (400 to 800 mg/l). The water is also hard (5 to 10 meq/l). Groundwater is as saline as the river water. It has about the same chloride content but it is much harder (up to 14 meq/l). This can be explained by the dissolution of the predominantly carbonate materials in the aquifer system by the CO₂ produced by dissolved organic water decay.

This high hardness is a serious problem for many industrial processes. Softening facilities are common, using NaCl as a regenerating chemical for exchange resins. The elution (regeneration) brines, produced periodically (daily to weekly), are disposed of into the river, directly or in most cases through small unlined ditches. The small quantity of these outflows, the uneven production and the impossibility of economically desalting them poses a discharge problem that regulations do not make adequate provision for. The Authorities

prefer to turn a blind eye to the problems while waiting for a sewer to be constructed along the river.

3. THE PROBLEM POSED

After a big river flood on November 7th, 1982, some industrial wells began to yield water that was much saltier than usual. A particular industry was seriously affected in the production process. Several sections were forced to close down for a few days and attempts were made to clean-up the aquifer by pumping its wells continuously, spending a significant excess of energy.

A complaint was made to the Authorities, who then had to determine the origin of the salting-up problem, the corrective measures to be applied and the way how to settle the company's claim for damages. Some nearby industries manipulating brines or salt and the operator of a brine pipeline passing near the affected area were pin-pointed as being responsible for the problem.

In such a case as this, survey and study methods should be the fastest possible, bearing in mind the limitations imposed by the impossibility of obtaining funds in a short time - or of authorising expenditures without lengthy, and therefore impractical, approval procedures - as well as the difficulty, if not practical impossibility, of directly surveying activities inside industrial settlements.

The following measures were taken:

- collection of geohydrological information existing on files;
- fast survey to find and identify local salt sources and their possible differences;
- some sampling to determine the extent and short-term evolution of the problem;
- recommendation of immediate action to clean-up the aquifer (sometimes more a measure of greater psychological rather than practical value);
- publication of a short report explaining the facts, proposing

solutions and pointing to technical and administrative actions to be taken to prevent similar situations occurring in the future.

In a situation where a complaint has been made after a rapidly changing situation has developed, studies have to rely on observations made after the problem is well developed and receding. By then, the full dimensions of the problem can only be inferred and the immediate causes have already disappeared. The only observations available are those from regional monitoring networks - generally too few - and data provided by the affected industries, generally incomplete, sometimes misleading and even faked.

Since groundwater chemical characteristics last longer than hydrodynamic changes, they are therefore more suitable for study in an attempt to solve the problem in hand. How the source of salinization was determined and how salinization occurred will be discussed below. Other aspects are not considered.

4. LOCAL SOURCES OF SALINITY

The different possible local sources of salinity, capable of producing salt concentrations higher than those observed in pumping wells are:

1. brine pipeline along the boundary of the area transporting residual salt from a chemical industry upstream. Relatively low in Br^- and K^+ content;
2. residual brines from the potash mines, imported in cisterns, stored in small tanks and used for regenerating the softening exchange resins. High in K^+ and Br^- ;
3. small salt pilings of residual salt from the potash mines used for regenerating softening resins after being converted into a brine. Normal in K^+ and moderate in Br^- . Small pilings of salt for winter road de-icing have similar characteristics;
4. brines intermittently discharged after regeneration of exchange resins. High in Br^- and K^+ . Point flows up to 2 l/s. Measured point salinity between 10 and 20 g/l Cl^- , but up to 50 g/l Cl^- can be expected in unmonitored ditches.

The most relevant data are summarized in Table 1.

Table 1. *Most frequent values of salt sources*

Water and salt source	salinity g/l Cl^-	rNa/rK	rCl/rBr	Other
1 pipeline	4 to 40	30	12000	pH 11; high alkalinity; very low hardness
2 brines for regeneration	50 to 200	7	1400	hard; high Mg
3 salt for regeneration	-	39	5500	
4 discharged	100	7	1200 to 2000	deficiency in Na; hard; high $\text{SO}_4^{=}$; 0.5-2 l/s intermittent
Llobregat river	0.5			
local recharge	0.3	5-8 30-50	1200 10000	

r= value in meq/l

5. ORIGIN OF THE SALT POLLUTION

The Cl/ Br ratio does not change in the ground. In polluted groundwater it is indistinguishable from river water, locally discharged brines and brines imported for resin regeneration, but it clearly differs from the pipeline brine and imported solid salt.

The Na/ K ratio in the polluted groundwater is similar to or lower than in river water and local brines, and much less than in the pipeline brine and imported solid salt. Some Na exchange in the ground can be expected, thus explaining the observed small decrease in the ratio in polluted groundwater.

Groundwater hardness increases lineally with salinity, as can be expected from residual regeneration brines. Cation exchange in the ground may produce a similar effect, but this is not as marked.

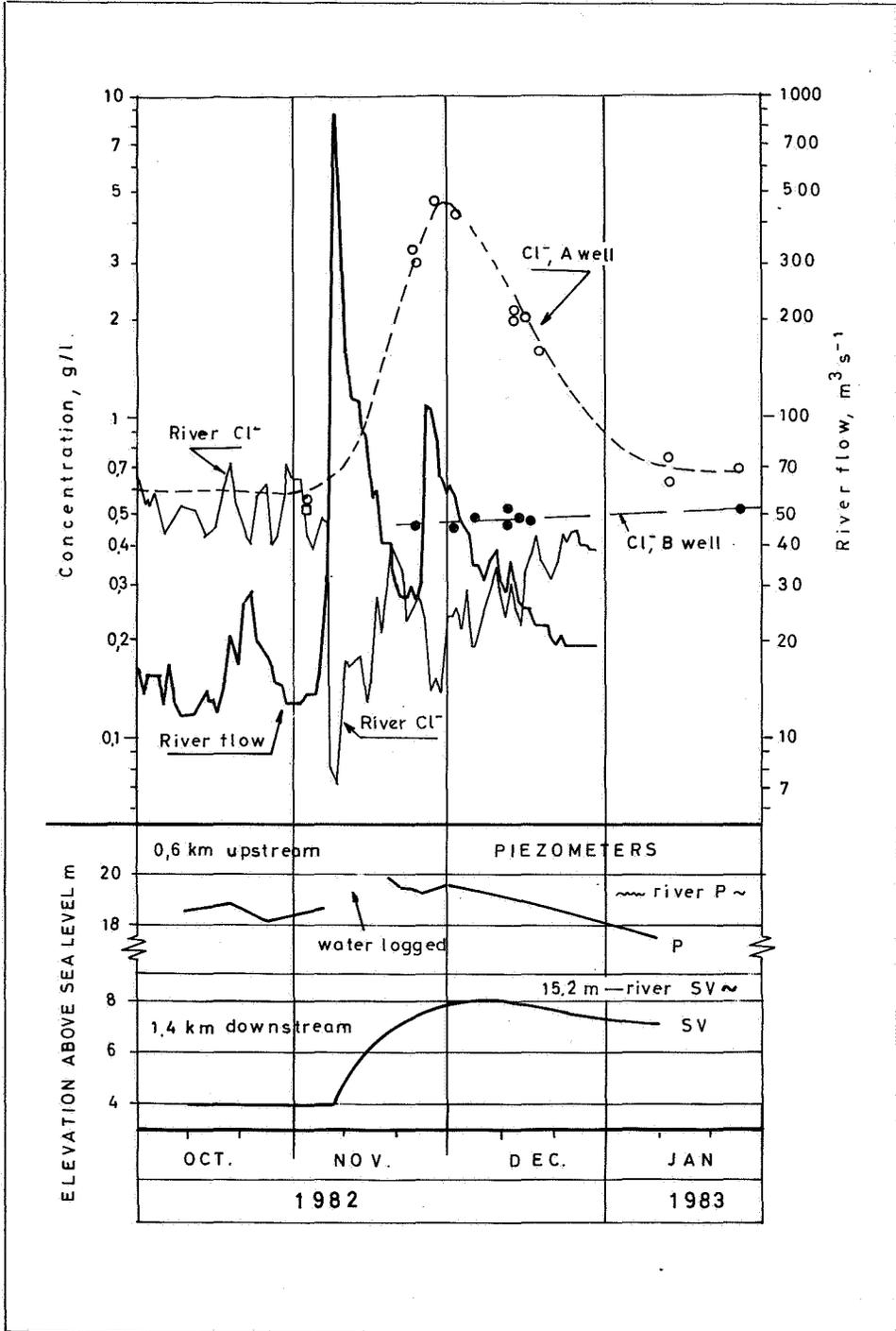
Both ratios and salinity values point to the discharge of regeneration brines as the source of salinity. The increase in water hardness would support this conclusion. Salinity does not come from the brine pipeline or the salt pilings.

The source of salt is therefore located inside or close to the industries affected by the increase in salinity. The problem can be linked to the softening process themselves carry out. No off-site activities can be blamed.

6. DATA TO EVALUATE THE SALINIZATION MECHANISM

- Date of the flood: 7-11-1982, not overflowing the banks.
- Depth to water table: 11 to 14 m.
- Saturated thickness about 13 m.
- Water table reaction at the site: about 3 metres, starting soon, peaking at about 10 days and fading out not before 1 month, as inferred from two piezometers, up and downstream. See Figure 2.
- Affected wells: those close to the river. See Figure 1.
- Affected surface: about 0.1 to $0.2 \cdot 10^6$ km².
- Excess salinity abstracted during the 1 month clean-up period (at about 70 l/s): $400 \cdot 10^3$ kg Cl⁻. This is a minimum value; the unknown discharge of other wells must be added. About $500 \cdot 10^3$ kg Cl⁻ would appear to be reasonable.
- Local brine discharge: according to an hourly sampling during a week at the main discharge ditch, 500 to 2000 kg/day of Cl⁻. Adding other ditches, the total amount is 1000 to 3000 kg/day of Cl⁻.
- Total point salt input into the aquifer (a pyramid-shaped distribution of concentration, varying between background level and 5 g/l is assumed): 450 to $800 \cdot 10^3$ kg of Cl⁻.

Figure 2. Water table altitude, river flow and river and well salinities (modified from Custodio et al., 1983)



7. MECHANISM OF SALINIZATION

Under normal conditions, regeneration brines infiltrate along the ditches, favoured by the intermittency of flow, the retention produced by some one-way gates in the outlet of the ditches through the river bank to prevent flooding, and the periodic mechanical clean-up of debris, vegetation and oils in the ditches. This produces an observed local increase in salinity of up to 0.1 g/l Cl^- , which extends downstream and fades away by dispersion. This amounts 50 to 100 kg/day of Cl^- , or about 5% of the total salinity discharge.

Water held in the unsaturated zone below de infiltration areas is also a brine moving downwards to the saturated zone. Heterogeneities in the ground (mainly fine interbedded lenses and back-filled gravel pits) allow for the lateral spreading of percolating brines. On the main aquifer a saline patch of 0.05 km^2 seems probable. Point discharges constitute the bulk of infiltration, with salinities of 10 to 30 g/l Cl^- . Recharge by rain water dilutes the salt water, though a large part of the surface is paved, therefore reducing this contribution. It can be reckoned that this recharge is about the same quantity of percolating salt water, thus reducing soil water salinity in the unsaturated zone to about 5 to 15 g/l Cl^- .

The fast water table recovery suddenly allowed the salinity stored in the drowned band to be incorporated into the saturated zone. A 3 metre rise the water table explains the introduction of 75 to $150 \cdot 10^3 \text{ kg}$ of Cl^- or about 0.5 to 1.5 g/l concentration increase, assuming an initial 0.1 water content.

The lack of precision of data and calculations produces errors that can explain the differences, but an additional mechanism will give a closer approximation.

The flood greatly extends the wetted river surface, up to the banks. River water easily percolates through the dry permeable materials - the water table being well below the river bed level. It allows for the lateral extension of infiltrating water, spreading over the area

in which the unsaturated zone is soaked with salt water. Thus, the salt water is displaced downwards and incorporated into the aquifer. This mechanism cannot be easily quantified. Assuming 1 m of river water infiltrating a strip 500 m wide, one quarter moving to the lateral formations, this produces the equivalent effect of a further water table rise of about 3 m. This is enough to account for the amount of salt apparently missing and the concentration peak. It is also a more satisfactoring explanation for the elongated form of the saline pollution, since the equivalent water table rise effect is greater near the river bank.

8. CONCLUSIONS

A fast survey of salt sources and simple salinity balances help in explaining the possible origin of the salt and the salinization mechanism. The ratio Cl/Br characterizes the source. Salinity comes from unlined outflow ditches from the industrial softening plants which use imported brines as a regeneration agent. The continuous percolation of these brines increases the local salinity background but do not produce high peaks of Cl^- . The high salinity peak which appeared in groundwater comes from the unsaturated zone, soaked with brine when, after an extraordinary river flood, there is a rapid rise in groundwater level and the lateral spread of locally infiltrated river water through the upper unsaturated zone.

9. ACKNOWLEDGEMENTS

The collaboration of the chemists J. Guardiola and S. Balagué is highly appreciated. Sociedad General de Aguas de Barcelona helped in obtaining field data and conducting some surveys. Relevant data come from the files of the Eastern Pyrenees Water Authority. Some new studies on the area have been carried out under project 8309/007 of the Joint US-Spain Committee for Scientific and Technological Cooperation. The above mentioned organizations jointly with the

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LEVELS OF FLUORINE POLLUTION IN DRINKING WATER (TAP AND WELL) IN ENTISOL SOIL AREA

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ABSTRACT

Fluoride is one of the major chemical parameters that determine the quality of drinking water. A total number of 120 water samples were collected from different sources in and around the entisol area of Allahabad district (U.P., India). The sources of water samples were Wells, Taps and Rivers. The fluoride determination was done spectrophotometrically using Aligarine Red S and Zirconium nitrate reagents. Out of the eleven tap water samples analysed it was observed that 72% sample contain fluoride much below the permissible limit. The rest of the samples contain fluoride in permissible limit (approximately 1 ppm). On analysing 49 well water samples, 34% were found to have either no fluorine or in a concentration which is much lower than the permissible limit i.e. 1 ppm. 32% of the samples were found to have fluoride within permissible limit. However, 18% of the samples were found to have a fairly high fluoride concentration (1.4-3.2 ppm). Thirty water samples each from river Ganga and Yamuna from depths of 15 cm and 30 cm were assessed for their fluorine content. It is interesting to note that water from river Ganges from both the depths does not show even permissible concentration of fluorine while the river Yamuna records fluorine content which is fairly high than the permissible limit (2 ppm). This is ascribed to the presence of fluorapatites ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ or $\text{C}_{10}(\text{PO}_4)_6\text{F}_2$) with other minerals in the beds of river Yamuna.

INTRODUCTION

Fluoride is one of the major chemical parameters that determine the

quality of drinking water in addition to lead, iron, arsenic, nitrates, chlorides, dissolved oxygen and ammonia. The permissible concentration of fluoride in drinking water should be about 1 ppm. A lower value than this one may lead to high incidence to dental caries that make the teeth more prone to bacterial attack (acidity) and with excess of this value (especially 1.5 ppm) dental fluorosis and ultimately endemic cumulative fluorosis with resultant skeletal changes (arthritis) in both children and adults may occur. (Robinson, 1972; Rich & Ensink, 1961 and Mishra et al, 1985).

MATERIALS & METHODS

A total number of one hundred twenty water samples were collected from different sources in and around the entisol area of Allahabad district (Uttar Pradesh, India). Special precautions were taken during collection of water samples, keeping following points under consideration:

- (a) The sample be representative of the water to be examined.
- (b) The sample be collected in either clean glass stoppered bottles made of neutral glass of capacity not less than 1 litre or in plastic bottles.
- (c) Before the collection of sample bottle should be rinsed well thrice with the water.

The sources of water samples in this study were from wells, taps and river Ganga and Yamuna.

The determination of fluoride was made spectrophotometrically by Barr and Thorogood's modification of De Boer process using Alizarine Red S and Zirconium nitrate reagents (De Boer, 1924 & Barr et al, 1934). The minerals from the beds of Jamuna river were chemically analysed and fluor-apatites were identified by usual X-ray method using powders of the minerals.

RESULTS AND DISCUSSION

Eleven tap water samples from different parts of Allahabad City were analysed for their fluorine content. It was found that about 72% of the tap water samples contain fluoride much below the permissible

concentration. The rest of the samples (Rasoolabad, Dhumdume and Saidabad) contain fluoride in suitable concentration (approximately 1.0 ppm).

Out of the forty nine well water samples, 34% were found to have either no fluorine or in a concentration which is much lower than the permissible concentration i.e. 1 ppm 32% of the samples were found to have fluorine around 1 ppm which is suitable for drinking purpose. However, 18% of the samples were found to have a fairly high concentration of fluorine (1.4 to 3.2 ppm). Higher concentration of fluorine (fairly high concentration than the permissible one) in well water was found in Baghambari, Tagore Town, Chowk, Bahadurganj and Rasoolabad areas. Thus, tubewell water in these areas should not be mixed up with tap water otherwise people in these areas in the long run will suffer from severe fluorosis. The other areas where the well water a bit higher concentration of fluorine than the permissible one are Saidabad, Sulem Sarai, Rajapur and Naini.

Thirty samples of water from river Ganges and thirty from river Yamuna from depths of 15 cm and 30 cm were taken to assess their fluorine content. It is interesting to note that water from river Ganges from both the depths does not show even permissible concentration of fluorine whereas river Yamuna records fluorine content which is fairly high than the permissible concentration (2 ppm), higher concentration being in water collected from the highest depth (30 cm) of river Yamuna. This is ascribed to the presence of fluorapatites ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ or $\text{C}_{10}(\text{PO}_4)_6\text{F}_2$) with other minerals in the beds of river Jamuna.

Recommendations:

- a. Water from river Yamuna may be supplied for drinking purposes through tap water after reducing its fluoride content to about 1 ppm. The possibility of supplying drinking water from river Ganges which contains little fluorine, to certain parts of Allahabad city like Baghambari, Tagore Town & Rasoolabad area, after adding sodium fluoride to about 1 ppm can also be explored.

- b. Tubewell water may not be mixed up with normal tap water to intensity its pressure where tubewell water contains fluorine more than 1.5 ppm
- c. Tubewell water may be supplied alongwith tap water in areas of Allahabad where the underground water contains almost no fluorine or where its concentration is at permissible level.

ACKNOWLEDGEMENT

The authors are thankful to Council of Science and Technology, U.P. (India) for the financial assistance provided for this work.

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Cu, As AND Cr-POLLUTION OF A DANISH TILL AREA

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ABSTRACT

The necessity of compiling a detailed conceptual geological model as the basis for evaluation of a given pollution is shown by an example from a Danish till area.

1. INTRODUCTION

The poster aims to describe the geological and hydrogeological situation of one of the localities within the research project: "Studies of soil properties related to heavy metal retention", carried out by Lund (1987).

The actual study is carried out in an area (200 x 50 m) which has been polluted by leakage from a wood impregnation industry during the period 1920 - 1968. A major leakage (15 m³) took place in 1968 in the northern half of the area leading to a first investigation, including ten investigation wells to a depth of 3 - 4 meters. The purpose of that investigation was to evaluate the risk of pollution of two nearby water supply wells (137 m north and 164 m northwest of P3 in Figure 1) pumping 250.000 m³ per year. A later investigation was carried out in 1984 including two new investigation wells each 6 m deep and ten 1.5 m deep pits (Vestsjællands Amtskommune 1984).

2. REGIONAL GEOLOGY

The glacial deposits forming the landscape of the investigated area is

of Weischelian age, from which three glacial advances are known in the area. The hill Galgebakken (Figure 1) west of the polluted area is interpreted as a, probably icepressed, kame, consisting of sand and gravel. The kame is an easterly part of a kame-esker system draining the central Seeland during deglaciation of the latest advance from south (Humlum 1976). The landscape east of the kame-esker system is an undulating till plain.

3. GEOLOGY OF THE INVESTIGATED AREA

The first coherent geological model of the area based on the investigation from 1968 and 1984 showed 25 - 30 m of clayey till overlying a regional aquifer of glaciofluvial sand. Locally a thin layer, up to one meter thick, of sorted material occurs on top of the till (Vestsjællands Amtskommune 1984).

The new investigation in 1986 consisted of three shallow pits for geochemical studies (Lund 1987) and six drilled observation wells with the aim of elucidating the geology. The resulting revised model of the uppermost ten meters is presented in a fence diagram (Figure 1), which shows a much more complex layer sequence than previously supposed. Four units can be identified.

Unit 1 consists of 1 - 1.5 m of redeposited till interlayered with 10 - 30 cm layers of fine grained sand and based on coarse sand and gravel; the sequence plunging downhill. Unit 1 is interpreted as flow till or solifluction deposits interlayered with downwashed sand.

Unit 2 is a clayey till with a high content of silt and sand. The firm consistency of the till observed in the pits indicates a lodgement till. At the base the till in five wells is separated from the underlying lower till by an only 10 - 30 cm thick layer of fine-medium grained sand. The sand is interpreted as a sandy sole, a phenomenon often seen in profiles in Denmark.

Unit 3 is a clayey till (lower till) which is very similar to the till of unit 2, but with an even firmer consistency.

Unit 4 is a wellsorted medium grained meltwater sand with a thickness of more than 2 meters (Pl in Figure 1).

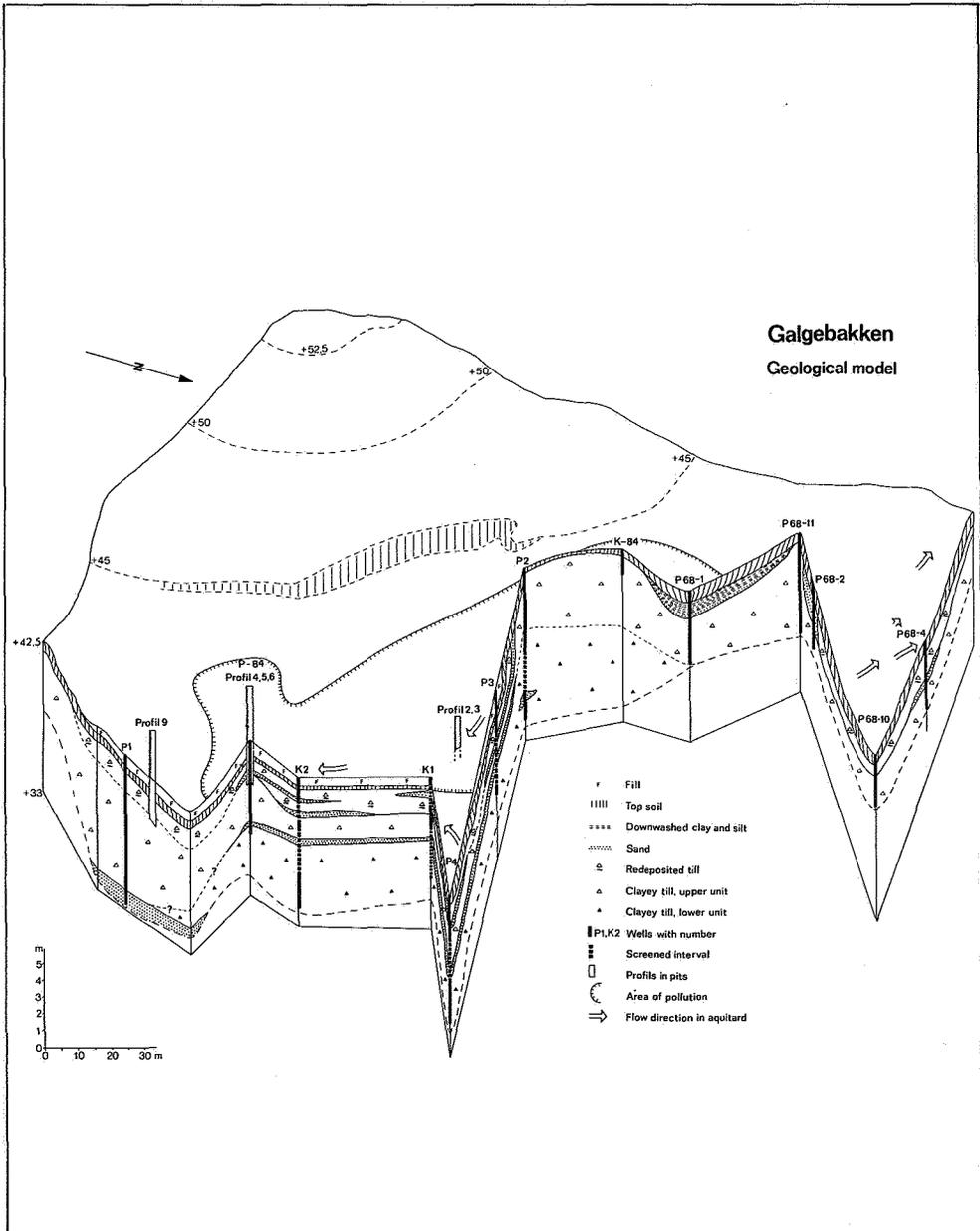


Figure 1. Fence diagram showing the geological model. Data from 1968 and 1984 are marked with -68 and -84 respectively followed by a current number. All other data are from 1986. The area of pollution is approximate and based on analyses of soil samples and on failure of vegetation

As a hypothesis the identified two tills are related to the two latest Weischelian advances in the area.

In the clayey till, soil structure described as blocky is seen. Furthermore clear joints with iron oxides are observed. The structure is fine and/or coarse and weakly to well developed. The coarse structure occurs even to a depth of more than 6 meters. A geoelectrical investigation has shown that the sandy till is resting directly on till (probably unit 2) and thus is separated from unit 4. Furthermore the geoelectrical investigation showed a surprisingly low resistivity of the depth interval 5-15 meters, which supports the observations (Vestsjællands Amtskommune 1984) of a rather deep penetration of the pollution.

4. HYDROGEOLOGY

The groundwater flow in the regional artesian aquifer has a direction towards the north and the piezometric surface is situated at +30 - +31. The seasonal variation of the piezometric surface of the aquitard overlying the regional aquifer is shown in Figure 2. The piezometric surface ranges from +37 to +41, and has constantly highest level in the upper screened interval. There is thus a downward gradient towards the primary aquifer, the upper limit of which is situated in 25 - 30 meters depth, (+15 - +10). The observed variation of the piezometric surface of the local secondary reservoirs in the aquitard is typical for this hydrogeological situation and the piezometric surface follows the topography. The flow direction in the aquitard in the southern part of the area has a minor lateral component which generally is towards the south in contrast to the northern part of the area (Figure 1). The sandlayer (unit 4) at P1 is dry (in May) indicating that the measured piezometric surface (Figure 2) in the upper sandlayers (in unit 2 and 3) is representing a perched aquifer.

The interesting observation of a dry but not penetrated sandlayer in P1 at a depth far below the waterlevel within the aquitard, and the fact that this sandlayer may occur all over the area, can result in a completely different model for the distribution of the pollution than first supposed, i.e. downward to the regional aquifer, because this

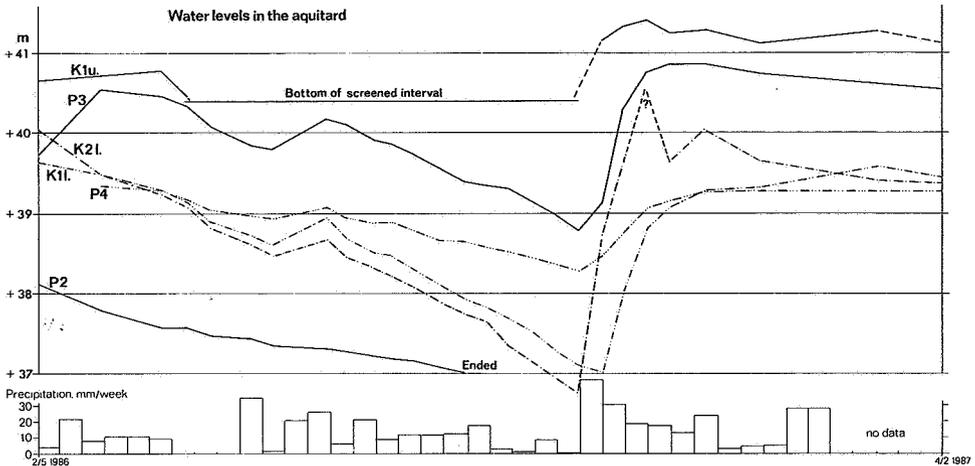


Figure 2. Measurement of groundwater levels in the aquitard and the weekly precipitation. The letters and numbers refer to the wells shown on Figure 1 where also the screened interval is shown. K1u and K1l refer to a separated upper and lower screened interval

sandlayer must have a rather good drainage capacity. If the flow direction is lateral the pollution consequently does not necessarily reach the regional aquifer, but may be concentrated somewhere else. However, this new conceptual model must be verified by studying the extension of the sandlayer and the hydraulic head of the probably enclosed water. The geoelectrical investigation has not excluded the occurrence of this critical sandlayer.

5. CONCLUDING REMARKS

The presented example stresses the necessity of compiling a detailed geological model as the first step in an evaluation of a pollution migration. The geological model is a tool, which makes it possible to use ordinary geological and stratigraphic methods in mapping. As shown by Lund (1987) a knowledge of the possible reaction between soil and

chemical elements should be the next step giving indications of pollutant retention.

6. ACKNOWLEDGEMENT

This work was supported by the National Council of Technology (grant no. 5.26.13.05)

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NITRATE POLLUTION OF GROUNDWATER FROM PRIVATE WELLS
IN THE PROVINCE OF GELDERLAND, THE NETHERLANDS

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ABSTRACT

A survey of the quality of water from private groundwater wells was carried out. The survey showed that the nitrate content of pumped groundwater is so high that in more than half of the cases the water is not fully suitable for human consumption, especially in eastern Gelderland. The main cause is thought to be intensive manuring of agricultural land. A secondary cause is thought to be infiltration of household waste water.

1. INTRODUCTION

A number of surveys have shown that the quality of the groundwater in various parts of Gelderland is deteriorating considerably (Verkooyen et al. 1985); Potter, 1986). In particular, a rise in the nitrate content of the groundwater has been noted. The principal causes are seen as the intensification of agriculture and the associated over-production of animal manures. Other causes to which the pollution of the groundwater can be ascribed are infiltration of household waste water and, to a lesser extent, atmospheric deposition of nitrogen compounds. About 98% of all households in the province of Gelderland are supplied with drinking water by the public water companies (provincie Gelderland, 1987), but outside the municipal built-up areas drinking water is still largely drawn from private groundwater wells, especially in the east of the province. Whereas the water companies have a statutory obligation to provide water of adequate quality (and do in fact take action to ensure

that this quality is maintained), drinking water drawn from wells by private individuals is not governed by any quality regulations. In recent years the authorities (municipal and provincial) and the water companies have been receiving expressions of concern from private consumers of groundwater about the quality of groundwater intended for human consumption.

2. OBJECT OF THE SURVEY

The object of the provincial survey is to examine the extent of the problems relating to the quality of groundwater from private wells and to discover the causes of well pollution. The survey will form the basis for decisions concerning possible measures to prevent or combat the pollution of private wells.

3. SCOPE OF THE PROBLEM

In recent years the provincial authority has noted the results of investigations into the quality of groundwater from private wells, and in particular the findings of a survey carried out jointly by the Vrije Universiteit van Amsterdam, Chemiewinkel Amsterdam and the Landbouw Universiteit Wageningen (1986). In addition, similar studies have been carried out by the provincial authority in cooperation with certain municipalities (for example Zelhem and Neede). Figure 1 summarises the findings of these surveys. As indicated, very high nitrate contents occur in many instances, in particular in the eastern part of the province.

If the findings are compared with the nitrate norm laid down by the Water Act (50mg NO₃ per litre), it will be seen that in most cases the water must be regarded as unfit for human consumption.

To clarify the causes of these high nitrate contents, the situation on the Needse Berg, part of the municipality of Neede, is examined in greater detail in the following section.

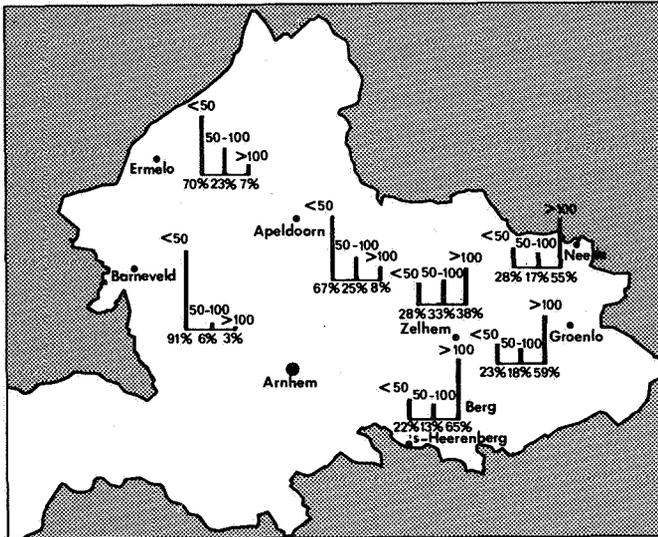


Figure 1
Nitrate concentrations
in ground water
from private wells
in the province of
Gelderland (mg NO₃/l)

4. SITUATION IN NEEDE

The Needse Berg lies in the north-east of the province of Gelderland. It is a hill, rising to 35 m above Amsterdam Ordnance Datum (NAP) and about 20 m above the surrounding countryside (Fig. 2). The Needse Berg was formed during the Saale Glacial Stage through damming by land ice of, among other things, Eocene clay and the subsequent deposit of sand during the Weichselian period (Stichting voor Bodemkartering, 1979). The regional hydrological system is characterised by a westerly flow of groundwater in a predominantly sandy layer about 60 m thick. The Needse Berg's hydrological system (radial run-off of infiltrated surplus precipitation) is superimposed on this.

Surface water also drains off in a westerly direction, via Schipbeek and Bolksbeek (Fig. 2).

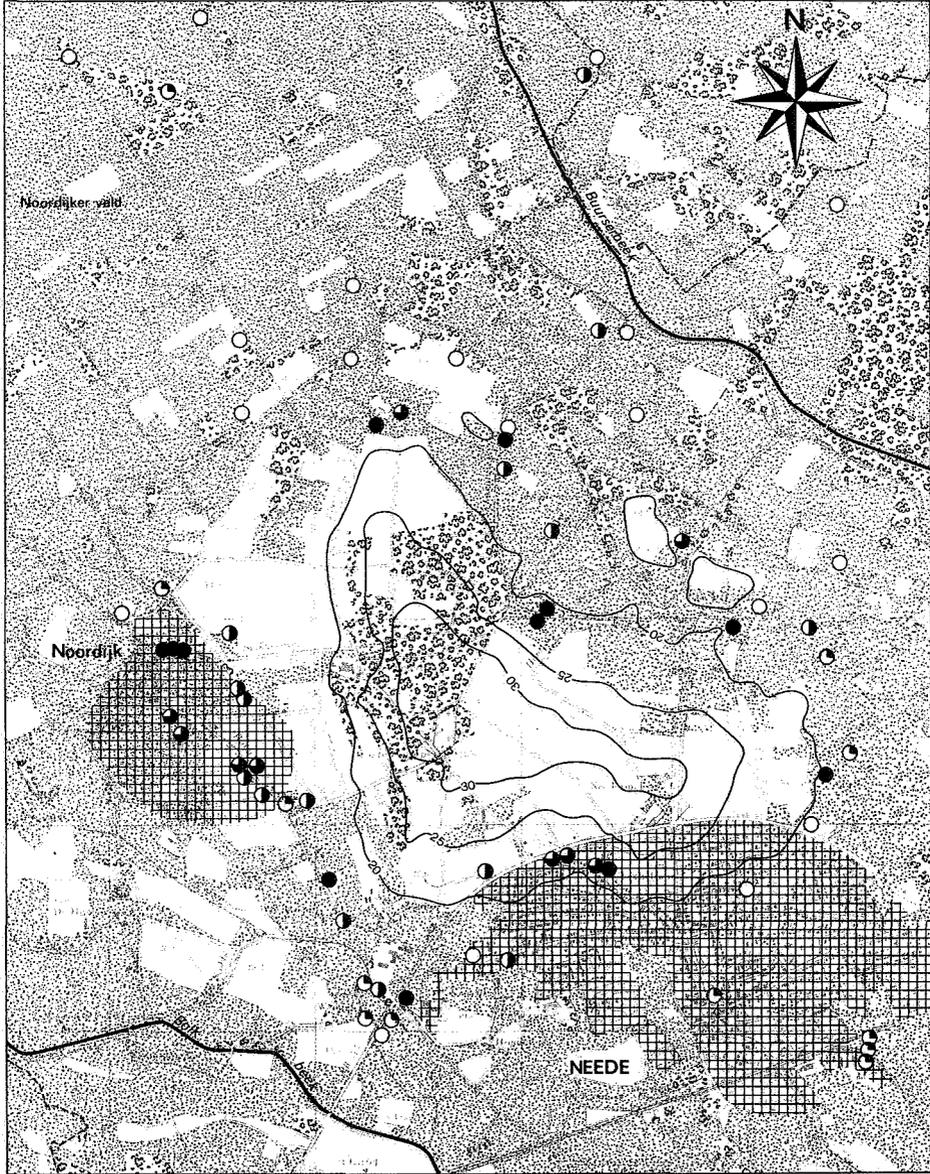
The land has been used for agriculture for many centuries (Fig. 2), as is proved by the presence of the ancient "es" type cultivation on large parts of the Needse Berg. The predominant type of farming has been arable, with green maize as the main crop since the 1970s. The maize is used as roughage for cattle, which were increasing constantly in numbers until a short while ago; in return the maize-growing land is fertilised with substantial quantities of cattle manure and manure from the still increasing pig population.

Besides agricultural use, there is a substantial proportion of residential use, which has grown rapidly over the last hundred years.

Figure 2 shows the towns of Neede and Noordijk, which have sewage mains. Outside these centres are scores of dwellings which discharge their (household) waste water directly into the ground.

Both centres are connected to the East Gelderland Water Company's public water mains. In the outlying areas scores of dwellings still have their own water supply, which is used for human for animal consumption. The water is drawn from depths ranging from 3 to 40 m below ground level.

The municipality of Neede, in cooperation with the province of Gelderland and the Eastern Water Laboratory, has examined almost all the private wells. Figure 2 shows the nitrate contents measured.



SITUATION IN NEEDE



- Arable land
- Grassland
- Residential use
- Nature
- Contour line in m + NAP

- < 50
- 50 - 100
- 100 - 150
- 150 - 200
- > 200

Nitrate contents measured in private wells (mg NO₃/l)



Fig.2

5. EVALUATION

The survey findings show that in 72% of cases the quality of the groundwater used by private households in Neede is not fully suitable for human consumption. It is not immediately possible, on the basis of available data, to give the causes of these high nitrate contents. They may be the result of heavy manuring of arable land on the Needse Berg, of very local pollution caused by penetration of household waste water into the ground, or of faulty storage of manure.

To pinpoint the causes, a survey commissioned by the province is currently in progress. At a limited number of locations the consultancy firm Chemielinco is compiling a list of possible nitrate sources of the pollution. The suspected sources will then be verified by sampling and analysis. The conclusions of the survey will form a basis for decisions to be taken on this problem.

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CHARACTERIZING SOIL MOISTURE COMPOSITION IN FOREST
SOILS

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ABSTRACT

A soil monitoring project in eight Douglas stands, located on four representative forest soils in the Netherlands, is being executed to characterize soil moisture composition. Soil samples are taken four times per year, near five randomly selected trees per stand, at four depths. Soil solution is extracted by centrifugation. Preliminary results on 15 element species show strong spatial and temporal variations in concentration levels. In all cases variance increases with concentration level. Analysis of variance on log-transformed concentrations shows that the variations are strongly related to differences in location and, to a lesser extent, to sampling depth and sampling period. However, the remaining unexplained variance is considerable. Nevertheless, the sampling programme gives a reasonable estimate of the mean log-concentrations of several element species in stands, per depth class and per period.

1. INTRODUCTION

The possible effect of atmospheric deposition of sulphur (SO_2) and nitrogen (NO_x and NH_3) compounds on forest vitality has received considerable attention in recent years. There is evidence to show that the decreasing vitality is partly due to changes in soil water chemistry. Damage may occur as a result of nutrient depletion, due to accelerated soil acidification (Zoettl and Huettl, 1985), an increase in toxic aluminium in acid soils (Ulrich, 1983) and an unbalanced nutrient

availability due to high N-concentrations (Roelofs et al., 1985). In order to get some idea of the soil moisture composition of forest soils in areas with different pollution levels, a biogeochemical monitoring programme has been started on eight Douglas stands in the Netherlands. The research focuses on spatial and temporal variations in soil moisture composition in relation to atmospheric deposition and soil characteristics. The project is being carried out in close cooperation with the Dorschkamp Research Institute for Forestry and Landscape Planning, Wageningen, where the spatial and temporal variations in tree vitality, within the selected Douglas stands, are being studied. The final aim of the project is to establish the relation between soil moisture composition and tree vitality, using statistical techniques. In this paper, some preliminary data on spatial and temporal variations in soil moisture composition are presented. The data are discussed in relation to research design, sampling procedures and data management.

2. RESEARCH DESIGN

In order to draw statistically reliable conclusions on the relation between soil moisture composition and tree vitality with a limited number of samples, we minimized differences in stand characteristics influencing tree vitality, by selecting Douglas stands of similar age, provenance and management practice. Furthermore, only dominant trees at a distance of more than 15 m from the border of the forest or path are being studied, in order to reduce the effect of differences in competition position and microclimate.

Eight stands have been selected on four soil types, that cover about 80 per cent of Dutch forest soils. Within each soil type, a relatively vital and a relatively non-vital Douglas stand were chosen. The selected population of Douglas trees therefore covers a broad range in vitality. Within each of the eight stands, five trees were selected by numbering all dominant trees to be considered and drawing lots using a random numbers table.

Close to the selected trees, within the crown projection on the soil surface, samples are being taken to study the soil moisture composition.

Sampling is done every three months (each season), at one place near each tree, at four depths. The monitoring programme thus comprises 8 (stands) x 5 (trees) x 1 (place) x 4 (depths) x 4 (seasons) = 640 samples per year. Furthermore, data are collected on solid phase characteristics (once), root condition (in spring and autumn), needle condition (once per year) and needle composition (twice: at the beginning and end of the study). Sampling was started in the summer of 1986 and will be continued for two years. The selected trees will then be cut to study growth characteristics.

3. EXPERIMENTAL SETTING

3.1 Locations and soil types



Figure 1. Location of the study sites

Figure 1 shows the location of the selected stands. Stands 6, 7 and 8 are located relatively close to each other, resulting in relatively small differences in atmospheric deposition. The same applies to stands 1, 3 and 4.

The soils under the selected stands are all non-calcareous and sandy.

According to the FAO system of soil classification, the soils are classified as Leptic Podzols (stands 1 and 2), Humic Podzols (3 and 4), Gleyic Podzols (5 and 6) and Albic Arenosols (7 and 8). With the exception of stand no. 2, the soils in all stands developed in medium fine to fine sand, which is loamy in the topsoils of the podzols. The podzol in stand no. 2 developed in coarse to very coarse sand, with gravel throughout the profile.

3.2 Field and laboratory methods

To study soil moisture composition, soil samples are taken beneath the litter layer, at 0 to 15, 15 to 30, 30 to 45 and 45 to 60 cm below the surface. A bi-partite hand auger is used for sampling. With this device, it is possible to take undisturbed samples with a relatively high degree of accuracy with respect to sampling depth. The soil solution is extracted from the samples by centrifugation, as described by Reynolds (1984). After centrifugation, the extracted solution is filtered, which increases the maximum preservation time. The pore-size of the filters is 0.45 μm .

The extracted solution is analyzed for 15 element species using High Pressure Liquid Chromatography (NO_3 , SO_4 , Cl), Inductive Coupled Plasma emission spectrometry (Si, Al, Fe, Mn, Ca, Mg, P, Zn, Cu), Atomic Absorption Spectrometry (Na, K) and Spectrophotometry (NH_4). The pH is measured potentiometrically, using a combined glass-calomel electrode.

3.3 Data-management and statistical analyses

So far, data on the soil moisture composition in June and September 1986 have been processed. The data are grouped according to stand, sampling depth and sampling period.

To get some idea of the relative influence of location (stand), depth and time (sampling period) on the concentration levels of several element species, two-way analysis of variance is used, comparing the

variance within the grouped data with the variance between these groups. Furthermore, the interactions between the three factors are tested. There are four possible ways of interaction, viz. the effect of time on concentration profiles, the effect of time on concentration levels in stands, the effect of location (stand) on concentration profiles, and the combined effect of time, location and depth on concentration levels.

4. RESULTS AND DISCUSSION

4.1 Analysis of variance

The analytical results show that for all element species the variance increases considerably with mean concentration level in each group of data. For this reason, the concentrations are transformed to $\log(10)$ -values, resulting in a reasonably constant variance for all element species in the grouped data, being a basic requirement in analysis of variance. Results for major element species show a significant relation between variance in log-concentrations and location, depth and time respectively (Table 1). The relative importance of these factors is different for each compound. However, the influence of location is very

Table 1 *Percentages of variance in log-concentration accounted for by differences in time (T), location (L), depth (D) and by interactions between these factors for several species*

	T	L	D	T.L	T.D	L.D	T.L.D
Al	5	40	8	-	-	0.5	-
Ca	10	53	-	3	-	-	-
Mg	10	48	8	-	-	-	-
K	3	10	9	3	-	-	-
NH ₄	-	35	31	-	-	-	-
NO ₃	14	36	-	4	-	1	-
SO ₄	8	59	6	5	-	-	-
pH	17	17	5	10	-	2	-

- = not significant

strong in all cases. With respect to the interactions, only the effect of time on variations in stands is important, which means that the change in concentration levels with time depends upon location. The interaction between stand and sampling depth is significant for aluminium, nitrate and pH (Table 1).

The remaining unexplained variance may be caused by local differences (within the stands) in soil characteristics, water flux and atmospheric deposition and by random errors in both field and laboratory procedures.

4.2 Variations in soil moisture composition

The spatial variations in soil moisture composition are very great, both on a regional scale (between several stands) and on a local scale (within stands). In several cases the variation coefficient of 5 observations within one stand, one depth class and one period exceeds 100 per cent. The temporal variations are also considerable: for most element species the concentration levels in September are increased compared to June; sometimes by a factor of 4 or more. The variation coefficients are reduced considerably by the log-transformation: the maximum variation in log-transformed concentrations within one stand, on one sampling depth for a single period is 25 per cent and in most cases does not exceed 10 per cent. In Table 2, figures of the concentrations of some element species, important with respect to growth and vitality of the trees, are given to illustrate the differences between stands and between sampling periods.

Differences in the concentrations of ammonium, nitrate and sulphate are mainly due to differences in input by atmospheric deposition. This is illustrated by the relatively small differences in the mean concentrations of these species between stands within the same region.

The figures in Table 2 show a relation between Al concentrations on one side and nitrate plus sulphate minus ammonium concentrations on the other, suggesting a strong mobilization of aluminium induced by atmospheric deposition.

The variation within single profiles is also very large. The ammonium concentration shows the strongest relation with depth: the concen-

Table 2 *The mean concentrations (in mol (+/-) m⁻³) of some element species in the first 60 cm of soils under eight Douglas stands in June (J) and September (S) 1986*

El.	Period	Stand no.							
		1	2	3	4	5	6	7	8
Al	J	1.2	3	1.1	1.0	4	2.6	6	4
	S	2.2	4	2	0.9	7	6	24	10.8
NH ₄	J	0.18	0.7	0.4	0.3	1.5	1.4	1.2	1.0
	S	0.16	1.0	0.5	0.2	1.7	2.2	0.9	1.7
NO ₃	J	1.4	2.5	1.2	1.0	3	1.8	3	2
	S	2.7	4.6	2.1	0.9	6	7	12	6.8
SO ₄	J	0.8	2.1	0.9	1.3	4	3	4	5
	S	0.9	2.0	1.6	0.9	6	11	11	11.9

tration strongly decreases in the topsoil, which may be caused by nitrification and uptake. At 45 to 60 cm below the surface, the ammonium concentration is 25 to 10 per cent of the concentration in the topsoil. The concentration profiles of other element species are strongly influenced by the mean concentrations. The aluminium concentration increases between 15 and 45 cm below the surface and decreases or remains constant below 45 cm, when the mean concentration is low (stands 1 to 4). When the mean concentration is high (stands 5, 7 and 8), it continues to rise to 60 cm below the surface. The pH increases with depth in stands 1 to 4, but strongly fluctuates in stands 5, 6 and 7. Nitrate and sulphate concentrations are rather constant throughout the profiles at low mean concentrations and fluctuate considerably at high mean concentrations.

4.3 Accuracy of the sampling programme

The number of observations needed to give a reliable estimation of the mean concentration of a certain solute in one stand at one depth on one date is calculated using the Z-distribution and the maximum variation coefficients in mean log-concentrations per stand, sampling depth and

period. Results are given in Table 3, which shows that for each element species, apart from sulphate, five observations per stand will give an estimation of the mean log-concentration with an error of 20 per cent at the most. However, in most cases the accuracy is much better, because the maximum variation coefficients overestimate the standard deviations.

Knowing the enormous variation in concentration level within stands, the question arises whether the samples taken at one place near a tree are representative of the soil moisture composition around that tree. In order to establish the relation between soil moisture composition and tree vitality it is necessary to have some knowledge of this variation in order to make the correct judgement concerning the significance of differences in mean soil moisture composition between trees. The sampling programme may then be optimized by increasing the number of samples near trees at those depths and during those periods where large variations in soil moisture composition occur.

Table 3 *Required sample size for estimating the mean log-concentration of several element species in one stand, at four different tolerable margins of error (D)*

Species	VCmax (%)	D (%)			
		5	10	15	20
Al	20	77	20	9	5
pH	10	20	5	3	-
Ca	10	20	5	3	-
Mg	13	32	8	4	3
K	12	28	7	4	2
NH ₄	20	77	20	9	5
NO ₃	15	43	11	5	3
SO ₄	25	120	30	14	8

To minimize the number of analyses, the samples may be mixed. Such a sampling programme, using a variable number of samples per stand and per period and with the possibility of taking mixed samples, is only possible with a very flexible sampling procedure. The chosen sampling

method, in which soil samples are taken with a hand-auger and the soil solution extracted by centrifugation, is very useful for this purpose. In optimizing the sampling programme, analysis of variance is an important aid to get some insight into the relative influence of the factors location, sampling depth and period on the variation in soil moisture composition.

5. CONCLUSIONS

- The present sampling programme gives a reasonable estimate of the mean log-concentration of several element species in stands, per depth class and per period.
- Spatial and temporal variations in concentration of a large number of element species in the soil solution increase significantly with the concentration levels.
- The variation in concentration levels is strongly related to location (stand) and to a lesser extent to sampling depth and time. The remaining unexplained variance is considerable.

ACKNOWLEDGEMENTS

We wish to thank the following members of the soil chemistry department of the Netherlands Soil Survey Institute: R. Zwijnen for his assistance with sampling, W. Balkema and M. Heijnen for the chemical analyses and Dr. A. Breeuwsma for his useful comments.

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GROUNDWATER POLLUTION UNDER FARMING-LAND AND WOODLAND
IN A WATERCATCHMENT AREA

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ABSTRACT

The investigation concerns: groundwater pollution, effect of a changed manuring-practice, denitrification in the saturated zone, transport-process in the unsaturated zone. The features of the area are: a coarse sandy unconfined aquifer, a deep groundwater level, mixed forest and plots of farming-land, rising nitrate contents in pumping wells. Soil and water samples are taken under arable land and woodland. The obtained data show deep farming-land pollution, high pollution under the forest borderzone and high aluminium contents in the woodland-leachate.

INTRODUCTION

The National Institute of Public Health and Environmental Hygiene (RIVM) is carrying out a research project on occurrence and behaviour of nitrogen compounds in groundwater. An investigation in the watercatchment area of Putten, in co-operation with the Water-supply Company Gelderland, forms part of this project.

Objectives of investigation are the determination of:

- The extent of agricultural groundwater pollution in the 10-year protection-zone
- The effect of a changed manuring-practice on the leaching of nutrients
- The quality of recharge water under woodland, as being effected by atmospheric pollutants
- The denitrification capacity of the saturated zone
- The transport process in the unsaturated zone

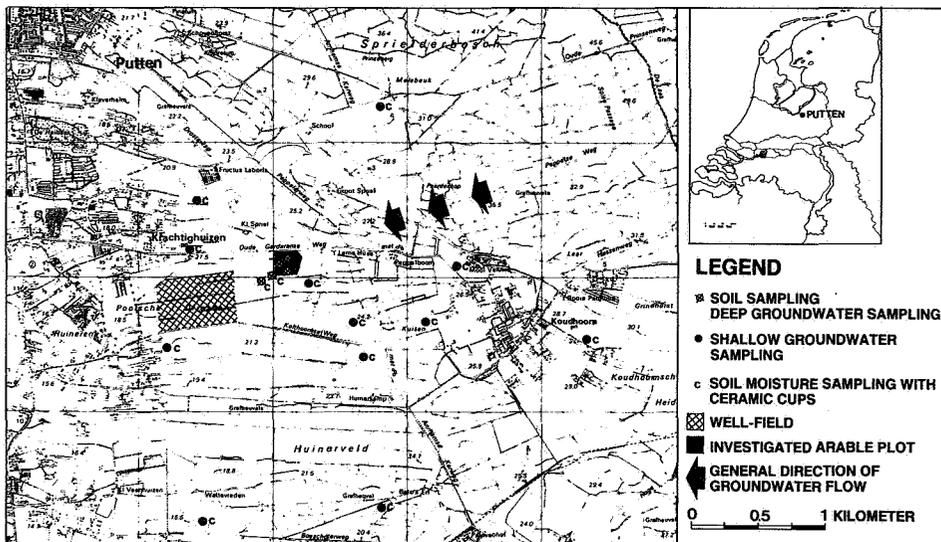


Figure 1. Area of investigation

AREA OF INVESTIGATION

The investigated area (figure 1) forms part of the total recharge area of pumping-station Putten on the NW rim of the Veluwe, a topographically elevated area of ice-pushed ridges in the middle of the Netherlands. The unconfined aquifer (about 180 meters thick) mainly consists of coarse sands. Inclined clay/loam layers (ice-pushed effect) can strongly determine the groundwater flowpattern. The land-use is mainly mixed forest and in places plots of farming-land.

From the beginning of the seventies the nitrate content in some wells is increasing (max. 23 mg N/l), probably because of groundwater pollution under farming-land at a distance of hundreds of meters. In 1983 the farmers voluntarily stopped the (abundant) application of cattle slurry in the winterperiod. Special attention is paid to the pollution under one plot of arable land (corn) with an area of about 3 hectares (figure 1). In the new manuring-practice only fertilizers (N,P,K,lime) are used in spring.

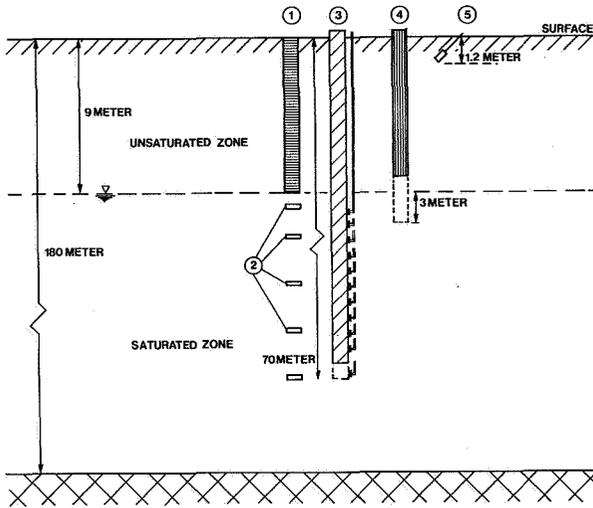


Figure 2. *Investigated system*

SAMPLING AND MEASURING

Figure 2 shows the investigated system. The numbering corresponds with the sampling description below.

1. Soil of unsaturated zone

On several places the unsaturated zone under arable land and woodland has continuously been cored down to the watertable. Mixed samples of every 35 cm depth interval have been analysed on soil and moisture (extraction method) composition.

2. Soil of saturated zone

The denitrification capacity of undisturbed soil cores has been measured in the laboratory by means of a shaking-method.

3. Deep groundwater

The sampling under arable land and woodland (figure 1) is carried out with miniscreens at 1 to 1.5 meter depth intervals, down to 70 meters below surface. The water is forced to the surface by a gas-lift-method.

4. Shallow groundwater under woodland

The toplayer of the groundwater (1 meter) is sampled at 3 cm depth intervals on several places, different regarding to vegetation and distance to agricultural areas. The sampling with the so-called multilayer-sampler is based on the dialysis-cell-method.

5. Soil moisture

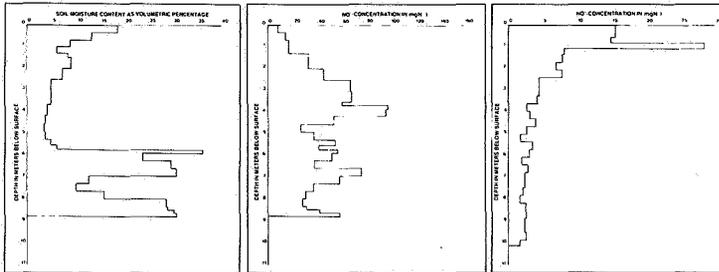
The soil moisture is directly sampled using ceramic cups and a vacuum-pressure-method. The sampling sites differ regarding to land-use and vegetation - arable land, various types of trees, open spots, heath/grass - and distance to agricultural areas. The monthly sampling takes place in the period November - May.

RESULTS AND CONCLUSIONS

Figure 3 gives an impression of the obtained data. It concerns profiles of several parameters in the unsaturated zone, the deep groundwater and the toplayer of groundwater. The table shows the soil moisture quality under a varying vegetation and land-use. The following conclusions can be drawn from the interim results:

- Groundwater under arable land has a maximum nitrate content of 70 mg N/l, while a value of 43 mg N/l has been measured at 60 meter below surface.
- The quality distribution in the (deep) groundwater is very heterogeneous. By preferential flowpaths polluted water reaches unexpected depths. On the other hand sometimes no pollution is found at places where it could be expected according to the general flow direction.
- The leachate quality under woodland strongly varies in space and time. High nitrate (up to 54 mg N/l) and sulphate (up to 286 mg/l) contents occur under coniferous trees in the forest borderzone (100-200 meter), where atmospheric deposition is relatively important.
- In comparison with soil moisture the groundwater toplayer under woodland shows lower concentration differences. Maximum contents in the forest borderzone: NO_3^- 21 mg N/l ; SO_4^{2-} 56 mg/l This phenomenon is probably caused by the mixing process in the groundwater and the dilution effect of recharge water of open spots.
- Especially the leachate under coniferous trees shows high aluminium contents (up to 56 mg/l under spruce). This corresponds with low pH-values, 3.9 - 4.5 .
- The pH of the groundwater toplayer under woodland varies from 4.3 to 7.9 . The great pH-differences between soil moisture and groundwater (sometimes 3.5 pH-units) indicate the importance of the (varying) buffering capacity of the (deeper) unsaturated zone.

UNSATURATED ZONE

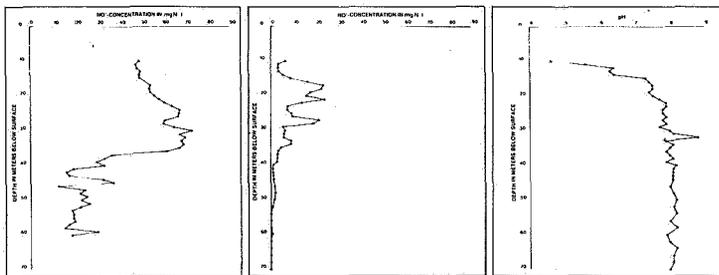


MOISTURE CONTENT

NO₃⁻
ARABLE LAND

NO₃⁻
WOODLAND

DEEP GROUNDWATER

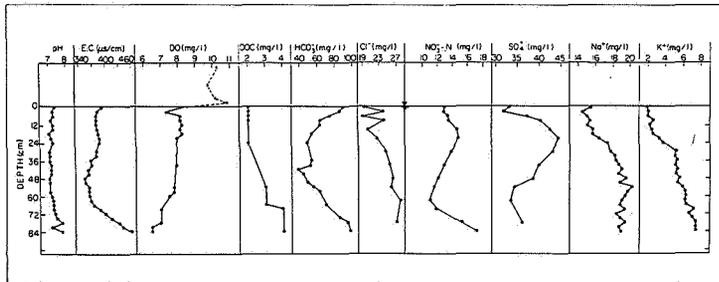


NO₃⁻
ARABLE LAND

NO₃⁻
WOODLAND, DOWNSTREAM OF
ARABLE LAND

PH
WOODLAND

SHALLOW GROUNDWATER WOODLAND



PINE FOREST

SOIL MOISTURE

PH, NO₃⁻, AND SO₄²⁻ CONCENTRATIONS IN SOIL MOISTURE AT 1.2 METER BELOW SURFACE, UNDER VARIOUS TYPES OF LAND USE/VEGETATION. LOCATION: ON AND NEAR THE INVESTIGATED ARABLE PLOT AT A DISTANCE OF 500-700 METER FROM THE WESTERN FOREST BORDER. MEASURING PERIOD: MARCH-MAY 1988 AND NOVEMBER-DECEMBER 1988.

LAND-USE/VEGETATION	MEASURING PERIOD	PH	NO ₃ ⁻ -N				SO ₄ ²⁻		
			R ¹	N ²	R ¹	C ³	R ¹	C ³	
OAK	M-M	4.2-4.7	6	5.2-12.4	8.0	8	22-38	30	8
	N-D	4.2-4.7	8	0.1-11.1	5.4	9	28-41	34	9
BEECH	M-M	4.3-4.4	4	1.9- 4.6	3.3	4	52-86	69	4
	N-D	4.2-4.5	5	1.3- 7.9	4.9	6	48-97	68	5
DOUGLAS SPRUCE (29)	M-M	4.1-4.2	3	5.9-23.0	14.8	6	26-152	134	5
	N-D	4.1-4.3	3	4.5-22.2	17.0	5	92-146	116	5
PINE (27)	M-M	4.3	3	8.8-14.9	12.9	5	45-68	47	5
	N-D	4.2-4.4	4	5.8-29.6	17.9	5	59-76	58	5
PINE (54)	M-M	4.2-4.5	4	9.4-51.5	20.9	6	39-42	41	8
	N-D	4.1-4.4	4	10.4-19.9	17.0	5	30-117	65	5
OPEN SPOTS/GRASS	M-M	4.5-4.6	5	0.7- 6.5	3.1	5	11-23	17	5
	N-D	4.3-4.6	6	0.2- 3.4	1.6	6	22-27	24	7
ARABLE LAND	M-M	5.7-6.3	6	14.5-23.5	17.4	10	10-61	29	8
	N-D	4.5-6.3	17	9.0-174	41.2	17	10-59	36	17

¹R: RANGE ²C: ARITHMETIC MEAN ³N: NUMBER OF DATA

Figure 3. Parameter profiles of unsaturated zone and groundwater and quality data of soil moisture

- The leachate quality under the arable plot has been improved by the changed manuring-practice (at present only fertilizers). However, mean nitrate contents (17 mgN/l in March-May; 41 mgN/l in November-December) still exceed the drinking-water-standard (11.3 mgN/l).
- In the laboratory nitrate-reduction has only been found in soil samples from depths of 60 meters below surface and more. These results generally correspond with other data from the region: nitrate profiles, iron-precipitation in pumping wells.
- The overall residence time of a waterparticle in the very heterogeneous unsaturated zone at the arable plot (about 9 meters thick) varies from 1.5 to 3.2 years.
- Chloride and nitrate profiles of the unsaturated zone indicate a fast watertransport via preferential flowpaths in (inclined) coarse sand and gravel layers.

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STUDIES OF SOIL PROPERTIES RELATED TO HEAVY METAL RETENTION

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ABSTRACT

The retention of the heavy metals, Cu, Cr and As, in two soils, a till and a meltwater sand, subjected to a heavy load of the three metals has been examined. It has been found, that variations in heavy metal concentrations correspond well with variations in organic and inorganic carbon, but other geochemical parameters also contribute to the retention. All variations in concentration can not be explained by geochemical factors alone, and it is suggested, that variations in permeability are responsible.

INTRODUCTION

The mechanisms for the retention of heavy metals in soil have been extensively investigated and the results cited in many reference books on trace metals (e.g. Adriano (1986), Kabata-Pendias & Pendias (1984)). The aim of the present work is to investigate the behaviour in the field of Cu, Cr and As in soils subjected to a heavy load of the three metals.

The study has been a field investigation at two sites formerly occupied by wood impregnation plants. The two sites are situated, one in a till area in the eastern part of Denmark, and one on meltwater sand in the western part of Denmark (Figure 1).

The geological setting of the till site has been described in detail by Fredericia & Lund (1987).

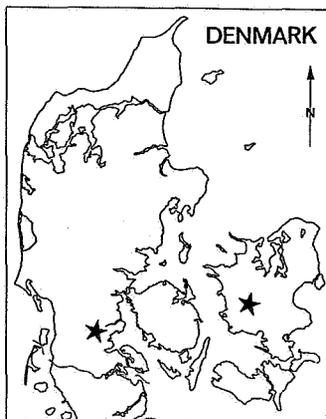


Figure 1. Localization of study areas

On both sites pollution started in the early nineteen twenties and has continued until 1968 on the till site and until 1982 on the site on meltwater sand.

MATERIALS AND METHODS

Soil samples

Soil samples have been taken in dug pits, 2.2 - 2.4 m deep. 1 - 2 kg of soil has been collected in polyethylene bags for every 5 cm's in the whole soil profile. After the determination of total residue, the samples have been air-dried and sieved to remove praticles larger than 2 mm diameter.

Undisturbed samples

In selected parts of the soil profile undisturbed soil samples have been taken in Kubiěna-boxes, 10 x 5 x 3.5 cm. Upon slow drying, the samples have been impregnated with an epoxy-resin (Ciba-Geigy HY 2996 resin and BY 158 curing agent). This resin, however, cures relatively fast, and

reimpregnation has been necessary in most cases.

The impregnated blocks have been sliced. Selected slices have been polished for macroscopic inspection. Also thin sections have been prepared, and the description and results from these will be published at a later date (Lund & Fobian, to be published).

Analyses

Total residue was determined by drying at 105°C for 20 hours. pH was measured in a 1:2.5 slurry of soil in water (pH, H₂O) and in 1 M KCl (pH, KCl). Total carbon was determined using a Leco, model 532, induction furnace, while carbonate was measured by titration. Organic carbon was found by subtraction of carbonate from total carbon. Due to analytical variability organic carbon could not be determined in samples having more than 0.5 % carbonate-carbon. Grain size distribution was measured in at least one sample for each horizon. Grain sizes larger than 63 µm were measured by dry sieving, while sizes smaller than 63 µm were measured by a sedimentation procedure. Free oxides of Fe, Mn and Al were extracted by the dithionite - citrate-bicarbonate procedure (Mehra & Jackson (1960)) and concentrations were measured by atomic absorption spectrophotometry (Perkin-Elmer model 5000). Cation exchange capacity (CEC) was determined by summation of exchangeable Na, K, Ca and Mg found by extraction with neutral ammonium acetate (Thomas (1982)), with exchangeable acidity. Exchangeable acidity was measured using a mini-column modification of the BaCl₂-triethanolamine procedure (Peech (1965)). The validity of the results by summation was checked at intervals by the measurement of total cation exchange capacity (Rhoades (1982)). Metal concentrations (Cu, Cr and As) were determined upon extraction in an autoclave with 7 N HNO₃ for 30 min. This procedure does not release heavy metals tightly bound in minerals, e.g. Cr in chromite is known to be largely unaffected by this treatment. In unpolluted samples it has been shown (Tjell & Hovmand (1978)) that Cu is released almost quantitatively, while only c. 50% of the Cr-content that could be found upon a HF/HClO₄-treatment, was extracted. The tightly bound metals are, however, of minimal environmental concern, and thus the use of 7 N HNO₃ is

considered justifiable. The concentrations of Cu and Cr have been determined by atomic absorption spectrophotometry in a flame (Perkin-Elmer model 5000), while As has been measured as arsine using a Perkin-Elmer, model 489 atomic absorption spectrophotometer, equipped with an MHS-20 hydride system.

RESULTS AND DISCUSSION

Three soil profiles have been examined in detail at each site. The profiles have been placed in such a way that the widest possible range of heavy metal load would be encountered.

The analyses showed that while the load was far higher in the most polluted soil profiles, compared to the medium polluted profiles, the distribution of the heavy metals in relation to geochemical parameters was similar. The profiles expected to have a minimal load of pollution were dug in areas supporting vegetation. The concentrations in the top soil were, however, higher than background levels for both Cu, Cr and As. Concentrations exceeding background level were found down to between 20 and 70 cm below surface. The distribution of heavy metals in these profiles did not contradict the results found for the most polluted profiles, and thus only results from the most polluted profile from each site are shown in the following, Figure 2, giving results from the site on meltwater sand, and Figure 3 from the till site (Galgebakken).

The maximum concentrations of Cu at the top of the two profiles are in the same range (12000 ppm and 8000 ppm, respectively), while the concentrations of Cr and As at the top are 6 - 8 times as high in the meltwater sand profiles as in the till profile.

A comparison of Figure 2 and 3 show, that the concentrations in the deeper part of the till profile are generally much higher than in the meltwater sand profile.

In the meltwater sand profile the concentrations of Cu exceed the background level (c. 10 ppm) at all depths, i.e. to 2.4 m below surface. Also As concentrations are over background level (c. 5 ppm), except between 0.9 and 1.5 m below surface, while the concentrations of Cr fall to background (c. 5 - 10 ppm) from 0.7 m below surface.

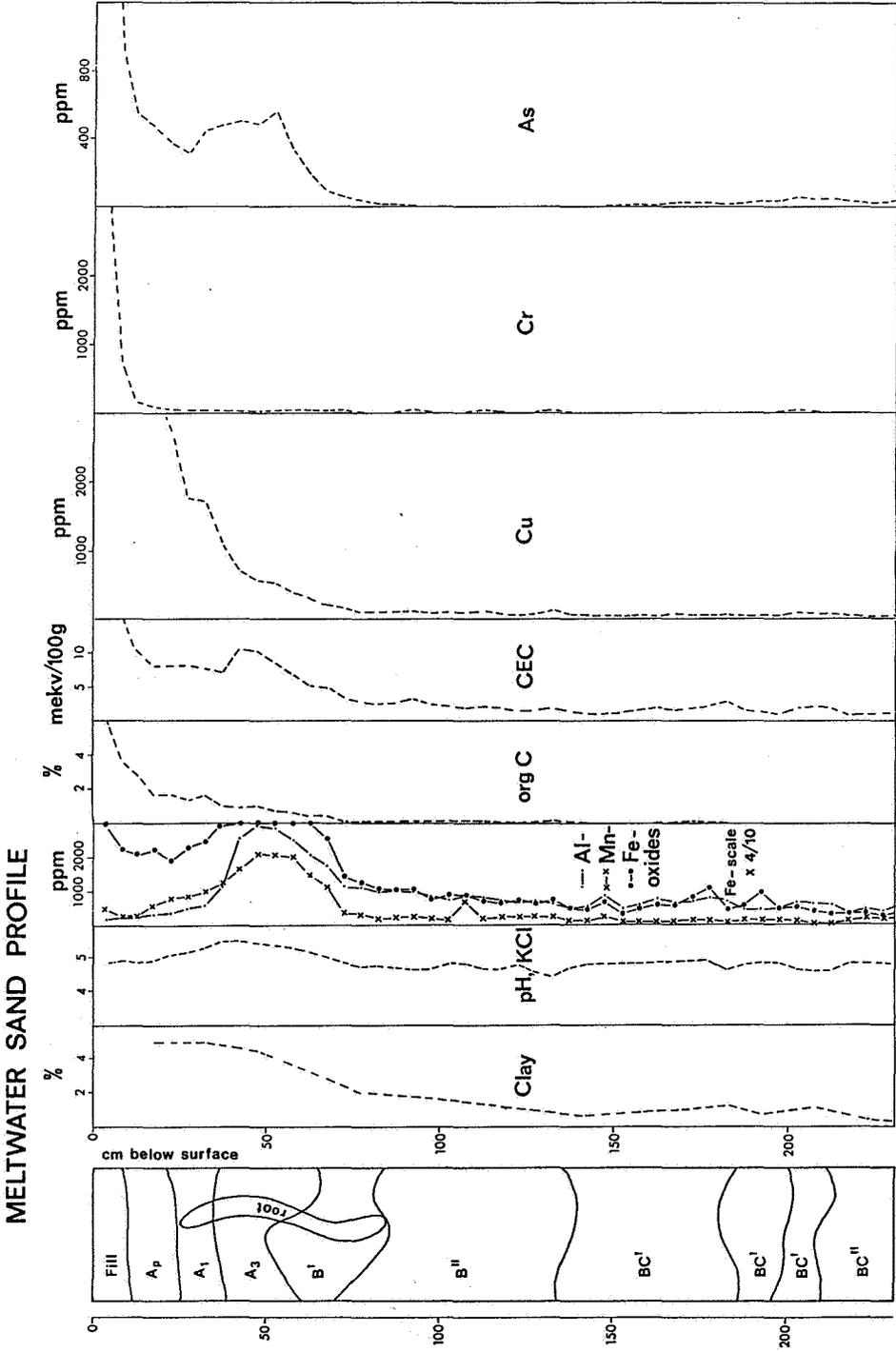


Figure 2. Geochemical parameters in a meltwater sandprofile

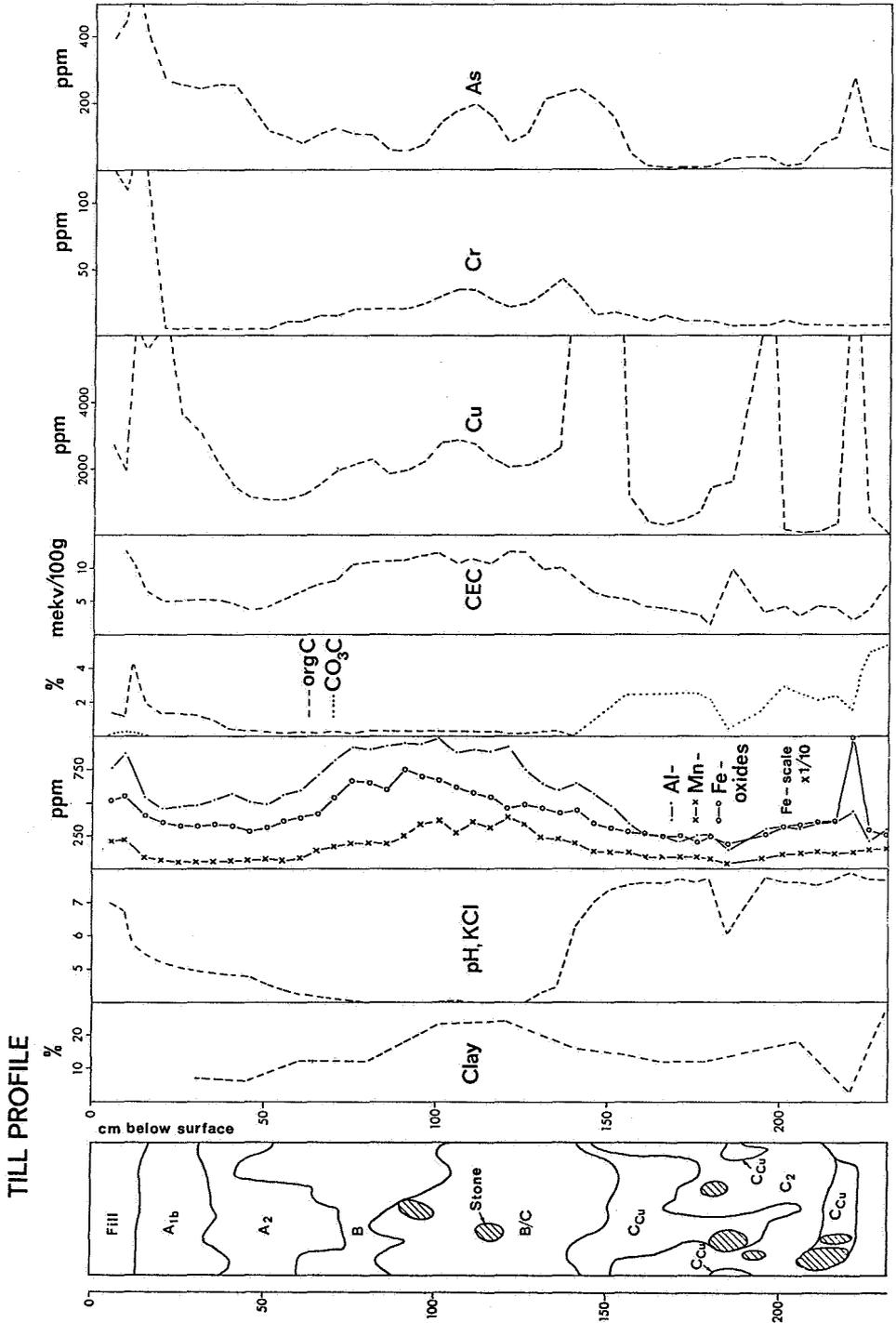


Figure 3. Geochemical parameters in a till profile

Only few samples are thus polluted by Cr, and apart from the evident connection between organic carbon (org C) and Cr retention, and the very high binding capacity in the fill at the top of the profile, no conclusions can be drawn from the data.

For Cu the best general correlation is found to organic carbon content ($r = 0.97$). It is also evident from Figure 2 that the sharp decrease in Cu concentration at the top of the profile can, out of the parameters examined, only be explained by an affinity to organic carbon. A similar decrease is, however, seen in the cation exchange capacity ($r = 0.82$), but as CEC is related to organic carbon, this is probably a derived relationship.

The clay content ($r = 0.83$) and, below the A1-horizon, the content of oxides, especially Mn- and Al-oxides, also seem to play a role (Mn-oxides: $r = 0.93$, Al-oxides: $r = 0.68$), but the correlation is not as good as for the organic carbon content.

The concentration of As correlates well with all geochemical parameters examined (r between 0.89 and 0.98), the best correlation being to organic carbon. The organic carbon content, however, fails to explain the increase in As concentration that is seen in the A1 and A3 horizons. In these horizons the accumulated oxides of Al, Fe and Mn probably contribute to the retention of As.

In the till profile (Figure 3) background levels are exceeded for Cu and As, except at short depth intervals. For Cr the concentrations are only above background in the fill at top of the profile and in the B/C horizon. The relationship of the retention of all three metals to organic carbon content is evident in this profile, as well as in the meltwater sand profile. But from the distribution of Cu and As it is clear, that in this profile other mechanisms must be important.

The most striking feature is the peaks in Cu concentration from 140 cm depth and down. The peaks correspond to horizons termed C_{Cu} in the profile drawing. These are recognized in the field as green areas, the green color originating from basic cupric carbonate (malachite, $Cu_2(OH)_2CO_3$), identified by X-ray diffraction. Precipitates of Cu in a calcareous soil have previously been identified as malachite by McBride & Bouldin (1984).

There seems, however, to be no ready geochemical explanation for the

very great variation in Cu concentrations within the calcareous part of the profile. It is believed, that this behaviour is due to differences in permeability, since high Cu concentrations are found below a partly disintegrated stone and in a gravel layer (in Figure 3 shown as the horizon 2.2 m below surface, having a low clay content).

The variation in As concentration within the calcareous zone is similar to the variation in Cu concentration, although the maximum concentrations are much lower. This supports the theory that variations in concentration are due to differences in permeability.

In the B and B/C horizons the wavy appearance of the curves for Cu, Cr and As cannot be related to variations in any of the measured geochemical parameters. The only trend seems to be a slight increase in metal concentrations in the B/C horizon, where concentrations of oxides and clay are high.

CONCLUSIONS

The geochemical parameters of the greatest importance for the retention of Cu, Cr and As in both the meltwater sand and the till profiles have in this study been organic and inorganic carbon. Within a soil profile also clay content and the concentration of Fe-, Mn- and Al-oxides play a role, but it seems to result in only slight variations in the general pattern governed by the two carbon parameters. The cation exchange capacity, being a parameter derived from the organic carbon, clay and oxide content, also gives a reasonable correlation in non-calcareous soil. The relationship between a geochemical parameter and a heavy metal, e.g. between organic carbon and Cu, is not the same for the two soil types and thus a general correlation between e.g. organic carbon and retention capacity for a heavy metal can not be made.

ACKNOWLEDGEMENT

This work was supported by the National Council of Technology (grant no. 5.26.13.11).

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ACCOUNT FOR WATER-ROCK INTERACTION FOR SOUNDING OF
GROUNDWATERS AND AERATION ZONE PROTECTION

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ABSTRACT

An interdisciplinary nature pertinent to the study of a water-rock ecological system requires a comprehensive approach considering moisture and salt transfer in an aeration zone and groundwaters. A set of equations describing both solution transport and physical-chemical interaction in a water-rock system is used to model moisture and salt transfer in unsaturated and saturated soils. Parameters and boundary and initial conditions should be provided for solution of equations. This approach to the study implies on experiments. Initial and boundary conditions are verified at field test sites. Pore solution sampling by a method of vacuum extraction in saturated and unsaturated soils is used to estimate a hydrochemical background. Hydrogeochemical parameters can be determined using soil monoliths either filtrated at their total saturation with salt solution or having moisture transfer in unsaturated soils. From the results of washing soils characterised by different moisture contents and velocities of moisture transfer one can find the values of molecular and convective diffusion and salt exchange (adsorbtion and cation exchange).

On irrigation conditions of the agricultural soils the importants change in the natural water and salt balance of soils, grounds of aeration zone, groundwater and their contamination take place. It is stipulated in the first turn by the increasing of the infiltrational groundwater recharge in comparison with natural recharge and also by the utilization of the groundwaters with the high mineralization, drain and sewage with the aim of irrigation.

It is necessary to research and to prognosis in time the processes of salt-transfer and salt-exchange in water-rock system for the elaboration of soil protection strategies in aeration zone and groundwaters from contamination. One of the studing methods is the

modelling. It's very important that mathematic models should reflect the main links between the most essential factors of hydrochemical processes and reproduce their main components. For the modelling of moisture - and salt transfer in the unsaturated-saturated grounds the known qualitative models of the natural processes described by Lyalko (1985), Nerpin and Chudnovsky (1976), Faibishenko (1986) are used. The models describe the solution migration and different kinds of interaction in water-rocks system, made on the bases of achievements in fundamental sciences - mathematics, physics, chemistry and etc. However the processes of interaction in water-rock system such as: dissolution, leaching, precipitation, crystallization, sorption, desorption, exchange processes and so on, which have taken place in natural environment are very specific especially in the conditions of land-reclamation. Predominance of this or that process is determined by the reciprocal influence and correlation of natural factors: climatic, geological, hydrogeological, by soil conditions and factors of land-reclamation: regime of irrigation, quality of irrigational waters, kind of plants and chemical land-reclamation.

The analyses of results on the previously irrigated soils in the South Ukraine illustrated, that such processes as alkalization of soil and soda salinization, gypsification, carbonatization, calcification are the main land reclamation - hydrogeochemical processes in water-rock system and are caused by the prevail effect of leaching processes and ion-exchange.

In the substantiation of different measures on the protection of groundwater and aeration zone one can take into consideration some categories of interaction processes: mechanical, physical, physico-chemical, chemical and biological ones.¹ Usually, they occur in the natural environment simultaneously, and to a certain extent mutual conditioning each other. The main factors provoked these processes of interaction are the peculiarities of grounds (mineralogical and mechanical composition and character of salinization - crystalline salts or in the exchange complex, structure and texture of the ground, swelling of soil, soil soaking, potential of colloidal particles and so on) and peculiarities of pore solution (mineralization and ionic concentration, density, volume and transport rate in the pore solution, osmotic potential and so on).

Mechanical processes it is redistribution in ground of colloidal silty particles and also dispersion of particles without their migration. The accumulation of substance on the boundary of well-pervious sandy sediments and underlying clayey sediments is the typical demonstration of mechanical processes. These processes resulted in the decreasing of permeable pore sizes and lowering of filtration coefficient. The last factor must be taken into consideration in the formation model of the salt-aqueous balance of the ground in aeration zone and groundwater. Mechanical processes may induce the manifestation of physical, physicochemical and chemical interaction in grounds. At the same time the mechanical processes may become the result of their manifestation. Physical processes are stipulated by the hydration phenomena of clay particles and adsorption (or desorption) on them the ions of pore solution. Molecules of water surrounding particles of grounds aim at the osmotic equilibration with the bulk of the pore solution. The increasing of mineralization of the bulk of the pore solution decrease the bulk of the solvate shells but its decreasing increase the latter solvate layers and, consequently, decrease the effective porosity and ground permeability. Processes of adsorption-desorption are generally described by the nonlinear Langmuire isotherm

$$\partial N_i / \partial t = a C_i / (1 + b C_i) \quad (1)$$

where

N_i = the mass of the adsorpted i-ion

t = time

C_i = the concentration in the pore solution of i-ion

a_i and b_i = coefficients

When $b_i = 0$ Langmuire isotherm transmute into the linear Henry isotherm, the equation of which is usually represented as:

$$N_i = H_i C_i \quad (2)$$

where

H_i = Henry coefficient

The nonlinear physical processes usually proceed not for the long time-during for the first twenty-four hours, weeks, months after the beginning of humidification of grounds. Then they satisfy a linear isotherm. For the majority of inorganic contaminants, for instance heavy metals, the numerical values of Henry coefficient reach dozens, hundred and even thousands. If in the equation of soil transfer

$$\partial (\theta C_i) / \partial t = \partial (D \partial C_i / \partial z) / \partial z - \partial (V C_i) / \partial z - \partial N_i / \partial t \quad (3)$$

where

- θ = the volume of pore solution per unit of groundvolume by which C_i is determined
- V = rate of transfer of the pore solution
- D = coefficient of convective diffusion

we substitute the expression of Henry isotherm (2) and get the following equation:

$$\partial (\theta + H_i) C_i / \partial t = \partial (D C_i / \partial z) / \partial z - \partial (V C_i) / \partial z \quad (4)$$

We can see, that if the high values of Henry coefficient the numerical values of θ ($\theta < 1$) can be neglected. This is very important simplification of investigations because the determination of θ is very difficult. The grounds of aeration zone with respect to the contaminant are geochemical barrier. In particular the interaction water-rock system can be accompanied by the sorption processes. The equation (4) shows that these processes decrease the distance of substance transfer in $(\theta + H)$ time or roughly in H time as it has been shown by Golubev and Garybyants (1968).

Natural processes of substance decay both in solid or in liquid phase and migration are typical for the majority of organic and inorganic contaminants. That is why equation of decay

$$C_i = C_{oi} \exp(-\alpha_i t) \quad (5)$$

where

α_i = half-decay constant

It is necessary to consider in same system with the équation (4) taking account of physical processes.

Physicochemical processes of interaction between the pore solution and ground the so-called exchange ones are stipulated by the ion-exchange of the pore solution and the ground exchanging complex.

Some difference between physicochemical and physical processes must be emphasized. Physical processes have taken place on the molecular level when the whole molecules of substance are sorbed, but the physicochemical processes occur the ionic level. Cation-exchange is generally typical for the grounds.

Nickolskoi linear isotherm is usually used for the characteristic of cation-exchange in soils and grounds:

$$N_1^{1/z_1} / N_2^{1/z_2} = k_{1,2} a_1^{1/z_1} / a_2^{1/z_2} \quad (6)$$

where

N_1, N_2 = the concentrations of i-ion in the exchange ground complex

a_1, a_2 = the activities of i-ion in the equilibrium pore solution

z_1, z_2 = valencies of i-ion

$k_{1,2}$ = exchange coefficient

However, as the deep model researches performed by Spozito (1984) have shown, the linear isotherm (6) is the particular case characterised the exchanging processes. Besides that there are three types of exchange isotherms: S-formed isotherm (when hard competition arises between the exchange ion and ion from the ground exchange complex or when exchange ions are distributed irregularly and aims at the formation of clusters), L-isotherm (ion has sufficiently high affinity to exchange complex), H-isotherm (ion has very high affinity to exchange complex).

More often the exchange of ions of equal valency is subordinated to the linear isotherm (G-type), and to the nonlinear one with different valency.

The chemical processes include a dissolution and extracting of easily-, middle-, and hard dissolved soils which occur in the ground as a crystall form. The chemical processes to a certain extent favour the manifestation of physical and physicochemical interaction between

ground and pore solution. Verigin et al. (1979) described of the dissolution and extracting by the model:

$$\partial N_i / \partial t = \beta_i (C_{mi} - C_i) a_i^{k_i} \quad (7)$$

where

β_i, a_i, k_i = coefficients

C_{mi} = limit concentration i-ion in the pore solution

It can be seen that these processes of interaction between ground and pore solution are described by different models.

Hence, for the transfer prognosis of the multicomponent pore solution. System included the equations 1,2,3,5,6,7 for each i-ion and corresponding equations of saltexchange has been used.

The authenticity of prognoses increases if instead of ion concentration data in models of salt-exchange will be used the ion activity data. The solution of salt-transfer equations requires the superposition of boundary conditions (initial and finite ones) and the provision of boundary parameters.

The full-scale researches advisable for the estimation of the initial and boundary conditions salt-transfer must be carried out on the basis of method of "vacuum extracts". Black (1974) described its principle which comes to sampling of pore solution from the grounds and water-bearing horizons by means of the rarefaction within the space of porous probe. Then the overflow of pore solution from the ground to the probe takes place. Faibishenko (1986) has shown that utilization of probes established on different levels within the boring well is the very reliable method of extraction of the pore solution. The probes are established along the boring well tube different depths and this pipe - bend needed for the rarefing and the sampling of the pore solution are fixed above the terrestrial surface. The free part of the boring well tube is temping with the ground or some other material. For the extracting of the pore solution on the terrestrial surface the air-lift principle is wed when air is injected into the input probe pipe to induce flowing of pore solution through the out put one, rising to the terrestrial surface. Such method of extracting of the pore solution allow to establish probes at different depths to about

some dozens metres. This method is reliable for the point control of soil and ground salinity. At the same time the area control is necessary for setting different irrigation measures. One method to extract the area information is setting of porous probes a lot of points within the studied area with regard to space salinity distribution and statistical test data processing.

The determination of hydrogeochemical parameters is advisable to carry out in the soil monoliths so in this case the dependence on molecular diffusion coefficient, convective diffusion, salt exchange parameters taking account of the variation of moisture and its sucking pressure is determined. Since salt transfer parameters dependent on the mineralization and chemical composition of pore solution, aqueous solutions for the experiments man-made prepared and corresponded to pore solution composition at nature conditions must be used. Thus, the prognoses of groundwaters and aeration zone contamination requires the account of processes simultaneously proceeding and interconditioned one another, such as mechanical, physial, physicochemical, chemical, biological ones where they are described by equation system (1-7). Since ion concentration in pore solution is assumed as a function in salt transfer equation describing transfer of salts in unsaturated-saturated grounds of aeration zone simultaneously and in water-bearing horizont, so the method of vacuum extract of pore solution is used to evaluate a boundary conditions for salt transfer equations. Its application is based on installation of porous probes at different depths in boring well tube. Further detailed improvement of interaction models in water-rock system must consider ion activities of multicomponential pore solutions.

NOTES

¹Biological factors in this paper aren't considered

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THE EVOLUTION OF IRON AND MANGANESE VALUES IN GROUNDWATER
ALLUVIAL SYSTEM - INTERPRETATION OF FIELD DATA

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ABSTRACT

Analyses of iron and manganese in the groundwater of the alluvial aquifer of the Saône river (EAST of FRANCE) are discussed from a program with multiple measurements. It is possible to verify the presence of several forms : ionic, strong or weak complexes and precipitates.

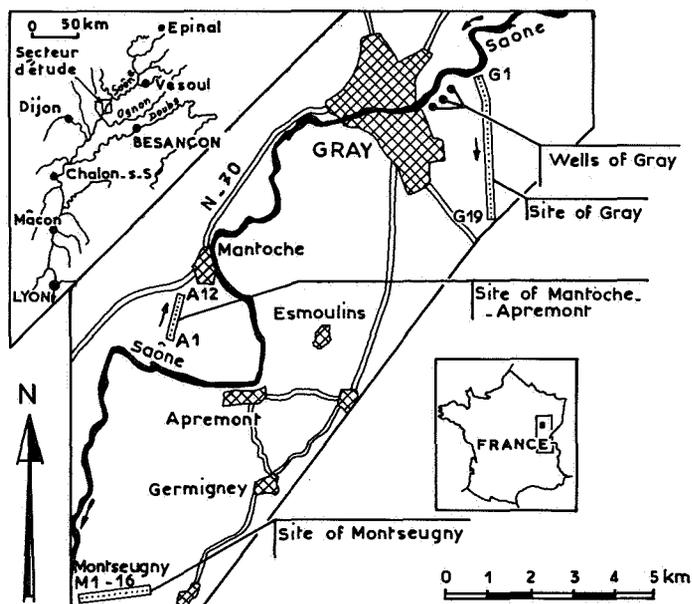
An essential fact discriminates manganese and iron in solution : while iron in many cases takes an organic-complex form (except in strong reducing sites), manganese is, on the contrary and in major part, in an ionic divalent state. The values of Eh and pH in groundwater determine the domains of stability of Fe and Fe(OH), while the values of manganese are rather placed in the stability field of Mn.

1 INTRODUCTION

This work deals with the mechanism of evolution of iron and manganese values in groundwater in the alluvial aquifer of the Saône river during two hydrologic cycles (1983-1984). The complex alluvial system, confined under superficial clay loams, is essentially silicious with large seasonal variations of Fe^{2+} and Mn^{2+} . Some sixty sampling

points of water (groundwater and superficial water) have been examined each month on three experimental sites (Gray, Apremont, Montseugny - Figure 1).

Figure 1 : *Geographical situation of the case study and location of site*



2. OPERATING MODE

The samples of water (after pumping) are immediately acidized on field by chlorhydric acid (HCl 0,7 m) without filtering. Classic method (Anonymous, 1980) recommends an acidizing but also a filtering with a mesh of 0.45μ which can separate "dissolved phase" from "suspended phase". But some studies (FIGUERES, 1978) have shown that metals can be transported with a colloidal form or fine grain susceptible to be stopped by filtering.

In our case all kinds of states of iron and manganese are considered : ionic form, soluted complexes, colloids and fine suspension. Only hydroxydes with a greater size and

technique)

$$y=1.79x-0.50 \quad (r=0.73-332 \text{ samples})$$

3.2 Different complexed forms of iron

Many authors (Singer et al., 1975 ; Buffle, 1977) mention complexed forms of iron with bicarbonate, chloride, phosphate, sulfate ions, silica and organic components. We have correlated the concentrations of iron with different anions on 330 samples (table 1).

Table 1 : *Correlation coefficients between Iron and anions (330 samples) * : significant coefficient*

	HCO_3^-	PO_4^{3-}	SO_4^{2-}	Cl^-	SiO_2
Total Iron	0.09	-0.09	-0.13*	-0.15*	-
Complexed Iron	0.02	-0.10	-0.12*	-	0.26*
Dissolved Iron	-	-	-	-	0.36*

The relations between iron and sulfate and chloride anions are significant but opposite. With bicarbonate and phosphate there is no chemical relation. But between SiO_2 and "Dissolved Iron" as well as "Complexed Iron" we found a high correlation respectively with $r=0.36$ and $r=0.26$.

3.3. Manganese

The correlation between concentration values of manganese obtained on field (y) (Merck's method) and by atomic absorption method (x) in laboratory gives good fitness :

$$y=0.67x+0.05 \quad (r=0.90-93 \text{ samples})$$

We can see the difference is 30% more important than in the case of iron because the ionic form of manganese is abundant. The statistical tests relating to the presence of anionic complexes have been negative.

3.4 Spatial evolution

The comparative evolution of the concentrations of iron, manganese and E_H (Redox potential) at a same time (01/17/84) on a alluvial site (Apremont section) shows (Fig. 2) :

- a good opposite fluctuation of manganese with E_H
- a translation of iron values in relation with the influence of complex formation phenomenon.

On the whole values (330) the correlation coefficients found are the followings :

dissolved iron/ E_H , $r=-0.395$ ($y=8.49x+4.43$)

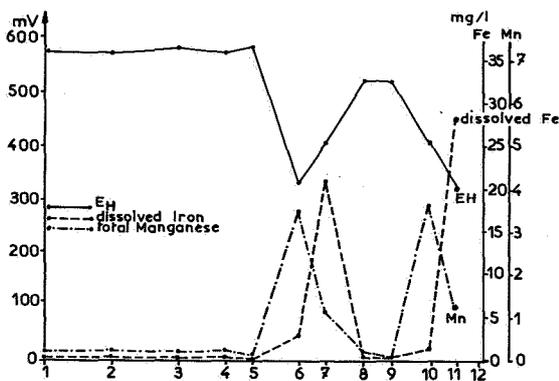
total iron/ E_H , $r=-0.35$ ($y=9.95x+5.86$)

complexed iron/ E_H , $r=-0.12$

manganese/ E_H , $r=-0.18$ (289 values)

All the correlation coefficients are significant.

Figure 2 : *Spatial influence of the E_H on the values of iron and manganese (Apremont section) measured on 01/17/84.*



4. INFLUENCE OF DISSOLVED OXYGEN AND CARBON DIOXIDE

The amount of dissolved oxygen which regulates the redox reaction varies between 0 and 10 mg l^{-1} with a maximum when subsurface clay loams are missing. The seasonal variations can reach amplitudes of 3 mg l^{-1} .

often better cristallized are not taken into account because trapped in the ground or in the peripheral part of the well.

The acidizing of water on field immediatly after the sampling causes the dissolution of hydroxydes newly precipitated. The weak complexes and colloidal clusters are destroyed and filtering ($d = 0.45 \mu$) retains only the matters in suspension (organic solids, clays, ...) and the big particles of iron and manganese not attacked by the acid (Edmunds in Lloyd, 1981).

Iron

The different methods used for the analysis of iron (appendix 1) do not take into account the same states of this metal. In fact the Merck's field method permits the measurement of the amount of ionic iron Fe^{2+} , the low complexe of iron and of the soluble form of Fe^{3+} , this kind of analysis being named "Field Iron". We also find here also the colloids of iron destroyed by HCl and the fine particles attacked by HCl.

The colorimetric analysis of "Total Iron", by addition of hydroxylamine (reducing medium) after heating, leads us to the knowledge of all the precedent forms but also of the strong complexes of iron which have resisted the cold acid attack.

The spectrophotometric method (atomic absorption) is equivalent to "Total Iron" colorimetric technique with additional complex forms which do not react with colorimetric solutions (Hem, 1960 ; Rodier, 1971 ; Anonymous, 1980).

Manganese

The analysis on field by the Merck's method gives ionic

forms of manganese Mn^{2+} (0.0-0.5 $mg\ l^{-1}$ range).

The atomic absorption technique takes into account all the forms : ionic Mn^{2+} , colloids, complexes and precipitates which have been destroyed by cold HCl.

3. ANALYSES RESULTS

3.1 Iron

A statistical approach ("least squares" method) by means of 1200 determinations on iron forms, realized on 47 piezometers, permits (Recoules, 1984 ; Chauve et al., 1986) the following remarks :

- values of "Field Iron(y)" (Merck's method) are greater than "Dissolved Iron(x)" (Colorimetric technique) with

$$y = 1.60x + 0.24 \quad (r = 0.82 - 290 \text{ samples})$$

This equation shows the presence in suspension of Fe^{2+} hydroxydes and Fe^{2+} oxydes.

- values of "Total Iron(y)" (Colorimetric technique+hydroxylamine) are higher than "Field Iron(x)" (Merck's method) with

$$y = 0.72x + 0.30 \quad (r = 0.89 - 334 \text{ samples})$$

because with the latest method strong complexes widely present in alluvial groundwaters are not analysed.

- the correlation between "Total Iron" by Colorimetric technique (y) and by atomic absorption(x) leads to a very good relation :

$$y = 1.01x + 0.05 \quad (r = 0.98 - 334 \text{ samples})$$

- between "Total Iron(y)" and "Dissolved Iron(x)" treated by colorimetric technique a great difference is seen in association with the presence of strong complexes in the first case :

$$y = 1.23x + 0.60 \quad (r = 0.93 - 332 \text{ samples})$$

- finally it is possible to evaluate the amount of complexed iron (x) and its relation with "Total Iron(y)" (colorimetric

Table 2 : Correlation coefficients between oxygen and iron, manganese. Values of dissolved oxygen.

n : number of samples * : significant coefficient.

Sites	Dissolved Iron		Manganese		Dissolved Oxygen		CO ₂ mgl ⁻¹
	n	r	n	r	mgl ⁻¹		
					mini	maxi	
Gray	86	-0.31*	49	0.03	1.5	8	10-40
Apré mont	42	-0.25	42	-0.40*	0	10	20-80
Mont seugny	78	-0.39*	78	-0.06	0	6	20-80

The linear regression between dissolved iron and dissolved oxygen gives, for 294 values, a significant correlation coefficient of -0.32. Manganese, for 256 values, is also correlated to oxygen ($r=-0.15$). The sites have been considered separately with a relative correlation too (table 2). The free carbon dioxide has been calculated by means of ionic activity of Ca²⁺, HCO₃, pH and temperature.

The concentrations of CO₂ are low in winter (average of 50 mgl⁻¹) for Montseugny and Apremont and very high in spring-time in relation with microbiological activity.

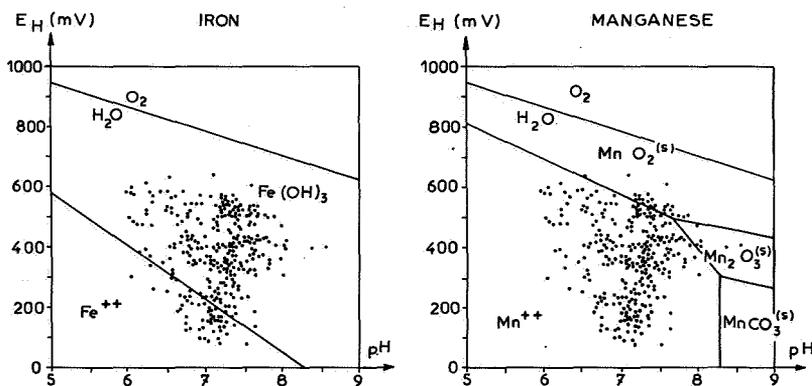
A correlation with 324 samples shows a strong opposite connection between pH and CO₂ ($r=-0.83$).

5. CONCLUSIONS : STABILITY DOMAIN

The amounts of dissolved oxygen and carbon dioxide influence the E_H values of groundwater. We have shown on Figure 3 the stability domains of different forms of iron and manganese in comparison with E_H and pH parameters. The iron values

are always close to the stability limit of Fe^{2+} and $\text{Fe}(\text{OH})_3$, whereas the manganese values are located in the stability domain of Mn^{2+} . In the alluvial groundwater of the Saône river it is logical to find more ionic Mn^{2+} than ionic Fe^{2+} . The latest automatically precipitates ($\text{Fe}(\text{OH})_3$) with presence of dissolved oxygen. The iron is often complexed (organic matter, silica) and in this case its reaction differs from that of the manganese which has a thermodynamical behaviour (in connection with pH and especially E_H) and drops off its concentration with oxidizing conditions (Verjus, 1984).

Figure 3 : $pH-E_H$ stability field diagrams for iron and manganese for an ionic activity of 0.01 ppm



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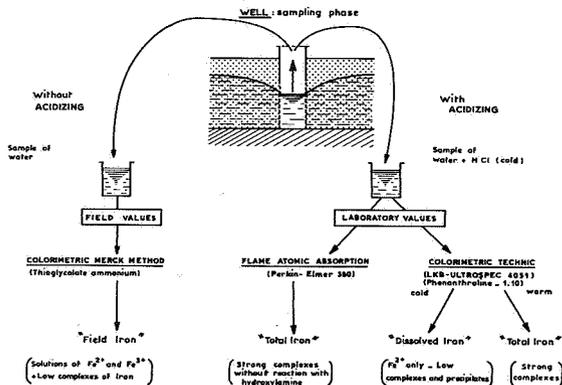
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APPENDIX 1: The different steps of the analytical process for the Iron in ground water

THE INFLUENCE ON THE QUALITY AND QUANTITY OF GROUND
WATER BY SPRINKLER IRRIGATION OF WASTE AND FRESH
WATER

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ABSTRACT

The tendency of leaching of nutrients (nitrate) into the groundwater is reinforced on high permeability soils by irrigation. If the geochemical environment is suitable, nitrate reduction is catalyzed by mikro-organisms. In the research areas groundwater recharge by irrigation is restricted to the winter months.

1. INTRODUCTION

In the Federal Republic of Germany, 60% of the drinking water supply is derived from ground water, in Lower Saxony this proportion can reach 80%. Attention must therefore be paid in all industrial and agricultural activities to the preventative protection of the ground water. In Eastern Lower Saxony, where our investigations were carried out, additional sprinkler irrigation is necessary due to the negative climatic water balance in the period of vegetation, and the high water permeability of the sandy soils. The amounts of ground water necessary for this often considerably exceed the supply rates of the local waterworks. Sensible recycling of the purified communal waste-water by land

treatment contributes to the protection of the ground water supplies.

In the following, investigations of the Abwasserverband Wolfsburg and the Beregnungsverband Hankensbüttel are presented (Figure 1).

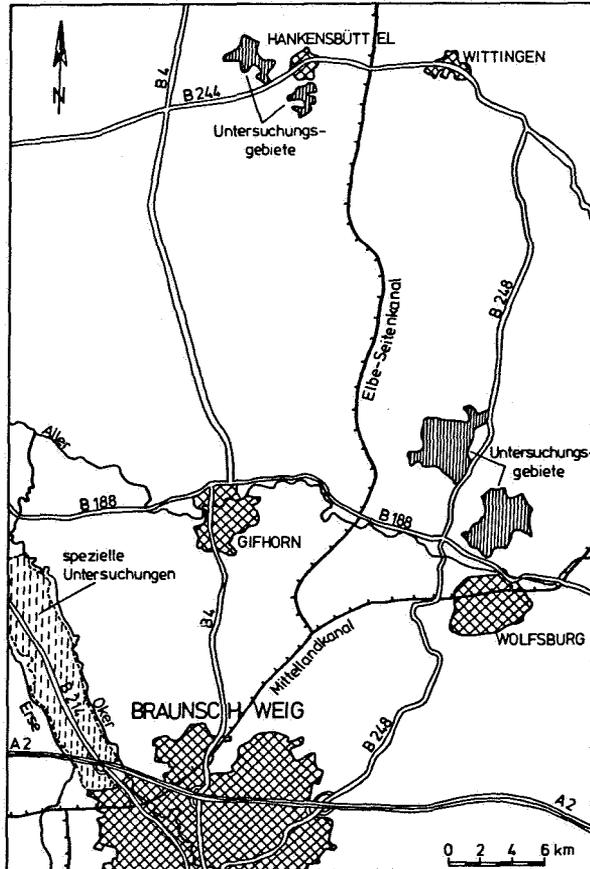


Figure 1. Location map of the investigation areas in Southeast Lower Saxony

The focal point of the following is flow rate and transport procedures in the upper, Pleistocene aquifer, and the description of a computer model in order to record local ground water recharge by intensive waste water irrigation and seepage.

2. GEOLOGY AND DESCRIPTION OF THE SITE

2.1. Abwasserverband Wolfsburg (after WOLFF and WACKER (1985))

Within the area of the Abwasserverband Wolfsburg, two local areas are irrigated - Jembke and Brackstedt, cf. Figure 1.

Sprinkler irrigation area	-	13 km ²
Flush irrigation area	-	3 km ²
Amount of waste water	-	6,000,000 m ³ /a
Precipitation	-	639 mm/a
Climatic water balance (N-ET _{Haude})	-	-118 mm/a

2.2. Beregnungsverband Hankensbüttel (after ENGELBACH (1984))

Ground water and local waste water are irrigated in the Beregnungsverband Hankensbüttel.

Sprinkler irrigation area	-	10 km ²
Amount of waste water	-	40,000 m ³ /a
Precipitation	-	665 mm/a
Climatic water balance (N-ET _{Haude})	-	-100 mm/a

2.3. Geology and hydrogeological parameters

The aquifer in both areas consists of Pleistocene (Saale period, Drenthe stage) glaciofluvial sands and gravels. The thickness of the Quaternary is approx. 60m (Figure 2). The base is mainly composed of Tertiary clays. Jurassic clays are also locally present.

The standard profile is as follows:

1. Upper aquifer. Sands and gravels. The thickness is approx. 15-20m.
2. Saalian tillite. Silts and clays. The thickness is approx. 20-40m.

Locally, 'hydraulic windows' are present.

3. Lower aquifer. Sands and gravels. The thickness is approx. 20m. The lower aquifer is the main source of the drinking water supply in Lower Saxony.
4. Tertiary or Jurassic clays.

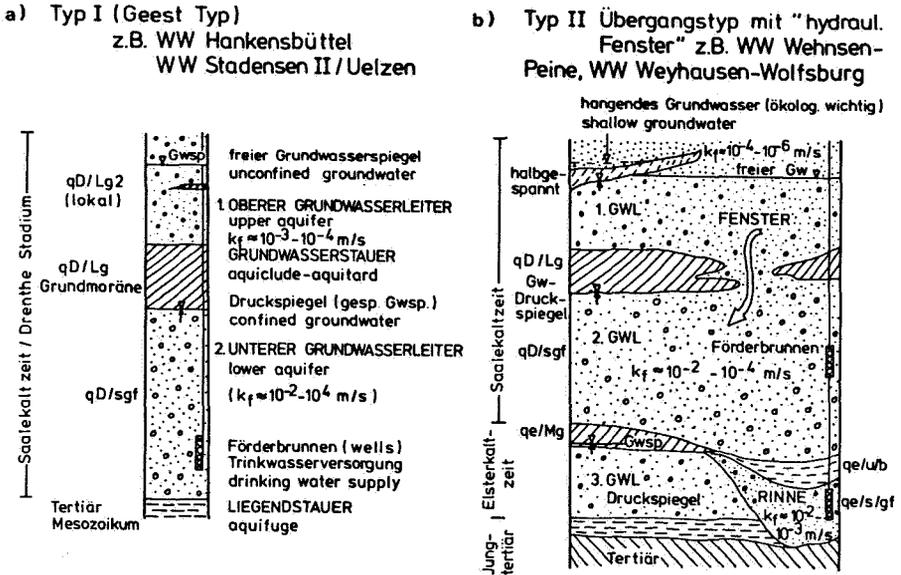


Figure 2. Schematic standard profiles of the Pleistocene aquifers in Southeast Lower Saxony

The evaluation of pumping tests for the upper, unconfined aquifer gave the following results:

a. Abwasserverband Wolfsburg:

- Coefficient of hydraulic conductivity: 1.0×10^{-3} m/s
- Transmissivity: 1.6×10^{-2} m²/s
- Apparent flow velocity (Jembke): 1.5×10^{-5} m/s (1.3 m/d)
- (Brackstedt): 4.8×10^{-5} m/s (4.0 m/d)
- Effective porosity: 0.13

b. Berechnungsverband Hankensbüttel:

Coefficient of hydraulic conductivity:	0.8×10^{-3} m/s
Transmissivity:	1.4×10^{-2} m ² /s
Apparent flow velocity:	2.0×10^{-5} m/s (1.7 m/d)
Effective porosity:	0.14

Tritium data in the Abwasserverband Wolfsburg showed an age of between one and ten years (layered ground water) for the upper aquifer and for the lower aquifer an age of more than 25 years.

3. INPUT AND FLOW RATE IN THE UPPER AQUIFER

Sprinkler irrigation, together with intensive manuring, results in improved leaching of nutrients (especially nitrate) into the ground water from the permeable sandy soils, which are low in absorption property. Figure 3 shows, for example, that the nitrate concentration in waste-water and fresh-water irrigation areas hardly differ. There are, however, clear differences in the geochemical environment of the two sites, which are particularly expressed in the higher O₂ contents and the higher nitrate permeability (NO₃⁻/Cl⁻) of the fresh-water irrigation area Hankensbüttel. The bacterially controlled nitrate conversion comes about exclusively in reducing environmental conditions, with the result that there are no favourable conditions for denitrification in the fresh water irrigation area. On the other hand, the environment in the ground water of the waste-water irrigation area Wolfsburg is favourable for nitrate reduction, because of the presence of sufficient organic carbon (Table 1, Figures 3 and 5). In addition elementary nitrogen (N₂), as the final product of the denitrification, was detected. The bacterially catalyzed denitrification could well take place according to the following reaction equation:



The microbiological investigations were carried out as follows:

The ground water of the irrigation area Wolfsburg was investigated with respect to its content of various physiological groups of microorganisms (WOLFF et al. (1985)). As the testing could not cover the whole of the area, individual wells with varying depths were tested at random.

Table 1. Arithmetic means of chemical data

	Wolfsburg		Hankensbüttel		
	waste water irrigation		fresh water irrigation		
	upper aquifer	lower aquifer	upper aquifer	lower aquifer	
O ₂	(ppm)	0.22	0.16	5.90	1.93
Eh	(mV)	396.20	339.00	420.70	376.00
pH		5.47	6.73	5.55	7.06
NO ₃ ⁻	(ppm)	90.70	3.00	88.30	4.50
NO ₂ ⁻	(ppm)	0.03	0.02		
NH ₄ ⁺	(ppm)	0.49	0.48		
Cl ⁻	(ppm)	98.10	62.90	76.70	16.80
NO ₃ ⁻ /Cl		0.84	0.04	1.24	0.36
Conduct. (μS/cm)		646.00	464.40	470.00	191.50
KMnO ₄	(ppm)	17.00	4.50		

In the case of the physiological groups of microorganisms, it was above all the nitrate reducers and the denitrifiers which comprised a large part of the investigation. Under anaerobic or O₂-limited conditions these organisms result in the decomposition of the nitrate. Further, the groups which are responsible for the development of nitrate were tested, i.e. the nitrifiers of the 1st and 2nd phases (1st phase: NH₄⁺-NO₂⁻; 2nd phase: NO₂⁻-NO₃⁻).

As regards the results, it can be stated in summary that a vertical zoning has developed in the ground water. In the upper aerobic zone of the upper aquifer, there are predominantly nitrifiers, which oxidize the reduced nitrogen brought up with oxygen. In the transitional zone to the anaerobic area of the aquifer, it is mainly the nitrite oxidizers

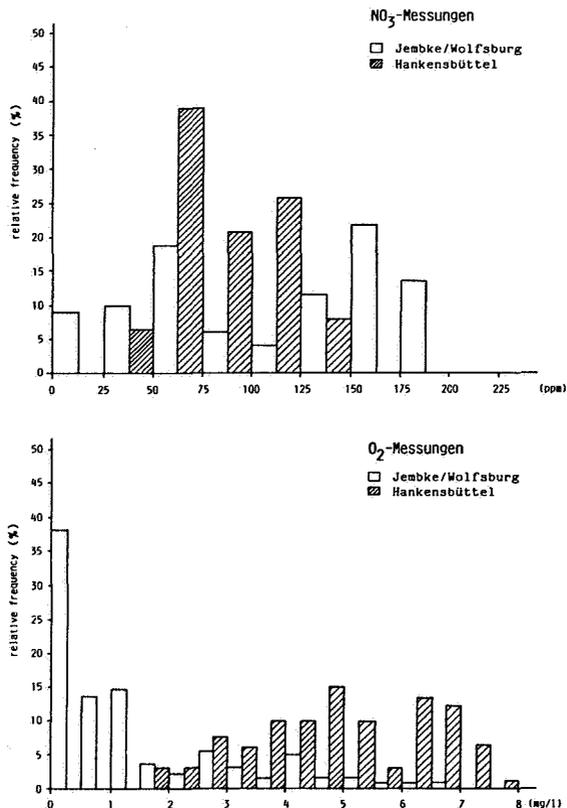


Figure 3. Nitrate and oxygen contents in the groundwater of the Abwasserverband Wolfsburg and the Beregnungsverband Hankensbüttel

(2nd phase nitrifiers) and nitrate reducers which dominate. In this area, with O₂ contents around 0.2 ppm, both metabolic processes take place alongside each other, albeit with reduced activity. Thus it can be presumed that the nitrogen going down from the upper layers of the ground water as nitrate is subjected to a circulatory process (Figure 4). It is reduced, above all by nitrate reducers, with diminishing O₂ contents and organic electron donors, to nitrite, whereupon nitrite oxidizers reverse the process by oxidizing the nitrite with the oxygen which is still presented in low concentration. In the anaerobic zone below this, a part of the nitrate and nitrite is completely decomposed to N₂ and N₂O by means of denitrification. This is also reflected in an

increase of the concentration of denitrifiers with diminishing O₂ concentrations.

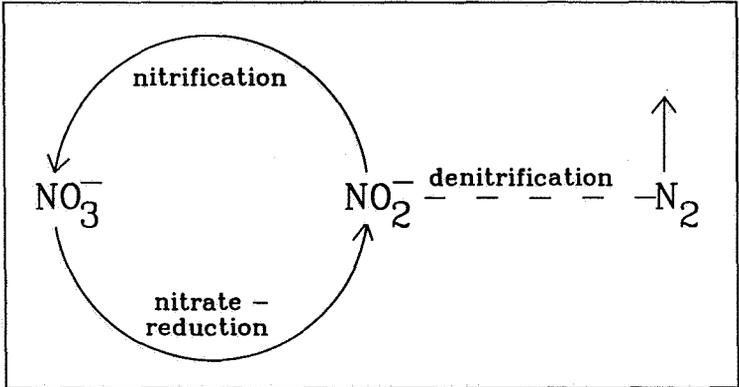


Figure 4. Scheme of the circulatory process

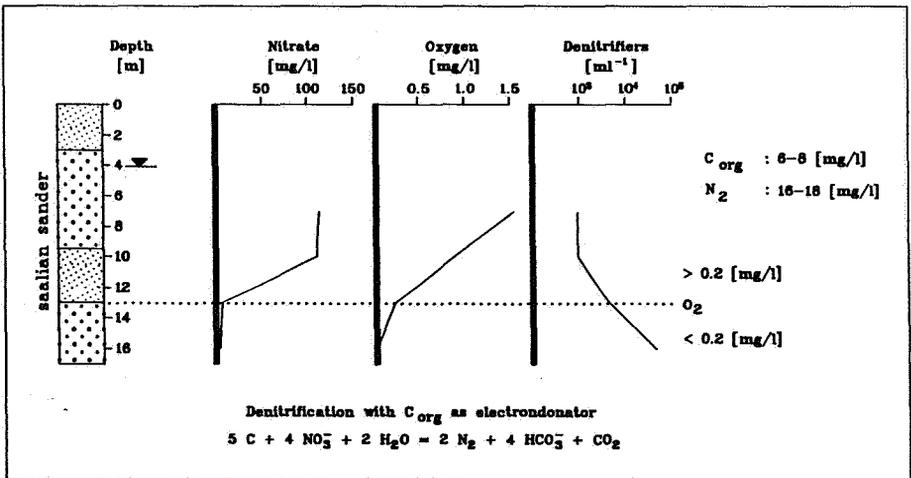


Figure 5. Depth related contents of nitrate, oxygene and denitrifiers in the groundwater of the upper aquifer (Abwasserverband Wolfsburg)

Since the drinking water in Eastern Lower Saxony is primarily derived

from the lower aquifer, the decomposition of nitrate that is described here is very important for the protection of the ground water. Wherever the environmental conditions are not favourable for the decomposition of high nitrate concentrations, it must be assumed that the lower aquifer will also be increasingly loaded with nitrate, especially, where the two aquifers are hydraulically connected. This is particularly true of areas in which the naturally present nitrate leaching into the ground water is increased by irrigation.

4. THE COMPUTER MODEL 'INFILTRATION AND GROUND WATER RECHARGE'

In order to estimate the proportion of anthropogenous influence on the upper unconfined aquifer caused in addition to the ground water recharge, a hydrological water-budget model was developed for the area of the Abwasserverband Wolfsburg.

The range for the model is the water year (Nov-Oct). Input parameters for this period are the daily values for precipitation, temperature and relative air humidity at 2 p.m. Alongside these climatic parameters, the value for effective porosity of the observed aquifer must also be considered as constant. These value was established by means of a pumping test carried out in May 1985 (see above). Likewise, the position and height above sea level of the stream channel must be known from ground water surface maps. In each case the time step is one day . As a reference level, two observation wells under agricultural use were taken. One of them is in the middle of the irrigation area, and is thus influenced by the irrigation of waste-water. The second one is outside the irrigated area. Both observation wells have about the same depth to water table.

During the start-up of the modelling process, additional variable parameters are required by the model. Amongst these are the initial soil moisture, the thickness of the upper soil, the humus content, statements concerning the distribution of grain size, the depth to water table and the depth of rooting. Further soil-specific parameters such as

field capacity are calculated from these statements by the programme.

The actual modelling begins for each time step with the soil profile being divided into compartments of 10 cm thickness. In the first time step, the soil moisture is allocated to these compartments. The precipitation on this day influences the upper compartment. After this, the potential evapotranspiration according to Haude is calculated. In accordance with RENGGER et al. (1974), the current evapotranspiration is calculated from this potential evaporation. Precipitation minus current evapotranspiration gives the variation of the soil moisture in the upper compartment. The variation in the soil moisture in all compartments of the soil profile is calculated on the basis of the different water contents in the compartments. Should a water content be calculated for the lowest compartment that is higher than the field capacity, then this difference is fed to the ground water and the ground water table is correspondingly raised. At the same time, the ground water table is lowered by the underground flow. The soil moisture that is fed to the ground water is then recorded as groundwater recharge. The new state of the system is the basis for the next time step.

The comparison between calculated and measured hydrograph (Figure 6) in the irrigation area Wolfsburg shows that their tendency is similar.

Above all significant deviations can be seen in the winter months during which, there is an increase in the ground water as a result of the irrigation of waste water, which is not explicable through precipitation. Due to this, the measured hydrograph at the end of winter is about 20-30 cm higher than the calculated one.

From the investigations carried out up to now, which are restricted to the hydrological years 1985 (dry) and 1986 (average), it can be deduced that during the vegetation period all the irrigated water is consumed by the transpiration of the plants. Considerable increases in the ground water are thus not to be expected if fresh water irrigation is restricted to the vegetation period. Thus it must be reckoned in the middle term that there will be noticeable deficits in the area water

budget in large-area fresh water irrigation areas.

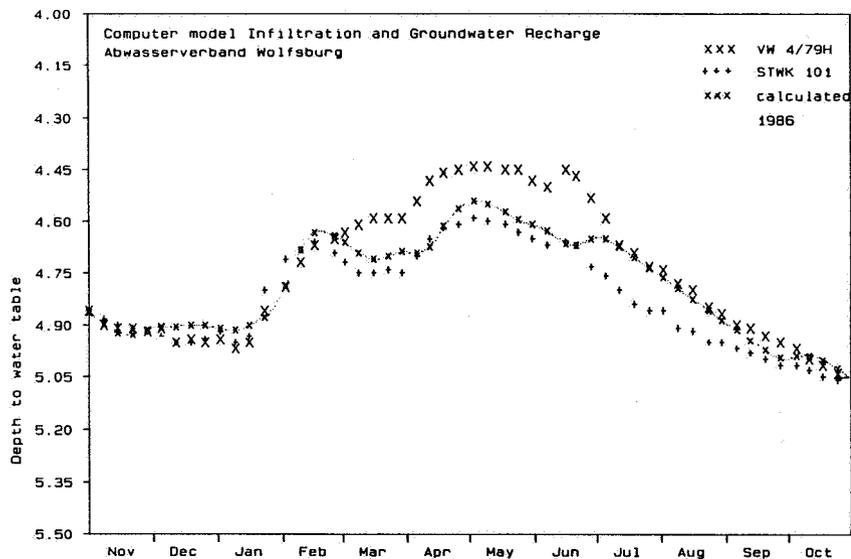


Figure 6. Hydrographs of the two reference observation wells and the computer calculated hydrograph. VW 4/79H: inside, STWK 101: outside of the waste-water irrigation area

ACKNOWLEDGEMENTS

The authors wish to thank the Umweltbundesamt Berlin for the support of investigations.

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GROUNDWATER POLLUTION BY EFFLUENTS FROM A PAPER AND PULP MILL,
IN THE PUNE INDUSTRIAL BELT, WESTERN MAHARASHTRA, INDIA

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ABSTRACT

Groundwater quality investigations were undertaken in the vicinity of a paper and pulp mill, situated on the bank of Pauna river at Thergaon, within the Pune Industrial Belt of western Maharashtra. The water-table of the groundwater aquifer, developed in alluvium and underlying basalt, shows little fluctuation and is located at a depth of about two metres. The aquifer has been highly contaminated by effluents discharged from the mill, into a waste-water pond, and then distributed by water-channels to agricultural fields in the surrounding areas. The groundwater has high values of HCO_3^- , Cl^- , NO_3^- and Na^+ , alongwith high BOD and COD values. It has been possible to delineate the contaminated zone by means of electrical resistivity surveys; the zone being characterised by low resistivity values. It has an areal extent of about 12.5 sq kms. In order to prevent further deterioration of groundwater quality it will be necessary to line the waste-water pond and distributory water-channels, and also give additional chemical treatment to the effluent.

INTRODUCTION

Within the Pune Metropolitan Complex of western India, which is spread over an area of 250sq kms, and has a population of about 1.7 million, groundwater is being increasingly polluted by industrial effluents released by a variety of medium to large scale industries. An extreme example of such pollution is recorded around a paper and pulp mill

located on the banks of Pauna river (Fig. 1). Chemical analyses of the effluents released by the mill, and of groundwater in adjacent area, were undertaken to evaluate the nature and extent of pollution. Resistivity surveys were conducted to delineate the contaminated zone and experiments were carried out to evaluate methods of chemical treatment of waste-water. The results of these investigations are presented in this paper.

MILL AREA

The paper and pulp mill under study is located on the right bank of the Pauna river, about 200 metres from the water course. Here a blanket of alluvium, about six metres thick, rests on weathered basalt. The water-table is at a depth of about a metre during the rainy season. The groundwater flow is in a northeasterly direction towards the river. The unlined waste-water pond of the mill, about 100 square metres in area, is situated about one kilometre from the river. The mill, which manufactures grease-proof glassine and special packaging paper, was started in 1968. The production of paper in 1975 was of the order of 470 tons/month with waste water discharge of $6175 \text{ m}^3/\text{day}$. By 1981, the production had increased to 600 tons/month and waste-water discharge to $13,500 \text{ m}^3/\text{day}$. A steady growth is visualised. The mill has a waste-water treatment plant which adopts the activated sludge method of water treatment. The effluent released after treatment is highly coloured and, like effluents from other paper and pulp mills, contains carbohydrates, lignis, sugars, acids, furfurials and other products.

MATERIALS AND METHODS

In accordance with the criteria adopted by GEMS/WATER programme (Helmer 1981) seven water sampling stations, four for groundwater (St. Nos. 1,2,4 and 5) and two for river-water (St.Nos. 3 and 7) were established. Additionally the waste-water pond was also sampled. The pH, conductivity and dissolved oxygen were determined at the site using a portable water-quality analyser and the remaining constituents

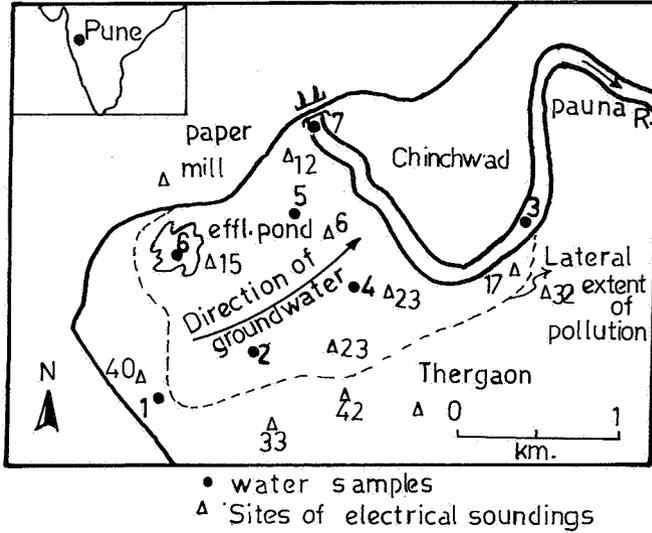


Fig 1. Map of the area showing locations of water samples and electrical resistivity soundings

viz. alkalinity, hardness, chlorides, sulphates Mg^{2+} , Na^+ , K^+ COD and BOD were determined in the laboratory, within 24 hours of collection of the samples, following the analytical procedures given by APHA, AWWA and WPCF (1975). The data for samples collected during summer and rainy seasons is presented in Table 1.

RESISTIVITY SURVEYS

Investigations carried out by a number of workers have shown that the electrical earth resistivity can be used to define the lateral extent and depth of a contaminated ground water body (Stollar and Roux, 1975). Accordingly resistivity surveys of the environs of the paper and pulp mill were conducted using a Sparkonix A.C. resistivity meter and employing the Wenner configuration. The resistivity values for different profiling stations are given in Table 2 and also plotted in Fig 1. It is observed from Table 3 that the electrical conductivity values for polluted ground water are approximately three times that of natural ground water. Further it is seen from Fig 1 that there is a marked contrast between earth resistivity values for areas of polluted and unpolluted water. This contrast enables the

Table 1. *Physico-Chemical characters of surface and groundwater from Thergaon area. Rainy Season & Summer.*

St.No.	pH	TDS	D.O.	Alk.	Hardness	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Nitrate	COD	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	El. Conductance
3	7.5	113	1.4	22	310	32	287	0.36	1.81	1160	12	3	20	63	150
6	8.2	728	Nil	250	480	170	857	0.50	2.34	1550	136	13	260	20	970
7	7.7	75	2.8	140	320	8	15	0.25	1.20	60	12	ND	15	9	120
1	7.4	480	1.0	95	710	184	276	Nil	0.44	140	38	ND	48	144	640
2	7.2	548	0.4	87	820	304	301	Nil	0.44	120	51	ND	60	163	730
4	7.6	338	1.2	77	550	169	89	0.36	0.53	300	77	ND	34	114	450
5	7.5	750	Nil	130	850	266	221	0.25	0.97	500	121	ND	50	177	1000
Summer Season:															
3	7.2	165	2.2	110	140	25	247	0.20	0.66	1200	5	ND	22	21	220
6	6.8	750	Nil	310	270	155	27	1.15	1.11	1530	88	ND	80	17	1000
7	7.5	128	4.8	120	100	25	48	0.01	1.08	50	3	ND	18	14	170
1	6.5	714	2.0	165	550	120	247	0.01	Nil	330	10	ND	122	59	950
2	7.1	900	Nil	350	480	135	37	0.01	0.49	410	13	ND	33	85	1200
4	7.3	750	1.8	300	480	130	15	0.21	1.11	490	24	ND	50	87	1000
5	7.6	1200	1.6	460	500	220	78	Nil	1.33	970	70	ND	33	101	1600

St.No.6 is waste-water pond.

All concentrations are reported in ppm except pH & conductance is in microsiemens/cm.

Table 2. *Earth resistivity and groundwater conductivity values from Thergaon area*

Sr.No.	Water Sampling Station Nos.	Earth Resistivity Ohm- m	Groundwater Conductivity $\mu\text{s/cm}$.
1	1	-	970
2	2	22	1128
3	4	23	991
4	5	6	1556
5	6	15	1230
6	8*	38	450
7	-	21	-
8	-	12	-
9	-	42	-
10	-	40	-

* Natural groundwater from other area.

Table 3. *Comparison between characters of industrial effluent, surface and ground waters*

St.No.	D.O.	Cl ⁻	Alkalinity	TDS	pH	COD	Hardness	Nitrate
1	2.48	152	232	702	7.32	240	557	ND
2	1.87	244	279	1010	7.28	268	618	0.85
3	3.22	147	90	125	8.53	484	180	1.56
4	3.20	155	252	669	7.72	282	458	0.55
5	1.57	289	365	1135	7.58	673	554	0.93
6	Nil	246	306	1068	7.50	1100	362	2.79
7*	5.18	27	91	158	7.60	24	167	1.07

* Uncontaminated surface water

demarcation of the polluted zone which is seen to have an areal extent of about 12.5 sq kms. The low resistivity values obtained over the contaminated zone is attributed to the presence of radicals with higher ionic content namely Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} etc. in the polluted zone (Howe, 1982). The vertical electrical soundings carried out at a few profiling stations indicate that the contamination has reached a depth of six metres. This suggests that the contamination is restricted to the alluvium and underlying weathered basalt. It also means that the basaltic flow underlying the weathered zone and alluvium has, because of its relative impermeability, prevented pollution at greater depths. This is evident from the fact that the polluted water, that percolates through weathered zone or alluvium, ultimately emerges out in the form of polluted springs in the Pauna river bed.

GEOCHEMISTRY AND MECHANISM OF GROUND WATER POLLUTION

The chemical analysis of effluent water collected from the waste-water pond, and of ground water samples collected from the wells in the surrounding area, show that the average chemical compositions of groundwater samples and that of industrial effluents are nearly the same. Water samples from three different stations out of four (St.Nos. 2,4 and 5) were found to be highly polluted and did not show much variation in composition from that of composition of industrial effluents (Table 3). The sampling station No. 1 shows periodic contamination of groundwater. During the rainy season the well water is polluted and during summer it is unpolluted.

Chlorides, nitrates and sodium are considered to be most useful indicators of groundwater pollution (Kwitz, 1972 and Ali,1980). Since chemical pollutants travel farther and persist longer as compared to bacterial pollutants, the present study was focused on the subsurface movement of chlorides, nitrates and sodium. However, other contaminants like total hardness, alkalinity etc. are also considered.

The shallow aquifers are more important sources of groundwater for water supply purposes, but upper portions of these aquifers are also susceptible to pollution. The most significant source of groundwater pollution in the area is the waste-water pond, and the network of

water-channels supplying waste-water to the agriculture. The infiltration of such waste-water through alluvium and weathered basalt is evidently the cause of contamination of the shallow groundwater in the area. From Fig 2 it can be seen that the entry of pollutants to shallow aquifers is due to downward percolation through the zone of aeration or recharge from surface water body ie. the waste-water pond. Here the polluted water from the waste-water pond flows downward to form a recharge mound at the water-table and then moves laterally below the water-table.

The polluting effluents drain downwards to the water-table and then flow laterally to form a line source of pollution beneath the ground surface. Pollutants entrained in saturated ground water flow (evidenced by nearly water logged conditions) have formed plumes of polluted water extending downstream from pollution source. Since there is slight water-table fluctuation and the waste input is increasing with the increasing production it can be inferred that the polluted plume is enlarging. However, the geomorphological, lithological and hydrogeological situation of the area is such that the plume cannot extend laterally. The zone of pollution demarcated with the help of earth resistivity surveys support this statement.

The periodic pollution of ground water in sampling well No.1 is related to the fact that during rainy season, the water-table comes upto the surface and the zone of pollution extends laterally, ultimately contaminating groundwater in well No.1. Subsequently when the water-table is lowered during summer the quality of water improves.

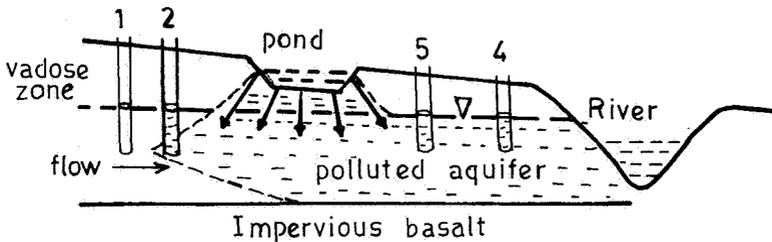


Fig 2. Cross section of the area showing the mechanism of pollution

A considerable deterioration of ground and surface water quality in the immediate environments of paper and pulp mill has been recorded. The observations made by the authors suggest that unless preventive measures are taken immediately the situation will worsen. The obvious remedial measure is to line the waste-water pond and the distributory water channel to prevent further percolation of the effluents. At the same time it will be necessary to increase the area of waste-water pond so that the evaporation would commensurate with the quality of effluent discharged. It is also desirable that the effluents be subjected to additional chemical treatment.

CONCLUSIONS

Ground water pollution is attaining alarming proportions in the vicinity of paper and pulp mill at Thergaon because of the large amounts of effluents released from the mill. The main source of groundwater contamination is the waste-water pond and network of distributory water-channels supplying water to the agriculture. The geophysical and geochemical investigations reveal that the earth resistivity values are very low in the zone of pollution and the electrical conductivity of groundwater is three times higher than natural groundwater. In order to reduce effluent percolation and groundwater contamination lining of waste-water pond and distributory channels would be necessary as also additional chemical treatment of effluents.

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DENITRIFICATION AND SULPHATE FORMATION, IN RELATION TO
NITRATE ACCUMULATION WITHIN THE GEOHYDROLOGICAL PROFILE
OF THE PUMPINGSTATION AREA AT VIERLINGSBEEK

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ABSTRACT

The (slowly) increasing nitrate concentrations during the last decade in the phreatic ground-water pumped up at Vierlingsbeek, located in the south-eastern part of The Netherlands, formed the basis for geochemical investigation. Next to a hydrological study (KIWA) also a geological survey including 3 medium deep drillings was executed (RGD). Representative samples were taken at various depths. Some of them were wend to Stiboka for geochemical analysis.

At a depth of about 25-35 metres below surface pyrite accumulations occur. These accumulations are mainly concentrated in the marine Formation of Breda and the above lying Kiezeloöliet Formation; a fluviatile deposit. Previous research from KIWA showed the possibility of pyrite-oxidation in relation to denitrification, together with sulphate formation. Though the hydrological investigation seems to show that only a minority of the pumped water passes through pyrite-bearing strata, the importance of this anaerobe reaction was recognized by the owner of the pumpingstation (W.O.B.).

If nitrate-concentrations reach these strata this may lead to an increase in sulphate content of the groundwater. At this moment the nitrate polluted water is not yet infiltrated to this depth, but the necessity for understanding and possible control is not limited to this local investigation only, but should be recognized as a broad-regional concern.

GEOLOGICAL OVERVIEW

Pumping-station Vierlingsbeek and surroundings are situated in a relatively depressed fault block area, called "the Slenk of Venlo". In the framework of this study only the first 40 metres of the soilprofile from the surface were investigated by means of drillings, and laboratory tests. Depths, mentioned in this paper, refer to ground level, with relative height differences of at most 5 metres. The "Formatie of Breda", a marine deposit of tertiary age is encountered from 40 to approx. 30 metre. It consists mainly of fine to coarse glauconite - bearing sands. In the upper part of these sands pyrite bearing clays or clay-lenses with organic matter reflect the near shore environment during deposition. The top of this "Formation of Breda" is sometimes cemented, indicating at an erosion period before subsequent sedimentation took place. The latter formation is followed by the "Kiezeloöliet Formation", generally composed of coarse sands (600 u) and gravel, reflecting the fluviate mechanism. Top of this formation lies at approximately 14 m below ground level and its thickness varies from 16 to 19 metre. The lower part of the Kiezeloöliet Formation is less coarse and frequently clay lumps with high pyrite content are found, probably as a result of accumulation from the underlying marine sediments by river-action at short distance to the coast. The Formation of Veghel overlies the latter and is characterized by fluviate sediments of the river Maas. Thickness of this formation is at most 9 metre and characterized by sands and abundant gravel deposits. The upper deposits belong to the Nuenen Group. They are of Holocene age and consist of sands, gravels and peat layers. Maximum thickness of this formation is 8 to 10 metre.

LABORATORY- AND MICROSCOPIC RESULTS

These tests were performed by Stiboka on samples, taken from various depths. They indicated that pyrite and iron-monosulphides are *not* present within the first 19 m of the soil profile. These first 19 m belong to the Veghel Formation and the Nuenen Group. Below this depth values up till 1,5% (weight) were recorded. Significant quantities of pyrite occurred at several places in two this sections at depths from 25 to 27 m. The pyrite exhibited various morphologies of which the most striking were framboidal, octahedral and cubic forms. The most common type of pyrite, however, occurred in masses of various sizes with different external forms, and without specific internal characteristics.

The pyrite was found at various places in the thin-sections and is interpreted as predominantly secondary in origin. The sites were on and in plantfragments, of which pyritized pseudomorphs could form (Figure 1), between grain boundaries (Figure 2) and in larger masses along layers or other directions such as burrow walls. Much of the pyrite was associated with glauconite of which a part was weathered, but it also occurred in porespaces between predominantly quartzgrains.

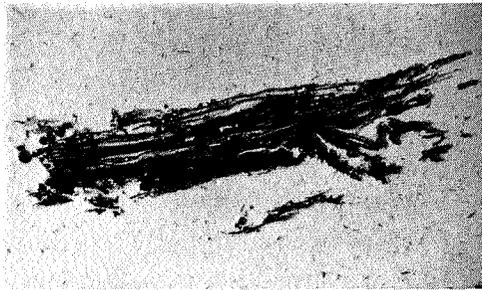


Figure 1. *Pyritized pseudomorphs after plantfragments*

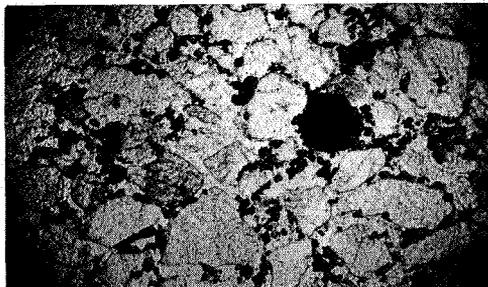


Figure 2. *Pyrite on surface of and between minerals*

HYDROLOGY

At Vierlingsbeek groundwater is extracted from the Formation of Veghel and the Kiezeloëliet Formation. To estimate the effects of denitrification by pyrite on the quality of the extracted water, both formations have been schematized onto one aquifer. The Formation of Breda was assumed to be an impermeable bottom-layer.

Recent bore-holes made it possible to estimate differences in permeability in this aquifer, by using the textural description of the sand and the formula of Koceny. The first calculations with a hydrological model (Boukes, 1986) showed that 35 - 45 percent of the abstracted water passes through the Formation of Veghel, and 40 - 50 percent through the Kiezeloëliet Formation (Figure 3). Only 27 percent of the water may have been in contact with the pyrite-containing layer, seem to be of very great importance for the nitrate-concentration. As pyrite is consumed, the boundary between the pyrite-containing and pyrite-less layer will lower, and the influence of the described processes upon the extracted water-quality will diminish. Further hydrological investigations are necessary to prove these first results.

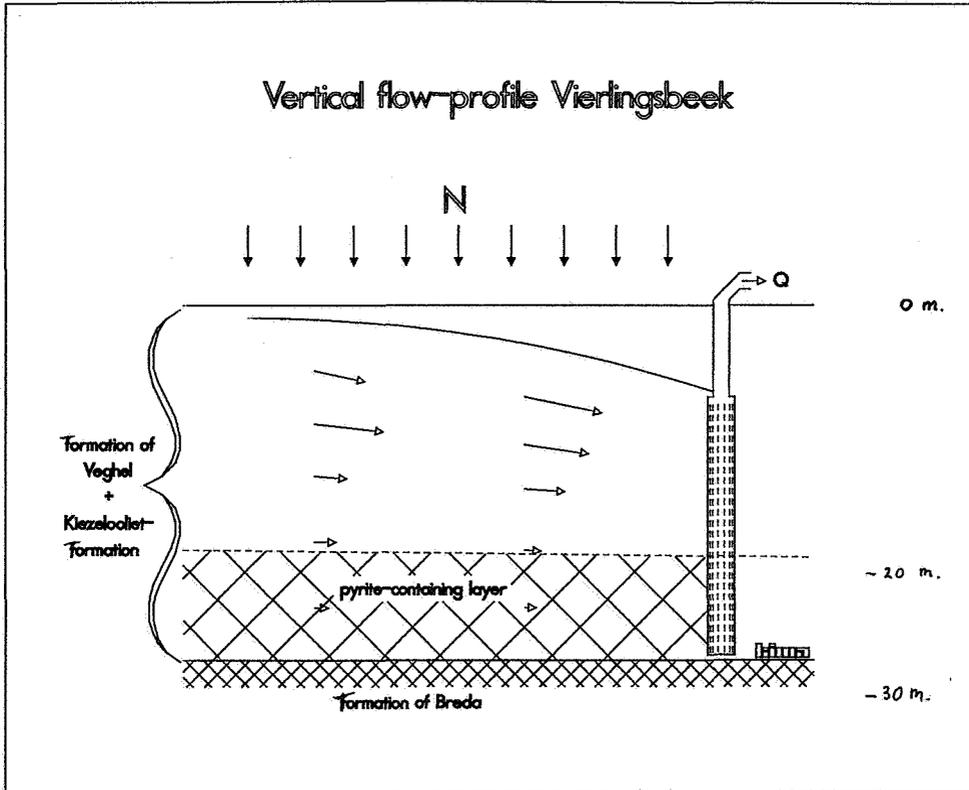


Figure 3. *Schematic hydrological profile*

ACKNOWLEDGEMENTS

The authors wish to thank the "Waterleidingsmaatschappij Oost-Brabant" for giving permission to publish the results of this investigation.

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DEGRADATION OF GROUNDWATER QUALITY IN A DENSELY POPULATED LOESS REGION

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1. INTRODUCTION

The deteriorating chemical quality of groundwater is one of the major environmental problems in Western Europe. High concentrations of nitrate in the groundwater form a particularly serious threat to the chemical quality of the groundwater, and hence, to the supply of drinking water.

In South Limburg, a densely populated loess region in the south of The Netherlands, the chemical quality of the groundwater in the unconfined aquifers is deteriorating. This region is characterized by undulating limestone plateaus with a thin covering of gravel and loess. Although unlike the rest of The Netherlands, similar geology and soils are found over large areas of Western and Central Europe. Furthermore, the density of population and the degree of industrialization in this region are very high. Thus, the groundwater problems in South Limburg illustrate the threats to the groundwater quality, and the resulting repercussions that could be experienced in the heavily urbanized and industrialized regions in Western and Central Europe in the future.

2. FUNCTIONS OF THE GROUNDWATER

Figure 1 gives the height of the water-table and the directions of groundwater flow in South Limburg. The water-table is considerably higher above sea level under the limestone plateaus than under the valley floors. Thus, the groundwater will flow from under the plateaus to the valley floors. The groundwater is mainly fed by the precipitation surplus (i.e. precipitation minus evaporation, Figure 2).

The groundwater has many functions. These can be summarized as:

- A. A source of drinking-water, and water for industry (Photo 1).
- B. A source of water and nutrients for the vegetation (by seepage and capillary rise, Photo 2).
- C. A source of water for the surface water system (Photo 3).
 - a. In south Limburg, groundwater is the sole source of drinking-water for the total population of about 600,000. Furthermore, the groundwater is of great importance to industry, e.g. chemical works and breweries (Table 1).
 - b. An important natural function of the groundwater is the supply of water and nutrients to the vegetation. This process can take place by:
 - Capillary rise. This can only happen if the water-table is within a few meters of the surface. In South-Limburg, this can only occur in the valley floors.
 - Seepage. Seepage takes place when the groundwater reaches the surface. This is the case on many hillslopes in South Limburg. Here, many natural springs and seepage zones occur, often supporting a groundwater-dependent vegetation.
 - c. The third function of the groundwater is to supply water to the surface water system. All the brooks and small rivers in South Limburg receive water from the groundwater.

3. THREATS TO THE CHEMICAL QUALITY OF GROUNDWATER

Throughout the region, the chemical quality of the groundwater is threatened by the use of fertilizers and manure in agriculture, and by the atmospheric deposition of pollutants.

In South Limburg, atmospheric deposition of pollutants is very high compared with that in regions without substantial air pollution, such as New Zealand, where human activities have little influence on the atmosphere (Table 2). The high rate of atmospheric deposition in South Limburg probably contributes to the high levels of nitrate (contribution up to 21 mg/l) and sulphate (contribution up to 17 mg/l) in the groundwater.

Recent changes in agriculture have resulted in increased use of fertilizers and manure. Some of the nitrogen in the fertilizers (about 10%) and in manure (about 40%) will leach to the groundwater. This leads to high levels of nitrate in the groundwater (Photo 4).

On a local scale, severe pollution of the groundwater may be caused by waste disposal, colliery spoil-heaps, and colliery mud. It is estimated that in South Limburg the total amount of colliery waste material is about 200 million tons. Most of this waste material can be found near the former coal mines, where it has been dumped or has been used for building roads and railways. These materials cause extremely high sulphate concentrations in the groundwater. Furthermore, when the groundwater reaches the surface, ferrihydrite ($\text{Fe}(\text{OH})_3$) is deposited, as a result of the oxidation and leaching of the pyrites (FeS_2) in the colliery spoil (Photo 5). There are also several dumps for domestic refuse in South Limburg, mostly in old sand and gravel pits. The material dumped here can have very adverse effects on the groundwater quality (Photo 6).

4. DEGRADATION OF THE GROUNDWATER QUALITY

Atmospheric deposition, the increased use of fertilizers and manure, and the leaching from rubbish dumps and colliery spoil have led to a degradation of the chemical quality of groundwater in South Limburg:

- a. There is a danger that EC standards for drinking water quality will be exceeded; this means the groundwater will no longer be suitable for the production of drinking-water. Figure 3 shows the increase in nitrate, sulphate, and chloride levels in the water from two groundwater pumping-stations. A comparison with Table 3 shows that in both cases the EC directives for nitrate and sulphate are already being exceeded. In Guttecoven station, the EC Maximum Concentration Standard for nitrate has been exceeded since 1970.
- b. The groundwater-dependent vegetation in woodlands may change or disappear. Changes in the vegetation of springs and seepage zones have been observed in some woodlands in South Limburg, ranging from a change in vegetation composition to the total disappearance of vegetation (Photo 7).

- c. The chemical quality of the surface water system is deteriorating as a result of the changed chemical properties of the groundwater that feeds it (Photo 8).

This degradation of groundwater quality does not occur on the same scale throughout South Limburg. There are several smaller regions whose groundwater quality differs. These differences partly result from different geological properties, e.g. thickness of the groundwater body and the residence time of the groundwater (Figure 4). Regions where the residence time of the groundwater is relatively short (10-20 years) show higher nitrate levels in the groundwater than other regions (Figure 5). Intra-regional differences are also caused by the locations of the rubbish dumps, colliery spoil heaps, and colliery mud.

Groundwater in the vicinity of these locations is strongly affected by chemical substances leaching from the dumped material. The highest sulphate concentrations in the groundwater in South Limburg are found near the colliery waste sites (Figure 7).

5. FUTURE

Further degradation of the groundwater quality in the future can only be stopped if:

- a. Dumping of waste materials is permitted only under very strict conditions, e.g. purification of the drainage water from rubbish dumps and colliery spoil.
- b. There is a decline in the use of fertilizers and manure in agriculture. This requires a reappraisal of the aims of agriculture: the goal should not only be an increase in production but also concern for the quality of the landscape and of the groundwater.

Even if this can be achieved, nitrate (and sulphate) concentrations in the groundwater in South Limburg will continue to rise for 20-80 years, because of the time lag before the contaminated water in the unsaturated zone reaches the groundwater.

DEGRADATION OF GROUNDWATER QUALITY IN A DENSELY POPULATED LOESS REGION

● Introduction

The degradation of the chemical quality of groundwater is one of the major environmental problems in Western Europe. South Limburg, a densely populated loess region in the south of The Netherlands, is one of the regions where groundwater quality is deteriorating.

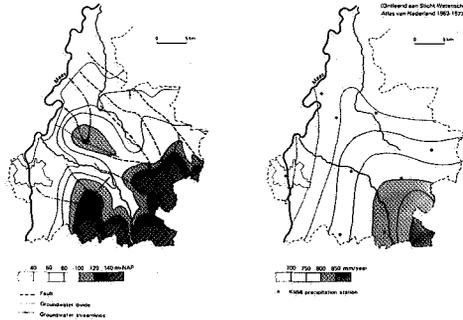


Figure 1
Groundwater in South Limburg

Figure 2
Average yearly precipitation in South Limburg (1930 - 1960)

● Functions of the groundwater

The groundwater has many functions. These can be summarized as:
 1 A source of drinking-water, and water used in industry.
 2 A source of water and nutrients for the vegetation.
 3 A source of water for the surface water system.

Table 1 The use of the groundwater in South Limburg for drinking-water and industrial water

User	Function	Volume (million m ³)
Waterleidingmaatschappij Limburg	drinking-water	19.0
Waterleidingbedrijf Heerlen	drinking-water	3.9
Waterleidingbedrijf Sittard	drinking-water	3.1
Cementwerken Maastricht	drinking-water	5.2
Industrial Users	process-water and household-water (1)	14.3
Industrial Users	cooling-water, and other industrial use	9.9

(1) partly also used as cooling-water and other industrial use.

Photo 1
Groundwater winning area (Photo: VEWIN)

Photo 2
Seepage zone with a groundwater dependent vegetation in a woodland in South Limburg (Bunderbos)

Photo 3
Spring, feeding a small brook

● Threats to the chemical quality of groundwater

Throughout the region, the chemical quality of the groundwater is threatened by the use of fertilizers and manure in agriculture, and by the atmospheric deposition of pollutants. On a local scale severe pollution of the groundwater may be caused by waste disposal, colliery spoil heaps, and colliery mud.

Table 2 Atmospheric deposition of some pollutants in South Limburg and New Zealand (kg/ha.y)

	nitrate	sulphate	chloride
South Limburg	30	52	8
New Zealand	5.3	2	3.2

Photo 4
Application of manure near Elsloo (South Limburg), leading to high concentrations of nitrate in the groundwater

Photo 5
Seepage zone in a colliery spoil heap. Leaching from the colliery waste material causes high concentrations of sulphate and iron in the groundwater

Photo 6
Domestic refuse dump

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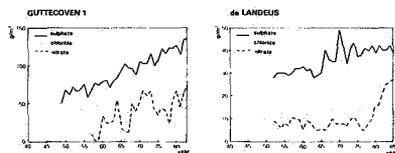
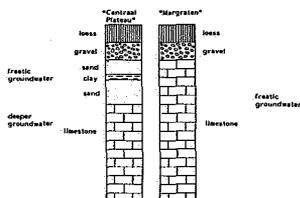


Figure 3

Increase in nitrate, sulphate, and chloride concentrations in the water from two groundwater pumping stations in South Limburg

Table 3 EC directives and EC Maximum Concentration standards for nitrate and sulphate in drinking-water

	EC Directive	EC Maximum Concentration (mg/l)
Nitrate (NO ₃)	25	50
Sulphate (SO ₄)	25	250



Regional differences in geological properties

Figure 5

Nitrate concentrations in the freatic groundwater in South Limburg

● Degradation of groundwater quality

Atmospheric deposition, the increased use of fertilizers and manure, and the leaching from domestic and industrial refuse dumps and colliery spoil have led to a degradation of the chemical quality of groundwater in South Limburg:

- 1 There is a danger that EC Maximum Concentration standards for drinking-water will be exceeded.
- 2 The groundwater-dependent vegetation in woodlands has changed or disappeared in several places.
- 3 The chemical quality of the surface water system is deteriorating.

The degradation of groundwater quality does not occur on the same scale throughout South Limburg. There are several smaller regions whose groundwater quality differs. These differences in groundwater quality result from regional differences in geological properties, and the location of the refuse dumps and the colliery spoil.

- Refuse dump of regional importance
- ▲ Refuse dump of local importance
- Average concentration
- 1 Standard deviation from the average
- Concentrations in mg/l

Figure 6

Sulphate concentrations in the freatic groundwater in South Limburg

● Future

Further degradation of the groundwater quality in the future can only be stopped if:

- 1 dumping of waste materials is permitted only under very strict conditions.
- 2 there will be a decline in the use of fertilizers and manure in agriculture.

Photo 7

Seepage zone in a woodland in South Limburg downstream of a domestic refuse dump (Kruisberg area). The groundwater-dependent vegetation has disappeared

Photo 8

Brook fed by polluted groundwater

CHEMICAL POLLUTION OF THE SOIL AND THE GROUNDWATER IN THE
KINGDOM OF NEPAL

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ABSTRACT

Nepal is facing problems of indiscriminate uses of chemical fertiliser, and insecticide in order to increase the food production by polluting the phreatic groundwater which is being tapped by masses for the purpose of drinking water. Furthermore, the untreated sewerages of the cities and factories which are poured in the rivers upstream also pollute the groundwater wherever the stream bed is influents and recharging the aquifers.

Such cases of pollution are becoming widespread in many areas and also may reach alarming state. Unless it is stopped or checked in time, Nepal will face problem of health hazard and the chemical salinity in the soil and water in the future.

1. INTRODUCTION

The Kingdom of Nepal lies in the middle belt of Himalaya sandwiched between India in the south and China in the north. It is a mountainous country with a plain area in the south (Figure 1). The southern plain is called Terai in Nepal and is a part of Indogangetic plain. The country has an area of 147,181 sq.km of which about one-third is in the plain of the south. The population at present is 16 million and is increasing at a rate of 27% per annum. Nepal is principally an agricultural country where about 90% of the population is engaged in agriculture work. Out of 2 million hectares of arable land of Terai only 20% is under the command of man-made irrigation. Groundwater and surface water both are utilized for the irrigation as well as for drinking water. As land productivity is a function of irrigation and other agriculture inputs, to feed the growing population, the

development of these input are bound to increase in the years to come. At present about 40% of the population of Nepal is under subsistence level.

After the throw away of the autocratic Rana Regime in 1950, Nepal opened its door to outside influences and thus breaking the self imposed isolation with the rest of the world. The modern influence has helped mainly in the development of infrastructures and also industries. It has also not spared the breaking of the tradition and culture.

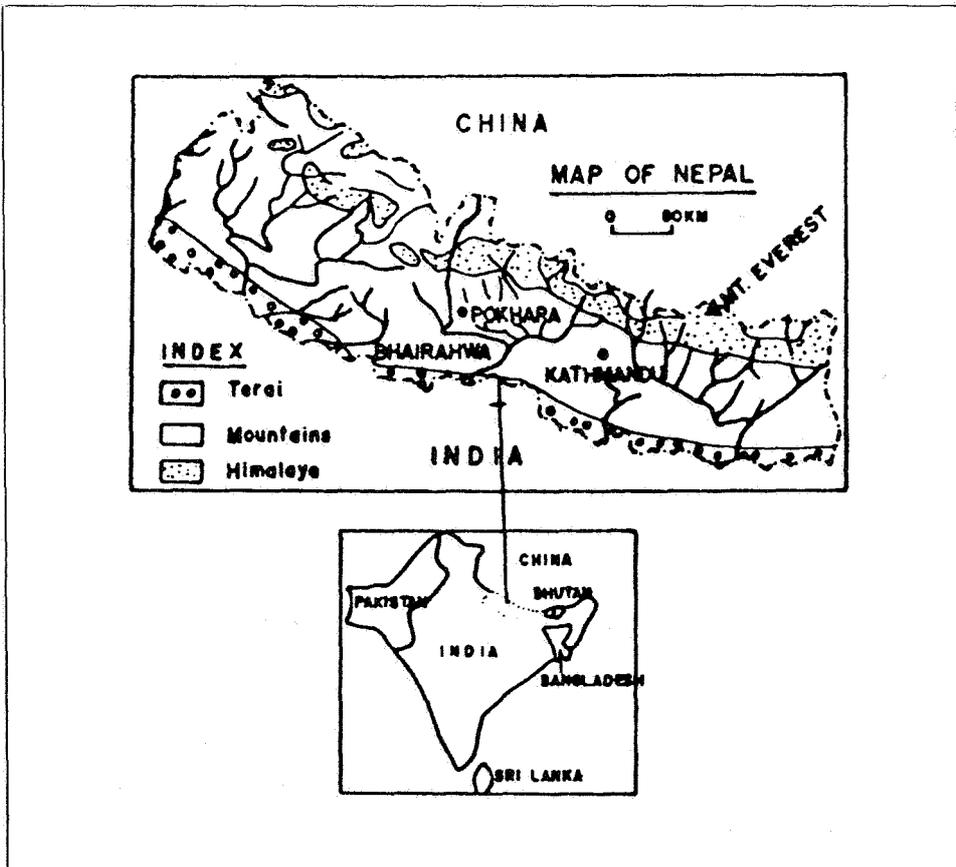


Figure 1.

2. CHANGE IN AGRICULTURE

In earlier days people were satisfied with rainfed monoculture, using organic matter as fertiliser. With the outside influence and also food pressure of the growing population, people started to grow two crops. This has resulted the development of irrigation projects primarily based on surface water and partially on groundwater. To get more yield new varieties of seeds were imported and transplanted all over the Kingdom. This has resulted to create two types of problems. They are the following:

- a. the old traditional varieties which could withstand the local eco-system have disappeared completely;
- b. the new varieties which were transplanted were found to be susceptible to disease and often require frequent change of varieties.

Furthermore, to get more food the introduction of concentrated chemical fertiliser and also to save the plant from infection, widespread and indiscriminate use of pesticide have started. People have abandoned old cumbersome technique of making fertiliser from the animal dung.

The use of chemical fertiliser and pesticide has increased the production considerably and still the demand of these chemical will grow more rapidly in the future years along with the food demand of increased population.

The present consumption pattern is presented in Figure 2. This indicates that farmers are demanding chemical fertiliser and dust type pesticide (DDT) and also malathion. Considering the rate of present demand based on the 20% irrigated area, the long term demand may be forecasted to be many fold when 100% of the arable lands are irrigated.

In addition to the above, some imports and distribution of insecticide were done by Nepal Malaria Eradication Organization which is active since 1950. Table 1 shown below gives data since 1982, with that one

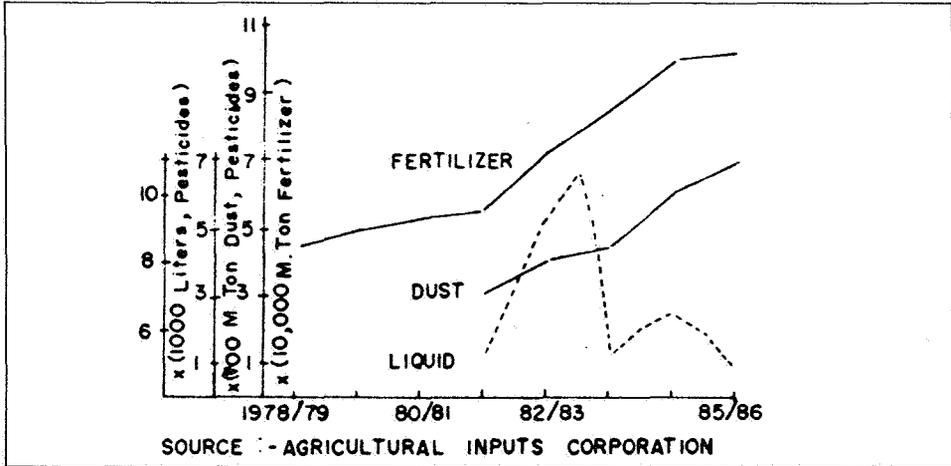


Figure 2. Total consumption of fertilizer and pesticides in Nepal

can imagine how much they have spread since 1950. In Nepal the local mosquitoes have been found to be immuned to DDT and new varieties of pesticide such as malathion is used.

In 1950's DDT was sprayed as the mosquitoes were supposed to be malaria carrier whereas, after three decades, it is found that they are spreading Japanese K variety of encephalitis which has taken a toll of many lives in the past.

Year	DDT 75% WDP	Malathion 50% WDP	Ficam 80% WDP
1982	-	-	-
1983	-	600	-
1984	-	600	-
1985	-	300	33
1986	195	300	34

Table 1. Use of different insecticides (unit in MT)

Water and mosquito-borne diseases as reported is given below.

	0-4 Yrs		5-14 Yrs		15-44 Yrs		45 Yrs +		NS*	TOTAL	
	Cases	Deaths	Cases	Deaths	Cases	Deaths	Cases	Deaths		Cases	Deaths
I Waterborne											
Typhoid	13	2	46	-	105	-	11	-	4	179	2
Amoebiasis	-	-	2	-	8	-	5	-	-	15	-
Dysentery, MOS	25	1	48	1	84	-	20	-	1	178	2
Gastro-Enteritis	298	21	108	2	435	1	76	4	56	973	28
Diarrhoea	87	7	40	-	26	-	11	-	2	166	7
TOTAL	423	31	244	3	658	1	123	4	63	1,511	39
(% Grand Total)	(41)	(32)	(23)	(9)	(10)	()	(8)	(5)	(3)	(15)	(8)
II Mosquito-Borne											
Viral Encephalitis	6	3	14	4	17	6	4	3	-	41	16
Malaria	2	-	2	-	21	-	11	-	-	40	-
TOTAL	8	3	16	4	38	6	15	3		81	16
III All other Diseases											
	600	62	784	27	5,880	287	1,426	69	126	8,816	445
GRAND TOTAL	1,031	96	1,044	34	6,576	294	1,564	78	189	10,408	500

*NS - Age Not Stated: TOTAL does not agree with published version because of minor arithmetic errors; the figures above assume individual entries are correct.

Source: (Proctor & Redfern International Limited, Canada, 1986)

Table 2. *Water and mosquito-borne diseases - nine hospitals 2040 (1983)*¹⁾

- 1) Epidemiological Bulletin, Vol. 5, No. 1-4, 1984, p. 37
Epidemiology and Statistics Division, Department of Health Services, Ministry of Health, HMG/Nepal, Kathmandu.

The data show water-borne diseases account for 15% of all cases and 8% of the deaths; but the proportions are higher among children and much higher for infants 0-4 years; 41% of all cases and 32% of all deaths.

3. PROBLEMS

As Nepal imports chemical fertiliser and pesticide it has created pressure on foreign exchange bill on one hand and wide and indiscriminate use of fertiliser and pesticide has increased the environmental problem on the other hand.

In environmental problem the soils of Terai plain of Nepal have become acidic and it often requires chemical treatment by lime. Some places zinc is found to be less and other places sulphur has increased. The farmers who used small dose of fertiliser in early parts are using more fertiliser now to get better yield as they are unaware of the acidity problem. The animal dung used to give fiberness to the soil in the past along with the required chemical nutrient. Now with use of chemicals the soil is hard and heavy.

4. IMPACT OF CHEMICALS ON WATER RESOURCES

Impact of chemical pollution in water resources is basically from three sectors:

- a. in most of cities and towns the effluents are directly discharged to the rivers. This increases not only coliforms but also chemical contents;
- b. the other is from the factories such as cement, jute, leather and paper. At present most of the factories are discharging their effluents to the stream and also to the atmosphere. From cement factories particulates and sulphur dioxide have been found to increase in the capital city of Kathmandu. Most of bricks used in the building are now producing white efflorescence and the copper roof temples are tarnished to copper sulphate;
- c. third source is from agriculture sector which is utilising chemical fertiliser and pesticide.

5. GROUNDWATER

It is found that the upper layer i.e. phreatic groundwater is mostly utilised by 50% of the population of Nepal for drinking purpose besides the use for irrigation and other works.

With the affluents from the stream and also widespread use of chemical fertiliser and pesticide in the agriculture sector. It has increased nitrate content considerably. This is particularly true near the village whereas the same layer of aquifer in other areas bear less chemical.

6. MONITORING OF GROUNDWATER

Now Nepal has put down several peizometers in different zones to monitor the water level and quality of groundwater and Nepal natural resources commission is considering to enforce law and measure to force the industries not to pollute the surface and groundwater.

Table 2 indicates that pure Himalayan water picks up chemical before it becomes groundwater and the concentration of chemical increases towards the down gradient even in both phreatic as well as deep aquifers. Micro elements have not been analysed in detail, but it is found that NO_3 and Cl are high in the dug well. Table 3 indicates that phreatic aquifer is more polluted compared to deep as the agricultural activities have more effect in the surface water. Within the Terai Table 4 shows how chemical variation occurs in the N-S direction. The chemical concentration increases down gradient towards the south where more agricultural activities and also heavy population are located. The SAR value even in the deep groundwater has at some places reached higher value as given in Figure 3.

With existing rate of present chemical warfare with the nature the chemical concentration has reached to a limit which may go beyond the dangerous level if the present trend of indiscriminate use of fertiliser and pesticide continue to grow. The salinity hazard seem to occur at some places of western Nepal in the form of white efflorescence

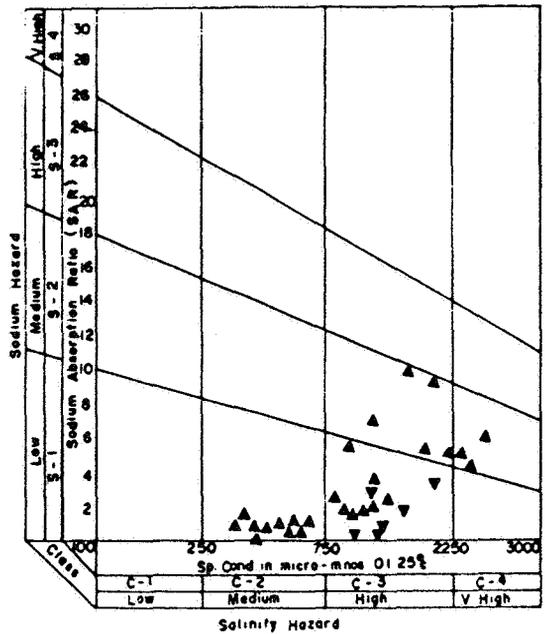


Figure 3. *Salinity hazard*

of NO_3 and other will cover wide areas in the future if surface and groundwaters are not used conjunctively and judiciously along with required correction for the chemical changes of the soil. At present in Terai wherever surface water is available, the farmers use water heavily as they believe more water means more productivity. In eastern Terai the water table has come to surface and productivity of the land is declining slowly. The drainage of ground and surface water is also a problem. As Nepal has 1800 mm rainfall per annum it is possible that chemical particulates and leachates can be washed away regularly as long as they do not enter into the groundwater system. For contaminated groundwater the only solution will be by pumping out the water and getting recharged from stream or rainfall. That may be eventually most costly and more time consuming.

7. CONCLUSIONS

There needs to be a close chemical and biological monitoring of ground as well as surface waters with regard to its toxic chemical quality. At the same time groundwater management should be introduced to reduce

Table 3

TABLE: 3 CHEMICAL CHARACTERISTIC OF SURFACE AND GROUNDWATERS OF NEPAL

(Unit parts per million)

Types of Chemical	Fresh and Unpolluted Water		Groundwater		
	Trisuli River	Tadi River	Pheratic	Bhairahawa	Deep Tubewell
Ca	11.12	2.3	20-200	43	8-68
Mg	3.8	1.3	30-100	20	18-79
Na+K	?	?	50-150	20	3-64
SO ₄	2.4	3	40-80	78	0-162
CL	5.6	7.9	59-250	10	5-8
Hardness	41.42	13.34	200-300	154	143-244
Alkalinity	36.35	16.44	299-300	300	159-346
PH	7.1-7.8	6.8-7.9	7-8	7	7.6-8.6
Specific Conductivity	91.96	31.96	771 M/Mo	335	293-683
CO ₂	0	0	0-20	20	0-14
Total Dissolved Solid	48.70	36.76	300-900	751	220-552
Fe	0.01	0.01			3-6-5

Table 4

TABLE 4
Chemical Characters of Water of Dug Wells in different Zones

Location	Ca++ + Mg++	Na+K	CO ₂	HCO ₃	SO ₄	Cl	Dis- solved Solid	Hard- ness	Non- Carb.	Sp. Cond.	PH	Alkali- nity	
Bhabar Zone													
1. Khairan	38	38	89	Nil	289	82	86	500	251	—	791	8.3	234
2. Sunawal	26	73	—	106	499	170	—	—	364	—	693	9.1	385
3. Materia	24	10	6	Nil	134	Nil	3	68	102	0	2176	8.35	110
4. Hasnapur	66	28	8	4	335	Nil	13	308	275	0	534	8.4	275
5. Jhim-Jhimia													
6. Chappar													
Middle Terai													
7. Tilaurs	70	74	120	Nil	391	120	209	1080	481	160	1477	7.25	321
8. Barwa	52	20	21	Nil	270	29	4	236	212	0	412	8.3	221
9. Dhunraha	79	72	57	Nil	263	114	199	1058	482	276	1207	8.1	216
10. Maraujaini	129	39	211	Nil	756	126	435	1504	482	0	1878	7.85	620
11. Hariharpur	107	1	184	Nil	628	44	78	1006	270	0	748	7.9	515
12. Harauatagar	74	—	—	Nil	514	20	83	436	157	0	1086	7.75	421
Southern flat Zone													
13. Krishnanagar	141	—	—	Nil	522	6	256	1268	—	—	1569	8.95	—
14. Azgara	6	29	267	Nil	581	64	112	872	126	0	1477	8.05	476
15. Bahadurgani	280	—	—	Nil	671	169	301	3228	484	0	2066	7.6	550
16. Bogri	123	—	—	Nil	440	12	157	538	—	0	839	8.0	360

the water logging and also over mining of resources. Nepal cannot be isolated with the development occurring in the rest of the world, but has to maintain its tradition and ecology which may be helpful eventually when high yielding varieties could not adjust the ecosystem of the country. Then there will be no time and no seed to come back to the traditional way.

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THE FIGHT AGAINST NITRATE LEACHING FROM AGRICULTURAL SOILS

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ABSTRACT

Nitrate pollution of surface waters and groundwater reservoirs is an increasing problem in many countries. Fertilizing activities in agriculture play an important role and therefore modified agricultural practices should be developed to reduce the nitrate leaching threat. Important factors determining the rate of nitrate leaching are soil use, soil type and hydrological situation. Nitrate leaching can be minimized by a good water management and by restrictions in the application of fertilizers and especially slurry with respect to time and amount of application. The growth of a cover crop after harvest of the main crop may cut nitrate leaching by 20 to 40%.

1. INTRODUCTION

There is increasing evidence of adverse effects of agricultural practices on nitrate leaching to groundwater reservoirs and surface waters. Interests such as water supply, recreation, fishery and nature conservation may be damaged by a rise in nitrogen content. Public awareness of possible effects of modern agriculture on environmental quality has provided an impulse to developing modified agricultural production systems. In this paper attention will be given to the effect of some measures which could be taken to reduce nitrate leaching from agricultural soils.

2. WATER MANAGEMENT

Water management influences some important processes and activities relevant for crop production and fate of nutrients. Examples are soil temperature, availability of water, nitrogen turnover and land trafficability. For each soil type and crop optimal drain depths or groundwater levels can be calculated based on long-term climatic data (Van Wijk and Feddes, 1986). At a certain level of N supply losses by nitrate leaching can be reduced by improving crop uptake (Steenvoorden and Bouma, 1986). Crop production can be raised by additional water supply in dry periods. Experiments with arable and horticultural crops show a decrease of the nitrate concentration in the leachate from irrigated fields compared with non-irrigated fields. This decrease ranges from 5 to 50 percent (Pfaff, 1958; Czeratzki et al., 1976). Irrigation experiments for grassland have recently been carried out on a sandy soil with a groundwater level of more than two meters belows soil surface. Especially at higher fertilization levels irrigation leads to lower nitrate concentrations (Figure 1). At the N-fertilization level of $400 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ (the level advised by the Agricultural Advisory Service) irrigation decreases the nitrate concentration by nearly 20 percent in the leaching period 1982/1983. At lower N inputs the N supply tends to be the limiting growth factor resulting in smaller reductions in nitrate leaching. Similar positive effects of grassland irrigation have been reported by Garwood and Ryden (1986).

Manipulation of water levels influences conditions for denitrification in the upper meter of the soil (Duynisveld and Strebel, 1987) and crop uptake. At higher groundwater levels both processes lead to lower losses by nitrate leaching at the same level of mineral-N supply (Figure 1). In this experiment fertilization was with mineral fertilizers and cattle slurry. The latter was applied in early spring via injection and surface spreading. Mineral-N supply is the sum of mineral-N in artificial fertilizers and mineral-N from slurry which has been calculated by multiplying total N in slurry with apparent N recovery in grass. The effect of water-table depth on leaching can be translated in a reduction coefficient by which nitrate leaching from deeply drained soils must be multiplied (Table 1).

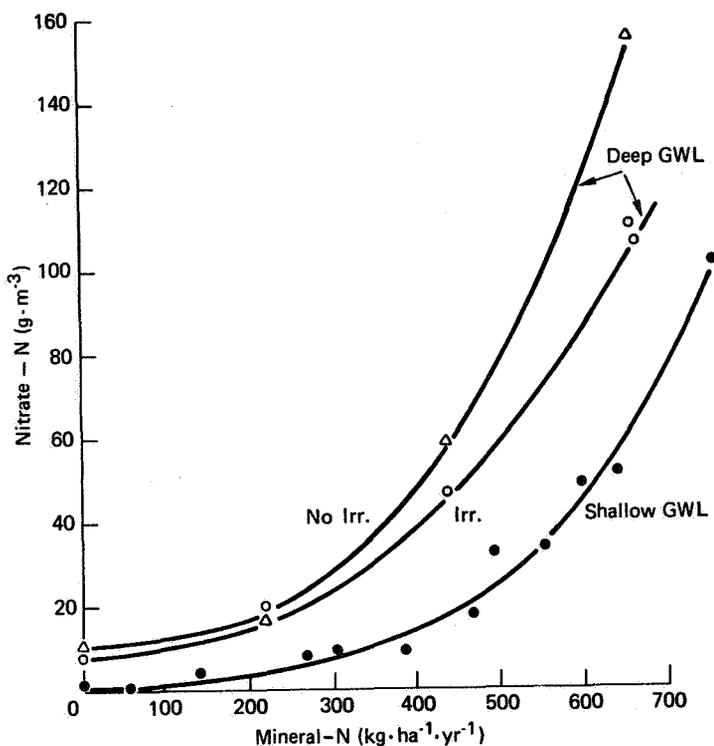


Figure 1. Nitrate concentration in the leachate in the leaching period 1982/1983 at roughly 1 meter below soil surface at different supply rates of mineral-N for cut grassland on sandy soils with shallow groundwater table (shallow GWL; max. 0.4 m below soil surface in winter and 1.4 m in growing season) and deep groundwater table (deep GWL; more than 2.5 m below soil surface). The field with the deep water table was with irrigation (Irr.) and without irrigation (No irr.) in dry periods. The field with the shallow groundwater table was not irrigated (Steenvoorden, 1987)

Table 1. The reduction coefficients by which nitrate leaching from deeply drained soils must be multiplied as a function of the mean depth of the groundwater table in winter

	Mean groundwater level (m - soil surface)						
	0.0	0.2	0.3	0.4	0.6	0.9	1.0
Reduction coefficient	0.04	0.10	0.15	0.22	0.41	0.73	1.00

3. COVER CROP

Nitrate leaching from arable land can be reduced by growth of a cover crop after harvest of the main crop. Cover crops can take up remaining nitrate and mineralized N after removal of the main crop. The effect of cover crops on nitrate leaching depends on time of sowing, type of crop and climatic conditions. The later the date of sowing, the lower N-uptake of the crops. Sowing at October 1 leads on average to a N-uptake of roughly 30 kg.ha⁻¹ which amounts to only 35 percent of the N-uptake when sown at September 1 (Elers and Hartmann, 1987). Total N-leaching in kg.ha⁻¹ was reduced by 40 to 95 percent depending on crop type (Vetter and Steffens, 1981; Nielsen and Jensen, 1985). Italian ryegrass, winter wheat and rape proved to be very effective. Nitrate concentration is negatively effected by the reduction in the amount of leachate resulting from an increase in evapotranspiration by the cover crop. The earlier the date of sowing the higher the amount of evapotranspiration and the lower the amount of leachate. Overall effects of cover crops on leachate-nitrate concentration are positive and on average the reduction in agricultural areas with a variety of crops may amount 20 to 40 percent compared to bare arable soils with the restriction that no extra N fertilization takes place.

4. TIME AND AMOUNT OF SLURRY APPLICATION

In areas in the Netherlands where excessive amounts of slurry are produced large parts of the slurry are put on silage maize land in autumn

Table 2. Effect of yearly application of $30 \text{ m}^3 \cdot \text{ha}^{-1}$ pig slurry (180 kg nitrogen) on nitrate leaching to shallow groundwater (2-3 m below soil surface) below arable land on sandy soil. Amount of leachate is $250 \text{ mm} \cdot \text{yr}^{-1}$ (Vetter and Steffens, 1981)

Application period	Leachate-nitrate concentration ($\text{g} \cdot \text{m}^{-3}$ as N)	Yearly extra N leaching compared to non-fertilized field	
		($\text{kg} \cdot \text{ha}^{-1}$)	(% of slurry-N)
August	56	54	30
October	51	39	22
February/March	41	14	8

Table 3. Effect of pig slurry dose in November for a sandy soil on N uptake in annual grass (sown: April; last cut: October; bare soil: October-April) and nitrate leaching to groundwater at 1 meter below soil surface. Results are an average over 6 experimental years. Groundwater-level fluctuation is between 1.0 and 1.5 m below soil surface. Amount of leachate is $327 \text{ mm} \cdot \text{yr}^{-1}$ (Oosterom, 1984)

Slurry dose ($\text{m}^3 \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	Slurry N ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	N uptake ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	Nitrate concentration ($\text{g} \cdot \text{m}^{-3}$ as N)	Yearly extra N leaching compared to non-fertilized fields ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$)	(% of slurry-N)
60	375	237	55	81	27
150	938	367	97	203	22
300	1875	512	156	431	23

and winter because of lack of storage capacity.

Application of slurry in spring in amounts not exceeding crop needs lead to nitrate-leaching losses of 8 percent of total N compared with no slurry application. When the same amount of slurry-N is applied in Octo-

ber or August leaching losses increase up to 22 and 30 percent respectively (Table 2). When slurry is applied in November leaching losses amount roughly 25% of total slurry N for slurry doses of 60, 150 and 300 m³.ha⁻¹ (Table 3). The best recovery of slurry N in crops and the lowest nitrate leaching results from application in spring and early summer in amounts not exceeding crop needs.

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DYNAMICS OF Cd, Cu and Zn IN COMPOSTED SLUDGE/
MINERAL SUBSTRATE LYSIMETRIC SYSTEMS

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ABSTRACT

Seasonal variations of the Cd, Cu and Zn concentrations in the gravitational waters of soil profiles reconstituted with composted sludges and non carbonated mineral supports are followed over a period of two years. Besides observing a greater retention of these heavy metals in sandstone soil profiles, the role of vegetation in the dynamics of heavy metals, the similarity in the behaviour of Cd and Zn, and the effect of soluble organic matter on the leaching of Cu are also studied.

1. INTRODUCTION

The restoration of mineral and degraded soils to organic soils, which is achieved by reconstituting the organic horizons with wastewater sludges or composts, poses the problem of the efficiency of such practices as well as of the potential environmental pollution risks by the micro pollutants found in these residues.

The experience using lysimetric systems, which started in May 1985, focuses on the leaching of heavy metals (Cu, Cd, Zn) through soil profiles reconstituted with wastewater sludge composts and non carbonated mineral supports.

2. MATERIALS AND METHODS

The soil profiles are of the AC type (36 cm diameter, 54 cm height): A₁ organo-mineral horizon (33% compost, 66% mineral material w/w d.m. 36 cm height), on top of the mineral horizon; the whole profile is passed through a 5 mm sieve. Eight different situations are examined:

(a) sandstone, granite - (b) spiked, non spiked - (c) naked soil, soil covered with vegetation (ray grass, clover)

	Horizon	Particle Size Distribution (%)			pH	pH	Fe (o/oo)		Organic matter	
		Sand	Silt	Clay	(eau)	(KCl)	Tamm	M-J	C (%)	N (%)
Arenite of sandstone (s)	C	68	13	19	6.90	5.60	1.0	7.4	0.30	0.11
Arenite of granite (g)	C	79	12	9	5.75	3.70	3.5	6.2	0.14	0.07
Non spiked systems	A1 (s)	76	13	11	6.77	6.60	25.4	33.5	11.40	0.59
	A1 (g)	75	15	10	6.62	6.41	29.8	35.3	13.00	0.67
Spiked systems	A1 (s)	75	13	12	6.32	6.00	27.0	33.8	11.50	0.56
	A1 (g)	74	14	12	6.15	5.90	26.4	30.0	11.40	0.54

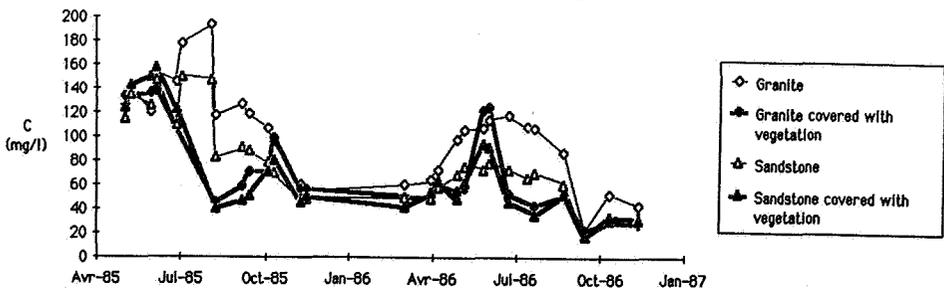
	Si	Al	Fe	K	Na	Ca	Mg	Mn	Cd	Cu	Zn
	(mg/g)										
Arenite of sandstone (s)	345	64	13	48.3	10.0	5.3	3.9	0.65	/	0.004	0.033
Arenite of granite (g)	334	68	18	47.2	16.0	6.6	8.1	0.54	/	0.007	0.042
Non spiked systems	A1(s)	221	44	37	30.4	6.8	13.8	3.6	0.36	0.005	0.17
	A1(g)	206	45	43	26.8	9.8	16.9	6.6	0.34	0.006	0.20
Spiked systems	A1(s)	231	45	37	30.2	9.3	8.5	3.4	0.36	0.01	1.10
	A1(g)	215	49	40	29.2	11.0	11.2	6.4	0.32	0.01	1.10

Table 1. and 2. Analytical characteristics of the A and C horizon

The lysimeters are subjected to discontinuous fluxes of demineralized water (annual height, 1 m approx.) in greenhouses (external climatic conditions prevailing except for rainfall). After taking gravitational water fluxes at the base of the C horizon, heavy metals and TOC are filtered (0.45 μ m) and titrated.

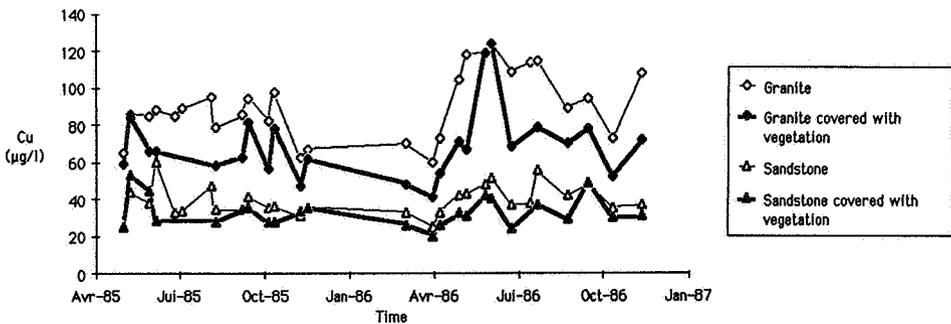
4. RESULTS AND DISCUSSION

About the pH evolution, one notes the gap (around 2 pH unit) existing between the sandstone and granite media at the beginning of the experimentation, and the convergence of the values towards neutrality at the end. The TOC concentrations present seasonal fluctuations (between 20 and 140 mg/l) with maxima during summer (Graphic 1.1)



Graphic 1.1. Mean organic carbon concentration in non-spiked systems

Over the six first months of experimentation, important Cd and Zn leaching is observed but thereafter their concentrations are stabilized around 0.1 ug/l and 50 ug/l respectively. There are no notable differences between the granite and the sandstone even though the Cd and Zn concentrations in the granite systems are greater during the first six months. The evolution of Cu (Graphic 1.2) is significantly different in sandstone systems from that in granite systems: the former shows a more efficient retention than the latter. Finally, systems covered with vegetation generally restrain Cu leaching.

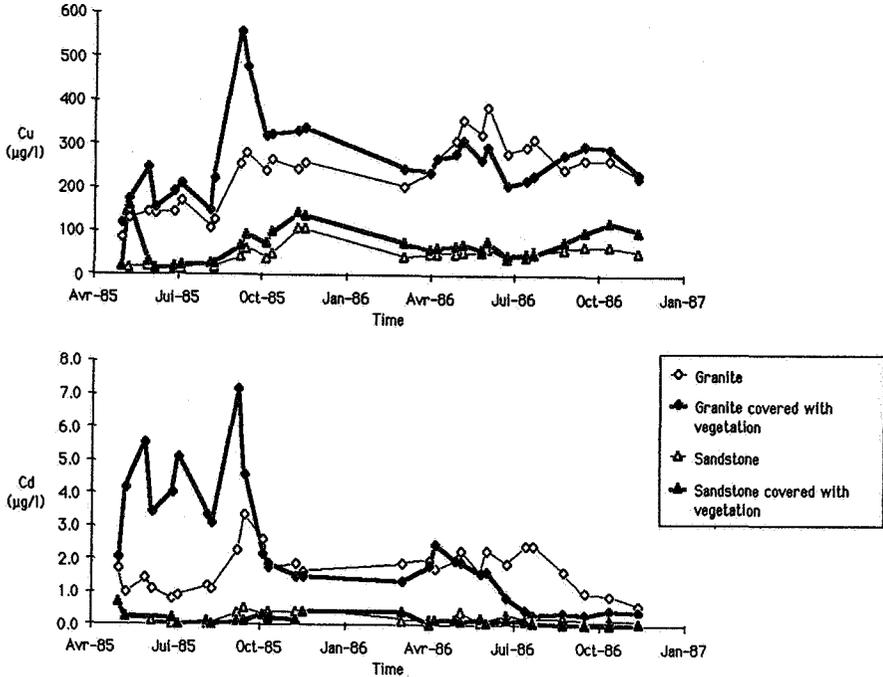


Graphic 1.2. Mean copper concentration in non spiked systems

As concerns spiked systems, the pH is subject to little evolution and always stays lower in filtrates of granite systems (between 5 and 6). The TOC concentration remain near 30 mg/l; the seasonal fluctuations are generally weak. The dynamics of Cu (Graphic 2.1) differs widely from sandstone to granite: in the latter, a leaching is 2 to 4 times greater; unlike non spiked systems, the presence of vegetation tends to increase the leaching of this element. Sandstone, contrary to granite, limits losses of Cd by drainage; in granite systems, moreover, seasonal variations are more important when vegetation is present. (Graphic 2.2)

The following points stand out:

- an important difference in the reactivity of sandstone and granite substrats with heavy metals: sandstone exhibits efficient sorption mechanisms limiting losses through drainage and thus pollution of ground water
- a difference of behaviour between metals. An important correlation (0.58-0.92) is observed between Zn and Cd especially in granite sys-



Graphic 2.1. and 2.2. Mean concentration in spiked systems

tems. Moreover, Zn and Cd appear negatively correlated to the pH (0.53-0.76). Therefore, Cu seems to be influenced by different factors than those governing the dynamics of Cd and Zn. Since May 1986, Cu has shown to be correlated to organic carbon

- a difference between naked soils and soils covered with vegetation, the presence of vegetation modifying, whether increasing or decreasing, the leaching of heavy metals
- a difference between spiked and non spiked systems. In spiked, the presence of heavy metals rapidly eliminates clover and leads to a drop of being subjected ray grass productivity. Otherwise, the presence of heavy metals reduces the microbial biomass which should obviously interfere with the biodegradation and humification processus of organic matter.

PLANT PRODUCTION INPUT-OUTPUT BALANCE AS CRITERION
OF SOIL AND GROUNDWATER PROTECTION AGAINST AGRI-
CULTURAL POLLUTION

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ABSTRACT

The dynamic growth of fertilizer consumption in Czechoslovak agriculture during the 1960-1980 period has lead to high nitrate concentrations in water sources.

The paper deals with the evaluation of the above mentioned period of twenty years that have witnessed an ever more pronounced degradating effect of vegetal production technologies upon the quality of groundwater sources, in particular upon the territory of the Českomoravská vrchovina /the Highlands/. Further an assessment is made relating to the development dynamics of balance relationships between inputs and outputs of plant production with regard to the differentiation range of geographical conditions of the territory of the Czech Socialist Republic. It appears to be sheer necessity to specify limit input-output values as criteria to be respected for the sake of rational functioning of both agriculture and groundwater protection.

1. INTRODUCTION

Since 1960 Czechoslovak agriculture went through a number of marked changes due to intensification processes aiming at production growth in order to make the country independent relating to basic foodstuffs. Intensive agriculture and its production technology based on high energetic and material inputs constitute substantial pollutants of groundwater and of soil environment in terms of their by-products.

A wide range of pesticides and fertilizers, in particular nitrogenous, play the crucial role in this respect.

Stibrál and Vagner /1979/, Moldan and Pačes /1980/, and Buček et al. /1980/ furnished quite evident correlations between levels of fertilizer consumption and nitrate concentrations in groundwater. Accordingly, on a general plan, the research proved the validity of correlation between the degradation of water sources and the application of fertilizers after exceeding a certain critical level of the latter. This relation, however, may be strikingly differentiated by the specific character of climatic and soil-ecological conditions, as well as by economic consequences of financial support rendered to agricultural production in relatively unfavourable natural conditions, such as hilly country and piedmont areas.

In order to document these relationships for the 1960-80 period a very simplified form of an example has been chosen as follows. The presented evaluations cover the district of Žďár nad Sázavou situated in the Českomoravská vrchovina /the Highlands/. On the one hand, this is an important territory from the viewpoint of water management and, on the other hand, it offers substandard conditions for agricultural production.

2. CORRELATION EXAMPLE: FERTILIZERS - PRODUCTION OF CROPS - CONCENTRATION OF NITRATES

2.1 Intensification of the production of crops through increasing consumption of fertilizers

Economic instruments functioning upon positive social principles, in compensating the negative effects by a differential rent, allow to maintain agricultural production also in marginal, i.e. productively weakest areas, while ensuring relatively high inputs into the production process. This can be documented by the dynamics of the development of fertilizer consumption, which is a considerable part of the plant production inputs. Figure 1 shows the consumption of pure NPK nutrients per 1 hectare of farmland in the district of Žďár nad Sázavou in 1960-1980. The average consumption increase from 62,7 kg in

1961 to 252,6 kg in 1980 represents a rise amounting to 302,8 %. Even more striking is the increase of nitrogenous fertilizer consumption amounting to 433,1 %. In pure N nutrients 17,5 kg were added in 1961, whereas the inputs soared to 93,3 kg in 1980. Let us subjoin that during the same period the gross value of the production of crops increased by 42,6 % /from 3 400 Kčs in 1961 to 4 850 Kčs in 1980/, as documented in Figure 2.

A detailed methodology of approaching this problem was dealt with in another contribution of the author /1980/.

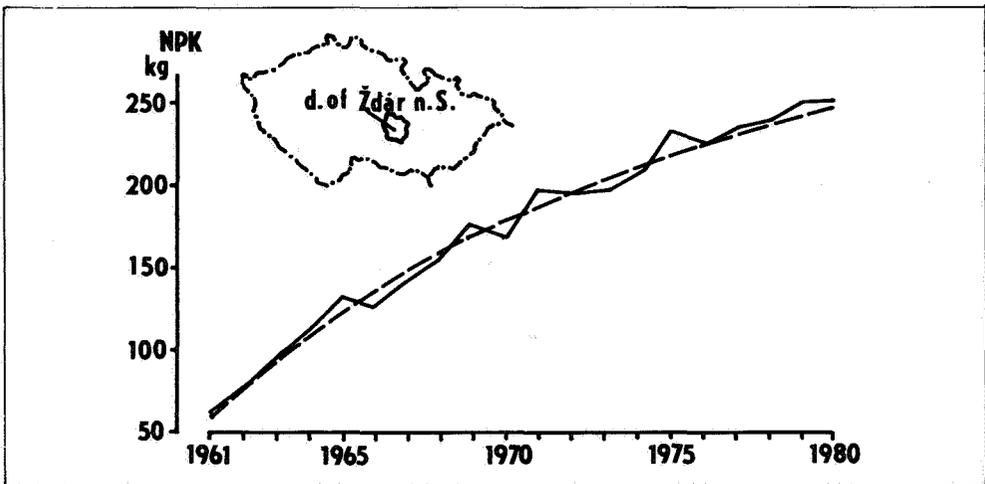


Figure 1. Consumption of fertilizers /NPK/ per hectare of farmland /district of Žďár nad Sázavou/

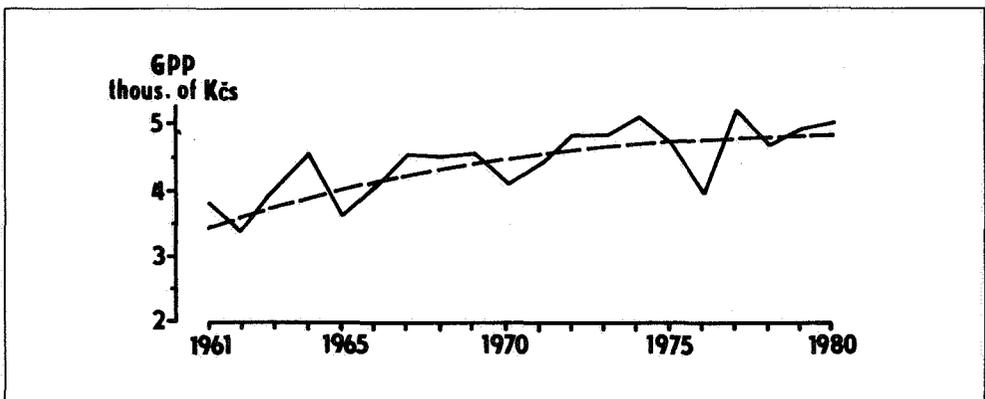


Figure 2. Gross plant production /GPP/ per hectare of farmland /district of Žďár nad Sázavou/

2.2 Undesirable consequences of the intensification process

The excessive rise of fertilizer consumption before 1980 did not account for the necessity of specific control measures within the important catchment areas of drinking water. The consequences can be seen in the following results of analyses carried out in the Highlands. Evaluations of file data comprising analyses of drinking water samples from 132 underground sources of local significance /supplying 100 and more inhabitants/ confirm that until 1960 most sources met the established limit of nitrates in artificial nourishment for small babies /15 mg.l⁻¹/ and no violation of the adult nitrate standard /50 mg.l⁻¹/ in the above area was found down to 1960. From 1960 down to the present day, only sources with complete afforestation of the catchment area have maximum nitrate values that do not exceed 15-20 mg.l⁻¹, fluctuating according to the season of the year. /Figure 3, sources /1/ Chlébské./

Contrariwise, sources with prevailing farmland catchment areas have had steadily rising nitrate contents. At present, it is seen to exceed the limit of 50 mg.l⁻¹ during the critical spring season almost as a rule. /Figure 3, sources /2/ Rovečné, /3/ Unčín./

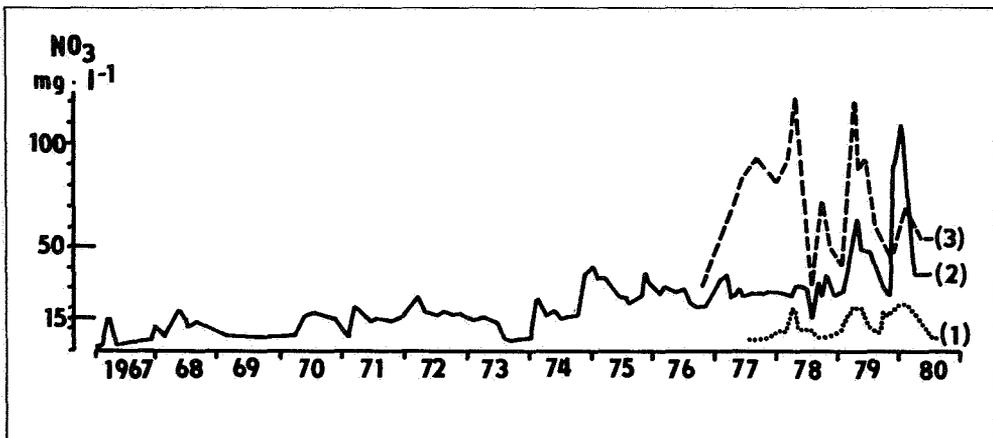


Figure 3. Concentration of nitrates in selected ground sources of drinking water. /1/ Chlébské, catchment area 41 ha, 100 % afforestation, /2/ Rovečné, catchment area 73 ha, 24 % afforestation, 76 % farmland, /3/ Unčín, catchment area 36 ha, 41 % afforestation, 59 % farmland

From this viewpoint, relating to the growth of nitrate concentrations due to agricultural production, the period after 1970 can be identified as critical.

These problems in correlation with production aspects within the territory under consideration are dealt with in another study of the author /1982/.

3. INPUT-OUTPUT BALANCE OF PLANT PRODUCTION

3.1 Economic and ecological aspects of the optimization of energetic and material balancing

In general terms, the introduction comprises a statement as to possible reductions of the undesirable effects of the production of crops on the quality of groundwater sources, provided optimum input.output ratios can be maintained so as to achieve the most favourable economic effects. In this connection it is most essential to change the fixed ready-made notion of intensified agriculture, while paying due attention to differentiated geological and environmental conditions of farming areas; only thus the particular orientation, the forms and the respective intensification degree of production can be determined. A representation of the development of the gross plant production over 1960-80 is in Figure 4, documenting the production relations within the range of different agricultural conditions of the Czech Socialist Republic /C.S.R. - Bohemia and Moravia, without Slovakia/. The graphical representation illustrates the positive dynamic trend of the gross production of crops, while disclosing the ever increasing difference between the achieved results of the extreme areas, relating to the suitability of natural conditions for agriculture.

Following the evaluation of the gross plant production, Figure 5 illustrates the balance ratio between gross plant production and fertilizer consumptions during the 1970-80 period. The comparison between the areas shows the range of fertilizer application to narrow down during the period under consideration.

The importance of the optimization of energetic and material balancing in agriculture is closely linked with questions of farming economics.

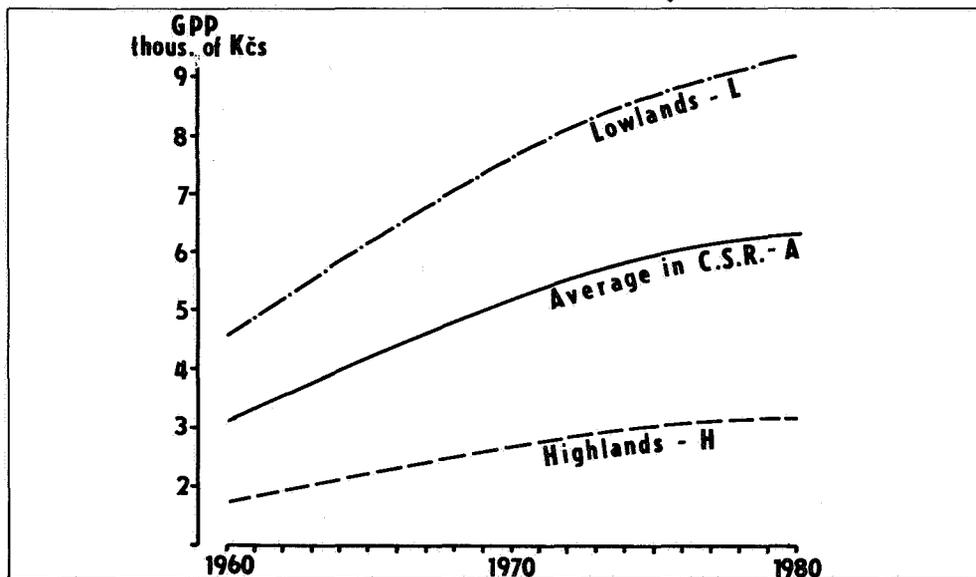


Figure 4. Representation of the gross plant production in extreme and average conditions of the C.S.R. during 1960-1980

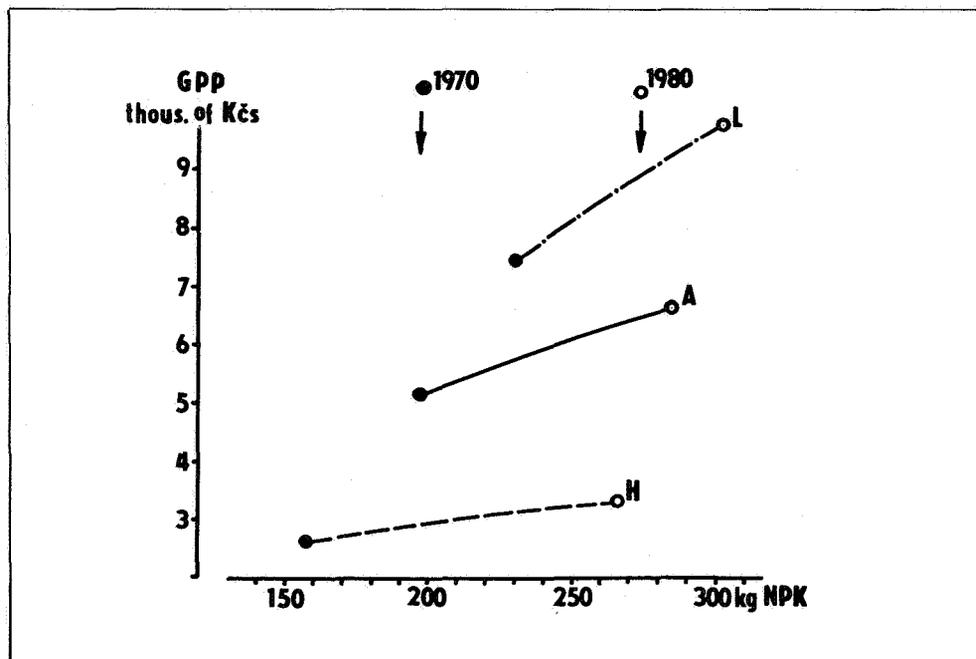


Figure 5. Balance relations between the consumption of fertilizers /NPK/ and the gross plant production /GPP/ in extreme and average conditions of the C.S.R.

Moreover, such optimization has a direct, essential impact upon the sphere of environment protection and its creation. Agricultural systems characterized by unfavourable energetic input-output balance, in other words by high losses of energy, usually in the form of escape beyond their boundaries, represent a serious threat to environment quality.

The optimization of the balance of material and energy within the farming production in the direction of their best effectivity is at the same time a valuable contribution to the protection of groundwater and of the whole sphere of environment.

3.2 Example of partial energetic balance of inputs and outputs of the production of crops

Table 1 shows a partial energetic balance that has been carried out upon the basis of retrospective evaluation of the development trends of input and output items of the production of crops during 1970-80 according to the extremely located areas from the viewpoint of geoeological conditions for agriculture and the average conditions in C.S.R. Due to lacking knowledge of adequate energetic representations of some component parts of plant production output the calculation comprises only directly applicable outputs. As to the inputs, only specific fuel consumption of agriculture machines and implements and the energy represented by the seed, the plantings, fertilizers and pesticides have been calculated. Accordingly, from the viewpoint of the energetic and material flow, such balance is only partial and can not be considered as complete.

The calculated data are represented diagrammatically in Figure 6. The extreme areas show a markedly broad range of output values as compared with minor variations of plant production input values. There is also an obvious general declining trend of the output-input relation within the framework of the calculated items, offering evidence as to the decreasing effectivity of additional energy that should boost the production of crops.

Table 1. *Partial energetic balance of plant production input and output items in extreme and average conditions of C.S.R. /in GJ per ha of farmland/*

Items of energy	Lowlands		Highlands		average in C.S.R.	
	1970	1980	1970	1980	1970	1980
Outputs from arable land	41,28	50,31	18,67	22,87	35,15	43,48
from other land	7,10	9,00	6,62	8,19	4,49	5,03
Total output from farmland	48,38	59,31	25,29	31,06	39,64	48,51
Difference of output 1980-1970	+10,93	= 22,6 %	+5,77	= 22,8 %	+8,87	= 22,4 %
Inputs - oil consumption, seeds, pesticides	7,46	9,22	6,06	6,29	7,04	8,16
- synthetic fertilizers	8,04	10,91	5,16	10,93	6,35	9,47
Total inputs to farmland	15,50	20,13	11,22	17,22	13,39	17,63
Difference in inputs 1980-1970	+4,63	= 29,9 %	+6,00	= 53,5 %	+4,24	= 31,7 %
Rate	3,12	2,95	2,25	1,80	2,96	2,75
t.outputs						
t.inputs						

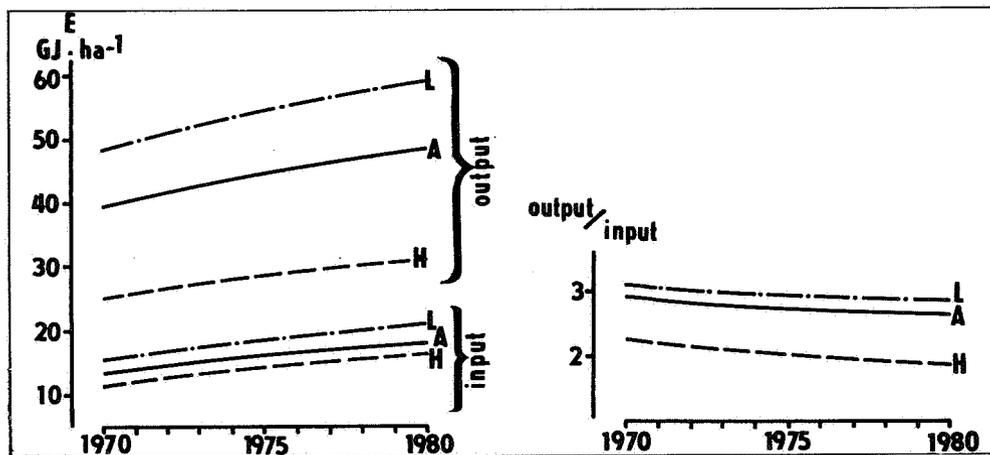


Figure 6. *The dynamics of partial energetic balance of plant production in extreme and average conditions of the C.S.R.*

4. CONCLUSION

A rationally oriented agricultural production process offers sufficient room for finding the appropriate relation between the production results on the one hand and the extent of additional energetic inputs on the other hand, while preferring such forms of energy that can be best utilized under the given conditions of climate, soil, and environment. The optimization of energetic and material balance in the sphere of the production of crops and, indirectly, in the whole agricultural domain, can effectively contribute to differentiated usage of rural areas. Such trend complies both with the requirements related to the particular degree of importance for agricultural production and with the importance of the given rural area for water management and for further nonproductive social functions.

ACKNOWLEDGEMENTS

The author wishes to express his heartiest thanks to the Czechoslovak Academy of Sciences, to the Czech Literary Foundation, and in particular to the organizers of the VSGP '87 Conference who helped him to

present the results of his research to a distinguished international forum.

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SELENIUM CONTAMINATION OF SOIL AND GROUND WATER
BY AGRICULTURAL DRAINAGE IN THE CENTRAL VALLEY
OF CALIFORNIA, USA

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ABSTRACT

Selenium contamination of surface and groundwater has occurred from leaching of sediments by agricultural drain water. Selenium is found to be mobile under oxidizing conditions encountered in surface water at the Kesterson Reservoir. Selenium is generally immobile under reducing conditions in anoxic bottom muds containing sulfate-reducing bacteria and in the deeper ground water aquifer in which dissolved oxygen is depleted by reaction with iron containing minerals. Local areas of ground water contamination occur in zones of high permeability and in the presence of nitrate. A semiquantitative relationship exists between aqueous oxidation-reduction potentials and selenium speciation although the mechanisms and kinetics of selenium reduction are not completely understood.

1. INTRODUCTION

Recently, extensive selenium contamination has occurred in agricultural areas of the Central Valley of California. The source of Se is Cretaceous marine shales containing iron sulfides with high concentrations of coprecipitated selenide. Weathering and sediment transport have created large alluvial fans which presently support intensive agriculture and which also contain high concentrations of mobile oxidized selenate and selenite. The mobilization of selenium has been aggravated by extensive irrigation which accelerates the rates of leaching, coupled with the practice of using tile drainage systems to prevent salt accumulation within the root zones of plants.

The sink for agricultural drainage from the region has been the 95 km long San Luis Drain which discharges to the Kesterson Reservoir. The Reservoir, consisting of 490 km² of shallow evaporation ponds, was originally designed as a midpoint regulatory structure after completion of the Drain to an estuary linked to the San Francisco Bay. Objections to the plan halted the completion of the Drain and Kesterson Reservoir, which is situated within a National Wildlife Refuge, became the terminus for agricultural drainage water.

Shortly after introduction of drainage water to the Reservoir, an excessive number of migratory water fowl deaths and deformities were caused due to selenium toxicity. In August, 1986, the U.S. Government ordered that drainage from 1.6×10^4 km² of farm land be stopped and discharge to the reservoir terminated. In addition to continued direct contamination of the food chain from residual selenium in surface water and bottom sediments in the reservoir, a potential threat to ground water also exists due to rapid infiltration rates (10 m/year) in the underlying shallow aquifer.

SELENIUM GEOCHEMISTRY

Four aqueous geochemical environments have been characterized in and beneath the Kesterson Reservoir. Selective representative chemical parameters for each environment are presented in Table 1.

The surface water in the reservoir contains up to 400 $\mu\text{g.l}^{-1}$ dissolved selenate with lesser amounts of selenite. Organic selenium species, including dimethyl selenide, dimethyl diselenide and seleno-amino acids, have been identified (Cook and Bruland, 1986). Dissolved oxygen (D.O.) is comparable to saturated atmospheric conditions (Table 1).

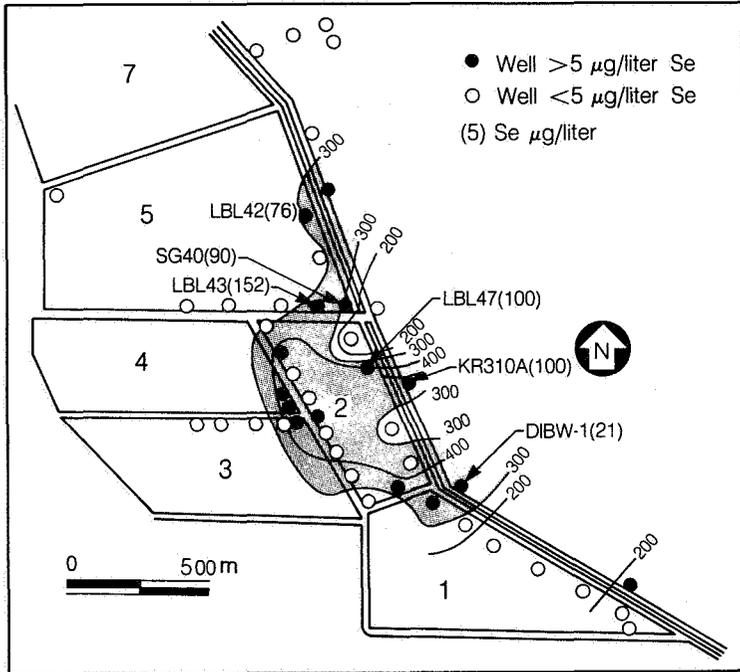
Directly underlying the oxidizing surface water in most areas is a 5 to 50 cm thick layer of anoxic organic-rich mud. High concentrations of H₂S (up to 300 mg.l^{-1}) indicate the presence of anaerobic sulfate-reducing bacteria. Pore water within these muds contains a chemistry almost identical to the overlying surface water (Table I) except for a lack of selenium which has been reduced and precipitated out as immobile elemental selenium. Substitution of SeO₄ for SO₄ in metabolic reduction by bacteria is assumed to occur although a highly selective partitioning required for selenium uptake relative to sulfur has not been demonstrated for specific strains of bacteria in the laboratory (Oremland, 1986).

Table 1. *Representative Chemistry (mg.l⁻¹ except at noted)*

	Surface	Sediment	Oxic	Anoxic
	Water	Pore Water	Ground Water	Ground Water
Site	PD2	H2	D2W2	D9W1
SeO ₄	0.261	0.000	0.115	0.001
SeO ₃	0.051	0.001	0.002	0.002
pH	7.75	7.05	6.80	7.70
Eh(mv)	372	-35	442	94
D.O.	9.30	0.00	0.80	0.00
Fe ⁺²	0.00	0.16	0.00	8.31
H ₂ S	0.00	38.0	0.00	0.00
Na	2481	6420	3305	3642
K	10.7	8.81	5.95	4.14
Ca	570	786	426	392
Mg	322	388	353	381
SO ₄	1560	10608	5933	7300
Cl	5720	4259	2021	1940
HCO ₃ ⁻	382	428	378	365

In most areas beneath the reservoir, both selenium and dissolved oxygen have been effectively excluded from the deeper (2 to 30 m) alluvial aquifer by prior infiltration through the bottom muds. Ground water is also generally reducing and contains significant ferrous iron.

An exception to the above condition occurs for high selenium concentrations associated with a number of monitoring wells on the eastern side of the reservoir (Figure 1). As shown by the Figure, high selenium concentrations (up to 152 ug.l⁻¹) occur in a plume of ground water which is oxidizing (> 300 mv, relative to the Pt-hydrogen electrode). This ground water generally contains similar major dissolved chemical components as adjacent reducing ground water but also has significant dissolved oxygen and nitrate and no ferrous iron. No elevated selenium concentrations occur in ground water outside the oxidizing plume, but selenium concentrations vary greatly within the plume itself.



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Figure 1. Lateral distribution of Eh relative to the hydrogen reference electrode in ground water at depths of 5-10 meters. Well numbers are shown at locations where selenium exceeds $10 \mu\text{g}\cdot\text{l}^{-1}$, with concentrations indicated in parentheses.

The cause of the selenium break through is related to several conditions. In the immediate area of contamination, the aquifer is overlain by a thinner layer of bottom sediments. This has the effect of both increasing the hydraulic conductivity and decreasing the effectiveness of reduction by anaerobic bacteria. In addition, the area of contamination is immediately adjacent to the San Luis Drain and has historically received high nitrate inputs.

Nitrate levels decrease rapidly away from the drain in other areas of the reservoir due to uptake as a nutrient by pond biota. The presence of this additional strong oxidant suppresses anaerobic bacteria in the bottom muds, and coupled with high movement rates, permits infiltration of oxidized selenium into the ground water.

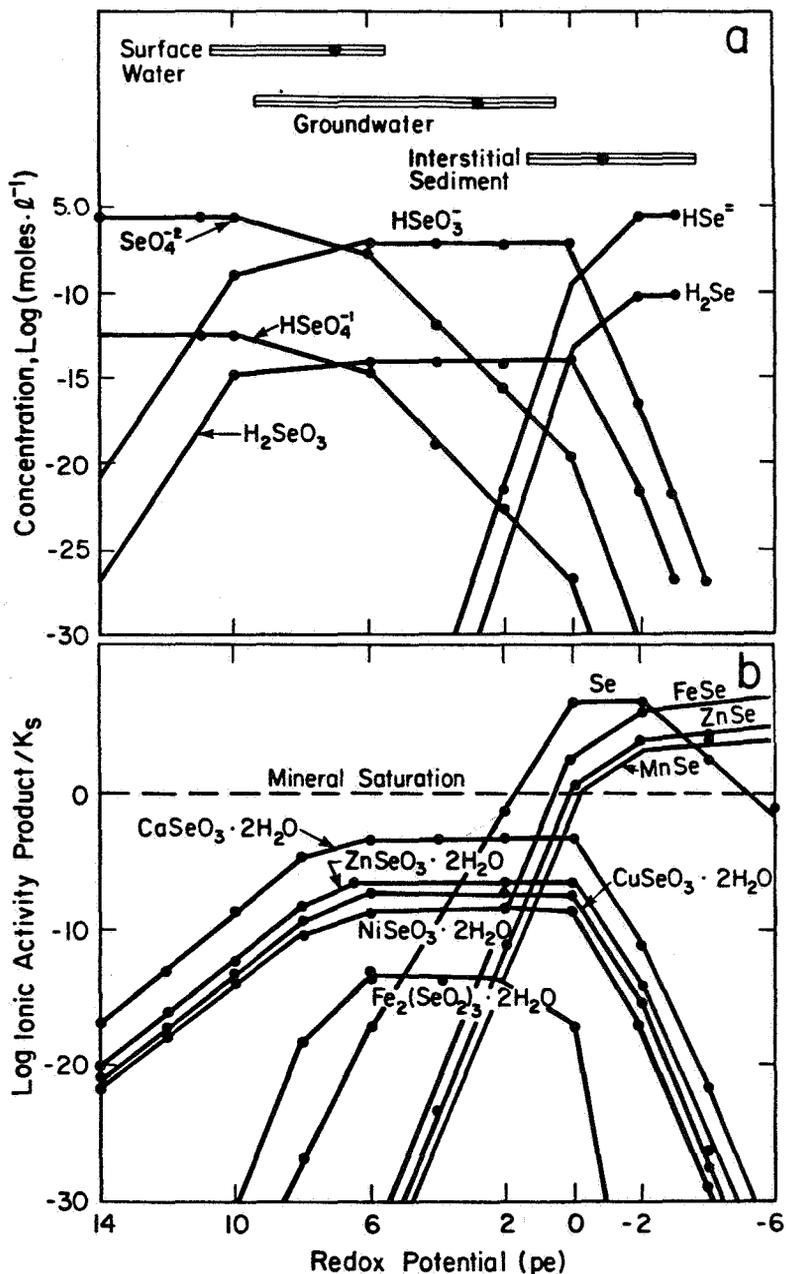
Selenium has penetrated to a depth of 15 m in the alluvial aquifer, significantly less than 40 m measured for drain water infiltration based on the presence of boron and sulfate and by tritium age dating. The lower limit of selenium penetration is coupled to the depth to which significant dissolved oxygen has penetrated into the aquifer. As oxygen is transported downward, it is gradually consumed by reaction with iron minerals and possibly by aerobic bacteria. At the point of oxygen depletion, selenium is precipitated and/or sorbed as a reduced species.

GEOCHEMICAL MODEL

The PHREEQE geochemical computer code (Parkhurst et al., 1980), along with a newly developed selenium thermodynamic data base, was used to model the relative stability of aqueous species (Figure 2a) and selenium phases (Figure 2b) in the Kesterson Reservoir. The horizontal scale in both Figures is the reduction potential of the system. Plotted at the top of Figure 2a are the measured redox potentials for surface water, pore water in interstitial sediments, and both oxic and anoxic ground water. The vertical scale in Figure 2a is the concentration (activity) of aqueous species assuming average surface water chemistry. The model correctly predicts that selenate will be the dominant species. As the drain water infiltrates into the bottom sediments, it is converted to reduced selenium species, dominantly selenide. The broad range in groundwater redox potentials permit a wide range in selenium speciation, including selenate, selenite, and selenide.

The vertical scale in Figure 2b is the ionic activity product of dissolved species divided by the solubility product, K_s , of a specific solid selenium-containing phase. Saturation with respect to a solid phase occurs at a log ratio of zero. The Figure indicates that under oxidizing conditions, selenate and selenite species are undersaturated with respect to any solid phase and will be mobile as evidenced by high concentrations in the surface water.

Under strongly reducing conditions, the fluids became supersaturated with respect to elemental selenium and metal selenides. The model successfully predicts that solid elemental selenium is the dominant phase in the interstitial sediments and in anoxic groundwater.



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Figure 2. Predicted dissolved Se speciation (a) and mineral saturation (b) for pond water undergoing progressive reduction. Bars are redox ranges measured by Pt electrode with mean averages shown by solid dots.

The above model assumes thermodynamic equilibrium and therefore must be considered only an approximation of the actual geochemical system. A more detailed characterization of redox controls on ground water indicates that while ferrous iron is in redox equilibrium with an amorphous iron hydroxide, the selenate-selenite aqueous couple is not in equilibrium. Likewise elemental selenium is most probably precipitated through metabolic reduction by bacteria and not as a result of thermodynamically controlled inorganic reduction. Even considering such complexities, selenium speciation and mobility at the Kesterson Reservoir is an important example of the control of soil-water contamination by geochemical oxidation-reduction processes.

ACKNOWLEDGEMENTS

The author worked in collaboration with Sally Benson, Tetsu Tokunaga, Oleh Weres, Harold Wollenberg, and Andy Yee, all of Lawrence Berkeley Laboratory. This work is supported by the United States Department of the Interior, Bureau of Reclamation.

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NITRATE, PHOSPHATE AND POTASSIUM CONTAMINATION OF
THE GROUNDWATER TOPLAYER RELATED TO SOIL TYPE, LAND
USE AND SPATIAL POSITION

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ABSTRACT

Under very intensive agricultural land use systems, especially in sandy-soil areas, the groundwater is heavily contaminated with manure elements. In the central part of the Netherlands a field study has been carried out on the actual nutrient contamination of sandy soils and the groundwater toplayer in relation to manure production, soil type and land use.

Results after chemical analysis of samples from 400 sample sites show very high nitrate and potassium levels in the groundwater of sandy soil areas with intensive agriculture (about 5 times EC-standards for drinking water). Arable land on clayey soils has a mean nitrate level of 2 times the EC-standard. All other soil and land use types have mean nitrate and potassium concentrations that remain far below EC-standards. Mean phosphate concentrations in groundwater do not exceed EC-standards in any combination of soil and land use type, due to the still existing adsorption capacity in most sand and clay soils.

In sandy soils, nitrogen, phosphorous and potassium availabilities show a clear relationship with land use types.

Measured potassium concentrations in groundwater of these areas can be positively correlated with concentrations computed from animal densities by the quantitative model "MANRUU".

1. INTRODUCTION

During the last decades, developments in agriculture have lead to very high production levels in the Netherlands. The number of cattle increased far above the fodder productivity of the soil, so that these products had to be imported from abroad. By export only dairy-products and meat are returned. The country is a manure-sink, because manure-production exceed crop demands. This results in problems with regard to soil-fertility (K, Cu), and soil (PO_4 , Cu), groundwater (NO_3 , K, PO_4) and air pollution (NH_3).

The level of groundwater contamination depends on manure and fertilizer input, land use, soil type and groundwater depth. In everyday agricultural management slurry is predominately applicated to arable land (silage maize) while natural areas receive no manure at all. Every manure element is subject to specific processes which are (partly) known from experiments and field analysis. Clay soils are less vulnerable than sandy soils for nitrate losses to groundwater. Except in peat soils, phosphates are adsorbed to soil particles and therefore less susceptible to leaching.

In cooperation with the regional government a field study started in 1985 on the actual nutrient contamination of the groundwater toplayer in the entire province of Utrecht.

2. METHODS

In order to obtain the relation between groundwater quality, soil type and land use systems, 400 sample locations (fields) were selected throughout the province of Utrecht (1400 km²).

Selection of sample locations has been carried out by means of a stratified random selection procedure (Blalock, 1972). Groundwater samples were taken in May and in October 1985 from 3 bore holes situated 25 m apart in the centre of each field, by means of groundwater tubes (PVC). The upper meter of the phreatic groundwater was sampled from the three borings. One single mixture sample was taken for chemical analysis. Part of each sample was soured with 18% HNO_3 to pH smaller than 2 to avoid complexation of metal ions. Nitrate (NO_3), ortho-phosphate (O- PO_4),

sulphate (SO_4), chloride (Cl), ammonium (NH_4) and hydrous carbonate (HCO_3) were analysed by colorimetry; calcium (Ca) and copper (Cu) by atomic adsorption and potassium (K) by flame photo-meter.

In sandy soils, samples were taken at 0-20 cm (plough-layer), and at 40-50 cm depth. These samples have been extracted with water and by colorimetric methods nitrogen (as nitrate), and phosphorous (as ortho-phosphate) were measured. Potassium was analysed by flame photo-meter.

3. RESULTS

From figure 1 it can be seen that mean NO_3 and K levels in groundwater show a clear dependency towards land use system within sandy soils.

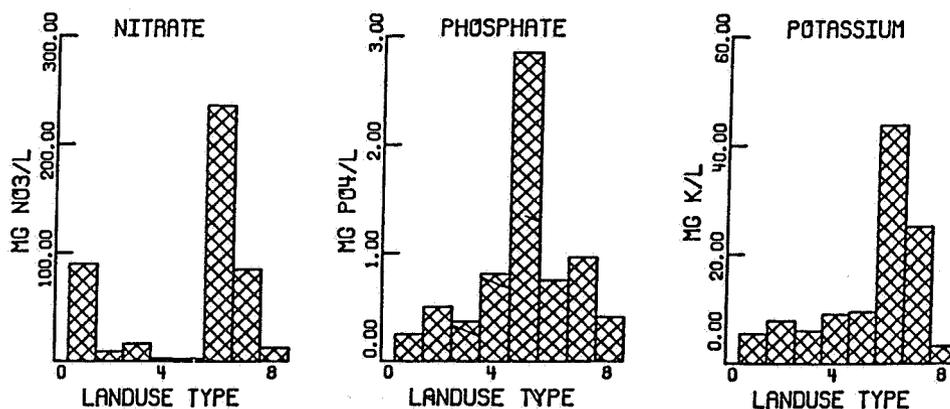


Figure 1. Mean concentrations of nitrate, phosphate and potassium in the groundwater top layer of soil and land-use types (October 1985)

Highest levels for the NO_3 and K concentrations, about 5 times the maximum EC-standards for the NO_3 and K concentrations in drinking water (50 mg NO_3/l , resp. 12 mg K/l), were found under arable land, which receives most slurry. Under natural ecosystems concentrations were low. Below arable land on clay soils the mean nitrate concentration in groundwater equals 2 times the EC-standard (Table 1).

Mean phosphate concentrations (figure 1, Table 1) in phreatic groundwater do nowhere exceed the EC-standard for drinking water (6.1 mg

Table 1. *Statistics of the measured concentrations of nitrate, phosphate and potassium in the groundwater toplayer of soil and landuse types (October 1985)*

A: NITRATE (NO ₃)		MEAN	MEDIAN	ST.DEV	MIN	MAX	N
1	CLAY-ARABLE LAND	95.34	74.55	76.59	.38	222.29	6
2	CLAY-GRASSLAND	13.13	2.44	35.10	.04	223.61	82
3	CLAY-NATURE	12.90	.87	26.14	.64	59.64	5
4	PEAT-GRASSLAND	2.75	1.18	4.07	0.00	17.37	41
5	PEAT-NATURE	3.62	3.71	2.91	.56	8.28	7
6	SAND-ARABLE LAND	275.60	233.11	191.04	1.39	754.92	71
7	SAND-GRASSLAND	105.30	77.15	110.05	.90	683.05	76
8	SAND-NATURE	9.86	5.55	11.77	2.52	48.95	15
B: PHOSPHATE (PO ₄)		MEAN	MEDIAN	ST.DEV	MIN	MAX	N
1	CLAY-ARABLE LAND	.26	.26	.10	.10	.42	6
2	CLAY-GRASSLAND	.33	.24	.45	0.00	3.91	88
3	CLAY-NATURE	.13	.07	.19	.02	2.46	5
4	PEAT-GRASSLAND	.81	.67	.62	.14	2.71	37
5	PEAT-NATURE	2.85	2.11	2.42	.31	6.36	7
6	SAND-ARABLE LAND	.54	.29	.73	.03	3.44	67
7	SAND-GRASSLAND	1.12	.43	1.86	.02	12.97	78
8	SAND-NATURE	.32	.20	.30	.10	1.23	13
C: POTASSIUM (K)		MEAN	MEDIAN	ST.DEV	MIN	MAX	N
1	CLAY-ARABLE LAND	5.49	1.60	7.29	.80	19.70	7
2	CLAY-GRASSLAND	7.85	3.40	10.20	.20	49.30	82
3	CLAY-NATURE	6.01	5.10	5.19	.40	14.50	7
4	PEAT-GRASSLAND	9.11	5.85	7.86	1.60	32.10	42
5	PEAT-NATURE	9.70	5.80	10.75	1.70	32.60	7
6	SAND-ARABLE LAND	43.87	30.15	34.16	2.40	139.90	62
7	SAND-GRASSLAND	25.29	15.55	26.32	.60	160.10	84
8	SAND-NATURE	3.26	2.85	1.66	1.50	7.30	14

PO₄/l). Also there is no significant relationship between mean phosphate levels in groundwater and land use types. Contrary to groundwater, the mean phosphorous levels in the soil show a clear relationship with land usetypes in the plough-layer as well as in the subsoil samples. The same goes for nitrogen and potassium concentrations (figure 2).

4. DISCUSSION

The results show a strong relationship between NO₃⁻ and K-concentrations in groundwater and mean slurry application levels on land use systems on sandy soils. The same holds for soil nitrogen, potassium and phosphorous. This may be concluded despite high standard deviations of concentration values (Table 1). This is caused by unknown differences in

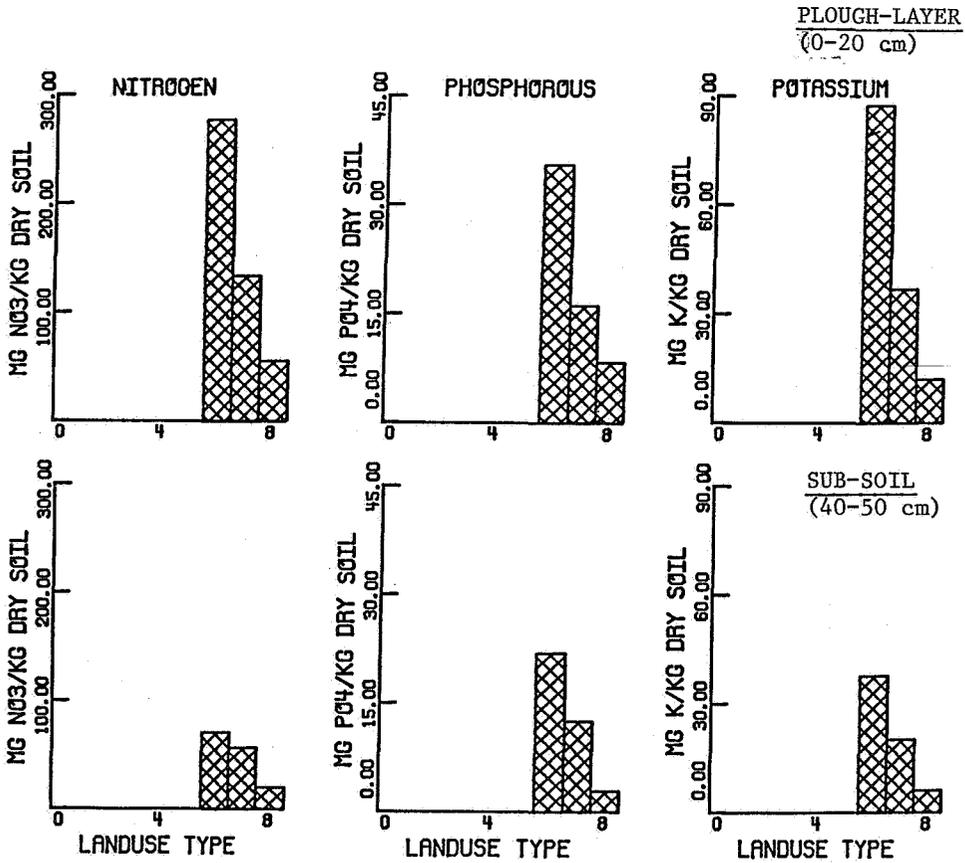


Figure 2. Mean contents of nitrogen, phosphorous and potassium in the plough-layer and sub-soil of sandy soils

the amount of slurry applied to each field, and short-distance variability in soil characteristics on each sample site which may affect the leaching process of manure elements.

Another phenomenon which affects the variability of groundwater concentration occurs mainly during summertime, as a result of higher evapotranspiration levels in forests compared to surrounding agricultural land use systems. As a result of this a local groundwater stream directed towards the forested area develops, and in this way nutrients are transported to the edges of these natural areas. The high phosphate concentrations in groundwater under natural areas on peat-soils (Figure 1, Table 1) are probably an example of this phenomenon. Those areas are small forests. They may therefore act as "nutrient-sinks" (De Wit and

Bleuten, 1986). The absence of a relationship between slurry application rates and the phosphate concentration in groundwater is caused by the adsorption of phosphate by mainly ferric and alluminous (hydr)oxides in the unsaturated zone. Only in a few cases high phosphate concentrations in groundwater of sandy soils point at phosphate leaching, indicating that the adsorption capacity has been totally used. The high nitrate content of groundwater under arable land (silage maize) on clay soils contradict general understanding about denitrification. Probably denitrification conditions are small compared to the high nitrogen input on these fields.

The proved relationship in sandy-soil areas between mean measured ground water quality and mean level of slurry application can be used to verify the quantitative model "MANRUU", which computes watershed groundwater quality from cattle densities per municipality and animal-specific manure production and composition (Vissers et al., 1985). Manure element production per ha. is calculated for the sandy soil part of the study area. From an environmental hygienic point of view it is possible to establish a maximum dose of slurry per ha. (EH-standard). Application up to this level will cause only minimal damage to soil and groundwater quality (STOM, 1983; Vissers et al., 1985). Total manure production minus the EH-standard gives the amount of excess production which causes soil and groundwater to be contaminated with manure elements.

Output of the model are computed mean nitrate and phosphate concentrations in the groundwater toplayer of watershed areas of shallow groundwater.

Comparison of these calculated values with measured values in the same watershed areas shows no significant correlation with respect to NO_3 . This can be explained by the behaviour of nitrogen in soil and groundwater systems, which varies widely even on a local scale as has been pointed out before. Apparently the mean characteristics of the sample sites in the watershed areas do not correspond with the mean characteristics with respect to nitrogen behaviour that were built in the model. For example, it is possible that the number of sample sites in infiltration and seepage zones (important with respect denitrification possibilities) does not correspond with the actual ratio of infiltration and seepage areas in the watershed (stratification in the selection-

procedure was on general soil type). This will lead to a mean measured concentration that deviates from the calculated value.

Compared to NO_3 , K is a better ion to compare measured values with model results, since potassium in sandy soils and groundwater is not subject to conversion processes.

Linear regression analysis between mean measured K-concentrations in the groundwater toplayer of watershed areas and the calculated mean model values leads to a correlation coefficient of .490 when all watershed areas (n=18) are taken into account. When only those watershed areas with at least 6 measured points of potassium concentrations are used, the correlation coefficient of the relationship is .998 (n=5). Both correlations are significant (95% confidence level).

5. CONCLUSIONS

- Groundwater toplayer load of nitrate and potassium is firstly dependent on soil type and
- Secondly, within each soil type on land use-type/manure application.
- Available nitrate, potassium and phosphate in (sandy) soil is up to depths of 50 cm significant correlated to land use type/manure application.
- In research on the spatial aspects of nitrate pollution of groundwater, sample site selection-procedure should include a stratification based on hydrological situation (infiltration/seepage zone).

6. ACKNOWLEDGEMENTS

The authors wish to thank the "Gedeputeerde Staten" of the province of Utrecht, the Inspectorate of Public Health for Environmental Hygiene, the "Waterleidingbedrijf Midden Nederland", and the municipal waterworks of Amersfoort and Amsterdam for their financial contribution to this study.

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**TOPIC 5: VULNERABILITY IN RELATION TO SUBSURFACE
BEHAVIOUR OF ORGANIC POLLUTANTS**

BEHAVIOUR OF ^{14}C -LABELLED ORGANIC INDUSTRIAL CHEMICALS
IN SOIL AND LEACHED WATER

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ABSTRACT

Laboratory and outdoor studies were carried out with ^{14}C -labelled chlorinated benzenes, chlorinated phenols, polychlorinated biphenyls and non-chlorinated organic pollutants. In a closed aerated laboratory soil system, mineralization rates to $^{14}\text{CO}_2$ as well as conversion rates to soluble metabolites and to soil-bound residues were established. In outdoor lysimeters, total recovery of ^{14}C and leaching into water at a 60 cm depth were determined after one growing period. For chlorinated compounds, degradation and conversion rates mostly were negatively correlated to the chlorine content; leaching of residues into water was negligible. Non-chlorinated compounds exhibited higher leaching rates of polar conversion products into water. Conversion products in soil were isolated and identified by gas chromatography/mass spectrometry.

INTRODUCTION

Numerous organic industrial chemicals come to the soil, either intentionally as agrochemicals or unintentionally by solid waste, by waste water or by deposition from the atmosphere. In order to assess the vulnerability of soils and groundwater to these contaminants, information on their degradation and conversion in soil and on mobility and leaching, both of parent compounds and of conversion products, is of paramount importance.

METHODS

Laboratory and outdoor experiments were carried out with ^{14}C -labelled, widespread industrial soil contaminants. For laboratory studies, a closed aerated soil system was used as described by Scheunert et al. (1986). Mineralization rates were determined by counting of radioactivity of $^{14}\text{CO}_2$ trapped in an alkaline scintillation liquid. Conversion rates to soluble metabolites and soil-bound residues were established after extraction of soil and separation of the extracts by chromatographic methods. Outdoor studies were carried out in lysimeters as reported by Scheunert et al. (1977, 1986). Radioactivity was determined in soil and in leached water collected at a depth of 60 cm for one growing period. Conversion products were isolated from soil extracts by various chromatographic methods and identified by gas chromatography/ mass spectrometry.

RESULTS AND DISCUSSION

The results obtained for benzene and some of its chlorinated derivatives are shown in Table 1. Mineralization to $^{14}\text{CO}_2$ as well as the amount of soluble metabolites and of bound residues found after one week decrease with increasing number of chlorine atoms in the molecule. Accordingly, under outdoor conditions after one growing season, total recovery of radioactivity is highest for hexachlorobenzene and lowest for benzene. Leaching into water at a depth of 60 cm was negligible. Conversion products of chlorinated benzenes are shown in Figure 1. Whereas tri- and pentachlorobenzene formed anisols, for hexachlorobenzene only traces of a conjugated thiophenol could be detected. From benzene, no conversion products could be identified due to very low recovery of residues.

Both 2,4,6-trichlorophenol and pentachlorophenol (Table 2) showed relatively high mineralization rates in soil, already after one week.

Table 1. Fate of ^{14}C -labelled chlorinated benzenes in soil (Scheunert and Korte, 1986)

Parameter studied	Benzene	1,2,4-Tri-chlorobenzene	Pentachloro-benzene	Hexachloro-benzene
Mineralization ($^{14}\text{CO}_2$, %*), 1 week, lab.	62.2	0.46	0.02	<0.01
Soluble metabolites (%*), 1 week, lab.	0.93	0.28	0.16	traces
Bound residues (%*), 1 week, lab.	8.99	3.52	1.10	0.72
Total recovery (%*), 1 season, outdoors	0.7	4.9	46.4	105.5
^{14}C in leached water (%*), 1 season, outdoors	n.d.	<0.01	n.d.	<0.01

* % of radioactivity initially applied

n.d. = not detected

For 2,4,6-trichlorophenol, only small amounts of soluble metabolites were found, but large amounts of soil-bound residues, probably formed by covalent binding to humic precursors and incorporation into humic compounds. From pentachlorophenol, larger amounts of soluble conversion products, mostly dechlorinated and/or methylated derivatives, were found in soil (Figure 2).

Polychlorinated biphenyls (Table 3) exhibited a negative correlation of mineralization, of soluble metabolites and of bound residues with the chlorine content under laboratory conditions. Chloroalkylene-9, an isopropylated derivative of 2,4'-dichlorobiphenyl, was even bet-

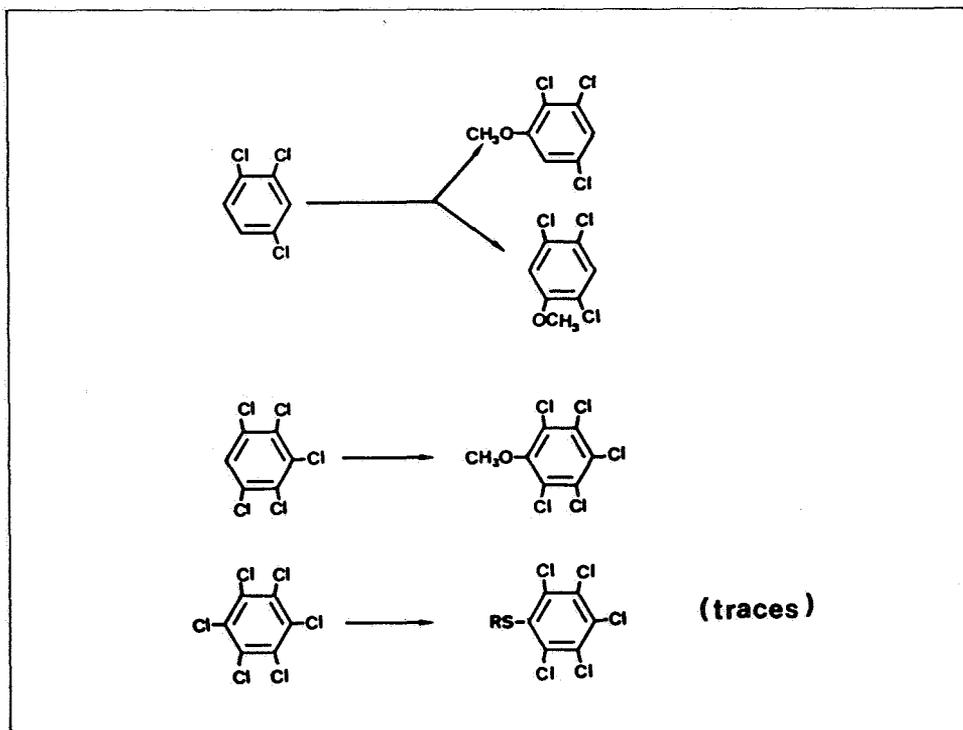


Figure 1. Conversion products of chlorinated benzenes in soil
(Scheunert and Korte, 1986)

ter degradable than 2,2'-dichlorobiphenyl. Under outdoor conditions, 2,5,4'-trichlorobiphenyl showed a relatively low persistence. Its soluble conversion products, as shown in Figure 3, comprised hydroxylated and methoxylated derivatives.

As examples of non-chlorinated organic pollutants, an anionic detergent, n-dodecylbenzenesulfonate, and a plasticizer, di(2-ethylhexyl)-phthalate, were studied (Table 4). Relatively high mineralization and conversion rates demonstrated a lower persistence as compared to most of the chlorinated compounds. The amount of radioactivity leached into water was significantly higher than in the case of chlorinated compounds. Leached radioactivity in both cases was not the parent compound but fully watersoluble conversion products whose chemical structure was not established. As soluble conversion products of the

Table 2: Fate of ^{14}C -labelled chlorinated phenols in soil
(Fragiadakis et al., 1979; Scheunert et al., 1986, 1987)

Parameter studied	2,4,6-Trichlorophenol	Pentachlorophenol
Mineralization ($^{14}\text{CO}_2$, %*), 1 week, lab.	22	10
Soluble metabolites (%*), 1 week, lab.	1	52
Bound residues (%*), 1 week, lab.	61	14
Total recovery (%*), 1 season, outdoors	64	58
^{14}C in leached water (%*), 1 season, outdoors	n.d.	0.1

*% of radioactivity initially applied

n.d. = not detected

phthalate in soil, products of ester hydrolysis were identified (Figure 4).

CONCLUSION

It may be concluded that, for a realistic evaluation of the vulnerability of soil and groundwater to organic pollutants, their elimination by mineralization to CO_2 is a main process to be considered. For the residues in soil and groundwater, not only the parent compounds but also their polar conversion products must be regarded.

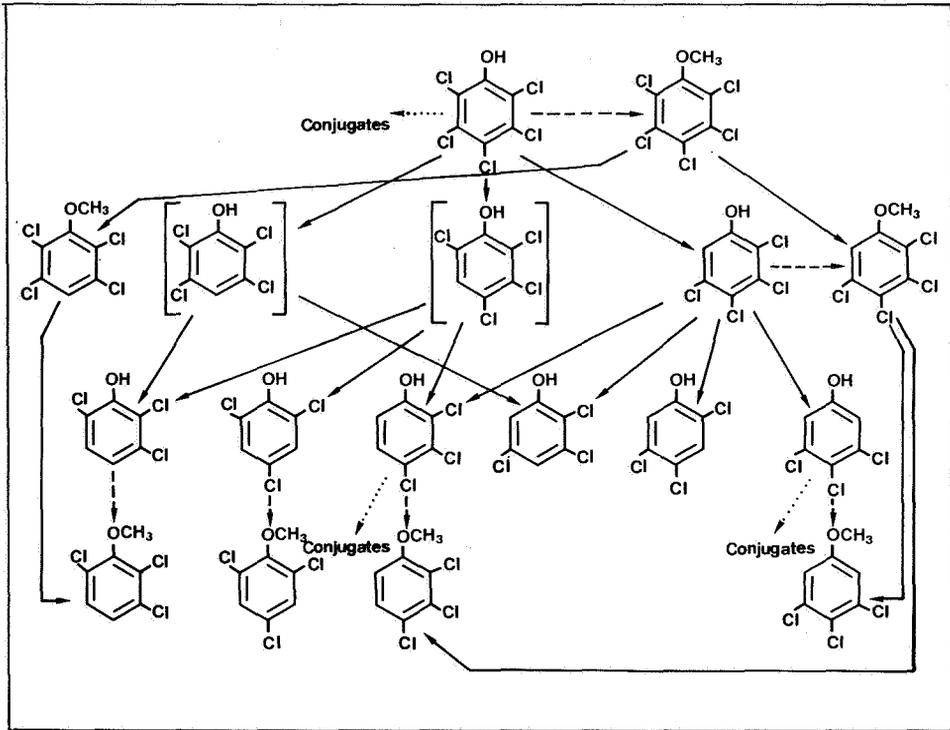


Figure 2. Conversion pathways of pentachlorophenol in soil
 Brackets = hypothetical intermediate;
 solid arrow = dechlorination; dashed arrow = methylation;
 dotted arrow = conjugation (Weiß et al., 1982)

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Table 3. Fate of ^{14}C -labelled polychlorinated biphenyls in soil (Moza et al., 1976; Moza et al., 1979 a and b; Kloskowski, 1981)

Parameter studied	Chloro-alkylene-9*	2,2'-Di-chloro-biphenyl	2,5,4'-Tri-chlorobi-phenyl	2,4,6,2',4'-Pentachloro-biphenyl
Mineralization ($^{14}\text{CO}_2$, %**), 1 week, lab.	3.4	2.5	0.7	0.1
Soluble metabolites (%**), 1 week, lab.	10.8	8.5	4.8	5.5
Bound residues (%**), 1 week, lab.	7.4	4.1	1.9	< 0.1
Total recovery (%**), 1 season, outdoors	17.4	44.4	29.3	55.9
^{14}C in leached water (%**), 1 season, outdoors	n.d.	n.d.	n.d.	n.d.

* isopropylated 2,4'-dichlorobiphenyl

** % of radioactivity initially applied

n.d. = not detected

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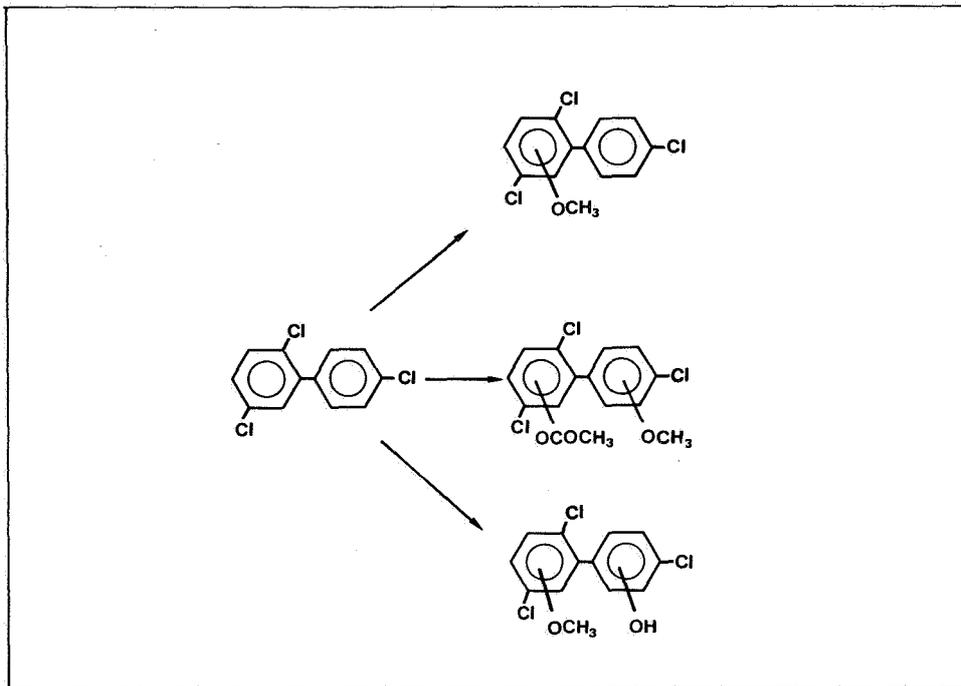


Figure 3. Derivatized (methylated) conversion products of 2,5,4'-trichlorobiphenyl in soil (Moza et al., 1979 a)

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Table 4. Fate of ^{14}C -labelled non-chlorinated organic pollutants in soil (Scheunert et al., 1983; Schmitzer et al., 1987)

Parameter studied	n-Dodecylbenzene-sulfonate	Di(2-ethylhexyl) phthalate
Mineralization ($^{14}\text{CO}_2$, %*), 1 week, lab.	11.1	8.2
Soluble metabolites (%*), 1 week, lab.	36.9	9.0
Bound residues (%*), 1 week, lab.	27.4	1.3
Total recovery (%*), 1 season, outdoors	10.7	6.9
^{14}C in leached water (%*), 1 season, outdoors	2.7	0.5

* % of radioactivity initially applied

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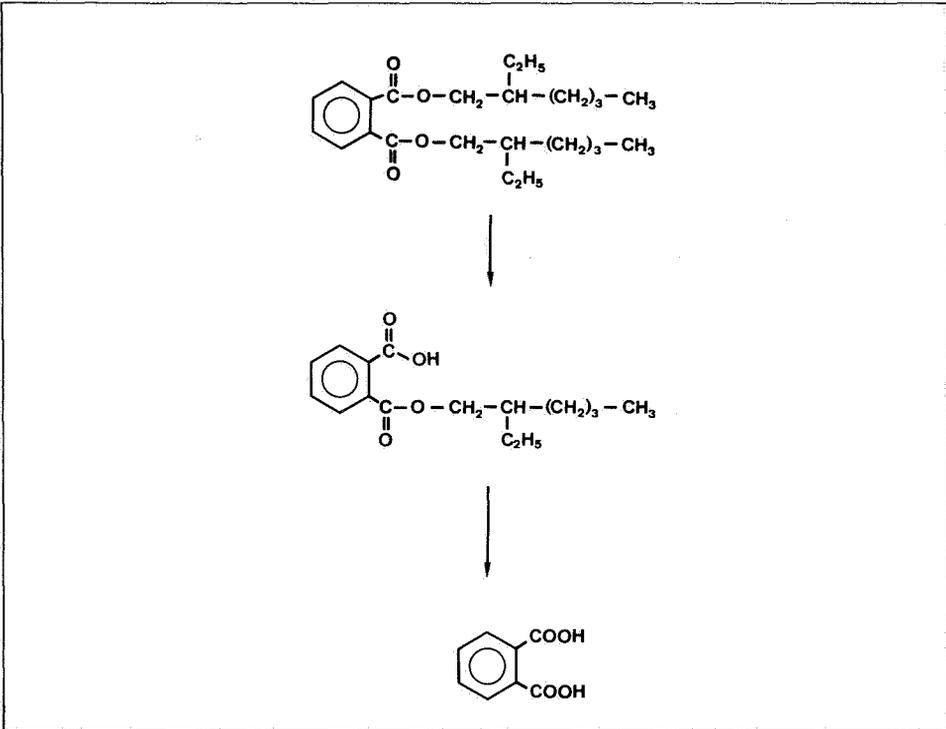


Figure 4. Conversion products of di(2-ethylhexyl)phthalate in soil
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VULNERABILITY OF GROUNDWATER IN RELATION TO SUBSURFACE
BEHAVIOUR OF ORGANIC POLLUTANTS

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ABSTRACT

The high number and different properties of potential organic groundwater contaminants on the one side and the great variability of conditions in the subsurface on the other side lead to a very complex constellation of possible processes and interactions in the subsurface.

These influence mobility and persistence of chemical substances and, in the end, they determine the vulnerability of a groundwater with respect to a substance in question.

Assessment of groundwater vulnerability demands that rules and regularities are found. In this paper some rules for processes of transport and metabolism are discussed with respect to examples and exceptions. So far they only allow rough estimates. It is concluded that more field investigations of contamination cases with varying contaminants under different conditions are necessary which must be subjected to combined evaluations.

1. INTRODUCTION

By end of 1985 more than 7 000 000 chemical substances had been registered in the Chemical Abstracts System. It is estimated that about 1% of these, i.e. 70 000, are produced and used somewhere in the world. Apart from these chemicals produced deliberately there is a large number of compounds generated as e.g. side products or in combustion processes. This may be exemplified with the chlorinated dibenzodioxines and -fura-

nes of which there are 210. This whole group only was identified in the environment because of the toxicity of some of its members. It may be estimated that there are some 100 000 chemical substances of potential concern for the environment. The vast majority of these are organic chemicals.

In a compilation of groundwater studies in the U.S.A. examining impacts of hazardous waste disposal sites Plumb (1985) reports that 782 organic chemicals were identified in groundwater. So it is probably justified to say that roughly 1 000 organic chemical substances so far have been found to be groundwater contaminants.

However, since only those substances are detected for which a sufficiently sensitive technique of isolation and identification exists the scope of known groundwater pollutants may be biased by analytical premises. Zoeteman et al. (1981) were the first to evaluate systematically groundwater contamination incidents and to link the groundwater contamination potential of a compound with its physico-chemical properties. The result - very simplified - was that compounds of a certain polarity, enough to be sufficiently water soluble, but too little to be easily available for biodegradation, were those which typically caused groundwater problems. Although there are very good reasons to follow this line of argument it must be pointed out that substances of higher polarity simply cannot be analysed at the low ppb level in water samples with conventional techniques, involving a concentration step by transfer into an organic phase. They stay in the aqueous phase and escape detection. The immunochemical analysis based on a completely different principle mechanism and especially applicable for polar substances may in the near future change views to a considerable extent.

In this contribution some rules and regularities with respect to processes of transport and metabolism are discussed. The basic premise is that generalizing approaches like those introduced by Zoeteman et al. (1981) and Schwarzenbach and Westall (1981) are needed. In such investigations rules were developed which are useful for estimating assessments and which are of growing importance as transport models are being developed. On the other hand so far our understanding of processes involving organic contaminants in the subsurface is not yet sufficient to be a basis for exact predictions.

Here only a few aspects of subsurface behaviour can be touched, more detailed information can be found in Mattheß et al. (1985).

2. ORGANIC CHEMICALS AND VULNERABILITY OF GROUNDWATER

Normally the vulnerability or protectiveness of a groundwater is defined by its openness to recharge, that is the permeability of covering strata for water. In numerous hydrogeological publications the movement of water through top soil, vadose zone and aquifer has been investigated. To discuss vulnerability specifically with respect to subsurface behaviour of organic chemicals is taken to mean considering those effects causing the movement of these substances to be different from the movement of water, that is changes of concentrations apart from those originating from dispersion and dilution. These are

- retardation,
- gas phase transport,
- chemical and microbial degradation.

This approach only is valid for pollutants dissolved in water. Massive contaminations where pollutants move in phases immiscible with water are not considered here, they have been discussed by Darimont and Lühr (1985) and Schwille (1984).

The effects named are - to a different extent - interactive, i.e. whether and how effectively they act is a function of the specific properties of the compound in question in combination with the respective conditions in the subsurface environment.

3. MOBILITY OF ORGANIC CHEMICALS IN SOILS

As a rule mobility of a contaminant in a soil with a given hydrological situation is a function of its concentration in the liquid phase, i.e. soil- and groundwater. This concentration is determined by

- solubility and vapour pressure of the compound in the respective aqueous solution and
- partitioning between solid and liquid phase (ad-/desorption).

3.1 Water solubility

Solubilities of organic compounds in water range from completely miscible (methanol) to very low (ng/l: highly chlorinated PCDDs and PCBs; higher PAHs). Solubility data for many compounds are readily available, and allow an estimation of possible maximum concentrations.

Tabulated water solubilities of organic compounds normally are based on experiments with pure water. These may be applicable for estimates concerning fairly clean ground water. In contaminated soil and groundwater solubility may be lowered in the case of high salinity or it may be heightened by "solubilizers". These may be either natural humic substances or anthropogenic co-contaminants.

Webster et al. (1986) report that the solubility of 1,2,3,7-TCDD in aqueous humic and fulvic acid solutions is increased in such a way that the amount additionally solubilized by the humic substances corresponds to a partition equilibrium where the solubilizing capacity of dissolved humic substances is equal to the sorption capacity of undissolved humic substances in soils, so that the K_{OC} can be used to calculate this effect.

Much more important could be effects in waters which are heavily contaminated by lipophilic organic compounds. Table 1 gives an example where chlorobenzenes and chlorophenols probably act as solubilizers for otherwise not groundwater endangering TCDDs and TCDFs.

Table 1. Chlorinated organic contaminants in a groundwater well (screens in 9-19m and 22-23m below surface) (sum of group named, CDDs = chlorinated dibenzodioxines, CDFs = chlorinated dibenzofuranes)

hexa CDDs	1.0 ng/l	hexa CDFs	1.5 ng/l
hepta CDDs	1.5 ng/l	hepta CDFs	0.9 ng/l
octa CDD	7.5 ng/l	octa CDF	1.5 ng/l
total CDDs and CDFs	13.9 ng/l		
chlorobenzenes	9 500 µg/l		
chlorophenols	5 200 µg/l		

Although effects of colloids and particulate matter cannot be excluded it is believed that in this groundwater actually dissolved dioxines and furanes occurred. Their presence is quite plausible: 13.9 ng CDDs and

CDFs in chlorinated solvents.

It is suggested to consider the solubility of a compound in a contaminated aqueous phase to be the sum of the "solubilities" of this compound in the various constituents of this aqueous phase, i.e. water, humic substances, and organic solvents etc.

3.2 Adsorption to the solid phase

Sorption processes for most compounds are the most important factor determining the velocity of transport in the subsurface environment. In numerous investigations experimental data on adsorption of different compounds to soils and sediments were collected and generalized in such a way that in many cases predictions can be made with respect to sorptive behaviour of substances of which only few physico-chemical parameters are known (Kenaga and Goring 1978, Schwarzenbach and Westall 1981, Lyman 1982, Friesel et al. 1985). Basically this involves an estimation of the Freundlich constant K of a given soil and compound by calculating the K_{OC} (constant of adsorption to soil organic matter of a compound) from the compound's water solubility (S) or the octanol/water partition coefficient (P_{OW}) and determining K of the soil from its percentage of organic carbon (oc):

$$\log K_{OC} = a \log P_{OW} + b \quad \log K_{OC} = c \log S + d \quad K = K_{OC} \cdot oc/100$$

The trustworthiness of estimated K_{OC} values may be very high if a compound is considered of which homologues or similars were investigated and where these results were used to determine a-d in the formulas given. This is demonstrated in Table 2.

In this case water solubility seems the superior base data in relation to P_{OW} for two reasons: data are easier to get and the correlation is better (higher r) for S than P_{OW} .

However, the more complex interactions of a compound with the aqueous phase and the soil organic matter become, the more advantages lie in experimental P_{OW} data. This can be shown for the herbicide atrazine (Table 3). Here the molecular structure causes a negative charge surplus at the periphery of the molecule, which reduces the water solubility without a corresponding increase of affinity to the soil organic phase.

Table 2. Experimental K_{OC} values of chlorinated hydrocarbons of which the relation $\log K_{OC} = 0.627 \log S + 4.026$ ($r = 0.97$) was calculated by which theoretical K_{OC} values were recalculated

compound	S(mg/l)	K_{OC} (l/kg)	
		exper.	recalc.
1,1,1-trichloroethane	1700	125	100
trichloroethene	1090	117	132
tetrachloroethene	160	275	441
1,2-dichlorobenzene	145	614	469
1,3-dichlorobenzene	123	554	520
1,4-dichlorobenzene	79	498	686
1,2,4-trichlorobenzene	30	1670	1260
1,3,5-trichlorobenzene	19	2090	1680
gamma-BHC (lindane)	7.6	2550	2980

Table 3. Experimental and calculated sorption data of atrazine

experimental data:	$S = 47$ mg/l (UBA 1982)
	$\log P_{OW} = 2.64$ (UBA 1982)
	$K_{OC} = 149$ (UBA 1982)
	$K_{OC} = 100-300$ (Friesel et al. 1984)
	K_{OC} calculated from P_{OW} : $K_{OC} = 184$
	K_{OC} calculated from S : $K_{OC} = 500-1000$

3.3 Transport and gaseous phase

Chemists have a thumb rule for diffusion velocity: diffusion in aqueous phase is 1 cm/a, in gaseous phase 1 m/d. Therefore diffusion processes in aqueous solutions in the subsurface only may become relevant at extremely low flow rates, e.g. if k_f is significantly below 10^{-9} .

For many volatile organic compounds in the unsaturated zone transport by gas diffusion is a major path of spreading. This process leads to fairly regular distribution patterns which are a condition for investigation strategies based on soil air sampling in cases of contaminations by chlorinated organic solvents (Nerger et al. 1987). To assess the possible extent of gaseous transport two questions have to be answered: How much of a compound is in the gaseous phase, and what will the diffusion

velocity of this fraction be?

Direct measurements of gas phase concentrations are not always easy. In these cases gas phase concentrations may be deduced from concentrations in the dissolved state: The partition between aqueous and gaseous phase $P_{a/g}$ is equal to the quotient of the water solubility of the compound (S) divided by its vapour pressure (P_V) both in mg/l:

$$P_{a/g} = \text{conc. aqueous} / \text{conc. gaseous} \approx S / P_V$$

Table 4 gives experimental evidence.

Table 4. Aqueous/gaseous partition coefficients from lysimeter experiment (lys), laboratory (lab), and calculation (cal) (Friesel et al. 1985)

compound	lys	$P_{a/g}$	lab
		cal	
trichloroethene	2.31	2.29	2.74
1,1,1-trichloroethane	1.63	1.79	0.71

If this calculation is applied to environmentally important substances like BHCs, PCB, or HCB it follows that even these compounds with very low volatility may to a considerable extent be present in the gas phase because they also have a very low water solubility. This explains results where e.g. PCBs were found in a previously uncontaminated soil cover over a hazardous waste disposal site.

Velocity of gas diffusion in soils was thoroughly investigated for the model gas CO_2 by Albertsen (1977). He found that in dry sandy materials the diffusion rate was roughly half of that in atmospheric gases. It decreased strongly with growing soil moisture and broke down at a point of 60% water saturation, apparently because at that state there was no continuous pore system left.

Field and lysimeter experiments with trichloroethylene and dichloropropene verified that these compounds reached a soil depth of 1 or 2 m much faster than percolating water would, that is after a few days.

This rapid dispersion in subsurface systems is one of the reasons why volatile substances have a comparatively high groundwater pollution potential. E.g., 31 of the EPA's 113 priority pollutants are volatiles and in the investigations on groundwater contaminations by hazardous waste

sites in the U.S.A. volatiles were the compounds found most frequently (Plumb 1985).

4. DEGRADATION AND METABOLISM

As opposed to heavy metals organic contaminants in the subsurface environment are object of chemical alterations which eventually lead to a breakdown into small molecules which also result from natural organic debris (e.g. CO₂, CH₄, H₂O, HCl). The complexity of these processes is demonstrated by Scheunert (1987).

When assessing a chemical compound with respect to soil and groundwater vulnerability the two main questions are: What is the half live of the compound in question in soils and groundwater and which are possible metabolites? The metabolites again may require a complete new evaluation procedure. For some compounds the third or fourth metabolite can be of a greater importance than the mother compound; this may be discussed for the following metabolism chain (Bouwer and Mc Carty 1984):

tetrachloroethene-trichloroethene-cis dichloroethene-vinyl chloride because of the carcinogenic potential of vinyl chloride.

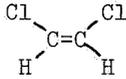
A systematic approach to degradation usually will involve differentiation according to the mechanisms causing chemical change of an organic contaminant (Table 5).

Table 5. Major mechanism types causing chemical changes of organic contaminants in the subsurface

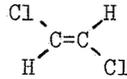
microbial metabolism	aerobic
	anaerobic
chemical reactions	hydrolysis
	oxidation/reduction

However, in many cases it may be doubted whether a purely chemical process occurs or e.g. a reduction of a compound is caused/catalyzed by microbial activity.

Clear evidence can be found in very few cases: For example, cis-dichloroethene is not infrequently detected in groundwater in absence of the trans-isomer. Since technical dichloroethene contains 60-70% of the trans-



cis-dichloroethene



trans-dichloroethene

isomer and since this dichloroethene is only used at few locations for rather special technical purposes the cis-dichloroethene in groundwater must be attributed to an origin different from dichloroethene spills. The most probable explanation is a microbial process in the metabolism chain mentioned above (a chemical dechlorination would produce a mixture of isomers).

It is suggested that most "chemical" degradation processes in the subsurface at least involve microbial action. Exceptions from this rule probably only occur where compounds are highly unstable with respect to hydrolysis and/or redox reactions. If that is so, evidently microbial activity is a major parameter to be considered in vulnerability studies. As a general rule the microbial activity in a soil decreases from surface to groundwater by about two orders of magnitude with the strongest gradient in the top meter (except for the winter season). Consequently differences in degradation rates may reach several orders of magnitude: E.g. for atrazine in agricultural soils normally half lives of 30-90 d are reported (Friesel et al 1986), while in groundwater 2500 d are assumed (Mattheß et al. 1985).

Likewise considerable seasonal influences may occur. In field experiments with 2,4,5-T Litz (1984) found a reduction of the degradation rate by a factor of almost ten from summer to winter and a consequent increase in leaching.

Of course microbial activity may also be influenced by a contaminant itself or co-contaminants. In a severe soil and groundwater contamination by cresols and other phenols used as disinfectants (up to 5 g/l in groundwater) the contamination did not seem to decrease within years although these compounds normally are readily degraded (half life of cresol in groundwater 4 d, Zoeteman et al. 1981).

Another rule with respect to microbial activity is that normally aerobic environments are much much more active than anaerobic ones. Therefore in general aerobic degradations are more effective. Notable exception to this rule is that some chlorinated compounds (DDT, ethenes) are stable in oxic environments but metabolised under anaerobic conditions.

5. CONCLUSIONS

In addition to classical concepts of groundwater protection based on the hydrological openness of and groundwater transport rates within an aquifer, considerations of possible processes involving reactions - physical, chemical, and/or biological - of organic contaminants in the subsoil environment are necessary. Although these reactions may be very complex and highly specific to a certain type of compound and /or of subsurface environment it is possible to use data accessible for many locations and substances for a first rough assessment of processes possibly leading to groundwater contaminations (Table 6).

In the practice of assessing groundwater vulnerability, be it with respect to a possible future use of a chemical compound or to a given soil contamination, one has to choose between very large safety margins or possible underestimates of groundwater vulnerability, because so far there is no safe data base.

At the minimum there is a demand to evaluate existing groundwater contaminations by various sources, e.g. non point sources like pesticide application and point sources like hazardous waste disposal sites or contaminated industrial sites, under various meteorological, pedological, and hydrogeological conditions to elucidate processes and to quantify factors which influence groundwater vulnerability. For this it is especially necessary to combine data from as many investigations as possible and to develop and extend those by Zoeteman et al. (1981) and Plumb(1985).

Table 6. Basic data relevant for assessment of mobility and persistence of a potential groundwater contaminant in a subsurface environment with respect to its groundwater vulnerability

data on soil and underground	data on contaminant
content of organic carbon	water solubility
water saturation	octanol/water partition
oxygen supply	adsorption (K_{oc})
nutrient status	vapour pressure
toxic substances	half life of hydrolysis
DOC	microbial degradability
pH	metabolites

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GROUNDWATER POLLUTION BY A CHEMICAL WASTE DEPOSIT
ABOVE ALLUVIAL GRAVELS, RHONE VALLEY, SWITZERLAND

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ABSTRACT

The spreading of a contamination plume in the groundwater is controlled by the particular hydrogeological conditions : high permeabilities and high hydraulic gradients. The spatial distribution of the pollutants is described. A remedial action of the pollution by lowering the groundwater under the deposit has been studied by a tridimensional hydraulic model; it is now in the planning stage.

1. THE AQUIFER, THE HYDRODYNAMIC CONDITIONS AND THE CONTAMINATION

In the Rhone Valley between Visp and Brig, the Quaternary alluvium is contaminated beneath and downstream of a waste deposit (24 hectares). The aquifer in this area is formed by an upper sandy silt (0-10 m) and by at least 25 m of sandy gravels. According to geoelectrical investigations, the total thickness of the gravels may reach up to 100 m. Measured permeabilities in the gravels range from $1-50 \cdot 10^{-4}$ m/sec. The average hydraulic gradient under the deposit varies with the seasonal groundwater fluctuations. The groundwater levels and the hydraulic gradients under the deposit are high ($i = 3.7$ o/oo) in July and August during snowmelting in the upper catchment of the Rhone. At that time, the groundwater is in contact with the lower 0-60 cm of the waste deposit. In winter, the gradients are low ($i = 2.5$ o/oo) and the groundwater levels are not in contact with the deposit.

The lower 10 m of the deposit consist of calcium-hydroxyde, which was elutriated between 1923 and 1962 in evaporation ponds. It was expected

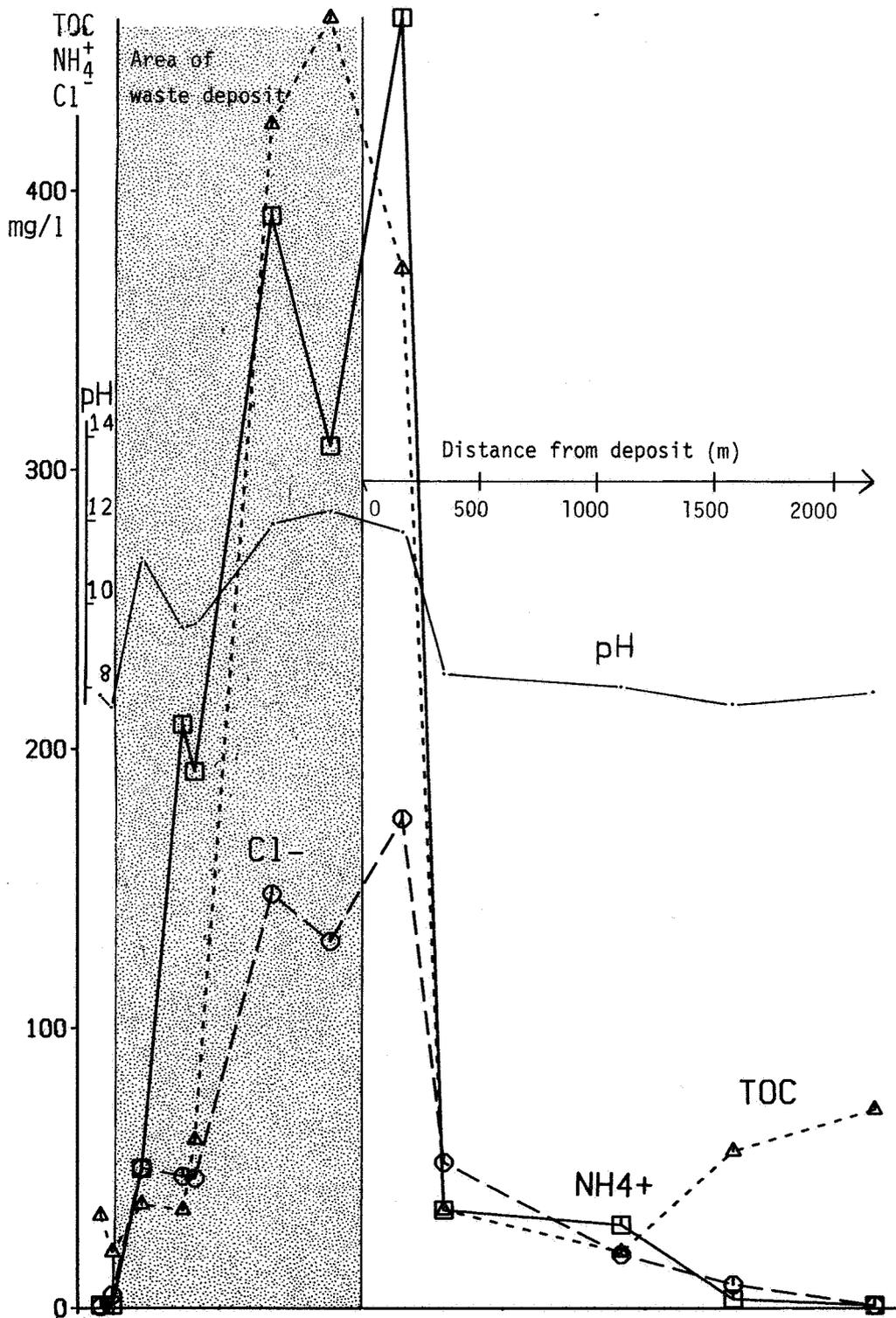


Figure 1. Profiles (pH, Cl^- , NH_4^+ , TOC) in flow direction, August 1986

that they would form a barrier against the more hazardous materials deposited above : acid sulphatic solutions, which were precipitated as stratified gypsum deposits, contaminated by organic and anorganic residues. These gypsum deposits appear to be causing the groundwater pollution. The total thickness of the deposit may reach 17 m.

Within the groundwater contamination plume the electrical conductivity, the pH and the TOC have elevated values and the water is anoxic. Figures 1 and 2 show the distribution of some typical parameters in flow direction. The front of the plume cannot be clearly defined, but an important decrease of concentrations occurs between 1100 and 1500 m. Recent observations in new drillings carried out for a motorway project gave the following results for the November 1986 simultaneous campaign (Table 1) :

Table 1. *Distribution of groundwater concentrations in relation to the distance from the deposit (m)*

Parameter	upstr.	175	870	1100	1500	2170	2475	2900
NH ₄ ⁺ mg/l	0.9	370	48	39	1.3	1.9	2.4	<0.5
Cl ⁻ mg/l	<0.5	129	43	19	11	3	<0.5	<0.5
SO ₄ ²⁻ mg/l	165	255	173	207	33	36	53	39
TOC mg/l	<20	235	25	<20	20	<20	20	<20
Phenol µg/l	<10	5850	220	<10	<10	90	<10	<10
Aniline µg/l	<10	26900	3380	140	20	50	20	<10

Other contaminants observed are : nitroaniline, PO₄³⁻, Fe, Hg, Co. The heavy metals do not migrate far from the deposit, as they have probably precipitated in the highly alkaline groundwater. Manganese appears only 300 m downstream from the deposit when the iron concentration decreases (Figure 2). More observation is required to define the geometry and behaviour of the plume in relation to the hydrodynamic conditions.

2. TRIDIMENSIONAL MODELLING OF THE REMEDIAL ACTION

We have applied the finite element model, developed at Neuchâtel by Kiraly (1985), to study different remedial actions of the pollution.

The solution chosen consists of pumping the groundwater under and upstream of the deposit. As the pumped water needs to be treated, it was necessary to evaluate the pumping rates required to prevent the contaminated water leaving the area of the deposit. The objective of the pumping is to create a groundwater divide along the border of the deposit. The hydrogeological data used as input- and calibration parameters are discussed in Geister-Frantz (1987) and the results of the simulations are presented in both horizontal and vertical hydraulic potential sections. The simulations showed that a double-circuit system will be necessary :

- 100 m upstream from the deposit six wells will intercept 80-150 m³/hour of uncontaminated water and release it into the Rhone;
- in the longitudinal axis of the deposit 12 wells will pump about 30 m³/hour contaminated water; this water will be neutralized and treated biologically before being released into the river.

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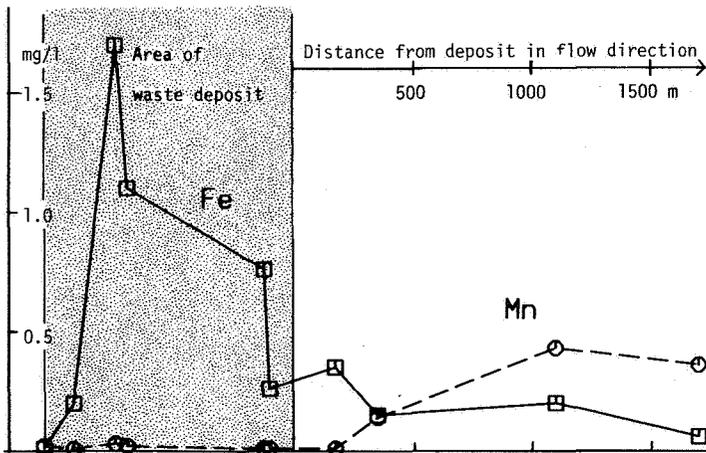


Figure 2. Profiles in flow direction (Fe, Mn), October 1985

AN INVESTIGATION INTO THE POTENTIAL EXTENT OF GROUND
CONTAMINATION BY HYDROCARBONS WITHIN A REFINERY

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1. INTRODUCTION

This paper presents the findings of Phase I of an investigation comprising a comprehensive "desk study" of available information and analysis of environmental samples to define the scale of a ground contamination problem within a refinery. Phase I additionally provided guidance to Phase II of the investigation, comprising a "field study" to establish/confirm likely sources of contamination, pathways for transport in the ground and the potential for oil reservoirs.

The refinery has been established for over twenty years, during which time development has proceeded gradually, such that the site now supports a mix of old (approximately twenty years), new (less than six years) and refurbished tanks, pipelines and associated plant.

It is inevitable that steel structures such as storage tanks, will experience corrosion, and this will be particularly enhanced where such structures are in intimate contact with ground and groundwaters, electrical equipment, and/or have water bottoms. Perforation will ultimately result from chronic or acute corrosion of tanks with consequent leakage of product. Such leakage can be relatively minor and contribute to "unexplained losses", but even a pinhole can over time lead to loss of a significant quantity to the general environment; should this be stored, rather than dissipated, then a "reservoir" of the lost product can be formed within the ground.

Relatively minor leakage rates can at any time become more serious because of the collective effect of multiple perforations, or because of a larger scale failure resultant upon multiple perforations. Similarly, should a reservoir of hydrocarbons develop within ground

strata, then a sudden change in ground conditions - such as may be caused by slippage or saturation - may lead to a sudden loss of stored materials over a short period of time.

2. HISTORY

- 1 Leakage is known to have occurred from various tanks on site over a period of at least 18 months or so but at the time of investigation only one tank was known to be leaking.
- 2 Significant contamination was detected in a paddock downslope of an eastern tank storage area with 26 tanks, but laboratory analysis was not able to isolate the source.
- 3 The contamination is downslope of multiple potential sources and occurs over a complicated but ill defined geology.
- 4 The contamination has effectively removed the refinery's buffer zone adjacent to the external site boundary, increasing the possibility of contaminating environmentally sensitive land/vegetation off site.

In general, the following points summarise the concerns which the problem raises:

- 1 they may be undetected leakage with resultant loss of product into the ground;
- 2 there may be a large reservoir of hydrocarbons in the ground as a result of past leakage;
- 3 the existing flow of hydrocarbons over groundwater is of concern because of both its quantity and volatility;
- 4 should leakage rates increase catastrophically, or ground conditions allow uncontrolled loss from a reservoir, then there are numerous undesirable consequences and dangers;
- 5 overall, the existing rate of release is only roughly estimated, and hence the magnitude of the problem presented is largely unknown;
- 6 the fractions lost are low flash products.

3. OBJECTIVES

The identification and quantification of the problem, with the following specific tasks:

- 1 to undertake a desk study of available geological information;
- 2 to review the history of tank developments, pipelines and leakage;
- 3 to examine existing laboratory data, and to undertake further analysis as necessary.

4. METHOD OF APPRAISAL

Phase 1(a)

This area of work involved a desk study amalgamating all available information from the following areas:

Geological study - the geological structure of the area was established using existing data (maps, surveys). The ground rock itself was assessed for its porosity/permeability and also for its theoretical liquid holding capacity; an estimate of the potential reservoir within the ground has been made from this data.

History - a review of the history of the tank developments has been undertaken and leak testing undertaken on tanks and pipelines has been examined to establish the precision of such determinations. This review is not included within this paper.

Environmental Impact Assessment - to establish the effects of oil contamination on the site, as well as the impact of leakage off site. This review is not included within this paper.

Phase 1(b)

This area of work involved laboratory and desk study amalgamating all available analytical data, and undertaking analysis as necessary:

Existing data - acquired and examined

Analysis - as necessary, analysis of groundwater and soil samples has been undertaken. This has established oil types at various locations and in addition the weathering characteristics and hence age of the oils present. The presence of TML/TEL has been established. Analytical data has provided theoretical origin(s) of contamination.

5. ANALYSIS OF GEOLOGICAL DATA

Anecdotal evidence that the superficial ground is very porous would appear to be commonplace; for example, it is cited that during water drawing from the tanks, within the bunds, the water is very quickly lost to the ground, and does not stand significantly. Similarly, during a preliminary tracing experiment, flushing water to carry a fluorescent dye also permeated into the ground rapidly. However, information regarding the specific geology of the refinery site has been gained from 3 main sources:

- 1 geological maps;
- 2 previous geological site investigation work;
- 3 site visit.

Much valuable information about the detailed site geology has been gained from the numerous site investigations carried out throughout the development of the refinery.

6. GENERAL GEOLOGY AND TOPOGRAPHY

The location is astride a syncline, the centre line which runs approximately east-west. The core of the syncline comprises carboniferous limestone shales while the limbs are of Devonian or old red sandstone. The sandstones compose east-west ridges across the area whilst the limestone shales correspond in position to two valleys, now almost completely occupied by the refinery. Within the valley areas silt and clay soils to various depths overlie the bedrock - these are

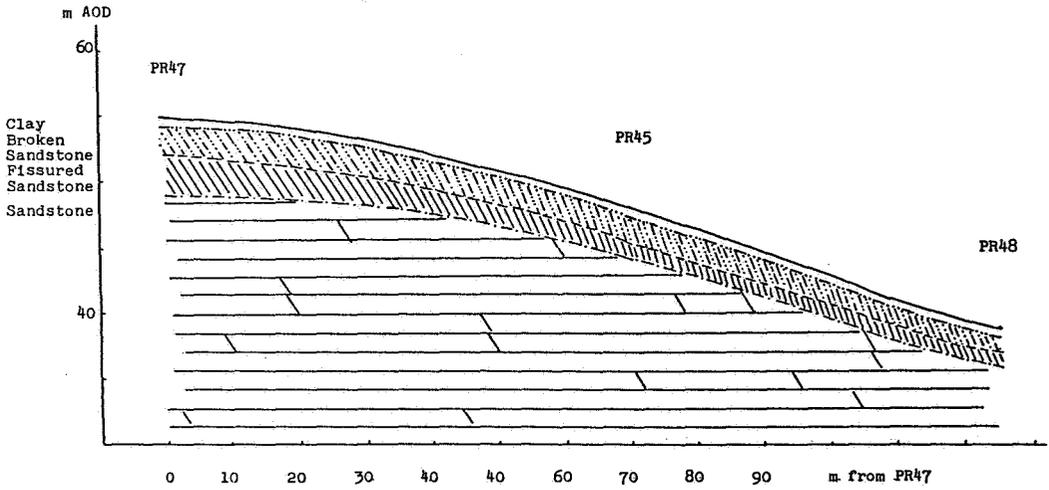


Figure 1. Section AA

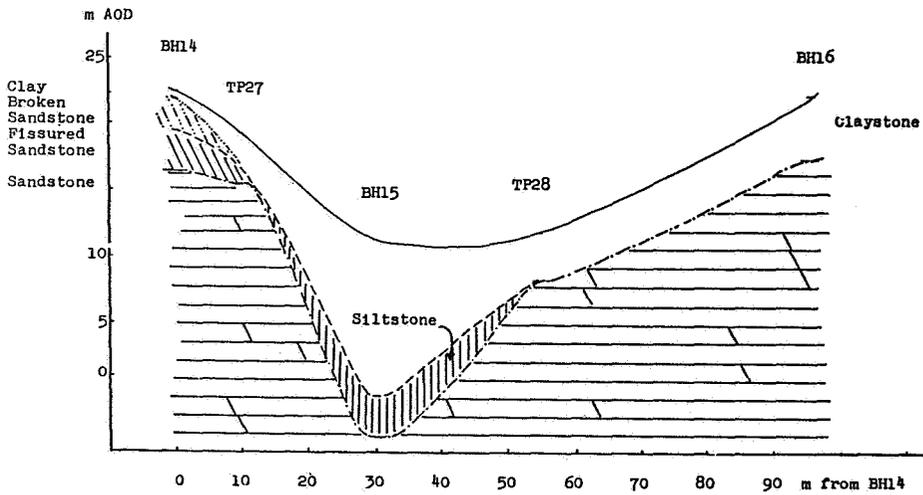


Figure 2. Section BB

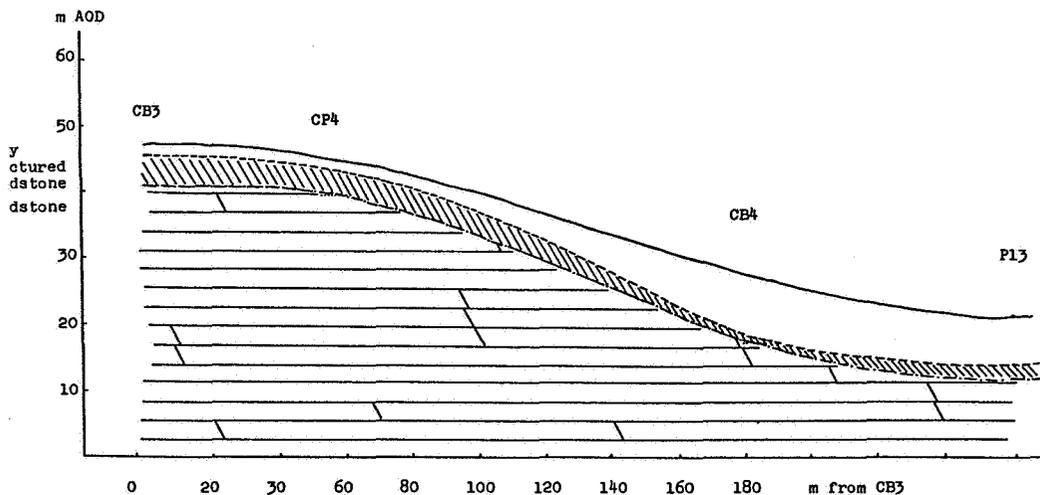


Figure 3. Section CC

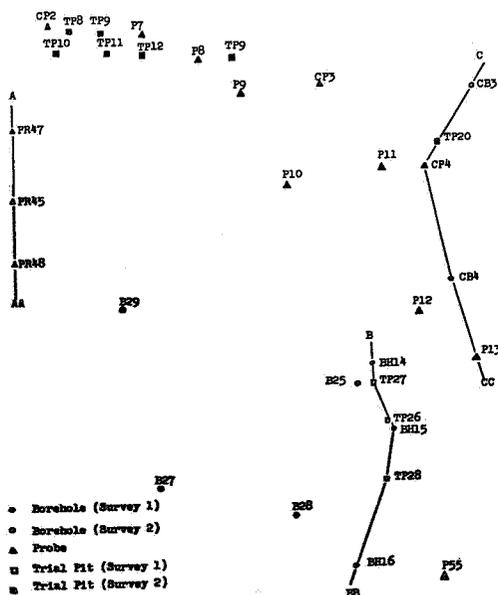


Figure 4. Schematic locations of various excavations across syncline

considered to be a product of the weathering of the carboniferous shaley mudstone.

The topography of the site is important since this obviously influences drainage.

7. POSITION OF SEEPAGE POINTS - GEOLOGY

Seepage is generally occurring in one area of the site. This occupies a south facing slope of an eastern valley basin, to the south and east of the eastern tank storage area.

From the information obtained from investigations it is apparent that storage tanks are built on sandstones, but to the south the sandstones give way to shales and mudstones which are overlain by varying amounts of clays and silts.

The sandstones on which the tanks are constructed are highly fractured especially within the upper weathered portion.

Leakage points, however, occur some considerable distance from the tank positions at the edges of an area of marsh vegetation, where there appears to be a considerable amount of clay overburden.

The sections drawn up from the borehole data show the approximate sequence of structures in a north-south direction, and are presented in Figure 3, constructed from the data derived from locations illustrated in Figure 4.

8. PERMEABILITY AND LIQUID HOLDING CAPACITY OF STRATA

There are 3 major ground type of importance:

- 1 sandstones;
- 2 clays;
- 3 shales/mudstone.

The sandstones visible on site are generally highly fractured especially at the surface. Fracture spacing is typically between 8 and 20 cm within the top 5 m of sandstone. At greater depth fracture spacing may increase, while close to the surface the rock is highly weathered and fragmented. Prior to tank construction a clay horizon overlay the fractured rock, however, this was removed, together with the uppermost portion of highly fractured rock during construction.

The development site investigation provided limited information on the permeability of the sandstone. Permeability tests were performed on the broken rock, re-compacted with standard and heavy compaction. This gave a permeability of 100×10^{-6} cms/sec. This compares to the clay overburden with an average permeability of 10×10^{-8} cm/sec.

The clays present on site are thus relatively impermeable and hence not likely to be important in retaining or transporting liquids. The shales and mudstone on site may be highly permeable and if contaminated may play a significant role in oil transport. The most likely strata capable of holding or transporting liquid is the fractured old red sandstone.

9. POTENTIAL HYDROCARBON RESERVOIRS

The known area of contamination between the seepage points and the only isolated source is approximately 15,000 square metres in size.

The potential depth of the reservoir in drifts, heavily fissured sandstones and superficial materials varies between zero and 5 m, averaging around 2.5 m, but it is unlikely that the top 1 m plays a significant role in the reservoir; hence the effective reservoir depth is 1.5 m.

The potential geological volume therefore, of the reservoir is 22,500 cubic metres.

Assuming a hydrocarbon content of 1% within this volume gives a total hydrocarbon reservoir of 225 cubic metres, or approximately 50,000 gallons.

The current rate of hydrocarbon accumulation within separators installed in the ground is approximately 250 gallons per month, only 0.5% of the potential reservoir. This does appear to be only a small proportion of the potential reservoir, hence it is likely that the separators are not highly efficient in trapping and removing the hydrocarbons.

Similarly, these calculations assume that there is no storage within the less fissured sandstones; it is unlikely that there will be no storage at all, and hence the data could underestimate the potential reservoir.

An alternative calculation could be based on the permeability of the sandstone, as reported in earlier test data. Such a calculation must be treated with extreme caution because of the method of rock testing used, and the use of the data for hydrocarbons rather than water. However, the sandstone has a reported permeability of 100×10^{-6} cm/sec., and if it is assumed that the leakage point is 300 linear metres from the current seepages, this gives an approximate travel time of 2.6 m/month, or approximately 115 months (9 years) to cover the distance from source to seepage. Given a current seepage rate (assuming 100% recovery) of 250 gallons/month, this gives a reservoir size of approximately 29,000 gallons, only assuming direct linear transport - that is, single dimension.

Given that there will be both 2nd and 3rd dimensions to the oil reservoir, this estimate is reasonably compatible with that calculated from rock volumes and storage capacity.

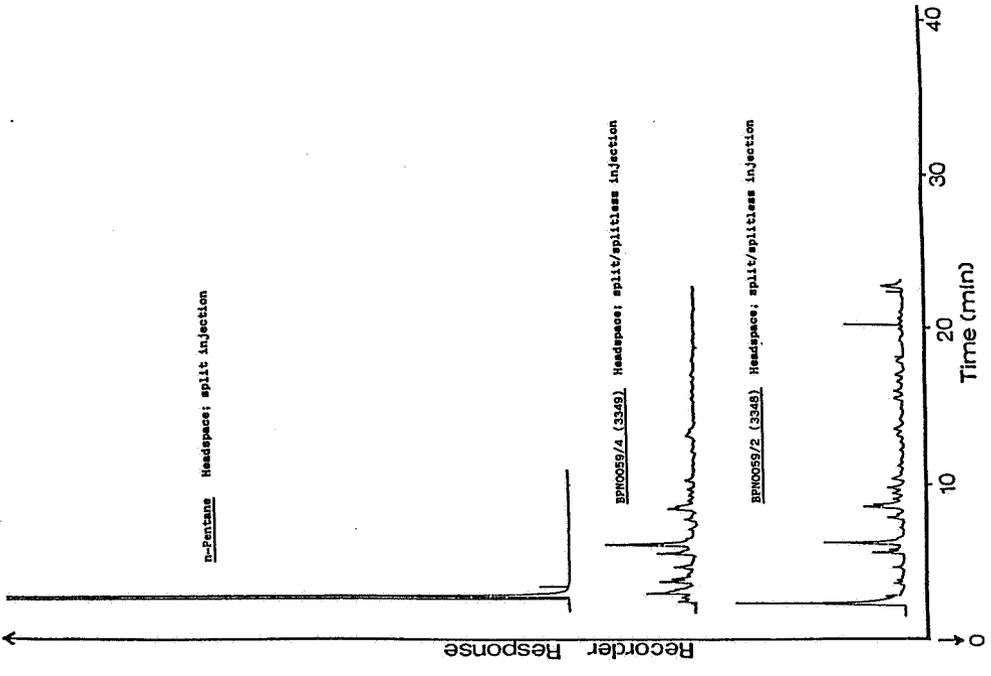


Figure 6. Hydrocarbons in environmental samples

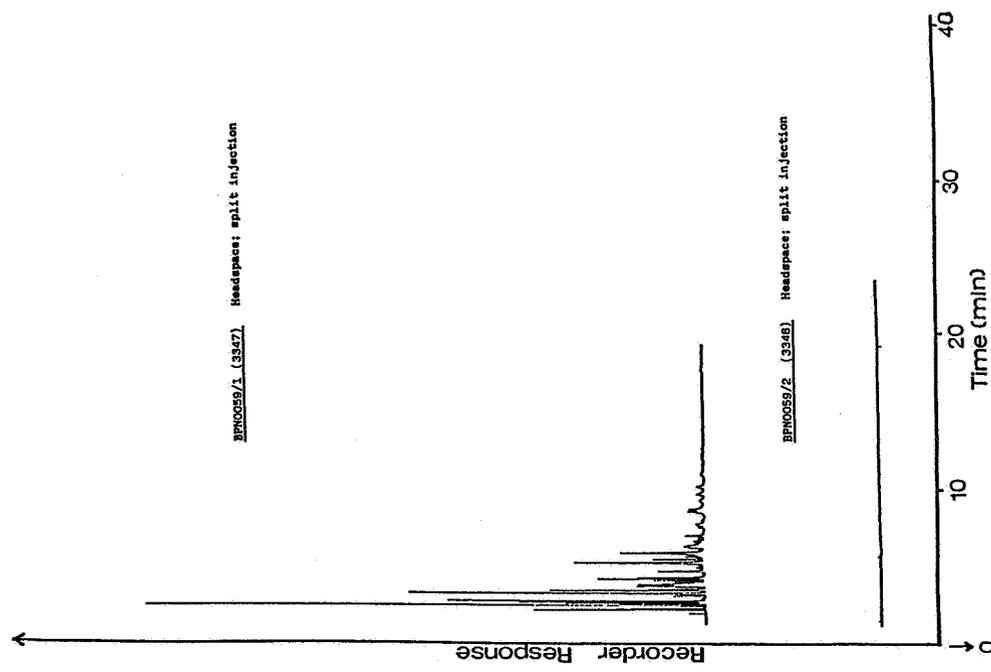


Figure 5. Hydrocarbons in stream bank sediments

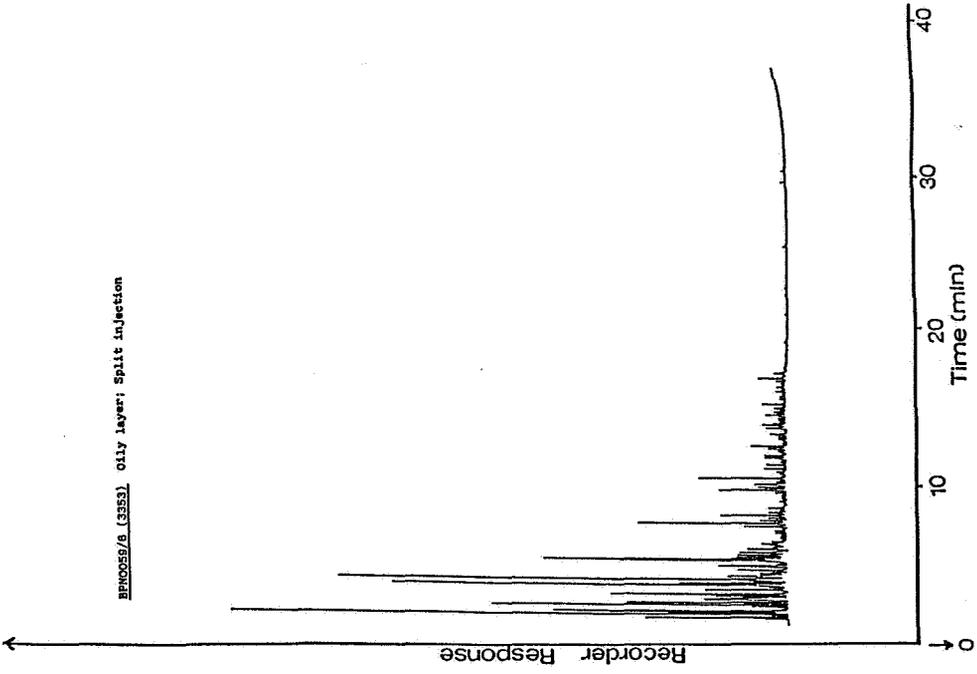


Figure 8. Supernatant in hydrocarbon separator

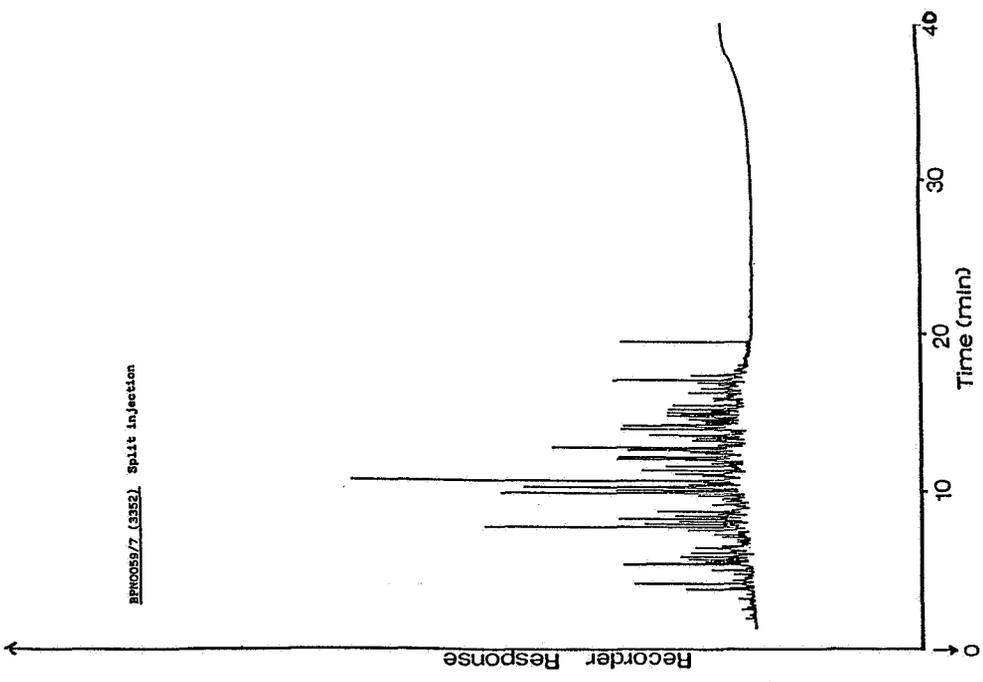


Figure 7. Supernatant in hydrocarbon separator

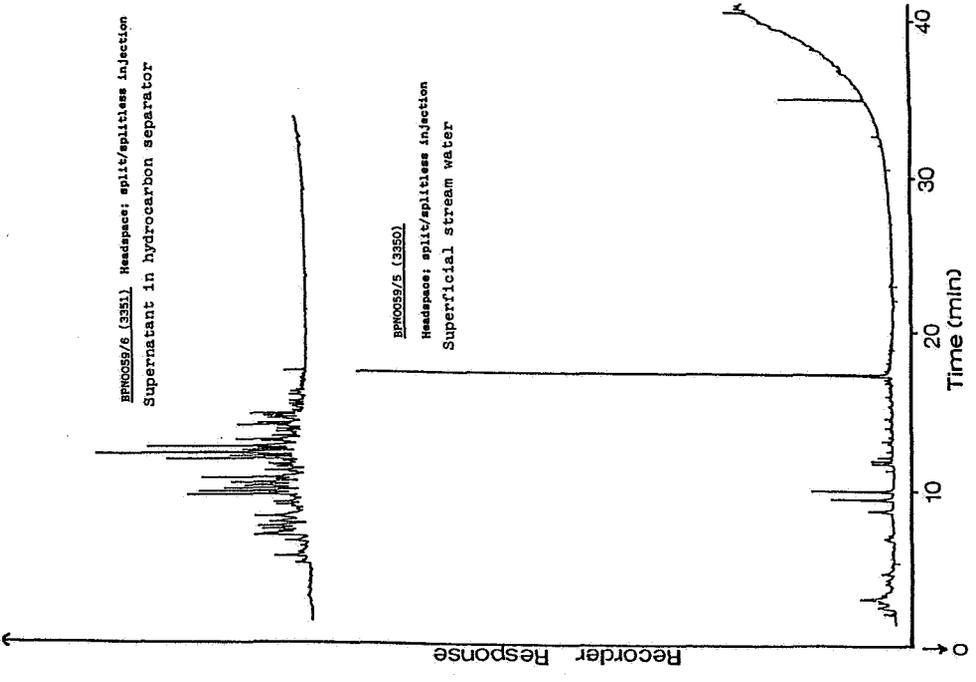


Figure 10. Hydrocarbons in environmental samples

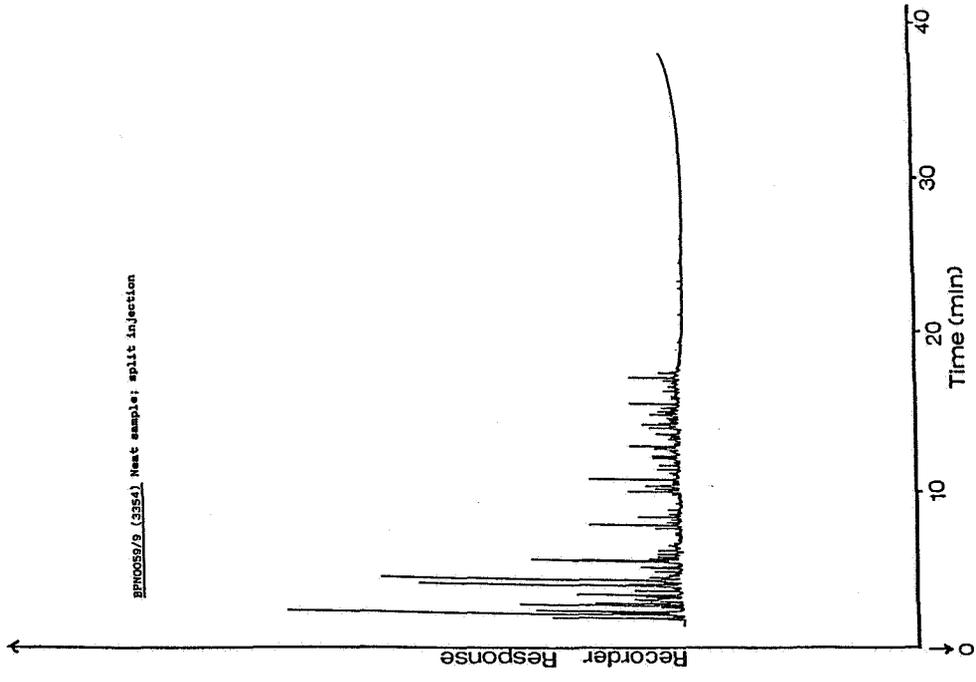


Figure 9. Supernatant in hydrocarbon separator

10. ANALYSIS OF SAMPLES FROM SITE

A number of tank, soil, water and separator content samples were taken on site, for analysis as required, to fill in gaps in existing knowledge.

Three separator samples were analysed for organo lead content, all showing the presence of TEL at up to 3.0 mg/l, approximately 1.5% of that present in gasoline.

This would suggest that there has been, or currently still is, a loss of leaded gasoline to the ground. The relatively small amount present, in the absence of highly absorptive strata, indicates that either the organo lead found here is "old", or that other leaks effectively dilute the concentration in the ground.

In either interpretation, this would suggest at least two sources of hydrocarbons.

A number of samples were subjected to capillary gas chromatography in order to characterise the hydrocarbons found (see Figure 5-10). Both unweathered and weathered light refined product (LRP), possibly naphtha (C4-C9), is found in soils and separators, while a weathered LRP containing some heavier fractions (C8-C12) is also found in the separators.

This would appear to be indicative of there being at least two sources of hydrocarbons in the ground, and consistent with the results of organo-lead analysis.

11. CONCLUSIONS

- 1 Hydrocarbon seepage is currently being collected at a rate of approximately 250 gallons/month.
- 2 Analysis of existing data appears to show that there may be a hydrocarbon reservoir on-site within the ground of up to approximately 50,000 gallons.

- 3 It is likely that this reservoir is held largely in the upper fissured sandstones and superficial deposits.
- 4 The lower sandstones are fractured and fissured to a degree and we have little knowledge regarding the extent of deep storage in this manner.
- 5 The seepages show evidence of organo lead compounds, and have in places the characteristics of weathered gasoline and naphtha.
- 6 The presence of neat and unweathered light refined products suggests a new nearby source of LRP, with short travel time.
- 7 The presence of low concentrations of TEL suggests either an old source of gasoline, or high dilution.
- 8 The known leak is either highly diluted before reaching the seepage points or is not reaching the seepage points because of faults and fractures. If it is reaching the seepage points, it may have been leaking for up to 9 years.
- 9 If the known leak is not reaching the paddock, then there is a secondary or historic source of gasoline.
- 10 There is evidence of historic gasoline contamination.
- 11 The known leak may therefore be transferring to a deep store through fissures.
- 12 The subsurface strata may be saturated with LRP over a wide geographic area, as evidenced by volatile components seeping on the far side of a stream bank, possibly by condensation of vapours of naphtha.
- 13 A buried run of pipelines appears to be effectively cutting off further transport of hydrocarbons to the south.

12. FURTHER WORK

Phase II is now in preparation, which will involve identification of the geological extent contamination by drilling and excavation.

MOVEMENT OF TETRACHLOROETHYLENE DEPOSITED ON AN
IMPERVIOUS LAYER DUE TO WITHDRAWAL OF GROUNDWATER

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ABSTRACT

Groundwater pollution by tetrachloroethylene (TCE) and its hydrogeological background are introduced. A numerical simulation model to investigate the basic movement of TCE when groundwater is withdrawn is developed. The relationship between pumping rate and the change in the concentration distribution of TCE is investigated.

1. INTRODUCTION

Groundwater pollution by chlorinated hydrocarbons such as tetrachloroethylene and trichloroethylene has been increasing in many places. These materials are widely used as organic solvents in dry cleaning of clothes or for cleaning metals in integrated circuit production.

Since this type of groundwater pollution has recently become apparent, we do not know much about the mechanism. Moreover the effective countermeasures against the pollution have not been established yet. In this paper, the groundwater pollution by TCE is briefly introduced and the relationship between the discharge of pumping and the change in the concentration distribution is simulated by numerical calculation.

2. OBSERVED GROUNDWATER POLLUTION BY TETRACHLOROETHYLENE

Figure 1 shows the polluted area by TCE. The shaded portion in the figure indicates the polluted area. Symbols b_1 to b_7 represent the locations of bore holes. Notations a to e indicate the boundary points

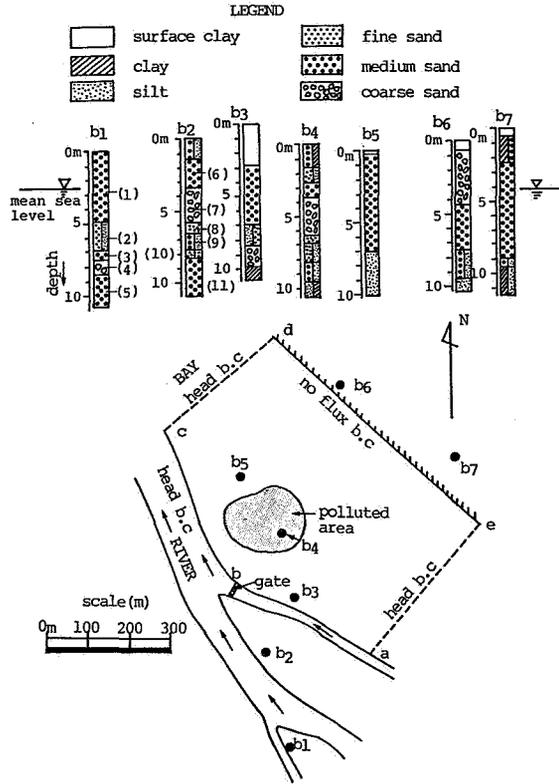


Figure 1. Polluted area and bore logs

Table 1. Permeabilities by Creager's formula in cm/sec

		Bore hole b ₁				
Section	(1)	(2)	(3)	(4)	(5)	
	7.37×10^{-2}	3.51×10^{-4}	1.30×10^{-2}	2.46×10^{-1}	3.24×10^{-2}	
		Bore hole b ₄				
Section	(6)	(7)	(8)	(9)	(10)	(11)
	2.00×10^{-2}	1.95×10^{-1}	1.75×10^{-1}	1.25×10^{-5}	2.15×10^{-3}	4.10×10^{-2}

used for the expression of boundary conditions in the numerical calculation of the two-dimensional groundwater flow.

The bore logs are shown in the upper part of the figure. Numbers in parenthesis indicate the segments whose permeabilities are obtained by the Creager's formula. Table 1 shows these values. Since the permeability in segment (9) of bore hole b_2 is considerably smaller than those in segments (7) and (8), the layer below the medium or coarse sand layer will be regarded as an impervious layer. The coarse sand layer contains gravel sized particles ranging from 10 to 20 mm in diameter. It is therefore expected that the permeabilities in segments (4), (7) and (8) are considerably large. The groundwater flow in this area is affected by both the water levels in the river and the sea. Figure 2 shows an example of the flow pattern by numerical calculation in which the variation of the water levels due to the tidal oscillation and the gate operation for the water level control are taken into consideration. In the figure, the larger arrows indicate that the flow velocity is ten times larger than those of the smaller ones. One of the measured concentration distributions of TCE is also illustrated. Since the water

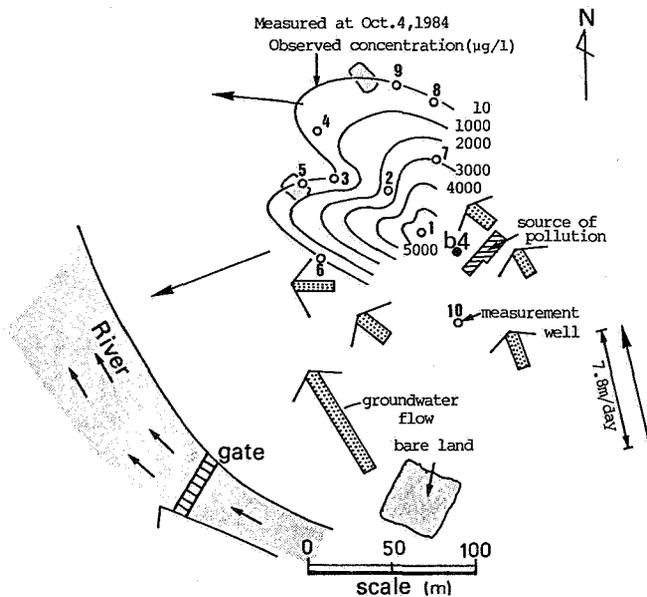


Figure 2. Observed concentration distribution of TCE and flow pattern

quality standard of the WHO for TCE is $10 \mu\text{g/l}$, serious pollution takes place in this area. Open circles with numbers from one to ten represent the measurement wells. The symbol b_4 is the bore hole which locates 5 m downstream from the suspected source of the pollution. A dry cleaning laundry was identified as the source. It was found that TCE leaked from a crack in the concrete floor of the factory and infiltrated underground. It is interesting that the dominant direction of the spread of pollution correlates with the flow direction. Readers who are interested in the correlation between the two-dimensional spread of the pollution and the groundwater flow patterns may refer to the papers (Jinno et al., 1986a,b).

3. CHANGE IN THE CONCENTRATION DISTRIBUTION DUE TO THE WITHDRAWAL OF GROUNDWATER

3.1 Calculation conditions

If the pollution by TCE can be regarded as a two-dimensional problem in a horizontal plane, we may simply apply the two-dimensional mass transport equation to the prediction of the movement of TCE. However, in this case, neither the effects of the density nor the viscosity of TCE will be taken into consideration. According to the observations through the experiment (Jinno et al., 1986b), the gravitational effect due to a large

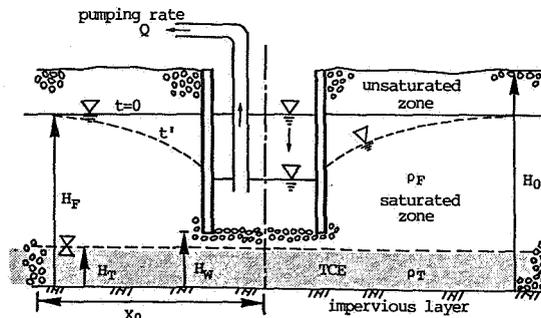


Figure 3. Schematic illustration of calculation region

density of TCE will not be neglected when an undiluted solution of TCE deposits on the impervious layer. In order to see the effect of the inherent properties of TCE on the movement of the deposited TCE, we will calculate for the simplified case in which the change in the vertical distribution of TCE in the unconfined aquifer is predicted. The numerical calculation here is executed for the two-dimensional cartesian coordinate system instead of the radial one. Figure 3 shows the schematic illustration of the calculation region. Strictly speaking, the results obtained by this calculation may not represent the exact groundwater drawdown and the change in the concentration distribution of TCE due to the withdrawal through a circular well as in the actual field. We will, however, expect that the basic responses to the withdrawal obtained here are still retained. If the present procedures are confirmed applicable to the prediction of the movement of TCE, then we will get reasonable implementation for the field data and effective countermeasures against the pollution.

The continuity equation and the equation of motion are used for the groundwater flow calculation. For the prediction of the concentration distribution, the two-dimensional mass transport equation is used. These equations are as follows:

[equation of groundwater flow in saturated/unsaturated zone]

$$(C_w + \alpha S) \partial h / \partial t = \partial (k \partial h / \partial x) / \partial x + \partial [k (\partial h / \partial y + \rho / \rho_w)] / \partial y \quad (1)$$

where

- C_w = specific moisture capacity = $d\theta/dh$, θ = water content
 S = specific storage coefficient , h = hydraulic head
 α = dummy parameter [1: for saturated zone, 0: for unsaturated zone]
 k = permeability (cm/sec) , k_w = saturated permeability of water
 k_w = $k' \rho_w g / \mu_w = 0.246$ cm/sec, μ_w = viscosity of water
 k' = intrinsic permeability (cm²)
 k_{TCE} = $k' \rho_w g / \mu_{TCE} = 0.300$ cm/sec

[unsaturated permeability of water, k_u]

$$k_u = k_w * k_r, \quad k_r = (\theta / \theta_{sat})^m, \quad \theta_{sat} = \text{saturated water content}$$

[unsaturated properties of soil]

$$\theta = \theta_{sat} : h > 0, \quad \theta = a \theta_{sat} / (a + |h|^b) : h < 0$$

$$C_w = 0 : h > 0$$

Table 2. Values of parameters used in the calculation

parameter	numerical value	parameter	numerical value
H_0	215 cm	$k' = k_{sat} \mu / \rho_F g r = 2.857 \times 10^{-6} \text{ (cm}^2\text{)}$	
H_W	110 cm	μ ; viscosity	
H_T	15 cm	k_{sat}	0.246 cm/sec (for water)
H_F	200 cm	k_W	0.246 cm/sec
ρ_F	0.999 g/cm ³ (15°C)	k_{TCE}	0.300 cm/sec
ρ_T	1.631 g/cm ³ (15°C)	$\alpha_T = d/25$	0.08 cm (d=2 cm)
Q	200 l/hour	$\alpha_L = d/1.5$	1.33 cm (d=2 cm)

$$= d\theta/dh = ab\theta_{sat} |h|^{b-1} / (a + |h|^b)^2 \quad : \quad h < 0$$

where $a=3500$, $b=2.5$, and $m=4$ are used in this calculation.

[convective-dispersion equation]

$$\begin{aligned} & \partial(\theta C) / \partial t + \partial u'(\theta C) / \partial x + \partial v'(\theta C) / \partial y \\ & = \partial[\theta D_{xx} \partial C / \partial x + \theta D_{xy} \partial C / \partial y] / \partial x + \partial[\theta D_{yx} \partial C / \partial x + \theta D_{yy} \partial C / \partial y] / \partial y \quad (2) \end{aligned}$$

where $u' = u/\theta$, $v' = v/\theta$, $u = -k \partial h / \partial x$, $v = -k(\partial h / \partial y + \rho / \rho_w)$,

$$C = (\rho - \rho_w) / (\rho_{TCE} - \rho_w) * 100 \quad (\%)$$

$$\begin{aligned} \theta D_{xx} &= \alpha_L u^2 / v + \alpha_T v^2 / v + \theta D_M, \quad \theta D_{yy} = \alpha_L v^2 / v + \alpha_T u^2 / v + \theta D_M, \\ \theta D_{xy} &= \theta D_{yx} = (\alpha_L - \alpha_T) uv / v, \quad \text{and} \quad v = (u^2 + v^2)^{1/2} \end{aligned}$$

Characteristic lengths of hydraulic dispersions α_L and α_T are determined by the Harleman's relation (Harleman, D.R.F. et al., 1963) as

$$D_L / \nu = n_1 (Vd / \nu)^{n_2}, \quad D_T / \nu = n'_1 (Vd / \nu)^{n'_2}$$

When $n_1 = 1/1.5$, $n_2 = 1$, $n'_1 = 1/25$ and $n'_2 = 1$,

$$\alpha_L = d/1.5 \quad \text{and} \quad \alpha_T = d/25$$

where d is the representative diameter of the porous medium.

The retardation factor of TCE due to chemical adsorption is neglected in this calculation. The values and the boundary conditions used in this calculation are given in Table 2.

3.2 Change in the concentration distribution

Figure 4 shows the results at 71.6 sec after pumping starts. The flow pattern and the concentration distribution are illustrated on the left

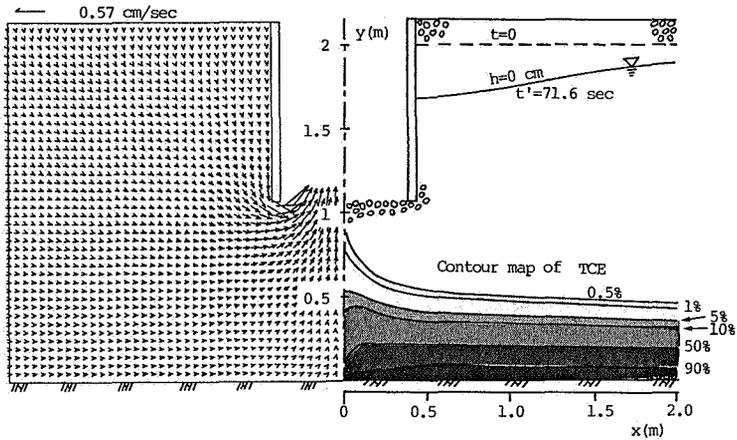


Figure 4. Flow pattern and change in the concentration distribution of TCE at 71.6 sec

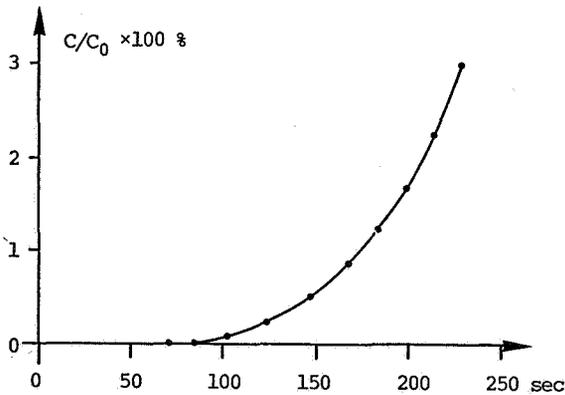


Figure 5. Change in the concentration of TCE at the pump outlet

and on the right sides, respectively. Since the initial height of undiluted TCE deposited on the impervious layer is 15cm in this calculation, the spread of TCE due to hydraulic dispersion and convection is large because the iso-concentration line of 0.5% reaches almost to the bottom of the well.

3.3 Change in concentration at the pump outlet

It is important for users to know how much of the deposited TCE will be pumped up. If we assume the complete mixing inside the well space, we

can estimate the concentration of TCE from the pump outlet. Figure 5 shows the change in the concentration of TCE with time. Since the concentration at the pump outlet changes with time after pumping starts, we may underestimate the concentration if the sampling period is not long enough until the converged value is obtained. It should also be noticed that the measured concentration at the pump outlet does not always represent the actual concentration of TCE in the aquifer.

4. CONCLUSIONS

A primary study on the prediction method of the movement of TCE due to withdrawal of groundwater is attempted, taking into consideration some inherent properties of TCE. It should be noted from the results that the sampling of polluted groundwater through an outlet should be carefully done taking into account the change in concentration of TCE with time. We believe that the present approach based on the numerical simulation will be helpful for better understanding of the mechanism and the establishment of countermeasures against the pollution.

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GROUNDWATER CONTAMINATION WITH THE PESTICIDES
CHLOROTHALONIL, CARBOFURAN AND 2,4-D UNDER AN
IRRIGATED CANADIAN PRAIRIE FARM

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ABSTRACT

The movement of pesticide residues to ground water was studied on a commercial farm (sandy soil with low organic matter content, a high water table, a tile drain system and an irrigation system using river water) southwest of Portage la Prairie, Manitoba. An initial (1981) random sampling of the tile drain water did not detect any pesticide residues in the outflow at the 0.02 $\mu\text{g/L}$ level. A subsequent extensive sampling (1982) detected residues of chlorothalonil on eight occasions ranging from 0.06 to 3.66 $\mu\text{g/L}$ in the tile drain outflow. Ground water from one of two stand-pipe wells in the northwest quarter was found to contain the fungicide chlorothalonil at a level of 10.1 to 272.2 $\mu\text{g/L}$ in 1982 and 0.4 to 9.0 $\mu\text{g/L}$ in 1983, the insecticide carbofuran at a level of 11.5 to 158.4 $\mu\text{g/L}$ in 1982 and < 0.5 to 1.0 $\mu\text{g/L}$ in 1983, and the herbicide 2,4-D at a level of 0.8 to 2.5 $\mu\text{g/L}$ in 1983.

1. INTRODUCTION

With the use of irrigation, intensive cultivation and pesticides, the coarse textured agricultural soils of Manitoba in the area of the old Assiniboine Delta of glacial Lake Agassiz, normally poor producers under conventional farm practices, can be made quite productive. A potential for ground water contamination exists when land is under irrigation. This is an item of concern in this region as ground water is quite close to the surface and soils are sandy and of relatively low organic matter content.

Concern has been expressed regarding potential contamination of ground water through movement and leaching of pesticides from irrigated farm

land. Ground water quality deterioration has been recorded in recent years (Page, 1981; Junk et al., 1980; Spalding et al., 1980), and the use of pesticides is coming under increasing scrutiny in this regard (Greenberg et al., 1982; Hogue et al., 1981; Rohde et al., 1981; Muir and Baker, 1978). Once ground water is contaminated, it is difficult and costly to restore it to its former high quality state.

2. MATERIAL AND METHODS

2.1 Farm site

The site (Krawchuk and Webster, 1987) was situated on a commercial farm which was irrigated using river water and had a tile drain system to counteract the high water table in the region. There were four major soil types at the site, with the predominant type being fine sand (Manitoba Soil Survey, 1972).

2.2 Tile Drain Outlets and Wells - Sampling and Analysis

Samples of the tile outflow water were collected during the period May 12 to August 5 in 1981 and from June 23 to October 1 in 1982 from the outfall of the tile drain systems (Krawchuk and Webster, 1987). During 1983 there was no further sampling of the tile outflow. Ground water was collected by autosampler in 1982 or peristaltic pump in 1983 from two stand pipe wells located in the northwest quarter. In addition to this weekly average sample, a bulk (4 L) grab sample was also collected weekly from each well.

The water extraction procedure using C₁₈ Sep-Pak extraction cartridges (Waters Scientific Ltd., Mississauga, Ontario) involving a 1000 fold concentration factor, residue analysis by High-Performance Liquid Chromatography, and confirmation by capillary GC-EC and GC/MS has been previously described (Krawchuk and Webster, 1987).

3. RESULTS AND DISCUSSION

3.1 Tile drain water

Pesticide residues were not detected ($<0.02 \mu\text{g/L}$) in the tile outflow water samples collected in 1981 which may have been due either to the sampling schedule or the manner in which samples were taken, or to there being insufficient pesticide residues present to be detected. Analysis of tile water from 1982 found residues of chlorothalonil in 9 samples (Table 1), 4 each from the east and west gravity outflows of

Table 1. *Chlorothalonil in tile drain water: 1982*

NE East outfall				NE West outfall				West side	
date	water	date	Sep-Pak	date	water	date	Sep-Pak	date	water
d/mo	$\mu\text{g L}^{-1}$	d/mo	μg	d/mo	$\mu\text{g L}^{-1}$	d/mo	μg	d/mo	$\mu\text{g L}^{-1}$
04/05	0.08	11/08	0.76	01/07	3.27	07/07	9.70	23/07	0.06
07/07	0.04	18/08	0.10	13/08	3.66	13/07	5.54		
17/08	0.74	15/09	0.08	17/08	0.09	18/08	45.50		
09/09	0.13			06/09	1.50	15/09	5.49		

the tile drain system and 1 from the sump well outflow on the west side of the site. The pattern of appearance is similar for the daily data and the weekly Sep-Pak data (Figure 1) indicating a common influencing factor. The difference in levels from the two tile systems is probably an effect of the area drained by that particular tile line system and the chlorothalonil application pattern with respect to the fields treated and the underlying tile system.

Carry-over of chlorothalonil residues in the subsoil from the previous year is indicated by the presence of residues in the tile water sampled on May 4th as the first application of chlorothalonil was not until July in 1982. Results for ground water analysis for 1983 agreed with this conclusion.

Subsequent appearances of residues in the tile water were usually only a few days apart, with residues first appearing in the tile outflow from the western system, then in the eastern system. This time

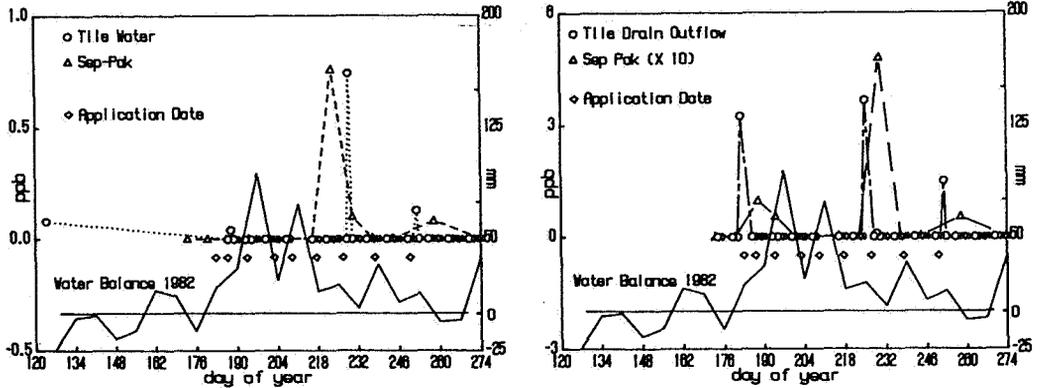


Figure 1. Chlorothalonil levels in tile water from a) NE East outfall and b) NE West outfall of monitored/grab samples and outlet Sep-Paks and water balance (rainfall + irrigation evaporation) in the area

differential may have been due to the distance the residues had to leach from the soil surface to ground water and the tile system. In both cases, residues appeared in the tile outflow water about 14 days after a period where there was a large positive water balance (heavy rainfall). Residues of chlorothalonil appear to have been leached into the subsoil by the positive water balance during the period day 190 to 197, and subsequently further leached to ground water by the positive water balance of days 204 to 211. Time of travel was between 28 and 35 days depending on the water balance and the distance to ground water.

Higher residue levels observed in the tile outflow from the west system was attributed to the difference in flow volumes from each of the two tile systems as well as the application pattern of chlorothalonil to the fields with respect to the tile drain pattern.

Chlorothalonil was detected in the outflow water from the sump well on only one occasion in the outflow water. This one occurrence of chlorothalonil in the outflow from the sump well occurred shortly before pumping ceased and while the tile system was actively drawing water out of the field. In addition, it occurred shortly after a period where there was a large positive water balance. The low level of chlorothalonil detected in the outflow is probably due to the relatively small drainage area for this tile system as well as the greater surface to ground water distance for this area.

3.2 GROUND WATER

In 1982, chlorothalonil and carbofuran were confirmed in the ground water samples taken from one of the sand-pipe wells (Table 2).

Table 2. Pesticide levels in ground water from a stand pipe well:
1982

date	chlorothalonil	carbofuran	date	chlorothalonil	carbofuran
d/mo	ppb	ppb	d/mo	ppb	ppb
12/08	107.2	20.9	15/09	81.7	145.5
16/08	225.5	74.6	16/09	10.9	11.5
16/08	125.8	53.1	22/09	10.1	24.6
17/08	272.6	67.1	23/09	72.3	158.5

Analysis of the 1983 well water samples from the two stand-pipe wells in the NW quarter found the following pesticides to be present: chlorothalonil, carbofuran, and 2,4-D (Table 3) (2,4-D was not applied in 1982).

A comparison of the relative amounts of chlorothalonil (Figures 2a and 2B) and carbofuran (Figures 3a and 3b) in ground water for the two years

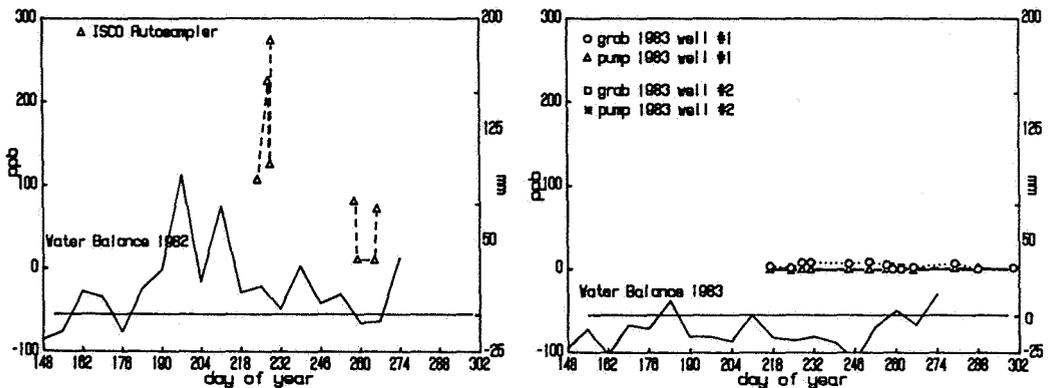


Figure 2. Chlorothalonil level in ground water from a) ISCO autosampler-1983 Well #1 and b) grab and pump ground water samples from Wells #1 and 2 in 1983 and the water balance (rainfall + irrigation-evaporation) in the area for each year.

Table 3. Pesticide levels (ppb) in ground water from two stand pipe wells: 1983 ($0.02 < tr < 0.1$; $-- < 0.02$)

date	chlorothalonil				carbofuran		2,4-D			
	Well #1		Well #2		Well #1		Well #1		Well #2	
	grab	pump	grab	pump	grab	pump	grab	pump	grab	pump
05/08	4.0	--	--	--	1.1	--	4.4	--	--	--
12/08	2.7	2.6	0.2	0.1	0.4	--	3.7	4.0	--	--
16/08	8.5	0.1	tr	--	--	--	3.5	--	0.8	--
19/08	8.6	--	--	--	0.9	--	4.2	--	--	--
01/09	7.2	--	--	--	--	--	6.8	--	--	--
08/09	9.0	0.4	0.3	--	--	--	9.1	1.9	0.8	--
14/09	5.6	--	--	--	--	--	9.9	--	--	--
16/09	0.9	3.4	--	--	--	0.8	2.4	7.2	--	--
19/09	1.0	--	2.4	--	0.6	--	--	--	2.5	--
23/09	2.7	2.1	0.1	0.3	0.6	--	4.4	4.0	--	--
06/10	7.6	1.6	--	--	--	--	3.6	6.3	2.1	--
14/10	1.0	1.3	1.4	--	--	--	7.0	4.2	--	--
26/10	2.0	--	0.3	--	--	--	9.9	--	--	--

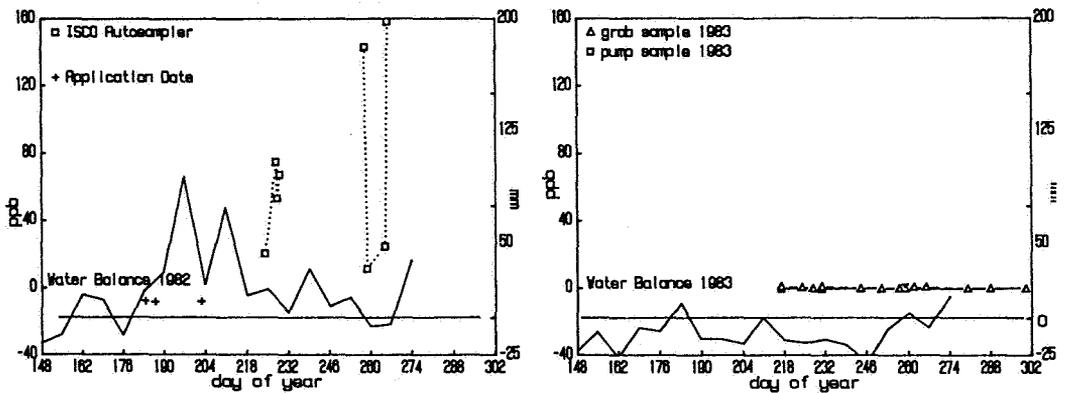


Figure 3. Carbofuran level in ground water from a) ISCO autosampler-1982 Well #1 and b) grab and pump ground water samples from Wells #1 in 1983 and the water balance in the area for each year.

shows that the levels dropped considerably in the second year. As chlorothalonil and carbofuran were not applied to the field in 1983, carry-over from the previous year and subsequent leaching down through the soil column is thought to be the probable source for these residues, since the levels of chlorothalonil and carbofuran were reduced by similar factors. In addition, when comparing the water balances for the two years, it can be seen that the lower amounts of these two pesticides detected in 1983 may also be a result of the lower water input into this particular field in 1983. Even with this largely negative water balance level, chlorothalonil, carbofuran, and 2,4-D were leached through the soil column into ground water in 1983. However, the amount of 2,4-D leached through the soil was lower than would have been expected probably reflecting the lower amount of input water. Ground water concentrations of chlorothalonil and carbofuran fluctuated quite markedly on a daily basis in August and September in 1982 (Figures 2a & 3a). A similar, but not as great a variation in concentrations was noted for the residue levels detected in the ground water for 1983. The pesticide concentration in water discharged into the municipal ditch from the tile drainage system in 1982 was generally below detectable limits ($<0.02 \mu\text{g/L}$) with only occasional occurrences where detectable levels of chlorothalonil residues were present in the tile outflow.

4. CONCLUSION

In summary, the fungicide chlorothalonil, the insecticide carbofuran, and the herbicide 2,4-D have been detected and identified in ground water from a farm site. Carbofuran, chlorothalonil and 2,4-D are leached through the soil profile fairly rapidly with residues appearing in ground water in a short time (28-35 days) after application. There appears to be a small amount of carry-over of chlorothalonil and carbofuran to the following year with these amounts still being detected in the ground water one year after application. Both the amount leached and the time of appearance appear to be functions of the water balance for the area. Some leaching of residues appears to occur even under a negative water balance. Laboratory studies currently in

progress confirm these observations and indicate that even "immobile" compounds may leach under certain conditions in coarse textured soils.

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VULNERABILITY OF VARIOUS SOILS TO LEACHING OF CHLOROPHENOLS

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ABSTRACT

Sorption isotherms for five chlorophenols have been determined in six natural Dutch soils and in two synthetic humus soils. Sorption coefficients at infinite dilution have been described in terms of the organic carbon fractions and the pH values of the soils and the octanol/water partition coefficients and dissociation constants of the chlorophenols. Single step desorption experiments revealed very slow desorption kinetics and formation of (practically) non-extractable residues. Calcareous soils and low-humic soils appear to be most vulnerable to leaching of chlorinated phenols.

INTRODUCTION

Chlorophenols occur in the environment as industrial waste, and because of their use as wood preservative and as pesticide. A number of them are inserted on the EC-list of priority pollutants. Published results on the behaviour of chlorophenols (CPs) in the environment are rather scarce. Boyd (1982) examined sorption of mono- and dichlorophenols in soil, whereas Choi and Aomine (1974) studied sorption of pentachlorophenol. Schellenberg et al. (1984) and Xie (1983) examined sorption of some CPs in sediments. Bio-degradation of CPs in soil was investigated by Murthy et al. (1979), and by Baker and Mayfield (1980). The occurrence of CPs in Dutch surface water and sediment has been established by Wegman et al. (1979, 1983).

The aim of the present work is to describe the sorption behaviour of CPs in soil-water suspensions by means of a number of readily available soil and solute data in order to estimate the vulnerability of soils in connection with transport of CPs to the groundwater.

THEORETICAL

Sorption of solutes to soil particles is usually described with a Freundlich isotherm, which in a logarithmic form reads

$$\log q = \log K_f + (1/n) \log c \quad (1)$$

where

- q = concentration of the sorbed solute ($\mu\text{g kg}^{-1}$)
- c = concentration of the solute in the aqueous phase ($\mu\text{g dm}^{-3}$)
- n = parameter with a value that is usually between 1 and 1.4
- K_f = Freundlich coefficient for solute sorption.

When c is sufficiently small, $1/n$ is equal to 1 and K_f is equal to the sorption coefficient, K_p ($\text{dm}^3 \text{kg}^{-1}$). Because hydrophobic solutes are mainly sorbed to the humin of the soil, it is convenient to define $K_{oc} = K_p/f_{oc}$, because the organic carbon of the soil, f_{oc} , appears to be proportional to the organic matter content of all kinds of soil. Consequently, K_{oc} data are less dependent on the soil type than K_p values. However, sorption of CPs depends also on the pH of the soil due to dissociation of these solutes. In order to account for this effect, it will be assumed that only the non-dissociated solute fraction in the aqueous phase is involved in the sorption process. This fraction is given by $f_{nd} = 1/(1 + K_a/a_H)$. Therein, K_a is the (apparent) solute dissociation constant and a_H is the proton activity in the aqueous phase. When the pK_a ($\equiv -\text{Log } K_a$) of the solute and the pH of the soil are known and $\text{pH} < \text{pK}_a + 2$, f_{nd} can be estimated. The influence of f_{oc} and f_{nd} on K_p is given by

$$K'_{oc} = K_{oc}/f_{nd} = K_p/(f_{oc} f_{nd}) \quad (2)$$

Notice that K'_{oc} is virtually independent of f_{oc} and f_{nd} , provided sorption of chlorophenolate can be omitted. When phenolate sorption is significant anomalously large K'_{oc} values are expected. Finally, the $\log K'_{oc}$ values are correlated with $\log K_{ow}$ data for the non-dissociated CPs. K_{ow} is the solute partition coefficient between n-octanol and a suitable (aqueous) buffer. The following equation will be examined

$$\log K'_{oc} = A + B \log K_{ow} \quad (3)$$

The values of the parameters A and B in this equation depend on the class of solutes, and -to a minor degree- on the soil type (Schellenberg et al., 1984).

EXPERIMENTAL

Materials

Soils. The topsoil samples were air-dried, homogenized and sieved. The < 400 μm fractions were collected and did not contain significant amounts of CPs. The humus soils were synthesized as follows. Sodium humate (Aldrich, Bruxelles, Belgium) was suspended in a solution of calcium chloride and sodium chloride (ratio Ca:Na= 2:1) at pH= 3.7 and 6. After centrifugation the humates were thoroughly mixed with quartz sand to a ratio of 1:19. The f_{oc} values of the soils were determined with a carbon analyzer (the amount of carbondioxyde was measured by IR-spectroscopy). The sampled soils and the properties of their < 400 μm fractions are given in Table 1.

Chlorophenols. The selection of the CPs was based on their occurrence (Wegman and Hofstee, 1979) and persistence (Verschueren, 1983) in surface water. Under aerobic conditions the CPs, given in Table 2, undergo a very slow bio-degradation (less than 50% after 72 days). Therefore, non-sterilized soil was used in the experiments described below.

Table 1. The examined soils, sample places, pH¹, f_{oc} and their fine silt (2-16 μm) and clay (< 2 μm) fractions²

Code	Soils	Sample places	pH	f _{oc}	Fine silt	Clay
1	Humic sand	Kootwijk	3.4	0.017	0.003	0.012
2	Humic sand	Rolde	4.9	0.022	0.006	0.015
3	Humic-rich sand	Holtjen	4.7	0.032	0.010	0.037
4	Peat	Schipluiden	4.6	0.298	-	-
5	Light loam	Maasdijk	7.5	0.009	0.038	0.087
6	Heavy loam	Opijnen	7.1	0.017	0.116	0.180
7	Humus soil	(synthetic)	3.7	0.027		
8	Humus soil	(synthetic)	6.0	0.028		

¹Measured in a suspension of 10 g of soil in 50 ml 1 M KCl after shaking for 16 h

²Weight fractions based on dry soil

Table 2. The examined CPs, code, pK_a¹ and logK_{ow}² values

Chlorophenols	Code	pK _a	LogK _{ow}
3-Chlorophenol	MCP	9.37	2.50
3,4-Dichlorophenol	DCP	8.62	3.22
2,4,5-Trichlorophenol	TrCP	6.72	3.88
2,3,4,6-Tetrachlorophenol	TeCP	5.22	4.42
Pentachlorophenol	PCP	4.74	5.05

¹Data given by Ugland et al. (1981)

²Data taken from Xie and Dyrssen (1984).

Methods

Sorption: In a typical experiment 4 g of soil (or 0.27 g of peat) was suspended in 20 ml of a standard solution of the CPs in 0.01 M calcium chloride. Sorption was studied at 5 CPs concentrations ranging from 30 to 3000 $\mu\text{g MCP dm}^{-3}$ and from 3 to 300 $\mu\text{g PCP dm}^{-3}$. The suspensions were shaken at 10°C for 16 h and were then centrifuged at 7500 rpm for 15 min. Borax solution was added to a known amount of the supernatants up to a final concentration of 0.067 g cm^{-3} and a fixed volume. These solutions were analysed as described below. The centrifugates were used in SSDW desorption experiments.

Desorption: In single-step desorptions with water, denoted by SSDW experiments, the above mentioned soil centrifugates were weighed (to correct for the amount of CPs solution left in these centrifugates). Thereafter, 20 cm^3 of a 0.01 M calcium chloride solution was added and the resulting suspensions were shaken at 10°C for 24 h. After centrifugation at 7500 rpm for 15 min and decantation, borax was added to known amounts of the supernatants, as indicated above. These solutions were analysed as described below. In desorptions with borax, denoted by DB, experiments 1.3 cm^3 of an aqueous solution containing 1 $\mu\text{g MCP}$, 0.5 $\mu\text{g DCP}$, 0.2 $\mu\text{g TrCP}$, and 0.1 $\mu\text{g TeCP}$ and PCP was added to 2 g of soil (or 0.13 g of peat). This suspension was thoroughly homogenized. After incubation for 16 h at 25°C, borax was added up to pH = 9.3 as indicated above. The suspensions were sonicated for 1 h and then directly (i.e., without centrifugation) extracted and analysed.

GC analysis: To the supernatants and suspensions a known amount of internal standard (3,4,5-tribromophenol) was added. Next, the phenols were acetylated and extracted at pH = 9.3 using a solution of acetic anhydride in hexane, according to Xie (1983). The extracts were analysed with a Hewlett-Packard M5880 gaschromatograph, equipped with an electron capture detector. The extracts in hexane did not need further cleanup. Sample volumes of 1 mm^{-3} were (splitless) injected. The CP acetates were separated on a fused silica CP Sil 8 CB capillary column (length 25 m, I.D. 0.33 mm), supplied by Chrompack (Middelburg, The Netherlands). Helium was used as the carrier gas, and argon + 5% methane as the make-up gas. The following temperature program was applied: 80° (3 min), 10°/min to 120°, 120° (1 min), 6°/min to 210°,

210° (1 min), 20°/min to 290°, 290° (10 min). Detection limits were in the low pg-range. All analyses were carried out within the linear range of the detector. Solute calibration was applied with 2,3,4,5-TeCP acetate as a reference compound to account for the variability of the injected sample volume. All results are based on replicate measurements.

RESULTS AND DISCUSSION

Sorption

Sorbed CPs concentrations, q , were calculated from the mass balance equation, using c values determined in the aqueous phase.

Log K_f and $1/n$ values from Equation 1 are given in Table 3. For the natural soils $1/n$ values are <1 for MCP, DCP and TrCP, where $0.05 < c (\mu\text{mol dm}^{-3}) < 20$, but virtually equal to 1 for TeCP and PCP, where $c < 0.5 \mu\text{mol dm}^{-3}$. From these results it is concluded that the Freundlich isotherms for the CPs are linear when $c < 0.5 \mu\text{mol dm}^{-3}$. Schwarzenbach and Westall (1981) and Karickhoff (1981) found linear isotherms at concentrations smaller than 1 and $10 \mu\text{mol dm}^{-3}$ respectively. The K_p values from the linear part of the isotherm for CPs with $\text{p}K_a + 2 > \text{pH}$ (soil) were corrected for f_{oc} and f_{nd} according to Equation 2. The obtained K'_{oc} values for TrCP, TeCP and PCP are within error equal to those given by Schellenberg et al. (1984). The following correlation between $\log K'_{oc}$ and $\log K_{ow}$ value is obtained

$$\log K'_{oc} = (0.62 \pm 0.14) + (0.75 \pm 0.04) \log K_{ow}$$

with a standard error of fit $s = 0.19$ which allows of predictions of K_p values within a factor of about 2 (see Figure 1). The $\log K'_{oc}$ values for PCP in the loamy soils are excluded from this correlation because contributions of phenolate sorption are significant (see Table 3).

Table 3. Log K_f , $1/n$ and log K'_{oc} data from sorption (equilibrium) experiments, log K_f and $1/n$ data from (non-equilibrium) SSDW experiments, and NEF data (see text) under DB conditions, for various soils (code given in Table 1)

Soil code	log K_f	Sorption			SSDW		DB NEF
		$1/n$	Log K'_{oc}	s.d.	Log K_f	$1/n$	
MCP							
1	0.9	0.8	2.31	± 0.13	0.9	0.9	0.34
2	1.2	0.8	2.49	± 0.22	1.6	0.7	0.34
3	1.5	0.8	2.62	± 0.25	1.7	0.7	0.49
4	2.5	0.7	2.64	± 0.15	2.4	0.9	0.16
5	1.1	0.6	2.48	± 0.43	1.9	0.5	0.18
6	1.0	0.7	2.26	± 0.43	1.9	0.8	0.28
7	1.2	0.8	2.49	± 0.10			
8	1.1	0.8	2.40	± 0.12			
DCP							
1	1.4	0.9	2.95	± 0.12	1.3	1.0	0.20
2	1.7	0.9	3.21	± 0.17	1.6	1.0	0.29
3	1.9	0.8	3.25	± 0.19	2.0	0.9	0.41
4	2.8	0.8	3.16	± 0.13	2.8	0.9	0.52
5	1.1	0.8	2.97	± 0.05	1.2	0.8	0.21
6	1.5	0.7	3.00	± 0.16	1.6	0.8	0.27
7	1.7	0.9	3.17	± 0.14			
8	1.5	1.0	2.96	± 0.17			
TrCP							
1	1.8	0.9	3.49	± 0.07	1.8	1.0	0.10
2	2.0	0.9	3.71	± 0.13	2.0	0.9	0.19
3	2.3	0.8	3.91	± 0.21	2.4	1.0	0.32
4	3.1	0.8	3.62	± 0.41	3.1	0.9	0.40
5	1.1	0.8	3.45	± 0.14	1.1	0.8	0.15
6	1.5	0.8	3.47	± 0.07	1.3	1.0	0.23
7	2.0	0.9	3.54	± 0.25			
8	1.9	0.9	3.44	± 0.19			
TeCP							
1	1.9	1.0	3.62	± 0.16	2.1	1.1	0.15
2	2.0	0.9	4.12	± 0.18	2.1	1.0	-
3	2.4	1.0	4.18	± 0.13	2.6	0.9	0.35
4	3.1	0.8	3.85	± 0.22	3.3	0.7	0.38
5	0.4	0.9	4.14	± 0.35	0.8	0.7	0.13
6	1.0	0.8	4.18	± 0.16	0.9	1.0	0.19
7	2.1	0.6	3.97	± 0.19			
8	1.7	0.9	3.72	± 0.09			
PCP							
1	2.2	0.9	4.02	± 0.14	2.5	1.0	0.25
2	2.2	0.9	4.80	± 0.14	2.4	1.0	0.40
3	2.6	1.0	4.65	± 0.03	2.9	1.1	0.60
4	3.3	0.8	4.38	± 0.24	3.8	1.1	0.59
5	1.1	0.9	5.55	± 0.18	1.2	1.2	0.20
6	1.5	0.8	5.39	± 0.15	1.6	1.2	0.38
7	2.3	0.7	4.05	± 0.20			
8	2.0	0.8	4.53	± 0.16			
Mean s.d.	0.2	0.15		0.2	0.2	0.13	

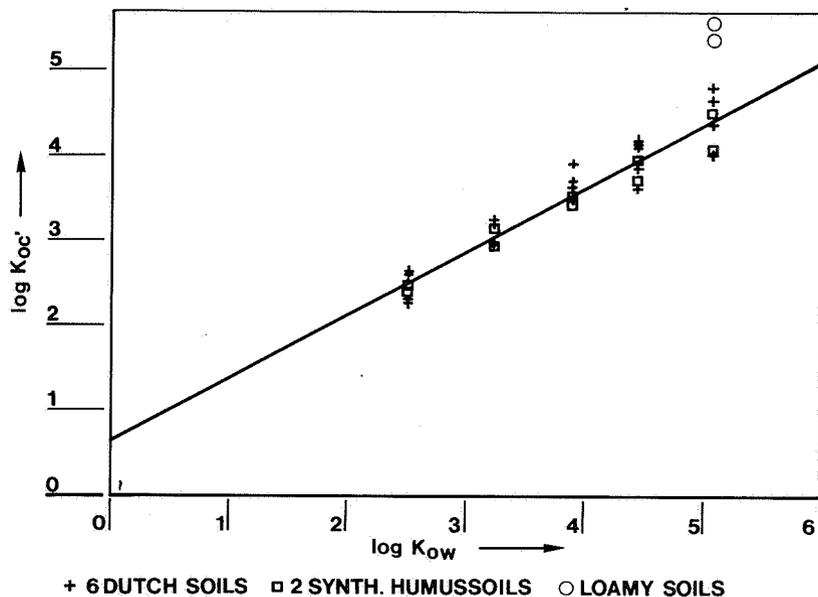


Figure 1. Log K'_{oc} versus log K_{ow} data for CPs in the examined soils. Data for PCP in loamy soils (o).

Desorption

For convenience the results from the SSDW experiments are presented in Table 3 in terms of log K_f and $1/n$ values. When applied in Equation 1, they give log q values which are consistently larger than those from sorption experiments at similar c values. Obviously, the desorption equilibrium is not attained within 24 h. Karickhoff and Morris (1985) estimated that solute diffusion in sediment particles is about a factor 10^6 slower than in bulk water. Analogously, the present result may be ascribed to very slow solute diffusion in humus. Notice that the $1/n$ data for sorption are only slightly smaller than those for desorption. This implies that the ratio of the non-extractable amount and the total amount of added CPs (NEF) is approximately independent of c under SSDW conditions. NEF values estimated according to Di Toro and Horzempa (1982) appear to increase from about 0.45 for MCP to 0.97 for PCP.

Even under the DB extraction conditions (sonication at pH = 9.3), the NEF values are still large (see Table 3). Under the DB conditions, the NEF values for the various CPs are not clearly related to their pK_a or K_{ow} values. However, they tend to increase with the amount of humus in the soil-water suspensions. The ratio NEF/humus for the natural soils appears to increase in the order: humic sand (Kootwijk) < humic sand (Rolde) \approx humic-rich sand < light loam < heavy loam < peat. Notice that this order is not related to the pH and f_{oc} of the soils. Obviously, the present results do not allow of a description of NEF data in terms of the variables used to describe the K_p values for CPs. From the diffusion and the two-compartment models by Karickhoff and Morris (1985) it may be expected that the NEF values increase with the incubation time, whereas according to Di Toro et al. (1982) also the soil/water ratio will influence the NEF value. Therefore, non-extractable residues in soil present an intricate, but important, phenomenon that should not be overlooked in leaching studies. Due to the slow desorption equilibrium, (bio-)degradation of CPs in the top-soil layer will become an important factor as well.

CONCLUSIONS

Sorption coefficients can be predicted within a factor 2 when $c < 0.5 \mu\text{mol dm}^{-3}$, $pK_a + 2 > \text{pH}(\text{soil})$ and when f_{oc} , f_{nd} and K_{ow} values are known. The vulnerability to leaching of CPs, based on K_f or K_p data, increase in the order: peat < humic-rich sand < humic sand (Rolde) < humic sand (Kootwijk) \approx heavy loam \approx light loam. This order is a result of decreasing f_{oc} and/or increasing pH values of the soils and will be maintained when non-extractable residue formation is taken into account.

Realistic estimates for leaching rates of CPs only can be expected from kinetic models that account for slow sorption-desorption and (bio-)degradation processes in the top-soil layer.

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TRANSFORMATION RATES OF CARBAMOYL-OXIME
PESTICIDES IN SOILS AND SUBSOILS :
CONSEQUENCES FOR GROUNDWATER QUALITY

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ABSTRACT

When carbamoyl-oxime pesticides like aldicarb and oxamyl are applied in spring, residues may remain in the soil in autumn and a fraction may leach from the soil with the rainfall surplus. In various regions, residues of aldicarb and oxamyl have been measured in ground water, with the highest concentrations in shallow wells near treated fields. The rate of transformation of carbamoyl-oximes in material from below the watertable shows tremendous variation, mainly dependent on redox potential and pH. In vulnerable regions, toxicologically based limiting values for drinking water can be met only when these pesticides are applied on a limited scale. Further studies on transformation in subsoil materials from vulnerable regions are needed.

1. INTRODUCTION

The carbamoyl-oxime pesticides aldicarb and oxamyl are mainly used for the protection of crops against nematodes in soil. In typical farming systems, for example with potatoes and sugar-beet, they are applied in spring at a rate of a.i. up to 3 kg/ha (aldicarb) and up to 4 kg/ha (oxamyl). These nematicides are applied at planting or sowing of the

crop in spring and they remain in the upper metre of the soil during the summer half-year, provided there is no excessive rainfall or irrigation. The amount of toxic residue remaining late in autumn is critical to the extent of leaching below 1 m depth. The adsorption of oxamyl and of the toxic oxidation products of aldicarb is only weak (Bromilow et al., 1980), so there is little retardation when these compounds are transported downwards by water flow.

Studies on the transformation rate of pesticides in material from the water-saturated zone have only been carried out in the last few years. The residence times of water plus dissolved substances in this zone is usually long, especially when wells are comparatively deep (as for public water supply). Even slow transformation results in a substantial reduction in the concentrations in pumped-up water. The carbamoyl-oximes have been used in transformation studies with subsoil material and the consequences for groundwater quality need to be evaluated.

When certain pesticide concentrations in the pumped water are estimated or measured, the question of toxicological significance arises. An evaluation scheme parallel to that for residues in foodstuffs may be followed, which strengthens the basis for possible measures taken to prevent or reduce contamination.

2. TRANSFORMATION IN SOIL AND LEACHING TO GROUND WATER

When aldicarb is applied in spring, substantial residues may still be present in autumn mainly in the top 0.3 m of the soil profile. After application to loamy soils, 4 to 7% of the dose was still present in autumn as the toxic oxidation products aldicarb sulphoxide and aldicarb sulphone (Smelt et al., 1983a). In the subsequent winter, 0.5 to 2.2% of the dose leached from 1 m long columns of these soils. The amounts of toxic residue remaining in humic sand soil in the autumn were distinctly higher: 17 to 20% of the dose. In winter, 10 to 16% of the dose leached from columns (0.8 m long) of this soil, mainly as the sulphone. These leaching patterns roughly corresponded to expectations based on computer simulations, after introducing adsorption coeffi-

cients and transformation rates measured in the laboratory (Leistra and Smelt, 1981).

The concentration of aldicarb residues in shallow ground water in an area with quite intensive potato growing in the north-east of the Netherlands can be estimated. Suppose that a rate of aldicarb of 3 kg/ha is applied in spring to fields with humic or peaty sand soils and that 15% of the dose leaches from soil (as sulphoxide plus sulphone) with a rainfall surplus of 300 mm in the winter half-year. The averaged concentration in water percolating below a depth of 1 m in the treated fields is then calculated to be 175 µg/l, expressed as the sulphone. Accounting for the other nematode control measures (crop rotation, growth of resistant cultivars, four other nematicides approved), it can be estimated that up to about 2% of a region may be treated with aldicarb per year. This estimate corresponds to the soil treatments compulsorily notified by the farmers to the Plant Protection Service. If 2% of the surface area in a region (e.g. a municipality) is treated with aldicarb per year, the average concentration in the water percolating in that region will be 3.5 µg/l.

In the Netherlands, aldicarb residues (22 µg/l; more than 90% sulphoxide) were measured in shallow ground water (2 m below the surface) in a sandy soil (pH 4.3) (Smelt et al., 1983b). A rate of aldicarb of 5.3 kg/ha was applied to this soil 18 months before. Later, concentrations up to 130 µg/l were found in shallow ground water below a field with sandy soil treated with aldicarb at 1.5 kg/ha in spring (Loch and Hoekstra, 1986). Aldicarb residues have been found in ground water in 15 states in the U.S.A. (Cohen et al., 1986). Many of the positive samples in the ground water of Long Island (New York) were in the range 1 to 50 µg/l, but some were higher. In the ground water of the Central Sand Plain (Wisconsin), the concentration of aldicarb residues ranged up to around 200 µg/l (Rothschild et al., 1982). The largest residues were found in comparatively shallow wells near potato fields. In the previous years, aldicarb was applied frequently at quite high rates and the amounts of rainfall plus irrigation were comparatively high.

The rate of transformation of oxamyl in various soils was found to be

fairly rapid; around 15°C, most half-lives were in the range 1 to 3 weeks (Smelt et al., 1979; Bromilow et al., 1980). However, in two soils with fairly low pH (5.4 and 5.2), half-lives were about 40 days. After application to such soils in spring, about 5% of the dose may be left at the beginning of the winter and a fraction of this could be leached from the soil. Oxamyl has been found in ground water in two states of the U.S.A. with positive samples ranging from 1 to 106 µg/l (Cohen et al., 1986; Kim et al., 1986).

3. TRANSFORMATION IN THE GROUNDWATER ZONE

Carbamoyl-oxime pesticides have been involved in some studies on the rate of transformation in subsoil material. Aldicarb sulphoxide and sulphone were incubated at 10°C in materials from 1 to 2 m depth within the groundwater zone of four fields.

The subsoils were in reduced condition and this was maintained during the incubations (Smelt et al., 1983b). The 50% transformation times for the sulphoxide were 6, 2, 3 and 27 days, respectively. The corresponding values for the sulphone were 6, 7, 8 and 131 days. The lowest transformation rates were measured for a subsoil with a comparatively high redox potential (Eh = 310 mV) and with a comparatively low pH of 5.0. After one of the anaerobic subsoils had been sterilized, transformation was not much retarded. This indicates that the transformation is catalysed by soil constituents in reduced state (Smelt et al., 1983b). The rates of transformation in the aerobic materials from above the watertable in the same profiles were much lower than those in the anaerobic materials.

The rates of transformation of oxamyl and methomyl in the four anaerobic subsoils were even faster: about 10% of the dose or less remained after one day (Smelt et al., 1983b). In a follow-up study, oxamyl was incubated at 20°C in three water-saturated subsoils, two with a fairly low and one with a high redox potential (Bromilow et al., 1986).

Transformation in the two subsoils with low redox potential was very rapid: it was largely complete within one day. On the contrary, transformation of oxamyl in the subsoil with high redox potential (500

to 600 mV) was very slow: for an incubation period of 120 days, there was no clear transformation. Similarly, there was no distinct transformation of the oxidation products of aldicarb in a period of 72 days in this water-saturated aerobic subsoil.

In incubation studies, ferrous ions occurring frequently in reduced subsoil conditions proved to be involved in the rapid transformation of carbamoyl-oximes. The reaction mechanisms and the products formed have been studied by Bromilow et al. (1986).

The results of a series of transformation studies with aldicarb sulphoxide and sulphone in materials from the groundwater zone were summarized by Jones (1986). Great differences in transformation rate were found, with half-lives at 25°C ranging from about a week to about a year. There was a tendency for comparatively slow transformation at lower pH (between 5 and 6). Extrapolation to a subsoil temperature of about 10°C indicates that half-lives in the field could range up to about 3 years. This was confirmed by one measurement at 13°C. Unfortunately, no redox potentials were reported for these studies.

In a series of measurements in shallow ground water (about 2 m deep) at thirteen places in the Netherlands, we found very great differences in redox potential: it varied from -250 to +600 mV. Most measurements indicated moderately reduced conditions. Great differences were found even at distances of less than 100 m. Changes from oxidized to reduced conditions with increasing depth and vice versa were found in the subsoil. The pH ranged from 4.4 to 7.2

Analysis of the composition of ground water pumped up gives an indication of the redox conditions in the main aquifer. In the north-east of the Netherlands, ground water for public water supply is usually pumped from 50 m or deeper. This ground water contained no free oxygen; it contained traces of H₂S; concentrations of iron were around 10 mg/l (Waterleiding Maatschappij Drenthe, 1982), so anaerobic conditions prevail in the main aquifers. The pH of this ground water is around 7.

4. RATES OF HYDROLYSIS

Studies on the rate of hydrolysis of pesticides in water are inte-

resting because they may provide a lower limit of the possible transformation rates in the groundwater zone. Rates of hydrolysis of carbamoyl-oximes in water with phosphate buffers at various pH values and at 25°C were reported by Chapman and Cole (1982). Comparatively short half-lives were found at pH 7 for aldicarb sulphoxide (0.44 year), the sulphone (0.21 year), methomyl (0.73 year) and oxamyl (0.03 year); at pH 8, these half-lives were even shorter. At pH 6, substantially longer half-lives were found: 1.9, 1.2, 1.0 and 0.3 year, respectively. At pH 4.5 (the lowest studied), these half-lives were found to be 1.6, 3.1, 1.1 and 5.8 year, respectively. These values should be extrapolated from 25°C to a common groundwater temperature of 10°C.

The rates of hydrolysis of aldicarb sulphoxide and sulphone in sterilized buffer solutions in water were studied by Hansen and Spiegel (1983). In an acetate buffer of pH 5.5 and interpolated between 5 and 15 °C to a common groundwater temperature of 10°C, they found half-lives of about 2 years for both compounds. In a phosphate buffer at pH 7.5, somewhat shorter half-lives were found. However these studies were relatively short (0.5 to 0.8 year) and the transformation pattern strongly deviated from a first-order pattern.

Rates of hydrolysis of the sulphoxide and the sulphone in ground water pumped from a depth of about 150 m (Florida) and at an initial pH in the range 7.7 to 8.5 were measured by Miles and Delfino (1985). The incubations were made under both aerobic and anaerobic conditions and some of the water samples were filtered (0.2 µm) beforehand to remove micro-organisms. At 20°C, the half-lives of sulphoxide were in the range 10 to 26 days and those for sulphone were in the range 4 to 33 days. No rates of hydrolysis were measured at lower pH.

5. TOXICOLOGICAL EVALUATION

Around 1980, the National Academy of Sciences in the U.S.A. recommended a limiting value of 7 µg/l for aldicarb residues in drinking water (Zaki et al., 1982). Below this value, the water was considered to be suitable for human consumption, whereas action had to be taken

to prevent consumption above this value. The calculation of this limit was based on the following assumptions (Guerrera, 1981; Zaki et al., 1982):

- the acceptable daily intake (ADI) is 0.001 mg/(kg d);
- the mass of a person is 70 kg;
- the water consumption is 2 l/d;
- 20% of the ADI is reserved for possible residues in drinking water.

This limit of 7 µg/l was adopted by the New York State Department of Health for actions to protect consumers against aldicarb residues in Long Island ground water. These actions included termination of water pumping from various wells and the installation of activated carbon filters for purification.

The Joint Meeting of FAO and WHO (1983) published a new "estimate of acceptable daily intake for man" of 0 to 0.005 mg/(kg d) for aldicarb residues. According to the calculation scheme, the new maximum concentration would become 35 µg/l.

An ADI of 0 to 0.03 mg/(kg d) was established for residues of oxamyl by the Joint Meeting in 1984. In combination with the assumptions above, this leads to a calculated limit of 210 µg/l for oxamyl in drinking water. The New York State Department of Health established a preliminary guideline of 50 µg/l for oxamyl in ground water (Kim et al., 1986).

The Council of the European Communities (1980) published a directive relating to the quality of water intended for human consumption. The maximum admissible concentration of pesticides and related compounds was set at 0.1 µg/l for a single compound and at 0.5 µg/l for the compounds together. The establishment of these values in the directive did not have a toxicological basis.

6. GENERAL DISCUSSION

Measurements of pesticide residues in shallow ground water evoke questions about their behaviour in the groundwater zone. Transformation rates can be measured in incubations with subsoil, in which the

conditions in the relevant groundwater zone should be closely simulated. Hydrolysis, catalysis and microbial activity may play a part. Further studies on the carbamoyl-oximes should concentrate on the most vulnerable areas with topsoils of fairly low pH and with aerobic ground water having a fairly low pH. The transformation of carbamoyl-oximes under certain groundwater conditions is very slow. However accurate measurements of rates are scarce. More attention is needed to the characterization of the conditions in the groundwater zone; there is a paucity of measurements of the redox potential.

Transformation rates of the carbamoyl-oximes can be introduced into computations with models simulating flow of water and behaviour of residues in particular groundwater-extraction areas. Recently, a review of this approach has been given by Leistra (1986).

The leaching of the carbamoyl-oxime pesticides to ground water had consequences for their status in the registration process. In certain regions of the U.S.A., registrations of aldicarb and oxamyl were cancelled and requests for extension of the registration were not granted (Creeger, 1986). In the Netherlands, no approval was given to extensions of the use of aldicarb in some crops grown in areas that seemed vulnerable to groundwater pollution by this pesticide. Additional research may be needed on the transformation in the groundwater zone before extensions of the registration can be considered.

In some countries, including the Netherlands, groundwater-extraction areas for public water supply are protected against pollution. The size of the protection zone corresponds roughly to the zone in which the residence time of water in the main aquifer is up to 25 years. The use of pesticides presenting a risk to groundwater quality, such as aldicarb, is not allowed in these zones. When a pesticides is applied outside the protection zones, it takes several years before possible residues reach the aquifer and after that it takes at least 25 years before the wells are reached. This provides ample time for transformation.

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VULNERABILITY OF GROUNDWATER TO PESTICIDE LEACHING

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ABSTRACT

The upper groundwater below agricultural fields on four vulnerable Dutch soils was sampled and analysed for residues of twelve pesticides. The soils have high water permeability and low binding capacity for residues of pesticides. The group of pesticides includes both compounds admitted and banned in Dutch groundwater protection areas. Atrazine, aldicarb, dinoseb and 1,3-dichloropropene are detected in a number of sampling tubes. Atrazine and dinoseb are admitted in groundwater protection areas. Conclusions are drawn with respect to admission requirements of pesticides.

1. INTRODUCTION

By order of the Ministry of Environment of The Netherlands a survey is being carried out of the presence of frequently applied pesticides and their metabolites in the groundwater in agricultural areas. In a first screening sampling is limited to the upper groundwater below agricultural fields on soils with high water permeability, low adsorption capacity for pesticides and shallow groundwater table. All pesticides selected for analysis have been tested in the laboratory for persistence and mobility in soils. These tests are prescribed by the Dutch government and carried out by the pesticide industry for admission purposes. In the admission procedure specific attention is given to use within groundwater protection areas. In these areas a pesticide is admitted if its chances of reaching the groundwater table are small or absent. The selected pesticides in this survey represent a wide range of mobility and persistence. Thus this investigation is a

check of the reliability of laboratory studies for admission purposes, specifically for permeable soils with low retention for solutes.

2. SELECTION OF SOILS, LOCATIONS AND PESTICIDES

2.1 Soil types and cultures

Selection of locations to be sampled was guided by the following criteria:

- The groundwater is vulnerable to leaching from the unsaturated zone. Soils with high water permeability and low retention capacity for organic xenobiotics meet this criterium. This implies soils with low content of clay and organic matter. Pronounced examples are soils with a thin, low-humic top layer upon a coarse-sandy subsoil. Another vulnerable group of soils is that with a high clay percentage in the surface layer, on top of a coarse-sandy subsoil. By dessication the top layer may develop cracks, which act as preferential flow paths for water (Bouma et al., 1978).
- Absence of impermeable layers and perched water tables.
- Depth of phreatic surface < 2.5 m.
- Yearly variation of phreatic surface < 1.5 m.
- The types of cropping have been practiced for many years over a vast area in the region, with regular use of the same pesticides.
- The soil type on each location is as homogeneous as possible over an area of ≥ 5 ha.

Thus the following cultures and soil types were selected. Soil nomenclature is derived from the Dutch soil classification system (De Bakker en Schelling, 1966). In parentheses the classification in the U.S. 7th Approximation is added.

- Flowerbulb culture on "Vlakvaag"-soil (Typic Psammaquent).

A Vlakvaag-soil is a low-humic sandy soil which among other places is found on levelled beach ridges behind the coastal dunes in The Netherlands. The selected location is between Hillegom and Lisse. Figure 1 gives a profile description. In figures 1 through 4 the average highest and lowest phreatic levels are indicated with arrows in the filter tubes.

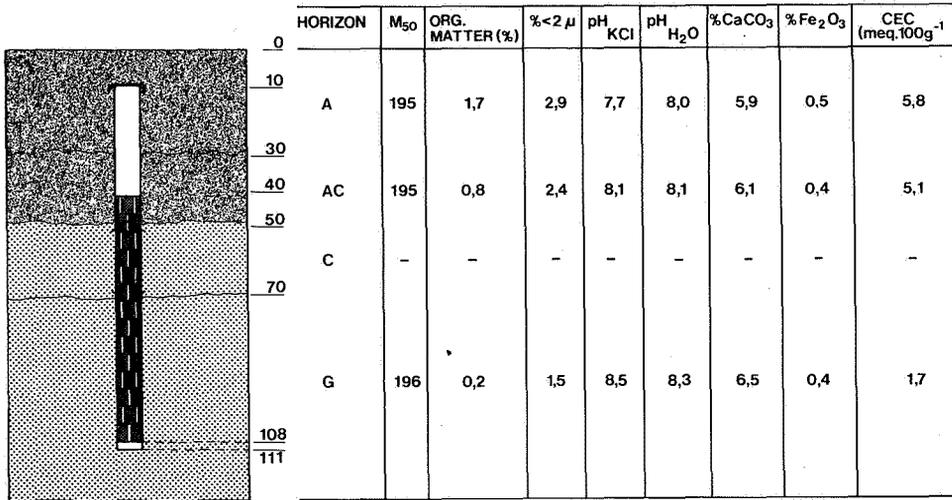


Figure 1. Soil profile description and filter location of the Vlakvaag-soil near Hillegom

- Industrial potatoes on "Gooreerd"-soil (Spodic Humaquept).

In The Netherlands industrial potatoe culture largely takes place in the northeastern provinces of Groningen and Drenthe. In the last few centuries the vast peat-moor in this region has been dug off. The plow layer now exists of a mixture of sand and peat remnants. The selected location is on a low- to moderately-humic sandy soil near Ter Apel. The soil type resembles a low-humic "veld"-podzol of which the typical B horizon is lacking. In most of the region, a crop rotation with 50% industrial potatoes is common practice. Figure 2 gives a profile description.

- Maize on "Gooreerd"-soil (Spodic Humaquept).

Maize culture has expanded rapidly on the eastern and southern sandy soils of the Netherlands during the past 15 years. In the province of Noord-Brabant, near Bergeijk, a location was found on a moderately humic sandy soil with a coarse sandy C-horizon, classified as a gooreerd-soil. On the selected parcels maize has been grown nearly continuously for over 20 years. Figure 3 gives a profile description.

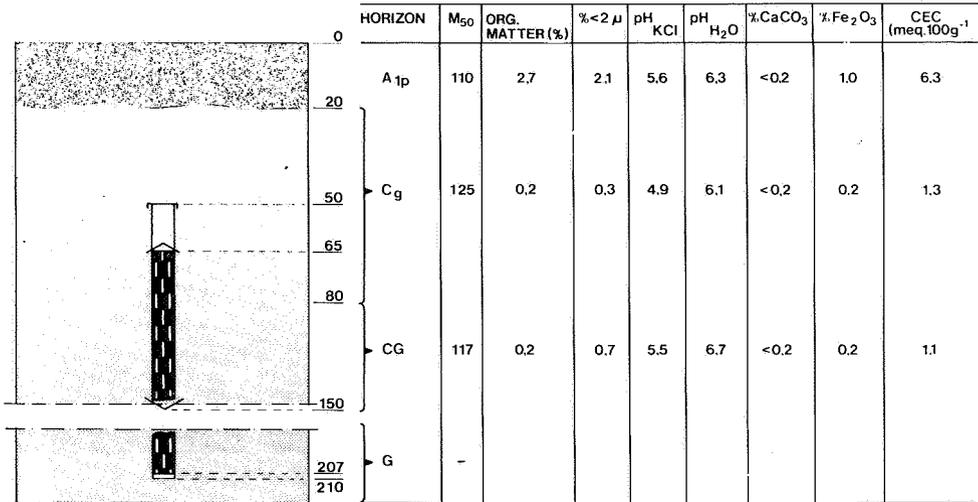


Figure 2. Soil profile description and filter location of the Gooreerd-soil near Ter Apel.

- Orchard on "Poldervaag"-soil (Typic Fluvaquent) and "Ooivaag"-soil (Fluventic Eutrochrept).

In the central part of the Netherlands the mechanism of deposition by meandering rivers created a succession of low flood basin deposits, with a high clay content, and high levée ridge deposits, consisting of coarser materials. Orchards used to be on the ridge deposits. On ridge deposits near Geldermalsen a low-humic light clay soil, becoming coarser with depth, with a sandy C-horizon was selected. The soils are classified as calcareous Polder- and Ooivaag-soils. Figure 4 presents a profile description.

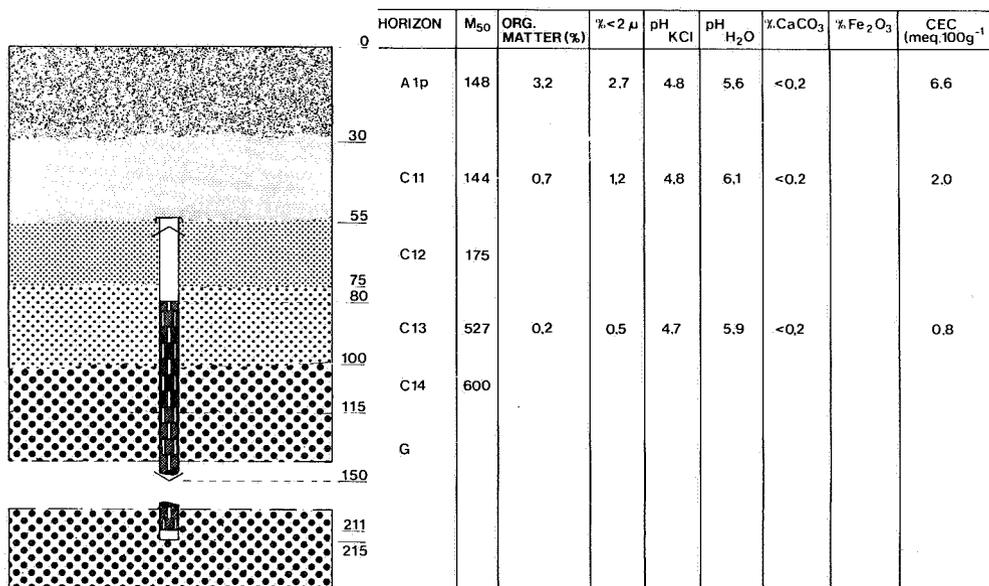


Figure 3. Soil profile description and filter location of the Gooreerd-soil near Bergeijk

2.2 Pesticides

Pesticides to be analysed were selected with the following criteria:

- They should be applied since several years in the four selected cultures.
- The applied dosages and/or frequency of use should be relatively high.
- Compounds should represent a broad range of mobility and persistence.

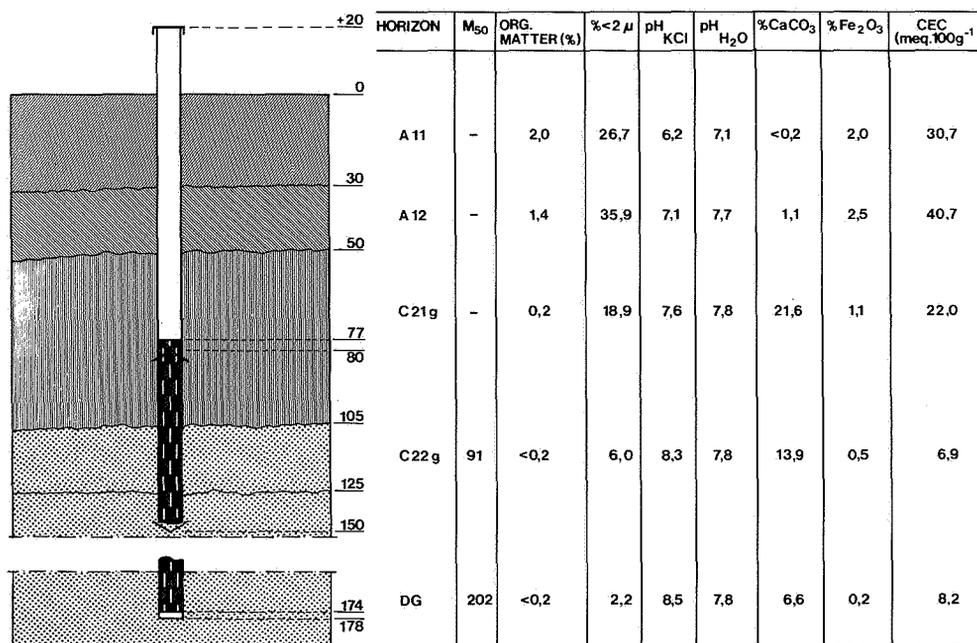


Figure 4. Soil profile description and filter location of the calcareous Ooivaag-soil near Geldermalsen.

The pesticides selected are presented in Table 1, along with their mobility, persistence and admission status in groundwater protection areas in the Netherlands. For maneb and metam-Na the metabolites ethylenethiourea (ETU) and methylisothiocyanate (MIT) respectively are analysed. For aldicarb the total concentration of aldicarb, aldicarb-sulfon and -sulfoxide are determined. For fentinacetate total tin is determined. The degree of mobility in Table 1 is based on a classification according to adsorption-coefficient and retardation-factor, comparable with the classification by Helling (1971). Admission in groundwater protection areas is based on mobility and persistence of both parent compound and metabolites, and on time of application.

3. MATERIALS AND METHODS

On each of the four selected locations five filter tubes for groundwater sampling were installed. The filter tubes were placed as much as possible in the middle of the cropped parcels. In order not to disturb tillage operations, the tops of the tubes in the bulb-, maize- and potatoe-regions are buried below soil surface. Only in the orchards the tops are above ground. The 100-200 cm long tubes are made of stainless steel. Their inner diameter is 57.5 mm. The filters were placed so that the upper groundwater (< 1.5 m below the phreatic surface) is sampled. Therefore the composition of the collected water is determined by the local soil treatment.

Sampling takes place with a submergeable pump. From the pump the groundwater is fed into a teflon filtering unit where, at N_2 -overpressure, it is led over a 0.45 μ m filter of cellulose nitrate and collected in a glass bottle for analysis. Sampling and subsequent analysis took place respectively in July and October 1985, and March, June and November 1986. Sampling is continued.

4. RESULTS AND DISCUSSION

For most compounds concentrations are below the detection limits. Atrazine; dinoseb; 1,3-dichloropropene and aldicarb were detected in a number of filters (Table 2). Included in this table is the application history of the four compounds detected. The influence of application history is only evident for dinoseb. Filter 3, which shows highest dinoseb concentrations, is located on the parcel which received the highest dosage ($8.3 \text{ kg}\cdot\text{ha}^{-1}$, partly as leaf killer). All filters on the parcels where dinoseb was applied in 1985 showed detectable concentrations at least once.

In the periods June 1 - October 1, 1985 and April 1 - October 1, 1985 (the time between the last application and the first observation of respectively dinoseb and aldicarb) the net precipitation was respectively < 5 cm and < 0 cm. Therefore it is not expected that dinoseb and aldicarb reach the phreatic surface within these periods. On the other hand residues of aldicarb and dinoseb (as leaf killer) are

Table 1. Selected pesticides, their persistence, mobility and admission status in Dutch groundwater protection areas.

culture	compound	mobility	DT ₅₀ (days) 10-25 °C	admission status ¹⁾
maize	atrazine	moderately mobile	40-130	white
	alachlor	moderately mobile	8-38	black
potatoes	1,3-dichloro- propene	mobile	3-45	black
	aldicarb	very mobile	22-44(aldicarb)	black
	DNOC	mobile	6-42	white ²⁾
	dinoseb	mobile	7->168	white
	fentinacetate	slightly mobile	4-100	white
	ethylene- thioureum(ETU, metabolite of Maneb)	mobile	<7(ETU) 28-56(Maneb)	white
	orchard	amitrole	mobile	2-61
captan		slightly mobile	1-42	white
flowerbulbs	chlorpropham	slightly mobile	43, 65	white
	methylisothio- cyanate	>moderately mobile	<1 (metam-Na)	
	(MIT, metabo- lite of metam- sodium)		<21 (MIT)	white

1) white = admitted; black = not admitted

2) application not allowed between October 1 and April 1.

transferred to some depth by tillage shortly after application. Besides a small temporary excess of precipitation can cause substantial downward movement. These factors, in combination with preferential flow paths may explain the earlier than expected arrival of these pesticides in the upper groundwater. The presence of 1,3-dichloropropene in the

Table 2. Concentrations of the compounds detected in groundwater samples

crop	pesticide	dosage (kg.ha ⁻¹)	filternr.	applied in												concentration*(µg.dm ⁻³)				
				'79	'80	'81	'82	'83	'84	'85	'86	July '85	Oct. '85	March '86	June '86	Nov. '86				
maize	atrazine	0,5-1,2	1	+	+	+	+	+	+	+	+	+	+	+	0,3	0,2	0,36	0,09	0,09	
		"	2	+	+	+										<0,3	0,1	0,17	<0,08	0,02
		"	3	+			+									0,5	0,5	0,58	0,23	0,16
		"	4	+			+									0,3	0,2	0,23	0,08	0,14
		"	5	+			+									0,4	0,2	0,29	0,15	0,09
potatoes	dinoseb	1,4	1				+								<0,3	<0,1	<0,1	<0,1	<0,1	
		2,5-6,3	2				+								<0,3	0,2	0,1	<0,1	<0,1	
		8,3	3	?	?		+								<0,3	5,0	9,2	4,6	0,78	
		2,5	4				+								<0,3	<0,1	<0,1	<0,1	-	
		2-2,5	5				+								0,3	0,1	0,1	0,1	<0,1	
"	aldicarb	-	1											-	-	-	-	-	-	
-		2												<2	-	-	-	-	-	
1,5		3												-	130	4,5	14	25		
-		4												<2	-	-	-	-	-	
-		5												-	-	-	-	-	-	
"	1,3-dichloro-propene	225	2				+								<1	<1	<0,5	<0,5	<0,5	
180		3					+								<1	<1	<0,5	<0,5	<0,5	
180-225		4				+									80	<1	<0,5	<0,5	<0,5	
210-225		5				+									30	3	<0,5	<0,5	<0,5	

*) < = below the detection limit

- = not analysed

upper groundwater 8 months after application can be expected from net precipitation and from downward gaseous diffusion after its application by injection. Its degradation in winter will be strongly reduced.

The relatively steady concentration of atrazine is an indication of a continuously present amount of atrazine residu in the plow layer. Long-term application of atrazine on the parcels has led to accumulation in this layer. From this supply a steady flux of solute leaches to the groundwater. Loch et al. (1985) find in column experiments that atrazine, while leaching from a podzol soil, is still present in the surface layer a year after application.

The overall decrease of concentrations of aldicarb; 1,3-dichloropropene and dinoseb in this investigation will be due to convective discharge to deeper groundwater and/or in situ degradation. Further analysis is required to distinguish these processes.

5. CONCLUSIONS

Of the pesticides atrazine; dinoseb; 1,3-dichloropropene and aldicarb part of the dosage reaches the groundwater in vulnerable soils under Dutch climatic conditions. The measured concentrations exceed the EC-guideline value for pesticides in drinking water. The vulnerable soils are sands with a thin A_1 -horizon (< 30 cm) of low organic matter content (< 4%) immediately overlaid with a C-horizon, and with an average lowest phreatic surface < 1.5 m below soil surface. They belong to the subgroup of Gooreerd-soils, in the U.S. classification named Spodic Humaquepts.

The present ban of aldicarb and 1,3-dichloropropene in groundwater protection areas in the Netherlands is supported by the observations. Atrazine and dinoseb apparently reach the upper groundwater in vulnerable soils whereas they are admitted within these areas. It is concluded that the admission procedure should pay more attention to pesticide behaviour in vulnerable soils.

If the four pesticides mentioned are applied on the indicated soils near private water wells, extracting water from shallow depth, chances

of contamination of drinking water are real. Whether, if applied outside groundwater protection areas, these compounds will reach (public) water supplies, depends on their degradability in the aquifer environment. This is unknown for most pesticides and urgently needs investigation.

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STRATEGIES FOR THE CONTROL OF UNDERGROUND CONTAMINATION
BY CHLORINATED HYDROCARBON SOLVENTS

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ABSTRACT

Use and handling of chlorinated hydrocarbon solvents led to subsurface and groundwater contamination in different cases in recent years. Thus it was necessary to develop and realize strategies for the recognition and evaluation of these subsurface pollutants, monitoring of groundwater contamination and ways of rehabilitation.

1. INTRODUCTION

Volatile organic pollutants have been detected in soil air, soil and groundwater at different sites. Such substances have been identified through improved analytical methods which make use mainly of gaschromatography. These analytical techniques allow the detection of synthetic organics at extremely low levels. Most frequently detected compounds are 1,1,1-trichloroethane, trichloroethene and tetrachloroethene because of their widespread use.

If pollution has taken place in catchment areas of drinking water supplies or even in the vicinity of groundwater wells used for potable water, complex control strategies are necessary to determine type and extent of contamination before restoration measures can be undertaken. The investigations follow three phases : screening, preliminary and main

investigations, in that order. The remedial action to be taken is indicated by results of these investigations (Figure 1).

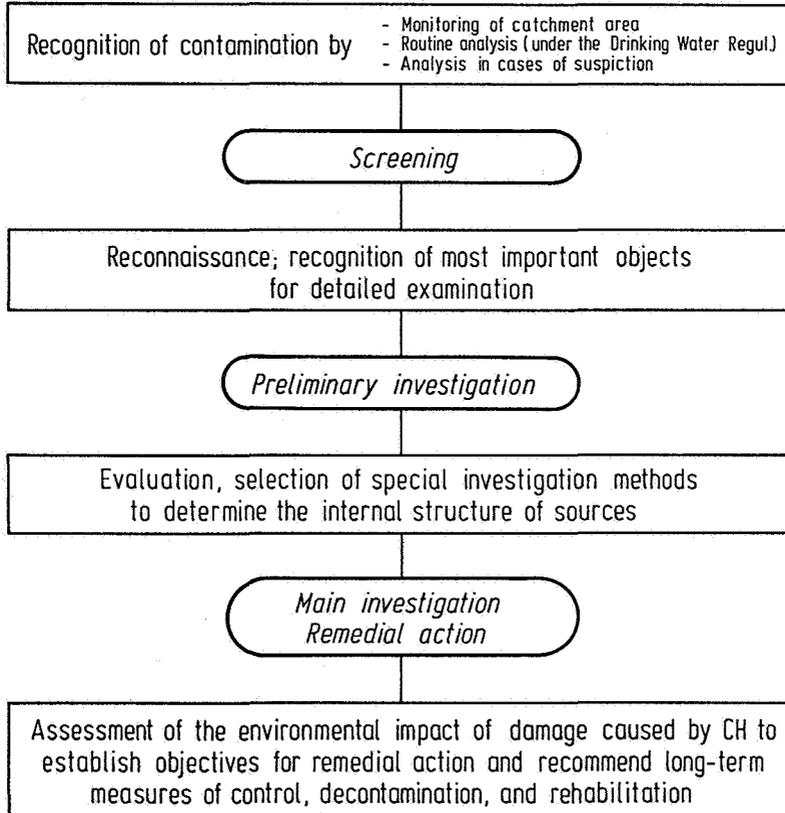


Figure 1. *Recognition, localisation and evaluation of subsurface contamination by readily volatile chlorinated hydrocarbons (CH)*

An example of severe and extensive underground contamination in the neighbourhood of a high capacity water works fed by a pleistocene aquifer is presented.

2. BACKGROUND INFORMATION

Wide experience with groundwater contamination has shown that it is necessary to have detailed knowledge about the spreading and reaction of pollutants in the subsurface before it is possible to start a successful

rehabilitation programme. Control and corrective measures means stopping the introduction of pollutants into the unsaturated zone during their technical use. Principally remedial measures include decontamination (such as in situ measures) and elimination of chlorinated hydrocarbons from the unsaturated and saturated zone (vacuuming up soil air and purifying groundwater). It seems important, for the planning of investigation work, that different methods are considered in order to determine the degree of contamination. This is necessary since the cause and the extent of damage are not known.

3. METHODOLOGICAL STEPS FOR RECOGNITION, LOCALIZATION AND EVALUATION OF SUBSURFACE CONTAMINATIONS

3.1 Recognition

Readily volatile chlorinated hydrocarbons in groundwater can be recognized by :

- monitoring of catchment areas (analysis of groundwater samples)
- routine analysis (according to Drinking Water Regulations) and
- analysis in cases of suspicion

3.2 Screening

If chlorinated hydrocarbons are detected, a screening process should be initiated.

In order to get a clear picture of all the factors which contribute to contamination it is necessary to record all data of the following phases of investigation :

- investigation of the hydrological situation
- determination of the extent of contamination by taking samples from all available wells in the catchment area
- survey of the handling of chlorinated hydrocarbons

The screening process results in the documentation of all accumulated information and data, which are presented in tables and maps, and provide the basis for the following investigations.

Subsequently that it is possible to recommend immediate measures, for instance, close wells which supply raw water and/or stop all readily apparent introduction of chlorinated hydrocarbons into the subsurface. The areas which need further investigation can be determined on the basis of the screening results and the results of the first counter-measures taken.

3.3 Preliminary investigation

Evaluation of the expected pollution in certain areas at first includes the following activities : sampling in and analysis of the unsaturated zone :

- soil air
- soil

the saturated zone :

- groundwater

areas of handling of chlorinated hydrocarbons :

- sewage and wastes
- surface water.

Furthermore it is important to record in detail the handling and operating conditions of chlorinated hydrocarbons by means of questionnaires and inspections in the respective areas. After having evaluated all data obtained from the preliminary investigation it is necessary to initiate intermediate-term measures for control and decontamination. Special methods of investigation to determine the internal structure of the contamination sources must be undertaken as well.

3.4 Main investigation

The main investigation programme includes a very detailed investigation of soil air, soil and groundwater to determine the horizontal and vertical distribution of chlorinated hydrocarbons at the individual contamination sites. This includes different drilling activities. The search for causes of contamination, e.g. losses and leakages, also

include studies of process engineering of chlorinated hydrocarbon usage. Data from all these investigations allow to delineate the contaminated sites and plumes of pollution as well as the potential hazard for the subsurface and thus for drinking water. The elimination of operation-related sources of contamination and introduction of preventive measures are the most important steps to be taken in the area of the user of chlorinated hydrocarbons.

On the basis of all the investigation results it is possible, and necessary, to recommend and carry out a monitoring programme to observe the development of the concentration of chlorinated hydrocarbons in groundwater. It is also important to look for possible degradation products in groundwater, like *cis*-1,2-dichloroethen and vinyl chloride which were found in this case.

3.5 Remedial action

The assessment of the environmental impact of pollution caused by chlorinated hydrocarbons is decisive in establishing the objectives of remedial action, which includes, in general, long-term measures of control, decontamination and rehabilitation by withdrawal of contaminated soil air and groundwater. The latter should be purified and, if possible, recirculated, so that groundwater resources are not exhausted. The detailed technical performance and management of this restoration depends on the position of the contamination site in relation to a water catchment area and on the geological and hydrogeological situation in and around the contaminated sites.

4. RESULTS

The strategies described are a result of a project where the contamination of the catchment area of a high capacity water works was investigated over a period of several years. They may serve as a model of general applicability in similar cases.

4.1 Recognition

When recognizing a pollution of about $50\mu\text{g}/\text{l}$ of chlorinated hydrocarbons in the raw water of two or three batteries of wells tested, it became clear that detailed investigation was necessary. The following analysis of the water of all 51 wells showed that 10 wells were contaminated with more than $25\mu\text{g}/\text{l}$ (up to a maximum of $2000\mu\text{g}/\text{l}$).

4.2 Screening

The geological and hydrogeological situation as well as technical and well output data showed the following :

The aquifer is composed of medium fine to fine sand and has a thickness

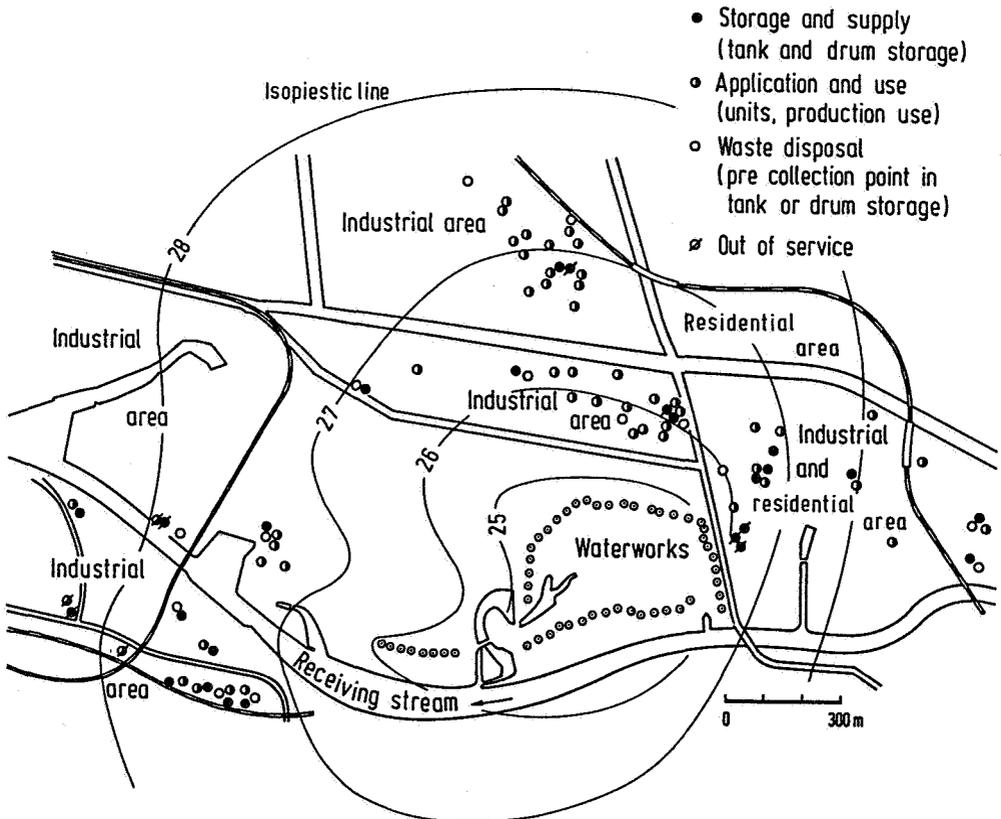


Figure 2. Hydrogeological situation and sites of handling and use of CH

of 35m. The permeability is good to very good. Each well is, on the average 40m deep and yields between 50 and 130m³/h. The daily pumping rates are 50 - 60.000m³ water.

The survey of the handling of chlorinated hydrocarbons in the vicinity of the water works shows that nearly 300.000 kg/a of these solvents are used. Only one fifth of this amount was eliminated by waste disposal. 83 places of handling were recorded (Figure 2).

On the basis of the initial survey it was found necessary to divide the investigation area into individual zones of contamination due to unknown sources of contamination, size of investigation area, number of establishments, type of business using chlorinated hydrocarbons.

4.3 Preliminary investigation

The fundamental principles for establishing the appropriate sampling and analyses procedures for chlorinated hydrocarbons were described i.a. in Schwille (1984), DVGW Review (1981) and Dähne (1982).

The preliminary investigation of soil air analysis was based on the description of the sampling technique by Neumayr (1983), Harres and Holzwarth (1983) and Gutöhrlein (1985). In the investigation area, a total of 1.400 soil air samples were taken and analysed by gaschromatography with the gaschromatograph PYE Unicam 204. Thus it was possible to subdivide the area into sections with comparable soil air concentration: up to 200µg/m³ (as background level in the respectively area); up to 100.000µg/m³ (handling areas); and up to 7.000.000µg/m³ (centres of contamination) (Figure 3).

The soil investigation, carried out in the areas of maximum concentration, gave information about the distribution of chlorinated hydrocarbons in the soil. The method of analysis principally used was the "multiple headspace extraction", described by Kolb et al (1982), followed by gaschromatography using gaschromatograph HS 100/Sigma 2000 Perkin Elmer. Concentrations between a few µg/kg as background level and 1.000.000µg/kg in the centre were found.

The investigation of water (ground, surface and waste water), also by using the headspace method, showed a different distribution of chlorinated hydrocarbons. When analyzing groundwater in the catchment area

only $1\mu\text{g}/\text{l}$ could be detected, but in a few sections, up to $15.000\mu\text{g}/\text{l}$ were found. The latter areas could be delineated in most cases by means of soil air analysis.

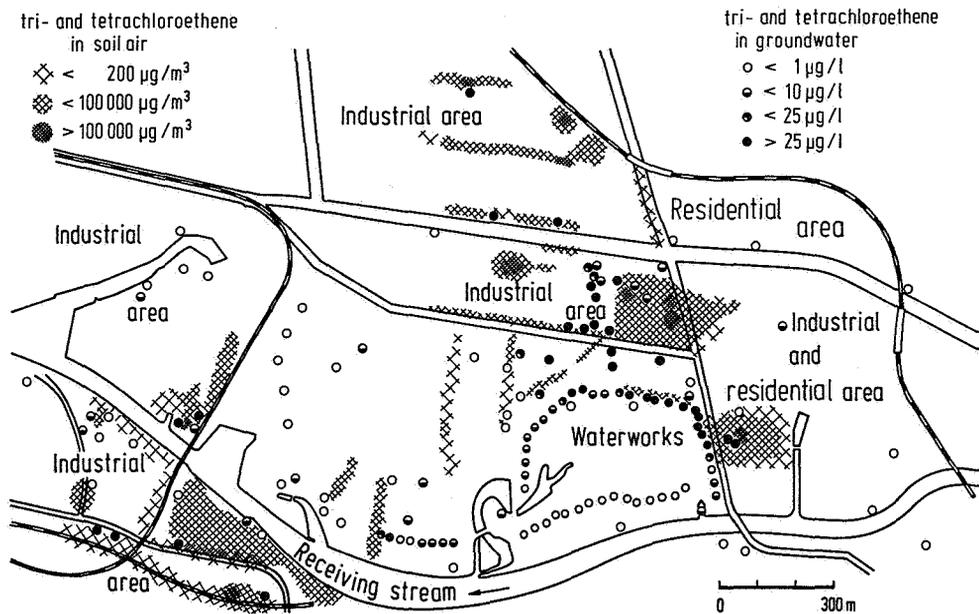


Figure 3. Groundwater and soil air contamination in the area of investigation

Surface water could be eliminated from the list of suspected sources of pollution, since it contained only a few $\mu\text{g}/\text{l}$. Investigation of the waste water was also very important. An examination of sewers which drain polluted waste water with high concentrations of chlorinated hydrocarbons (sometimes up to $120\text{mg}/\text{l}$) for possible leakages often proved to be successful.

4.4 Main investigation

The determination of the horizontal and vertical distribution of chlorinated hydrocarbons in the contaminated sites was made possible through the use of flexible inner tube core drilling and probing of bores. Soil air and soil samples were taken at points differing by $0,50\text{m}$ in depth.

The horizontal distribution of chlorinated hydrocarbons in groundwater

was determined by sampling in all available wells, mainly the newly installed monitoring wells in the individual zones of contamination. The vertical distribution in the aquifer could be determined by sampling in the well with a pump and a 2m packer. The pumping time was fixed at 15 and 60 minutes. So it was possible to locate the exact position of the well in relation to the actual centre of contamination or the respective plume of contamination.

The investigation of leakages in sewers and waste water collecting reservoirs was at first carried out on an ever-increasing scale and then stopped as leakages were discovered.

4.5 Remedial action

After cessation of all leakages, long-term measures to restore the contaminated sites were initiated. In the majority of cases soil air as well as groundwater were withdrawn from the sites and the effect of the concentration of chlorinated hydrocarbons in the groundwater were monitored. The groundwater was purified by stripping. By this the concentration of chlorinated hydrocarbons in a well decreased from 360µg/l to 10µg/l during one and a half year. In another well it was possible to reduce the pollution load from 2000µg/l to 50µg/l within one year. The necessary pumping quantities were about 700.000 and $1 \cdot 10^6 \text{ m}^3$, respectively. All measures taken were long-term activities.

5. CONCLUSION AND RECOMMENDATIONS

- All results of the three phases of investigation and remedial action such as concentration of chlorinated hydrocarbons, groundwater level differences etc. should be very carefully recorded.
- During the restoration measures water and soil air should be purified before released into the aquifer or atmosphere.
- Systematic monitoring of water catchment areas will provide protection of groundwater for drinking water supply and can help to recognize cases of pollution at a very early stage.

- Absolute prevention of a further introduction of harmful substances as well as remedial action against subsurface contamination are of importance in all these cases.

NOTES

- ¹All above mentioned concentrations of chlorinated hydrocarbons are given as sum of single substances of all volatile chlorinated hydrocarbons, tri- and tetrachloroethene being the main pollutants in the most cases.
- ²In the Federal Republic of Germany in general there are three zones of protection around water works. They cover areas up to different distances from the wells: zone I (10m), zone II (100m), zone III (varying distances depending on the hydrogeological situation).

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GROUNDWATER POLLUTIONS ON THE AREAS OF PETROCHEMICAL FACTORIES

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1. INTRODUCTION

In this paper results of 3-years long investigations on groundwater pollutions on the area of petrochemical factory are presented.

2. GEOLOGY

Taking into consideration the results of 2500 shallow bore-holes geological maps on the depths of 0, 1, 2, 4, 6 and 8 m were elaborated. In the zone investigated by bore-holes quaternary deposits were identified: boulder-clays, gravels, sands and silts. On the investigated area were found two glacial troughs, eroded in boulder-clays and filled with sands and gravels. These two troughs have general direction NW-SE and are separated by boulder-clay gibbosity.

3. HYDROGEOLOGY

The groundwaters were found in the sands, filling the glacial troughs as well as in the sandy interbeddings in boulder-clays. Geological section confirmed that waters in sandy interbeddings have a junction with the waters in the troughs. The map of watertable countours has proved, that the groundwater runoff from the area of the factory in SE direction.

4. GROUNDWATER QUALITY INVESTIGATIONS

Investigations of groundwater pollution were executed in 10 points on the factory area. The tests were carried on during 3 years, one per week. The content of: sulphates, chlorides, nitrates, phenols, iron, hydrocarbons as well as the value of pH, total hardness and oxygen consumption were determined. Analysis of contents of the components mentioned above takes into consideration such sources of pollution as: atmospherical precipitation, over-flood of chemicals on the surface and leaks from sewage system.

The results of investigations were analysed in comparison with Polish Standard for drinkable water.

Results of determinations are shown in Table 1.

Undrinkability of waters was mainly caused by presence of hydrocarbons and high concentrations of phenols, iron and periodically high total hardness and O_2 consumption.

Presence of hydrocarbons and phenols was result of surface overflow and increases in time.

High content of iron especially in waters in sandy interbeddings in boulder-clays, may be explained by complex formation with dissolved phenols.

High total hardness was coupled with existence of great contents of Mg^{2+} and Ca^{2+} (up to 1000 mgdm^{-3}).

High oxygen consumption was caused by presence of phenols and hydrocarbons.

The quantity of sulphates and nitrates was higher than allowed by Standard only in some periods and in few points.

Considerable quantitative differences were identified between the water samples taken from different piezometers situated in the same aquiferous layer as well as great changes of content of the respective components were observed in the successive samples taken from the same piezometer. The pollution was a result of direct infiltration to the soil from defected sewage system or surface overflow as well as an indirect infiltration from polluted atmospheric falls. The reaction of groundwater changed generally to the basic.

Table 1. Average values of determined quantities and concentrations

Determination	Number of piezometer										Polish
	2	8	9	11	12	20	21	50	53	58	
pH	7,70	7,6	8,2	7,1	7,7	7,5	7,6	7,6	7,6	7,3	6,5-8,5
SO ₄ ⁻ /mgdm ⁻³	186,0	148,0	40,0	39,0	47,0	123,0	130,0	142,0	150,0	113,0	200
Cl ⁻ /mgdm ⁻³	12,0	11,0	10,0	13,0	15,0	15,0	16,0	24,0	33,0	20,0	250
NO ₃ ⁻ /mgdm ⁻³	0,83	1,0	0,68	0,88	0,54	7,89	1,59	0,55	0,43	3,04	10
Fe ^{tot} /mgdm ⁻³	112,0	94,0	84,0	109,0	81,0	69,0	74,0	181,0	94,0	229,0	0,5
total hardn.											
mval CaOdm ⁻³	6,3	6,2	3,6	13,6	5,4	6,2	7,3	11,4	10,4	4,2	10
phenols mgdm ⁻³	0,18	0,29	0,45	0,89	0,54	0,56	0,43	0,53	0,53	0,13	0,02
O ₂ consump											
mgO ₂ dm ³	15,2	20,6	23,1	165,4	35,8	17,7	19,8	14,4	17,0	10,2	5
hydrocarbons											
% vol				10							3

5. CONCLUSIONS

1. Groundwater pollutions appear as a result of industrial activity of factory. Pollution agents infiltrated directly into aquiferous layer from surface overflows, sewage leakage and indirectly with atmospheric falls.
2. Hydrocarbons presence above the groundwater table changes its chemism: increase acidity, electrochemical potential change to more negative values, increase total hardness and O_2 consumption. Also content of phenols rapidly increases.
3. Sulphates and nitrates concentrations change depends on season.
4. Generally reaction of groundwater change to basic.
5. Although there were many sulphates sources, their concentrations decrease with time.
6. For prevention of pollutions propagation out of factory area depression well system was designed on water runoff line for lowering water table. The last investigations showed, that polluted groundwater do not leave factory area.

BEHAVIOUR OF CERTAIN INSECTICIDES AND FUNGICIDES IN SELECTED
SOILS OF KARNATAKA, INDIA

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1. INTRODUCTION

The use of pesticides has become indispensable for modern strategy of crop production in India particularly under an intensive agricultural programme.

Were a pesticide entirely specific in its action, there would be no controversy about its use. Movement out of the intended zone of activity, threshold levels of hazard in other segments of the environment and persistence beyond the critical period of control lead to residue problem. Therefore, a thorough knowledge and understanding of the soil processes affecting pesticides is imperative if methods for controlling pesticide persistence and minimising their undesirable effects are to be devised.

Microbiological and chemical degradation of pesticides in soils are decisive factors for the overall performance of these compounds in soils. The physico-chemical aspects of interactions such as adsorption, leaching and movement and their interaction with organic amendments and fertilizers are not fully understood, the need for such a knowledge would help in their efficient and economic use has been realised. The present investigation was undertaken to study the behaviour of some commonly used insecticides and fungicides in selected soils of Karnataka, India.

2. MATERIALS AND METHODS

Incubation studies:

Twenty grams of soil (Table 1) passed through 2 mm sieve was placed in test tubes of 20 x 200 mm size test tubes. The technical grade pesticides (Table 1) dissolved in suitable organic solvent were added to soil, mixed thoroughly after evaporating off the solvent and the moisture adjusted to field capacity (non-flooded) or flooded conditions created by the addition of 20 ml distilled water. Soils receiving organic amendments were treated with either rice straw, farm yard manure (FYM) or neem cake at 0.5% carbon basis. The effect of nitrogenous fertilizers viz., urea, ammonium sulphate applied at 100 ppm N was also studied. The role of soil micro-organisms in the degradation of pesticides was tested by autoclaving one set of soils. Appropriate control was maintained in all the experiments. The treated soils were incubated in an incubator maintained at $30\pm 1^{\circ}\text{C}$. At periodic intervals the residues in soil were extracted and analysed for fenitrothion (Tokimoto et al., 1976), phorate (Getz and Watt, 1964), carbaryl and carbofuran (Rajagopal and Sethunathan, 1984), carbendazim (Austin and Briggs, 1976) and tridemorph (Anon, 1970).

Leaching studies:

The leaching loss, movement and distribution of added insecticides (40 mg) was studied by employing soil columns (Austin and Briggs, 1976).

Plant uptake:

The uptake of soil applied phorate by sorghum was studied in a greenhouse experiment. Phorate granules at 16 kg/acre were applied to soil. Soil and plant parts were analysed periodically for phorate residues. The persistence in flooded soil and uptake of carbofuran by rice plants was studied in a greenhouse experiment. Carbofuran at 2 kg a.i. per hectare was applied either as (i) broadcast to paddy water, (ii) incorporated into the rootzone of rice plant. At periodic intervals the residues of carbofuran in soil and rice plant was determined.

3. RESULTS AND DISCUSSION

The recovery of added pesticides from soil at various incubation periods (Table 2) have revealed that the degradation of pesticide occurred in all the four soils and the rate followed the order saline soil > black soil > red soil > laterite soil for all the chemicals except phorate where red soil > laterite soil > saline > black soil. Thin layer chromatographic analysis of the residues have confirmed the formation of their degradation products in soil. The degradation of carbaryl, carbofuran and fenitrothion was related to initial pH of the soil. Alkaline conditions favoured the hydrolysis of carbaryl and carbofuran to 1-naphthol and carbofuran phenol respectively. Fenitrothion was hydrolysed to 3-methyl-4-nitrophenol. Alkaline hydrolysis of these insecticides has been reported (Rajagopal and Sethunathan, 1984; Baarschers et al., 1980). Soil flooding further enhanced the rate of degradation process. More rapid degradation of pesticides in flooded than in non-flooded soils has been reported (Rajagopal and Sethunathan, 1984). Autoclaving the soil resulted in appreciable inhibition of the degradation process implicating the role of soil micro-organisms (data not given). The degradation of tridemorph and carbendazim occurred in all the soils, though slow, and flooding slightly enhanced the rate. Carbendazim was relatively more persistent in soil among the chemicals studied. Addition of organic amendments to flooded soil resulted in more rapid degradation of all the four insecticides. Application of rice straw and FYM were more effective than neem cake for fenitrothion and phorate while it was neem cake and rice straw rather than FYM for carbaryl and carbofuran. Thus addition of organic matter to soil, a useful agronomic practice followed in Indian agriculture, may help in the decontamination of soil pollutants (Table 3). Application of nitrogenous fertilizers such as urea, ammonium sulphate had no significant effect on the degradation process except for carbaryl where the degradation rate was slightly inhibited (data not given).

The leaching loss, movement and distribution of the three insecticides in soil is given in Table 4 and 5. The loss of insecticides due to leaching was more in coarse-textured (red and laterite) soils than in

fine-textured (black and saline) soils. Freed and Haque (1973) has made similar observations.

Besides soil texture, the hydraulic conductivity has affected the movement and leaching loss of insecticide in soil. Bulk of the insecticide was retained in 0-7 cms and the concentration decreased with the depth. Apparently the sandy soils exhibit higher loss by leaching thus resulting in contamination of the soil and groundwater.

The uptake of soil applied phorate (Table 6) by the sorghum and carbofuran (Table 7) by rice plants was gradual but further translocation to apical parts of the plant was rapid. Among the different methods of application of carbofuran to rice, the root zone application and soil incorporation were superior to paddy water broadcast. The former methods have resulted in the reduced degradation rate in the soil and increased availability of the chemical to rice over longer periods. Rapid degradation of carbofuran applied to paddy water has been reported (Siddaramappa et al., 1979). Recognising the possible surface loss of carbofuran from paddy water, the root zone placement of systemic insecticide may be a better practice for increasing efficiency of the applied chemical.

4. ACKNOWLEDGEMENTS

The authors are grateful to Dr S.V. Patil, Vice-Chancellor and Dr K. Krishnamurthy, Director of Research, University of Agricultural Sciences, Bangalore, India for encouragement. This project was funded, in part, by grants from the Department of Environment, Government of India.

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Table 1. *Particulars of the soils and the chemicals used in the study*

i) Soils

Properties	Black soil	Red soil	Laterite soil	Saline soil
pH	6.7	6.6	5.8	8.3
E.C. (mmhos/cm)	2.3	0.3	0.2	13.5
Organic carbon (%)	0.99	0.44	1.65	0.45
Exchangeable sodium percentage	9.50	6.4	5.2	10.9
Hydraulic conductivity (cm/hr)	1.72	16.1	17.55	0.25
Texture	Clayey	Sandy clay	Sandy loam	Silty clay

ii) Chemicals

1. Carbaryl 1-naphthyl N-methyl carbamate
2. Carbofuran 2,3-dihydro-2, 2-dimethyl-7-benzofuranyl N-methyl carbamate
3. Fenitrothion O, O-dimethyl O-3-methyl-4-nitrophenyl phosphorothionate
4. Phorate O, O-diethyl S-(ethylthio) methyl phosphorodithionate
5. Tridemorph N-Tridecyl-2, 6-dimethyl morpholine
6. Carbendazim 2-(methoxy carbamoyl)-benzimidazole

Table 2. Persistence of pesticides ($\mu\text{g/g}^{-1}$) in different soils under flooded (A) and non-flooded (B) conditions

Chemicals/Weeks		Black soil		Red soil		Laterite soil		Saline soil	
		A	B	A	B	A	B	A	B
		Carbaryl	0	17	18	17	18	17	19
	6	5	6	5	7	7	11	0	0
Carbofuran	0	37	37	38	37	38	39	35	34
	6	5	10	5	8	5	10	5	6
Fenitrothion	0	122	122	109	106	121	115	109	105
	6	3	5	0	11	3	5	4	4
Phorate	0	22	23	22	22	22	23	22	23
	6	6	7	4	8	5	6	6	7
Tridemorph	0	19	19	19	20	20	22	17	18
	6	5	10	7	10	7	11	4	5
Carbendazim	0	34	32	35	34	35	34	32	31
	6	25	26	26	30	27	29	24	26

Initially added concentration differed with the pesticide

Table 3. Persistence of pesticides ($\mu\text{g/g}^{-1}$) in organic matter-amended and unamended soils under flooded conditions

Soils/Chemicals	Control		Rice straw		FYM		Neem cake		
	weeks	0	6	0	6	0	6	0	6
Black soil									
Carbaryl		17	5	17	4	17	3	17	3
Carbofuran		39	6	37	3	39	4	37	1
Fenitrothion		122	3	125	0	122	0	121	0
Phorate		22	6	22	5	24	5	23	5
Red soil									
Carbaryl		17	5	17	4	17	4	17	3
Carbofuran		37	5	38	4	38	4	37	3
Fenitrothion		109	4	115	0	122	Tr	109	0
Phorate		22	3	21	2	22	2	22	2
Laterite soil									
Carbaryl		18	7	18	6	19	7	18	6
Carbofuran		40	8	40	6	38	5	37	5
Fenitrothion		116	3	121	0	122	0	117	0
Phorate		22	5	22	4	23	3	23	4
Saline soil									
Carbaryl		17	2	17	2	17	2	17	1
Carbofuran		35	4	36	2	36	3	35	1
Fenitrothion		109	Tr	110	Tr	100	0	110	Tr
Phorate		22	6	23	5	23	5	22	5

Initially added concentration differed with the pesticide

Table 4. *Leaching loss of insecticides (mg) in different soils maintained at a constant head for 72 hrs.*

Time (hr.)	Carbaryl	Carbofuran	Phorate
Black soil			
0-12	1.30	1.55	1.26
12-24	2.26	2.80	2.08
24-48	2.63	4.00	2.44
48-72	2.84	5.00	2.85
Red soil			
0-12	4.16	6.00	2.51
12-24	6.14	11.10	6.55
24-48	5.72	7.20	4.89
48-72	5.86	6.40	5.00
Laterite soil			
0-12	2.64	3.50	1.89
12-24	6.68	8.10	3.69
24-48	4.92	6.40	4.22
48-72	5.43	5.90	4.64
Saline soil			
0-12	0*)	0*)	0*)
12-24	0.35	0.75	0.37
24-48	0.94	0.90	1.02
48-72	1.35	2.80	1.86

*) No leachate was collected

Table 5. *Distribution of insecticides (mg) in different soils maintained at a constant head for 72 hrs.*

Depth (cm)	Carbaryl	Carbofuran	Phorate
Black soil			
0- 7	12.90	15.00	10.45
7-14	5.26	6.30	7.11
14-18	0.98	1.20	1.26
Red soil			
0- 7	2.32	1.30	4.57
7-14	1.19	1.00	3.67
14-18	0.32	0.45	1.02
Laterite soil			
0- 7	3.94	4.40	6.25
7-14	1.83	2.55	5.91
14-18	0.70	0.65	1.66
Saline soil			
0- 7	12.60	20.00	15.94
7-14	4.20	7.00	8.28
14-18	0.68	0.50	1.14

Table 6. *Distribution of phorate residues (ppm) in sorghum plant grown on black soil*

Duration (Weeks)	Soil	Roots	Stem	Leaves
0	4.8	0	0	0
2	2.5	0.3	0.9	1.0
4	1.5	0.1	0.4	2.4

Table 7. *Persistence in soil and uptake and uptake of carbofuran (μg) by rice under different methods of application to black soil under flooded conditions*

	0 Week	2 Weeks	4 Weeks
Paddy water broadcast:			
Flooded soil	430	100 (3.6)*)	42
Root	0	20	20
Shoot	0	88	95
Soil incorporation:			
Flooded soil	430	100 (2.56)*)	56
Root	0	30	17
Shoot	0	100	110
Root zone application:			
Flooded soil	430	120 (1.25)*)	86
Root	0	26	19
Shoot	0	115	130

*) Figures in parenthesis indicate the concentration of carbofuran (ppm) in the standing water

THE EFFECT OF FLOW RATE ON THE ADSORPTION
OF PESTICIDES IN SOILS

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ABSTRACT

Adsorption kinetics of diquat, linuron, phenamiphos and simazine were studied using a flow technique in columns of a sand and a sandy loam soil from Western Australia. A decrease in the rate of adsorption with time to a constant value was observed for all pesticides. This constant rate of adsorption could be fitted to a first order kinetic equation. The batch method and the flow technique gave comparable adsorption results for similar equilibration times. Extrapolation of the results from the column experiments show that considerable deviation from equilibrium in the adsorption of pesticides can occur under field conditions.

1. INTRODUCTION

Adsorption and degradation are the major processes affecting pesticide transfer through soils. Both the extent and the rate of adsorption at the solid-liquid interface determine the susceptibility of a particular pesticide to leaching. Little information on kinetics of adsorption of pesticides in soils is available from the literature (Yaron et al. 1985).

The batch slurry method, which is commonly used to study adsorption kinetics, has many limitations. The solution concentration of pesticide decreases with time and alterations in the surface chemistry of soil particles can occur with vigorous mixing (Barrow and Shaw 1979). It is also difficult to distinguish between adsorption and degradation when using the batch method. Because of these factors, data cannot be reliably applied at the field scale. Flow techniques in columns of soil provide a better representation of field conditions (Murali and Aylmore 1983). Mechanical agitation is absent and degradation can be measured by comparing column input and output.

This paper reports on studies of the adsorption kinetics of diquat, linuron, phenamiphos and simazine. The adsorption data obtained by a flow technique were fitted to a first order rate equation in two soils of different texture. Equilibrium adsorption isotherms obtained by the flow technique and batch method were compared. The effect of the rates of adsorption on distribution of pesticides under flow velocities encountered in the field situation is discussed.

2. MATERIALS AND METHODS

2.1 Soils and Pesticides

A sandy soil of the Bassendean association of the Swan Coastal Plain near Perth (Western Australia) and a sandy loam soil of the Gascoyne association near Carnarvon (Western Australia) were used in this study. The characteristics of Bassendean sand are given by McArthur and Bettenay (1974) and of Gascoyne sandy loam by Bettenay et al. (1971). Relevant properties of the Bassendean sand and Gascoyne sandy loam are respectively, clay (%) 6.3, 16.8; silt (%) 0.7, 11.8; organic carbon (%) 0.63, 0.84; and pH (1:5, 0.01 M CaCl₂) 5.4 and 7.1.

Horticultural crops are grown on both soils. The groundwater below Bassendean sands is used for domestic and irrigation purposes. On the Gascoyne soils, the groundwater is used for irrigation but drinking water is supplied mainly from the Gascoyne River.

Four pesticides were used in this study, three herbicides: diquat, linuron, simazine, and a nematicide, phenamiphos. Analytical grade samples (+99%) of pesticides were obtained from ICI Australia Ltd. (diquat); Hoechst Australia Ltd. (linuron); Bayer Australia Ltd. (phenamiphos) and Ciba-Geigy Australia Ltd. (simazine).

Diquat, linuron, phenamiphos and simazine are some of the commonly used pesticides in Western Australia. The amounts generally used per application are: diquat (3 l/ha), linuron (4 kg/ha), simazine (4 kg/ha) and phenamiphos (20 l/ha).

2.2 Equilibrium adsorption study

Batch distribution isotherms for the four pesticides in the two soils were determined at $20 \pm 2^\circ\text{C}$. Five grams of air-dried soil were equilibrated in polypropylene centrifuge tubes with 10 ml of pesticide solution in 0.01 M CaCl_2 . Pesticide concentrations ranged from 150 to 6000 $\mu\text{mole/litre}$ (diquat) and from 50 to 600 $\mu\text{mole/litre}$ (other pesticides). The tubes were shaken (end over end) for 16 h (diquat) or 24 h (other pesticides). Soil adsorption was found to be almost complete after this time. Pesticides were not noticeably adsorbed to the walls of the centrifuge tubes. After shaking the suspension was centrifuged at 12000 rpm for 15 minutes. The supernatant was pipetted off and analysed. The adsorbed amount was calculated from the initial and final concentrations of pesticides in solution.

2.3 Pesticide analysis

Simazine and linuron were analysed directly in the soil solution phase by liquid chromatography (Vickery et al. 1980) using a Spherisorb 10 μm ODS column, 30 cm x 1.6 mm ID (Phase Separation Ltd.) and a mobile phase of methanol and water (65:35 v/v). The pesticides were detected at 220 nm with a variable wavelength UV detector (ETP-Kortec).

Detection limit for simazine was 0.1 $\mu\text{g/ml}$ and for linuron 0.5 $\mu\text{g/ml}$. Diquat was measured colorimetrically at 376 nm after reacting the soil solution phase with sodium dithionite (Lott et al. 1978). Detection limit was 0.1 $\mu\text{g/ml}$.

Phenamiphos was analysed by capillary gas chromatography (Hewlett-Packard) using a HP-5 column (25 m x 0.31 mm ID) and He as carrier gas at 44 cm/sec. Operating conditions were, injection port temperature was 250°C, initial column temperature 175°C programmed to 250°C at 25°C/min. Detection was with a single ion monitoring mass spectrometer (Hewlett-Packard 5970) at $m/e = 303$. Detection limit for phenamiphos was 0.05 $\mu\text{g/ml}$. Phenamiphos was analysed after extracting the soil solution phase with 15% methylene chloride in hexane. The average recovery was 97%.

2.4 Soil column studies

Air-dried soil was vibrated into columns. A HPLC pump (ETP-Kortec) supplied a solution of 0.01 M CaCl_2 to the columns. Saturated flow rates were varied from 0.01 ml/min to 2.0 ml/min. Samples were injected in a volume of 300 μl with a six port stainless steel valve (Rheodyne). Details of experimental conditions for soil columns are given in Table 1. To avoid slaking of the Gascoyne sandy loam, a mixture of soil and diatomaceous earth (2.4:1) was used. Pesticide adsorption by diatomaceous earth was negligible. Breakthrough curves (BTCs) were monitored with a UV detector and chart recorder or alternatively off line from analysis of automatically collected fractions.

Dynamic distribution isotherms of pesticides were measured from BTCs at various rates of flow in small columns of soil under saturated conditions. The isotherms were obtained by applying the peak maxima method (Huber and Gerritse 1971). This method is based on the transport equation for non-linear distribution of a solute:

$$(\delta\langle C \rangle / \delta t) + ((1-\theta)/\theta)(\delta\langle S \rangle / \delta t) = -(\delta\langle VC \rangle / \delta z) + D(\delta^2\langle C \rangle / \delta z^2) \dots (1)$$

where z = length co-ordinate

t = time

S = adsorbed concentration

C = solution concentration

V = pore water velocity

- < > = average over corresponding cross-sectional area
 θ = fraction of cross-sectional area occupied by solution
 $1-\theta$ = fraction of cross-sectional area occupied by solid phase
 D = longitudinal dispersion coefficient

Assuming the dispersion coefficient to be effectively zero, an expression describing the residence time (t_c) of the maximum solution concentration in the BTC from a column of soil can be derived.

$$(t_c - t_0)/t_0 = ((1-\theta)/\theta)(d\langle S \rangle/d\langle C \rangle) \dots\dots\dots(2)$$

where t_0 = retention time of non-retained solute (C_1^-)

The adsorbed concentration (S) can be calculated by applying Equation 2 to the locus of concentration maxima of the BTCs and integrating. The adsorption rate coefficients were calculated from the change in the amount of adsorbed pesticide with residence time (t_c in Equation 2).

Table 1. Soil column characteristics and experimental conditions

Properties	Bassendean sand		Gascoyne sandy loam	
	Diquat	Other Pesticides	Diquat	Other Pesticides
Length (cm)	4.9	15	4.9	13
Internal diam.(cm)	0.44	1.0	0.44	1.0
Soil wt. (g)	1.2	18.6	1.1	6.0+2.8*
Bulk density (g/cm ³)	1.54	1.6	1.48	0.9
Porosity (cm ³ /cm ³)	0.46	0.44	0.60	0.73
Pore volume (ml)	0.36	5.4	0.45	7.5
Pesticide injected (μ g)	10-80	1-20	30-150	1-20
Range of pore water velocities (m/day)	20-500	1-40	10-300	2-30

*Diatomaceous earth (BDH, particle range 5-10 μ m)

3. RESULTS AND DISCUSSION

Results of applying the flow technique to the breakthrough of simazine from a column of Bassendean sand are shown in Figure 1a and 1b. Recoveries calculated from the BTCs were always better than 90%, showing that pesticide degradation during the column experiments was not significant. A comparison of adsorption isotherms measured by batch and by the flow technique is shown in Figure 1b for simazine and in Table 2 for all pesticides. Results from the flow technique and batch method are similar.

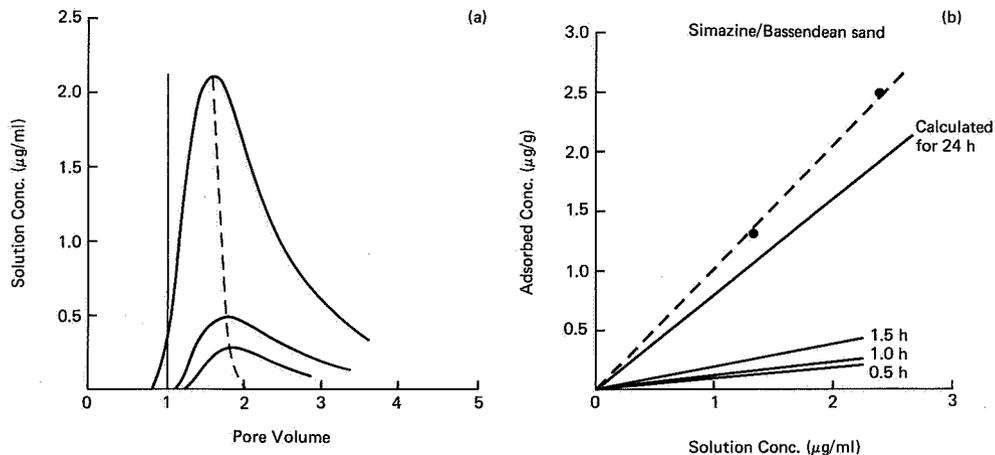


Figure 1a. Dynamic adsorption isotherm obtained by peak maxima method. Pore water velocity 2.2 m/day. Amount of simazine injected 3-12 µg. Chloride ———: Pesticide - - - - -

Figure 1b. Dynamic adsorption isotherms of simazine obtained by flow technique and comparison with batch values. Observed batch values after 24 h ----•; adsorption isotherms by flow technique at various residence times (t_c)———.

Data from the column experiments were fitted to a first order kinetic equation derived for constant solution concentration of the pesticide:

$$\ln(1 - S_t/S_\infty) = -bt$$

where S_t = amount adsorbed at time t

S_∞ = amount adsorbed at $t = \infty$ obtained from batch experiment

b = adsorption rate coefficient

Table 2. Distribution constants (K_∞) of pesticides by batch and flow technique measured after 24 h *

Pesticide	Bassendean sand		Gascoyne sandy loam	
	(ml/g)		(ml/g)	
	Flow	Batch	Flow	Batch
Diquat	234	260	755	800
Linuron	5.6	7.0	5.8	9.0
Phenamiphos	4.3	4.5	4.0	4.0
Simazine	1.0	1.6	2.4	2.5

* Diquat - 16 h

The first order plots of four pesticides in the two soils are shown in Figure 2. A decrease in the rate of adsorption with time to a relatively constant value is observed for all pesticides in both soils. Similar results have been reported by Graham-Bryce (1972). The limiting values of the rate coefficients as calculated from Figure 2 are shown in Table 3.

Table 3. Limiting values of rate coefficients of pesticides

Pesticide	Bassendean sand	Gascoyne sandy loam
	(day ⁻¹)	(day ⁻¹)
Diquat	3.2	3.6
Linuron	1.3	0.8
Phenamiphos	1.9	2.6
Simazine	1.2	2.7

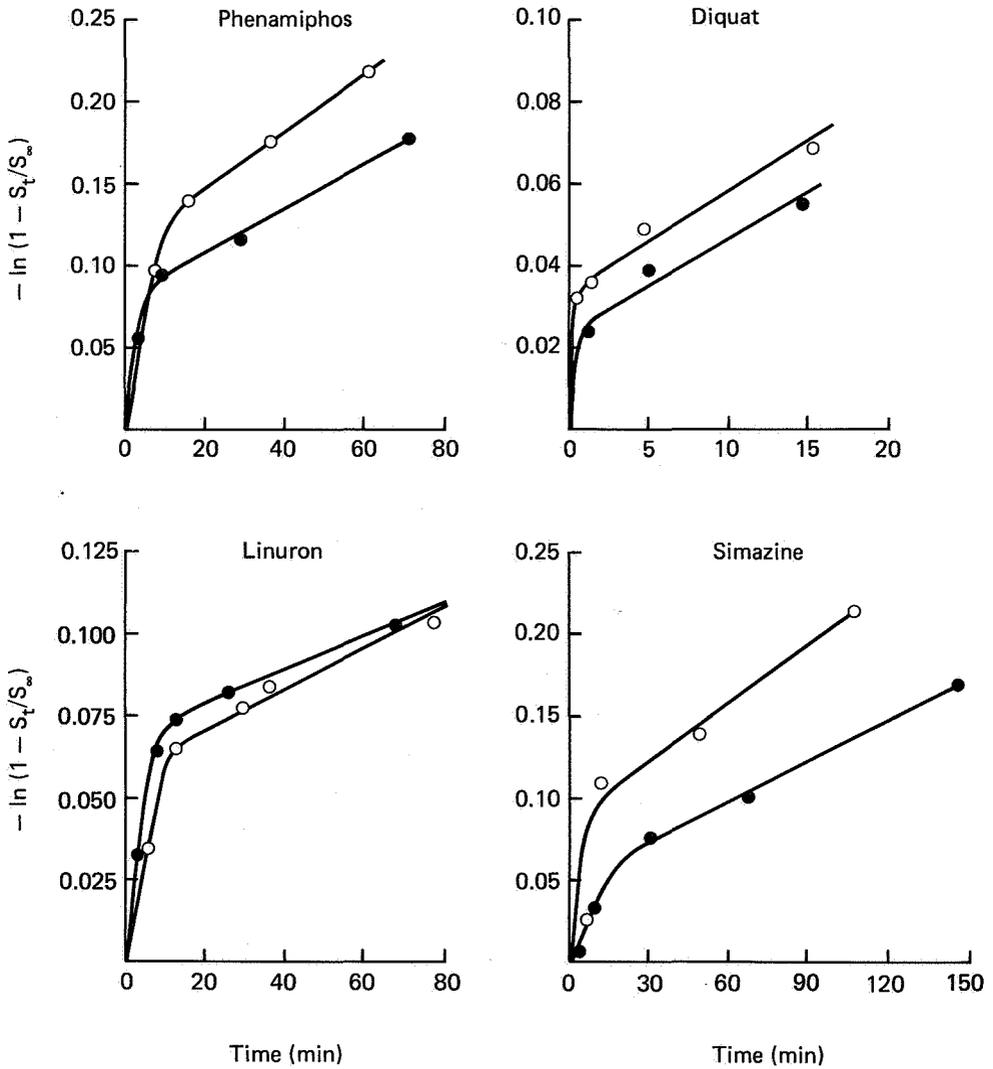


Figure 2. First order plots of diquat, linuron, phenamiphos and simazine. in two soils. Bassendean sand ---●; Gascoyne sandy loam---○.

The effect of pore water velocity on the distribution of the various pesticides in the soils used in this study are shown in Figure 3a and 3b. In the calculations dispersion length (Disp) is taken as the smallest soil unit within which complete mixing of solute occurs.

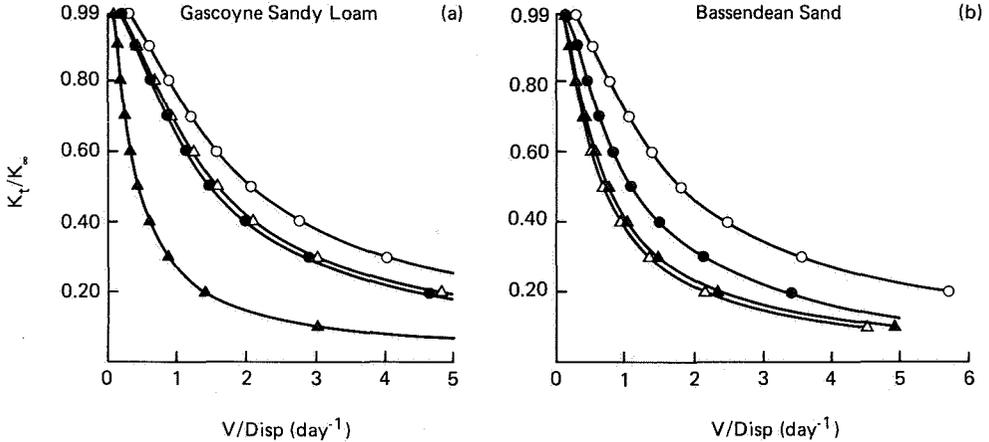


Figure 3. Effect of pore water velocity (V) on distribution (K_t/K_∞) of pesticides in soil. The pore water velocity is expressed relative to dispersivity (V/Disp) and the distribution relative to the equilibrium value approached at $t = \infty$ ($V \rightarrow 0$). Diquat -- \circ ; Simazine -- Δ ; Phenamiphos -- \bullet ; and Linuron -- \blacktriangle

The time necessary to attain complete longitudinal mixing at a pore water velocity V is then Disp/V . The value of the dispersion length in the literature for sand/sandy loam varies from 0.2 mm to 7.9 cm (Rose 1977). In surface soils of Western Australia used in the study, the value of V/Disp can range from 0.1 to 10.0 day⁻¹ showing that significant departure from equilibrium distribution is possible during pesticide transfer.

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HYDROLOGICAL CHARACTERISTICS OF GROUNDWATER CONTAMINATED BY TRICHLOROETHYLENE AND OTHER POLLUTANTS IN SEVERAL AREAS OF JAPAN

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ABSTRACT

Several areas in Japan whose groundwaters are polluted by trichloroethylene and other material have been studied by examining the relationship between hydrogeology and the spatial distribution of the pollutants. Areas with high permeability of geologic units are particularly vulnerable to pollutants, and careless construction of wells causes direct pollution from the land surface.

1. INTRODUCTION

Water for drinking, agricultural and other uses has been important for humans throughout the world for all time. It is often thought that water resources in Japan are relatively abundant because of its rather rainy climate; however, since rainfall is not constant during all seasons and in every area, there are often problems of supply. Almost all water for industrial use in Japan is dependent upon groundwater, placing a heavy demand on supply in some areas. Issues such as land subsidence and salt water intrusion caused by heavy pumpage of groundwater, exacerbated by the growth of industrial demand for water, are some of the severe social problems in Japan. Following the realization of the importance of qualitative and quantitative groundwater management, groundwater has been checked throughout Japan to determine where it did not conform to the environmental standard of Japan.

This is a preliminary report of our study over the last 20 years on groundwater pollution by trichloroethylene and other toxic substances.

Among several polluted areas studied, the following example illustrates a typical case of groundwater pollution.

2. HYDROCHEMICAL ASPECTS OF THE POLLUTED GROUNDWATER

The studied area, located in the western part of the Kanto plain, central Japan, is the lower part of an alluvial fan consisting of sand and gravel. Unconfined groundwater lies about 30 m below the land surface and several aquifers of confined groundwater exist at deeper levels. Most of the pumping wells in this area have multi-screened casings.

We analyzed the water quality of confined groundwater in 1965 and again in 1985; the unconfined groundwaters were also analyzed in 1985 (Fig.1). Well No.3, first sampled in 1965, was repeatedly sampled in 1985. The concentration of NO_3^- ion was also determined in the 1985 samples. The original 1965 pattern of water quality of confined groundwater is a diamond-shaped, Ca- HCO_3 type (e.g. Nos. 52, 54, 55, and 3; Fig.1). This water quality has changed dramatically during the last two decades due to pollutants originating from the land surface; in particular, there

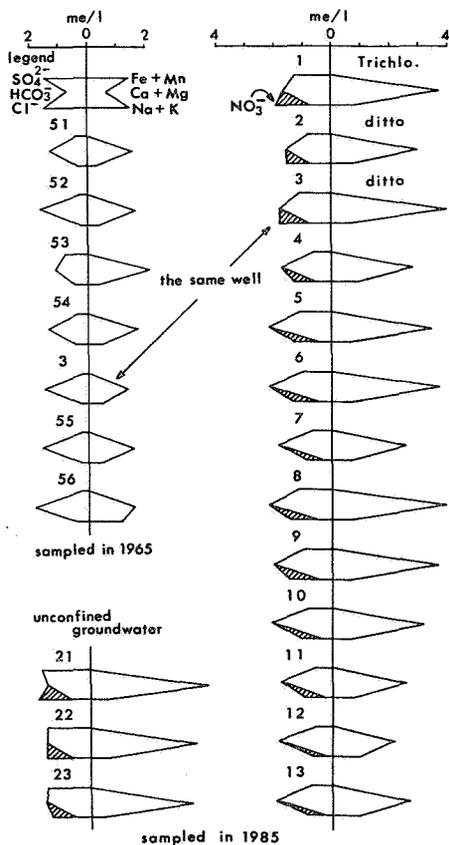


Figure 1. Groundwater quality in hexadiagram.

Number in this figure indicates that of the sampling wells.

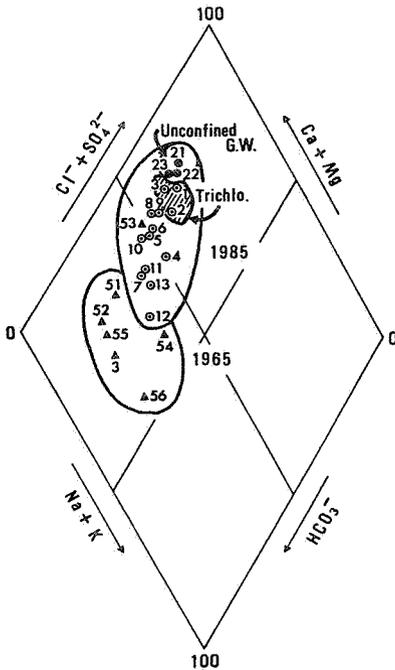


Figure 2. Groundwater quality in key-diagram.

Numbers are the same as those in Fig.1. Trichloroethylene was detected in 1985 from three samples in the shaded area.

waters of 1985.

Similar results were obtained in the other areas studied, including low angled talus and gently sloping upland covered with permeable lava.

3. CONCLUSIONS

The following important factors were found to be common in all the areas studied.

- 1) Surface geology of the polluted area is composed of highly permeable

has been a significant increase in the concentration of SO_4^{2-} , NO_3^- and Ca. The water quality pattern of the confined groundwater evolved to become similar to that of unconfined groundwater. High trichloroethylene was also detected in 1985 in wells 1 to 3.

The water quality of both sampling periods is also expressed in a key-diagram (Fig.2). The quality of the 1985 confined waters plots between that of the 1965 sampling and that of the 1985 unconfined groundwater. Three samples with high concentration over 30 ppb of trichloroethylene from wells 1 to 3 of 1985 plot particularly close to that of the 1985 unconfined groundwater. This result is not surprising since the source of trichloroethylene and other pollutants originates from human activities on the land surface. Among the 1965 samples, No. 53 was already polluted, and plots within the area of confined ground-

sand and gravel or lava with many fissures. These conditions allow downward percolation of pollution from the land surface. In terms of geomorphology, groundwater pollution mainly occurs in areas of alluvial fans, talus accumulation and those covered by permeable lava flows.

2) The notable common factors of groundwaters polluted by trichloroethylene and other substances are high contents of NO_3^- or SO_4^{2-} ; these originate from fertilizers, insecticides and other chemicals used in agriculture. Conversely, areas with high NO_3^- or SO_4^{2-} content in groundwater are generally susceptible to pollution by chemicals such as trichloroethylene.

3) Most cases of such pollution in deep confined aquifers are considered to occur not by direct infiltration from the land surface but by continuous percolation from polluted unconfined aquifers through the gravel surrounding well casings.

ACKNOWLEDGEMENTS

The authors wish to thank the Yoshida Science and Technology Foundation of Japan for supporting one of the authors to participate in the international symposium on vulnerability of soil and groundwater to pollutants.

LABORATORY INVESTIGATIONS ON THE MIGRATION OF PESTICIDES
IN POROUS MEDIUM

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ABSTRACT

The migration behaviour of several pesticides (i.e. atrazine, saturn, phenitrothione) used most frequently in agriculture are studied under static and dynamic conditions. Some of the major methodological problems discussed here are as follows: a) it is shown in what cases the use of a first order kinetic equation for describing the pesticide elimination is correct; b) a special computer program KINEL is designed for selecting the most suitable kinetic model of irreversible elimination; c) it is concluded that the distribution coefficient characterizing the sorption ability of the organic pollutants has to be determined mainly for substances of high stability ($\tau_{1/2} > 200$ d). The values of the basic migration parameters for the pesticides studied are computed. The greatest damage to groundwater is atrazine, while saturn and especially phenitrothione are practically harmless.

1. INTRODUCTION

Pesticides are amongst the most dangerous potential pollutants of groundwater in agricultural regions (Gavich 1985, Mattess et al 1985). That is why the study of their behaviour and migration in porous (filtration) medium is of great scientific and practical interest.

The present paper is a study of the behaviour of these pesticides: atrazine (2-chlor-4-ethylamine-6-isopropylamine-sym-triazine), saturn S-/4-chlorbenzyl/-N-N-diethylthiocarbamate) and phenitrothione (o,o-

dimethyl-o-/3-methyl-4-nitrophenyl/thiophosphate), under static and dynamic conditions. These pesticides belong to different chemical subgroups (Melnikov et al 1977) and are used worldwide.

The aim of the investigations was, on the one hand, to specify some methodological problems concerning the performance and interpretation of the experiments, and on the other hand, to determine the values of certain basic migration parameters characterizing the transport of pesticides in the aquifer.

Particular attention is paid to the processes of sorption retardation and mostly to the irreversible elimination (hydrolytic and oxidizing) which plays an essential part in the migration of organic pollutants, bearing in mind that most of the pesticides, particularly the ones under study, are actually organic pollutants.

2. METHOD OF INVESTIGATION

As was mentioned above, static and dynamic laboratory tests were carried out (at 18°C).

The static tests involve all model experiments performed in the absence of a filtration flow. Usually they are carried out at first in the absence of a solid phase (i.e. a sample of porous medium). Thereby in a homogeneous system the processes of interaction between the particles of the respective ingredients (pollutants) and the water molecules, ions and other substances dissolved, are investigated. These tests most often include studies of the thermodynamics and kinetics of complex-forming and degradation processes, and sometimes studies of bioaccumulation and precipitation processes. The results obtained from the tests in a homogeneous system are practically usable when the influence of the filtration medium is fairly slight or easy to evaluate.

As usual, after having obtained the parameters characterizing the interactions in a homogeneous water disperse system, static tests are carried out in the presence of a sample of real porous medium (in heterogeneous system). Thus, usually the distribution coefficients, the rate constants of elimination, and sometimes the elimination capacity, are determined. The tests in a heterogeneous system in the presence of a

filtration flow (i.e. the dynamic tests) are carried out at constant ($C_0 = \text{const}$) or variable ($C_0 = 0$) input concentration of the ingredient under study. A variety of the second type is the so-called impulse water input for which $C_0 = \text{const.}$ only for definite time t , whereas for the remaining time of the experiment $C_0 = 0$.

Apart from the input and output concentration, the volume of liquid phase flowed through (in dynamic tests), as well as the basic hydrochemical parameters - t° , pH, Eh, specific conductivity, etc, are measured in the course of the experiments. The water samples taken (usually 100 cm^3 in size) are placed in darkness, at $t^\circ - 3-4^\circ\text{C}$ and, if necessary, are additionally conserved (Velikov, 1986).

The solid and liquid phases used are characterized in Table 1, and as regards the scheme and conditions for carrying out static and dynamic tests, the manner of dissolving and analyzing the pesticides, more details can be found in Gavich (1985), Velikov (1986) and Mohammed (1986).

Table 1. *Chemical characteristics of the solid (in %) and liquid phase (in mmol/l) used*

	Upper level	Lower level	Liquid phase	
	sand	sand		
Dampness	4,48	3,43	pH	7,3
Ignition lost	9,90	11,87	spec.conductivity($\mu\text{s}/\text{cm}$)	168,3
SiO_2	53,44	50,64	SO_4^{2-}	0,250
CaO	7,00	10,15	Cl^-	2,630
MgO	3,20	3,50		
Na_2O	2,02	2,05	Ca^{2+}	0,430
K_2O	2,29	1,89	Mg^{2+}	0,380
Al_2O_3	15,28	14,14		
Fe_2O_3	6,58	5,98	Na + K	2,870
TiO_2	< 0,1	< 0,1	ANC to pH 4,4	1,36
SiO_3	0,53	0,20	BNC to pH 8,3	0,09
Organic subst.	0,86	0,20	Ionic strength	5,55
Σ	100,24	100,42		

We shall just note that 'upper' level sand in this case means sand taken from 0,5 m underground whereas a sample from 4 m underground is designated as 'lower' level sand.

As a result of the experiments, a dependence $C = f(t)$ is obtained. When the kinetic relationships are studied, it is usually assumed that these dependences are described by kinetic equations of the first order (Velikov and Pentchev 1984, Gavich 1985). The test we performed to verify the assumption that the rate constants of elimination obtained by different kinetic equations for pairs of values $C \div t$ will have approximately the same values only for $n = 1$ (i.e. for the first order equation), showed that this assumption is not always correct. The basic kinetic dependence are related to solutions of the differential kinetic equation of elimination

$$-dC/dt = \gamma \cdot C^n \quad (1)$$

where n is the order of the reaction, and γ = the rate constant.

For interpreting the results of the static tests from a kinetic point of view, we developed an algorithm and realized a computer program KINEL on a Pravets-82 in BASIC. The block diagram of the algorithm is given in Figure 1, and in Mohammed (1986) the listing of the program is presented. Two main points were taken as a basis, viz.

- a. the experimental investigation data are successively processed according to the method of least squares by several of the integral forms of the kinetic equations (for $n=0\div 6$), the values of the kinetic parameters being determined for each version;
- b. the individual versions are compared on the basis of a quantitative statistic criterion and the most adequate kinetic equation in the particular case is selected objectively. This criterion is the so-called index of correlation (correlation coefficient) R which is calculated by the formula:

$$R = \sqrt{1 - \frac{\sum_{i=1}^m (C_i - \bar{C}_i)^2}{\sum_{i=1}^m (C_i - C_{aver})^2}} \quad (2)$$

where C_i - the values of the concentrations obtained by experiment for

a moment of time t_i , \bar{C}_i - the concentration values predicted according to the respective kinetic equation for a moment of time t_i , C_{aver} - the arithmetic mean of the concentrations obtained by experiment.

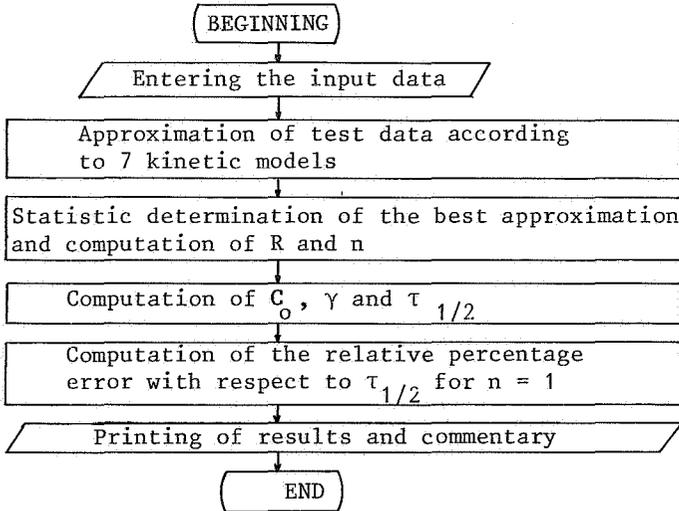


Figure 1. Algorithm of the KINEL program

The program also includes computation of the relative percentage error Δ which could be made if, instead of using the most adequate kinetic equation of the n -th order for the particular case, an equation of the first order is used. The respective half-decay times $\tau_{1/2}$ having equal dimensions (unlike the rate constants) are used as a basis for comparison:

$$\Delta = (\tau_{1/2}^n - \tau_{1/2}^1 / \tau_{1/2}^n) \cdot 100 \quad [\%] \quad (3)$$

The input data required are inserted in a dialogue mode thus excluding the necessity of a special instruction for operation with the program. When the elimination is irreversible or the value of its rate constant is small (i.e. below $1 \cdot 10^8 \text{ min}^{-1}$ for first order reactions), the thermodynamic approach gains importance. In practice its application in interpreting the data from the static tests consists in determining the values of the distribution coefficients K_d [dm^3/kg] for the respective ingredient by the formula:

$$K_d = (1/C^* - 1) V/m \quad (4)$$

where $C^* = C_i / C_0$ - a ratio between the concentrations of the substance studied for a contact time t_i and at the beginning (t_0), V - volume of the water sample studied in dm^3 , m - mass of the sample from the filtration medium in kg.

In the literature on the problem there are a number of methods for interpreting the dynamic tests such as the grapho-analytical method (Bochever et al, 1979), the method of characteristics points (Gavich, 1985), the method of the maximum (Maluszewski and Zuber, 1983), etc. However these methods are suitable for cases when the physico-chemical processes and especially the irreversible elimination processes occur slightly or do not occur at all. That is why for our purposes we chose the approach proposed in Galabov and Penchev (1986) for using the linear migration model, the computations being performed according to two basic variants: a disperse elimination variant (DEV) and a disperse-diffusion variant (DDV). By means of the TRINT program the experimental data $C^* = f(w^*)$ are interpreted by the two variants, a comparative analysis is made on the basis of quantitative criteria, analogous to (2) and the values of the corresponding migration parameters are determined.

3. RESULTS FROM THE EXPERIMENTS

Some more important results from the static experiments carried out are summarized in Table 2 and 3, and the data obtained from the dynamic migration tests are illustrated in Figure 2 ('lower' level sand), Figure 3 ('upper level sand') and in Table 4.

We should note that when the experiments are performed in a homogeneous system, the reaction is always of the first order. In a heterogeneous system, however, apart from the first, it can be of the second, third and even fourth order. It is probably due to the fact that along with the hydrolytic elimination processes, other processes (mechanisms) also take place such as degradation catalyzed by clay particles, chemical sorption accompanied by formation of covalent bonds, biochemical decomposition, etc. These assumptions are verified by comparing the data obtained for a different ratio of solid to liquid phase. It is evident

that in most cases these relative errors are below $\pm 30\%$, i.e. within the error bounds of the analytical method of thin-layer chromatography used. Therefore in such cases it is quite possible to use the simpler first order equation. This does not apply to phenitrothione where the nature of the errors necessitates the use of equations of a higher order and corresponding elimination constants with their characteristic dimensions.

Table 4. Values of migration parameters determined under dynamic conditions

Parameters	Lower level sand				Upper level sand			
	n_s	$D(m^2/d)$	$\gamma(1/d)$	B_d	n_s	$D(m^2/d)$	$\gamma(1/d)$	B_d
Atrazine	0,62	0,10	0,061	-	0,27	0,44	0,017	-
Saturn	0,8	0,024	3,84	-	0,79	0,25	4,23	-
Phenitrothione	0,82	0,02	4,64	-	1,61	0,53	6,18	-
Cl^-	0,54	0,15	-	-0,13	0,18	0,45	-	-0,026

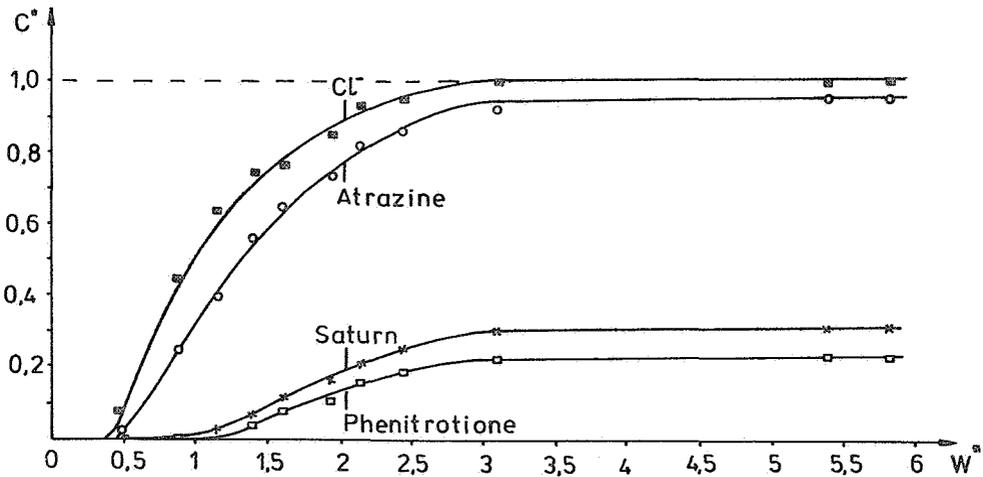


Figure 2. Dependence $C^* = f(w^*)$ for the test with 'lower' level sand

The distribution coefficient K_d was computed for all pesticides though we can speak of reaching thermodynamic equilibrium only for atrazine.

That is why K_d was computed for definite contact times (Table 3).

From the experimental data obtained by static tests we may conclude

that the additional mechanisms of decomposition cause considerable acceleration of the irreversible elimination in the heterogeneous systems as compared to the rate in a homogeneous system.

Table 2. Values of kinetic parameters of elimination for static tests in a homogeneous and a heterogeneous system by using only a first order equation

Parameters	Sand(level) ratio solid:liquid phase	γ [min^{-1}]	τ [d]	Δ [%]
Atrazine	-without sand	$2,58 \cdot 10^{-6}$	186,7	0
	'lower' 1:1,5	$3,5 \cdot 10^{-4}$	1,37	-9,25
	'lower' 1:3	$8,8 \cdot 10^{-5}$	5,47	-23,7
	'upper' 1:3	$5,5 \cdot 10^{-5}$	8,76	-25,1
	-without sand	$1,93 \cdot 10^{-5}$	24,9	0
Saturn	'lower' 1:1,5	$5,96 \cdot 10^{-4}$	0,81	0
	'lower' 1:3	$2,4 \cdot 10^{-4}$	2,01	-1,72
	'upper' 1:3	$2,0 \cdot 10^{-4}$	2,39	-6,0
	-without sand	$2,4 \cdot 10^{-5}$	20,0	0
	'lower' 1:1,5	$1,77 \cdot 10^{-3}$	0,27	270,7
Phenitrothione	'lower' 1:3	$2,9 \cdot 10^{-4}$	1,64	0
	'upper' 1:3	$3,4 \cdot 10^{-4}$	1,43	568,1

Table 3. Values of the distribution coefficient K_d (dm^3/kg)

t_i	'Lower' level sand m/V = 1/1,5			'Lower level sand m/V = 1/3			'Upper' level sand m/V=1/3		
	4h	24h	48h	4h	24h	48h	4h	24h	48h
Atrazine	0,165	1	2	0,07	0,43	0,86	0,045	0,25	0,51
Saturn	0,23	2,04	6,86	0,83	3,56	5,77	0,2	1,19	2,38
Phenitrothione	3,25	19,5	39,07	0,21	1,55	3,92	6,73	11,58	14,2

The data about the value of errors in assessing the half-decay times of elimination, made if, instead of the correct kinetic equation, a first order equation is taken, are of certain interest. It was found (table 2)

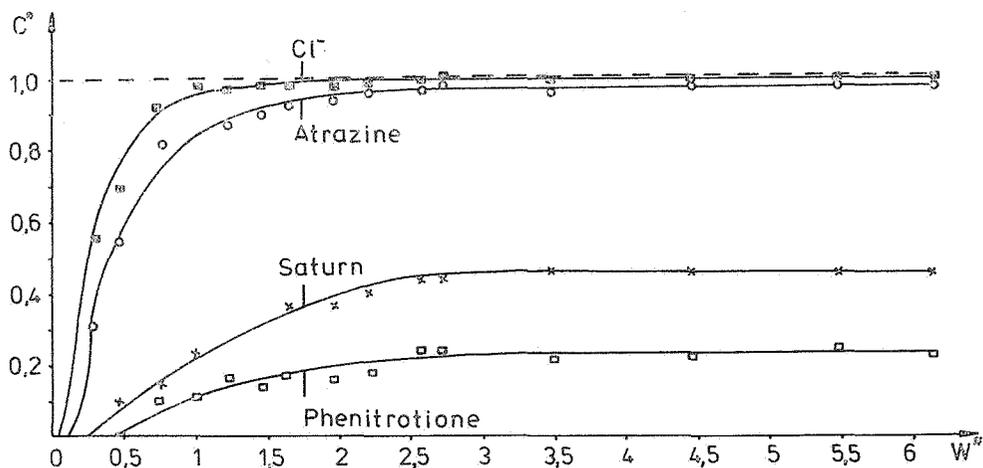


Figure 3. Dependence $C^* = f(W^*)$ for the test with 'upper' level sand

for K_d and especially for γ , the elimination processes have the strongest effect on the migration of phenitrothione, and a lesser effect on saturn, and still lesser effect on atrazine.

These results and tendencies were compared with the data from the dynamic tests and a satisfactory coincidence was noticed. From Figure 2, Figure 3 and Table 4 it becomes clear that atrazine has the highest migration mobility (approximate to that of Cl^-) whereas the migration mobility of saturn and especially of phenitrothione at the given filtration rate and under the other hydrodynamic and hydrochemical conditions, does not allow for reaching even $C^* = 0,5$.

4. CONCLUSIONS

a. The laboratory studies carried out show the applicability of static tests for determining some basic parameters of the migration (elimination) of pesticides and other organic substances in aqueous-disperse systems, particularly in groundwater. The advantages of these tests are mainly in the simple apparatus, lower expenses for chemicals and energy and very often, in the shorter time for performing.

b. The determination of the distribution coefficient is reasonable only for organic substances (pesticides in particular), which have higher stability (half-decay time $\tau_{1/2}$ exceeding, say, 200 d). For the other substances it is sufficient to determine and use only the rate constants

of elimination in predicting their migration in groundwater.

c. The dependence $C=f(t)$ obtained in the static tests should be interpreted by means of all kinetic models and by using objective mathematical-statistical criteria, the most reliable one should be determined. The use of a first order equation is possible only if the error made in interpreting by means of this equation does not exceed the error of the corresponding hydrochemical method. For increasing the accuracy of computations and easy implementation of the method, it is desirable to use the KINEL program for a personal computer.

d. In a number of cases it is sufficient to determine the kinetic parameters in a homogeneous system, because it gives more convenient experimental possibilities, and the kinetic dependences are well approximated to a first order equation. The values obtained for the parameters can be used for predicting the migration of the corresponding ingredients not only in a water-saturated heterogeneous system, but also in the zone of aeration, and even in the topsoil. This is true, because the values obtained, say, for the rate constant of elimination in a homogeneous medium are the lowest possible, and, hence, provide a certain amount of security.

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USE OF GROUND WATER QUALITY MONITORING DATA IN
DETERMINATION OF DECAY COEFFICIENTS FOR ORGANIC
CHEMICALS IN SHALLOW GROUND WATER

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ABSTRACT

Ground water beneath a chemical waste burial site in saprolitic material of the North Carolina piedmont has been closely monitored for more than 4 years. The water table lies approximately 8 meters below the bottom of the burial trenches. Monitoring well data permit calculation of decay constants for several organic compounds commonly found contaminating ground water, and carbon tetrachloride is used to describe the technique used in their determination. The geohydrology of the site suggests a near steady-state condition for contaminant movement and decay. By treating the well situated nearest the site as the source and wells and contour values along a given traverse as sampling points, one can determine the decay coefficient for a given contaminant. Semilog plots aid in the determination of the position of the non-detectable concentrations (zero contour), and calculations using an exponential decay equation determine both the distance-dependent and the time-dependent decay relationships. From this information it is possible to estimate spatial and time relationships for movement of the plume.

1. INTRODUCTION

A small chemical waste burial site near Raleigh, N.C. has been studied for approximately four years. Organic compounds used in the various teaching and research laboratories of N.C. State University were buried at the site between 1969 and 1980. These included pesticides and

herbicides as well as a variety of common solvents.

Of concern is the extent to which the ground water has become contaminated and the distance to which the contaminants may move over the next 30 years. Four of the most common volatile organic contaminants have been studied with respect to their distribution and seasonal behavior. It seems possible to use the analytical data to predict the future behavior of their respective plumes and the decay of the contaminants in the ground water system without extensive mathematical modelling. The chemicals have been buried for a time sufficiently long to permit consideration of the system as a steady state system with a decaying source. Carbon tetrachloride will be used to describe the technique.

2. GEOLOGY AND BURIAL OF CHEMICAL WASTE

The area is underlain by felsic gneiss and schist which in turn is overlain by approximately 30m of weathered rock (saprolite). Red and red-brown, very fine clayey sand and clayey silt with a median grain diameter of about 3.5 phi comprise the weathered zone. Both coarser and finer materials are present. The foliation preserved in the saprolite trends northwards with both east and west dips, reflecting the character of the underlying rocks.

Hydraulic conductivity determinations from both the laboratory and field indicate an average hydraulic conductivity in the 10^{-4} cm/sec. range. The water table slopes to the northwest as is indicated in Figure 1. Locally more permeable zones parallel to the foliation may control movement of the water and organic compounds. The water table sustains this general relationship through the seasons as the top of the saturated zone moves up and down. The saprolite appears to have an average porosity of about 43 percent.

The chemical waste was buried in trenches about 3m deep and 1m to 2m wide. Material removed from the trenches was used as backfill and compacted with the equipment used to dig the trenches.

3. OBJECTIVES

Objectives of the work described were first to determine the possibility of using the hydraulic conductivity and water table conditions to evaluate and understand movement of common organic pollutants in the saprolitic materials. A second objective was to determine constants which might be applicable in similar situations and which might aid in siting monitoring wells and evaluating the risk of ground water pollution from a specific site. It is of course possible that many ground water contamination problems are relatively small and amenable to a simple, low-cost approach to their understanding.

4. DATA COLLECTION

Chemical analysis for Volatile Organic Compounds (VOC) were done by Gas Chromatograph/Mass Spectrometer techniques. Chemical data from the site includes as many as 15 VOC analyses from some of the monitoring wells. Sampling has been by bailing. Rainfall and water data have been collected at the site for a period of approximately 4 years.

5. PROCEDURE

The VOC analyses for the various wells have been contoured as individual sets of analyses from samples collected within one or two weeks of each other, and the geometric mean of the data has been computed for the analyses from each well. The geometric means have been contoured to show the distribution of the contaminants.

The geometric mean was chosen as the best treatment of the data to account for variations associated with the sampling technique and the chemical analyses. This statistic is less affected by the extremes of the data than the arithmetical mean and with small numbers of samples seems the most appropriate statistical measure for the present study. Diethyl ether, chloroform, methylene chloride (dichloromethane), carbon tetrachloride, and benzene are important contaminants at the site. Figure 2 shows the distribution of the carbon tetrachloride and forms the basis of the interpretations discussed below. Under commonly

accepted theory of ground water flow the plume for each compound should extend in the downgradient direction (Figure 1). However, as the contours for carbon tetrachloride indicate (Figure 2) a significant northward component exists to the movement of the contaminant.

The organic carbon content of the saprolite is typically less than 0.01 percent. Thus any retardation effect of organic carbon is probably masked by other processes.

Examination of the data and plots of concentration vs distance in several orientations northerly and westerly from the boundary fence permit the determination of a constant related to the decay and dispersion/diffusion of the particular compound along the selected traverses. Two of these profiles are indicated on Figure 2, A and B. The ultimate goal of determination of a "decay" constant is the ability to estimate how far a particular contaminant may move from its source in a given direction. In the case at hand it is necessary to deal with multiple sources within the site and the probable overlapping of small plumes and mixing of compounds from several small sources. The fence line around the site has been taken as the position where any analysis should begin.

From contour maps and various plots of concentrations and concentration ratios vs distance it appears that the "decay" of a particular compound at the N.C. State University site is related exponentially to the distance the contaminant has traveled from the site boundary. A plot of the concentration vs log distance approximates a straight line, the slope varying somewhat with the particular set of analytical data used.

6. DISCUSSION

Since the analytical data and the maps drawn from the them suggest an exponential change in the contamination levels with distance from the source, the equation $C = C_0 e^{-uS}$ applies to the relationship,

where,

- C_0 = initial concentration
- C = concentration at some distance S
- S = distance from the origin
- u = "decay constant"

For two wells, or one well and the position of a concentration contour along the profile, it is then possible to solve for u , the decay constant, or the rate at which concentration changes with distance along the chosen direction. In the case of the N.C. State University site there probably exist overlapping plumes. Therefore, u is a function of the profile chosen and reflects the existing conditions within the contaminant plume.

Profiles A and B are two of the traverses used to estimate a decay constant for the site (Figure 2). A plot of concentration ratio vs log distance is shown in Figure 3. By extending the plot across one log cycle, one can calculate the slope of the line, and from the plot it is possible to estimate the distance to the non-detectable concentration of the particular compound (zero contour). For some profiles it is also possible to estimate the concentration at a point near the fence line marking the burial site.

Use of the above equation makes possible calculation of the rate of concentration change along each profile. Generally, the profile should be drawn normal to the concentration contours. Table 1 summarizes this information for carbon tetrachloride along the two profiles.

Establishment of the distance-dependent decay rate permits estimation of the time-dependent decay rate. The required velocity factor can be estimated from the time required for the zero contour to have moved from the edge of the burial site to its current position S_0 as determined from the plot of Figure 3. Thus $S = \text{velocity } (v) \times \text{time } (t)$, and the decay equation can be rewritten for time as $C = C_0 e^{-(uv)t}$. For the example given along Profile B, $S_0 = 30\text{m}$; $t = 15 \text{ yr}$; $v = 2.2\text{m/yr}$.

If the profile is constructed normal to the water table equipotential lines, v can be chosen as the seepage velocity. For determination of the outer limit of detectable contaminant concentration, C_0 can be

TABLE 1. *Decay Constant Calculation*

Profile A

Concentration	C/C ₀	Distance (S)	Decay Constant(u)
2.24	1.0	0	-
2.0	.89	1.5	.076
1.0	.45	10	.081
0.1	.045	38	.081
.015	.007	65	.077
.01	.005	70	.077
GEOMETRIC MEAN			.078

Profile B

2.24	1.0	0	-
2.0	.89	2	.057
1.0	.45	15	.053
.71	.31	24	.048
.10	.045	48	.065
.01	.0045	80	.067
GEOMETRIC MEAN			.058

selected as a value at an outer well, or it can be taken from the contour map of the concentrations. The decay equation is then applied, assuming a contaminant concentration approaching zero.

A calculation along Profile B for $C_0 = 0.01$ ppm and $C_t = 0.001$ ppm at some time in the future shows that it will take approximately 13 years for the 0.01 ppm concentration to decay to .001 ppm. In that time the zero contour will have moved approximately 29m northward. However, the concentration of carbon tetrachloride behind the zero contour will be essentially undetectable, and certainly in the parts per trillion range.

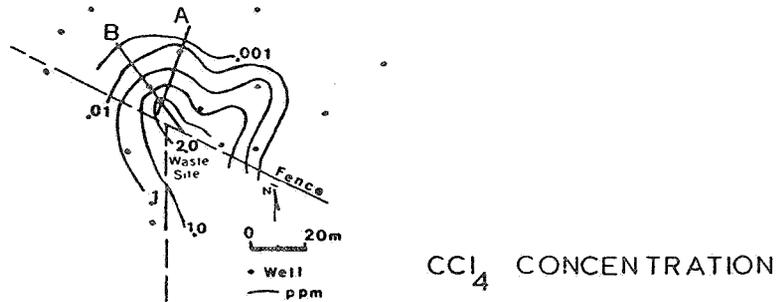


Figure 1. Typical Water Table Map. Theoretical water movement is to northwest.

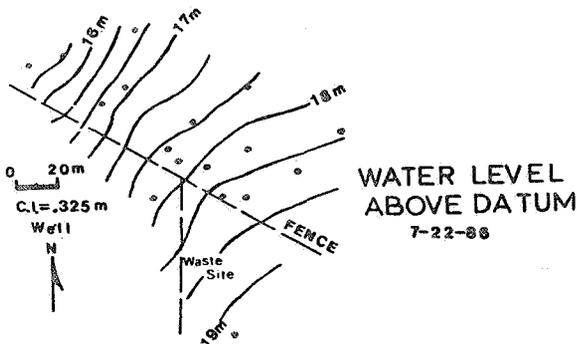


Figure 2. Distribution of CCl₄ based on geometric means of analyses. A and B are profiles for determination of decay constant.

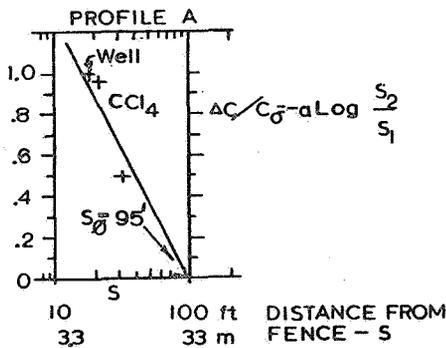


Figure 3. Concentration Ratio vs. Distance. CCl₄ concentration at the well closest to boundary is taken as C₀. This plot is used to establish the position of the zero (non-detectable) concentration. It can also be used to determine probable concentration at site boundary.

7. CONCLUSION

Study and analysis of the data collected at the N.C. State University chemical waste burial site suggests strongly that decay of the common organic compounds can be determined cost effectively and with reasonable accuracy by contouring the concentrations and plotting the concentration distribution along various traverses on semilog plots. It appears that an exponential decay relationship exists and that this can be exploited in evaluating sites.

The outward limit of the detectable concentrations can be quickly determined, and reasonable estimates of the concentrations at the boundary of a site can be made by back-plotting from the well, or point on a concentration contour, chosen to provide the C_0 concentration. In addition, it appears possible to demonstrate within the accuracy of the field data and the complexities of the system the limits to which the contaminant may be reasonably expected to move.

The technique described can be utilized where movement of the contaminant appears to be at angle to the ground water equipotential lines. Because of the general similarity of saprolitic materials from similar rocks over significant areas of piedmont North Carolina, the decay constants determined from study of the N.C. State University site can serve as guidelines for evaluation of other similar sites.

8. ACKNOWLEDGEMENTS

This work has been supported by North Carolina State University. The cooperation of the Department of Public Safety, and the assistance of several graduate and undergraduate students is gratefully acknowledged.

CONTAMINANT HYDROGEOLOGY AND THE ROLE OF GEOLOGY AND FLUID DYNAMICS
IN THE INVESTIGATION OF SUBSURFACE POLLUTIONS

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What has been called "Contaminant Hydrogeology" by its proponents in North-America, has often not been suited to deal adequately with the complex migration pattern of polluting heavy organic compounds and immiscible multi-phase flow in general. This is due to the widespread overemphasis of chemical aspects of pollutants and the neglect of fluid dynamics and the inadequate definition of the geologic environment. After ten years of the chemically dominated "Contaminant Hydrogeology" the order of the day should once again be "plain" hydrogeology, fluid dynamics, fluid chemistry, rock-water interaction and their proper application to particular problems.

1. INTRODUCTION

The term "Contaminant Hydrogeology" has been introduced into North-American literature by Cherry et al. (1975). Today "Contaminant Hydrogeology" in North-America stands for a particular and characteristic scheme of investigations and research of subsurface pollution problems. It appears that, in the mind of its proponents, "Contaminant Hydrogeology" has established itself as the science to deal with subsurface contaminations. This is presently reflected in the great number of consultants and governmental agencies advertising for "Contaminant Hydrogeologists" in North-America. Supposedly a "mere" hydrogeologist would not be suited for the job. More recently the term "Contaminant Hydrogeology" experienced a modification by the used of the descriptor "Contaminant Hydrology" as the title for a new Journal by Elsevier Publishers.

2. CONTAMINANT HYDROGEOLOGY

Contrary to what one might expect from the name, "Contaminant Hydrogeology" does not stand for a method of investigations which would place particular

emphasis on the geologic methods of hydrogeology and the intrinsically related fluid dynamics. In "Contaminant Hydrogeology" investigations and research of subsurface pollution problems usually excell in the chemical and physico-chemical aspects of dissolved pollutants as for example in regard to dispersion, sorption, retardation and partitioning behaviour of the dissolved pollutants, often in conjunction with the application of mathematical models and very simplified geologic parameters. From this paper's point of view there are two things missing, namely the proper emphasis on the geologic framework and the associated fluid dynamics. This would apply for the one-phase flow situation and, to a much more obvious degree, to the two-phase immiscible flow with densities higher than that of the groundwater present.

Schwille (1986, p. 32) characterized the situation as follows:

"In the considerable environmental literature that is concerned with the migration of organic chemicals underground the retention of the immiscible phase has up until now hardly been featured as a fluid mechanical phenomenon but explained generally as adsorption. This way of configuring the situation, practiced predominantly by the physico-chemically oriented environmental scientist, requires use of the expression "water solubility" rather than the expression "immiscibility". Correspondingly the migration of organic chemicals in soluble form is treated almost exclusively while the initial spreading stage of the immiscible phase which so decisively determines the shape and extend of the pollution centre is usually not treated at all. Thus one should not be surprised that for the investigation and restoration of polluted zones the methods corresponding to the newest scientific knowledge are not always applied."

This paper illustrates its points by discussing typical investigations and results layed down in several publications (Jackson et al., 1985, 1986; Walther et al., in print; MacKay et al., 1985). The publications referred to take a somewhat prominent place within North-American "Contaminant Hydrogeology" either by virtue of its presentation as an invited paper (Jackson et al., 1986, in: Hitchon and Trudell, 1986), or by virtue of the prominence of the authors (MacKay et al., 1985) and by virtue of the importance of the client and supporters of the investigation (Walther et al., in print).

The papers by Jackson et al. (1985, 1986) show how a lack of application of basic geologic, hydrogeologic and fluid dynamic principles make the result of a study rather academic. The second and third paper indicate an underestimation of the influence of geology and fluid dynamics on the migration of heavy organic liquids and dissolved pollutants.

3. FLUID DYNAMICS AND GEOLOGY

Only a general outline of fluid dynamics can be given here in regard to the migration behaviour of pollutants. Additional information is contained in the literature cited. When dealing with subsurface pollution one first needs to assess the general fluid dynamical situation as outlined in table 1.

A. miscible flow = one phase aqueous flow with dissolved pollutants

B. immiscible flow = multi-phase flow

B1. liquid phase lighter than water; volatile phase lighter than soil gas i.e. gasoline, oil

B2. Liquid phase heavier than ground water; volatile phase heavier than soil gas i.e. heavy organic compounds

Table 1: Basic fluid dynamic principles applied to migration of pollutants

The migration of inorganic pollutants usually falls into the domain of the one phase flow (Table 1, case A). For the one phase miscible flow the principles of potential theory (Hubbert, 1940; Weyer, 1978) and its further development, the groundwater flow systems theory, apply as outlined by Toth (1962, 1963) and by Freeze and Witherspoon (1966, 1967). The migration of the dissolved part of organic pollutants is governed by the very same principles (Figure 1). Of general importance is (1) in recharge areas the migration of dissolved pollutants from the groundwater table into the groundwater body and (2) in discharge areas the migration from the groundwater body towards the groundwater table.

Multi-phase immiscible flow is subdivided into multi-phase flow with the organic liquids lighter than water (Table 1, case B1) and with organic liquids heavier than water (Table 1, case B2).

The migration behaviour of organic liquids lighter than water (Table 1, case B1) is generally well known and has been summarized by Schwille (1984). The liquid phase migrates towards and along the groundwater table until residual saturation has been reached. A plume of dissolved pollutants migrates as one phase aqueous flow away from the source of the dissolved pollutant i.e. the areas with liquid phase pollutant.

The multi-phase flow behaviour of organic liquids heavier than water has only been understood since about 1980 due to Dr. Schwille's research at the Federal Institute of Hydrology, Koblenz, F.R. Germany (Schwille, 1981, 1984, 1986; Schwille and Ubell, 1982; Schwille et al., 1984). The migration and pollution behaviour of the heavy organic liquids is fundamentally different from light organic liquids as gasoline or oil due to the comparatively high density of the liquid and the gaseous phase. The light organic liquids float on groundwater while the heavy liquids sink to the bottom of the aquifer. Accordingly the light organic liquids are sometimes called floaters while the heavy organic liquids are called sinkers. In figure 1 the results of Dr. Schwille's research are schematically combined with groundwater flow systems theory and the occurrence of an aquitard which, under the polluting source, dips in a direction opposite to the direction of groundwater flow. Heavy immiscible organic liquids sink through the groundwater body to the top of the first low permeable layer (aquitard). Further gravity driven migration of the liquid immiscible phase proceeds along the surface of the aquitard to a local or regional topographical low, regardless of the configuration of the hydraulic gradients within the groundwater flow systems. The migrating liquid as well as the residual saturation along the flow path act as a continuous source of dissolved pollutants. Vapors heavier than soil gas are emitted in the unsaturated zone and eventually dissolve near the groundwater table.

In nature the geologic environment is usually more complicated than that shown in figure 1 due to a limitless number of structural, lithological and facies variations within the three-dimensional rock space. Some of these variations may be difficult to detect but may still exert a pronounced effect on the flow of water and organic liquids. For example within a 10 m thick seemingly uniform sand aquifer the migration of heavy organic liquids can be significantly modified by a layer of lower hydraulic conductivity.

One needs creative geologic thinking, drilling and the application of other investigative tools to unravel the intricate migration path followed by heavy organic liquids in the subsurface. The matter at hand becomes even more complicated because of the fingering tendencies of heavy organic liquids which occurs within unconsolidated rocks as well as in fractured bedrock (Schwille, 1984; Schwille et al., 1984). Except for easy cases it is next to impossible for the non-geologist and difficult for an unexperienced geologist to outline satisfactorily these sources of pollution in the subsurface. This condition may be one of the reasons for the increasing popularity of soil gas investigations. These measurements tend to create the impression of reliable and solid data. They are, however, usually only a first and often incomplete help in determining promising areas for drilling. In this way they can, of course, be one of the tools used in the preparation of a thorough geologic investigation.

The previous discussions do not take into account the "aggressive" behaviour of heavy organic liquids which tend to sink through clay layers regardless of their low permeability for water. This behaviour is now subject of research on dense-non-aqueous-phase liquids (DNAP) by clay mineralogists in the context of the performance of clay liners at landfill sites.

4. CASE HISTORIES

4.1. Case 1

The investigation by Jackson et al. (1985, 1986) is an instructive case in point and shall therefore be discussed in some detail. References are given to the 1985 publication because its figures are better readable and more details are given within the text.

At the Gloucester landfill site near Ottawa, Ontario, Canada, government agencies disposed off inorganic and organic pollutants including heavy organic liquids at the special waste compound and possible at other parts of the Gloucester landfill site. The special waste compound (S.W.C. is situated topographically near the crest of a topographic high (Figure 2) in a recharge area. The surface of the limestone under unconsolidated sediments (Figures 3 and 4) shows a very irregular bedrock topography

(Jackson et al., 1985, p. 23). The surface of metamorphic rocks at the bottom of the rock column shows an undulating topography (Wilson, 1964). Hence the situation at the special waste compound site is in principle similar to the situation shown in figure 1 regarding the bedrock topography and the positioning of the polluting source.

A comparison of figures 16 and 24 of Jackson et al. (1985; this paper: Figures 3 and 4) reveals that the authors show significant geological differences in the two figures for the rocks under the same special waste compound site in regard to the occurrence of coarse angular cobbles and boulders (Figure 3) versus sand and gravel, angular clasts (Figure 4) and regarding the occurrence of fine-coarse sand (Figure 3) versus fine to coarse sand, some gravel and fine silty sand and sandy silt (Figure 4). The boundaries of the angular cobbles and angular clast layers are shown horizontal in figure 3 and strongly tilted in figure 4. Jackson et al. (1985) based their differing "Geologic" evaluation on the very same boreholes, in that particular area namely on borehole 37.

For the underlying "limestone bedrock at depth" Jackson et al. (1985, p.23) assume a permeability of 10^{-7} m/s, taken from a textbook by Freeze and Cherry (1979), while there occurred circulation loss within limestone in the two boreholes 37P-3 and 47P-5 drilled into limestone (ibid, p. 35). Private water supply wells nearby encountered highly permeable zones 7 to 20 m into the limestone (ibid, p. 23). The authors finally expect "that the upper portion of the limestone has been weathered resulting in a more permeable zone with a hydraulic conductivity several orders of magnitude higher than that for intact limestone or dolomite" (ibid, p.23).

From the data available it is obvious that heavy organic liquids could and would migrate into the underlying limestone and also over the surface of the bedrock to the west of the special waste compound. Jackson et al. (1985) basically limit their investigation to the eastward migration of inorganic and organic dissolved pollution plumes within the unconsolidated rocks of the overburden. An example is given in figure 5 showing the migration of the conservative ion chloride. In figure appears, however, to be indicative for two conditions at the Gloucester landfill site, namely (1) that chloride seemingly migrates into the limestone and (2) that a

second pollution plume may be migrating from the special waste compound towards the west (left side of the diagram). The latter should be expected due to the position of the special waste compound near the crest of the recharge area and the groundwater flow directions recorded in figure 2. It appears that the occurrence of the migration of dissolved pollutants towards the west is probable.

Regarding fluid dynamics Jackson et al. (1985) deal to some degree with the solute transport by groundwater. They practically do not discuss the multi-phase flow of organic liquids, both those lighter and those heavier than water. Their figure 41 (partly reproduced in figure 4) contains, however, a plume of dissolved carbon tetrachloride pollution along the borehole 37 and therefore convincing evidence that at least carbon tetrachloride (density higher than water) migrated from the special waste compound vertically downwards to an undetermined depth and possibly laterally towards the West. Hence there must exist additional sources for pollution and additional plumes of dissolved pollutants which have neither been discovered nor even suspected by the authors. Jackson et al. (1986) have, however, already determined, modelled and optimized a scheme for the restoration of the aquifers at the Gloucester landfill site.

4.2. Case 2

Walther et al. (in print) on behalf of the EPA Environmental Monitoring Systems Laboratory in Las Vegas and with funding of the US Air Force prepared a strategy for detecting subsurface organic contaminants making "use of the experience of a team of North-American experts in hydrogeology, geophysics and soil gas sampling". The strategy was presented in November 1986 at the Houston NWW/API Conference on Petroleum Hydrocarbons and organic Chemicals in Ground Water: Prevention, Detection and Restoration.

Figure 6 shows their case 2 of the 10 schematical cases evaluated. It is noticed that a very simple geologic framework has been adopted and that it is assumed that the groundwater flow gradient pushes (or pushed) the heavy organic liquid (in this case a solvent) along a horizontal aquifer base for more than 1 km. A similar assumption is made in their case 7 where hydraulic gradients are assumed to push or have pushed a solvent in opposite directions in the two confined aquifers.

From the above it appears that the authors did not take fully into account the role geology and gravity as well as some general conditions of one-phase and multi-phase fluid dynamics take in determining the migration pattern of heavy organic liquids and dissolved organic chemicals and in determining the position of sources for dissolved organic pollutants and the plumes of dissolved pollutants originating from there.

4.3. Case 3

The paper by MacKay et al. (1985) presents an overview of the transport of organic chemicals in groundwater. There is not much mention of geologic parameters. The discussion is explicitly confined to horizontal flow in horizontal aquifers. All figures in the paper, however, show non-horizontal flow conditions. The paper does not make mention of the gravity driven migration of heavy organic liquids along the topographic gradients of the surface of low permeable layers (aquitards).

5. CONCLUSIONS

During the last decade investigations of subsurface pollution have mainly been dealt with by methods which have been labelled "Contaminant Hydrogeology" in North-America. The methods applied have been dominated by physico-chemical, hydrological and engineering thinking. Geologic and fluid dynamic methods seemingly appeared to be secondary importance. Geologic and fluid dynamic parameters are, however, usually more important for the practicable assessment of underground pollutions and the restoration of the aquifers involved. There is no need for a limited "Contaminant Hydrogeology" without emphasis on hydrogeology and fluid dynamics.

The order of the day should once again be "plain" hydrogeology, fluid dynamics, fluid chemistry, rock water interaction and their proper application to particular pollution problems. The listing sequence above ranks the practical importance of the subjects dealt with. Investigation and restoration of subsurface pollution needs to be done by teams controlled by and experienced hydrogeologist with a good understanding of fluid dynamics.

Although all the examples for this paper have been taken from North-American literature and though the term "Contaminant Hydrogeology" is rarely used in Europe it is nevertheless obvious from the European environmental literature and also from reading some papers in this issue that development in Europe have, to some degree, been similar to those in North-America. One also often finds a lack of geologic understanding and a disregard of fluid dynamics reflected in the methods applied and results obtained. And neither in North-America nor in Europe can this be compensated for by the application of computer models due to the nasty GIGO (garbage in, garbage out) principle.

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Figure 1

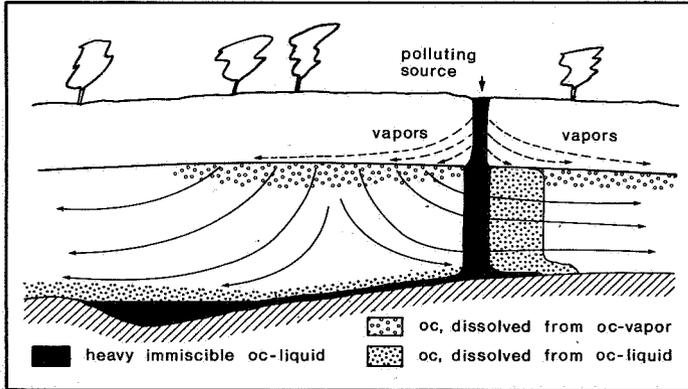


Figure 2

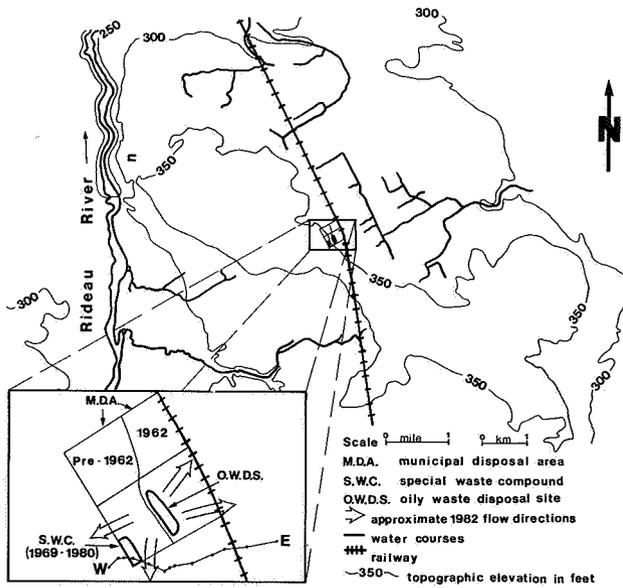


Figure 3

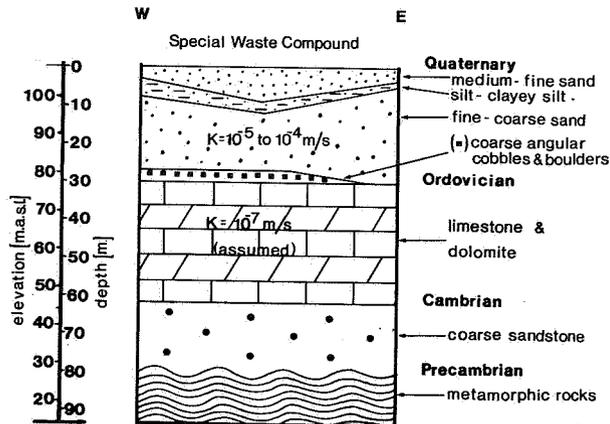


Figure 4

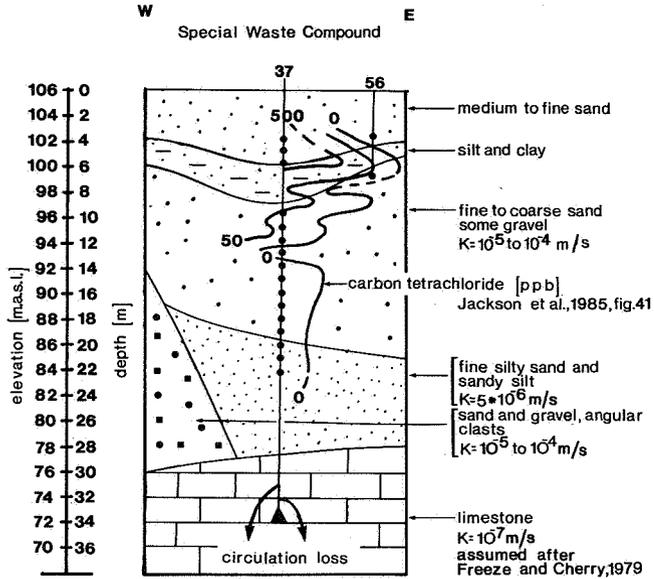


Figure 5

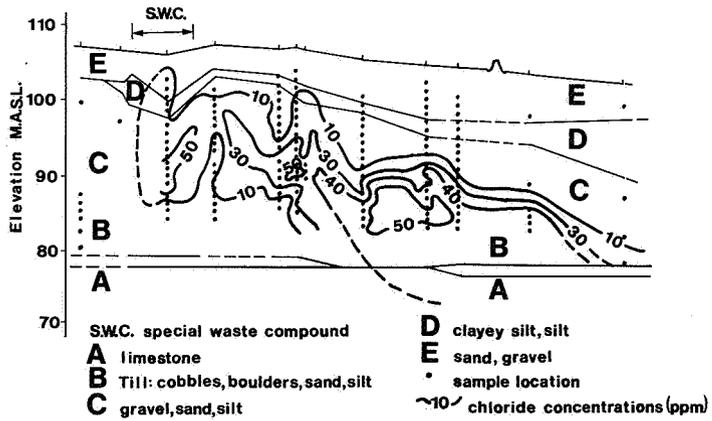
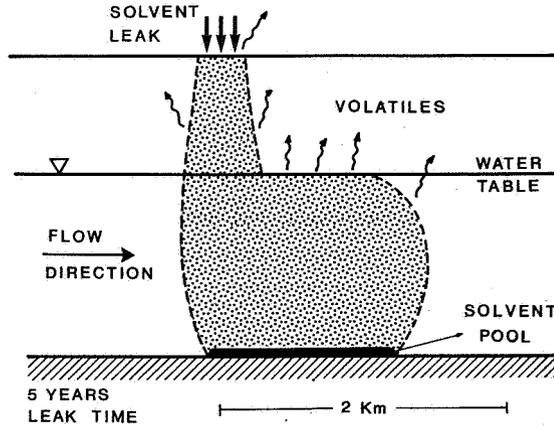


Figure 6



INTERACTIONS BETWEEN SOLID SOIL AND GROUNDWATER:
EXPERIENCES FROM THE MONITORING OF GROUNDWATER
CLEAN UP OPERATIONS AND IN SITU TREATMENT OF
CONTAMINATED SOIL

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ABSTRACT

Some case studies of groundwater clean up and in situ soil treatment are described. Results obtained in the field are compared to the results of shake and column experiments. In order to clean both groundwater and solid soil, many extractions may be needed. This can be achieved by the application of infiltration techniques.

1. INTRODUCTION

Since 1980 remedial action techniques for removal and treatment of contaminated soil and groundwater have become an important issue in The Netherlands. Within this scope, in situ soil and groundwater treatment techniques will be applied more and more. The first drafts of groundwater clean up operations were based on the rule of thumb, that a certain volume of contaminated soil and groundwater should be clean after 3 to 5 extractions of an equivalent volume. This so-called extraction factor of 3 to 5 implies a certain amount of subsequent release of contaminants from the solid soil to the groundwater leading to a prolongation of the clean up process. During the last few years it turned out, that most groundwater clean up operations actually took much more time than had been calculated initially by this method.

In this paper some groundwater clean up and in situ soil treatment projects, executed by De Ruiter Milieutechnologie B.V., will be discussed (de Zeeuw, 1986). The results obtained in the field will be compared to the results of laboratory experiments.

Special attention is paid to interactions between soil and groundwater.

2. CASE STUDIES

2.1 Project Cuyk

In Cuyk a volume of 150,000 m³ of groundwater over an area of 100 x 200 m² was contaminated with tri- and perchloroethylene. A clean up operation started in november 1984. From a well with a depth of 18 m the contaminated groundwater was extracted with a discharge rate of 80 to 90 m³/hr. The contaminant concentrations in the well, ranging from 50 to 500 ug/l (average 90 ug/l), were much lower than the expected value of 10,000 ug/l, based on the concentrations measured in the piezometers. In figure 1. the concentrations versus time are drawn for 4 different piezometers : two (no. 11 and 12) at 4 m depth along the border of the contaminated zone (see figure 1.), and two (no. 19.1 and 19.2) at 4.5 and 17 m depth respectively. The piezometric levels, rainfall surplus and discharge rate are also drawn in figure 1.

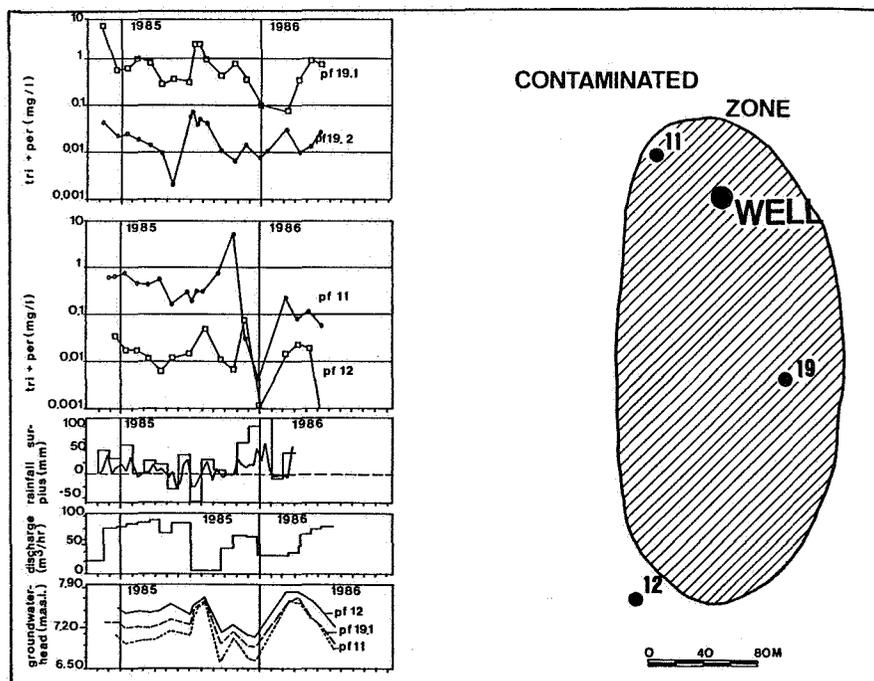


Figure 1 : Location map and results groundwater clean up Cuyk

In periods of a high discharge, and consequently a stronger groundwater flow, in all piezometers a decreasing trend in concentrations has been observed. During periods of no discharge (july/august 1985) or low discharge, the concentrations increase again. This may indicate the release of contaminants from the solid soil to the groundwater by desorption processes. Contaminants are released very slowly from the soil particles by diffusion processes and then mix on a micro-scale with the flowing groundwater. This mixing on a pore-scale is called the mechanical dispersion or convective diffusion (J. Bear, 1979).

Pumping reduces travel and contact time of the groundwater resulting in lower concentrations in the groundwater. Near the border (piezometers 11 and 12) also mixing on a macro-scale may contribute to this effect. The low concentrations in the well itself are mainly caused by mixing with relatively clean groundwater from below. During periods of stagnation contact times between soil and groundwater are much higher resulting in a higher equilibrium concentration in the groundwater. In this way a dynamic chemical equilibrium is present between soil and groundwater. The calculated time needed for the clean up operation amounted to $1\frac{1}{2}$ to 2 years, based on an extraction factor of 4. Up to the end of 1986 already about 6 times the original volume of contaminated groundwater has been extracted, but still the results are not sufficient yet. Meanwhile a second well has been installed to enhance the clean up process, and a plan has been made to install a vacuum drainage system in combination with an infiltration system in order to remove the most heavily polluted groundwater at shallow depths.

2.2 Project Amsterdam

On a former petrol depot in Amsterdam the ground in the unsaturated zone (fine sand) and also the groundwater were contaminated with oil and volatile aromatics. Before the start of the clean up, shake experiments with soil samples from 4 representative locations were carried out in the laboratory. From each soil sample with known contaminant concentrations, 100 g was put into a bottle together with 500 ml of clean water. After 6 hrs of shaking and 16 hrs of rest both the aqueous phase and the soil material were analysed.

In the period of may to august 1986 the soil was treated by a combination of groundwater extraction and subsequent infiltration of this water after purification. Groundwater was extracted from 4 strings of vacuum filters with a total discharge of about 4 m³/h. The purified water was infiltrated again through 3 ditches, filled with coarse sand. Each month, soil samples were taken from 0.25 to 1.25 m below landsurface on the 4 representative locations. The average results of chemical analyses for the 4 locations are shown in table 1.

	the project in Amsterdam (in mg/kg drymatter)			% calculated from shake experiments	
	21/5/'86	7/7/'86	12/8/'86	% removed	
Mineral oil	1,478	496	425	71 %	50 %
Benzene	0,06		0.01	-	99 %
Toluene	0.05		0.17	-	91 %
Ethylbenzene	7.0		0.26	96 %	75 %
Xylenes	82.6		1.7	98 %	63 %
Btex-total	89.7		2.1	98 %	-

From the shake experiments the percentages of contaminants removed from the solid soil after one extraction could be calculated. These percentages ranged from 12% for mineral oil up to 60% for benzene. During the period may - august 1986 a volume equal to 5 times the contaminated volume of solid soil and groundwater was extracted. Assuming that the removal percentages remain constant for each extraction, the removal percentages after 5 extractions can be calculated. These results are also given in table 1. From these results it appears that under field conditions more contaminants have been removed from the solid soil than was calculated from the shake experiments. The following processes contribute to the removal of the contaminants:

- transport by dissolution
- colloidal transport
- microbiological degradation
- evaporation/volatilization

The first two processes are believed to be realistically modeled in the shake experiments. Because the time span of the shake experiments was much shorter than the actual project execution, it is believed that the

microbiological degradation may account for the differences between the results obtained in the field and the results from the shake experiments. The effect of volatilization of the contaminants may also account to some extent for the observed differences.

2.3 Project Amersfoort

Because of leakage from underground storage tanks or pipelines, both the solid soil and the groundwater around a petrol station were contaminated by petrol and volatile aromatics. The underground storage tanks and pipelines were removed when the petrol station was dismantled. In the course of the rebuilding of the petrol station however, not all the contaminated soil could be removed, because the clean up operation had to be carried out in such a way, that the petrol station and also a garage could remain in operation. This implied that some of the contaminated soil has to be treated in situ. Column experiments have been conducted in order to simulate the clean up of the soil.

The actual clean up operation started only recently. Groundwater is extracted by a number of shallow wells, and is infiltrated again through a central infiltration drain, after purification. This drain is placed in such a way that the most severely contaminated soil will be flushed the most intensively.

2.3.1 Column experiments

Two columns were identically filled with soil samples from the location in Amersfoort (fine sand) with known concentrations of mineral oil and volatile aromatics. Column A was flushed by tap water with a discharge rate between 0.3 and 4.3 l/day. Column B was flushed by a fertilizer dissolution, with a discharge rate ranging from 0.8 to 1.2 l/day. In the beginning of the experiment the influent of column B contained 0.6 mg N/L. After 21 liter the fertilizer concentration was raised to 6 mg N/L. On regular time intervals effluent samples were taken and analysed. The soil in the columns was contaminated so severely, that the first liter of effluent for both columns contained an immiscible oil phase.

This oil phase was analysed separately. After the experiment the soil in the column was analysed again.

In figure 2. the concentrations of volatile aromatics are shown against the number of extractions (extraction factor). The concentrations in the first samples have been corrected for the presence of the immiscible oil layer.

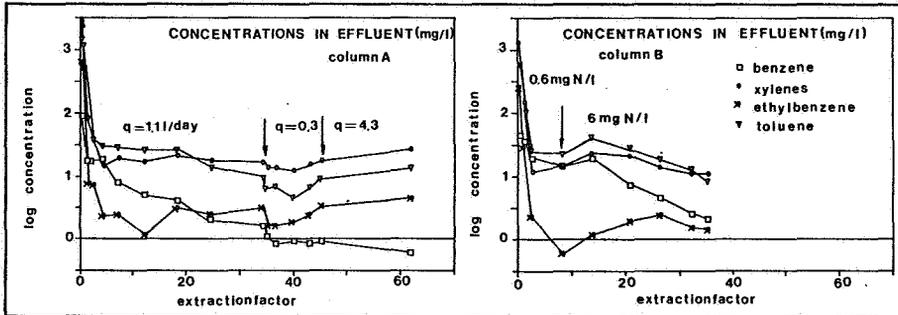


Figure 2 : Effluent concentrations column A and B

An increase in discharge leads to an increase in concentrations. This is in contradiction with the theory of chemical equilibria, which states that a higher discharge leads to lower concentrations due to the lower contact and travel time of the water, as has been described earlier in this paper for the project Cuyk. An explanation for the observed relation between discharge and effluent concentration is that a "drag-effect" is present. At a higher discharge rate more fine soil particles are transported by the water phase. Relatively high amounts of aromatic compounds may be adsorbed on these small, "colloidal" particles. Also an increase in fertilizer-concentration leads to higher effluent-concentrations. This is most likely caused by ion-exchange reactions, where the aromatic compounds are replaced by ions of the fertilizer dissolution. The extra addition of fertilizer may also lead to a strengthening of the drag-effect.

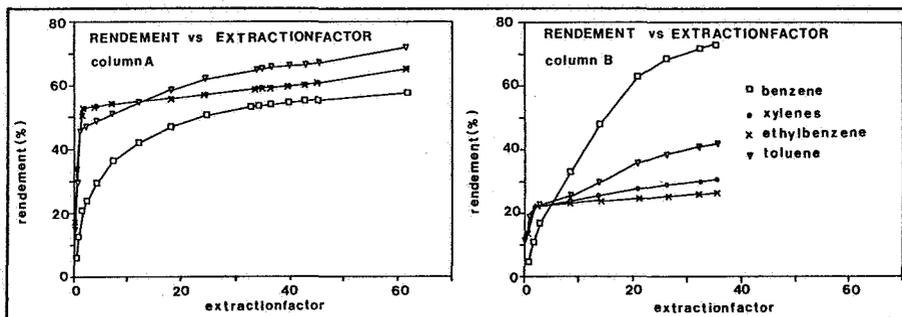


Figure 3 : Amount of aromatics flushed with the effluent as a percentage of the total original quantities in the soil.

In figure 3 the percentages of the volatile aromatics are shown, that were released from the columns with the effluent.

Three processes are considered to contribute to this release:

- flushing the immiscible oil phase at the beginning of the experiment
- flushing the water phase
- the drag-effect.

In table 1. the percentages of the volatile aromatics are shown, that have been removed from the soil on the basis of analysed soil samples before and after the experiments. For comparison also the percentages, that have been flushed, are given (water + oil phase, and water phase only).

Table 1 : Percentages of volatile aromatics flushed out of the columns

	Column A				Column B			
	b	t	e	x	b	t	e	x
(1)	99,8	98,4	93,8	92,9	98,7	95,3	90,9	86,6
(2)	54,0	65,5	59,5	62,9	73,4	41,9	26,7	30,7
(3)	57,8	72,1	66,6	70,2	-	-	-	-
(4)	48,9	42,0	31,7	34,7	71,0	31,2	14,0	17,9
(5)	52,7	48,6	38,8	42,0	-	-	-	-

b = benzene, t = toluene, e = ethylbenzene, x = xylenes

(1)= based on analysed soil samples before and after the experiment.

- (2)= based on effluent concentration (oil and water phase)after 36 extractions
- (3)= as (2), but after 62 extractions
- (4)= based on effluent concentration (water phase only) after 36 extractions
- (5)= as (4), but after 62 extractions.

The percentages of the volatile aromatics that have been flushed out of the soil by the water phase only, are in agreement with the adsorption/desorption characteristics, as can be derived from the distribution coefficients and the octanol-water partition coefficients (Chiou and Schmedding, 1982 ; Rogers et.al., 1980 ; Garbarini and Lion, 1986). Hence : % benzene > % toluene > % xylenes > % ethylbenzene.

This is not the case for the volatile aromatics that have been flushed out of column A by both the water and the immiscible oil phase. From column A relatively much more xylenes, toluene and ethylbenzene were removed, because the oil phase contained relatively much more of these compounds than of benzene.

The differences between the percentages based on the effluent concentrations (water + oil phase) and the analysed soil samples indicate, that volatilization and microbiological degradation may account for a large part of the release of the contaminants from the soil. In column B relatively smaller amounts of toluene, ethylbenzene and xylenes have been flushed out than in column A. This indicates that the addition of fertilizer has increased the microbiological degradation within the column. However, this is not the case for benzene, because volatilization is probably dominating the release from the soil.

The column experiments show, that the volatile aromatics can be removed almost completely from the solid soil. In the end of the experiment however, concentrations in the effluent for the individual volatile aromatics remain relatively high (> 1 mg/l). This means that in practice after the cleaning of the solid soil still further extractions are needed to clean up also the contaminated groundwater.

3. CONCLUSIONS

The first groundwater clean up operations have been based on the rule of thumb that an equivalent volume of contaminated groundwater should be pumped a number of times (3 to 5) before the groundwater is cleaned. However, it has become clear that more extractions are needed.

The number of extractions needed to clean up soil and groundwater (extraction factor) is strongly related to the adsorption/desorption equilibria between the solid soil and groundwater.

In this paper some case studies have been given, where the extraction factor was determined by laboratory experiments. From the case studies it has become clear, that for some contaminants both the groundwater and the solid soil can be cleaned. In order to do so an intensive flushing of the soil can be reached when infiltration techniques are applied. In practice, for volatile aromatics the extraction factor may lie between 25 and 250, and for tri- and perchloroethylene between 10 and 30, depending on the degree and nature of contamination, the soil characteristics, the influence of microbiological activities, and the desired residual concentrations. As in case, where only the groundwater is cleaned, it is important to monitor the contaminant concentrations in both solid soil and groundwater. Sometimes the concentrations of the contaminants in the solid soil may be very small (or even below the detection limit), while still significant concentrations of the contaminants are present in the groundwater.

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**TOPIC 6: USE OF DATA REQUIRED FOR MODELING
QUALITY OF SOIL AND GROUNDWATER**

THE ROLE OF SOIL DATA IN ASSESSING THE LARGE-SCALE
IMPACT OF ATMOSPHERIC POLLUTANTS ON THE QUALITY OF
SOIL WATER

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ABSTRACT

The regional application of process-oriented models of water quality is generally limited by a lack of input data. Consequently, to meet the need for data on a regional scale, the level of generalization selected for process description (process aggregation) must be appropriate. This is illustrated for a regional model of soil acidification, in which the soils processes considered of major importance in mitigating the effects of acid deposition on soil water chemistry (mineralization, weathering and cation exchange) are represented by simple first-order reactions and exchange equations. Rate constants and exchange (selectivity) coefficients are obtained from literature, descriptive research and process research. The physical and chemical soil properties are derived from soil characteristics collected routinely during soil surveys using 'transfer functions'. The key role of soil maps and associated soil survey information in obtaining data on model parameters is illustrated in relation to the use of these transfer functions.

1. INTRODUCTION

The large-scale input of pollutants to the soil by atmospheric deposition and the application (often excessive) of organic fertilizers is threatening the water quality in large, mainly sandy, areas of the Netherlands. High concentrations of nitrate, and locally of phosphate and aluminium, are observed in both soil water and groundwater.

In order to ascertain the impacts of pollutants on future water

quality, process-oriented simulation models are being developed at the Netherlands Soil Survey Institute, aimed to predict water quality on a regional scale for various input scenarios. Three notable examples are:

- A regional soil-acidification model (RESAM) relating soil-water quality (e.g. aluminium concentrations) to atmospheric deposition of SO_2 , NO_x and NH_3 (De Vries, in prep.).
- A regional phosphate-transport model (REPTRAM) predicting the impact of phosphate application via animal manure on phosphate transport in the unsaturated zone (Breeuwsma and Schoumans, in prep.).
- A regional nitrate-leaching model (RENLEM) estimating nitrate leaching from nitrogen input by atmospheric deposition, fertilizers and organic manure (De Vries et al., in prep. (a)).

Such models are valuable tools to decision-makers, assisting them to evaluate abatement strategies.

The regional application of process-oriented models is generally hampered by a lack of input data. Therefore, it is necessary to select an appropriate level of generalization of the model and its parameters in relation to the data available on weather, crops, soil, and groundwater. As regards the soil data, the complexity of the model and the associated data requirements should be in balance with the availability of data from soil surveys and soil research.

In this paper, the role of soil research and soil survey information in obtaining data on parameters for models of regional water quality is illustrated for the regional soil-acidification model (RESAM). It was decided to focus on this environmental problem, because atmospheric deposition affects all major ions in the soil solution through a multitude of biochemical and geochemical interactions with the vegetation and the soil. The discussion on data derivation is limited to forest ecosystems acid sandy soils.

2. MODEL COMPLEXITY AND REGIONAL APPLICABILITY

Models relating the response of water quality to atmospheric inputs can either be based on an empirical approach or on mechanistic descriptions of processes. The great drawback of empirical input-output models is

that they lack a theoretical basis for establishing confidence in the predictions. However, the disadvantage of physically-based (i.e. process-based) models is the general lack of the input data required to enable the model to be applied on a regional scale. This dilemma between detail (and reliability) of information obtained and regional applicability is illustrated in Figure 1.

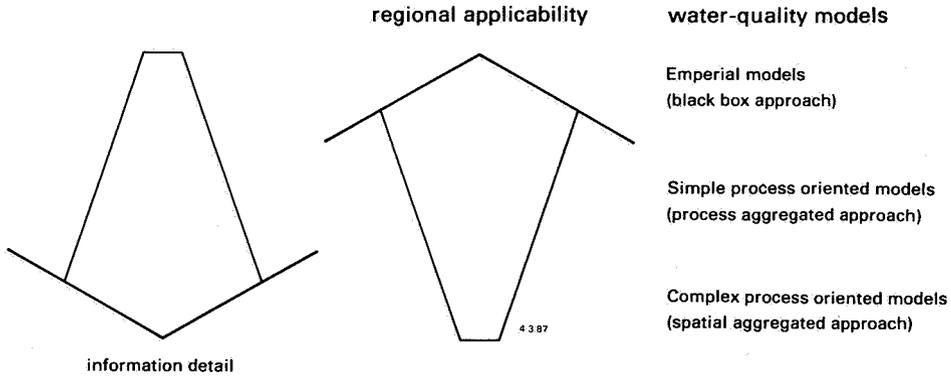


Figure 1 *Schematic diagram illustrating the contrast between the complexity of water a model of quality and its adequacy for regional application*

The desired degree of spatial resolution in model output is of crucial importance when selecting the level of detail that is appropriate for both the model and its parameters. For example, understanding the bulk chemical composition of stream water at the outlet of a catchment may not require precise knowledge of the spatial variation in soil properties, but understanding the vertical distribution of ions in the unsaturated zone certainly does.

Consequently, insight in the hydrological and chemical response of surface water to inputs (e.g. precipitation, acid deposition) is generally obtained from physically-based lumped parameter models, which 'average' or lump the spatially distributed physical and chemical processes in a catchment (spatial aggregation) (Cosby et al., 1985). However, the response of soil-water chemistry to input of pollutants has to be ascertained using a physically based distributed parameter model, because soil types and soil horizons influence the hydrological

and chemical behaviour of the soil system.

The use of "distributed" models allowing for spatial variations within a catchment (region) is a new development in the field of soil science (Goldstein et al., 1983; Bathurst, 1986). In order to apply these distributed models on a regional scale, the multitude of hydrological, biochemical and geochemical processes occurring in soils must either be represented by simple conceptualizations or be limited to a few key processes controlling the gross behaviour of the soil system (process aggregation) (Figure 1). Failure to do this leads to complex, multi-parameter simulation models with a large potential to explain system behaviour but few possibilities for regional application. At the Netherlands Soil Survey Institute, we believe that an intermediate level of generalization is most appropriate. It is sufficiently detailed to allow quantitative and reproducible predictions of water quality based on current knowledge of important processes, and it can be applied on a regional scale.

3. MODELLING APPROACH

In order to understand the probable long-term effects of acid deposition it is necessary to use a conceptual framework of the acidification process. One concept that is consistent with established physicochemical principles is to regard the acidification process as a disturbance in the nitrogen and sulphur cycles induced by the deposition of SO_2 , NO_x and NH_3 (De Vries and Breeuwsma, in prep.). This causes the input of strong acid anions (SO_4^{2-} and NO_3^-) to exceed base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) associated with proton production.

Figure 2 is a simple relation diagram of a conceptual model of soil acidification, depicting major processes influencing element cycling and proton transfer.

In order to illustrate the use of soil data in this water-quality model we shall focus on processes directly affecting the cation composition of the soil; viz. mineralization, weathering and cation exchange. Hydrological processes influencing the water flux and moisture content in each soil layer will not be discussed in this paper. How-

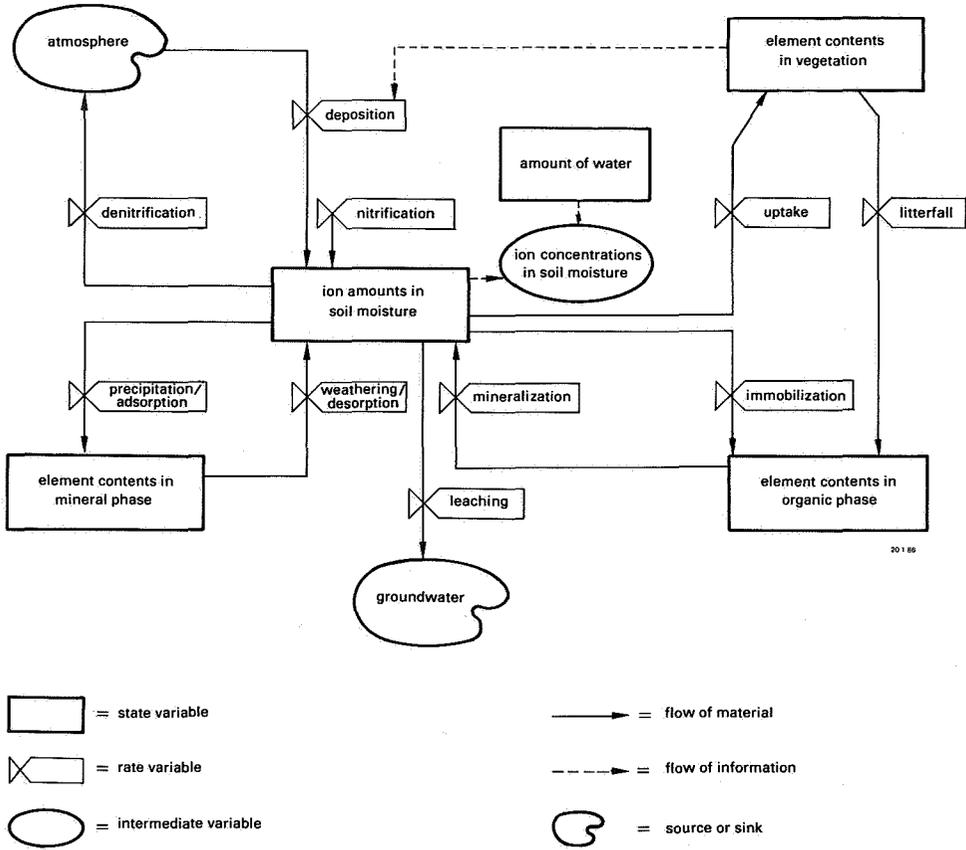


Figure 2 A simplified relation diagram of the regional soil acidification model

ever, some attention will be paid to the derivation of crucial physical properties of the soil; viz. the moisture retention curve ($\theta-h$) and the hydraulic conductivity curve ($K-h$), which affect water transport, and bulk density (ρ), which affects nutrient transport. Both mineralization and weathering can be described by simple first-order reactions according to:

$$\frac{\Delta AX_{om}}{\Delta t} = - km * AX_{om} \tag{2}$$

where:

AX_{om} = amount of nutrient X in organic matter (litter) ($\text{mol}(+)\text{kg}^{-1}$)
 km = mineralization rate constant (yr^{-1})

In this simple equation, the mineralization rate is assumed to be the same for all elements. In acid forest soils, this may not be true for nitrogen. The mineralization of this element is generally less than that of carbon, because of the high C/N ratio of the litter layer.

$$\frac{\Delta AX_m}{\Delta t} = - fX_w * K_w * ANC_m (c_H - c_{He}) \quad (3)$$

where:

AX_m = amount of element X in mineral soil ($\text{mol}(+)\text{kg}^{-1}$)

fX_w = equivalent fraction of element X released by weathering (-)

K_w = weathering rate constant ($\text{m}^3 \text{mol}(+)^{-1} \text{yr}^{-1}$)

ANC_m = acid-neutralizing capacity of mineral soil ($\text{mol}(+)\text{kg}^{-1}$)

c_{He} = equilibrium concentration of H (controlled by gibbsite solubility) ($\text{mol}(+)\text{m}^{-3}$)

In this equation, mineral weathering is greatly simplified, because the influence of pH on weathering stoichiometry (values of fX_w) is not included and the influence of pH on weathering rate is assumed to be the same for both aluminium and base cations. However, in acid sandy soils, these are not severe restrictions.

The exchange of an arbitrary ion X against a reference ion (e.g. Ca) can be described by:

$$\frac{(EX_{ads})^{1/z_x}}{(ECa_{ads})^{1/2}} = K_n(X, Ca) * \frac{(cX_{dis})^{1/z_x}}{(cCa_{dis})^{1/2}} \quad (4)$$

where:

EX_{ads} = equivalent fraction of element X on the exchange complex

z_x = valency of element x

$K_n(X, Ca)$ = the exchange (selectivity) coefficient of X with respects to Ca

'ads' and = adsorbed and dissolved respectively

'dis'

The major elements included in these processes are Al, Fe, Ca, Mg, K,

Na, NH_4 and H. The sum of all adsorbed (exchangeable) cations (AXads) equals the cation exchange capacity (CEC), and the sum of all weatherable cations (AXm) equals the acid-neutralizing capacity (ANCm).

4. SOIL DATA REQUIRED AND THEIR DERIVATION

4.1 General

The data required by a physically-based model of water quality can be divided into: (i) model inputs or forcing functions like weather data and input of pollutants; (ii) parameters like crop factors, rate constants and physical and chemical soil properties, and (iii) variables like amounts of elements in vegetation, organic matter, minerals and soil solution. If these data are limited to the parameters (and variables) associated with the processes mentioned above, the data given in table 1 are required.

Table 1 *Important soil data required by a model of soil acidification*

Processes	Constants	Soil properties	Elements
Water transport	-	ρ , θ -h, K-h	-
Mineralization	km	AXom (ANCom)	Ca, Mg, K, Na, N
Weathering	kw, fXw	AXm (ANCm)	Ca, Mg, K, Na, Al
Cation exchange	Kn (X, Ca)	AXads (CEC)	Ca, Mg, K, Na, NH_4 , Al, H

Specific soil research is needed to obtain values of constants, whereas values of soil properties can be derived from soil survey information.

4.2 Derivation of rate constants, weathering fractions and exchange coefficients

The methodology for deriving parameter values for constants describing the relation between the solid phase of the soil (organic phase, mineral phase and exchange phase) and the soil solution is summarized in table 2.

Table 2 *Parameter derivation for the model of soil acidification: 1 = process research; 1A = incubation experiments; 1B = titration experiments; 2 = descriptive research; 2C = solid phase analysis; 2D = soil solution analysis.*

Processes	Parameters	Elements	Parameter derivation			
			1A	1B	2C	2D
Mineralization	km	-	X		X	
Weathering	kw, fXw	Al, Ca, Mg, K, Na		X	X	(X)
Cation exchange	Kn (X, Ca)	H, Al, NH ₄ , Mg, K, Na		X	X	X

Rate constants of organic matter decomposition (mineralization) can be derived from incubation experiments by measuring the rate of carbon dioxide evolution from moist (soil) samples, placed in an incubator at constant temperature (Gilmour et al., 1985). Both moisture content and temperature strongly influence the value of km. An indication of the mineralization rate constant can also be obtained from field experiments by measuring the amount of organic matter on fallow land over a long time period (years). Values thus obtained for tree litter vary between 0.05 yr^{-1} and 0.3 yr^{-1} for old and fresh litter from spruce-trees and between 0.2 yr^{-1} and 0.6 yr^{-1} for old and fresh litter from deciduous trees (derived from Kolenbrander, 1974).

The rate (kw) and stoichiometry (fXw) of mineral weathering can be derived from column-type or batch-type titration experiments. However, relatively long-term experiments are needed to obtain these parameters, because rapid exchange of base cations is the main neutralizing process during the initial stage of proton consumption. In these experiments, the rate of acid neutralization with progressive proton consumption is directly obtained by measuring at rate acid must be added to maintain a constant pH. With column-type experiments, a titrator set up can be used with a continuous automatically adjustable rate of acid addition to keep a fixed pH value (pH-stat); batch type experiments require intermittent adjustment of pH. The release of cations with proton consumption is derived from intermittent solution analysis (De Vries et al., in prep.). The values of kw obtained at pH 3 ($cH = 1 \text{ mol m}^{-3}$) for B and C horizons of gleyic, humic and leptic podzols (the dominant

forest soils in the Netherlands) vary between $0.005 \text{ m}^3 \text{ mol}^{-1} \text{ yr}^{-1}$ and $0.030 \text{ m}^3 \text{ mol}^{-1} \text{ yr}^{-1}$, with an average value of $0.019 \text{ m}^3 \text{ mol}^{-1} \text{ yr}^{-1}$. In other words, the annual weathering rate ($\Delta\text{ANC}/\Delta t$) of these horizons at this low pH is 0.5 to 3% of the acid-neutralizing capacity (ANC). Average values of fX_w for these horizons at this pH are given in table 3, together with the results of a historical profile analysis. The principle of the historical approach is the analysis of the cation composition of a soil profile. The weathering stoichiometry is ascertained by comparing the distribution of a given element (in $\text{kmol}(+)\text{ha}^{-1}$) between the parent material (C horizon) and the overlying A and B horizons (De Vries and Breeuwsma, 1986). The results given in table 3 are average values for the A and B horizons of six gleyic podzols, three humic podzols and three leptic podzols.

Table 3 *The fractions of elements released from A-, B- and C-horizons of podzolic soils as obtained by profile analysis (historical approach) and column experiments (actual approach)*

	fAlw	fFew	fCan	fMgn	fKw	fNaw
Profile analysis	0.74	0.09	0.03	0.03	0.06	0.05
Column experiments	0.89	0.02	0.03	0.01	0.03	0.02

The results of the historical profile analysis indicate that mineral weathering induced by natural proton production (organic acids) has been dominated by aluminium release in these acid podzolic soils. The column experiments (at pH 3) indicate a relative increase in aluminium mobilization. This may be more realistic with respect to present weathering stoichiometry which is mainly induced by atmospheric deposition (sulphuric and nitric acids).

Column and batch experiments can also be used to derive exchange coefficients by measuring the exchangeable cations at the end of short term experiments (at different pH values) and comparing the reduced cation ratios at the exchange complex with the ratios in solution. Similarly, exchange coefficients can be obtained by analysing the exchangeable cation composition of a soil profile and comparing this with data on the soil solution. The latter data can be obtained by

monitoring: Kn values are currently being derived in forty forest soil profiles (mainly podzolic soils) in which the soil solution is monitored regularly (Kleijn and De Vries, in prep.). Soil solution analysis also reveals aspects of the weathering stoichiometry.

4.3 Derivation of physical and chemical soil properties

Physical and chemical soil properties, as described before, can often be related to known soil (and land) characteristics, such as texture and organic matter, obtained during soil surveys using so-called transfer functions. A subdivision is made between continuous characteristics that have a continuous range of values (e.g. % clay) and class characteristics that are characterized by either a specified range of values (e.g. texture class) or by a symbol (e.g. soil type, horizon designation). Similarly, transfer functions, relating soil properties to soil (and land) characteristics, are divided into continuous and class transfer functions (Bouma et al., 1986).

The use of soil survey information in deriving physical and chemical soil properties with transfer functions is illustrated in figure 3.

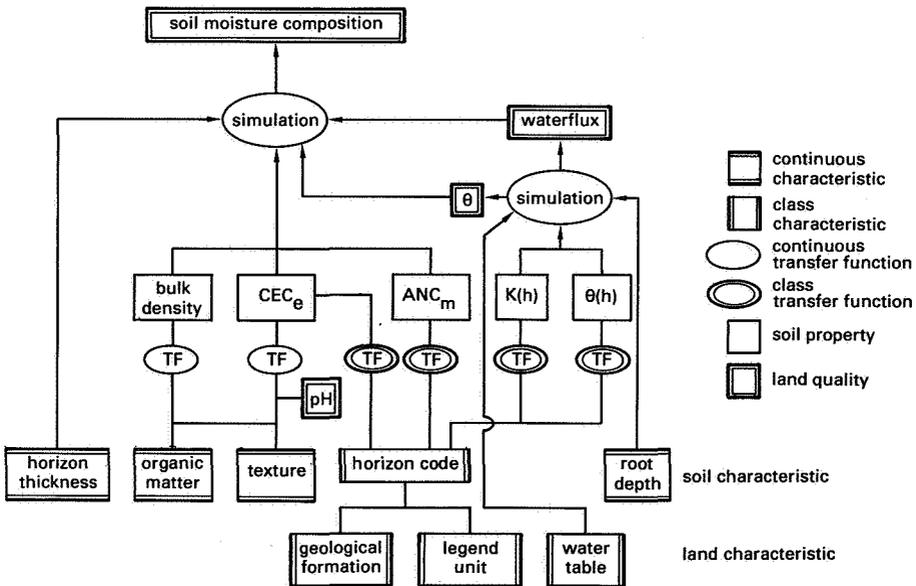


Figure 3 Diagram illustrating the use of soil survey information in regional water quality models

Bulk density has been related to organic matter content and texture with a continuous transfer function using regression analysis (Hoekstra and Poelman, 1982). The same method has been used to derive CEC values (measured at pH 6.5) from the clay- and organic matter contents of the soil (Breeuwsma et al., 1986). Further investigation is needed to obtain continuous transfer functions deriving the effective CEC (CECe) at field pH, because pH influences the exchange capacity of organic matter. The physical soil properties $\theta-h$ and $K-h$ have been related to well-defined horizon designations for soil types distinguished in soil surveys (class transfer functions). The significance of physical differences between soil horizons has been tested in relation to functional properties such as travel time (Wösten et al., 1986). In a similar way, class transfer functions can also be derived for the chemical soil properties ANCM (including weatherable cations) and CECe (including exchangeable cations). Average values of the ANCM and CECe of the A, B and C horizons of the gleyic, humic and leptic podzols mentioned before are given in table 4.

Table 4 *Indicative values of ANCM and CECe (mmol(*)kg⁻¹) of podzolic soils in the Netherlands*

Horizon	Gleyic podzol		Humic podzol		Leptic podzol	
	ANCM	CECe	ANCM	CECe	ANCM	CECe
A1	1150	40	800	40	2000	60
B2	2000	55	2000	55	2550	20
C1	2400	5	2400	5	2400	5

Information on the amount of cations in the Ao horizon or litter layer (ANCom) is very scarce and further investigation is needed to derive (class) transfer functions.

Table 4 shows that the B2 horizons of the gleyic- and the humic podzol and the C1 horizons of the three soil types have the same ANCM and CECe: the other combinations of soil horizons and soil types differ. The same applies to the amount of weatherable and exchangeable cations. Average values of the equivalent fraction of weatherable cations (EXm) are given in table 5.

Table 5 Average values of EXm as a function of soil type and soil horizon

Elements	EXm	Soil types ²⁾	Horizons
Al	0.72	Hn, Hd, Y	A, B, C
Fe	0.08	Hn, Hd	A, B, C
Fe	0.11	Y	A, B, C
B ¹⁾	0.20	Hn, Hd	A, B, C
B	0.17	Y	A, B, C

¹⁾ B = Ca + Mg + K + Na

²⁾ Hn = Gleyic podzol

Hd = Humic podzol

Y = Leptic podzol

Equivalent fractions of weatherable cations appear to be fairly constant, irrespective of soil type and soil horizon. The main differences between equivalent fractions of exchangeable cations are those between the H and Al and base saturation of A horizons and B/C horizons. In the A horizon, H and base saturation are higher and Al saturation is lower than in the underlying horizons. Furthermore, the equivalent fraction of all exchangeable cations in the A and B horizons of a leptic podzol is generally different to that in gleyic and humic podzols.

Tables 4 and 5 illustrate the phenomenon that pedogenetic differences do not necessarily correspond to functional differences from a chemical viewpoint.

The class transfer functions derived for these sandy soils illustrate the important role of soil type and soil horizons as carriers of physical and chemical soil properties that are important input data in regional water quality models. The soil map, which shows where the soil horizon ('building blocks') in various soil types can be found, allows a geographical presentation of the results.

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CAN THE DISTRIBUTION COEFFICIENT (Kd) CONCEPT ACCOUNT SUCCESSFULLY FOR THE ADSORPTION OF POLLUTANTS IN HYDRODYNAMIC MASS TRANSFER MODELS?

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ABSTRACT

Traditionnally, for solutes capable of interacting with solid surfaces, mass transfer models have used the Kd concept (i.e. a constant distribution coefficient) to account for the partition of the solute between the solid and the liquid phases. This approach, strongly criticized by many, has nevertheless in some cases produced acceptable mass transport predictions. Actually the applicability of the Kd approach is subject to the effect of solution chemistry (hydrolysis and dissolved complexation) on adsorption. The migration of weakly chemically reactive species (such as nonpolar hydrophobic organics and some metals) can be modeled using constant distribution coefficients. Modeling of limited predictive use for vulnerability assessment can also be achieved for small concentrations of highly reactive species provided that the chemistry of the aquifer is at equilibrium.

1. INTRODUCTION

The migration of non-biodegradable and non-volatile pollutants in aquifers is the result of the competition between solution transport and retention by insolubilization (adsorption, precipitation). Even though many questions still need to be answered, it is now recognized that adsorption processes are significant controls on the fate of pollutants in aquatic systems [Jenne (1968) ; Stumm (1982) ; Bourg (1987a)].

Convective and dispersive transport models of substances capable of reacting with solids must therefore introduce a chemical sorption term. Many such models have used the K_d concept (i.e. a constant distribution coefficient for the partition of the element or compound of interest between the solid and the liquid phases). This approach has the advantage of merely modifying the transfer functions by a retardation factor, which affects the time scale. It has been strongly criticized by many [Mc Kinley and Greenwood (1980) ; Reardon (1981) ; Bourg (1982) ; Bourg and Mouvet (1984) ; Leckie and Tripathi (1985) ; Cremers and Maes (1986) ; Bourg (1986) (1987b)] but has nevertheless, in some cases, produced acceptable mass transport predictions [Schwarzenbach and Westall (1981) ; Curtiss et al. (1986)].

Kd or not Kd, that is the question.

[After Shakespeare, Hamlet (Act III, Scene I)]

This philosophical statement will now be addressed in terms of the situations (i.e. pollutant and aquifer conditions) for which a constant partition coefficient is acceptable and those for which it is completely inadequate. This short paper will be presented elsewhere in greater details [Bourg and Sauty (1987)].

1. THE DISTRIBUTION COEFFICIENT K_d

The partition of an element or compound between a solid and a liquid phase can be quantified by the parameter K_d , typically defined as :

$$K_d = \frac{\text{total concentration in solid phase (per unit mass of solid)}}{\text{total concentration in solution (per unit volume of liquid)}} \quad (1)$$

This coefficient is easily measured for natural systems but one should be aware of the fact that the numerator does not discriminate between the various possible solid species (adsorbed on the surface, present as pure precipitates or as impurities in other precipitates).

If K_d is restricted to the quantification of adsorption, equation (1) can be written as :

$$K_d = \frac{C_0 - C}{C} \times \frac{v}{m} = \frac{S}{C} \quad (2)$$

where C_0 = dissolved initial or total (adsorbed + dissolved) concentration ; C = dissolved concentration, v = volume of liquid phase, m = weight of solid phase and S = adsorbed concentration (per unit mass of solid).

The partition of an element or compound between adsorbed and dissolved fractions can follow various mathematical relationships as a function of the equilibrium dissolved concentration (figure 1). For metals, adsorption isotherms are usually either of the Freundlich (parabola) or Langmuir (hyperbola) type. For hydrophobic organic pollutants, adsorption isotherms are often linear, and thus the corresponding K_d is independent of the total concentration of the compound. For metals it is generally accepted that, at low solute concentration, the partition coefficient can be realistically assumed to be constant.

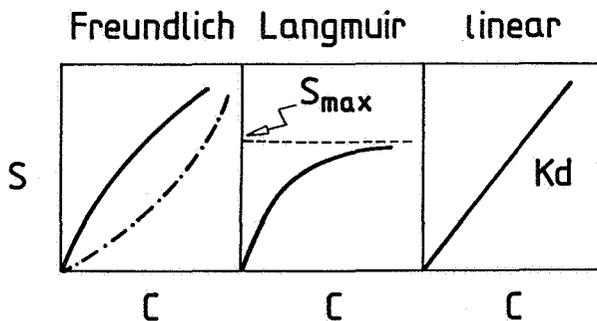


Figure 1 The most common types of adsorption isotherms (S and C are the equilibrium concentrations of adsorbed compound, on a solid weight basis, and dissolved compound, on a liquid volume basis).

A distribution coefficient can be measured at any time during the course of an adsorption reaction, a process which may not actually be reversible. However, it should be emphasized that the traditional K_d concept usually implies the notions of equilibrium and fully reversible adsorption.

Several investigations have reported that distribution coefficients decrease as the concentration of solids increases [O'Connor and Connolly (1980)]. This is indeed not surprising as K_d is not a properly defined reaction constant [Bourg and Sauty (1987)].

3. K_d AND THE MASS TRANSPORT EQUATION

The general equation of convective and dispersive monodimensional transport and solid-solution exchange reaction, assuming uniform parameters, is given by [Bear (1972)] :

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - \frac{\rho}{\theta} \frac{\partial s}{\partial t} \quad (3)$$

Dispersion convection exchange

where c = total dissolved concentration, t = time, D = dispersion coefficient, x = distance from source, u = interstitial velocity, ρ = bulk density, θ = porosity, s = solid phase (adsorbed) concentration of component.

The last term in equation (3) is the adsorption or exchange term. A number of models have been used, some for equilibrium conditions, others accounting for the rate of approach to equilibrium [Boast (1973)].

For example :

$$\frac{\rho}{\theta} \frac{\partial s}{\partial t} = k_f c^n - k_b s \quad (4)$$

where k_f and k_b = rate constants of adsorption and desorption, n = empirical parameter. At equilibrium $\partial s / \partial t = 0$ and thus

$$\frac{s}{c^n} = \frac{k_f}{k_b} \times \frac{\theta}{\rho} = K_d \quad (5)$$

The distribution coefficient K_d is independent of c or s if $n = 1$ (linear adsorption isotherm). Otherwise equation (5) describes a Freundlich isotherm.

It is possible to estimate K_d coefficients from column or field experiment, by comparing the rate of movement (V) of the element of interest relative to that of water :

$$\frac{V_{\text{water}}}{V_{\text{element}}} = 1 + \frac{\rho}{\theta} K_d \quad (6)$$

The expression $(1 + (\rho/\theta)K_d)$, called the retardation factor, can be used to estimate how rapidly a pollutant may migrate. This relation holds only, however, for a linear, reversible and instantaneous adsorption.

4. K_d AND THE WATER CHEMISTRY:

So far the chemical reactions in the water phase involving the adsorbable species have not been considered. It is however quite evident that hydrolysis and dissolved complexation can substantially compete with adsorption [Vuceta and Morgan (1978)]. For example the rate of migration of mercury through a quartz sand column is strongly dependent on the water composition (Table 1). [Behra and Bourg (1987)].

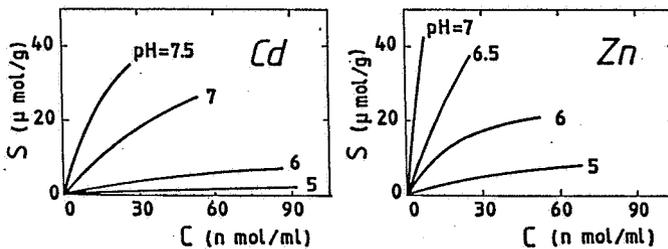
The denominator in equations (1) and (2) is the total dissolved concentration. For chemical elements undergoing solution reactions this term is strongly dependent upon water chemical parameters such as pH, total carbonate, chloride, organic matter or other complexing agents [Bourg and Mouvet (1984) ; Leckie and Tripathi (1985)]. The importance of solution chemistry on adsorption is demonstrated by the effect of pH and complexing agents on adsorption isotherms (figure 2).

Kd for mercury in contact with a quartz sand column¹
 [from Behra (1987)]

Water composition	Kd (m ³ /g)
H ₂ O	> 137
0.01 M NaNO ₃	> 68
0.01 M NaCl	41
0.01 M HNO ₃	67
0.01 M HCl	25
1.0 M NaNO ₃	> 47
1.0 M NaCl	4.7

¹ 5×10^{-7} M of Hg (II) ; Kd calculated when eluent Hg conc. = input Hg conc. ; $\rho = 4.8 \times 10^3$ g/l

PODZOL-B_S (Cl⁻=0.1 M)



PODZOL-A_p (pH=5 and 7.5)

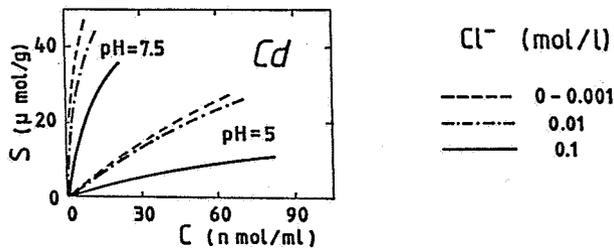


Figure 2 : Sorption isotherms of Cd and Zn in presence of podzol horizons [after Gerth et al. (1981)]

5. CONSEQUENCES FOR MODELING THE MASS TRANSFER OF POLLUTANTS IN SOILS AND AQUIFERS

The distribution coefficient of species involved in reversible adsorption can be expected to vary over time at a given point in a flow system until steady state chemical evolution conditions are reached [Reardon (1981)]. The safest way is therefore to use a chemical adsorption model which accounts for the formation of aqueous complexes. [Miller and Benson (1983) ; Cederberg et al. (1985) ; Bourg et al. (1987) ; Jauzein et al. (1987)].

Kd coefficients do make transfer models much simpler and in some cases they can provide reasonable model predictions. As hinted in the preceding section the applicability of the Kd coefficient (provided that the adsorption reaction is sufficiently fast, with respect to water flow, and reversible) will be subject (1) to the chemical behavior of the element or compound of interest and (2) to the stability (steady state, equilibrium) of its water environment.

The uptake of nonpolar hydrophobic organic pollutants should not depend on the composition of the water phase since the process is mostly a physical partitioning. Successful modeling of the migration of nonpolar trace organics was achieved by Schwarzenbach and Westall (1981) and Curtiss et al. (1986). The presence of high molecular dissolved (or colloidal) organics such as humic substances can however decrease the adsorption of hydrophobic trace organics.

The adsorption of weakly hydrolyzed or complexed metals (such as alkali and alkaline-earth metals) is also poorly dependent on the chemistry of the water phase. The Kd approach was used by Jackson et al. (1980) to quantify the migration of ^{90}Sr and ^{137}Cs in a shallow sand aquifer. Finally, if the chemistry of the aquifer system is at equilibrium, the migration of small concentrations (small enough to not affect the speciation of major elements of strongly complexable elements (such as heavy metals) can be modeled by using "conditional" Kd values. Relative solute velocity equations (based on the Freundlich

isotherm and the linear isotherm) predicted successfully the migration of low concentrations of cadmium in soil columns [Christensen (1985)]. Such models are however of limited use as tools for the assessment of the vulnerability of groundwater to pollution. Their applicability is restricted to the prediction of transfer rates under very specific conditions. They cannot predict desorption or increase in transport rate due to variations in the chemistry of the aquifer. Let us emphasize that the vulnerability of an aquifer to pollutants is not only a matter of pollutant input, but also of remobilization due to seasonal or permanent trends provoking changes in the functioning of the ecosystem (e.g. acidification, oxidation or reduction and the effect on the solubility of iron hydroxides, production or introduction of complexing agents).

ACKNOWLEDGEMENTS

This paper was written with financial support of the French Geological Survey program EG 08 on the "Migration of Micropollutants in Groundwater". Many thanks to Anna Kay Bourg for editing the English and to Sylvie Matrat for typing the manuscript.

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DESCRIBING CHEMICAL TRANSPORT IN THE UNSATURATED
ZONE OF THE SUBSURFACE

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ABSTRACT

Predictive models describing chemical transport in the unsaturated zone of the subsurface contain many transport variables and coefficients for which adequate data do not exist. To develop better predictive models for this zone of the subsurface, areas of needed research are identified and approaches suggested to give estimates of required data.

1. INTRODUCTION

With the introduction into the unsaturated zone of a wide variety of chemicals from agricultural operations and chemical waste dumps, the contamination of underlying aquifers is the result of many simultaneous coupled transport and transformation processes that occur in both the subsurface and atmospheric domains. Conceptually, the processes and their interactions are shown in Figure 1.

For transport in the unsaturated zone, the set of transport equations derived from Figure 1 are given in integral form in Table 1. Data and process information needed in transport models of this type are many. Clearly there are many processes in this set of equations for which a complete understanding of their mechanisms of action do not exist. In addition, there are situations in which many of these processes make negligible contributions to transport and can be eliminated from the model. In this regard, conditions when models can be simplified should be carefully documented.

In this paper, data and process needs for the chemical transport equation will be examined. Areas of concern include processes for transformation and retardation. In addition, a very simple criterion will be presented that allows single chemical models to act as surrogates for multiple chemical transport.

2. CHEMICAL TRANSFORMATION PROCESSES

In the chemical field equation given in Table 1, transformations of chemicals by abiotic and biotic processes have been lumped together into the general rate constants for transformations in the liquid and vapor phases, Λ_l and Λ_v . If it is assumed that Henry's law applies, then:

$$C_v = H_c C_l \quad (1)$$

where

$$H_c = \text{Henry's constant}$$

Then:

$$\begin{aligned} \Lambda_l \theta C_l + (\epsilon - \theta) \Lambda_v C_v &= \Lambda_l \theta C_l + (\epsilon - \theta) \Lambda_v H_c C_l \\ &= ((\% \text{ org}) \beta_l + \gamma_l) \theta C_l \\ &\quad + (\alpha_l \rho_w \theta + \alpha_v (\epsilon - \theta) H_c \rho_{wv}(T)) C_l \end{aligned} \quad (2)$$

where

- % org = percent of organic matter
- β_l = rate constant for 1st order biodegradation in the liquid phase
- γ_l = rate constant for 1st order chemical reaction in the liquid phase
- α_l = rate constant for hydrolysis in the liquid phase
- α_v = rate constant for hydrolysis in the vapor phase
- ϵ = porosity
- θ = moisture content ($< \epsilon$)
- ρ_w = density of water
- $\rho_{wv}(T)$ = density of water vapor at temperature T

In describing chemical transformations in the subsurface, the chemical characteristics of the pollutants are very important. For synthetic organic chemicals, the arrangement of atoms in the molecular structure profoundly effects chemical reactivity either in the liquid or vapor phase, interactions with abiotic and biotic substrates present in the liquid, vapor or solid phases of the subsurface and interactions with solid constituents of the subsurface. As a general rule, organic chemicals that are nonreactive and have low water solubilities will persist unchanged in the subsurface for long periods of time.

Chemicals that are not easily transformed by abiotic or biotic processes have been found at great distances from their original point of entry (Schwarzenbach and Westall (1981)). In many cases, these same low water solubility, refractory chemicals also tend to be toxic. In the example from Schwarzenbach and Westall (1981), tetrachloroethylene has been shown to be carcinogenic in laboratory animals in gavage studies (NCI (1977)), and by inhalation (NTP (1986)).

Ten years ago, it was estimated that there were about 25,000 synthetic organic chemicals in significant production in the United States along, with 700 new chemicals being introduced each year (NCI (1976)). In this number are chemicals added to the land in agriculture and chemicals and their synthesis by-products added to the land in disposal sites. Not all of these chemicals represent potential public health problems. With such a wide variety of chemical structures, the common denominator in determining the potential of chemicals to induce cancer and other chronic diseases is their electrophilicity (electron-deficiency) (Shubik and Clayson (1976), and Miller and Miller (1976)). Using this criterion, Fishbein (1977) has analyzed the many types of chemicals in commercial production and has identified groups of chemicals that have a high potential for cancer induction.

With regard to the longterm damage to aquifers and the potential for causing adverse effects in human populations, organic chemicals that are electrophilic, have low water solubilities and are unreactive are of greatest concern. They can persist in ground waters for long times. Usually, they are not primary carbon sources for microorganisms at any level of the subsurface domain. However, when ingested from drinking waters taken from contaminated aquifers, many of these chemicals can be metabolically converted into chemicals that can play a significant role in the initiation and progression of many chronic diseases.

For chemicals with low reactivities, the removal processes given in Equation 21 can be neglected reducing the chemical field equation to a form of the convective-dispersion equation. However, it is not possible to dismiss totally the degradation activities of diverse populations of microorganisms and to say that they are inconsequential over long periods of time. The dynamics of population changes in response to the

presence of chemicals with a wide variety of molecular structures have not been studied in a consistent manner. As a first step, data correlating types and numbers of different microorganisms with soil composition and depths in the absence of xenobiotic chemicals are very important.

For inorganic chemicals, compounds of greatest concern contain metal ions such as cadmium, nickel, mercury, and lead. In many instances transport behavior in the subsurface is a function of the ability of microorganisms to form electronically neutral coordination complexes with the element. From studies by Cataldo and Wildung (1978) certain species of aerobic fungi were found to be very efficient in forming these complexes with metal ions. In this chemical form, Cataldo and Wildung (1978) have shown that metals such as cadmium and nickel have surprisingly high rates of transport in the subsurface and uptake by plants. Toxicities of many toxic metals are given in Friberg (1977). The transformation of metals in the subsurface is not well understood and requires additional research in soil columns.

3. SINGLE CHEMICAL ADSORPTION

Retardation of transport due to adsorption to components of the porous media is a function of the molecular structures of the chemical and the porous media constituents. The chemical field equation given in Table 1 assumes that adsorption is an equilibrium process that can be described by a Freundlich isotherm (Freundlich (1926)). Further, it is assumed that the equilibrium constant is composed of contributions from each of the different solid components. With these assumptions, the liquid phase adsorption equilibrium constant is given as:

$$K_{dl} = K_{l \text{ sand}}(\% \text{ sand}) + K_{l \text{ org}}(\% \text{ org}) + K_{l \text{ clay}}(\% \text{ clay}) \quad (3)$$

where

$K_{l \text{ sand}}$, $K_{l \text{ org}}$ and $K_{l \text{ clay}}$ = the equilibrium constants for adsorption to sand, organic matter and clay

% sand, % org and % clay = the percentages of sand, organic matter and clay in the soil

There have been numerous attempts to develop correlations between the octanol-water partition coefficient and the equilibrium constant for adsorption to organic matter (Lyman et al (1982)). In another approach, Sabljic (1984) uses molecular properties of the chemicals to develop correlations that cover a much broader range of molecular structures and functional groups. Neither this method nor any other method have been extended to other soil components because they were considered of negligible importance as substrates for adsorption. It is not at all clear that this assumption is valid, and research is needed to examine the role of clay minerals and silica in the retardation of chemical transport.

Methods would be greatly improved if ways could be found to incorporate more extensively the characteristics of the sorbate and sorbent.

Because the porous media through which the chemicals are transported are not inert, such considerations will greatly expand our capability to examine the processes of adsorption on heterogeneous surfaces.

Recent studies by Wershaw (1986) have provided a more comprehensive molecular model for humic acids. The exact molecular structures of humic acids are not known for certain, but Wershaw (1986) suggests that humic acids aggregate into a micellar structure. The humic acids are arranged so that the hydrophilic part faces out towards the water phase and the hydrophobic part faces inward.

Chiou et al (1983) suggests that adsorption of hydrophobic organic chemicals to these humic acids is a process of solubilization. In this process, the hydrophobic organic chemical in the aqueous phase is transported into the interior of the humic acid aggregate. The amount of material removed by adsorption is a function of the rate of diffusion into the interior of the aggregate and the binding strength between the organic chemical and the hydrophobic interior.

Using this model and assuming that adsorption can be partitioned in the same manner as in Equation (3), a first order kinetic rule for adsorption to organic matter from the liquid phase in the unsaturated zone is given as:

$$\rho_{\text{org}} \frac{\partial S_{\text{org}}}{\partial t} = K_{\text{Aorg}} (\theta + (\epsilon - \theta) H_c) C_l - K_{\text{Dorg}} \rho_{\text{org}} S_{\text{org}} \quad (4)$$

where

ρ_{org} = the density of organic matter
 S_{org} = the amount of chemical adsorbed to organic matter
 K_{org} = the equilibrium constant
 K_{Dorg} = the rate constant for desorption

Similar equations must be given for adsorption to other subsurface solid components in both the liquid and vapor phases.

The missing data in Equation (4) are values for the equilibrium constant and the diffusion rate constant. With methods of molecular mechanics it may be possible to construct molecular models for the binding of chemicals to substrates (Allinger (1976); Blaney et al (1982); Boyd and Lipkowitz (1982); and Kollman (1985)). With reaction rate theory and thermodynamics, rate constants and equilibrium constants can be estimated. These methods have already been used to obtain binding constant data for chemicals with biological substrates (Blaney et al (1982)).

4. MULTICOMPONENT ADSORPTION

Contamination of aquifers is not usually by single chemicals but by mixtures of chemicals. The chemicals are present either in the aqueous phase or in multiple liquid phases which may or may not be miscible with water. Because of the wide variety of chemicals that could be present in a mixture flowing out from a buried chemical waste dump, adsorption to solid surfaces is competitive. Santacesaria et al (1982) developed a model for multicomponent adsorption to saturated Y zeolites that was adapted from Helfferich and Klein (1970) for multicomponent chromatography. The model assumes that there are no losses of chemicals due to abiotic or biotic transformations, transport is isothermal, there is intraphase mass transfer resistance, the porous media is saturated and that adsorption follows linear Langmuir isotherm behavior.

The behavior observed by Santacesaria et al (1982), Radke and Prausnitz (1972), Wang and Tien (1982) is a function of how tightly held

individual chemicals are to the adsorbing substrate. Because there are different affinities, multiple breakthroughs are observed for saturated porous media, a situation much like that observed with multicomponent chromatography. However, the results were observed for adsorption to only one type of surface, whereas in the subsurface, there are many different surfaces. Laboratory studies with soil columns would provide a large amount of useful information on mechanisms and values for adsorptivities and rate constants.

5. SINGLE CHEMICAL MODELS

In many studies, single chemical models are used to analyze the behavior of chemical mixtures. The implied assumption is that each chemical is acting as if no other chemicals are present. It is essential to identify conditions when single chemical models are appropriate surrogates because many submerged disposal sites contain mixtures of chemicals with a wide range of solubilities not only in water but in other solvents. If this is not done, single chemical models will be applied incorrectly. For organic chemicals, Lindstrom and Piver (1985) suggest that for chemicals with low water solubility (less than 100 $\mu\text{g}/\text{cc}$) single chemical models can be used as surrogates for the transport of chemical mixtures. Chemicals with significant toxicities fall into this category. This includes many agricultural chemicals and many commercially important chlorinated organic chemicals. Clearly this assumption would not hold for organic solvents such as acetone and methanol which have significant water solubilities and toxicities when ingested. Also these solvents can dissolve many organic chemicals with low water solubilities. The transport behaviors of mixtures of this type represent situations that have not been explored.

Along with the identification of conditions when single chemical models are appropriate, models that have been developed must be validated in field studies. In this process, sources of error in numerical methods of solution must be identified. Then steps must be taken to minimize their impact on calculated values of dependent field variables. At the same time, multi-component, multi-phase models must be developed and

validated for both the unsaturated and saturated zones of the subsurface. With validated models, better methods can be developed to estimate exposures for epidemiology studies and to reclaim contaminated aquifers.

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Figure 1. Conceptual model of transport in the unsaturated zone of the subsurface

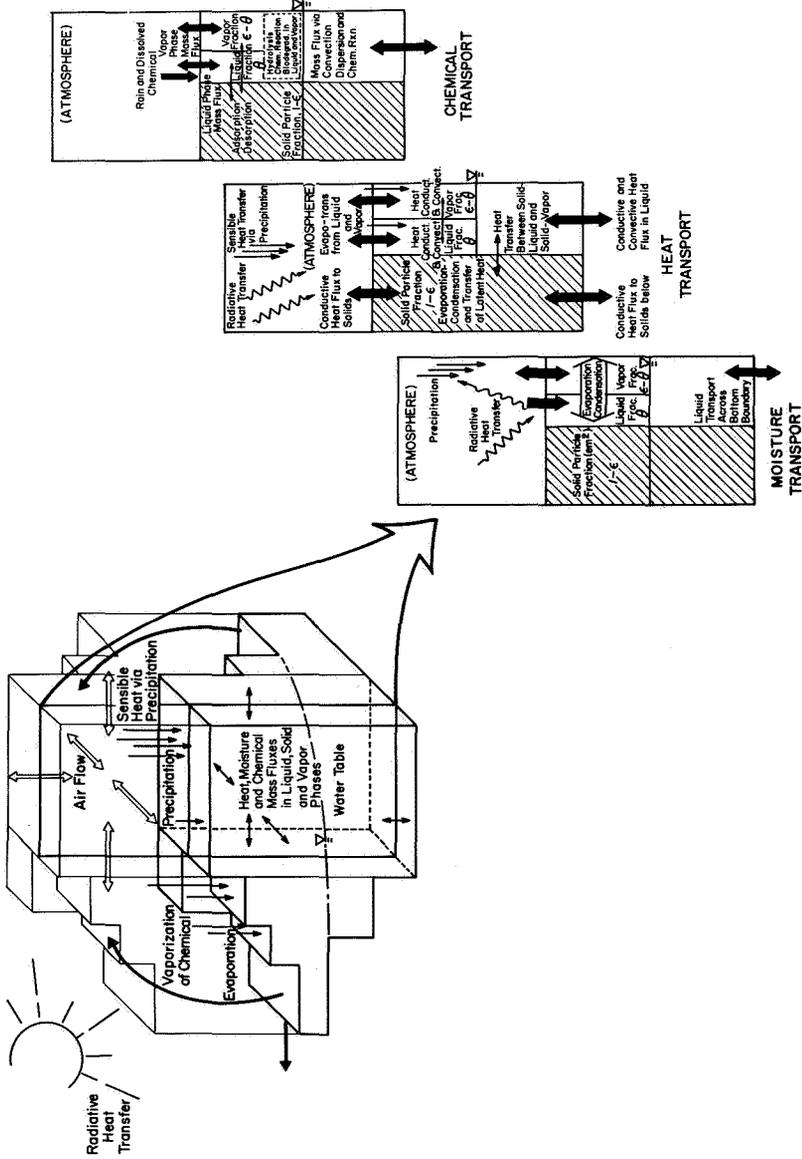


Table 1. Field equations for transport in unsaturated zone of the subsurface

A. Moisture Content Field Equations

$$\int_V \frac{\partial}{\partial t} (\rho_w \theta + \rho_{wv}^{sat}(T) h(\epsilon - \theta)) dV + \int_{\Sigma} \vec{q}_T \cdot \hat{n} ds = 0$$

The total moisture flux vector \vec{q}_T is defined as

$$\vec{q}_T = \vec{q}_l + \vec{q}_v \quad \text{with: } \vec{q}_l = \theta \rho_w \vec{V}_l \quad \text{and: } \vec{q}_v = (\epsilon - \theta) \rho_{wv} \vec{V}_v$$

where ρ_w is the density of water, ML^{-3} ; θ is moisture content, dimensionless; ϵ is soil porosity, dimensionless; $\rho_{wv}^{sat}(T)$ is the density of water vapor at saturation, ML^{-3} ; \vec{V}_l and \vec{V}_v are the velocities of moisture in the liquid and vapor phases, Lt^{-1} ; h is relative humidity, decimal percent; and, ρ_{wv} is the density of water vapor at temperature T , ML^{-3} .

B. Temperature Field Equation

$$\int_V \frac{\partial}{\partial t} (((1 - \epsilon) c_{solids} \rho_{solids} + c_{air} (\epsilon - \theta) \rho_{air} + c_w \theta \rho_w) T) dV = \int_{\Sigma} -\vec{H}_s \cdot \hat{n} ds$$

The total heat flux vector \vec{H}_s is defined as

$$\vec{H}_s = (1 - \epsilon) \vec{H}_{ss} + \theta \vec{H}_{sl} + (\epsilon - \theta) \vec{H}_{sv}$$

with:

$$\vec{H}_{ss} = -\lambda_{solids} (\alpha, \gamma, z) \nabla T \quad ; \text{ heat conduction through the solid particles}$$

$$\vec{H}_{sl} = -\lambda_w \nabla T + c_w \rho_w \vec{V}_l T \quad ; \text{ heat conduction and convection in the water phase}$$

$$\vec{H}_{sv} = -\zeta D_{atm} \alpha_{torf} \nabla \rho_{wv} - \lambda_{air} \nabla T \quad ; \text{ heat conduction in the vapor phase and the transfer of latent heat}$$

where λ_{solids} is the heat conductivity of solid particles, $ML^{-2}t^{-1}$; c_{solids} is the heat capacity of solid particles, $L^2t^{-2}t^{-1}$; λ_{air} is the heat conductivity of air, $L^2t^{-2}t^{-1}$; ρ_{solids} is the density of solid particles, ML^{-3} solids; ζ is latent heat of vaporization, L^2 ; D_{atm} is the diffusivity of air, L^2t^{-1} ; α_{torf} is the tortuosity, $0.33 \leq \alpha_{torf} \leq 0.66$, dimensionless; and, c_w and c_{air} are heat capacities of water and air, $L^2t^{-2}t^{-1}$.

C. Chemical Field Equation

$$\int_V \frac{\partial}{\partial t} \{ \theta (1 + \rho_B K_d) C_l + (\epsilon - \theta) (1 + \rho_B K_{dv}) C_v \} dV = - \int_{\Sigma} (\theta \vec{q}_{Cl} + (\epsilon - \theta) \vec{q}_{Cv}) \cdot \hat{n} ds + \int_V (\Delta_b \theta C_l + (\epsilon - \theta) \Delta_v C_v) dV$$

The mass flux vectors, \vec{q}_{Cl} and, \vec{q}_{Cv} , are defined as

$$\vec{q}_{Cl} = -D_{Cl} \cdot \nabla C_l + \vec{V}_l C_l \quad \text{and: } \vec{q}_{Cv} = -D_{Cv} \cdot \nabla C_v + \vec{V}_v C_v$$

where ρ_B is bulk density of the porous media, ML^{-3} ; K_d is liquid phase adsorption coefficient to solid surfaces, L^3M^{-1} ; K_{dv} is vapor phase adsorption coefficient from the vapor phase to solid surfaces, L^3M^{-1} ; C_l is liquid phase concentration, ML^{-3} ; C_v is vapor phase concentration ML^{-3} ; D_{Cl} is the liquid phase dispersion coefficient, L^2t^{-1} ; D_{Cv} is vapor phase dispersion coefficient, L^2t^{-1} ; Δ_b and Δ_v describe chemical transformation by chemical and biological processes in the liquid and vapor phases, t^{-1} .

HAZARDOUS WASTE CO-DISPOSAL WITH DOMESTIC WASTES
IN LANDFILLS - ACCEPTABLE OR UNACCEPTABLE?

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ABSTRACT

The mobility of the hazardous components of an industrial waste co-disposed with domestic waste in a landfill can be controlled by complex interactions between the physical, chemical and biological processes which occur as wastes leach and degrade within a landfill. Although process control is rudimentary, careful site management can exploit these mechanisms to restrict the leaching of toxic components and degrade other constituents. Using phenolic waste as an example, it is argued that the environmental acceptability of hazardous waste co-disposal with domestic wastes should not be based solely on criteria used to assess impact on leachate quality. Consideration must also be given to the variation in site water balance which determines leachate generation patterns.

1. INTRODUCTION

In order to investigate the co-disposal of industrial waste with domestic wastes under controlled conditions, four 360 m³ experimental landfills were constructed at Edmonton, N. London, U.K. Waste emplacement was carried out to simulate current landfill disposal practice. As an example, the leaching of a co-deposited phenolic and domestic waste mix, under natural infiltration conditions, has been compared to that of domestic wastes alone.

2. LEACHING OF PHENOL-CONTAINING WASTE

Small scale studies, designed to investigate the attenuation of phenols in landfills have shown that aged and fresh domestic wastes can adsorb these compounds. This mechanism was found to delay the release and reduce the concentration of phenol sufficiently to allow microbial degradation to occur under anaerobic conditions, DoE (1978). In order to confirm a simple mathematical model incorporating adsorption isotherm and kinetic data for physical and biological phenol removal respectively, small scale anaerobic experiments (0.2 m^3) were filled with pulverised domestic wastes and irrigated with solutions containing 25 g/l as phenol, Blakey and Barber (1980). The results showed that at infiltration rates of 300-900 mm/y more than 99% of added phenol was degraded within a 0.7 m depth of domestic wastes. At much higher rates of infiltration (2500 mm/y), significant leaching of phenol occurred (up to 400 mg/l), although 72% of added phenol was degraded.

An experimental landfill at Edmonton, N. London was loaded with 40 tonnes of a phenolic lime mud waste (0.55% phenol wet weight) deposited as a layer above a 2 m depth of domestic waste (surface area 90 m^2 ; domestic waste density 0.55 t/m^3). The wastes were leached by natural rainfall infiltration (Table 1). Analysis of the leachate over a five year period showed that the prediction of minimal leaching of phenol was not fully realised (Figure 1). High levels of infiltration particularly during the winter months associated with low landfill temperatures coincided with phenol concentrations in the leachate in excess of 100 mg/l. Despite this, less than 1% of the added phenol had been leached over the five year period, with less than 0.01% present within the lime mud and approximately 2% still resident within the 2 m depth of domestic waste beneath.

3. LEACHATE GENERATION PATTERN

Annual and seasonal variability of infiltration may not be directly proportional to rainfall. During 1981/82, annual rainfall at the site was at least 13% greater than the two preceding years and yet calculated infiltration was shown to be less, (Table 1). This was due to heavy rainfall events during the summer months when evapotranspiration was

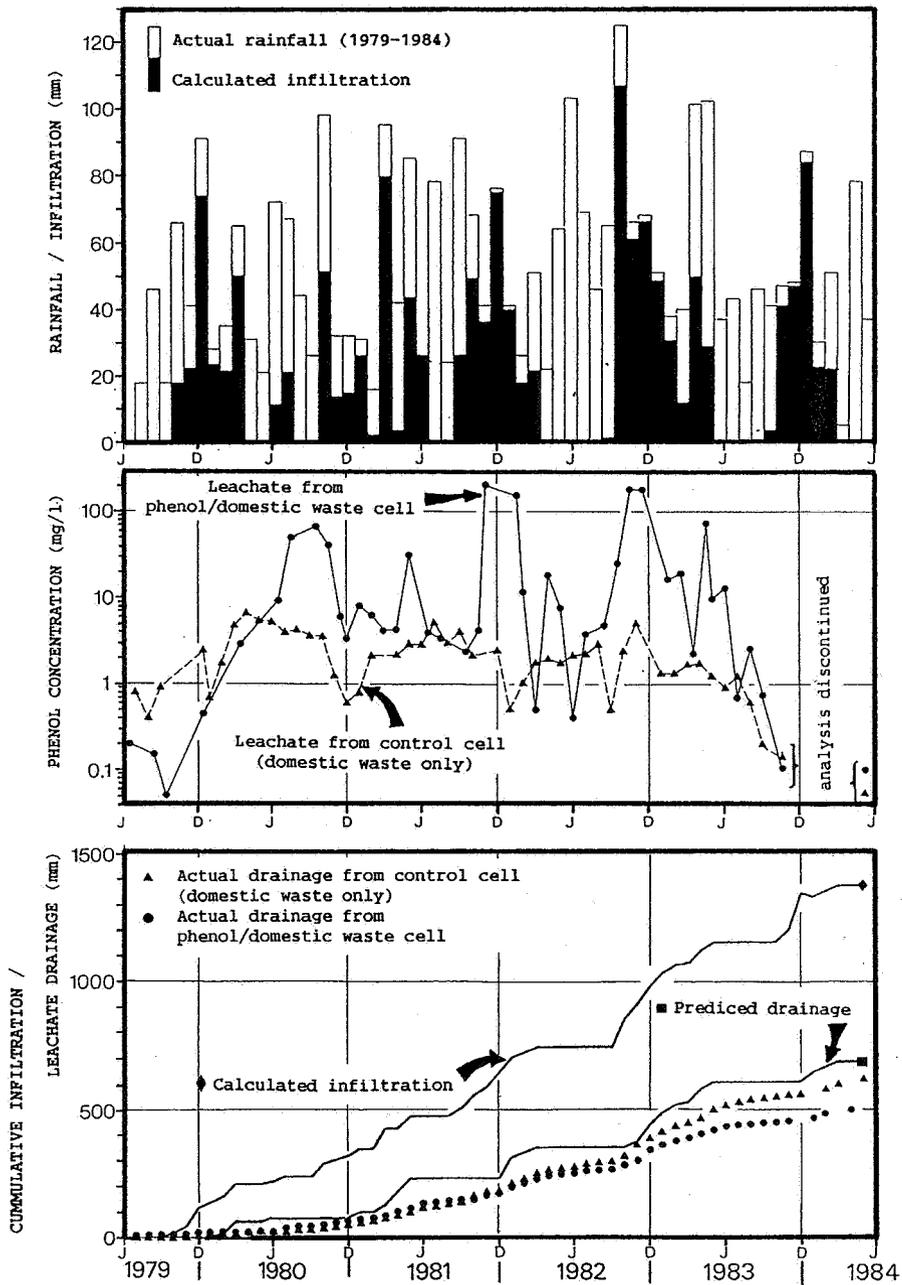


Figure 1. Phenol release from the experimental landfills, Edmonton related to rainfall infiltration and leachate discharge.

highest.

Table 1. Annual rainfall (mm) and calculated infiltration (mm) totals 1979-1984, Edmonton landfill cells, North London

Year	Rainfall (R)*	Calculated infiltration (I)	I/R (%)
1979/80	532	219	41
1980/81	594	255	43
1981/82	685	266	39
1982/83	808	403	50
1983/84	531	222	42

* Average data collected from 4 Meteorological Office Stations within 4 km of the site

Annual infiltration data shown in Table 1 is not unusual for the operational phase of a landfill. However, national or regional data cannot be relied upon as a guide to local infiltration. In contrast typical values of infiltration through cover soils at restored landfills have been shown to range between 14-34% of annual rainfall. These levels may be reduced further by installing clay caps, sub-surface drainage systems or by encouraging surface water run-off by surface contouring, DoE (1986).

At waste densities commonly achieved in the U.K. ($0.7-0.8 \text{ t/m}^3$) absorptive capacities of between $0.16-0.27 \text{ m}^3$ per dry tonne have been reported by Blakey (1986). Other work cited has shown that where emplacement densities approach 1 t/m^3 absorption may be as little as $0.02-0.03 \text{ m}^3$ per dry tonne.

In the experimental landfills at Edmonton, N. London, the widening discrepancy between calculated infiltration and predicted drainage from the control and phenol containing cells respectively (Figure 1) indicates that where wastes have received prolonged periods of infiltration, additional uptake of liquid is of the order $0.4-0.65 \text{ m}^3$ per dry tonne, (over and above initial moisture content of approx. 35% dry wt). Potential exists therefore for the exploitation of liquid

retention during the operational phase of a landfill in order to delay the production and reduce the volume of leachate.

4. CONCLUSIONS

Landfills are not efficient bio-reactors since control over chemical and biochemical processes is rudimentary. The environmental acceptability of hazardous waste co-disposal with domestic wastes in landfills cannot be assessed solely on identified attenuation mechanisms used to calculate relative loadings. Potential leachate generation patterns should also receive thorough examination.

ACKNOWLEDGEMENTS

This paper is published with the permission of the Director, WRc Environment, and describes studies funded by the U.K. Department of the Environment.

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SPATIAL VARIABILITY OF PLEISTOCENE SEDIMENT PARAMETERS TO BE USED IN GROUNDWATER QUALITY MODELS

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ABSTRACT

Spatial variability of pleistocene sediment parameters has been researched. Using the semivariogram method most variability within members of formations has been found to occur within 0.20 meters. Using the Student's T test differences of means of various parameters have been checked for significance. The formations of Urk and Sterksel are internally inhomogeneous; those of Drente and Kedichem are not. All formations differ significantly from each other.

1. INTRODUCTION

Various human activities result in groundwater contamination. By groundwater flow pollutants may reach pumping stations and/or sensitive ecosystems in seepage areas. During this transport pollutant concentrations are controlled by the physio-chemical properties of the aquifer which are difficult to study in real time and place. Therefore these properties are being studied presently in the laboratory for Physical Geography of the Utrecht State University in column-percolation experiments with undisturbed saturated field samples. For extrapolation of experimental results knowledge is needed about the spatial variability of

Table 1. Formations and members

Formation	Pit (1)	Code	Sedimentological structures	Sedimentological environment	Colour	Texture (2)	Remarks	Dimensions (3) (4)	
Drente	P	PD	low angle to parallel bedding with cross bedding	braided rivers & sandur	pale brown	moderately coarse sand and gravel	sorting from well to very poor	m hm km	
	P	KD10	parallel bedding		brown	gravely coarse sand and gravel		m km hm	
	K	KD9		gravity flow near ice front	brown	fine to coarse sand	fining upwards	m km hm	
	W	D	parallel to low angle lamination	sandur	pale brown	moderately coarse sand		dm	
Urk	P	PU4	parallel and cross lamination	braided river	green	sandy loam and fine sand	CaCO ₃ concretions	m hm km	
	K	KU8			brown	mod. fine to mod. coarse sand	few pebbles	m hm km	
	K	KU6	semibubular cross bedding	meandering river	brown	coarse gravelly sand		m hm km	
	K	KU5		fluvial deposits	brown	coarse gravel and gravely coarse sand	cobbles and clay-lumps in layer 'A'	m hm km	
	W	WU2c	parallel lamination	river deposits	blue/grey	clay with shells		dm hm km	
	W	WU2b	cross bedding	river deposits	brown	coarse sand			
	W	WU2a	cross bedding	river deposits	brown	coarse sand & gravel	some gravel		
	W	WU1		river deposits	pale green	sand		m hm km	
	Sterksel	W	WS2b	cross bedding	river deposits	orange	mod. coarse sand		dm hm km
		W	WS2a	cross bedding	river deposits	pale brown	mod. coarse sand		
W		WS1c		river deposits	pale green	very fine sand			
Kedichem	W	WS1b		river deposits	pale brown	mod. fine sand			
	W	WS1a		river deposits	pale green	very fine sand	with CaCO ₃		
	K	KK3		fluvial backswamps	brown	silty loam	homogeneous	m km km	
	K	KK2	some parallel lamination	meandering backswamp deposits	blueish grey	clay	organic carbon in up-per part, some peat	m km km	
	K	KK1	parallel and cross lamination	eolian deposits	pale green/grey	very fine sand thick loamy layers		m km km	

(1) Pit: P: 'De Palts' at Soesterberg (description partially after Augustinus (1971))

W: 'Fransche Kamp' at Wageningen (description partially after Ruegg (1985))

K: 'Kwinteloijen' at Rhenen (description after Ruegg and Zandstra (1981))

(2) Texture classification as used by the Geological Survey of the Netherlands

(4) after Alphen (1984)

(3) Dimensions: thickness / lateral / longitudinal

(order of) m: meter

dm: decameter

hm: hectometer

km: kilometer

oven-AAS. Distribution coefficients (as (cadmium adsorbed/gram soil)/(cadmium in solution/ml)) varied between 48 and 200,000. The entire procedure was repeated for the same samples at a pH lowered to ± 5 by acidifying with HCl. The amount of acid required was predetermined by making a titration curve for each sample. This was not satisfactory, however; large deviances in pH occurred which dominated the cadmium adsorption of the samples, thus obscuring differences between the samples.

3. STATISTICAL ANALYSES

Selected for analyses of variability were the parameters pH(H₂O), pH(KCl), weight loss at 850 °C, CEC, fraction smaller than 16 micron, fraction smaller than 2 micron and cadmium adsorption. Emphasis is put on the parameters weight loss and CEC as these are expected to dominate the soil properties with respect to ad- and desorption and thus of transport of contaminants in saturated groundwater flow through these sediments.

For all formations, members of formations and for the entire data set averages and standard deviations were calculated for each parameter (see Table 2). Using the Student's T test differences of means of CEC and weight loss at 850 °C between the formations were tested for significance.

In the Urk and Kedichem formations the results of both parameters tend to agree closely, in the Sterksel formation only weight loss at 850 °C gives significant differences between the members.

In the Urk formation as sampled in the Wageningen pit only the Urk 2c member differs significantly from the other four members. The members of the Urk formation in the Kwintelooijen pit are significantly different from each other. The weight loss at 850 °C shows a significant difference between the Urk formation in the Wageningen and the Kwintelooijen pits. All Sterksel formation members differ from each other except for the 1b and 1c members. In the Kedichem formation only the no. 1 member differs from all other members.

Significant differences have been found between all formations, except for between the Urk and Sterksel formations. With respect to cadmium adsorption only the Kedichem formation is significantly different from

all others.

Formation/ member	pH(H ₂ O)		pH(KCl)		weight loss at 850 °C		CEC		n	under 16 micron		under 2 micron		n
	\bar{X}	sd	\bar{X}	sd	\bar{X}	sd	\bar{X}	sd		\bar{X}	sd	\bar{X}	sd	
All data	7,44	(1,24)	6,55	(1,59)	2,72	(3,25)	4,43	(4,60)	155	14,0	(21,6)	6,74	(10,7)	23
Drente (P)	6,17	(0,83)	5,43	(0,94)	0,35	(0,06)	2,17	(0,73)	10	0,00	-	0,00	-	1
Drente (K)	8,22	(1,43)	8,01	(1,68)	0,94	(0,47)	1,55	(0,98)	11	0,40	(0,55)	0,00	-	2
Drente all	7,24	(1,56)	6,78	(1,88)	0,61	(0,42)	1,78	(0,92)	21	0,27	(0,45)	0,00	-	3
Urk:														
8 (K)	6,32	(1,62)	5,10	(1,44)	0,38	(0,26)	1,78	(0,91)	8	1,28	-	0,77	-	1
a5 (K)	7,55	(1,55)	6,44	(1,91)	10,6	(5,74)	10,6	(3,16)	9	50,9	-	25,06	-	1
5 (K)	7,44	(1,48)	6,94	(1,69)	0,24	-	1,81	(0,74)	32	0,99	-	0,00	-	1
4 (K)	7,49	(1,15)	6,11	(1,60)	2,96	(2,19)	4,09	(1,92)	13	8,34	-	4,31	-	1
4 (P)	8,60	(0,93)	7,94	(1,38)	7,18	(0,66)	2,60	(1,38)	9	4,96	(1,46)	1,64	(0,62)	2
2d (W)	7,41	(0,21)	7,36	(0,18)	0,45	(0,05)	2,57	(0,44)	2	-	-	-	-	0
2c (W)	7,99	(0,00)	7,54	(0,23)	10,8	(2,42)	16,1	(5,79)	2	72,8	-	35,4	-	1
2b (W)	8,92	(0,07)	8,99	(0,10)	0,79	(0,14)	0,79	(1,15)	4	1,05	-	0,52	-	1
2a (W)	6,60	(0,91)	5,73	(1,57)	0,66	(0,10)	2,41	(1,63)	4	0,86	-	0,48	-	1
1 (W)	7,19	(0,74)	5,27	(0,57)	0,60	(0,09)	1,24	(1,33)	13	0,43	(0,76)	0,52	(0,02)	2
Urk all	7,50	(1,38)	6,65	(1,74)	3,91	(4,23)	3,48	(3,75)	89	13,5	(24,5)	6,45	(12,1)	11
Sterksel:														
2b (W)	6,73	(0,66)	5,93	(0,87)	0,79	(0,29)	2,20	(1,17)	4	0,25	-	0,00	-	1
2a (W)	7,64	(0,08)	6,81	(0,11)	0,43	(0,03)	1,85	(1,24)	4	0,50	-	0,25	-	1
1c (W)	7,61	(0,42)	6,58	(0,40)	1,30	(0,24)	3,44	(1,74)	4	7,79	-	2,85	-	1
1b (W)	8,06	(0,20)	7,05	(0,10)	1,29	(0,20)	3,59	(1,96)	4	8,76	-	5,42	-	1
1a (W)	8,63	(0,17)	8,41	(0,16)	6,73	(0,85)	2,57	(1,95)	4	5,51	-	2,14	-	1
all	7,73	(0,72)	6,96	(0,92)	2,11	(2,42)	2,73	(1,62)	20	4,54	(3,98)	2,13	(2,20)	5
Kedichem:														
3 (K)	6,73	(0,22)	4,81	(0,15)	2,88	(0,31)	13,2	(2,91)	6	38,1	-	20,8	-	1
2b (K)	7,27	(0,34)	5,80	(0,55)	3,16	(0,22)	14,0	(4,09)	7	46,7	-	28,3	-	1
2a (K)	7,06	(0,33)	5,83	(0,64)	3,39	(0,99)	11,0	(3,41)	6	52,9	-	18,1	-	1
1 (K)	7,63	(0,21)	6,20	(0,44)	1,07	(0,24)	4,01	(1,75)	6	11,6	-	6,32	-	1
all	7,18	(0,42)	5,67	(0,69)	2,59	(1,05)	10,7	(4,99)	25	37,4	(18,2)	18,4	(9,11)	4

Legend: CEC is expressed in meq. per 100 grams of air dried soil. Weight loss at 850 °C, fraction smaller than 16 micron and fraction smaller than 2 micron are in % by weight of air dried soil. Colon denotes decimal point. Letter in brackets denotes the pit: P=Palts, K=Kwinteloijen, W=Fransche Kamp.

Table 2. *Averages and standarddeviations*

With fractions smaller than 16 and 2 micron as parameter significant differences have been found between the Kedichem and Drente and between the Kedichem and Sterksel formations, but not between Kedichem and Urk. Spatial variability within the members was studied using the semivariogram method (Burrough, 1986). In all cases nearly all variability occurred within the first 0.20 meters, increasing only at a scale of kilometers (between the pits).

Correlations between the parameters were calculated for the entire data set, for data sets of the four formations, for the data sets of cadmium adsorption and for the data sets of clay content. pH(H₂O) and pH(KCl) are significantly correlated with weight loss but not with CEC. In the Urk and Kedichem formations a significant correlation was found between

weight loss and CEC.

For cadmium adsorption the distribution coefficient, CEC and pH were correlated for both neutral and acidified solutions. No significant correlation was found in the neutral solution. Only in the Urk formation a significant correlation between the distribution coefficient and CEC was found. As in many cases distribution coefficient values show high extreme values results were checked for spurious correlation by recalculating correlations without these extremes after a visual inspection of the scatterplots.

As expected, strong significant correlations (r^2 over 0.90) were found between CEC and fractions smaller than 16 micron and smaller than 2 micron; weaker, but significant, correlations ($r^2 = 0.35$) were calculated between these fractions and weight loss at 850 °C.

4. DISCUSSION

From the table of averages the most striking results are the extremely high pH(H₂O) values. Partially this may be caused by not equilibrating the sample/water mixtures properly with the atmospheric CO₂ pressure (a maximum pH value of 8.40 may occur in the CO₂-CaCO₃ equilibrium), which can result in an increase of ± 0.5 pH units. The values of the other parameters agree with those found by Gerringa and Obdam (1985) and Chardon (1984). Weight loss at 850 °C, CEC and fractions smaller than 16 and 2 micron show a wide range of values; high values of each variable usually coincide with each other.

In the Sterksel formation no significant correlation was found between CEC and weight loss at 850 °C, which explains why only one parameter gives significant differences between the members. pH(KCl) is correlated with weight loss, but not with CEC. The positive correlation between CEC and organic matter content in the Urk and Kedichem formations was to be expected as these formations have (members with) a large fraction smaller than 16 micron, which usually has a high CEC.

The fact that only in the Urk formation a significant correlation between CEC and cadmium adsorption was found probably results from the high pH values which, in combination with a surplus of cation exchange sites, causes nearly all cadmium to be adsorbed. This also may explain

why cadmium-adsorption parameters donot show significant differences between the formations.

Comparison of means of CEC and weight loss at 850 °C of the formations and their members shows that nearly all formations are statistically significant (at 95% confidence level) different from eachother, and that within the formations some Urk members and nearly all Sterksel members are significantly different from the other members of the same formations. The other formations studied are statistically not inhomogeneous. It can be concluded that results of percolation tests for the formations studied may be extrapolated to members of formations as long as these are developed in the same sedimentary environments as those found in the pits studied. For the formations of Drente and Kedichem extrapolation to entire formations is possible, in the other formations great care must be taken in extrapolating, probably because of the presence of members with a large fraction smaller than 16 micron in otherwise sandy strata.

Spatial variability of the analysed parameters with the semi-variogram methods as suggested by Gerringa and Obdam (in RIVM (1985)) within members give poor results (nuggets seem to be within 0.20 m, indicating that small-ripple structures dominate variance). Either this method or the sample method needs improvement.

5. ACKNOWLEDGEMENTS

The authors acknowledge the kind cooperation of mr. Ruegg and mr. Zandstra of the Geological Survey of the Netherlands who pointed out the various formations and their members in the pits. The laboratories of the Institute of Earth Sciences (department of Soil Science) and of Geography (department of Physical Geography) of the Utrecht State University provided facilities for the analyses. The student M.T.M. Vossen collected the samples, calculated some of the statistics and carried out the analyses together with K.J.I. Vossen.

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INVENTORY AND PROGNOSIS: TOOLS TO DEAL WITH THE PROBLEMS OF
GROUNDWATER POLLUTION IN URBAN AREAS

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1. INTRODUCTION

The recent environmental investigations in the Netherlands have made clear that in urban areas a large number of polluted sites can be found. These pollutions are a result of many industrial activities, at very different scales.

Comparing the inventory of potential polluted sites and areas where actually investigations have been made, makes clear that there is still a larger number of undiscovered sites.

Soil contamination often introduces groundwater pollution which is spread into the environment by means of as well natural groundwater-transport as human activities (c.q. groundwater recovery).

Decisionmakers in environmental, public and regional planning are confronted with a confusing number of (often suddenly appearing) contaminated sites. An overview has to be gained to make a priority assessment in sanitation programs possible.

To get an overall view an inventory of data on hydrogeology, groundwater flow, land use and environmental investigations is necessary. TAUW Infra Consult B.V. initiated such an inventory on a regional scale in a specific urban area. Necessary support and information was gained from provincial authorities etc.

The results of the inventory have been described in a systematic way, presenting an overall view of those factors which are influencing the groundwater quality in the area under study. By means of computer simulated groundwater flow modelling future developments in groundwater quality are predicted.

The inventories and simulations have resulted in a report which can be seen as a model for a "Groundwaterplan in urban area". The essential parts of the case study and the contributions that this kind of "groundwaterplan" might have in decision-making are presented in this paper.

2. GEOLOGY AND HYDROGEOLOGY

To obtain an overall picture of the groundwaterflow in the area a geological and hydrogeological inventory was made. This inventory covered a greater region than the concerned urban area. The eastern boundary of the region is formed by a watershed situated approximately north-south at distance of 5 km from the urban area. Figure 1 shows a South West - North East cross-section of the subsoil in the region.

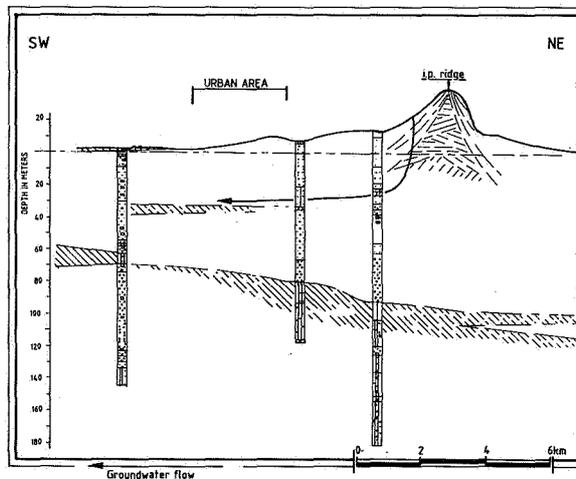


Figure 1. Geological cross section

From the ground level to greater depths the soil matrix consists of sandy materials with locally fine sands, clay and loam layers. The subsoil therefore can be described as a freatic aquifer. The impermeable base of this aquifer is formed by very clayey sands and clays belonging to the formation of Maassluis (Under Pleistocene).

Below the urban area this base is found at a depth of about 125 m -g.l. (minus groundlevel). The deposits which form the aquifer belong to the formations of Harderwijk, Sterksel, Kedichem, Twente and Drente and consist of fine, medium and very coarse sand with locally existing rather thin loam and clay layers.

West of the urban area the aquifer is split up into two parts by the loam and clay layers within the formation of Sterksel and Kedichem at a depth between 30 and 40 m -g.l. The above mentioned eastern watershed is an ice pushed ridge formed during the Saalien iceperiod (Middle-Pleistocene). Rainwater is infiltrating on the western side of the ridge determining the westward natural groundwater flow in the urban area. Table 1 shows the main hydrogeological parameters for the aquifer.

Table 1. Hydrogeological parameters

groundwaterlevel	: 2 m -g.l.
aquifer thickness	: 125 m
permeability	: 44 m/d ($0,51 \cdot 10^{-3}$ m/s)
porosity	: 35%
natural groundwater flow	
velocity	: 25 m/year
direction	: west

3. GROUNDWATER RECOVERY

The magnitude and the direction of the groundwater flow are altered due to groundwater recovery. As prescribed in the Groundwaterlaw all information about groundwater recovery in the Netherlands is gathered by the provincial authorities.

In this area information about recovery is available from 1966. Recovery of groundwater took and takes place for different purposes; within the urban area drinking water is recovered (about 4 million m³ in 1983), 11 locations of groundwater recovery for industrial purposes and a few major (temporarily) dewatering projects were included in the investigation. With some extrapolations it was possible to obtain the main recovery figures for the period 1945-1985.

4. HISTORICAL FLOWPATHS

To calculate the flowpaths of the groundwater due to natural groundwater flow and changing groundwater recoveries a computer model was used. The chosen model Flowpath calculates the migration of waterparticles under steady state conditions during a certain period.

The total period of time taken into consideration is divided by the program in sub periods with steady state condition. The length of a sub period is determined by whatever alteration in magnitude of groundwater recoveries takes place. Historical flowpaths, for instance over a period of 40 years, are calculated this way.

The check of a steady state groundwater flowpattern can be done by comparing the flowpattern with the pattern of lines of equal groundwater potentials. These patterns should be perpendicular. For the situation in august 1986 this check was done and the result was satisfying.

The results of the historical flowpath calculations were verified by studying the migration of a pollutant (trichloroethylene) as described later. The results were again positive.

5. NATURAL GROUNDWATER QUALITY

The results of the analyses of 35 groundwater samples, taken from existing sampling points, were used to get an impression of the natural groundwater quality. From these samples the concentrations of macro-parameters were determined: Cl^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ . It appeared that, especially in the infiltration zone east of the urban area, the natural groundwater quality was good. In the direction of flow, towards the urban area, the hardness of the water is rising (from about 5 to about 20 °DH). In the urban area the concentrations of some parameters are higher then in the area east of the city.

In the upper groundwater (10-20 m -g.l.) in most of the samples a higher concentration of Cl^- , SO_4^{2-} an NO_3^- was found. Only locally at greater depth (70-80 m) enhanced concentrations of Cl^- and SO_4^{2-} were found. The highest concentrations found for Cl^- , SO_4^{2-} and NO_3^- were 2,6, 2,5 and 0,5 meq/l respectively.

6. POLLUTION MIGRATION IN(TO) THE GROUNDWATER

Once a spill has taken place pollution of the saturated zone occurs quite rapidly as the unsaturated zone is rather thin. Once the pollution has reached the groundwater level, migration of pollution takes place in horizontal direction caused by the groundwaterflow.

The migration of pollutants however is not only depending on the groundwater flow but also on the nature of pollutant and the soil characteristics (processes as retardation, dispersion and decay can play a significant role). Nevertheless a first assesment of the flow direction of the pollutant and to what extent it will migrate can be made, based upon groundwater flow calculations.

7. KNOWN POLLUTED LOCATIONS

In the years since 1980 some 30 locations within the urban area were investigated with respect to soil and groundwater pollution.

The pollutants that were found are categorised in five groups:

A: chlorinated hydrocarbons

B: heavy metals

C: polycyclic aromatic hydrocarbons

D: oil products

E: aromatic hydrocarbons

For each of these five groups a map was drawn indicating the locations where pollution with the considered material was found. Also shown is, as far as known, the migration of the pollution from this locations.

Figure 2 shows the map drawn for pollution with chlorinated hydrocarbons.

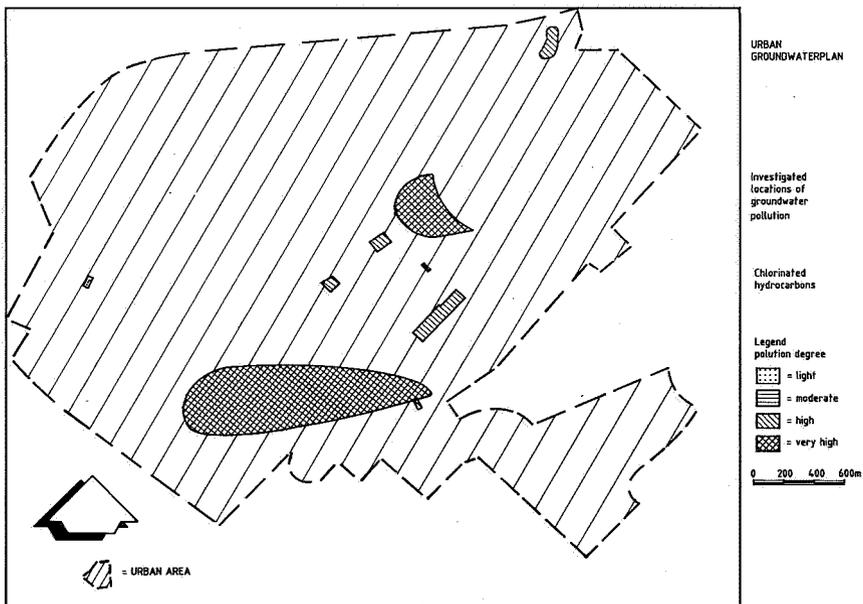


Figure 2. Investigated locations, chlorinated hydrocarbons

The migration of trichloroethylene from one location as investigated in 1985/1986 presented an opportunity to check the calculations of the historical flowpaths.

The pollution is spread over a much wider area than could be expected based on calculations of the natural groundwater flow and the greatest permanent groundwater recoveries. It appeared that a temporarily recovery of groundwater for dewatering a building pit has had a great influence on the migration of this pollution.

This dewatering project took place during 40 weeks in 1966. (capacity: ca. 700 m³/h). This effect is shown in figure 3.

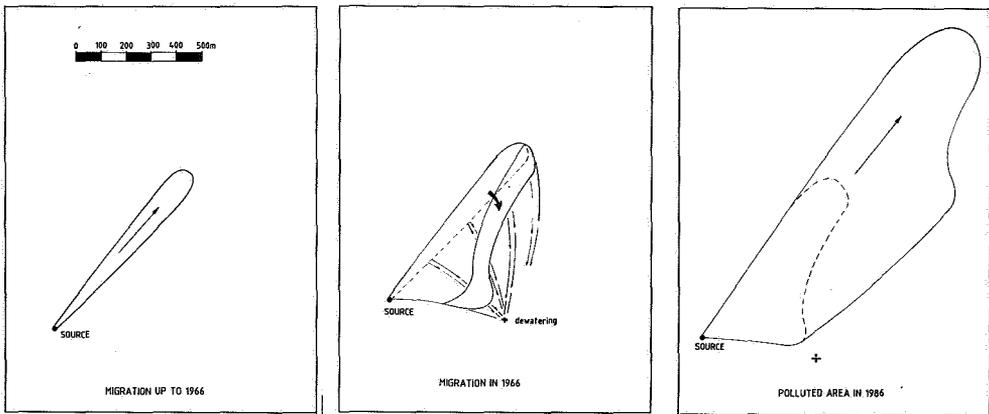


Figure 3. Influence of temporary groundwater recovery on pollutant migration

8. POTENTIAL POLLUTED SITES

Apart from the presently known polluted locations a lot of formerly used or existing sites may be polluted.

An inventory of potential polluted locations has been made based on industrial activities which are or have been located on these sites. The information necessary for such a selection was gathered at the Chamber of Commerce for this area.

Based on potential risk for soil and groundwater pollution different groups of industrial activities were formed.

The inventarisation for existing companies could be done by computer research.

The data of former industries were collected by handpicking from the archives of the Chamber of Commerce.

Table 2 shows the numbers of industries per group.
 In total about 1100 sites were selected.

Table 2. Industrial activities with a potential risk for soil and groundwater pollution

	<u>description</u>	<u>number of companies</u>	
		<u>existing</u>	<u>former</u>
group 1	fuel, trading	30	10
group 2	metals, trading and processing	110	70
group 3	chemicals, trading and production	225	165
group 4	wood, trading and processing	30	20
group 5	building companies	120	5
group 6	cars and machinery	155	125
group 7	others	<u>60</u>	<u>15</u>
	total	730	410

In this way the real number of polluted sites can be estimated. It is expected by estimation that in about 40-50%, of the total 1100 potential polluted sites, to some extend pollution of soil and groundwater occurs.

The potential polluted locations are also presented on maps.
 Figure 4 gives the sites of the former metal industries.

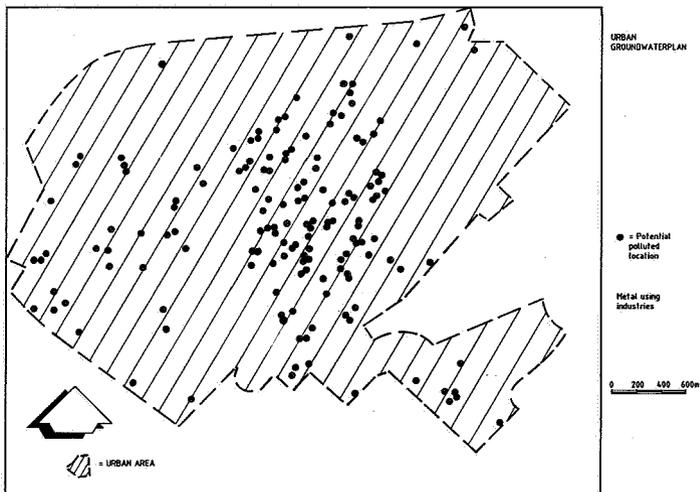


Figure 4. Potential polluted locations, possible pollutants: metals

9. DISCUSSION

The geohydrological data combined with the inventory of all known groundwater pollutions and the estimation of potential polluted sites in an urban area form the basis for a Groundwater plan in an urban area. This plan is useful for:

- estimating the total amount of polluted groundwater in the area. The groundwaterplan gives information about the number of polluted sites and the migration of the pollution from these sites.

- making priority decisions

The Groundwaterplan can be used in priority decisions for investigation of locations.

The same holds true for priority of groundwater sanitation projects.

- an integrated approach for groundwater sanitation.

When a site containing a large groundwater pollution is sanitized by recovery of polluted groundwater, the groundwater flow in a larger area is then afflicted during the sanitation period (some years of more).

This can influence the migration of other pollutions in the aquifer. An integral approach is made possible by the information given in the Groundwaterplan.

- groundwater recovery plans

The influence of present and future groundwater recoveries on the migration of pollutants can be made clear by calculating historical (and/or future) flowpaths as discussed.

- the design of monitoring systems.

Based on the Groundwaterplan a system for monitoring groundwater quality can be developed.

Industrial activities with a high potential risk for soil and groundwater pollution could be controlled by installing one or more sampling points in the direct vicinity of the site. Samples should be taken periodically (every half year or year) and should be analysed for chemicals used in the industrial processes.

In areas with a high density of polluted sites in addition some general sample points should be installed (also at different depths within the aquifer). Regular sampling and analysis on a wide range of elements should be carried out. Choice of location for sampling points could be based on (historical) groundwater flowpaths as presented in the groundwaterplan.

Based on data and calculations with respect to the groundwater quality (as presented in the Groundwaterplan), better decisions can be made concerning as well the installation of new groundwater recovery stations as the termination of existing groundwater recoveries which are threatened by these pollutions.

OBTAINING DATA FOR MODELS THAT PREDICT PROPERTIES OF AREAS OF
LAND USING SOIL SURVEYS

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ABSTRACT

Modeling forms an essential tool for defining practical effects of various land-use scenario's in terms of soil- and groundwater pollution. Modeling for areas of land requires massive quantities of data because models usually have been designed for well defined point observations. This may have resulted in a degree of detail that is not necessarily representative for processes occurring in areas of land. In general, extrapolation of point to area data may be based on the following procedures:

- Use of soil- or geologic maps which define delineated areas in terms of "representative" profiles with associated data;
- Use of (geo)statistical methods for point data.

The latter have the advantage that they are quantitative and reproducible while statistical reliability is known for any estimate being made. Use of these techniques is recommended within sub-areas in a landscape defined by soil- and geological maps. Data needed for modeling processes in areas of land are often not available. Various procedures are being used to fill this gap:

- Use of empirical "standard tables" which present data obtained elsewhere;
- Use of statistical relationships between simple soil- or geological data, to be obtained from published reports, and more complex data to be used for modeling;
- Use of an operational analysis to define simple, cheap methods; optimal

- sample volumes and optimal distances between sampling points;
- A critical analysis of the problem being studied which allows definition of the optimal degree of detail of research.

Soil surveys form a widely available data-base which can be used in an innovative manner in the context described above.

1. INTRODUCTION

Simulation models for characterizing physical and chemical soil processes are widely being used now to study nutrient fluxes in soils. Usually, models are one-dimensional and sometimes rather drastic boundary conditions have to be met to allow application of mathematical expressions characterizing fluxes and diffusion rates. Aside from the fact that natural soils in the field are usually quite heterogeneous, we must also consider the fact that environmental questions often relate to areas of land rather than to specific sites. This is also true for point sources of pollution that tend to spread into the surroundings. Detailed simulation models, tested in soil column studies, may be quite suitable for soils in the field, particularly when dealing with relatively homogeneous sandy soils. What is simulated for a soil at a specific site may be representative for a homogeneous area of land in which this particular type of soil occurs, or is expected to occur. However, if this is not the case it is difficult to make statements for areas of land. Urgent practical questions and problems often dictate a pragmatic research approach. In this context, available soil surveys are often used when making rather general statements about environmental properties of areas of land even though their internal heterogeneity is hardly known. Such areas of land are represented on soil maps by different mapping units consisting of well defined soil types that are assumed to occupy at least 80 % of the area of each of the units. Such soil types are well described in terms of soil horizons, textures, structures etc. The purpose of this paper is to review common and more innovative procedures that use soil survey information to obtain data for modeling environmental properties of land.

2. POINT AND AREA DATA

Soil maps of an area with sandy soils of 400 ha, were made at four different scales (Figure 1). The largest scale map (1 : 10 000) shows most details in terms of soil types, as expressed by the codes on the map (Table 1), and water-table fluctuations as expressed in classes indicated by roman numerals (Table 2). For further details, the reader is referred to Wosten et al., 1987. The number of delineated areas on the maps decreases with decreasing map scale.

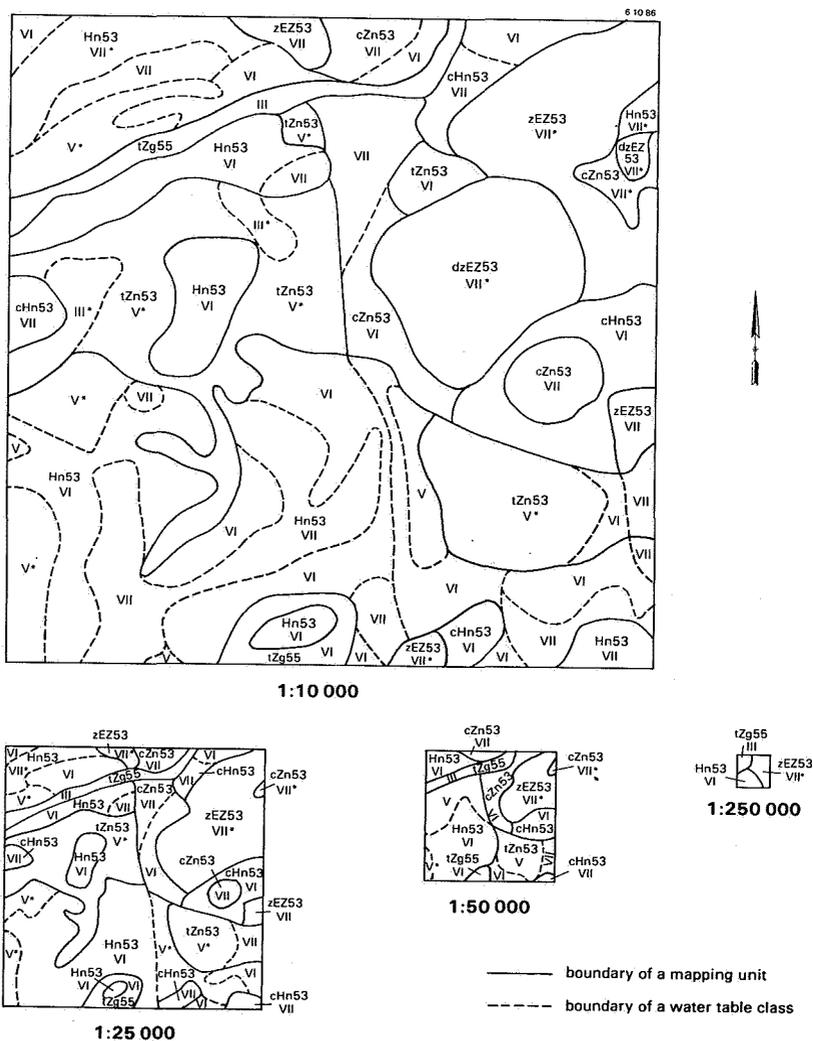


Figure 1. Segments of the soil maps of the sample area on four scales.

Maps are made by soil surveyors who translate point observations, using an auger, into areal patterns by observing various land features such as slope, vegetation etc. The number of observations decreases as the scale of the map to be published, decreases. Here, 606, 135, 54 and 1 borings were made for the four maps, respectively. Traditional soil survey interpretations define a "representative" soil profile for each mapping unit, based on the experience of the surveyor who synthesizes all his observations. This procedure is rather subjective and relatively large differences may occur among surveyors (e.g. Marsman and de Gruijter, 1986). The "representative" profile does not indicate variation within the mapping unit which is important as it determines the variability of soil behavior within the unit. For example, the water supply capacity or the phosphate adsorption capacity calculated for a "representative" profile are usually assumed to be representative for the mapping unit named after this particular type of soil. The variability within the mapping unit can be expressed by indicating the range of soil properties observed within the mapping unit and by making calculations which reflect this range of values. An alternative procedure is to use the individual point observations for making calculations. Next, these point values are transformed to areas by using interpolation techniques. Geostatistical procedures, such as kriging, are particularly useful in this context (e.g. Nielsen and Bouma, 1984 ; Webster, 1985). Some studies have been reported in which results of classical soil-mapping were compared with maps obtained from interpolation of point data. So far, results have been of comparable quality (e.g. Kuilenburg et al., 1982 ; Bregt et al., 1987). There is a tendency to emphasize use of point data and interpolation, certainly in large scale surveys, if only because standard deviations for any point estimate can be derived from kriging. However, it is advisable to make observations within well defined sub-areas of land in a landscape rather than at random. Soils in valleys and uplands, for example, are quite different. Observations along a regular point-grid could mix both types of soils, creating a much higher variability than when sampling both areas separately.

Table 1. Soil classification according to Soil Taxonomy (Soil Survey Staff, 1975) of the mapping units occurring in the sample area. All families are sandy, siliceous and mesic.

Mapping unit	Thickness Al or Ap horizon (cm)	% < 50 um in surface soil	Classification (Soil Taxonomy)
Hn51	< 30	0 - 10	Typic Haplaquods
Hn53	< 30	10 - 17.5	Typic Haplaquods
cHn53	30 - 50	10 - 17.5	Plaggeptic Haplaquods
zEZ53	50 - 100	10 - 17.5	Plaggept
dzEZ53	> 100	10 - 17.5	Plaggept
tZg53	15 - 30	10 - 17.5	Typic Humaquepts
tZg55	15 - 30	17.5-32.5	Typic Humaquepts
tZn51	15 - 30	0 - 10	Typic Humaquepts
tZn53	15 - 30	10 - 17.5	Typic Humaquepts
tZn55	15 - 30	17.5-32.5	Typic Humaquepts
cZn53	30 - 50	10 - 17.5	Plaggeptic Humaquepts
zWz	< 30		Histic Humaquepts

Table 2. Description of water table classes.

Water table class (Gt)	II	III	V	VI	VII
MHW	<40	<40	<40	40-80	>80
MLW	50-80	80-120	>120	>120	>120

MHW = mean highest water level and MLW = mean lowest water level in cm below soil surface.

A * behind the code Gt III and V refers to a "drier part", that means with a MHW deeper than 25 cm below soil surface.

A * behind the code Gt VII refers to a "very dry part", that means with a MHW deeper than 140 cm below soil surface.

3. OBTAINING DATA

3.1 Measurements

Many methods are available to measure physical and chemical soil

characteristics. Method-books tend to emphasize technical aspects of methods rather than operational aspects, such as complexity, cost and applicability, which are often crucial for obtaining representative results (e.g. Bouma, 1983). Emphasizing the aspect of applicability, the following examples will be presented to illustrate use of existing soil survey information for improving the planning and execution of physical and chemical measurements:

- a. As mentioned in the previous section, sampling and data handling within the context of well defined land-units as distinguished by soil survey, will reduce variability as compared with systems where sampling occurs at random, irrespective of soil patterns.
- b. Data on soil texture and organic matter content can be used to derive more complicated soil characteristics needed for simulation (see next section).
- c. Data on soil structure in terms of sizes and shapes of natural aggregates and soil pore patterns are useful to define representative elementary volumes of samples. In a sand such samples can be relatively small because sands consist of a packing of individual sand grains. In soils with aggregates, much larger samples are needed. Studies have indicated that measured infiltration rates are a function of sample volumes. A wide range of values can be obtained when varying the area of measurement, as indicated by Lauren et al., 1987 (Table 3). They measured infiltration rates into a silt loam soil with natural aggregates with sizes of approximately 4 cm diameter. Small infiltrative areas yielded highly variable replicate measurements; because only a few aggregates were present in the sample. Very large areas also yielded a relatively high variability due to technical, experimental reasons. A general rule was developed in this study requiring the presence of at least 30 peds in an infiltrative surface, for measurements to be representative. Soil descriptions in soil survey can thus be used, in principle, to define representative sample volumes in different soils.
- d. Descriptions of porosity patterns, particularly in terms of relatively large pores such as worm- and rootchannels and cracks in swelling clay soils can be used to define deterministic models for water movement. In these models (e.g. Hoogmoed and Bouma,

1980 ; Bouma et al., 1982) water movement into and through the large pores is considered separately from movement into the soil matrix. Applications are also relevant for the placement of e.g. tensiometers and neutron-access tubes in the soil. Whether or not these instruments intercept large pores may determine results obtained. The latter are more representative when porosity patterns of the soil are well defined in relation to the volume of measurement.

Table 3. Statistical parameters for K saturated measured by different sampling volumes.

Volume (cm ³)	Mean	Mode (cm/d)	Median	SD	CV %	No samples
240,000	21.3	10.3	16.6	16.9	79	37
120,000	13.7	6.4	10.7	11.0	81	36
50,000	14.4	6.3	10.9	12.5	96	37
6,283	36.6	6.3	20.3	54.9	150	37
884	34.5	4.8	16.3	64.0	186	35

3.2 Estimation

Simulation of physical and chemical processes requires basis data that are often not available. Various procedures are being used to derive basic data for modeling from existing soil survey data. Some examples follow:

- a. Soil texture can be related to hydraulic conductivity (K-h) and moisture retention (h-0) data that are needed for dynamic hydrological simulation models. The simplest form of this approach presents measured curves from literature as a function of

standard texture classes. A typical Dutch example is the "Rijtema" series, which is still being used (e.g. Driessen, 1986). However, uncertainty about procedures used during measurements makes such series rather unreliable. Van Genuchten (1980) used a mathematical analysis to relate K-h and h-0 to a number of parameters, which are, in turn, correlated with soil texture. Comparable, in principle, is the procedure by which Fe and Al contents of the soil are related by regression analysis to the phosphate sorption capacity (Breeuwsma et al., 1986). Functions obtained have been called "continuous transfer functions" (Bouma and van Lanen, 1987).

- b. At random replicate measurements in well defined soil horizons and soil types can be combined to allow predictions for unmeasured sites where the same horizon occurs in the same type of soil. Examples for hydraulic conductivity were presented by Baker (1977) and by Wosten et al. (1985) who also included moisture retention data. Measurements made in different soil horizons may turn out to be insignificantly different from a soil physical or chemical point of view. Thus, different horizons may be combined into one "soil physical" horizon. The procedure is illustrated for a Typic Haplaquod with four soil horizons of which only two had significantly different soil physical properties (Figure 2). Use of soil horizons as "carriers" of information is considered to constitute a "discontinuous transfer function" (Bouma and van Lanen, 1987).

4. THE QUESTION OF SCALE

This paper focuses on use of soil surveys which always cover areas of land. These areas can be represented at different scales (Figure 1). The choice of a particular scale for any given study is important as it governs the cost of the fieldwork to be made and the degree of detail of interpretations. As discussed in chapter 2, more observations in a given area of land allow more specific interpretations. However, sometimes questions are of a general nature only and there are many examples where the degree of detail of studies being made is not in agreement with the

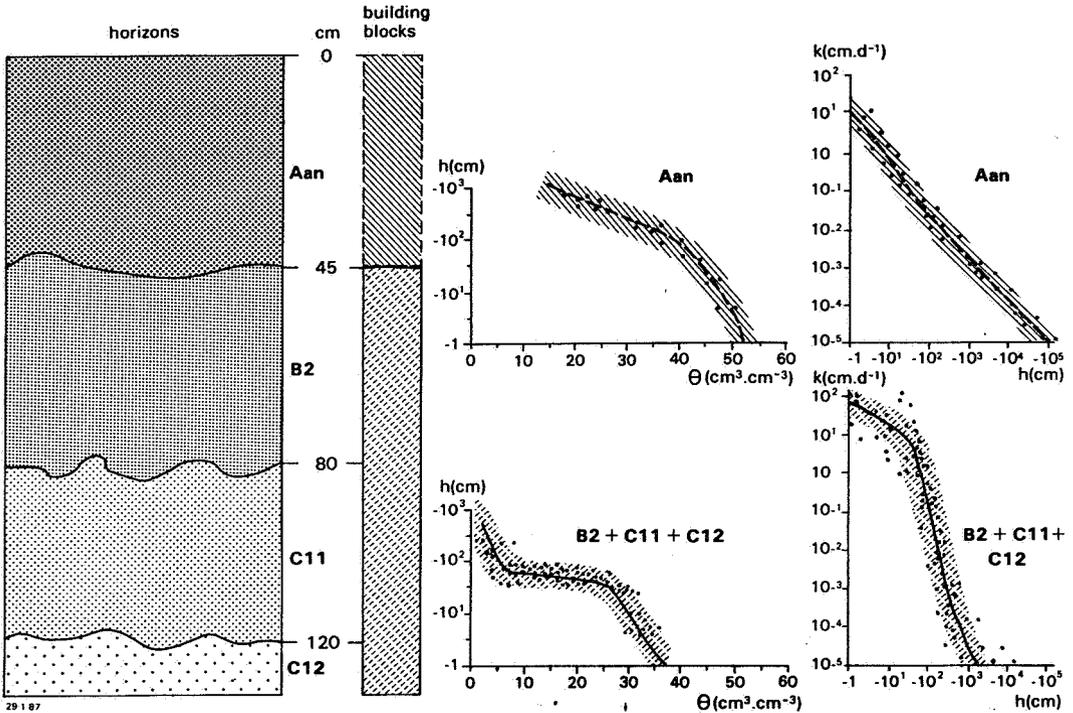


Figure 2. Translation of soil horizons in "soil physical" horizons and the corresponding soil physical properties.

problem to be solved.

A major aspect being emphasized in this paper is the use of soil survey for deriving basic physical and chemical data to be used in simulation models. So far, the discussion has focused on technical and operational aspects. However, a critical analysis of the problem to be solved can result in a sharp reduction of data needs (and costs) when a semi-detailed answer will be adequate. An arbitrary example will be presented to illustrate this aspect. The example relates to calculations of the reduction in crop production following lowering of the watertable by pumping for municipal water supply. Farmers receive a financial compensation for the loss of production. Large sums of money are involved and decisions have often to be made in court. The soil scientist must define the "old" and "new" watertable levels with corresponding crop productions. Computer simulation is used to obtain quantitative and reproducible predictions (Bouma et al., 1980). The maps (Figure 1) were used to make calculations for

each unit, on the basis of a defined "representative" soil profile. This involved application of different procedures discussed in chapter 3.2. Results were presented in terms of the absolute change of grass production, comparing the "old" and the "new" situation. One percent change corresponds with Dfl. 50.-. Two questions were being asked : (1) What is the average change in yield per year for the entire area, and (2) What is the change in yield per year for any given parcel of land. Average changes per year, considering all delineated areas of the various maps, were calculated. They were 2.7 % , 2.5 % , 2.6 % and 2.5 % for maps on scales 1 : 10 000 , 1 : 25 000 , 1 : 50 000 and 1 : 250 000 respectively. In other words, the relatively cheap small scale maps are quite suitable to estimate the average change in yield for the entire area. To analyse the second question, twenty parcels were selected at random and they were located on the different maps. Calculations were made for the soil types occurring within the parcels. Results are presented in terms of deviations from results of the 1 : 10 000 map which is considered as a reference (Figure 3).

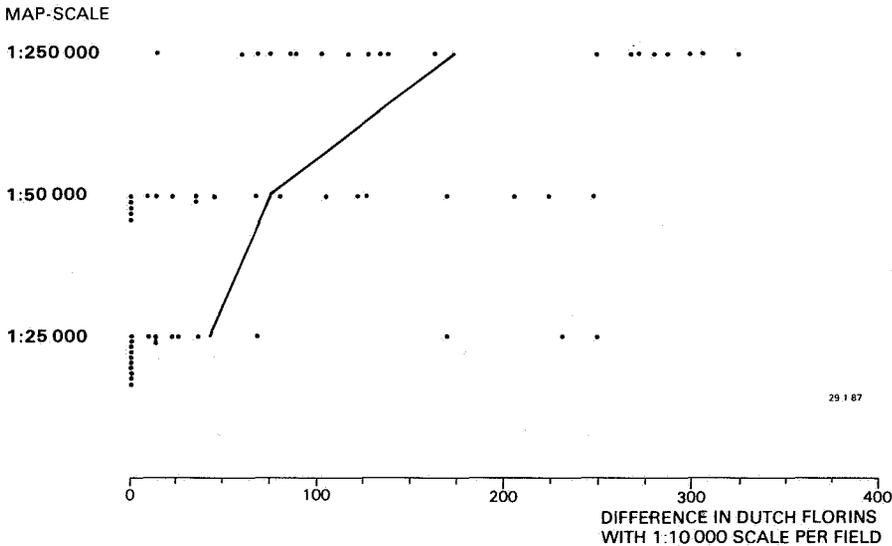


Figure 3. Absolute differences in yield, expressed in Dutch florins per parcel per year, of twenty parcels calculated on four map-scales with the 1 : 10 000 map as a reference. Average absolute differences in yields are indicated by a line connecting averages for each scale.

Deviations increase as the scale of the map decreases. The average deviation per parcel per year is Dfl. 43, Dfl. 76 and Dfl. 173 for the 1 : 25 000, 1 : 50 000 and 1 : 250 000 maps respectively. More significant, perhaps, is the observation that deviations for individual parcels can be very high up to Dfl. 300. On the other hand, no differences were observed for ten parcels at the 1 : 25 000 scale and for five parcels at the 1 : 50 000 scale. Each landowner must balance the cost of a survey versus the benefits resulting from the calculations. The conclusion here was that the higher cost of a 1 : 10 000 survey was less important than the associated increased accuracy of the calculation. Using cheaper smaller-scale surveys resulted in more variable data that would be less valuable when making a claim in court.

The example is meant to illustrate that the scale to be chosen for field work in soil survey should primarily be a function of soil variability but also of the type of question being asked and of a specific cost/benefit analysis. This aspect has largely been ignored within soil survey so far, as emphasis has been on country-wide surveys at a given scale using a fixed legend.

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FORECASTING PHOSPHATE LEACHING FROM SOILS ON A
REGIONAL SCALE

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ABSTRACT

High application rates of manure in areas with intensive livestock farming may eventually cause phosphate leaching to ground water and surface water. In the Netherlands, the capacity of the topsoil (unsaturated zone) to sorb phosphate is already exhausted at some locations. In other words, the soil has become saturated with phosphate to the groundwater level.

In this study we simulated the effects of different manure-application scenarios on the long-term development of the area of phosphate-saturated soils, using a regional model.

The process-oriented, spatially-distributed model is characterized by

- the use of a simplified transport model
- the application of soil survey data to assess the phosphate sorption capacity (a model parameter)
- the use of spatially distributed data.

Data on soils and land use were obtained by superimposing the soil map over the topographic map (scale 1 : 50 000). The phosphate input in the past was assessed from data on manure production and distribution. The input data for phosphate were average values for agricultural areas of 10 000 - 100 000 ha. The data on soils, land use and phosphate application were integrated for each area.

The results indicate that there would be a significant increase in phosphate-saturated soils if present application rates were maintained. The general levels for manure application stipulated recently in proposal legislation would only partly reduce the phosphate-saturated area. Additional measures have been planned, therefore, to prevent phosphate

leaching from the most vulnerable soils.

1. INTRODUCTION

During recent years, the leaching of nitrate from agricultural soils to groundwater and surface waters has received much attention. The widespread occurrence of this leaching is caused by the relatively high application of fertilizers in modern agriculture. Less well-known, but no less important locally, is the leaching of phosphate from soils that receive excessive amounts of manure. Most of the soils thus affected are under maize fields that are heavily manured because maize can tolerate high rates of manure application. The soil horizons in these soils eventually become saturated when the sorption capacity of the soil is exhausted. In the Netherlands, very high concentrations of phosphate, up to 90 mg P per litre, have been recorded locally in shallow groundwater.

Recently, measures have been imposed by law to restrict the spreading of manure. The regulations stipulate a decreasing application rate. The final rate is based on the phosphate requirement of the crop that is being sprayed with manure. This study presents some of the results of a study done to provide recommendations for the proposed regulations. We will focus on the general approach taken to forecast the transport of phosphate to the groundwater on a regional scale. It will be shown how regional transport models can benefit greatly from soil survey and other geographical information if the models are adjusted to the information that can be obtained from these systems and vice versa.

2. MODELLING APPROACH

The regional phosphate transport model (REPTRAM) developed in this study is typified as being:

(i) deterministic

Contrary to empirical input-output models, deterministic process-oriented models allow predictions to be made under changing conditions.

(ii) process-aggregated

Regional models usually require processes to be simplified or aggregated to a fair degree, if the spatial resolution is high (see iv). In this investigation we simplified the description of the process by assuming a stepwise movement of the phosphate front in the soil. Above the solute front the soil solution was considered to behave as a saturated phosphate solution (Schoumans et al., in prep.). Each soil layer was assumed to sorb the maximum amount of phosphate as given by the total phosphate sorption capacity. The average rate of penetration of the phosphate front, V_p , was calculated (in cm per year) by:

$$V_p = \frac{\text{annual effective phosphate load (kg P ha}^{-1}\text{y}^{-1})}{\text{total phosphate sorption capacity (kg P ha}^{-1}\text{cm}^{-1})} \quad (1)$$

The annual effective phosphate load was calculated from the amount of phosphate applied, the uptake by the crops and the amount dissolved from supersaturated layers. The maximum load was defined by:

$$EPL_{\max} = NNc_{\text{sat}} \quad (2)$$

in which:

EPL_{\max} : the maximum, annual, effective load of phosphate (kg P y^{-1})

NN : the annual precipitation excess ($m^{-3} y^{-1}$)

c_{sat} : the phosphate concentration in a saturated solution (kg P m^{-3})

(iii) soil survey-oriented

Describing a regional model in terms of model parameters that can be related to soil survey data greatly improves its regional applicability. The complex phosphate sorption capacity shows a satisfactory correlation with simple soil characteristics, viz. oxalate-extractable iron and aluminium (Schoumans et al., in prep.). In turn, these characteristics correlate well with soil type and horizon (Figure 1). The latter relation has been referred to as a class transfer function and the former as a continuous transfer function (Bouma et al., 1986). The continuous functions apply to soil data that have a continuous range of values. The class functions apply to soil data characterized

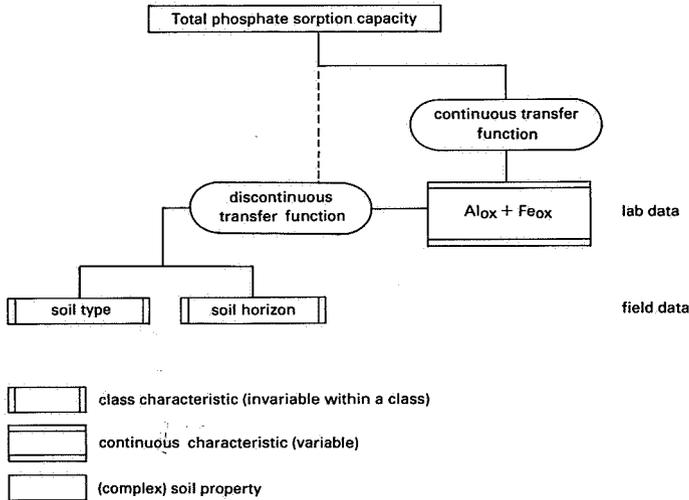


Figure 1 Diagram relating the total phosphate sorption capacity to soil survey data by "transfer functions"

by a specified range of values (e.g. texture classes) or by a symbol (e.g. soil type). The class functions allow a direct use of field data (dotted line in Figure 1).

(iv) spatially-distributed

The spatial distribution of the data is taken into account by using the highest available spatial detail or "resolution". Hence, spatial "lumping" (averaging) of parameters is minimized. Obviously, for economic reasons some averaging (for example, by extrapolating point data to areal data) is inevitable. A minimum degree of averaging is particularly recommended for vulnerability studies, because vulnerable areas can readily be overlooked when point data are averaged over larger areas. The last two points, especially, are considered to be the nub of what we call a "regional" model.

To our knowledge, the use of model parameters that can be directly or indirectly related to soil survey data is a new approach. The use of spatially-distributed models is well known to hydrologists (see e.g. Bathurst, 1986).

3. GEOGRAPHICAL INFORMATION USED

To be able to forecast phosphate leaching from soils, information is required on the geographical distribution of soils (including the water regime), land use (crops) and application of phosphate in fertilizers and manure. The data on manure production were collected for agricultural areas of 10 000 - 100 000 ha of crop land and the information on soils and land use from maps scale 1 : 50 000 (Breeuwsma and Schoumans, in prep.). The size of the areas was mainly determined by economic factors and by the accuracy that was requested.

3.1 Soils

The soils studied were acid sandy soils from the regions in the Netherlands with intensive livestock farming. The variables used in the model, viz. the phosphate concentration and the reaction time, were assumed to be constant for every soil, as described by Schoumans et al. (in prep.). The derivation of the phosphate sorption capacity from soil survey data is also discussed in that paper and by Breeuwsma et al. (1986). Table 1 gives some data on the phosphate sorption capacity of frequently occurring combinations of soil type and water-table class.

Table 1 *Average total phosphate sorption capacity to the mean highest water (MHW) level of five sandy soil types in the Netherlands as a function of the water-table class*

Soil type		Water-table class ¹⁾				
FAO class	USDA class	IIIIa/Va	IIIIb/Vb	VI	VII	VIIb
Arenosol	Psammaquent	3.7	6.1	-	-	-
Humic Gleysol	Typic Humaquept	8.3	11.9	17.1	-	-
Gleyic Podsol	Haplaquod	6.2	11.9	25.2	37.0	-
Plaggen soil	Plagept	-	-	18.9	36.4	>77
Humic Gleysol	"Ferric" Humaquept	24.4	34.2	-	-	-

¹⁾ Mean Highest Water level:
(cm below surface)

<25	25-40	40-80	>80	>140
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The figures demonstrate the effect of soil type and, especially, the depth to the water table. The distribution of the soil types and water-table classes within each area was obtained from the soil map.

3.2 Land use

The land use considered in this study was maize land, because maize fields are likely to receive the highest loads of manure. The distribution of maize fields over soil types and water-table classes was assumed to be similar to the distribution of arable land. Maize is still primarily grown on land that was arable land in the past, and to a much smaller extent on land previously used for grassland. Information on the soil conditions for arable land was obtained by superimposing the soil map over the topographic map of the same scale and by determining soil units and water-table classes of arable land at the intersection points of coordinates in a grid of 1 km x 1 km.

3.3 Phosphate Application

The total amount of phosphate present in the soil was assessed from estimates of the annual spreading of manure in the past and from the phosphate content of the soil before maize cultivation started (Breeuwsma and Schoumans, in prep.). Figures on manure production for each area were obtained from agricultural statistics and corrected to take account of applications to other crops and export to areas with a shortage of manure. At present, phosphate surpluses on maize land have reached average values in the order of 500 - 1000 kg P_2O_5 per ha per year for the major manure-surplus areas.

4. RESULTS

REPTRAM was mainly used to calculate areas of phosphate-saturated soils at various penetration depths and future scenarios for application of manure. Figure 2 demonstrates the effect of the penetration depth on the area of phosphate-saturated soils for the entire district, under the benchmark scenario (no change in application rates). Some 10 000 ha appear to be saturated to the mean highest water level already and this

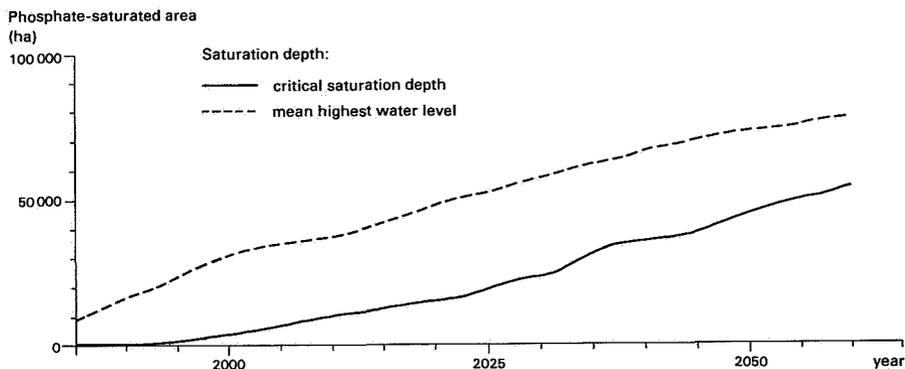


Figure 2 Long-term development of the area of phosphate-saturated maize land in the Netherlands for two saturation depths (no change in application rates)

area increases steadily in the future if no measures are taken. The area saturated to the "critical" depth, (i.e. the depth below which no permanent leaching is expected) is as yet very small. However, the most vulnerable soils may soon be saturated even at this depth, if the present rates of manure application continue.

Figure 3 shows the impact of some application scenarios on the area saturated with phosphate to the mean highest water level. Two of the scenarios have a phased reduction of rates with time. The first scenario, with annual rates of phosphate application decreasing from 420 to 215 kg of P_2O_5 per ha, is based on finally meeting the nitrogen requirement of the crop with manure. The other scenario, with annual rates decreasing from 350 to 75 kg of P_2O_5 per ha, is based on meeting the phosphate requirement. This scenario has now been imposed by law. The currently saturated area is actually higher than shown in Figure 2 because the phosphate sorption capacity was assumed to be somewhat smaller. The decreasing level of application has a limited effect on the phosphate-saturated areas (see Figure 3). Additional measures have been included in the regulations, therefore, involving the mapping and sampling of soils that are likely to be saturated with phosphate. Furthermore, farmers will no longer be allowed to apply more phosphate than the amount required by the crop if a field is found to be phosphate-saturated.

The tracing of the precise location of phosphate-saturated soils re-

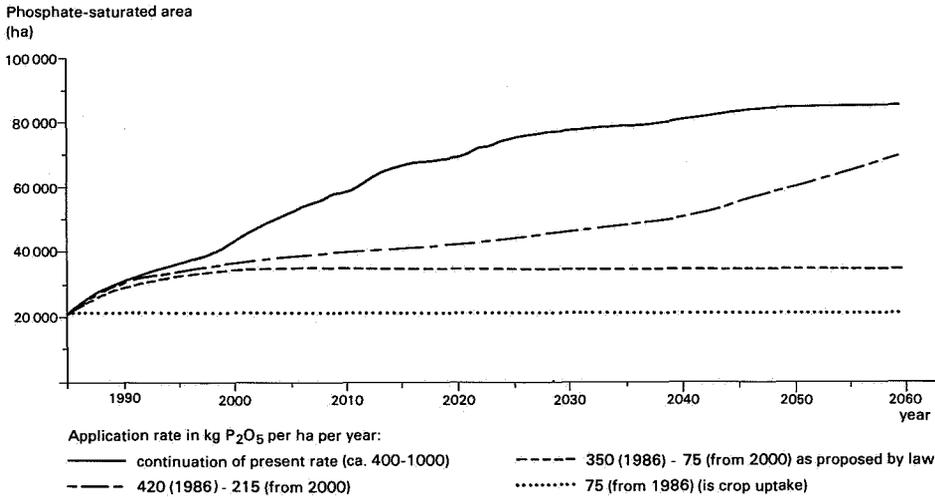


Figure 3 Long-term development of the area of phosphate-saturated maize land in the Netherlands for four scenarios of phosphate application (saturation depth: mean highest water level)

quires a more detailed study using data on manure application of higher spatial resolution and studying other crops too. In addition, the transport of phosphate could be described in more detail (see e.g. Raats et al., 1982). The present model could easily be adjusted to allow for the latter alteration in future studies, provided that model parameters can be related to soil survey data. This method for combining geographical data bases with geographically-oriented transport models is now being elaborated further, to locate vulnerable areas more precisely.

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EXPOSURE ASSESSMENT FOR THE PESTICIDE ALDICARB
IN FLORIDA, USA

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ABSTRACT

In this paper, computer modeling work related to an exposure assessment for the pesticide aldicarb in the state of Florida, USA, is presented. The work was divided into two phases: deterministic modeling of contaminant transport under various soil/climate/management scenarios for both the unsaturated and saturated zones, and uncertainty analysis of transport in the unsaturated zone using Monte Carlo simulations. The paper briefly describes the modeling study, reports results of the unsaturated zone modeling and compares the loading estimates for aldicarb to groundwater utilizing both deterministic and probabilistic techniques.

BACKGROUND

The pesticide aldicarb is used extensively in Florida citrus for the control of nematodes and other pests. Evidence of aldicarb contamination in groundwaters of the state sparked public concern and prompted a March 1983 suspension of the use of the compound in all but three Florida counties. In September 1983, the use of aldicarb was reinstated with the restrictions that it would not be used within 90 m (300 ft) of drinking water wells and that application would be at half the label rate of 11.2 kg/ha.

In 1984, a modeling study was performed to assess aldicarb concentrations in drinking water wells in the vicinity of citrus groves (Dean and Atwood, 1985). The modeling study was part of a coordinated risk assessment conducted by the U.S. EPA. Areas in the citrus-growing region were identified, with respect to the unsaturated and saturated zones, in which fate and transport of aldicarb were thought to be uniquely different. An extensive literature search was conducted to determine degradation and transformation rates, and adsorption coefficients for aldicarb. These regional and chemical data were used to define various simulation scenarios. The fate and migration of aldicarb was then simulated in the unsaturated zone using PRZM (the Pesticide Root Zone Model; Carsel, et al., 1984) and in the saturated zone using CFEST (Combined Fluid-Energy-Solute Transport model; Gupta, et al., 1982). Continued interest in the problem lead to subsequent work in which the transport of aldicarb to groundwater was again modeled (using PRZM), this time taking into account uncertainty in the pesticide and soils parameters used as model coefficients.

The objectives of this paper are twofold; to briefly describe the modeling study and to answer two questions: what is the impact of making misjudgements about the mean values of model parameter, and, what is the impact of neglecting uncertainty in model parameter estimates?

ENVIRONMENTAL SETTING AND PESTICIDE CHARACTERISTICS

Environment

Citrus is grown throughout most of central and southern Florida (Figure 1). A great deal of fruit is grown in the "ridge" area, a region of sand hills running north-south in the center of the state, and in the "flatwoods" area, a region of lowlands which flank the ridge area on both the east and west coasts. In each of these areas, climate, soils, management practices, and thickness of the unsaturated zone can be quite different. These factors cause substantial differences in the fate and transport of aldicarb to groundwater.

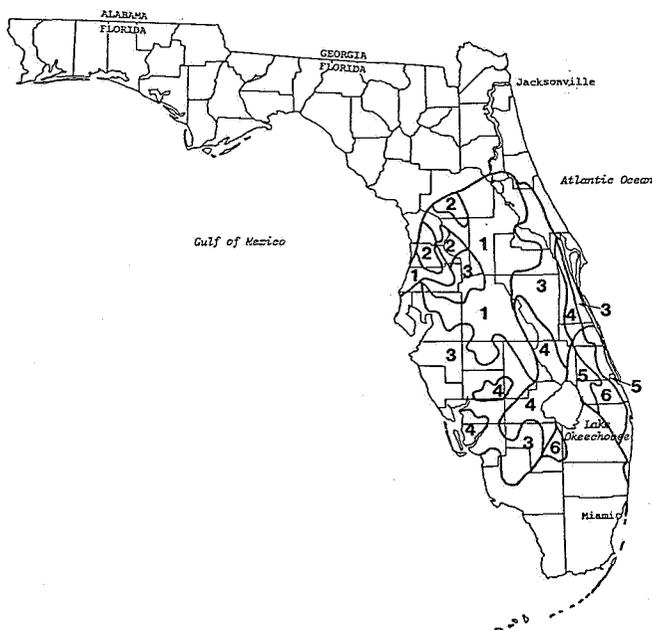


Figure 1. *Subareas delineated for unsaturated zone modeling*

Critical climatic variables are precipitation and evaporation which determine the quantity of water available for percolation through the soils. In the soil, water content and saturated hydraulic conductivity, soil organic matter content, and soil pH are important factors. Water content and hydraulic conductivity determines the velocity at which water moves through the soil, while organic-matter content affects chemical adsorption, and pH strongly affects aldicarb degradation. Data analysis indicated that differences in these factors were pronounced among four soil orders on which citrus is grown in Florida: the entisols, ultisols, spodosols, and alfisols.

Based on climatic, soils, management, and physiographic considerations, the Florida citrus-growing region was subdivided into the six areas shown in Figure 1. Area 1 is an area of primarily ultisols, while area 2 consists primarily of entisols. Areas 3 and 5 consist primarily of spodosols, while areas 4 and 6 contain primarily alfisols. Management practices vary somewhat between these areas. Areas 5 and 6 receive about 10% more rainfall on an annual basis than areas 3 and 4.

For the sake of brevity, only the results for unsaturated transport in thin ridge soils (i.e., ridge areas having a shallow groundwater table) are discussed in this paper. Loadings to groundwater are greatest in this area. The results of the deterministic modeling of all the unsaturated and saturated zone scenarios have been reported elsewhere (Dean and Atwood, 1985).

Pesticide Characteristics

Aldicarb is a nematicide, acaricide, and a systemic insecticide. Its environmental fate is dominated by two factors: it forms two toxic daughter products, and is highly mobile in soils. Degradation of the toxic residues of the compound is of intermediate duration compared to other pesticides. Aldicarb is rapidly oxidized to aldicarb sulfoxide, which in turn is more slowly oxidized to aldicarb sulfone.

Concurrently, these three carbamates are transformed by hydrolysis to corresponding oximes. These products of hydrolysis are far less toxic than aldicarb, its sulfoxide or its sulfone, and are of little environmental concern. A schematic of these processes is shown in Figure 2. The chemistry and environmental fate of aldicarb have been described by a number of researchers. A thorough review of its properties has been compiled in Dean, et al., 1986.

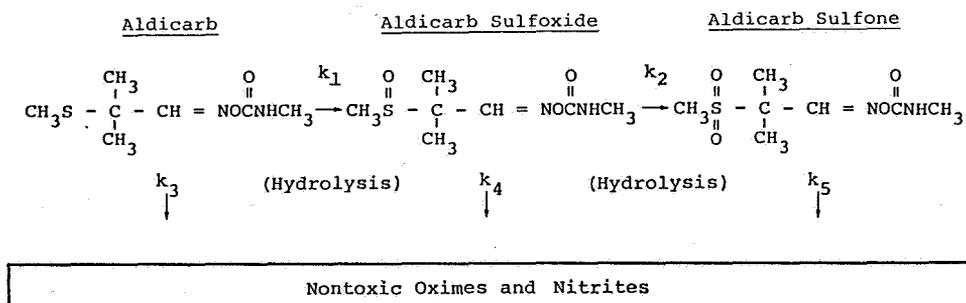


Figure 2. Schematic of aldicarb environmental chemical pathways

MODEL IMPLEMENTATION

PRZM was modified in this study so that the transformation of aldicarb to its daughter products could be simulated in the unsaturated zone. Therefore, the rates k_1 through k_5 had to be estimated for each transformation/degradation pathway and adsorption partition coefficients had to be estimated for aldicarb, its sulfoxide, and its sulfone. This was accomplished by taking rates from the literature and regressing the values on concurrently measured variables such as pH, temperature, soil water content and organic matter. Rates were predicted for each modeling scenario using these regression equations and mean valued data on local soil conditions. Adsorption partition coefficients were determined using average values of K_{oc} found in the literature with localized values of soil organic carbon. Two parameter sets were derived by two independent groups of experts to evaluate the "accuracy" of the selected values.

Deterministic Approach

Mean values for pesticide parameters were estimated by experts from Syracuse Research Corporation (SRC) without knowledge of the values used in the 1984 modeling study. Deterministic model runs were then made to compare the output obtained using the two sets of mean valued input. Meteorological data from Lake Alfred, Florida was used to drive the model. Because a number of years were run, the output was summarized into frequency distributions of the annual leaching load.

Probabilistic Approach

One of the purposes of this study was to evaluate the impact of having neglected uncertainty in the mean values of pesticide coefficients in the original (1984) modeling effort using PRZM. A classical method of doing this is by using Monte Carlo analysis. The Monte Carlo method and yields the distributions of model output variables.

The variability of parameters was taken into account while utilizing the mean values of the parameters from the 1984 modeling study and the more recent SRC estimates. The parameters under consideration for the uncertainty analysis were the following:

- adsorption coefficients (K_{oc}) for each species (aldicarb, AS; aldicarb sulfoxide, ASO; and aldicarb sulfone, ASO₂),
- transformation rate constants ($AS \rightarrow k_1 \rightarrow ASO$, $AS \rightarrow k_2 \rightarrow ASO_2$),
- degradation (hydrolysis rate) constants (k_3 , k_4 , k_5), and
- soil parameters (pH, organic carbon, water holding capacity, bulk density).

Details of the parameter estimation process are given in Dean, et al., 1986. Results are reported in the following section.

The approach for performing the Monte Carlo analysis was designed to conserve computer time while providing the information necessary to answer the question posed above. Ideally, the way to perform the analysis would be to rerun each of the deterministic scenarios run previously, considering the uncertainty in climate as well as in pesticide parameters. This information could then be used to calculate an ensemble of frequency distributions of pesticide leaching loads. Confidence bands could then be calculated for each distribution. Projections of the computer time and budget required to do so showed this to be infeasible. Instead, the following approach was used. Values of pesticide loads were taken at the 90%, 50%, and 10% exceedance probability levels from the previously derived frequency distribution. For each of these "target" simulation loads, a year having an annual load closest to the target was selected. These three years were then used in the subsequent Monte Carlo simulations.

This approach has some distinct advantages and disadvantages. A definite advantage is the savings in simulation time. Only a fraction

of the original simulation years had to be rerun. Another advantage is that the variability in the output due to pesticide parameters (from single year Monte Carlo runs) versus meteorological variability (from multiple year deterministic runs) is differentiated. The variation in the original frequency distribution is due primarily to time variability in rainfall, evapotranspiration, and/or temperature, and secondarily to differences among scenarios in soils and management (e.g., irrigation practices). The variability in the ensemble runs generated about the old frequency curves at selected exceedance values, is due primarily to uncertainty in pesticide parameters. Although there was some statistical interaction between results, the two analyses should show the relative effects of variability of climatic factors versus pesticide properties. A disadvantage is that the distribution of the integrated effects of variability in climatic factors and uncertainty in pesticide parameters is not directly obtained.

SIMULATION RESULTS

The annual pesticide loading results for thin ridge soils from the 1984 modeling study is shown in Figure 3. The points in the distribution consist of results from simulations of both entisols and ultisols for all appropriate management factors considered. These results were found not to be significantly different statistically. By combining the simulation results from several scenarios, better estimates of the probabilities are obtained. The 90%, 50%, and 10% exceedance probability loads are 0.006, 0.04 and 0.3 kg/ha, respectively.

Table 1 shows a comparison of the results of deterministic runs and means from the Monte Carlo analyses. The first column shows the annual pesticide leaching loads from the original simulations for the years chosen to represent the 10, 50 and 90 percent exceedance levels. The second column shows the results of using values estimated by SRC for chemical parameters. For the 10% exceedance level, the load was slightly lower (0.29 kg/ha) than the original simulations (0.32 kg/ha). At the 50% exceedance level, the SRC output was lower by 37% and at the

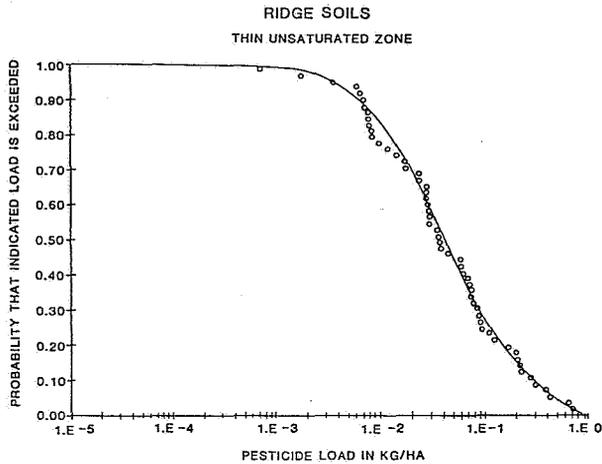


Figure 3. Frequency of annual quantity of pesticide leached to the unsaturated zone from thin Entisols and Ultisols

90% level, the SRC output was about one third of the original output (0.002 kg/ha versus 0.006). It is noteworthy that the results are most similar at higher loading values. This makes sense because the highest leaching loads occur in years in which large storms occur soon after application. Under these circumstances, degradation parameter selection is less likely to have an impact in the results.

Table 1. Deterministic results, means and coefficients of variation from Monte Carlo simulations for thin ridge soils¹

Exceedance Level	Deterministic Results		Monte Carlo Results		
	Original Coefficients	SRC Coefficients	Original With Correlation	Original Without Correlation	SRC With Correlation
0.10	0.320	0.29	0.78 (70.5)	0.72 (80.5)	0.63 (107.9)
0.50	0.038	0.024	0.24 (79.2)	0.20 (95.0)	0.22 (159.1)
0.90	0.006	0.002	0.065 (109.2)	0.065 (153.8)	0.049 (244.5)

¹ Units are kg/ha

Table 1 also shows the results of Monte Carlo simulations. Three cases were run: Dean and Atwood (original) parameters both with and without estimated correlation among inputs, and SRC parameters with correlation. The values shown in the table are the ensemble means of 200 simulations for each case. The parenthetic numbers are corresponding coefficients of variation (expressed as percents) for each case.

Because of the uncertainty in the estimates of correlation coefficients, Monte Carlo simulations were performed both with and without correlation. As can be seen in Table 1, correlation produced slightly higher mean responses and slightly lower coefficients of variation than when correlation was not considered.

The effect of considering uncertainty in pesticide parameters used in the original simulations PRZM was to increase the mean annual leaching output. The mean response for the thin ridge soils at the 10% exceedance level increased by a factor of 2.4 over the original output of 0.32 kg/ha. At the 50% exceedance level, the response increased by a factor of 6.3 over the original output of 0.038 kg/ha. At the 90% exceedance level the mean increased over an order of magnitude.

As in the case just discussed, consideration of uncertainty with SRC parameter estimates produced higher ensemble mean responses than the corresponding deterministic outputs. SRC parameters produced outputs with slightly lower means than the simulations produced with the original parameter set. However coefficients of variation were higher with the SRC parameter set.

These analyses have demonstrated that although the leaching output produced by PRZM is sensitive to chemical parameters, the difference in results produced by data sets derived independently by two groups of experts was small. However, consideration of the variability in parameter estimates can have dramatic results on the leaching output produced. Results were relatively insensitive to estimates of parameter covariance.

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MODELING OF NITRATE LEACHING IN THE DUTCH SANDY AREAS

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ABSTRACT

The NITRIN model is an empirical model, predicting the steady state nitrate leaching in sandy soils after several years of unchanged land-use and manuring practice. The model is used on the scale of a municipality. In this study nine scenarios are calculated. The application period of the animal waste (winter or spring) and the maximum percentage of the nitrogen requirement of the crops, given as animal waste, are variables. Calculations of the nitrate leaching have been done for 164 municipalities in the main four sand districts of the Netherlands. Some preliminary conclusions of this study :

- the nitrate leaching of grassland is not sensitive to restrictions of the application of animal waste. (47 % of the area is grassland)
- if the applied amount of animal waste is reduced to 75 % of the production and application is in spring instead of in winter a decrease of 35 % of the nitrate leaching of arable land is computed.

FRAMEWORK AND GOAL

By order of the Ministry of Housing, Physical Planning and Environment the occurrence and the behaviour of nitrogen in groundwater is studied. This should enable the Dutch government to estimate the effects of restricting the dumping of animal waste on sandy soils. Part of this study is modeling of the nitrate leaching as a function of application rate of animal waste and application time.

THE NITRIN MODEL

NITRIN (NITRin INflow model, Hoeymakers, 1986) is a regional nitrate leaching model, that is derived from the model NIMWAG (WNW, 1985). NITRIN is an empirical model, predicting the steady state nitrate leaching in sandy soils after several years of unchanged land-use and manuring practice. The calculations are made for a municipality (1,000 - 10,000 ha). Required inputdata are:

- production of various types of animal waste
- excess of various types of animal waste
- nitrogen requirement of the crops
- area of each combination of land-use and watertable class

The excess of animal waste is not used for farming land in the municipality. The applied amount of animal waste in the municipality is the difference between production and excess of animal waste. In fertilizer 100 % of the nitrogen is considered to be effective. In animal waste this ratio varies between 20 and 80 % . Discriminated types of land-use are: grassland, crop rotation, silage maize, extensive horticulture and woodland. Watertable-classes are numbered from 1 to 7; nr. 1 is wet marschy land; nr. 7 has a watertable > 1.25 m below landsurface. Only the mean nitrate concentration in the grondwater top layer is calculated for the various types of land-use in a municipality. Thus spatial variations of the nitrate leaching concentration are not concerned of. For the application of animal waste in relation to the Nitrogen requirement the following procedure is used.

1. apply a minimum amount of fertilizer N (table 1)
2. add animal waste up to the effective N-requirement
- 3a. If there is less animal waste than required:
fill up with fertilizer N up to the N-requirement
- 3b. If there is still animal waste left after 2 :
apply additional animal waste up to a the maximum level (table 1)
in the sequence : maize, grassland, arable land
4. If there is still animal waste left after 3b :
apply the rest on the silage maize fields (dumping).

Table 1 : Agricultural standards for the effective N-requirement of the crops and the application of animal waste and fertilizer

land use	nitrogen requirement kg N/ha/an	minimum fertilizer kg N/ha/an	maximal eff. N app. by animal waste kg N/ha/an
grassland	400	360	140
crop rotation	164	25	239
silage maize	210	50	560 (excl. dumping)
ext. horticulture	650	500	150

The proces of nitrate leaching is modeled as a set of empirical functions of the application of animal waste, fertilizer, land-use and depth of the watertable :

$$N\text{-flux} = f(\text{GHG}) \cdot [f(\text{N-fer}) + f(\text{N-man}) + f(\text{N-cat}) + f(\text{N-dep})]$$

N-flux = nitrogen mass-flux in kg N/ha/an; the approximate N concentration is found dividing by the annual nett precipitation (forest : 200 mm/an ; agricultural land : 300 mm/an)

f(GHG) = coefficient for the denitrification loss as function of the mean highest watertable (GHG) (Steenvoorden, 1984).

f(N-fer) = leaching as a function of the application of fertilizer N :
grassland :

$$f(\text{N-fer}) = 0 \quad \text{N-fer} < 270 \text{ kg N/ha/an}$$

$$f(\text{N-fer}) = 0.5 (\text{N-fer} - 270) \quad \text{N-fer} > 270 \text{ kg N/ha/an}$$

arable land:

$$f(\text{N-fer}) = 0.25 \text{ N-fer}$$

f(N-man) = leaching as a function of the application period and applied amount of Nitrogen in animal waste (Hoeymakers, 1986)

f(N-cat) = leaching as a function of the amount of nitrogen of cattle excrements on grassland : 20 % of 130 kg N/ha/an

f(N-dep) = leaching as a function of the N-deposition (NO_x + NH_x) on woodland (Hoeymakers , 1986)

USED DATA

In this first large scale application of the model 164 municipalities in the main four sandy districts of the Netherlands are involved. For each farm in a municipality the nitrogen requirement of the crops and the production and excess of animal waste is calculated (Luesink and Wijnands, 1985). Only the accumulated amounts of requirement, production and excess of the municipality are input for NITRIN.

Nine scenario's have been examined, in which the application period and the maximum percentage of the nitrogen requirement, given as animal waste, are variables (table 2).

Table 2 : Scenario's of application time and maximum percentage of applied nitrogen by animal waste

scenario	app. time	max. % of N by animal waste
1*	winter	no limit
2	winter	100
3	winter	75
4	winter	50
5	winter	25
6	spring	100
7	spring	75
8	spring	50
9	spring	25

* the total produced animal waste is spread over the farming land

Scenario 1 generally agrees with the present situation in the east, central and south sandy districts of the Netherlands. To get an estimate of the area of each combination of soil type, land-use and watertable class in a municipality topographical maps, soil maps, land-use statistics and agricultural production statistics are used. An area distribution of watertable classes (GT) is available for grassland and arable land (Haans and Van Soesbergen, 1977), table 3. From the GT an estimate the mean highest watertable depth (GHG) is made.

Table 3 : Distribution of the grassland area over the watertable classes (in % of the area)

sandy-district	watertable class:						
	1	2	3	4	5	6	7
north	1	15	25	2	38	16	3
east	0	2	30	5	37	18	8
central	1	6	41	5	4	16	10
south	0	3	23	6	32	26	10

RESULTS OF THE EASTERN SAND DISTRICT

Table 4 : Land-use of 39 municipalities in the eastern sandy district

land-use	% of the area	land-use	% of the farming land
farming land	75	grassland	78
wood	13	silage maize	12
urban area	12	crop rotation	2
		ext. horticulture	1

Table 5 : Total applied and total excess of animal waste in the eastern sandy district

scen.:	applied million kg	excess (*) million kg
1	13323	0
2	10177	3146
3	9931	3392
4	9600	3723
5	6235	7088
6	9926	3397
7	9692	3631
8	8931	4392
9	4927	8396

* not applied on farming land in the district

Table 6 : Mean NO₃-N concentration under grassland (mg/l)
scenario:

GT:	1	2	3	4	5	6	7	8	9
1	4.4	4.5	4.5	4.5	4.5	4.2	4.2	4.3	4.4
2	4.4	4.5	4.5	4.5	4.5	4.2	4.2	4.3	4.4
3	4.4	4.5	4.5	4.5	4.5	4.2	4.2	4.3	4.4
4	5.9	6.0	6.0	6.0	6.0	5.6	5.7	5.7	5.9
5	4.4	4.5	4.5	4.5	4.5	4.2	4.2	4.3	4.4
6	8.9	8.9	8.9	8.9	9.0	8.5	8.5	8.5	8.8
7	20.7	20.8	20.8	20.9	21.0	19.7	19.8	19.9	20.5

Table 7 : Mean NO₃-N concentration under arable land (mg/l)

GT:	scenario:								
	1	2	3	4	5	6	7	8	9
1	3.6	3.2	3.2	3.1	2.7	2.4	2.4	2.3	2.2
2	3.6	3.2	3.2	3.1	2.7	2.4	2.4	2.3	2.2
3	3.6	3.2	3.2	3.1	2.7	2.4	2.4	2.3	2.2
4	4.8	4.3	4.2	4.1	3.6	3.1	3.1	3.1	2.9
5	3.6	3.2	3.2	3.1	2.7	2.4	2.4	2.3	2.2
6	7.2	6.4	6.3	6.2	5.5	4.7	4.7	4.7	4.4
7	16.8	14.9	14.7	14.5	12.7	11.0	11.0	10.9	10.3

Table 8 : Mean NO₃-N concentration under silage maize (mg/l)

GT:	scenario:								
	1	2	3	4	5	6	7	8	9
1	4.4	3.9	3.9	3.8	3.4	3.0	3.0	2.9	2.8
2	4.4	3.9	3.9	3.8	3.4	3.0	3.0	2.9	2.8
3	4.4	3.9	3.9	3.8	3.4	3.0	3.0	2.9	2.8
4	5.9	5.2	5.2	5.1	4.5	4.0	4.0	3.9	3.7
5	4.4	3.9	3.9	3.8	3.4	3.0	3.0	2.9	2.8
6	8.8	7.9	7.8	7.7	6.8	6.0	5.9	5.9	5.6
7	20.6	18.3	18.2	18.0	15.9	13.9	13.9	13.7	13.0

Table 9 : Mean NO₃-N concentration under woodland (mg/l)

GT:	scenario:								
	1	2	3	4	5	6	7	8	9
1	5.6	4.3	4.3	4.2	3.1	2.8	2.7	2.6	1.9
2	5.6	4.3	4.3	4.2	3.1	2.8	2.7	2.6	1.9
3	5.6	4.3	4.3	4.2	3.1	2.8	2.7	2.6	1.9
4	7.4	5.8	5.7	5.5	4.1	3.7	3.7	3.5	2.6
5	5.6	4.3	4.3	4.2	3.1	2.8	2.7	2.6	1.9
6	11.1	8.7	8.5	8.3	6.1	5.6	5.5	5.2	3.9
7	26.0	20.3	19.9	19.4	14.2	13.0	12.8	12.2	9.1

Table 10 : Percentage of the districts area in each nitrate (NO₃) concentration class

class: (mg/l)	scenario:								
	1	2	3	4	5	6	7	8	9
< 25	55.	56.	56.	57.	60.	63.	62.	61.	67.
25- 50	26.	26.	26.	26.	24.	23.	23.	25.	21.
50-100	16.	17.	17.	17.	16.	14.	14.	14.	12.
>100	3.	1.	1.	1.

CONCLUSIONS

- The nitrate leaching of grassland is not sensitive to restrictions of the application of animal waste. Because 90 % of the nitrogen requirement of grassland is provided with fertilizer (table 6).
- If the applied amount of animal waste is reduced to 75 % of the production a decrease of 11 % of the nitrate leaching of arable land and silage maize is computed (table 7 and 8).
- If also animal waste is applied in spring instead of in winter, a decrease of 35 % of the nitrate leaching is computed (table 7 and 8).
- The nitrate leaching of woodland is high, because of the high ammonia deposition. The ammonia deposition is sensitive for a decrease of the applied amount of animal waste (table 9).
- In the present situation (no restrictions) in 20 % of the eastern sandy district the calculated nitrate concentration in the groundwater toplayer exceeds the EG drinking water standard of 50 mg NO₃/l (table 10).
- If applied amount of animal waste is decreased by 25 % and application is in spring this will be 15 % (table 10).

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HYDRODYNAMICAL EXCHANGES BETWEEN GRAVEL PITS AND
THE AQUIFER : A RISK FOR GROUNDWATER QUALITY.
FIELD OBSERVATIONS AND MODELLING.

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ABSTRACT

A new methodology has been applied to the site of La Wantzenau (Alsace-France) to locate and quantify the hydrodynamical exchanges between gravel pits and groundwater. The usual distinction between upstream and downstream is insufficient. A complex sectorization of the banks sets up with time under the influence of many factors such as : gravel pits morphology, vegetation of the slopes, geochemical characteristics of the material of the banks, water turbidity (eutrophication)... After interpretation of aerial thermographies, sampling sites for carrying out sediments were chosen in the upper zone of the banks. Sediments were also collected at the bottom of the gravel pit by scuba diving. The results show that a vertical sectorization has to complete the horizontal one. The modelling of the transient groundwater flow at a local scale has been done on the basis of these results. It appears that, in case of a pollution of the water of the gravel pits, the pumping wells situated downstream would be contaminated.

1. INTRODUCTION

The excellent mechanical characteristics of the alluvial deposits in the plain of the river Rhine motivate the exploitation of underground granulates. In Alsace, 94 % of the 120 exploited gravel pits and of 1500 abandoned gravel pits cut the groundwater table situated

a few meters under the soil surface. French administrative department in charge of underground resources has been lead to elaborate a new legislation. The main objective is to favour the rational exploitation of alluvium deposits by insuring the operator interests and also to control the equipping of privileged sites. In such sites, where several gravel pits will be exploited, the hydrodynamical impact of the gravel pits can be quite important and the risk of accidental pollution of the groundwater will be high.

2. THE EXPERIMENTAL SITE OF LA WANTZENAU

The experimental site of La Wantzenau is situated 10 km North of Strasbourg (Figure 1). The aquifer is constituted of alluvial deposits (sand and gravel of Pliocene and Quaternary) and is 90 m deep. In the studied zone, a clay layer situated 20 m under the soil surface separates two stages of this aquifer. The experimental site includes :

- two gravel pits aged differently, an exploited one with mean depth of 20 m and a surface of 12 ha and an abandoned one 15 m deep and with a surface of 18 ha ;
- the river Ill, which supplies partially the aquifer by infiltration ;
- a water catchment situated downstream of both gravel pits.

Several piezometers exist near the gravel pits and water level gauges were settled in the gravel pits and in the river Ill.

3. THE EXPERIMENTAL STUDY OF THE HYDRODYNAMICAL EXCHANGES

Usually, hydrodynamical exchanges between a gravel pit and the aquifer are described by considering an upstream zone where groundwater supplies the gravel pit and a downstream zone where groundwater drains the gravel pit. The downstream zone is expected to become clogged in time according to sedimentation and transport processes. The ecological heterogeneity of the banks has to be added to these

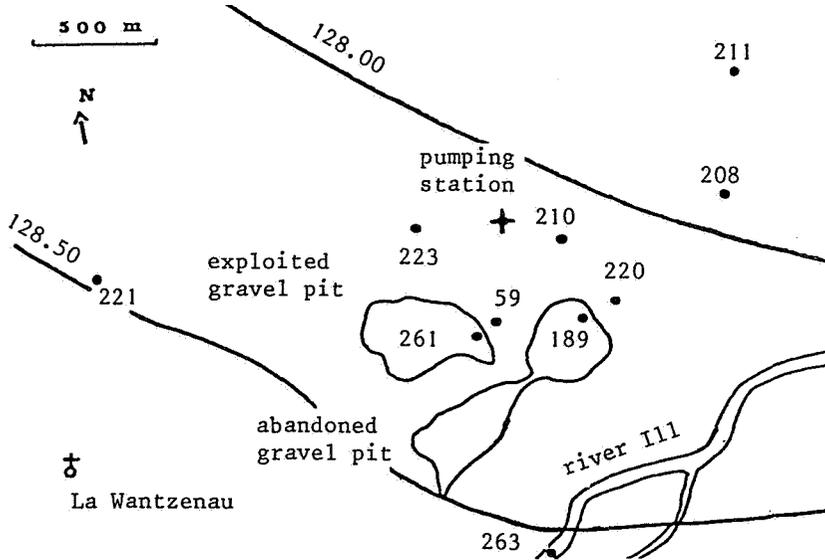


Figure 1. *The experimental site of La Wantzenau*

• piezometer or water level gauges, — piezometer head

multiple causes of banks clogging. Does this visible heterogeneity of the banks induce a spatial variability of the clogging and, thus, create privileged zone for hydrodynamical exchanges ? How can we locate these privileged zones ? How can we apprehend the gravel pit aquifer system in his whole heterogeneity ? These are some of the fundamental questions which motivate this research.

3.1 Location of hydrodynamical exchanges at a regional scale

Piezometric observations are the most widely used to appreciate hydrodynamical exchanges between the aquifer and a watery gravel pit. Nevertheless, these observations are rough and limited by the density of the measurement network. This problem can be solved by using remote sensing. We have used the thermal tracing with the natural stenothermic source : the groundwater (Colacino et al., 1976 ; Durbec et al., 1986). The measurements have been made on

February 1985 because of the good thermal contrast (average temperature of the air -15°C , of the groundwater $+9^{\circ}\text{C}$). A first sectorization of the banks of the gravel pits has been shown by detailed analyses of the photographs (Figure 2). Also, the supplying role of the river Ill was visualized.

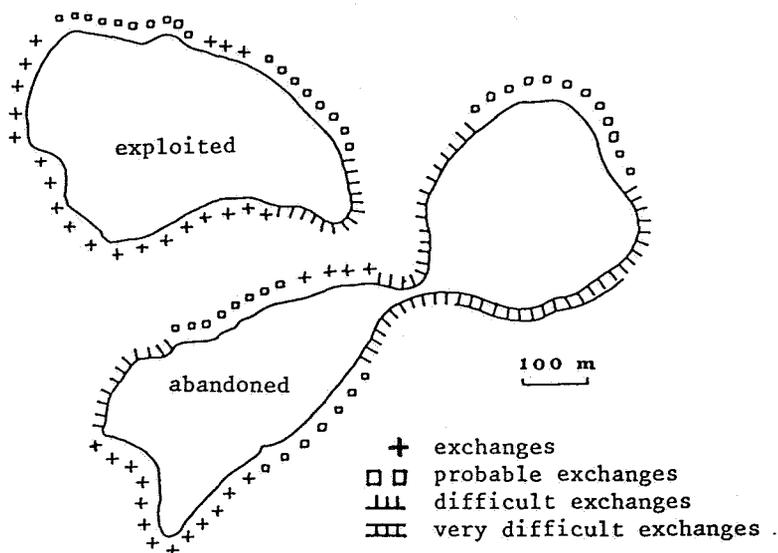


Figure 2. Localisation of the hydrodynamical exchanges by remote sensing

3.2 Location of hydrodynamical exchanges at the scale of a gravel pit

The clogging of the banks and his spatial variability is under influence of hydrogeological, hydroecological and hydrodynamical factors. Thus, our methodology is based on observations of these three processes.

3.2.1 The hydrogeological aspects

The following parameters have been studied by core sampling :

- fine grain fraction with an equivalent diameter less than 80 μm
- fine grain fraction with an equivalent diameter less than 10 μm
- fine grain fraction with an equivalent diameter less than 5 μm
- organic matter, carbonated matter and uncarbonated matter, Fe, Cu, Mn, Zn, Ca.

The data have been computerized by Main Component Analysis. The results of this statistical analysis show the duality mechanical - chemical processes of the clogging of the banks. Three fictive variables C1, C2, C3 describe approximatively the explained variancy (86,2 %) :

- C1 : chemical composition of the deposit on the fine grains (48,8 %)
- C2 : fine grain size distribution (29,6 %)
- C3 : fine material nature (13,8 %)

On the basis of these three variables, a trilinear diagram has been built (Durbec, 1986). The hydraulic properties of the banks can be appreciate with this diagram (Figure 3).

- + : no clogging
- P : probable exchanges
- D : difficult exchanges
- TD : very difficult exchanges

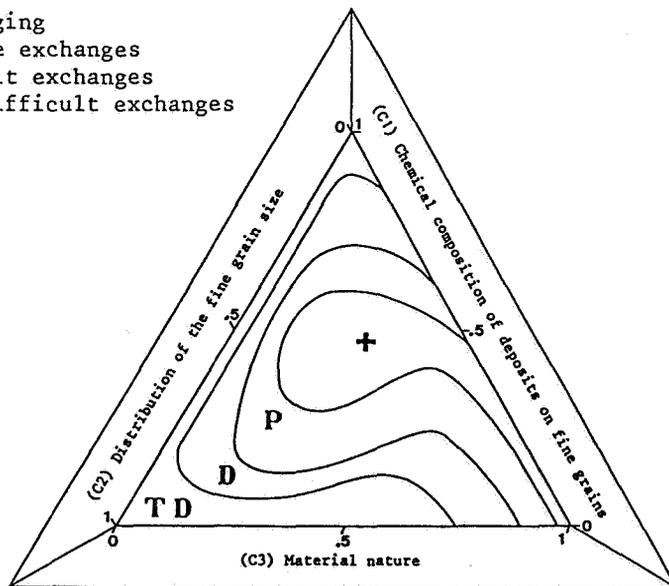


Figure 3. Explanation graph of the spatial variability of clogging

3.2.2 The hydroecological aspects

The ecological environment notion includes physical and chemical parameters and particularly those of the clogging of the banks. The purpose is to study if environmental peculiar conditions in a watery gravel pit suited to some macroinvertebrate species which could be used as an indicator for hydrodynamical exchanges. The results call the three following verifications :

- the more important the clogging is, the less diversified is the settlement,
- as indicator of an important clogging we retain : a high density of Crustacea (F. GAMMARIDES, F. ASELLIDAE) associated with molluscs (F. HYDROBIIDAE or F. PLANORBIDAE),
- as indicator of good hydrodynamical exchanges, we retain : a low density of Crustacea (F. GAMMARIDES, F. ASELLIDAE) and the presence of molluscs *Bythinella* or *Bithynia*.

3.2.3 The hydrodynamical aspects

Sample of sediments at the banks and at the bottom of the abandoned gravel pit were collected by scuba diving with a core of our conception (Durbec, 1986). The spatial variability of the hydraulic conductivity is important for the bank material. Only little fluctuations over the bottom of the gravel pit were noticed. The ten first centimeters are the most clogged and the vertical stratification of the permeability at the bottom of the gravel pit may be correlated to the rate in organic matter.

4. MATHEMATICAL MODELLING OF THE HYDRODYNAMIC OF THE AQUIFER - GRAVEL PITS SYSTEM

Though the exchanges phenomenon is threedimensional, the particular geological conditions on the site (clay layer 20 meters under the soil surface) and the depth of the gravel pits entitle the choice

of a bidimensional approach as a first approximation. In an alluvial medium, hydrodynamics can be calculated by the classical equation solved by finite element (Pinder and Gray, 1977).

The river-aquifer exchanges are described per leakage (Prickett and Lonquist, 1971). The exchanges between the aquifer and the gravel pits may be taken into account whether by fixing the potential at the aquifer/gravel pit interface, or by expressing them as we can do between the aquifer and a river, or by allocating high transmissivities (Winter, 1976) and a storage coefficient equal to 1 to the gravel pits. The third method has been chosen because it is more sensitive to the fluctuation of the banks permeability and the water balance can be controlled. The good adequation between measured and calculated piezometric heads during a whole hydrologic year and the few of calibrated parameters show that the model is suitable. The groundwater flow field is more disturbed by the abandoned gravel pit because of its clogging (Figure 4).

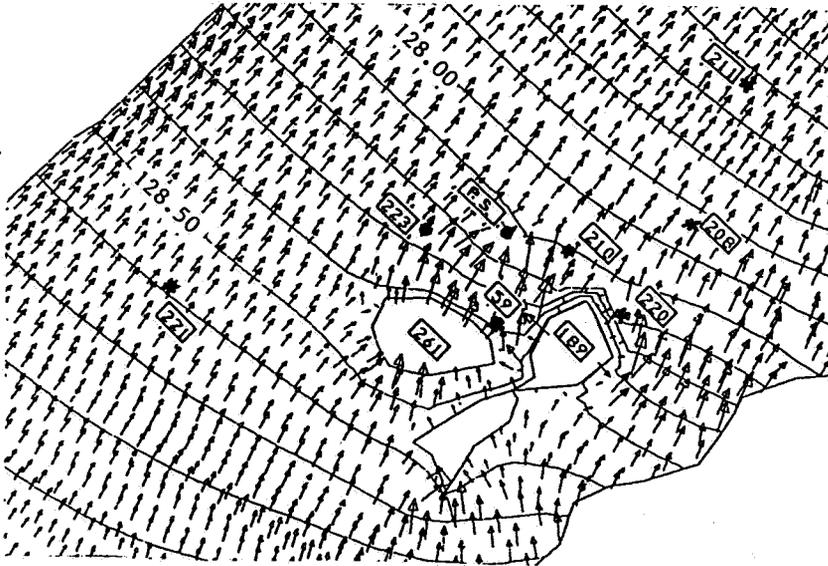


Figure 4. Simulated piezometric head and velocity flow field
(October, 1985 - detail of the modelled zone)

5. CONCLUSIONS

First of all, we confirm the fact that the bank heterogeneity is linked with a hydrodynamical sectorization of the upper zone. The usual way of considering the banks ("upstream-downstream") is insufficient. In fact, the superficial zone is not divided in an ideal upstream zone and a clogged downstream zone. Our results lead us to the suggestion of the "hydraulic working" of an old watery gravel pit (Figure 5).

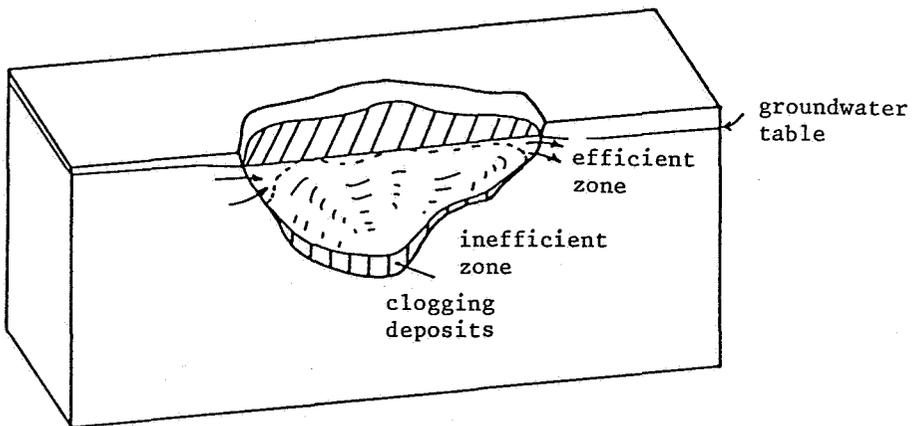


Figure 5. *Hydraulic scheme of aquifer-gravel pit exchanges*

There is a superficial zone not very affected by sedimentation processes but where a hydrodynamical sectorization occurs under the influence of chemical and mechanical factors ($10^{-5} < K \text{ m}\cdot\text{s}^{-1} < 10^{-3}$) with the depth, a clogging sediment deposit delimits a hydrodynamical inefficient zone in exchanges ($K < 10^{-7} \text{ m}\cdot\text{s}^{-1}$). We notice that this deposit causes the most of the clogging in the 10 upper centimeters. The indirect means we use are easy to bring into operation and show the complementary of the three studied fields : hydrogeology, hydroecology, hydrodynamics. At the regional scale, infrared remote sensing constitutes a first approach of the clogging of the banks and its spatial variability. Mathematical modelling based on all the

observations made on the experimental site bring some more information on the hydrodynamical behaviour of the gravel pit. Moreover, the potential danger concerning downstream water catchments in case of pollution of the gravel pit can be estimated. Nevertheless this observation synthesis by a model can only be applied when the number of parameters measured on the site and being necessary to the modelling is sufficient. The accuracy of the modelling results is indeed closely bounded to the parameters values provided by calibration. According to the quality of the information provided by remote sensing and modelling, these two approaches are both fundamental within the framework of the study of gravel pits impact on the aquifer in alluvial medium.

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UNSATURATED ZONE POLLUTANT TRANSPORT BENEATH
A LOW-TECHNOLOGY WASTEWATER REUSE FACILITY

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ABSTRACT

The aquifer pollutant load generated by human activity at the land surface is often the most difficult parameter to estimate when modelling groundwater quality. The pollutant load issuing from a typical low-technology wastewater reuse facility, which had been in operation for 22 years on the coastal alluvial aquifer of Lima, Peru, has been evaluated. Detailed investigations of the occurrence and attenuation of numerous groundwater pollutants in the unsaturated zone, both beneath the wastewater stabilisation lagoons and the adjacent desert land brought under cultivation by wastewater irrigation, permit the prediction of the likely pollutant load in other hydrogeological environments and enable the effects of modifications to the design and operation of such schemes to be assessed. More than 60% of the wastewater delivered to this site accidentally ends-up as groundwater recharge, mainly as a result of excess irrigation. The loading and penetration of fecal pathogens and nitrogen compounds is greater beneath the cultivated land than the stabilisation lagoons, and infiltration from the former is also somewhat more saline. There is evidence of some hydrocarbons and one common chlorinated solvent reaching the groundwater table at 25m in troublesome concentrations, despite the essentially non-industrial origin of the wastewater.

1. INTRODUCTION

1.1 Low-Technology Wastewater Reuse

In many developing countries, rapidly growing urban population and the desire to reduce river and coastal pollution are leading to increasing interest in wastewater reuse. This is especially the case in more arid regions where the use of wastewater for irrigation can help overcome acute water shortage and serious nutrient and organic deficiency in many soils, and offer scope for increasing agricultural production or improving suburban amenity.

Wastewater treatment in elaborate plants prior to reuse will generally be unrealistic, on both technical and economical grounds. Simpler and cheaper methods, notably stabilisation lagoons, are favoured.

Unless carefully controlled, these practices involve significant risks to human and animal health through pathogen propagation and to soil fertility due to toxic element buildup. Aside from the benefit of incidental groundwater recharge, there is often the likelihood of various types of groundwater pollution because such facilities will normally be sited on alluvial valleys or coastal plains adjacent to towns and cities.

1.2 Conditions at Lima Site

The wastewater reuse project at San Juan de Miraflores, close to the Peruvian coast on the southern outskirts of metropolitan Lima, was developed in 1964 for experimental agriculture and silviculture. The stabilisation lagoons occupy about 20 ha of former desert land, and comprise a series of 21 shallow unlined excavations in sand each less than 2m deep with a design retention time of 5+ days, arranged in batteries of primary and secondary, and sometimes tertiary, lagoons. About 360 l/s of raw sewage is delivered from three neighbouring, primarily residential, low-income areas, and somewhat more than half is treated in the lagoon complex.

Biochemically the lagoons function as complex facultative systems (Yanez, 1980) producing major reduction in BOD, elimination of most

fecal parasites, some reduction in pathogenic bacteria and viruses (at the secondary and any subsequent stages) and in total nitrogen load, but very low rates of nitrification.

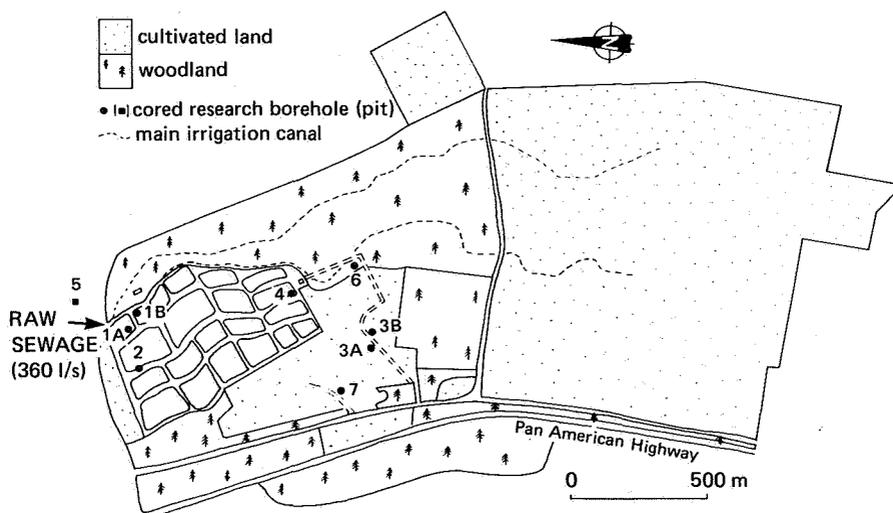


Figure 1. Wastewater reuse facility at San Juan de Miraflores, Lima

Lagoon effluent and raw sewage are used for channelled flood irrigation (at average rates of 5–10 mm/d) in an area of some 375 ha to enable cultivation of agricultural crops and amenity woodland respectively. The main crops grown are alfalfa, beans, papaya and bananas. Local rainfall averages less than 20 mm/a, but average potential evaporation rates of 3–4 mm/d are low for this latitude.

The lagoons are underlain by well-sorted, permeable, fine-to-medium grained (mainly 100–300 μm diameter) aeolian and alluvial sands. Long-term infiltration rates to groundwater have been measured at 10–20 mm/d (Figure 2), which is equivalent to about 35 l/s overall. The regional groundwater table is some 25m below ground level.

There are no direct measurements of unsaturated zone flow rates, but estimates can be made based on knowledge of grain-size distributions, moisture contents and infiltration rates. The moisture content of sands beneath the lagoons and cultivated land (6–12% by weight or about 10–20% by volume) approaches the specific retention. Under normal conditions the moisture content will vary between this value and saturation

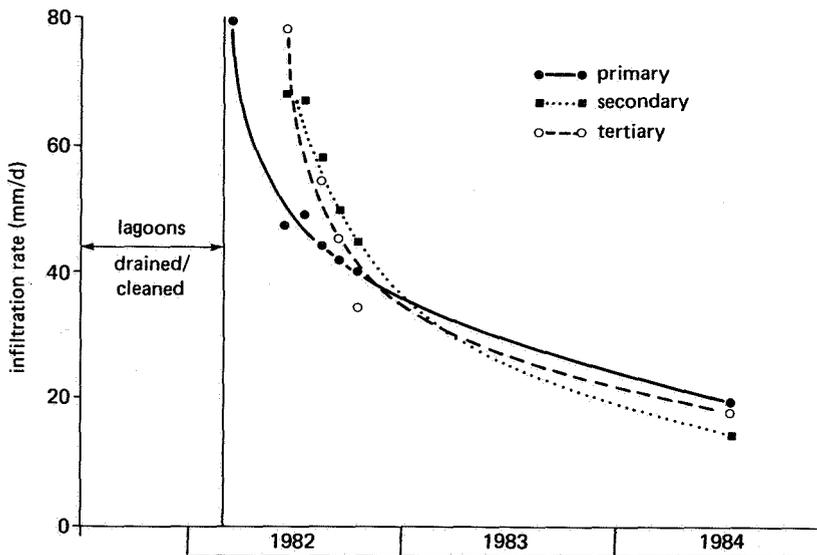


Figure 2. Infiltration rates from wastewater stabilisation lagoons

(estimated to be about 30% by volume) depending on the hydraulic loading at the surface. The moisture present beneath adjacent non-vegetated desert land (0.5-1.5% by weight) can be regarded as static.

Taking lagoon infiltration to be 15 mm/d and volumetric moisture contents in the unsaturated zone of 15-20%, then downward flow rates will be 0.07-0.10 m/d, representing transit times of 250-350 days to the groundwater table at 25m.

The corresponding values beneath cultivated land are 0.03-0.05 m/d and 500-850 days, because volumetric moisture contents are slightly lower (10-15%) and excess irrigation is estimated from the chloride mass balance data (presented below) to be 4-5 mm/d.

1.3 Research Scope and Method

A lightweight drilling rig was used to drill 8 investigation boreholes into the floor of lagoons (drained for the purpose) and on land irrigated with wastewater (Figure 1). Sand samples were obtained where feasible by driving a steel coring device. The use of drilling fluid was avoided as far as possible to prevent sample contamination. When

water had occasionally to be added, lithium chloride was used as a label to determine whether any samples had been contaminated. A deep pit was excavated into non-vegetated desert land to sample for comparative purposes. In certain boreholes unsaturated zone suction samplers or phreatic sampling piezometers were installed.

Sand samples were centrifuged at 50 rps to extract pore-water (about 10 ml) which was filtered through a 0.45 μm filter. In the case of samples from the uncultivated desert site, which were less moist, pore-water samples had to be eluted with distilled water. A wide range of chemical analyses were undertaken mainly in Peru, but stabilised or refrigerated samples were also shipped to Britain for a complementary programme, all with methods appropriate for small volume samples (Geake et al, 1986).

Sand samples were assayed directly for bacterial populations using a modified MPN procedure, with subsamples being transferred to sterile replidishes in selected weight series before addition of primary broth media. Presumptive positive results were confirmed by standard procedures. Rotavirus densities were estimated by elution, physicochemical flocculation of eluents and subsequent indirect immunofluorescence of suspended concentrates in Britain. Microbiological populations were initially expressed per 100g sample but have been adjusted to the equivalent per 100ml for comparison with data on raw sewage and lagoon effluent.

A further discussion of the problems, results and reliability of the sampling and analytical methods adopted has been given elsewhere (Geake et al, 1986), but it is believed that reasonable results for water phase concentrations of pollutants and solutes were obtained. These concentrations will be accompanied by higher concentrations in the sorbed phase for all constituents thus retained. However other methods were used for the determination of ABS detergent and of microbiological populations and these results represent total concentrations for both phases.

2. UNSATURATED ZONE PORE-WATER PROFILES

2.1 Electrical Conductivity (EC)

EC, a general guide to salinity, is relatively high in the wastewater itself and below the lagoons, and somewhat higher beneath cultivated land (Figure 3), as a result of evaporative concentration. The profile beneath non-vegetated desert land shows very high values, but the associated moisture contents are very low and the solute load in the profile essentially static. If this land were to be brought into cultivation a large lamina of irrigation water would first need to be applied to flush-out and to dilute soil salinity, which would result in very highly saline recharge to groundwater.

2.2 Nutrient Species

The total nitrogen concentration in raw domestic sewage of this area is 40-50 mg N/l, mainly in the organic and ammonium forms. Under the

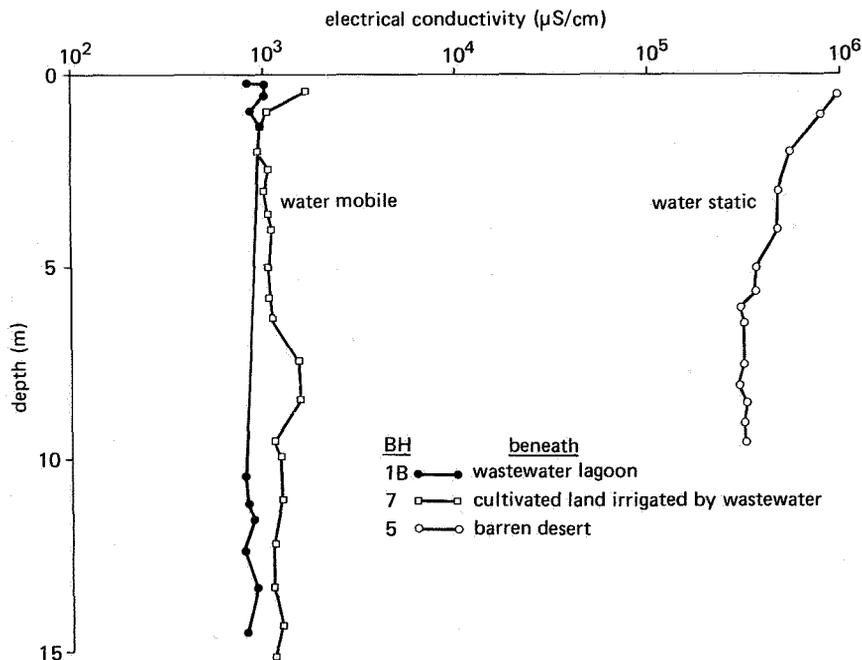


Figure 3. *Unsaturated zone pore-water EC profiles beneath wastewater reuse facility*

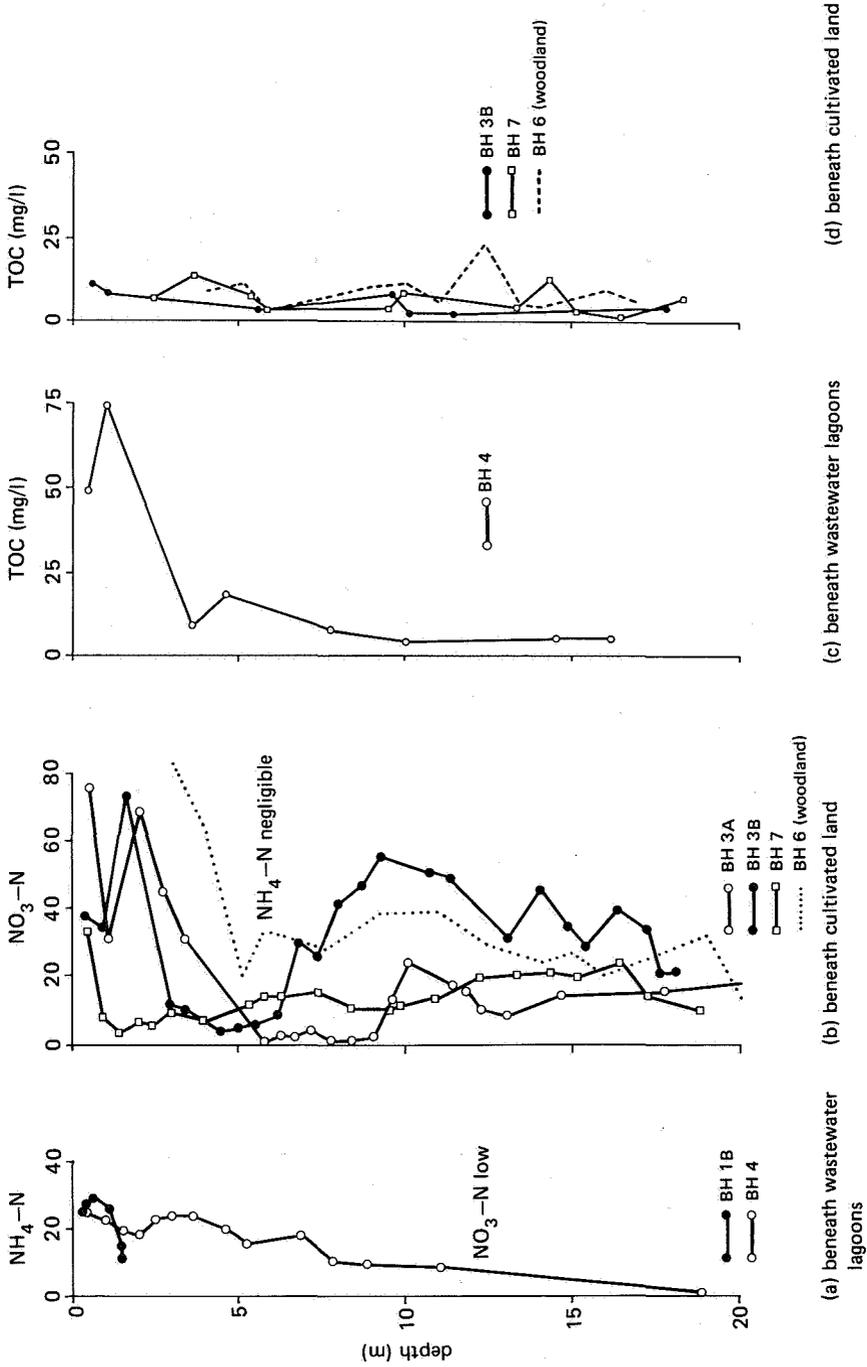


Figure 4. Chemical pore-water profiles in the unsaturated zone beneath wastewater reuse complex

lagoons, $\text{NH}_4\text{-N}$ concentrations are similar to those of raw sewage (30 mg $\text{NH}_4\text{-N}/\text{l}$) in the top 2m, and gradually decrease with depth becoming very low below about 10m (Figure 4). This attenuation is due initially to cation exchange on certain clay mineral surfaces, which appears to have almost reached saturation in the surface layers. It is thus probable that high $\text{NH}_4\text{-N}$ concentrations will advance slowly down the pore-water profile with further inputs, but for the present the nitrogen load reaching the water table is low, despite the fact that 700+ tonnes N have probably been input to the unsaturated zone beneath the lagoons during their 22 years in operation. The presence of $\text{NH}_4\text{-N}$ with only very low levels of $\text{NO}_3\text{-N}$ confirms that conditions are, as expected, anaerobic.

Under cultivated land, $\text{NH}_4\text{-N}$ concentrations are negligible because soil aeration occurs between flood irrigation events and promotes oxidation to $\text{NO}_3\text{-N}$ in the sandy soils. About half of the applied nitrogen load (estimated at around 840 kgN/ha/a) is taken-up by crops or lost by ammonia volatilisation, in addition to that generated by soil mineralisation, but an excess to crop requirements is applied and almost 400 kgN/ha/a are leached in excess irrigation water. The resultant $\text{NO}_3\text{-N}$ concentrations are considerably higher than the recommended WHO guideline for drinking water (Figure 4). The corresponding values for woodland are some 440 kgN/ha/a leached with an application of about 1260 kgN/ha/a.

Phosphate appears to be precipitated and/or adsorbed beneath the lagoons and eventually immobilised by reaction with carbonate and oxide minerals. Beneath the cultivated land it is somewhat more mobile and penetrates to depths of more than 5m at concentrations in excess of 2 mg $\text{PO}_4\text{-P}/\text{l}$.

2.3 Major Ions

Unsaturated zone chloride profiles show some effects of evaporative concentration at the surface, even in the case of the lagoons. A Cl mass balance calculation for cultivated land and woodland suggests that about 70% of the applied irrigation water infiltrates to groundwater at rates of 5.1 and 4.3 mm/d respectively.

Unsaturated zone sulphate concentrations are lower than for raw sewage,

especially beneath the lagoons where they also are strongly attenuated in depth. This is likely to be due to bacteriological sulphate reduction and sulphide precipitation in the anaerobic environment close to and below the base of the lagoons.

Sodium concentrations of pore waters increase markedly with passage through the unsaturated zone beneath the lagoons, probably as a result of cation exchange involving ammonium which shows progressive decrease. In contrast, sodium concentrations decrease somewhat with depth beneath cultivated land probably as a result of cation exchange with magnesium and calcium.

2.4 Organic Compounds

TOC concentrations in unsaturated zone pore-waters beneath the lagoons are high but rapidly attenuated in depth, although only to levels of 5-10 mg/l (Figure 4). Similar concentrations were recorded beneath cultivated land and compare to inferred values considerably in excess of 100 mg/l for raw sewage and lagoon effluent.

The principal detergents in use in Peru are based on the less biodegradable ABS type and this was detected at levels of 1-5 mg/l to beyond 10m depth beneath the lagoons.

Analysis of specific hazardous organic compounds was not possible on unsaturated zone pore-water samples. Although most WHO-listed compounds were below detection limits in all phreatic samples, total hydrocarbons up to 160 mg/l and 1,1,1-trichloroethane (a common industrial solvent) up to 60 µg/l were recorded. These were most probably derived from small workshops and garages in the area sewered, and probably penetrated below the lagoons where the hydraulic loading is higher and conditions are anaerobic. In addition to the synthetic industrial solvents, deodorants of the dichlorobenzene group are expected to be increasingly present in wastewaters and to persist in groundwater recharge.

2.5 Fecal Pathogens and Indicator Bacteria

The populations of the indicator bacteria (fecal coliforms and streptococci) and pathogens (Salmonella and human rotavirus) decrease by

1-2 orders of magnitude during passage through primary and secondary lagoons. Infiltration through the microbiologically-active sludge at the base of the lagoons under anaerobic conditions results in further elimination by competing bacteria, mechanical straining and adsorption. Nevertheless, high concentrations of both bacteria and viruses penetrate into the upper part of the unsaturated zone (Figure 5), but there is rapid elimination within the top 3m mostly by physicochemical interaction.

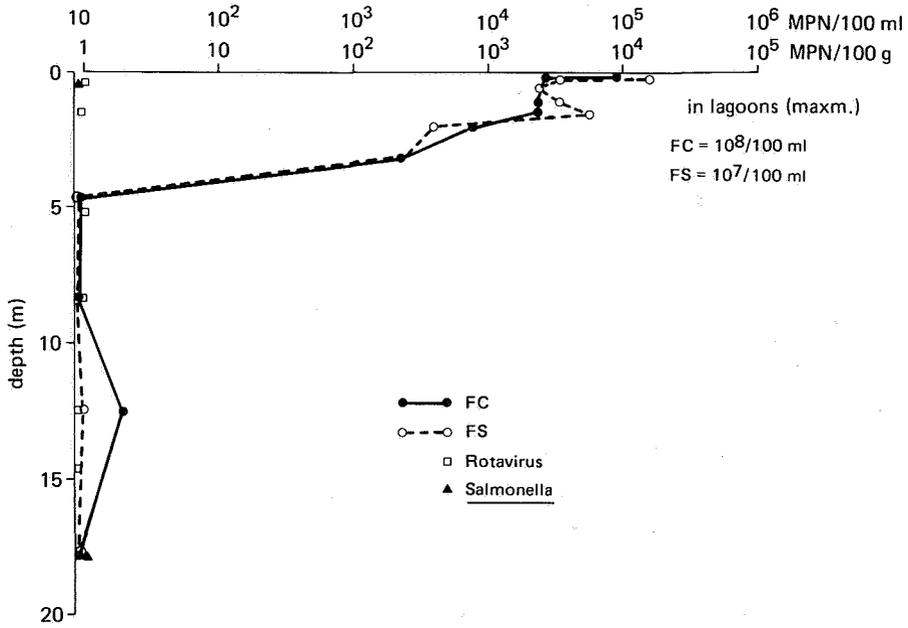
Beneath cultivated land, populations of the fecal indicators are as high in the surface layers despite lower incident concentrations from the secondary effluent and although they decrease rapidly over the top 3m, there are positive counts of these bacteria, and the robust human rotavirus, throughout the profiles right down to 20m depth (Figure 5). The reduced scale of attenuation, when compared with the situation beneath the lagoons, is probably because of the lack of a sludge mat at the infiltration surface. The ineffectiveness of an unsaturated zone of fine-to-medium sand of this thickness in eliminating fecal pathogens is surprising, but consistent with recent data on their subsurface survival (Pekdeger et al, 1985).

The pathogenic bacteria *Salmonella* appears to be eliminated rapidly in all unsaturated zone environments and was not detected in almost all samples analysed.

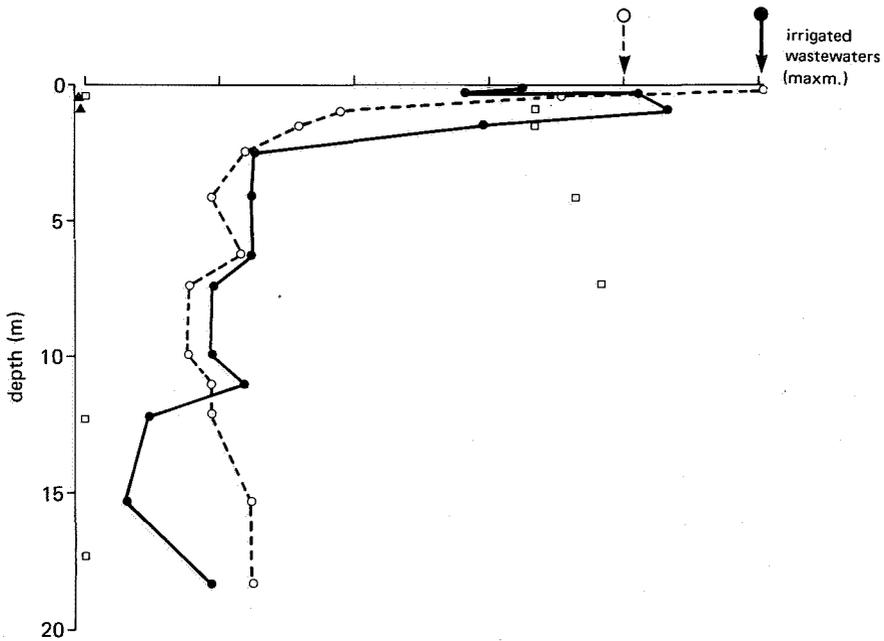
3. CONCLUDING DISCUSSION

3.1 Characterisation of Aquifer Pollutant Loading

The research demonstrates the groundwater pollution threat posed by low-technology wastewater reuse schemes and, while there is little published work on closely-comparable conditions, this conclusion is corroborated in some respects by other authors (Kehew et al, 1984; Rowen & Magaritz, 1985). While the thick unsaturated zone at the Lima site results in substantial attenuation of some pollutants, the resultant (somewhat saline) groundwater recharge remains unpotable in respect of nitrates, synthetic organic solvents and fecal indicator bacteria, and restriction on the construction of municipal and domestic water-supply boreholes is



(a) beneath wastewater lagoon (BH 4)



(b) beneath cultivated land irrigated with wastewater (BH 7)

Figure 5. Attenuation of fecal pathogens and indicator bacteria in unsaturated zone beneath wastewater reuse complex

required in the general vicinity.

The magnitude of aquifer pollutant loading generated by wastewater reuse schemes in terms of unit area of unlined stabilisation lagoons and of land cultivated by wastewater irrigation now can be assessed (Table 1) for these, and other, hydrogeological conditions. If, for example, the groundwater table had been much shallower, as would often be the case, then the pollutant load would have been much larger in respect of ammonium, organic compounds (Table 1) and fecal pathogens (Figure 5).

A similar or larger pollutant load could be expected for most other types of aquifer, with the exception of finer-grained formations with higher clay content. At the Lima site rainfall is negligible; under more humid conditions the pollutant load is likely to be somewhat less, or, at least, subject to greater dilution because of higher overall infiltration rates. Wastewater originating from more industrial areas might be characterised by lower pH and higher concentrations of trace metals and synthetic organics. In the low pH-Eh conditions then likely beneath the stabilisation lagoons, these pollutants could penetrate to the groundwater table.

3.2 Implications for Design of Wastewater Reuse Schemes

The unsaturated zone research at the Lima site allows the pollutant load generated by the various elements of a wastewater reuse scheme (stabilisation lagoons, irrigated crops and woodland) to be separately assessed (Table 1). This, in turn, permits an appraisal of the beneficial effects for groundwater quality of modifications to the design of such schemes, assuming they can be justified in terms of public health or financial saving.

The provision of impermeable linings for stabilisation lagoons should reduce the risk of groundwater pollution by organic compounds and almost eliminate subsurface $\text{NH}_4\text{-N}$ penetration. The introduction of more efficient irrigation techniques will reduce the pollutant load in terms of nutrients and pathogens, but the salinity and nitrate content of groundwater recharge will be increased because of the much lower rates of infiltration (Foster, 1985). The use of wastewater for silviculture alone, if carefully-controlled, probably offers the best prospect of

POLLUTANT LOAD (kg/ha/a)						
Site	lagoons			cultivated land		
	at base	2-3	20-25	to soil	2-3 ^a	20-25 ^a
NH ₄ -N	2190 ^c	1090	0 ^d	840 ^c	0	0
NO ₃ -N		0	0		390 ^e	390 ^e
PO ₄ -P	220	50	<10	90	40	<10
Cl ^b	7580	7580	7580	3280	3280	3280
SO ₄ ^b	13660	5260	1050	6320	3710	3710
Na ^b	3780	4410	5040	1670	1330	1250 ^d
TOC	9310	550	270	3010	100	100
ABS	110	110	60	50	40	20
hydraulic load (Ml/ha/a)	320	55	55	27	18	18

^a woodland values similar despite lower hydraulic load (15 Ml/ha/a)

^b will vary with chemistry of water-supply generating wastewater

^c total N mainly in organic and ammoniacal forms

^d will increase with time as cation exchange capacity exhausted

^e considerable variation on this average value

Table 1: *Estimation of groundwater chemical pollutant load generated by Lima wastewater reuse facility*

minimising groundwater pollution, although the salinity of any residual excess irrigation water is likely to be high.

On overall public health grounds it would be preferable to allow wastewater to infiltrate from intermittently-filled, spreading basins, following primary treatment in lined oxidation ponds. In this way natural unsaturated zone processes can perform secondary treatment and a wastewater of superior quality permitting unrestricted use for agricultural irrigation can be recovered from pumping wells purpose-drilled in the vicinity (Bouwer et al, 1980; Idelovitch & Michail, 1984). However, the much higher capital and running costs of this type of scheme coupled with the incidental loss of plant nutrients due to ammonia volatilisation and nitrate reduction, still tend to make this option economically unattractive to many developing nations.

ACKNOWLEDGEMENTS

The research project described was funded by the British Overseas Development Administration, the Pan-American Health Organisation (PAHO) and SEDAPAL (the Lima Water-Supply and Sewerage Undertaking). The programme was undertaken by a joint British-Peruvian team and the valuable contribution of the following is most gratefully acknowledged: Lionel Bridge (BGS), Maria-Luisa Castro and Guido Canales (PAHO-CEPIS Laboratory), Nelly Nakamatsu, Mary Valverde and Tadeo Vitko (SEDAPAL). The paper is published with permission of the Director of the British Geological Survey and with the encouragement of the Director of the PAHO-CEPIS Laboratory.

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COMPUTERIZED EVALUATION OF WASTE-DISPOSAL SITES: EFFECTS ON THE ENVIRONMENT

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ABSTRACT

Computerized evaluation of effects of waste-disposal sites on the environment, based on data collecting by a questionnaire appears feasible and saves time and costs. Data processing follows the physical mechanism of contaminant migration. Resulting conclusions and recommendations are fairly specific. The presented method has been adjusted by means of the results of investigation on 40 sites.

1. INTRODUCTION

As mechanisms of soil and groundwater pollution are better understood nowadays, the time has come to develop standardized and simplified ways to perform an investigation into a site's pollution. To tackle its 500 abandoned waste-disposal sites, the province of Noord-Brabant asked IWACO to design such a method. The method - hereafter called "Survey" - should be reliable and yet inexpensive. For the actual performance of the Survey a certain minimum of specialized expertise is required.

2. APPROACH

A number of simplified methods, often computerized, have been tried by various agencies. Generally, the different causes of pollution and its migration are given a numerical value and the total value is taken to represent the risk of pollution and health hazards. Sites with high total values should be dealt with prior to sites with lower values. Disadvantages of these methods are:

- the individual values should not simply be added together, as only certain combinations result in a risk. For instance, a harmful contaminant does no harm without possibilities for migration;
- since the individual values are no longer visible, no conclusions can be drawn from them as to specific hazards or remedial actions.

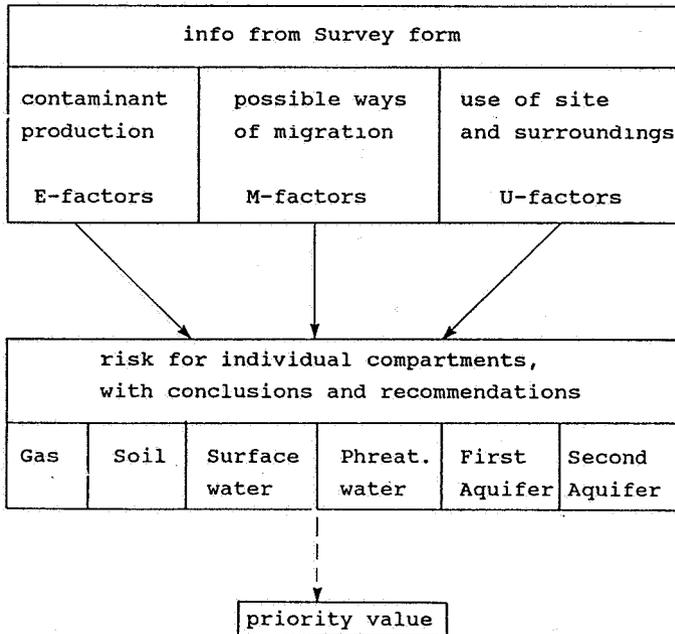


Figure 1. Flow chart of the Survey-method

Because of these shortcomings, IWACO decided to keep the various causes apart as long as required. The Survey has thus been made both more reliable and more useful.

The Survey has been set up similar to a tax form - as unattractive as this may seem to many of us - and is likewise accompanied by a booklet with instructions. The answers as entered into the form for a specific disposal site are again entered into a computer program, which yields a brief report as to risk and urgency, including recommendations and desired (remedial) action. The flow chart of the Survey and the computer program is shown in Figure 1.

3. DATA COLLECTION

The questions of the Survey form concern the following items:

- a. physical dimensions of the site;
- b. depth of groundwater;
- c. nature of the deposited waste, including indirect indications about its nature;
- d. vegetation of the site, together with visible gas damage;
- e. depth and type of the layer covering the waste;
- f. dimensions and intensity of drainage system;
- g. surface water management;
- h. geohydrologic system and groundwater potentials;
- i. land use of the site and its surroundings;
- j. use of surface water and groundwater.

A sketch of a typical site situation is shown in Figure 2.

Some 50 questions should be answered. The instruction booklet also contains help as to readily accessible sources of information in The Netherlands as well as practical guidance for field visits.

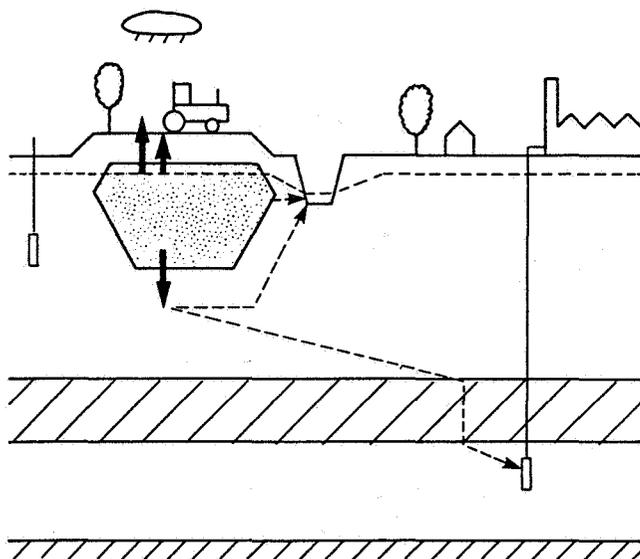


Figure 2. *Typical site situation*

4. RESCHEDULING OF DATA

The computer program reschedules the information into 25 factors of three types:

- 5 E-factors, describing the contaminant production of the site (E= Emission);
- 14 M-factors, describing the potential migration of contaminants in various ways (M= migration);
- 6 U-factors, describing the various uses threatened by migrated contaminants (U= use)..

The factors and their interrelations are shown in Figure 3.

They represent the individual contributions to the risk of contaminant migration as were mentioned in the second paragraph of this paper. The numerical value of the factors in specific cases are calculated by algorithms based on the mechanism of contaminant production and migration. However, no absolute value may be assigned to these factors at this stage.

After this step, no further use will be made of the detailed information as entered initially.

	Egas	Mgas					
	Esoil		Msoil				
leachate	Econs			Msc	Mpc	M1c	M2c
	Ehcarb			Msh	Mph	M1h	M2h
	Emet			Msm	Mpm	M1m	M2m
		U gas	U soil	U surf	U phre	U aq1	U aq2

E = emission
M = migration
U = use
c(ons) = conservative pollutants
h(carb) = hydrocarbonates
m(et) = heavy metals
s(urf) = surface-water
p(hre) = phreatic water
(aq)1 = first aquifer
(aq)2 = second aquifer

Figure 3. E-, M- and U-factors

The U-factors each represent the use of the compartments of the environment which may be endangered by the presence of the disposal site. The value of the U-factor is an indication of the sensitivity for contamination of the compartment concerned.

The compartments are:

- a. the atmosphere;
- b. the ground surface of the disposal site;
- c. the surface waters surrounding the site;
- d. the phreatic groundwater;
- e. deeper groundwater, for which two different aquifers are distinguished.

5. EVALUATION OF A SITE

The second step of the computer program is to determine the degree to which each compartment is endangered. This degree is expressed as a score from 0 to 3; 0 stands for negligible danger while 3 means that urgent action is required. The score is determined by an algorithm depending on the appropriate combination of E-, M- and U-factors.

	atmosphere	ground surface	surface water	phreatic grwtr	aquifer 1	aquifer 2	
actions	A						0
	B						1
	Gas	Soil	Surf	Phre	Aq1	Aq2	2
							3
							urgency

Figure 4. Key to specific action

Since the scores apply to individual compartments, they incorporate a specific risk for health or environment, much more than one total score for the complete site would do.

Also, the individual scores may be translated into fairly concrete remedial actions, monitoring programs or other recommendations. The key to these specific actions is shown in Figure 4, where the following packages of conclusions and recommendations are shown:

A and B: a general conclusion about of a low level of risk, with general recommendations for proper care of a waste-disposal site.

Gas through Aq 2: a warning for a specific emission together with suggestions for monitoring or remedial action. The actual action still depends on the individual situation (which may initially be obtained "by hand" from the original survey forms) and administrative requirements.

Score 3 indicates that action is urgently required, while 2 represents a lesser risk.

Finally, the program combines the various individual scores resulting in a double digit priority value for planning purposes.

6. CALIBRATION

IWACO has compared a first draft of the Survey with the results of "Survey" investigations on some 40 sites and has revised it accordingly. Revisions were required to the algorithms determining the risk scores and to the action packages. No revisions were needed for the E-, M- and U-factors.

7. APPLICATION

The thus adjusted Survey has yielded very satisfactory results since. An example of the final Survey output of a wast disposal site in Noord-Brabant is shown in Figure 5.

Compartment	Action	Urgency
Gas	A	0
Soil	Soil	3
Surface water	A	0
Phreatic water	B	1
Aquifer 1	B	1
Aquifer 2	A	0
Priority value		3.2

Figure 5. *Final Survey output (site H from Figure 6)*

The results of Figure 5 should be read as follows:

- For use of the site and surroundings, very low risks are calculated for gas, surface water and second aquifer and low risks for the phreatic water and first aquifer.

Proper care of the site and no change (or if possible limitation) of the destination are required for these compartments.

- With regard to the soil (covering layer) urgent action is needed, for instance:

- . increasing the thickness of the covering layer;
- . lowering groundwater level;
- . diminishing the accessibility by fences or ditches;
- . restriction of the destination;
- . sampling the soil (covering layer).

The manual offers a number of alternative treatments for each compartment.

The results of ten sites are shown in Figure 6.

Code site	Gas	Soil	Surf	Phre	Aq1	Aq2	Priority value
A 505.02	1	2	3	2	3	0	10.1
B 505.01	1	2	3	2	2	0	9.1
C 420.09	0	3	3	1	1	0	6.2
D 170.17	1	2	3	1	0	0	5.2
E 170.16	1	0	3	2	0	0	5.1
F 070.01	0	3	0	1	2	0	5.1
G 170.18	2	2	0	1	0	0	4.1
H 070.06	0	3	0	1	1	0	3.2
I 375.05	0	0	0	1	1	0	0.2
J 235.03	0	1	0	0	0	0	0.1

Figure 6. Results of ten sites

The results of 40 abandoned waste-disposal sites, in three geohydrologically different areas in Noord-Brabant, can be summarized as follows:

- for 11 sites no actions are needed, only proper care and no change of destination;
- 14 sites need actions focussed on only one, 12 sites on two and 3 sites on four compartments;
- the compartments scoring highest are: soil (covering layer) 18x, groundwater first aquifer 13x and surface water 11x;
- practically a Survey takes one to three days and will cost f 1,000.-- to f 3,000.-- depending on the circumstances, the number of sites to investigate and the experience in handling the model.

ACKNOWLEDGEMENTS

The authors thank for their cooperation and advice: T.C. Merkuur, M.J. Biet and F.A. van Zandbrink (WMV Noord-Brabant), D. Brouwer and F.A. Swinkels (Inspectie Milieuhygiëne) and J. Hoekst (ICW-Wageningen).

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SOIL QUALITY STANDARDS AND THE CHEMICAL PHYSICAL
EQUILIBRIUM BETWEEN SOIL AND GROUND WATER

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ABSTRACT

In the soil there is an equilibrium between the concentration of a compound in the waterphase, the gasphase and the solid phase. In setting quality standards for soil and groundwater this relation should be taken into account. The equilibrium relation of organic compounds was studied and a model is described which gives the partitioning of an organic component between the soil and the groundwater. For 127 black list organic compounds the partitioning between soil and groundwater is quantified.

1. INTRODUCTION

Thus the concentration of a compound in the groundwater is by way of this physical-chemical equilibrium directly related to the quantity of it sorbed to the solid phase. This means that in developing quality standards for soil and groundwater the equilibrium relations should be taken into account: if a quality standard for groundwater has been established then the standard for the soil is set by way of the equilibrium.

In order to underpin soil quality standards (Discussienota bodemkwaliteit, Ministry of Housing, Physical planning and Environment, 1986) in the Netherlands DHV Consulting Engineers have studied the equilibrium relation of organic components between soil and groundwater. This study was assigned by the Dutch Ministry of Housing, Physical Planning and the Environment.

Based on all the relevant literature, which was available at that moment (1985), a formula is derived, describing this relation on the basis of soil and compound characteristics. Processes, like degradation and gas transport, which influence the concentration of a compound in the soil, are not taken into account in this study.

2. SORPTION DESCRIBED BY THE OCTANOL-WATER PARTITION COEFFICIENT

The sorption of organic compounds in the soil can be described by the empirical Freundlich-equation:

$$C_s = K_p * C_w^{1/n} \quad (1)$$

where

C_s	= concentration in the soil	(mg/kg)
C_w	= concentration in groundwater	(mg/L)
K_p	= adsorption constant	(L/kg)
$1/n$	= a constant	

For low concentrations, as is the case for organic compounds in groundwater, one may take $n = 1$:

$$C_s = K_p * C_w \quad (2)$$

Studies of the uptake by soil of nonionic compounds from water have indicated that soil organic matter is the principal adsorbent (Hamaker and Thompson, 1972). For these compounds the value of the adsorption constant (K_p) can be derived out of the octanol-water partition coefficient and the organic matter of the soil.

In 1973 Briggs presented a concept for the calculation of the soil-sorption of a number of pesticides by means of the octanol-water partition coefficient (K_{ow}) of the compound and the organic matter content of the soil. It can be described as:

$$\log K_{oc} = a \log K_{ow} + b \quad (3)$$

where

K_{oc} = sorption constant for the organic carbon fraction
 a, b = constants

The sorption constant for a certain soil is dependent on the organic carbon fraction of the soil:

$$K_s = f_{oc} * K_{oc} \quad (4)$$

where

K_s = sorption constant for a soil
 f_{oc} = fraction organic carbon in the soil (%)

There are several limitations to the use of predicted K_{oc} values from octanol-water partition coefficients:

- the K_{oc} - K_{ow} correlation is a log-log relationship; hence, small deviations from the regression line can represent significant deviations in actual and predicted K_{oc} values;
- the model is based on sorption on the organic matter in the soil. At low organic matter content (organic carbon fraction < 0.1%, Schwarzenbach and Westall 1981) other sorption media, like 2:1 clay minerals, will be of greater importance. Other authors mention the ratio of the clay content to the organic matter content to be decisive for the contribution of the organic matter to the sorption. The sorption on clay minerals is important if this ratio exceeds 30 (Hassett et al 1983).

At high organic matter content the calculated sorption is over-estimated (Voice and Weber 1985). Also, the kind of organic matter may influence the sorbed amount of organic components;

- the model predicts less accurately for the sorption of hydrophylic, polar or ionizable components. For these, probably dissociated components, the sorption on charged surfaces is more important.

For the Dutch situation it is expected that the model is applicable, as:

- there is hardly any montmorillonite or any other 2:1 clay mineral present in the upper layer of the soil;
- the fraction of organic carbon is expected to be 0,1% or higher, also in (confined) aquifers;
- the ratio of clay fraction to organic carbon fraction in clay soils is roughly 10.

There are various ways to achieve the value of the octanol-water partition coefficient (K_{ow}):

- measure the value of K_{ow} , this may give problems because of the low concentrations (Means et al 1979);
- calculate it from the solubility of the component in water (Chiou et al 1977).
- calculate it from the structure of the molecule (Leo et al 1971);
- search the values in a manual or in the literature (e.g. Verschueren 1983).

Instead of calculating K_{oc} via the calculated value of K_{ow} (eq. 3), a direct calculation of K_{oc} from the solubility is preferred:

$$\log K_{oc} = c \log S + d \quad (5)$$

where

S = solubility (mole/L)

c, d = constants

3. THE MODEL

At first the measured values of K_{ow} were achieved. If there was no measured value available the value of the solubility (S) was gathered.

For the above described study the values of K_{ow} of 127 organic components were collected from the literature. Also the model parameters a and b for eq. 1 and c and d for eq. 5 were collected and evaluated. Figure 1 gives a review of the collected relations between $\log K_{ow}$ and $\log K_{oc}$. From this figure the dashed line is chosen as the best description the relation between K_{ow} and K_{oc} . For the relation between S and K_{oc} the same procedure is followed.

The following equations were found to give the most accurate values for $\log K_{oc}$:

$$\log K_{oc} = 0,989 \log K_{ow} - 0,346 \quad (6)$$

$$\text{and } \log K_{oc} = -0,729 \log S + 0,231 \quad S \text{ in mole/L} \quad (7)$$

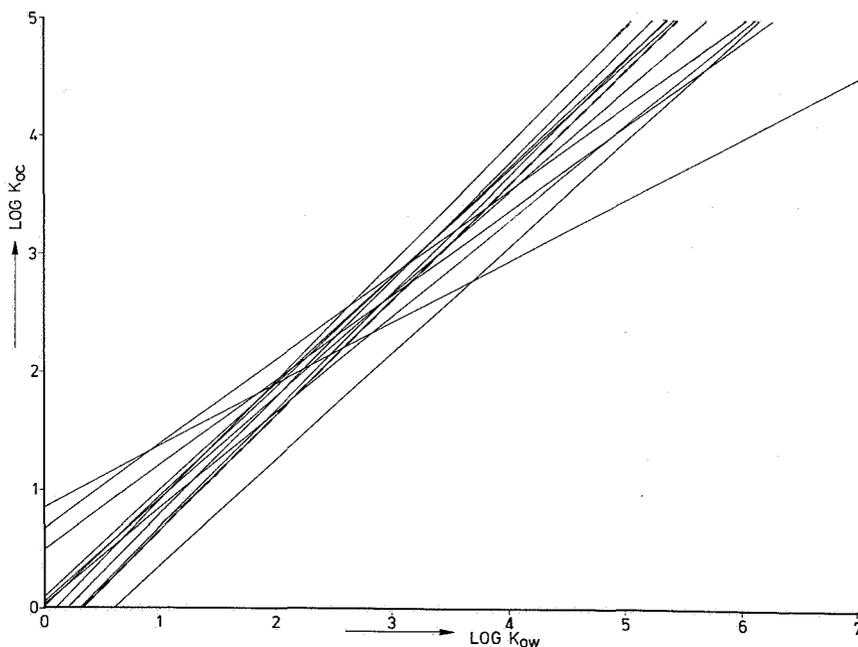


Figure 1. The from literature collected relations between $\log K_{oc}$ and $\log K_{ow}$. The chosen relations is marked by a dashed line.

The collected values of K_{ow} were evaluated and for every component the most probable value was selected. If the value of K_{ow} was available K_{oc} was calculated with eq. 6, if there was no available value of K_{ow} the K_{oc} was directly calculated from the solubility (eq. 7). In table 2 the values for K_{ow} (or S) and K_{oc} are given for a selection of components. The values of all the studied components are given in the report of the above described study (Van der Meijden and Driessen, 1986).

From the given values of the parameters a and b in the literature (figure 1) it is estimated that the variation in $\log K_{oc}$ for a certain value of $\log K_{ow}$ will be plus or minus half a logarithmic unit ($\sqrt{10}$). As goes to show when the calculated values are compared with the measured values of K_{oc} given in the literature (figure 2). The variation in $\log K_{oc}$ calculated with $\log S$ will be in the same order of magnitude.

The estimated overall error, including variations in the value of K_{ow} or S, in the value of K_{oc} is a factor 5 à 7.

The calculated values for K_{oc} are compared with measured values. Loch et al (1985) have measured the sorption of some volatile chlorinated components for three Dutch soils. Table 1 gives a summary of the results of these measurements with next to it the with the above given equation calculated values of K_{oc} .

It can be seen in table 1 that for the examined Dutch soils the model predicts the sorption reasonably well. It appears that there is a difference in sorption for the 3 soils, this is probably due to the nature of the organic carbon, which will be different for the 3 soils.

In the literature there were no quantitative models found which take simply into account the sorption on clay minerals and the polarity of the component. So the calculations for rather polar components like phenols, chlorinated phenols and MCPA also have been made with the above given equations 6 and 7, in spite of the expected large variance for these sorts of components.

Table 1. Comparison of measured and calculated values for K_{oc} for three Dutch soils

component	log K_{oc} measured ¹⁾				log K_{oc} calculated ²⁾
	"podzol"	"eerdgrond"	"veengrond"	mean	
chloroform	2,0	1,5	1,5	1,7	1,6
trichloro- ethylene	2,2	2,6	1,8	2,2	2,1
tetrachloro- ethylene	2,3	2,4	2,6	2,4	2,2
1,4 dichloro- benzene	3,2	2,7	3,3	3,1	3,0

1) Loch et al (1985)

2) Calculated with eq. 6

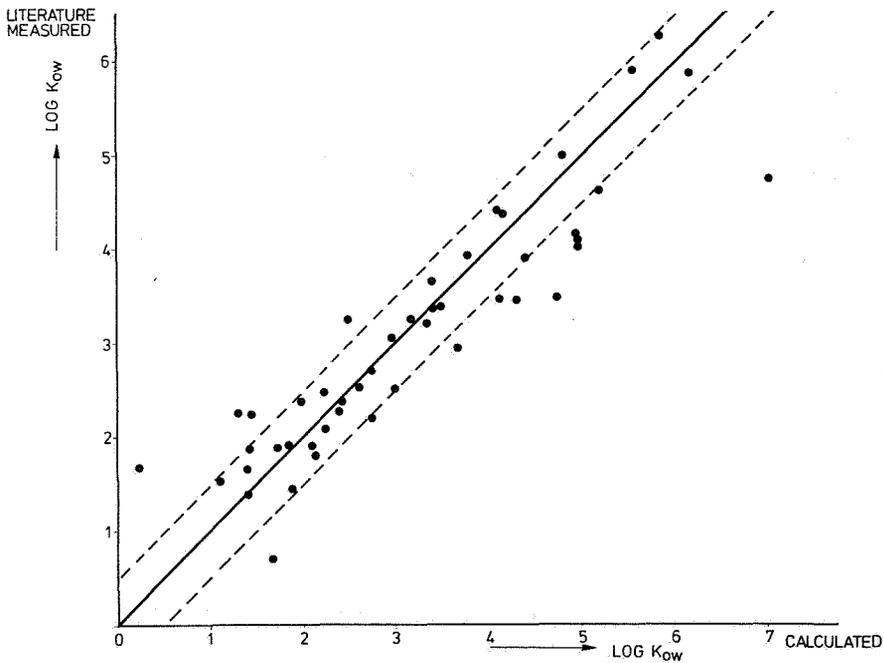


Figure 2. Measured values of $\log K_{oc}$ compared with the calculated values

4. CALCULATIONS AND RESULTS

The equilibrium concentration in the soil was calculated with the adsorption constant K_{oc} for the required maximum concentration level of the component in drinking water (if such a concentration is not known the A-level from the Dutch soil clean-up guidelines: "Leidraad" (1983) has been taken). The following equation was used:

$$\text{conc. soil (mg/kg d.m.)} = \frac{K_{oc} * f_{oc} * \text{conc. groundwater } (\mu\text{g/l}) * 10^{-3}}{1,7} \quad (8)$$

where

$$1,7 = \text{soil density (g.cm}^{-3}\text{)}$$

The calculations have been executed for the 127 organic components which are mentioned in the "Black-list" for 3 different organic carbon contents in the soil (1, 10 and 40%).

The calculated equilibrium concentrations in the soil are compared with the detection limit in soil for the component considered. Based on this comparison, the components can be divided into 3 groups (in table 2 is a selection of these components given, for all the components is referred to v.d. Meijden and Driessen (1986)):

- a. the calculated equilibrium concentration in the soil lies for all 3 values of the organic carbon content under the detection limit;
- b. the equilibrium concentration lies under the detection limit for one or two values (1 or 10%) of the organic carbon content;
- c. the calculated equilibrium concentration lies for all 3 values of the organic carbon content above the detection limit.

For some components in the third group, like benzo (k) fluoranthene and benzo (ghi) perylene, the calculated concentration in the soil which is in equilibrium with the drinking standard in water is so high that the standard concentration (the Dutch standards) for hazardous waste is exceeded! These components sorb very strongly to the soil.

Table 2. Examples of calculated equilibrium concentrations in soil for the standard concentration in drinking water (for 3 organic carbon contents) compared to the detection limit of the component considered.

component	log K_{oc1}	concentration in water ($\mu\text{g}\cdot\text{dm}^{-3}$)	equilibrium concentration in soil ($\text{mg}\cdot\text{kg}^{-1}$)			detection limit in soil ²⁾ ($\text{mg}\cdot\text{kg}^{-1}$)
			1% oc	10% oc	40% oc	
2a: equilibrium concentration (ec) < detection limit (dl)						
Dichloromethane	0.69*	1.0	0.000	0.000	0.001	0.010
Dichloropropane	1.41*	1.0	0.000	0.002	0.006	0.010
Linuron	2.01	0.1	0.000	0.001	0.002	0.050
Benzene	1.76	0.2	0.000	0.001	0.003	0.050
Toluene	2.31	0.5	0.001	0.006	0.024	0.050
Napthalene	2.98	0.2	0.001	0.011	0.045	0.050
Hydrazine	-1.71	0.1	0.000	0.000	0.000	0.050
Dichlorovos	1.04	0.1	0.000	0.000	0.000	0.010
2b: ec < dl (low organic carbon %) and ec > dl (high organic carbon %)						
Trichloromethane	1.60	1.0	0.000	0.002	0.009	0.001
Xylene						
metha	2.82	0.5	0.002	0.019	0.078	0.050
para	2.77	0.5	0.002	0.017	0.069	0.050
Acenafthylene	3.68	0.2	0.006	0.056	0.220	0.050
Phenanthrene	4.14	0.2	0.016	0.160	0.660	0.050
Dichlorobenzene	3.02	1.0	0.006	0.061	0.240	0.010
Trichloroethene	1.75*	1.0	0.000	0.003	0.0013	0.001
2c: ec > dl						
Aldrin	6.97	0.1	5.500	55.000	220.000	0.001
Dieldrin	4.96	0.1	0.053	0.530	2.100	0.001
beta-HCH	3.41	0.1	0.002	0.015	0.061	0.001
gamma-HCH	3.33	0.1	0.001	0.013	0.051	0.001
Tetrachloromethane	2.26	1.0	0.001	0.011	0.043	0.001
DDT	5.77	0.1	0.340	3.400	14.000	0.001
Fluoranthene	4.93	0.2	0.099	0.990	4.000	0.050
Pyrene	4.80	0.2	0.074	0.740	2.900	0.050
Benzo (a)						
pyrene	5.93	0.2	1.000	10.000	40.000	0.050

¹⁾ If the value of log K_{oc} is calculated out of the solubility (eq. 7) the value is marked with a *. The other values are calculated with eq. 6.

²⁾ The given detection limits are for methodes of analysis which are commonly used. For detailed information is referred to Van der Meijden and Driessen (1986).

5. CONSEQUENCES FOR THE DEVELOPMENT OF QUALITY STANDARDS

For the development of quality standards for soils and ground-water one has to take into account the equilibrium between the three phases in the soil. In the foregoing a model was described which gives the partitioning of an organic component between the soil and the ground-water. To determine the values for the parameters of the model all the relevant literature was studied (state of the art 1985). The meaning of this model for the development of quality standards is that if a standard concentration for groundwater is chosen the standard concentration for the soil is set and can be calculated with the model. Thus the standardization has to take place for the groundwater or the soil, the concentrations which apply to soil or groundwater can be calculated with the model.

For organic components which sorb weakly (roughly $\log K_{oc} < 2,5$) the effect of a small addition of that component to the soil shows a marked increase of the concentration in the groundwater. This may lead to unacceptable concentrations in the water while such a component is, because of its low concentration, not detectable in the soil. For these components the acceptable concentration in the water is the decisive factor for the development of quality standards.

Examples of such components are: chlorinated hydrocarbons (dichloropropane, dichloromethane and dichlorovos) and hydrazine.

If a component sorbs strongly (roughly $\log K_{oc} > 4$) the acceptable concentration in soil is the determining factor for the quality standards. For such components a significant increase of the concentration in the water is noticeable only for extreme high concentrations in the soil. Examples of these components are aldrin, hexachlorocyclohexane, benzo(a)pyrene and pyrene.

There are also components whose sorption behaviour lies between the two above given groups (roughly $2,5 < \log K_{oc} < 4$). For these components it has to be specified whether the quality standard will be formulated for the ground-water or for the soil. It concerns components like dichlorobenzene and acenafthylene.

The error in the obtained value of K_{oc} can be rather large, but the results are sufficient for the aim of the standardization. For other applications, like models for the prediction of the transport of pollutants, the value of K_{oc} has to be more accurate.

6. RECOMMENDATIONS

To use the model for the setting up of soil quality standards some supplementary research is useful:

- the range of validity of the model, especially the contribution of the mineral fraction to the sorption of organic components at a low organic carbon fraction;
- to find a quantitative way to distinguish polar, hydrophobic and ionogenic components in order to know if the model can be used for such components;
- if the model is applied for the development of quality standards, it is necessary to determine the organic carbon content of the soil. Because this content might change in a soil profile it is important to set up a sample strategy.

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AN APPLICATION OF AN AGRO-ECONOMIC MODEL TO ENVIRONMENTAL
ISSUES IN THE EC; A CASE STUDY

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ABSTRACT

The paper provides an application of IIASA's Basic Linked System (BLS) to environmental issues in EC-agriculture. In order to find out whether such an integrative exercise can be done without exceeding the limits of the model, a nutrient balance of EC-agriculture was constructed, which reflects the differences between nutrient extraction and delivery of nutrients to the soil; this balance was then run together with selected model scenarios. One of the conclusions is that the BLS can indeed be considered a suitable instrument for policy analysis, because it provides insights into the possible economic and environmental consequences of certain EC-policies for the medium to long term. A second important conclusion drawn is that policy measures to protect and improve the environment do not need to be at variance with agricultural income objectives. The results provide a basis for further research, which may become possible with a more detailed EC model of the same type, developed at the Centre for World Food Studies, which specifies the EC countries separately and distinguishes a larger number of agricultural commodities.

INTRODUCTION

EC agriculture is increasingly faced with problems caused by the very intensive use of agricultural land, surplus production and pollution of soils, surface- and groundwaters. Most studies link these issues to the economic policies and objectives for the agricultural sector adopted in the past. The questions presently discussed concern

therefore the effectiveness of changes in the present agricultural policy regime designed to reduce both the financial costs and the environmental harm being done by present agricultural practice. In what follows, an attempt is described to demonstrate the potential usefulness of agro-economic models for this purpose. As an example a summary analysis is given of the effects of alternative patterns of agricultural growth on the environment, using IIASA¹⁾/FAP's²⁾ Basic Linked System (BLS), (IIASA, 1986).

The BLS is a global modeling system consisting of national models with special focus on agriculture and based on applied general equilibrium concepts. Although it can be extended to the analysis of environmental issues, this has previously not been given much attention. The analyses described here are thus a first attempt to demonstrate the potential for extending the model system.

One of the important characteristics of the BLS is the linkage of national models represented in the system, which ensures that the effects of one country's policies can be traced through changes in trade patterns to all other countries, whereas over time a picture is obtained of the effects of third country adjustments on the country which initiated the policy. Because international relations in agriculture are strong and the effects of policies in each country can not be analysed properly within the confines of a national or regional model, the BLS approach is an attractive one for policy analysis. The demonstration presented here concerns the generation of potential polluting agents like nitrogen, phosphorus, potassium, Cu, Cd and Zn, as a consequence of agricultural production. Through estimation of the relevant parameters and coefficients for the base year (1980), a nutrient balance can be constructed. An agricultural nutrient balance describes inflows, uses and outflows of each nutrient associated with agricultural activities. Thus, the first part of the exercise consists of estimating the parameters of pollution associated with the production of particular agricultural commodities. These parameters are then inserted into the EC-model which forms a part of the BLS. The other part of the exercise consists of a comparison of two model projections, each with a particular set of policy assumptions. The

first one is labeled the reference scenario (RO) which projects agricultural developments to the year 2000 on the assumption that all countries continue to apply similar policies as in the past. It provides a base-line projection to which any other projection based on specific policy changes can be compared. The differences observed between the outcomes of a policy scenario and the reference scenario constitute the effects of the policy change.

The policy scenario used here, which was developed by G. Fischer of IIASA (Fischer 1985), assumes some changes of European agricultural policies designed to reduce negative consequences of agricultural production for the environment. It is formulated more or less along lines advocated by 'green' (environment-oriented) political groups. This 'greens' scenario (GR-1) assumes that two measures will be implemented in the years 1980-2000:

- (a) an annual reduction of arable land, of average productivity, of 1.1 per cent per year in the EC, and
- (b) a tax on fertilizers which raises their price to European farmers by 50 per cent.

The scenario does not specify how the transfer of land would be achieved, nor its direct budget costs. The measures are presumed to stimulate alternative uses of land (for example for forestry and recreation) and to reduce the use of polluting synthetic inputs, thus limiting present agricultural surpluses.

MAIN CONCLUSIONS; COMPARISON OF SCENARIOS

The results of the comparison are encouraging as they suggest that measures to protect and improve the environment are not necessarily at variance with economic objectives, particularly farm incomes and maintaining farming as an economic activity. However, some specific farm groups will be affected in their activities and consequently in their income. There are still other specific consequences which should not be overlooked:

- (a) agricultural products become significantly more expensive, putting part of the environmental costs on consumers,
- (b) agricultural land becomes very expensive, which hampers the transfer of farms to younger generations and adds considerably to the capital costs of young farmers,
- (c) it increases the agricultural trade deficit of the EC in constant prices by about one third (by one half in current world prices) and reduces self-sufficiency by about 4 per cent,
- (d) the impact on the net output of pollutants is significant: a reduction of 29 and 23 per cent for nitrogen and phosphorus, and 18 per cent for potassium; see figures 1 and 2. As agricultural land use decreases at a slightly lesser rate, this implies slightly less intensive use on a smaller total arable area.

In assessing measures of the kinds suggested here, these costs and estimates of effectiveness should all be taken into account, together with costs which may be passed on to other countries. The BLS is capable to estimate those effects; for example, it indicates that the 'greens' scenario causes a decline in calorie-consumption in the developing countries by raising world food prices which reduce the purchasing power of low-income groups.

The structure of the BLS, together with information on the supply and use of nutrients by crops and livestock, provides a useful instrument for policy analysis with respect to the possible economic and environmental consequences of certain EC-policies for the medium to long term.

The estimates presented here do not purport to be anything more than a demonstration of the potential value of an economic model to study potential policy impacts on the environment. For a reliable set of projections more work needs to be done to collect appropriate information, to estimate relevant coefficients and to provide more specific geographical detail. A more detailed policy model of the EC³⁾ has been constructed at the Centre for World Food Studies and may provide the basis for future work.

* The author is indebted to Prof.dr. Wouter Tims and Dr. Doeke C. Faber of the Centre for their helpful suggestions and comments on the manuscript.

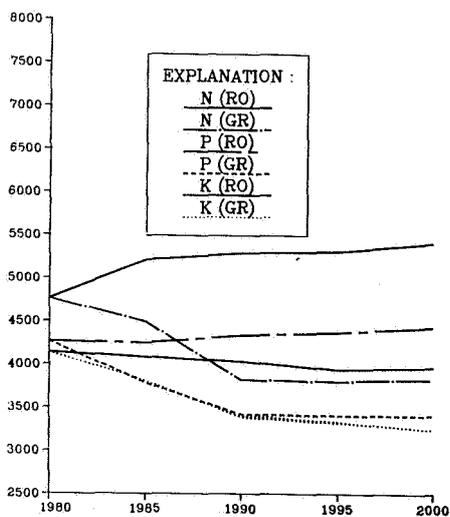


Figure 1: Projections of the total net delivery to the environment of N, P and K according to the reference (RO) and greens run (GR-1) of the BLS for the EC for 1980-2000 (in '000 tonnes of nutrients).

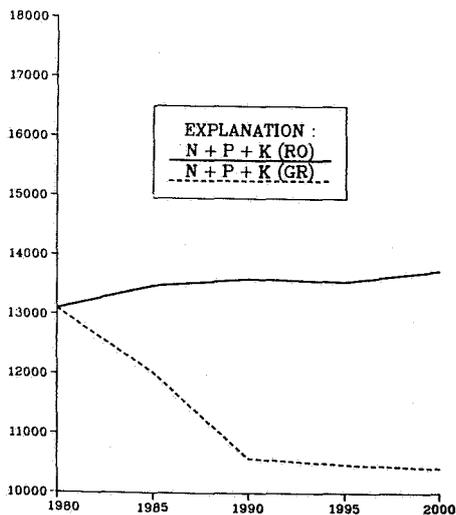


Figure 2: Projections of the total net delivery to the environment of the sum of the main nutrients (N+P+K), according to the reference run (RO) and green runs (GR-1) of the BLS for the EC for 1980-2000 (in '000 tonnes of nutrients).

NOTES

- 1) International Institute for Applied Systems Analysis, Laxenburg, Austria.
- 2) Food and Agricultural Programme of IIASA.
- 3) This model is developed in a joint effort of the Centre for World Food Studies in Amsterdam, the Central Planning Bureau and the Agricultural Economics Institute (LEI) in the Hague and the Agricultural University in Wageningen. In addition scientific support is given by other member-states.

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AN EXPERT SYSTEM FOR GROUNDWATER VULNERABILITY

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The number of locations, where the soil might have been polluted or should be protected against pollution, appears to increase rapidly. Precise evaluation of the vulnerability of groundwater at a location is often expensive and time-consuming. Because of this, there is a growing need for a low-cost method using easily accessible data to determine the vulnerability of groundwater to pollutants.

Information obtained from various maps and a visit to the site, contains indications, that can be used to approximate the vulnerability of groundwater. However, appropriate expert knowledge is needed for interpretation. Such knowledge is seldom readily available. As a consequence, optimal use of this information is not widely spread.

IWACO is building this expert knowledge into an expert system for groundwater vulnerability, i.e. a special computer program which can be used by non-experts to determine the vulnerability of groundwater with an accuracy which is acceptable for many purposes.

An expert system is better suited to handle uncertain or indicative information than other computer software like data bases, FORTRAN, BASIC, etc. In addition, the user may ask the expert system to explain a question the system poses, to explain why a question is asked by the system or through what reasoning the expert system comes to a certain conclusion.

The indirect, indicative information used by the expert system include: soil type, groundwater level, drainage pattern, land use, vegetation, relative elevation, slope, etc. At the end of the consultation the expert system gives its conclusions about vertical migration (seepage/infiltration) and horizontal migration of (polluted) groundwater.

TRANSPORT FROM A DIFFUSE SOURCE OF CONTAMINATION -
A FIELD EXPERIMENT

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ABSTRACT

To study the solute transport mechanism from a diffuse source of contamination, a tracer has been applied to an intake area of a drain (11 x 260m) in the Hupsel catchment area (The Netherlands).

The tracer was monitored in the unsaturated zone as well as in the drainage water. From the results of the observations in the unsaturated soil, the breakthrough curve of the combined - unsaturated/saturated - transport system is predicted and discussed.

Solute transfer functions were used to describe transport in the unsaturated zone and to simulate transport in the combined unsaturated/saturated system. In the latter case, the use of a recently developed linear systems approach was applied. Results of the experiment indicated an accelerated breakthrough from the unsaturated zone probably due to the mechanism of fingering.

INTRODUCTION

In the last years more and more evidence has shown that diffuse sources of contamination may play a dominant role in the conservation of groundwater quality (Bruyn, 1984; Van der Veen, 1986). The leaching of nutrients from agricultural lands causes an increasing concern for the supply of good quality water.

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Mechanisms of transport from a diffuse source initially involve transport in the unsaturated zone, followed by transport in the saturated system, the time scale of the latter process often being larger than the transport time in the unsaturated zone. The magnitude of the time scale of saturated transport has been discussed previously by Van Ommen (1986). From this study it appears that experiments concerning the migration of solutes from a diffuse source are limited to situations where shallow aquifers - hence short characteristic times - occur. Such a situation is also found at a field in the Hupsel catchment area, where a thick Miocene clay layer underlies fluvial and eolian deposits of a thickness of approximately two meters. The field under investigation has recently been drained, and a diffuse source of contamination was created by applying a pulse of KBr solution uniformly to a strip of land, twice as wide as the drain distance and as long as the drain itself. The experiment has been carried out to study and evaluate the transport mechanisms on a field scale, both in the unsaturated zone and in the coupled unsaturated/ saturated transport system.

THEORY

Unsaturated transport

Transport in the unsaturated soil profile can be described using a steady state water flow model, as has been discussed by Wierenga (1977). In his study, the concentrations plotted versus the amount of drainage water from the soil profile yielded results that were comparable with the results of a transient water flow model. In our approach the amount of drainage water will be used as the time-controlling variable.

Two frequently used transport models will be tested against the experimentally obtained data:

- a. the classical convection-dispersion (CD) model, which assumes an average solute migration velocity v ; the distribution around this average is based on a normal Gaussian probability density function

(PDF), and characterized by a dispersion coefficient D (L^2T^{-1}):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (1)$$

where c =concentration (ML^{-3}), x =depth in the soil (L), t =time (T). D is supposed to be given by:

$$D = \alpha_1 v \quad (2)$$

where α_1 represents the dispersion length (L). Van Genuchten & Alves (1982) present solutions of eq. 1 for various sets of initial and boundary conditions.

- b. the transfer function (TF) model, based on a log-normal distribution of the migration velocity v (Amoozegar-Fard et al., 1982). This model assumes the field being represented by a number of independent non-interacting soil columns in which vertical transport is described by the CD-model. However, each column has its proper migration velocity v , considered to be log-normally distributed with a mean μ and a standard deviation σ :

$$\rho(v) = \frac{1}{v\sigma\sqrt{2\pi}} \exp \left\{ - \frac{(\ln(v) - \mu)^2}{2\sigma^2} \right\} \quad (3)$$

The first moment of this distribution - the field mean velocity - $\langle v \rangle$ is given by:

$$\langle v \rangle = \exp (\mu + \sigma^2/2) \quad (4)$$

The spreading of a solute pulse in the 'average' soil profile can thus be attributed to two mechanisms: the dispersion in the column itself and the differences in the migration velocity between columns quantified by the standard deviation σ of the log-normal velocity PDF.

Saturated transport

Transport in the saturated zone is simulated using the analogy between flow to drains and ditches with the outflow of a perfectly stirred

reservoir (Eldor & Dagan, 1972; Ernst, 1973; Gelhar & Wilson, 1974; Raats, 1983; Van Ommen, 1986). The calculation of the convolution integral of the impulse response of the saturated transport system with the input of solutes coming from the unsaturated zone gives values of the concentration in the drainage water as a function of time. For details, see Van Ommen (1985).

EXPERIMENTAL SETUP AND METHODS

In December 1985, 4.5 mm of KBr solution (2.55 g Br /l) was applied to a drained strip of land of 20 x 260 m in the Hupsel catchment area. Land use on one half of the strip was permanent grassland, the other half was used for the cultivation of maize during the growing season; at the time of application it was uncultivated.

Drain distance was found to be approximately 11 m; hence nearly two times the theoretical catchment area of one drain received the bromide in order to assure a total application of the catchment area. Soil type was a loamy sand Haplaquod (Wösten et al., 1985) with a top soil having a finer texture than the deeper soil layers (Dekker, 1986). A cross-section of the situation is presented in Fig. 1.

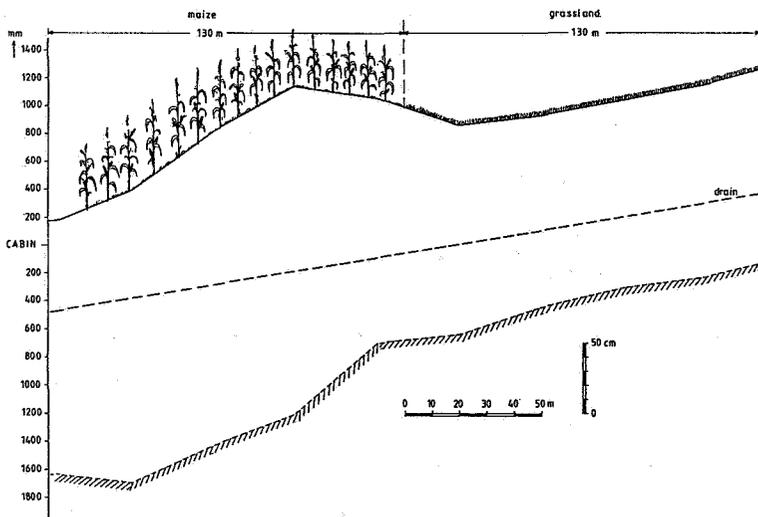


Figure 1. Vertical cross-section of the experimental field

This figure shows the position of the drain with respect to the surface and the depth to the clay layer. After application of the bromide pulse with a high precision dosage installation, drainage samples were taken every 0.5 mm of discharge. In addition, soil samples were taken after drainage amounts of 69.5, 167.0, 225.0 and 304.5 mm. These were taken with a 6 cm diameter auger, every 5 cm depth up to a depth of 1 m at 10 equally spaced locations, both in the maize field and grassland. From every sample a 1:2 extract was prepared and analysed on bromide concentration. With this value the bromide concentration in the soil solution is easily determined. Bromide concentrations were determined using an ion-chromatographic method with UV detection at a wavelength of 193 nm (Neele, 1987).

RESULTS

Soil samples

In order to determine the transport parameters of the two discussed unsaturated transport models, a non-linear least squares optimization program developed by Parker & Van Genuchten (1984) was used. For simplicity, the time-controlling variable is given in mm drain discharge. In this way the flow velocity v is taken with respect to the flux density of the discharge. Thus, a calculated velocity v of say 4.0 means the pore water flow velocity being four times larger than the water flux density. In this example the mobile water content is 0.25. In fig. 2 the observed and fitted concentration profiles are given for the first sampling time after 69.5 mm discharge, for the maize as well as for the grassland. Only samples to a depth of 70 cm are taken into consideration, since, as shown in fig. 1, some sampling locations may be situated in the saturated zone when using sampling depths up to 1 m. The field average concentration at a certain depth was calculated according to a normal distribution of the concentrations.

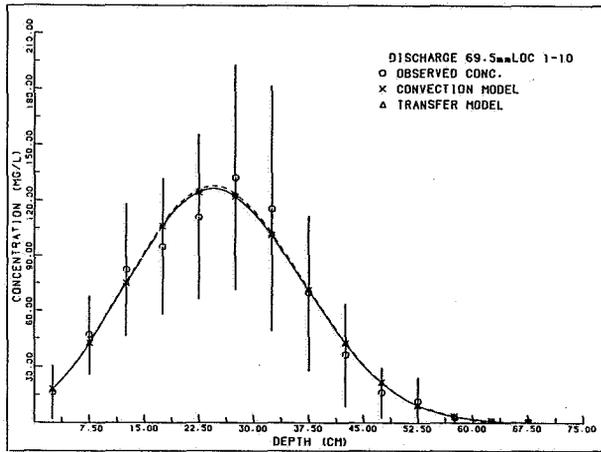


Figure 2a. Observed and fitted concentrations for 'maize' land

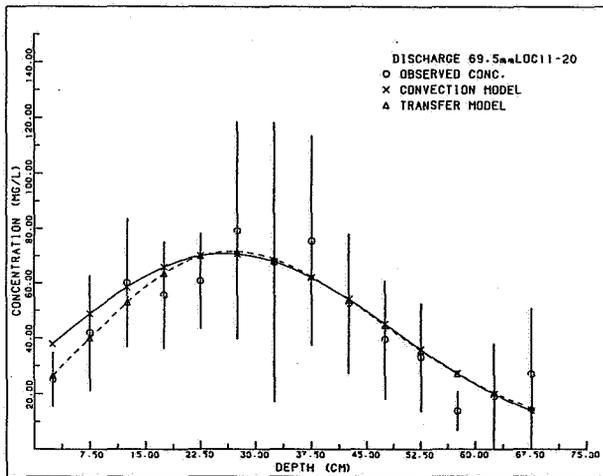


Figure 2b. Observed and fitted concentrations for 'grassland'

In table 1 all the values concerning the fit of the observed concentrations to the transport models are given. For the CD-model, two transport parameters v and α_1 were optimized. For the TF-model, a three parameter fit was performed, i.e. $\langle v \rangle$, σ and α_1 . Finally the R-square values of observed versus predicted are given, along with the minimum sum of squares attained with the optimization procedure.

Table 1. Results of the optimization procedures for different sampling times and land use

Convection-Dispersion model

Location: 1-10
Land use: maize

Sampling time	V	ALFA1	R**2	SSQ
1	3.2700	37.00	0.974	791.5
2	5.4040	195.76	0.890	201.5
3	3.7744	95.12	0.976	52.9
4	3.6768	94.87	0.972	14.1
1,2,3,4	3.1925	62.10	0.863	8274.1
1,3,4	3.3257	42.43	0.957	2204.9
2,3,4	4.3084	178.28	0.867	814.2

Location: 11-20
Land use: grassland

Sampling time	V	ALFA1	R**2	SSQ
1	3.0406	144.84	0.828	1004.2
2	7.1640	322.21	0.550	591.5
3	3.2792	210.55	1.000	35.0
4	3.7790	173.49	0.910	36.3
1,2,3,4	3.0306	198.08	0.871	3250.8
1,3,4	3.0863	154.40	0.951	1329.0
2,3,4	4.1498	353.02	0.639	1230.8

Transfer model

Location: 1-10
Land use: maize

Sampling time	<V>	ST.DEV	ALFA1	R**2	SSQ
1	3.2700	0.0001	37.00	0.974	773.6
2	8.2583	0.6510	64.22	0.937	112.1
3	4.7114	0.4566	33.49	0.988	26.0
4	3.6654	0.0024	94.60	0.972	14.1
1,2,3,4	4.1903	0.4111	15.15	0.890	5579.8
1,3,4	3.5327	0.1857	33.21	0.959	1999.6
2,3,4	6.4231	0.6070	45.89	0.908	541.7

Location: 11-20
Land use: grassland

Sampling time	<V>	ST.DEV	ALFA1	R**2	SSQ
1	3.8481	0.3032	84.90	0.863	800.8
2	20.0331	1.0100	0.15	0.786	278.7
3	3.2437	0.0020	212.08	0.953	35.0
4	5.9702	0.6468	70.07	0.925	30.2
1,2,3,4	4.7085	0.5205	60.83	0.893	2079.3
1,3,4	3.6955	0.3001	102.91	0.942	1053.6
2,3,4	8.8507	0.8397	33.08	0.753	853.3

From table 1 it appears that the CD-model describes the bromide transport very well for the first sampling time; v seems to correspond with the measured volumetric moisture content profiles showing slightly higher values for grassland than for maize. The dispersion length α_1 appears to be larger for grassland than for maize. This might be attributed to a more prominent continuous pore system, resulting into a

larger variation of pore flow velocities. For the other sampling times, the TF-model gives a slightly better fit to the observations; the minimum sum of squares for the TF-model optimization is less than the CD-model optimization.

Drainage water samples

After every 0.5 mm of drain discharge a water sample was taken by using a specially constructed automatic sampling device. The relation between mm discharge and measured drainage water concentration is shown in fig. 3.

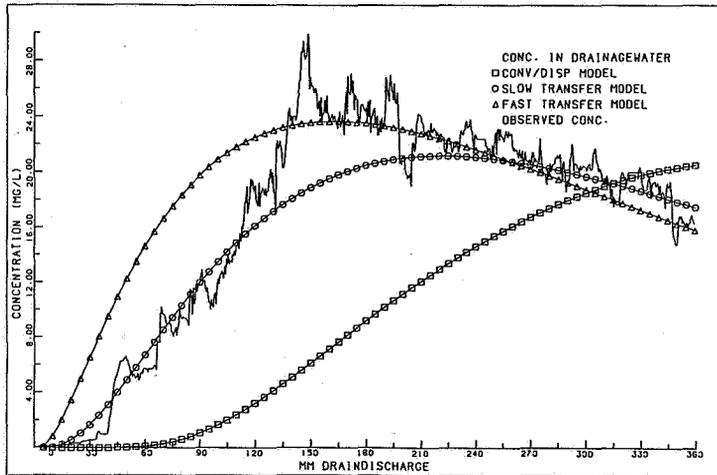


Figure 3. Bromide concentrations as a function of drain discharge

Synthesis

Knowing the transport mechanisms in the unsaturated zone it should be possible to predict the concentration of bromide in the drainage water. In order to account for the differences in thickness of the saturated and unsaturated zones along the length of the drain, the concentration in the drainage water was calculated as the average solute concentration of 20 equally spaced locations, each having its proper breakthrough curve depending upon land use, thickness of the

unsaturated zone and the thickness of the saturated zone. This has been calculated for three scenario's: 1) CD-model transport with parameters from sampling time 1, 2) the fastest TF-model: the parameters from sampling time 2 for maize and grassland, 3) the parameters obtained from the TF-model optimization for sampling times 2, 3 and 4 (the slow transfer model). These three cases are shown in fig. 3 as well.

DISCUSSION AND CONCLUSIONS

Using the soil sampling data one may conclude that the classic CD-model adequately describes the transport in the unsaturated zone - at least for the first sampling time. The values for the migration velocities and dispersion lengths seem to be acceptable from a physical point of view (Van Hoorn, 1981). However, validation of these transport parameters by prediction of the breakthrough curve (BTC) in the drainage water shows a severe underestimation as compared with the observed concentrations. The BTC in the drainage water is relatively well predicted using the TF-model parameters from the second sampling time ('fast model'). In this case, the migration velocities are much higher than estimated from the moisture profiles, i.e. part of the soil matrix seems not to be active in transporting water and solutes, thereby causing an accelerated breakthrough of the solute. The predicted concentrations appear even 'earlier' than observed. Possibly solute transport in the top soil may be described quite well with the CD-model - compare the CD-model parameters of the first sampling time in table 1 - while at a certain depth instability of the moisture front occurs and bypass of water flow takes place. Thus a CD-model transport in the top soil might be followed by a 'fast' process in the subsoil, as described by the fast TF-model. Such a combination of the CD-model for the top soil with the TF-model for transport in the subsoil may result in a BTC that fits the measured data.

The predicted BTC based on parameters of the 'slow' TF-model using the last three sampling times describes the observed data relatively well; only the peak around 150 mm discharge is not well predicted. This may be caused by an underestimation of the migration velocity around that

amount of discharge, corresponding with the presence of the solute in a soil layer where fingering might occur. Experimental evidence for this 'fingering' is not yet present, however, its existence is indicated by:

- a. the presence of a textural change from a low permeable to a more permeable layer, which may cause unstable wetting fronts (Raats, 1973), even in wet conditions (Oosting, 1986)
- b. the presence of water repellent layers throughout the field (Hendrickx & Dekker, 1986)
- c. the increase of the coefficient of variation in the volumetric water content at a depth of approximately 30 cm

The fingering mechanism renders a physical interpretation of the TF-model parameters from the soil sampling doubtful; moreover these have to be considered as parameters describing a fast breakthrough.

A strong recommendation is therefore made to quantify the mechanisms that produce the observed accelerated leaching of solutes from soils.

ACKNOWLEDGEMENTS

Thanks considering practical and theoretical realisation of the project are given to Mr. Dijksma, Mr. Hulshof, Mr. Stricker, Mr. Post and Mr. Van den Abeele of the Agricultural University Wageningen, Mr. Verstrate of the Inst. for Inland Water Management and Waste Water Treatment, Mr. Van der Plicht and Mr. De Klein of the Water Quality Control Service East-Gelderland, Mr. Neele of the National Institute of Public Health and Environmental Hygiene and Mr. Van Genuchten of USDA/ARS Riverside. I would like to acknowledge the Province of Gelderland and the Institute for Inland Water Management and Waste Water Treatment for their financial contribution to the project. I also would like to thank Mr. Dewachter for his help in the interpretation of data. Finally, Mr. Jorjani and Mr. Hopmans are friendly rewarded for reviewing the draft of this paper.

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A PROCEDURE AND NOMOGRAMS FOR DESIGNING SANITARY
PROTECTION ZONES AROUND WATER WELLS

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ABSTRACT

Presented are a procedure and nomograms for designing of Sanitary Protection Zones (SPZ) around water wells. The procedure has been standardized for the construction of water wells in Bulgaria. With the aid of the nomograms, it is now possible to design several types of SPZ around water wells with regard to different potential contaminants (bacteriological, chemical, etc.). This is of particular importance for the rational utilization of terrains for agricultural use. The procedure can also be applied for a group system of interacting wells, provided the system is considered a 'large' well.

The so called Sanitary Protection Zones (SPZ) are usually designed for local protection of ground waters within the zone of influence of water wells. The shape and territory of these zones depend on a number of factors, the most important of which are the structure of the filtration flow and the type of the potential contaminants. A procedure for designing of SPZ with regard to a concrete contaminant, as well as for determining the territory of SPZ, has been proposed by the authors on the basis of the 'Migration principle'. The latter has been reduced to two essentials as follows:

- The protection line coincides with the isochrone of the critical time (T_c) from where a given contaminant would reach the well. T_c depends on the contaminant type, which is adopted to be 25 to 50 years for chemical contaminants and 300 to 400 days for bacteriological contaminants.
- Mass transfer solutions with respect to reactive components are used

for the identification of points of the protection line.

Following three major cases have been taken into consideration:

- a well located in natural groundwater flow, far from aquifer boundaries (Case A);
- riverside well without existence of a natural flow from/to the river (Case B);
- riverside well with existence of a natural groundwater flow (Case C).

In order to determine the coordinates of the protection line and the total territory of SPZ, the authors have developed a procedure and the corresponding computer program SOZ. The essence of the procedure and the complete program codes in FORTRAN have been presented in detail by Galabov and Penchev (1986) and shall not be considered herein. A series of nomograms for the purpose of designing SPZ for the cases as described above have been made up by means of a multivariant numerical study under application of SOZ.

The exact shape and territory of SPZ have been investigated. For practical application a simplified shape for SPZ has been adopted, which can easily be determined using the attached nomograms.

1. CASE A

The exact and simplified shape of SPZ for the particular case is as shown on Figure 1.

To determine the distances L and M, which are used for definition of the simplified shape of SPZ, the nomogram shown on Figure 2 can be used.

The dimensionless quantities \bar{X}_{\min} , \bar{X}_{\max} , \bar{Y}_{\max} and R are presented as:

$$\bar{X}_{\min} = \bar{X}_{\min} / X_a; \quad \bar{X}_{\max} = \bar{X}_{\max} / X_a; \quad \bar{Y}_{\max} = \bar{Y}_{\max} / X_a; \quad R = \frac{V_e T_c}{n_s X_a}$$

where

\bar{X}_{\min} , \bar{X}_{\max} , \bar{Y}_{\max} = real coordinates of points on the protection line (m);

X_a = distance from the well to the saddle point (m);

V_e = velocity of the natural flow (m/d);

T_c = critical time (d).

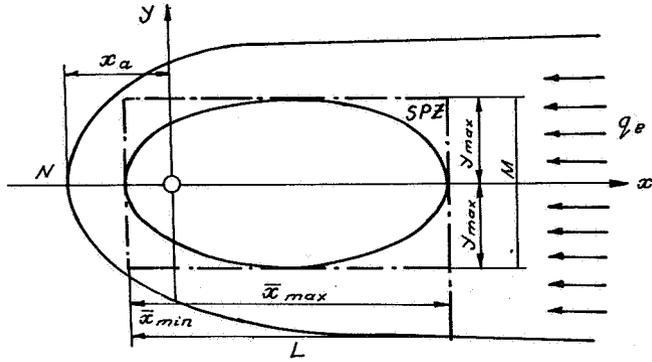


Figure 1

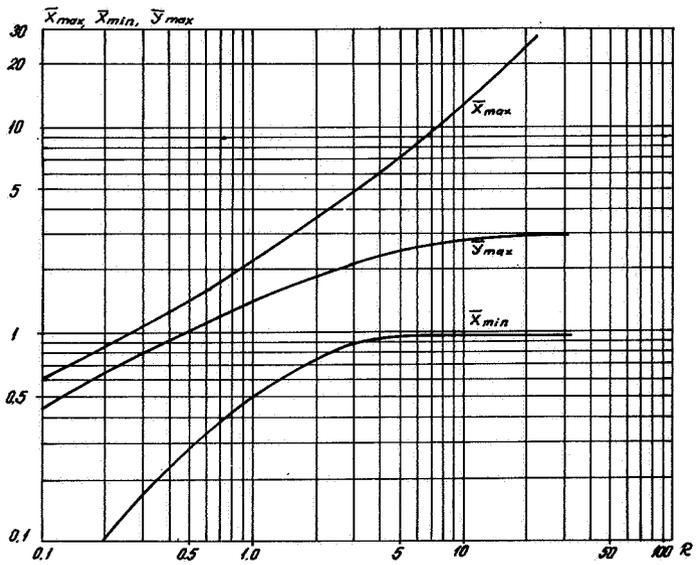


Figure 2

The distance X_a can be determined using the formula:

$$X_a = Q / (6.28mV_e)$$

whereas the filtration velocity is to be determined by the formula:

$$V_e = k.I_e$$

where

Q = well discharge (m^3/d);

m = aquifer thickness (m);

k = hydraulic conductivity (m/d);

I_e = gradient of the natural flow

The parameter n_s represents the so called sorption porosity of the porous medium and can be defined by the formula:

$$n_s = n.R_f$$

where

n = active porosity of the medium

R_f = retardation factor

The practical work with the proposed nomogram (Figure 2) is to be carried out in following steps:

- the parameter R is calculated for the particular conditions;
- $\bar{X}_{min, max}$ and \bar{Y}_{max} are defined as per Figure 2;
- L and M are calculated using the formulas:

$$L = (\bar{X}_{max} + \bar{X}_{min}) \cdot X_a \quad \text{and} \quad M = 2\bar{Y}_{max} \cdot X_a$$

2. CASE B

The exact and simplified shape of SPZ is shown on Figure 3.

To determine the distances L and M , which are used for definition of the simplified shape of SPZ, the nomogram on Figure 4 can be used.

The dimensionless quantities \bar{X}_{max} , \bar{Y}_{max} and R are presented as

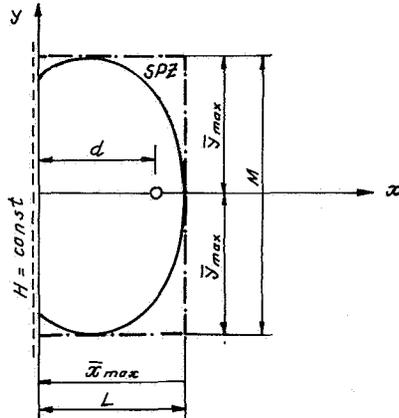


Figure 3

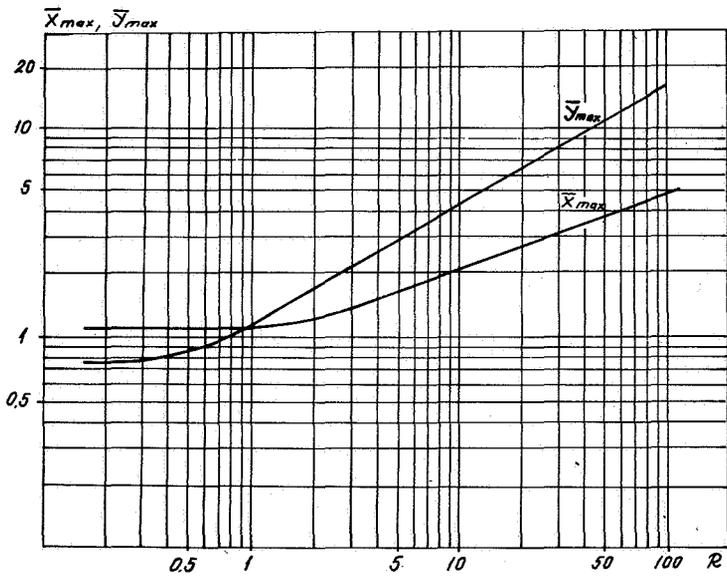


Figure 4

follows:

$$\bar{X}_{\max} = X_{\max} / d; \bar{Y}_{\max} = Y_{\max} / d; R = QT_c / (6.28mn_s d^2)$$

where

d = distance from the well to the river (m).

All remaining symbols are equal to those explained for Case A. The nomogram application procedure is analogous to the procedure for Case A, with the exception that the distances L and M are defined here by the formulas:

$$L = \bar{X}_{\max} \cdot d \quad \text{and} \quad M = 2\bar{Y}_{\max} \cdot d$$

3. CASE C

In this case a preliminary test has to be carried out in order to establish the existence of a saddle point between the well and the river. Following equation is used as criterion:

$$\mathcal{E} = Q / (3.14dmV_e)$$

In case $\mathcal{E} \leq 1$, there is a saddle point between the well and the river. SPZ designing is then carried out as for Case A.

In case $\mathcal{E} > 1$, there is no saddle point between the well and the river. Water flows to the well from both the aquifer and the river.

The exact shape of SPZ for this case is very complicated and not suitable for practical application. In view of this fact, a simplified rectangular shape for the SPZ is adopted, which most closely approximates the exact one exceeding its territory to an insignificant degree only. The adopted SPZ shape is shown on Figure 5.

The coordinates of the four points \bar{X}_1 , \bar{X}_2 , \bar{Y}_1 and \bar{Y}_2 of the protection line can be defined with the aid of the nomograms shown on Figures 6, 7, 8 and 9 and following formulas:

$$\bar{X}_1 = X_1 / d; \bar{X}_2 = X_2 / d; \bar{Y}_1 = Y_1 / d; \bar{Y}_2 = Y_2 / d \quad \text{and} \quad R = V_e T_c / (n_s d)$$

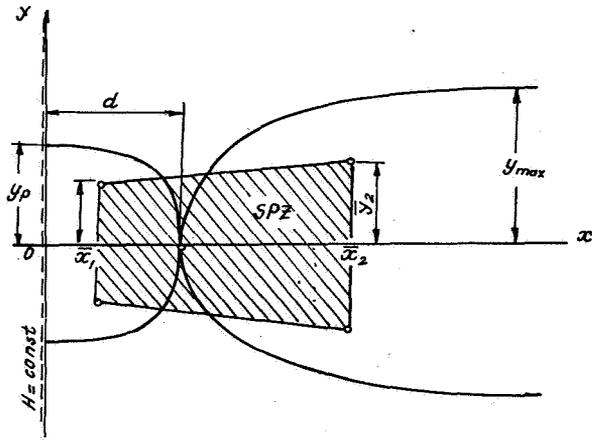


Figure 5

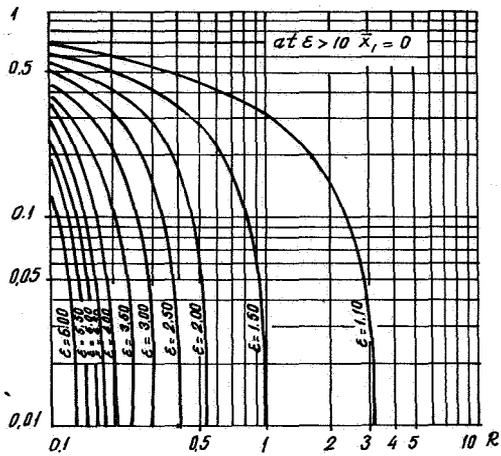


Figure 6

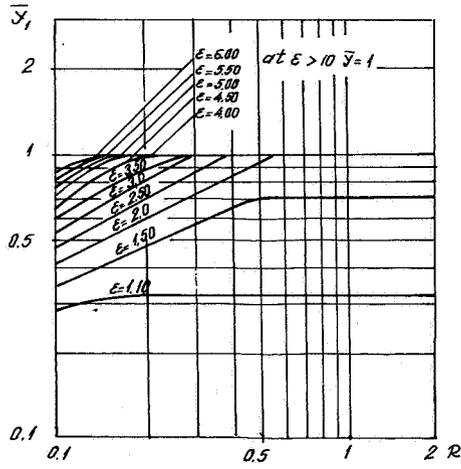


Figure 7

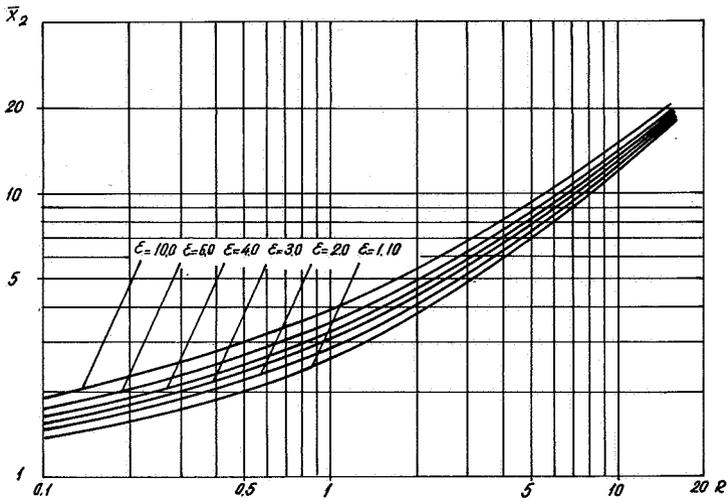


Figure 8

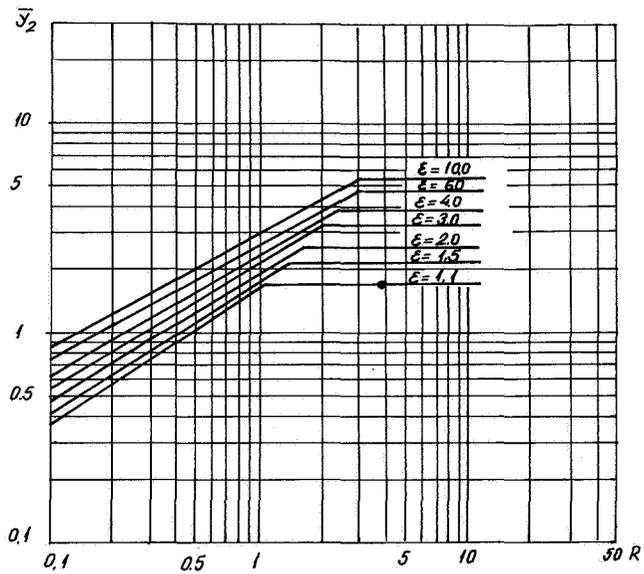


Figure 9

The nomogram application procedure is analogous to the procedures used for the other two cases.

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USE OF SOIL SURVEY INFORMATION FOR ASSESSING THE
PHOSPHATE SORPTION CAPACITY OF HEAVILY MANURED
SOILS

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ABSTRACT

Phosphate leaching from soils threatens the future quality of ground-water and surface water in areas with intensive livestock farming. This study shows how soil data can be used to assess the total phosphate sorption capacity (PSC) of the soil. The available PSC is a dynamic property depending upon pH, phosphate concentration, reaction time and previously sorbed phosphate. The influence of concentration and time were studied at phosphate concentrations of 25-100 mg P per litre in manured soils and with reaction times of 1 day to 1 month at pH 5.5. Adsorption isotherms were described by a "modified Freundlich" or a "Freundlich-Elovich" equation. The equations were used to extrapolate routinely measured values of available PSC at 50 mg P per litre and one day to other concentrations (e.g. 90 mg per litre) and with longer reaction times (1-5 years) as found under field conditions. The total PSC was obtained by adding the previously sorbed phosphate to the extrapolated available PSC.

The total PSC thus determined correlated strongly with oxalate-extractable aluminium (Al_{ox}) and iron (Fe_{ox}) in the non-calcareous sandy soils studied. Al_{ox} and Fe_{ox} are simple soil characteristics that are routinely measured during the soil survey in "representative" profiles. This procedure allows a rapid assessment of the total PSC of the soil types presented on the soil map.

1. INTRODUCTION

Since 1970 the intensification of animal husbandry has resulted in manure surpluses in the sandy districts of the Netherlands where there are large concentrations of livestock. These manure surpluses are primarily spread on maize fields, because maize is not adversely affected by high application rates. In these districts, the area under maize increased from 3% of the arable land in 1970 to about 60% in 1985. High application of phosphate, leads to phosphate leaching-sooner or later-depend- ing on the vulnerability of the soil. This in turn depends on the phos- phate sorption capacity (PSC). Phosphate sorption takes place at the edges of clay minerals, aluminium oxides, iron oxides, organic matter and calcium carbonate. The intensive animal husbandry is mainly found on non-calcareous sandy soils low in organic matter. Consequently, in this case the major soil characteristics important to phosphate sorp- tion are aluminium and iron oxides or hydroxides. This paper shows how the phosphate sorption capacity can be measured and how the phosphate sorption capacity can be related to these soil characteristics (which are measured during soil surveys) by means of a "transfer function". The soil survey data can then be used to assess the phosphate sorption capacity of tracts of land.

2. MEASUREMENT OF THE PHOSPHATE SORPTION CAPACITY (PSC)

2.1 Standard conditions

In our laboratory, the available PSC is routinely measured at a concen- tration of 50 mg P per l^{-1} during one day at pH 5.5. Most research on the influence on the concentration on phosphate sorption has been done at low concentrations, because of the low background concentrations in soil solution. However, heavily manured soils are characterized by high concentrations of inorganic phosphate in soil solution of the order of 50-100 mg l^{-1} (Van Riemsdijk et al., 1983). The concentration is fairly constant, because the solution can be considered to be a saturated calcium phosphate solution (Gerritse, 1976). Organic phosphate is

rapidly mineralized and, therefore, can be ignored when considering adsorption (Gerritse et al., 1982). The reaction time has to be taken into account, because the sorption process is slow possibly because of diffusion into the solid (Van Riemsdijk, 1979) or into mesopores (Madrid and Arambarri, 1985). The reaction time can therefore be in the order of years. For this reason, short-term experiments have to be extrapolated to longer reaction times to approximate the field situation. Finally, pH is also known to affect phosphate sorption in soil. However, the variation in pH is relatively small in the sandy soils considered in this study (pH 4-6). Therefore, our study of the impact of different variables on the phosphate sorption capacity focusses on the effect of concentration and reaction time.

2.2 The influence of the phosphate concentration

The influence of the concentration on phosphate sorption at a constant reaction time (1 day) was studied in 18 samples from major horizons (A_1 , A_2 , B_2 , B_3 , C_1) of representative sandy soil types in the Netherlands. The phosphate sorption was measured at concentrations of 25, 50, 75 and 100 mg P l⁻¹. The phosphate sorption at any concentration was related to the phosphate sorption capacity at a standard concentration of 50 mg per litre by a "normalized" Freundlich equation:

$$PSC_m^a(c, t_o) = PSC_m^a(c_o, t_o) * (c/c_o)^n \quad (1)$$

where:

PSC_m^a = available massic phosphate sorption capacity (mmol kg⁻¹)

c = concentration (mg l⁻¹)

c_o = standard concentration (50 mg l⁻¹)

t_o = standard reaction time (1 day)

n = constant (-)

The exponent of the Freundlich equation (n) of each adsorption isotherm was determined by linear regression of the natural logarithm of the phosphate sorption versus the natural logarithm of the relative concen-

tration. Table 1 shows the average values of the Freundlich exponents for the above-mentioned horizons. The mean value is 0.25 ± 0.12 . The value of n decreases from A to C horizons, suggesting that the organic matter content has some effect.

Table 1 *Soil data and statistical data on n values for soil horizons from sandy soils*

horizon code	number of samples	Al _{ox} + Fe _{ox} (mmol kg ⁻¹)	Organic matter (%)	\bar{n}		\bar{V}^2	
				\bar{x}	st. dev.	\bar{x}	st. dev.
A ₁	3	8- 38	2-14	0.46	0.15	94.0	4.5
A ₂	2	17- 43	1- 2	0.26	0.07	96.4	4.5
B ₂ , B ₃	6	48-120	1- 6	0.24	0.05	85.2	8.2
C	7	5- 73	< 1	0.17	0.07	85.2	11.9

note: V^2 = percentage variance accounted for

2.3 The influence of the reaction time

The influence of the reaction time on the phosphate sorption capacity at a constant phosphate concentration (50 mg l^{-1}) was studied for 23 samples from the equivalent horizons in podsollic soils. These data were fitted to an Elovich equation (Atkinson et al., 1970) and a "modified" Freundlich equation (Barrow et al., 1975):

$$dS/dt = k_1 e^{-k_2 S} \quad (2a)$$

$$S = k_3 c^n t^m \quad (2b)$$

where:

S = amount of phosphate sorbed (mmol kg^{-1})

k_1 = rate constant at a given c ($\text{mmol kg}^{-1} \text{ day}^{-1}$)

k_2 = constant at a given c (kg mmol^{-1})

k_3 = rate constant at a given c (day^{-1})

n, m = constants

In this study we define: $S = \text{PSC}_m^a$ and illustrate the calculation of the PSC as a function of the reaction time for the Elovich equation.

Integrating Eq. 2a using the boundary condition $q = 0$ at $t = 0$ and $t \gg 1/k_1 k_2$ yields

$$\text{PSC}_m^a(c_o, t) = (\ln k_1 k_2 + \ln t) / k_2 \quad (3)$$

Using equation (3), the phosphate sorption at any time can be related to the phosphate sorption capacity at a standard reaction time of 1 day by:

$$\text{PSC}_m^a(c_o, t) = \text{PSC}_m^a(c_o, t_o) (1 + a \ln t) \quad (4)$$

where:

$$a = 1/\ln k_1 k_2$$

t = reaction time (days)

The Elovich equation parameter 'a' was determined for each horizon from the slope and intercept of a linear plot of phosphate sorbed versus the natural logarithm of the reaction time. Table 2 gives the range of the Elovich coefficients 'a' for the horizons mentioned before. The mean 'a' for these horizons is 0.118 ± 0.026 . The mean percentage accounted for is high ($V^2 = 86.9$) and there is no effect of oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}). Using data from Van Riemsdijk (1979), it can be shown that 'a' is also independent of the concentration over the considered range. Furthermore, the exponent of the Freundlich equation is not affected by the reaction time (Kuo and Lotse, 1974). Consequently, Eq. 4 can be combined with Eq. 1, to:

$$\text{PSC}_m^a(c, t) = \text{PSC}_m^a(c_o, t_o) (1 + 0.118 \ln t) (c/50.0)^{0.25} \quad (5)$$

Table 2 *Soil data and statistical data on 'a' values for soil horizons from sandy soils*

horizon code	number of samples	Al _{ox} + Fe _{ox} (mmol kg ⁻¹)	a		V ²	
			\bar{x}	st. dev.	\bar{x}	st. dev.
					(%)	
A ₁	1	18	0.177	-	-	-
A ₂	2	10- 27	0.091	0.002	58.1	6.0
B ₂ , B ₃	14	37-429	0.115	0.002	88.7	9.5
C	5	29- 72	0.123	0.027	91.0	5.3

note: V² = percentage variance accounted for

This equation was used to extrapolate routinely measured values of available PSC, at 50 mg P per litre and one day, to other concentrations (e.g. 90 mg per litre) and longer reaction times. Routinely measured phosphate sorption capacities were extrapolated to a reaction time of 5 years. The effect of the reaction time on the PSC appears to be small after this period. The total PSC was obtained by adding the previously sorbed (oxalate-extractable) phosphate to the available PSC according to:

$$PSC_m^t(c,t) = PSC_m^a(c,t) + P_{ox} \quad (6)$$

where:

PSC_m^t = total massic phosphate sorption capacity (mmol kg⁻¹)

P_{ox} = oxalate-extractable phosphate (mmol kg⁻¹)

3 RELATION OF PSC WITH SOIL SURVEY DATA

3.1 Soil characteristics

To enable soil survey data to be used to calculate the total PSC, the

statistical relation between PSC and the amount of aluminium and iron oxides and hydroxides was examined, because it are these soils characteristics that mainly determine the phosphate sorption. The amorphous and fine particles in particular are able to sorb phosphate, because of their large specific area. These "active" compounds can be extracted with an acid oxalate solution.

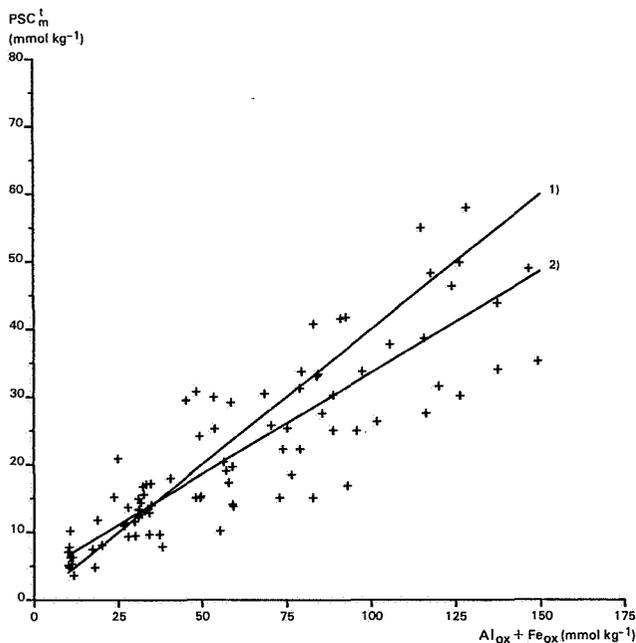


Figure 1 The total phosphate sorption capacity of sandy soils as a function of oxalate-extractable aluminium (Al_{ox}) and iron (Fe_{ox})

Figure 1 shows the total phosphate sorption capacity as a function of Al_{ox} and Fe_{ox} , a concentration of 90 mg P l^{-1} and a reaction time of 5 years. The lines in this figure were calculated by averaging (1) and by linear regression analysis (2). The corresponding mathematical expressions are:

$$PSC_m^t = 0.40 * (Al_{ox} + Fe_{ox}) \quad (cv = 35.5) \quad (7)$$

$$PSC_m^t = 3.6 + 0.30 (Al_{ox} + Fe_{ox}) \quad (V^2 = 78.3) \quad (8)$$

in which PSC_m^t , Al_{ox} and Fe_{ox} are expressed in mmol kg^{-1} , cv is the

coefficient of variation and V^2 the percentage variance accounted for. These relations demonstrate the possibility of obtaining data on a complex soil property (the PSC) by a "transfer function" from simple soil data collected during soil surveys (see Bouma et al., 1986).

3.2 Soil type and water regime

Using Eq. (7) the PSC of any horizon or profile can be calculated from:

$$PSC_a^t = 2.84 D_i d_i (Al_{ox} + Fe_{ox}) \quad (9)$$

where:

PSC_a^t = total areic phosphate sorption capacity ($kg P_2O_5 ha^{-1}$)

D_i = thickness of soil horizon i (cm)

d_i = bulk density of soil horizon i ($g cm^{-3}$)

The phosphate sorption capacity varies with soil horizon and soil type, because oxalate-extractable Al- and Fe-components are strongly affected by soil formation. The horizons of representative profiles can be characterized by mean thickness, bulk density and concentration of oxalate-extractable aluminium and iron. The phosphate sorption capacity can thus be calculated for each horizon, using (Eq. 9). Table 3 illustrates this for two soil types: a Plaggept soil and a Humaquept soil. The soil map can thus be converted into a phosphate sorption capacity map (Breeuwsma et al., 1986) and used in forecasting phosphate leaching on regional scale (Breeuwsma and Schoumans, in prep.).

Table 3 *Soil data used and results obtained for the phosphate sorption capacity (PSC) of horizons from two soil types*

Soil type	Hori- zon	Depth (cm)	bulk density (gr cm ⁻³)	Al _{ox}	Fe _{ox}	PSC _m ^{t¹}	PSC _a ^{t²}
				---(mmol kg ⁻¹)---			(10 ³ kg P ₂ O ₅ ha ⁻¹)
Plaggept	Aan	0- 70	1.30	37	32	27.6	17.8
	A ₁ b	70- 80	1.45	51	16	26.8	2.8
	B ₂ b	80-100	1.35	111	9	48.0	9.2
	B ₃ b	100-140	1.55	128	24	60.8	26.8
	C	140-	1.65	37	7	17.6	-
Typic	Aan	0- 30	1.15	44	104	59.2	14.5
Humaqept	C	30-	1.70	15	36	20.4	-

¹) calculated by Eq. 7

²) calculated by Eq. 9

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FINITE-DIFERENCES METHOD FOR MODELLING TRANSPORT OF ION EXCHANGING POLLUTANTS IN HETEROGENEOUS AQUIFERS

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ABSTRACT

Migration of pollutant components in natural hydrogeological conditions take always place on backround of physic-chemical interactions of transferred species with rock medium. Very often for great range of practical problems it is necessary to take into account schemes of migration such processes as sorption, complexation and especially ion exchange. The purpose of this paper is an analysis of ion exchangeable reactions in fissure-porous media. The evaluation of possibilities to use analytical relations is given.

1. INTRODUCTION

Analytical solutions defining ion exchange exist only for very simple schemes of hydrogeological conditions. E.g.Charbeneau /1981/ formulates solution of one-dimensional mass transfer without dispersion by the method of characteristics. The presence of both dispersion and non-linear exchange requires methods of numerical simulation to be used. Rubin and James /1973/, Valocchi et al./1981/ presented Galerkin's finite element method for describing the transport of multicomponent ion exchanging solutes. Their models was based upon steady, 1-D flow in homogeneous saturated porous medium. Pandey et al./1982/ used Cranc-Nicolson's finite-differences scheme for solution of the 1-D equations of mass transfer by non-linear sorption. In our paper we present numerical modelling of 2-D mass transport ion exchanging pollurants in heterogeneous media.

2. BASIC EQUATIONS

The equilibrium relationship for ion exchangeable interaction between fluid and solid phases into groundwater-rock system may be written as / Valocchi et al, 1981/

$$K_{ij} = (q_i / C_i Q_v)^{Z_j} (C_j Q_v / q_j)^{Z_i} \quad / 1 /$$

Where K_{ij} is the constant derived from laboratory, Z_{ij} are valences of the cation species, C_i , C_j and q_i , q_j are concentrations of the cations in solution and in the solids, Q_v is total cation exchange capacity. With the requirements of preservation electroneutrality of solution and filled exchange sites states during the reaction

$$\sum C_i = C_a \quad \sum q_i = Q_v \quad / 2 /$$

where C_a is the general anion which does not undergo ion exchange. We obtain the Freundlich exchange isotherm.

In particular, for binary heterovalent exchange we have

$$q_1 = P Q_v \left[(1 + 2/P)^{1/2} - 1 \right] \quad \text{by } Z_1 = 1, Z_2 = 2 / 3 /$$

and

$$q_1 = (Q_v / R) \left[R + S \left(S - \sqrt{S^2 + 2R} \right) \right] \quad \text{by } Z_1 = 2, Z_2 = 1$$

where $P = R C_1 / 4 S$, $R = 2 K_{12} C_1$ and $S = C_a - C_1$: / 4 /

Taking into account above-mentioned assumptions, the system of basic equations for mass transport in 2-D steady states saturated flow including binary ion exchange is / Golubev et al.1968, Valocchi et al. 1981/

$$n(\partial C_a / \partial t) + v \nabla C_a - D \nabla^2 C_a = 0 \quad / 5 /$$

$$n(\partial C_i / \partial t) + \partial q_i / \partial t + v \nabla C_i - D \nabla^2 C_i = 0, \quad i=1,2$$

where ∇ is gradient operator, ∇^2 is Laplace operator, t is time, x, y are Cartesian coordinates, n is porosity of medium, v is velocity vector,

D is tensor of hydrodynamic dispersion, C_1 and C_2 are concentrations of ousting and ousted cations, respectively.

Substituting to second equation / 5/ the relations of type / 3 / - / 4 / and using equation / 2 / by following initial and boundary conditions, respectively

$$C_1(x, y, 0) = 0, \quad C_2(x, y, 0) = C_2^0, \quad C_a(x, y, 0) = C_a^0 \quad y > 0 \text{ and } x > 0$$

$$C_1(0, 0, t) = C_1^b, \quad C_2(0, 0, t) = C_2^0, \quad C_a(0, 0, t) = C_a^b \quad t > 0 \quad / 6 /$$

the equations system / 5 / can be rewritten in form :

$$n(\partial C_a / \partial t) + v \nabla C_a - D \nabla^2 C_a = 0$$

$$\bar{n}(\partial C_1 / \partial t) + v \nabla C_1 - D \nabla^2 C_1 - (C_1 \bar{B} / C_a)(\partial C_a / \partial t) = 0$$

$$C_2 = C_a - C_1$$

where $\bar{n} = n + \bar{b} / C_a$, $W = (1 + 2/P)^{1/2}$

$$\bar{b} = Q_v C_a P \left[(2/C_1 + 1/S)(W-1) - (8/RC_1 W)(S/C_1 + 0,5) \right]$$

$$\bar{B} = \bar{b} / (2 C_2) \text{ for isotherm / 3 / and}$$

$$\bar{b} = (Q_v C_a / R) \left[(C_a + C_1) (W_0^2 - R) / WC_{01} - (C_a^2 - C_1^2) / C_1 \right], \quad W = S^2 + 2R^{1/2}$$

$$\bar{B} = 2\bar{b} / (C_a + C_1) \text{ for isotherm / 4 /}$$

For initial conditions when $C_1(x, y, 0) \neq 0 = C_1^0$ it is necessary to substitute the value C_1 for $C_1 + C_1^p$ in the parameter B . C_1^p is equilibrium concentration.

3. RESULTS AND CONCLUSION

For investigation of ion exchange processes in heterogeneous media the wide-spread approaches of fissure-porous rock approximation were used by means of more and less permeable layers system. The first one of them simulate fissures where convective transport dominates the second one approximates porous blocks where molecular diffusion and ion exchange prevails / fig.1 /.

For such kind of the medium three schemes corresponding to different mass exchange regimes between separate elements of this medium can be

distinguished : the scheme of infinite capacity, of concentrated capacity and the asymptotic scheme.

The analysis of exchanging cations transfer at beginning period of time, i.e. for infinite capacity scheme, is highly difficult. The simulations of this problem were run using a following parameters : the fissures capacity n is 0.01, the fissure fluid specific discharge v_y is 0.055 m/day the coefficients of longitudinal and trasverse hydrodynamic dispersion, respectively D_y is 0.06 m²/day and D_x is 0.05 m²/day the blocks porosity n_2 is 0.1, the coefficient of molecular diffusion in blocks D_m is 1.10⁻⁵ m²/day, the layers thickness m is m_0 is 0.4 m. In figure 4 the concentration profiles of anions C_a and cations C_1, C_2 at time t is 5 day for linear homovalent exchange / $Z_1 = Z_2 = 1$ or 2 and $K_{12} = 1$ / are illustrated. Here the C_1^0 is 0. In this case, in porous blocks is going always the cation exchange sorption decreases the transfer intensity in fissures. If the exchange isotherm is concave transfer velocity of the C_1 cations rises significantly in fissures, but concentration distribution remains monotonous / fig.3/.

At initial conditions when value of C_1^0 is not equal zero both exchangeable sorption and desorption processes are possible in dependence on input and on equilibrium concentrations relation. Figure5 shows C_1 profiles in fissures at $C_1^b > C_1^p$, i.e. for the case, of ion exchangeable desorption in porous blocks. We can see that the oustin cations deform output curves in comparison with the curve for non-reactin ions / by identical mass transfer parameters/. This paradox has been explained by inverse / contrary/ diffusion of cations from blocks / see fig. 2', which causes that the increase of cation contents in fissures exceeds input concentration values. Simultaneously takes place the infingement of concentration functions monotony.

Results of numerical experiments have indicated that the mass transport of exchanging ions in heterogeneous media for infinite- and concentrated capacity schemes can be describe by analytical solutions only in the case of linear isotherm when C_1^0 values are zero. For asymptotic scheme the medium with double porosity is identical to homogeneous aquifer.

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FIGURES

- Figure 1 : Migration scheme of two-layer aquifer imitatin the porous-fissured medium. 1,2 - more or less permeable layer, 3,4 - flow directin: 3 - convective, 4 - diffusive.
- Figure 2 : Distribution of cation C_1 concentration for infinite capacity scheme without ion exchange /curve 1/ and with ion exchange /curves 2 - 4/
- Figure 3 : Distribution of concentrations in the layers 1 and 2 if no mass transfer exists, there is a homovalent exchange in the layer 2.
- Figure 4 : Concentration curves for zero initial concentrations C_1^0 . The infinite capacity scheme.
- Figure 5 : Influence of non-linear exchange on concentration. Figures on graphs show the K_{12} value.

Z_1	Z_2	C_1^p	curve	K_{12}
1	1	8,0	1	1
2	2	8,0	3	1
1	2	6,09	2	$1/C_a^b$
2	1	10,35	4	C_a^b

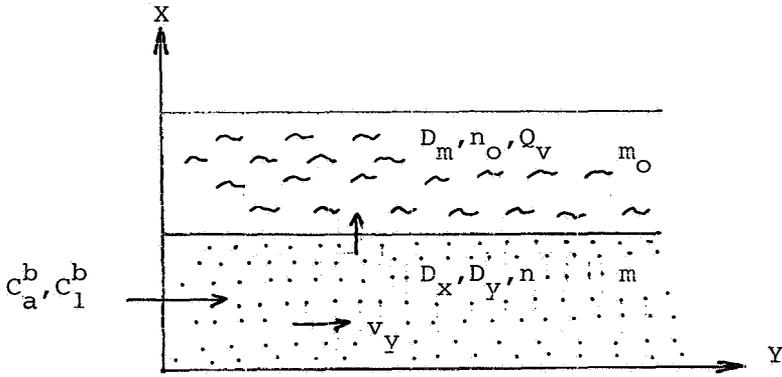


Fig.1

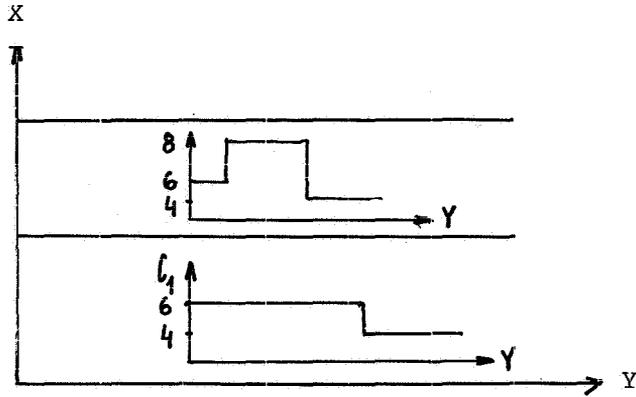


Fig.2

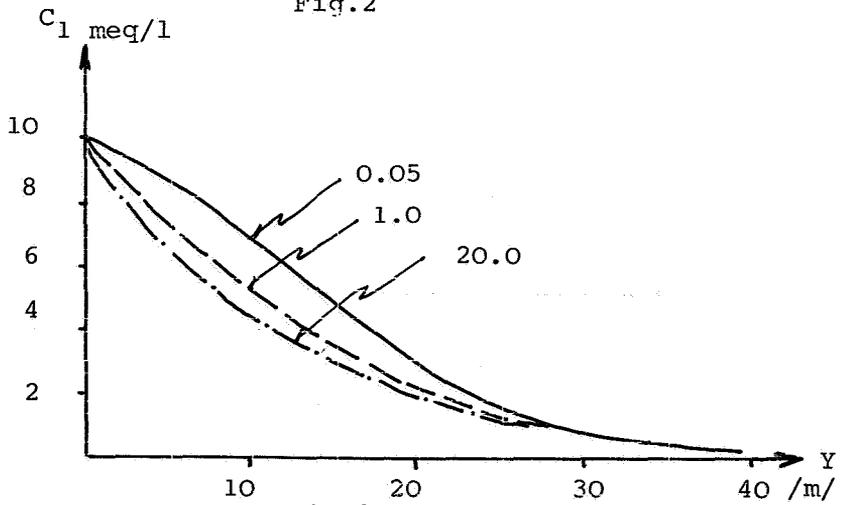


Fig.3

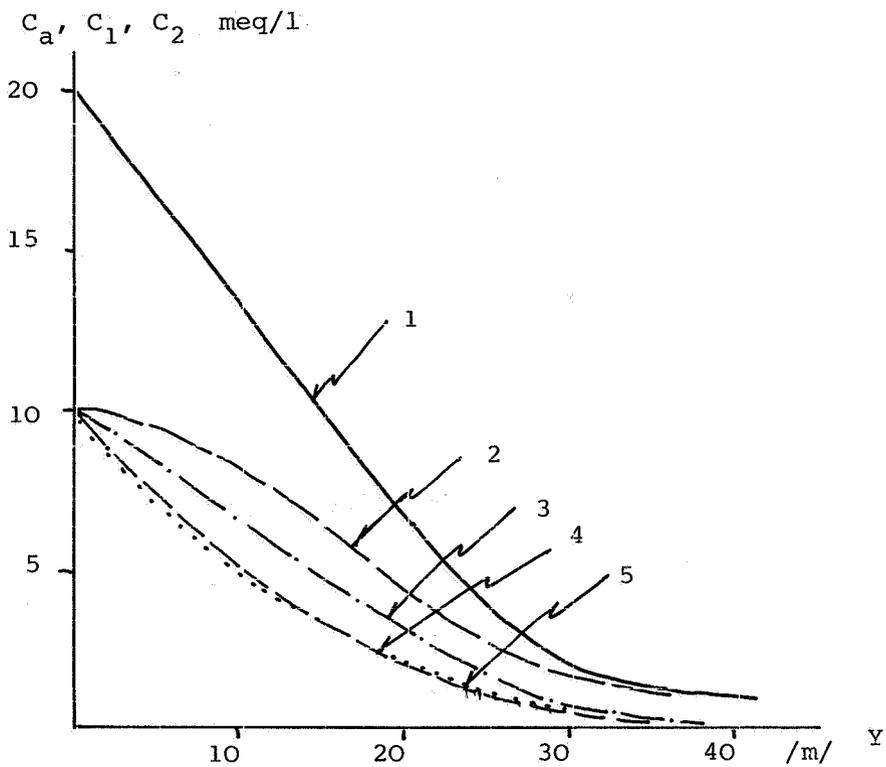


Fig. 4

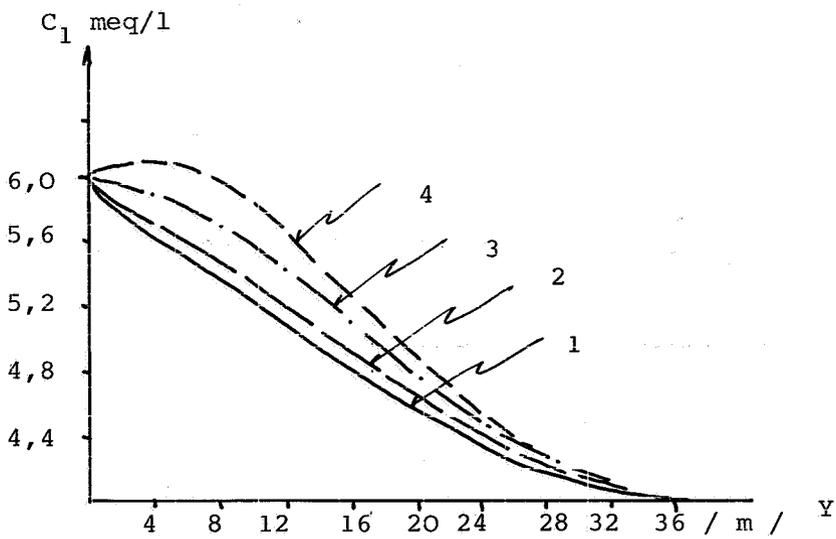


Fig. 5

A NEW MODEL FOR THE EVALUATION OF GROUNDWATER VULNERABILITY TO
NON-POINT CONTAMINATION BY PESTICIDES

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ABSTRACT

Though relatively recent, problems involving the contamination of soils and groundwater by pesticides are becoming more and more worrying. Such contamination results from the increased use of pesticides (treated areas and application rates), and their high toxicity, persistence and accumulation in the system.

Various degrees of alteration of the quality of groundwater may be caused by this non-point source contamination, as a function of the soil type, subsurface media, and the nature of the pesticide(s). These site-specific characteristics will determine the vulnerability of the groundwater to contamination.

It is important to characterize and quantify this vulnerability, in order to effectively protect the groundwater resources from contamination due to pesticides. Such quantification can be done on the basis of the values of the physical and hydrodynamic parameters of the system, as well as the physico-chemical properties of the pesticide(s). Numerous methods have been developed for this purpose; three major categories of methods can be distinguished - expertises (site-specific evaluation by a specialist in hydrogeology), rating systems, and simulation models of the transport and the fate of pesticides.

The model we have developed belongs to the third category. The purpose of the model is to predict the quantity of pesticide reaching the

water table. It is designed to take into account the major processes governing the movement and the fate of pesticides in the unsaturated zone. Destined to be used by planners and resource managers, the model is a practical tool which allows the visualization of the input and the output data. The application of the model for the evaluation of site vulnerability is done on the basis of Monte Carlo simulations.

The model proposed is thus a useful tool for decision making, for the planners and managers involved in the protection of groundwater quality and in the control of the use of pesticides. For a given water quality criterion, the model determines the potential vulnerability level of the system to contamination.

1. INTRODUCTION

Groundwater is an increasingly utilized resource. As we become more dependent on this resource, we also become more aware of the necessity to protect it. For more than ten years, we have been witnessing the multiplication and the aggravation of cases of groundwater pollution by organic contaminants. Facing this problem and the difficult task of decontamination, managers have rapidly become aware of the importance of prevention in the struggle against this type of pollution. It is within the general context of environmental protection and more particularly in order to safeguard the potential of groundwater resource that the VULPEST model has been developed.

The groundwater vulnerability to contamination is a complex matter that involves numerous interactive phenomena. However, the physical, chemical, biological and even human laws that control these phenomena are not yet very well mastered. The VULPEST model should allow the user to prevent the aggravation and the proliferation of contaminated sites. This model of evaluation of the vulnerability should be proving an essential tool for those involved in the planning of the territory, for those who select waste disposal sites or delimit protection areas, and also for those who supervise and control the quality of groundwater.

2. SETTING OF THE PROBLEM

The concept of groundwater vulnerability to contamination can be considered at three different levels. The first level concerns the evaluation of the contaminant risk of penetration, while the second one is linked to the contaminant propagation into the groundwater system. The third level deals with the effects of the contaminant presence on the quality of the resource, mainly as regards its use by man.

According to these three levels, the groundwater vulnerability thus appears as a function of (1) the aptitude of the soils that host or overlie the water system to be penetrated by the contaminant, (2) the possibility of the contaminant to migrate into the system, (3) the water quality criteria linked to water consumption, and finally (4) the persistence of the contaminant, a phenomenon that intervenes at all three levels.

Factors that affect the migration of the contaminant, and hence the vulnerability of a groundwater system, can be classified into several categories. These are the geological, hydrodynamic, hydrogeochemical and biological factors of the unsaturated and saturated zones, the bio-physico-chemical characteristics of the contaminant, and the water use.

The evaluation of the groundwater vulnerability to contamination, according to its definition level, is based on the interaction of these factors and on their influence as regards the migration and the fate of the contaminant into the groundwater system. Several methods attempt to take these various factors into account. Mainly, these methods are categorized as expertise-type approaches, matrix or decision tree methods, ranking-indexation system, or simulation models.

These different evaluation approaches are not related to the same definition level of the vulnerability and their objectives are distinct. They usually do not use the same information and they do not

take the same influential factors into account. Finally, the nature of their results varies accordingly, so that these are not always aimed at the same use. Most of the currently used methods provide a qualitative or relative evaluation (sometimes even subjective) of the vulnerability, without quantifying the aggression level, that is to say without establishing the quantity of contaminant that is likely to reach the water table, and beyond the user.

3. METHODOLOGY

Under certain circumstances, the spreading of pesticides can represent a problem of diffuse contamination. The model that we have developed is designed for the evaluation of the risks of groundwater contamination by pesticides.

In our approach, the phenomenon of vulnerability is defined as any contaminant penetration into the groundwater system (aquifer). The evaluation of the vulnerability within this context is based on the evaluation of the quantities of pesticide that are susceptible to reach the water table. This predictive approach relies on the modelling of the various phenomena that control the transport and the fate of the contaminant in the unsaturated zone of the soil. The main phenomena considered for the modelling are the advection and the dispersion processes that are linked to water flow, as well as the pesticide adsorption and degradation processes.

Given the diffuse nature of the contamination, the spatial variability of the various parameters and the uncertainties that characterize them, we have adopted a Monte Carlo approach. This approach consists in performing a sufficient number of simulations so that the overall results obtained are representative of the processes and of the parameters variability. Hence, for each simulation, values of the parameters used in the model are determined by random drawing from these parameters distributions. This approach is especially interesting for it takes into account the spatial variability of the processes and it provides results that can be statistically analysed.

The characteristic quantities obtained for each simulation are the maximum pesticide concentration reaching the water table along with the time at which this maximum occurs, and the cumulated mass of pesticide per unit of area that arrives at the water table. We thereafter perform a statistical analysis of each one of these characteristics, their values coming from the set of simulations realized. The interpretation of the results, which is carried out among other things by means of comparison with either norms or references, allows us to evaluate the groundwater level of vulnerability to contamination by pesticide.

4. DESCRIPTION OF THE VULPEST MODEL

The VULPEST model being aimed at management purposes, we tried to establish a tool that could rapidly provide a result, and thus allow managers to quickly reach a decision. Since the Monte Carlo approach requires a large number of simulations, the model execution speed is directly linked to the volume of calculations needed to solve the transport equation.

For these reasons, we opted for an analytical solution of the one-dimensional transport equation. This analytical solution is very easily written and allows reliable and rapid calculations. The equation that controls the transport is written as.

$$R \frac{dC}{dt} = -V \frac{dC}{dz} + D \frac{d^2C}{dz^2} - \lambda C$$

where:

$$R = 1 + K_d \frac{\rho}{\theta}$$

Van Genuchten's solution (1981)¹⁾ was adopted, its analytical formulation being very well suited to the description of the limit conditions that describe concentrations at the source. This solution indeed allows one to consider the source as either a constant concentration supply over a finite or infinite period of time, an

exponentially decreasing supply, or the sum of both; this initial condition is expressed as follows:

$$V C - D \frac{dC}{dz} = V (C_a + C_b e^{-\alpha t})$$

where:

$$C_a = 0 \text{ for } t > t_a$$

The analytical solution of the transport equation asks for the spatial and temporal invariability of the model parameters. Hence, the model transforms the parameters inferred from non-permanent phenomena into constant parameters, by means of functions that integrate the various processes involved. For instance, the speed parameter "V" is calculated from the monthly averages of rainfall and potential evaporation, the plant transpiration, the porosity and the vertical permeability of the unsaturated medium, and the date of application of the pesticide. This simplification does not impair the quality of the results, on account of the Monte Carlo approach that implicitly introduces the variability of the processes by making the initial parameters vary for each simulation.

The VULPEST model allows the user to explicitly take the vertical variability into account, owing to a vertical discretization according to the different horizons of the unsaturated zone. In order to do so, the analytical solutions are calculated independently for every stratum defined through the discretization process. The model uses the output quantity of pesticide calculated for a given level as a source of pesticide for the underlying level. The output quantity of pesticide is converted into a source that respects the initial limit conditions and appears under the previously specified form. This conversion is carried out by means of an algorithm of integration and adjustment.

The probabilistic distributions from which the parameters are fixed by random drawing for each simulation, can be of five types: ponctual value (deterministic case), uniform distribution over a given interval, normal, lognormal, or asymmetrical distribution. The

distribution of each parameter can be provided by the user. For lack of doing so, these distributions can be determined from standard values by the program and validated by the user. The model uses the characteristic parameters of the soil and the pesticide, the climatic data, and some crop data. All these data are easily gathered, which constitutes a fundamental quality of the model. The values of the parameters and variables used by the model can be entered by means of either interactive window menus, already existing files, or a combination of both.

5. USE OF THE VULPEST MODEL

The evaluation of groundwater vulnerability to contamination by pesticide rests on the prediction of the quantities of pesticide that can reach the water table. The VULPEST model can be applied to either a punctual site of a sufficiently homogeneous zone. The homogeneity of the zone must be expressed by unimodal distributions for the parameters and input variables, and by the similarity of the processes involved. For instance, this condition of homogeneity implies that the zone in question belongs to a same pedologic unit, is submitted to a same climate, has a somewhat uniform plant-cover, and is treated by one or several pesticides belonging to a same family and showing similar properties.

The data required for the application of the model on a site or on a zone are defined at the scale of this site or zone. They must be representative of the statistical distributions of the parameters and variables over the considered domain, this domain being defined and delimited in terms of the spatial homogeneity of these same parameters and variables.

The results and the statistical treatment of the various characteristic quantities inferred from the simulations can be interpreted by comparison with norms or other water quality criteria. On a given site, the water table will be considered vulnerable if for a certain percentage of simulations the maximum concentration of

pesticide reaching the water table exceeds a fixed norm. Hence, the quantitative notion of vulnerability will be linked on the one hand to imposed norms, and on the other hand to threshold values set by the user for different levels of vulnerability. Being related to norms, this approach will simultaneously allow the quantification of the incurred risk in terms of probability.

At the scale of a region or drainage area, one can utilize computerized data sets previously established according to a spatial discretization (square, zone, etc.), as input data for the model and perform simulations on each discretized element. The risk probabilities obtained for each zone considered homogeneous at the discretization scale can be mapped over the entire region. This approach combined with the use of an interpolation method, such as the kriging technique, could in some degree allow the automatic mapping of the level of vulnerability of the water tables within the studied area.

Being simple, the VULPEST model can be used by non-specialists. However, these eventual users will have to be sufficiently critical with respect to the model input variables and parameters. The representativity of the results at one site is directly linked to that of these variables and parameters which are provided by users. Users will also need to be qualified to analyse and interpret statistical results of the model in terms of the level of vulnerability and with respect to the norms that they will have themselves established.

6. CONCLUSION

The VULPEST model appears as a useful tool for the evaluation of groundwater vulnerability to contamination by pesticides. It allows the quantification of the contaminant risk of penetration, by evaluating the quantities of pesticide that can reach the water table. Making use of input parameters distributions that represent their spatial and temporal variability, it provides a statistical result.

This result can be interpreted in terms of level of vulnerability by means of comparison with pre-established norms.

This approach allows the mapping of groundwater vulnerability to a given pesticide as well as the study of the impact of this pesticide (thus permitting one to lighten the regulation and the technical aspects of its use).

Finally, given its simplicity of use, its rapidity of execution and the usual availability of the required data, the VULPEST model is accessible to competent, but not necessarily specialized managers.

7. ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Ministry of the Environment, Canada; and to the Donner Canadian Foundation for financial support for this study.

NOTES

- 1) Van Genuchten, M.Th., 1981. Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. *Journal of Hydrology*, 49, 213-233.

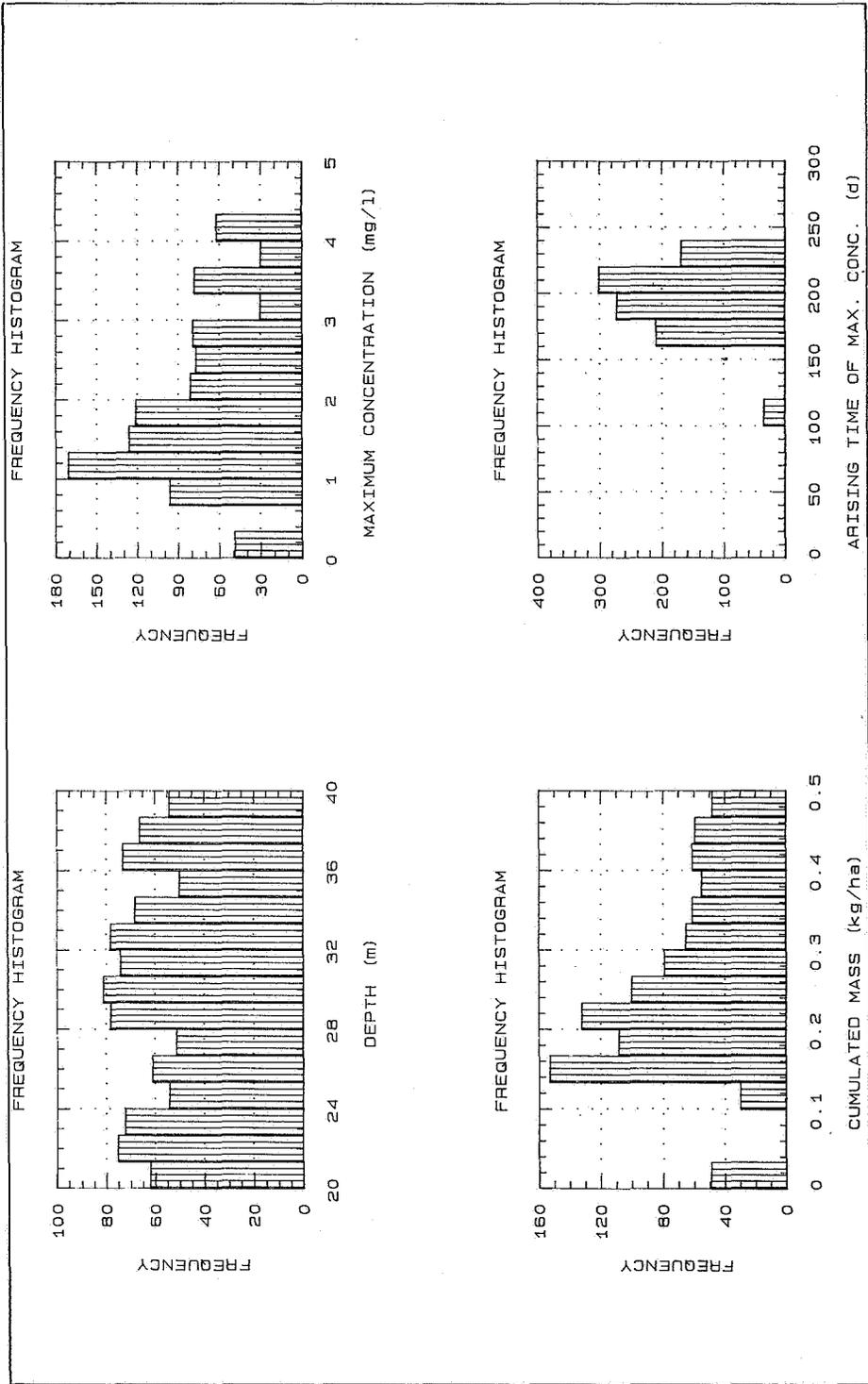


Figure 1. Effect of an uniform distribution of depth values

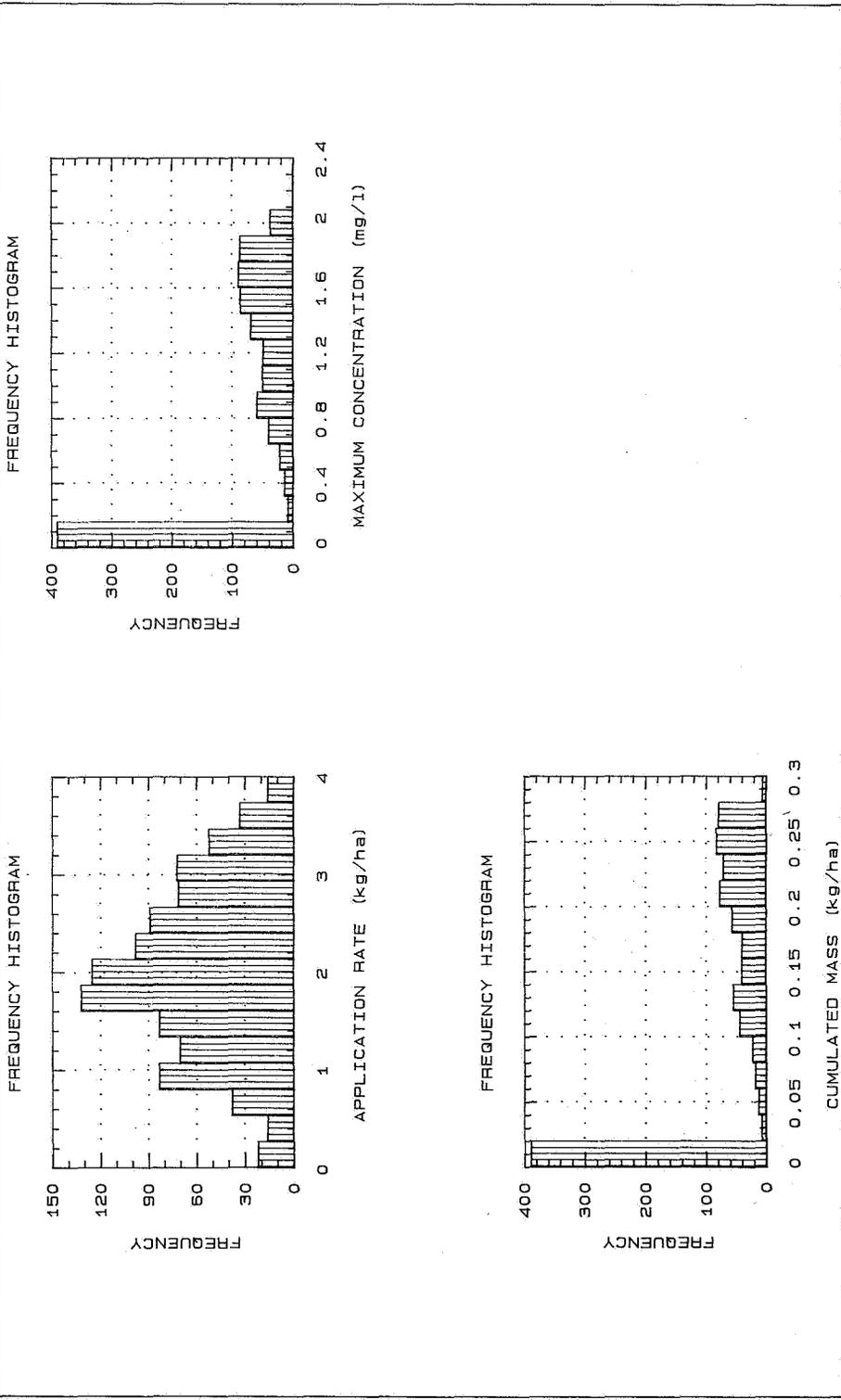


Figure 2. Effect of a normal distribution of application rates

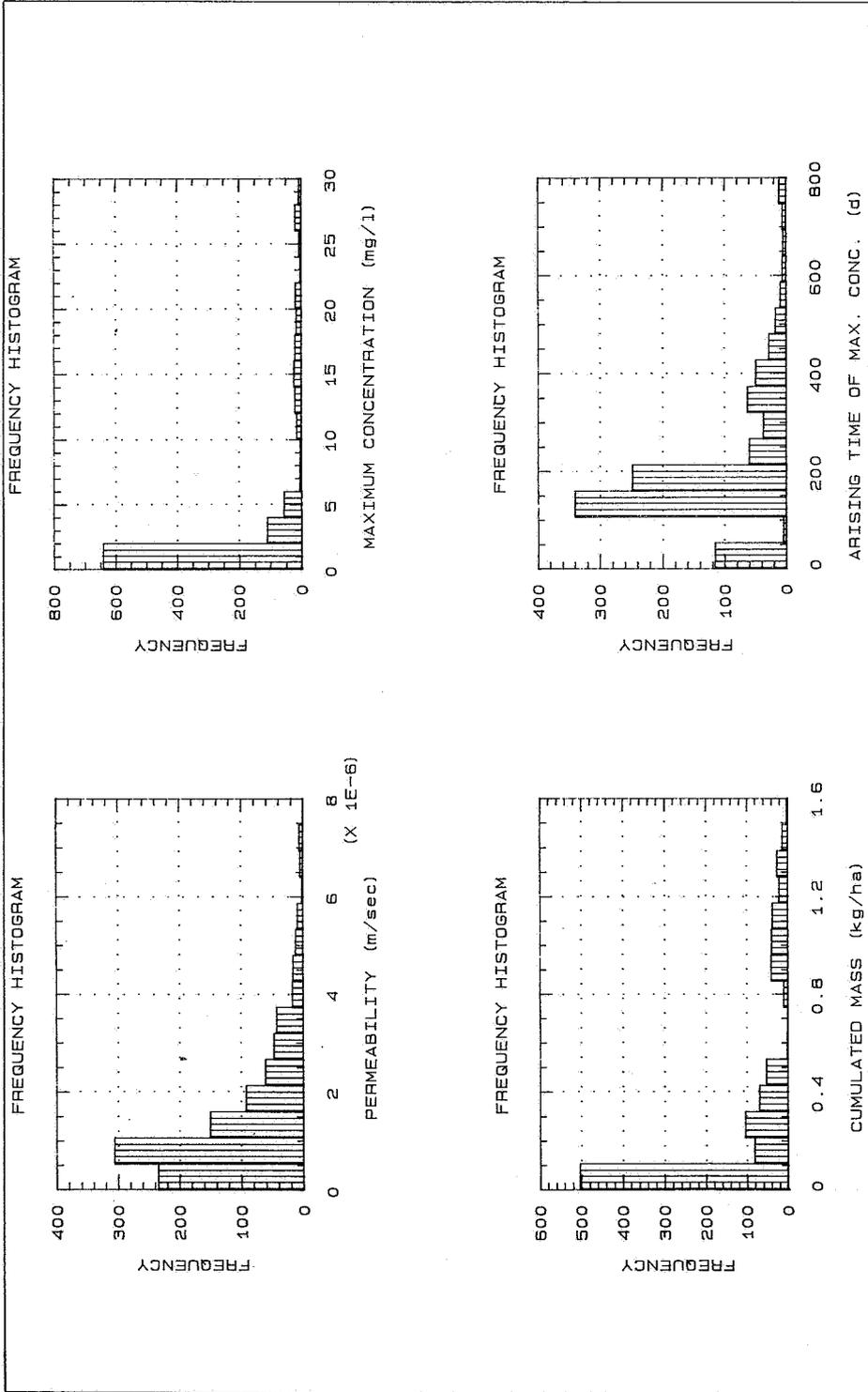


Figure 3. Effect of a lognormal distribution of permeabilities

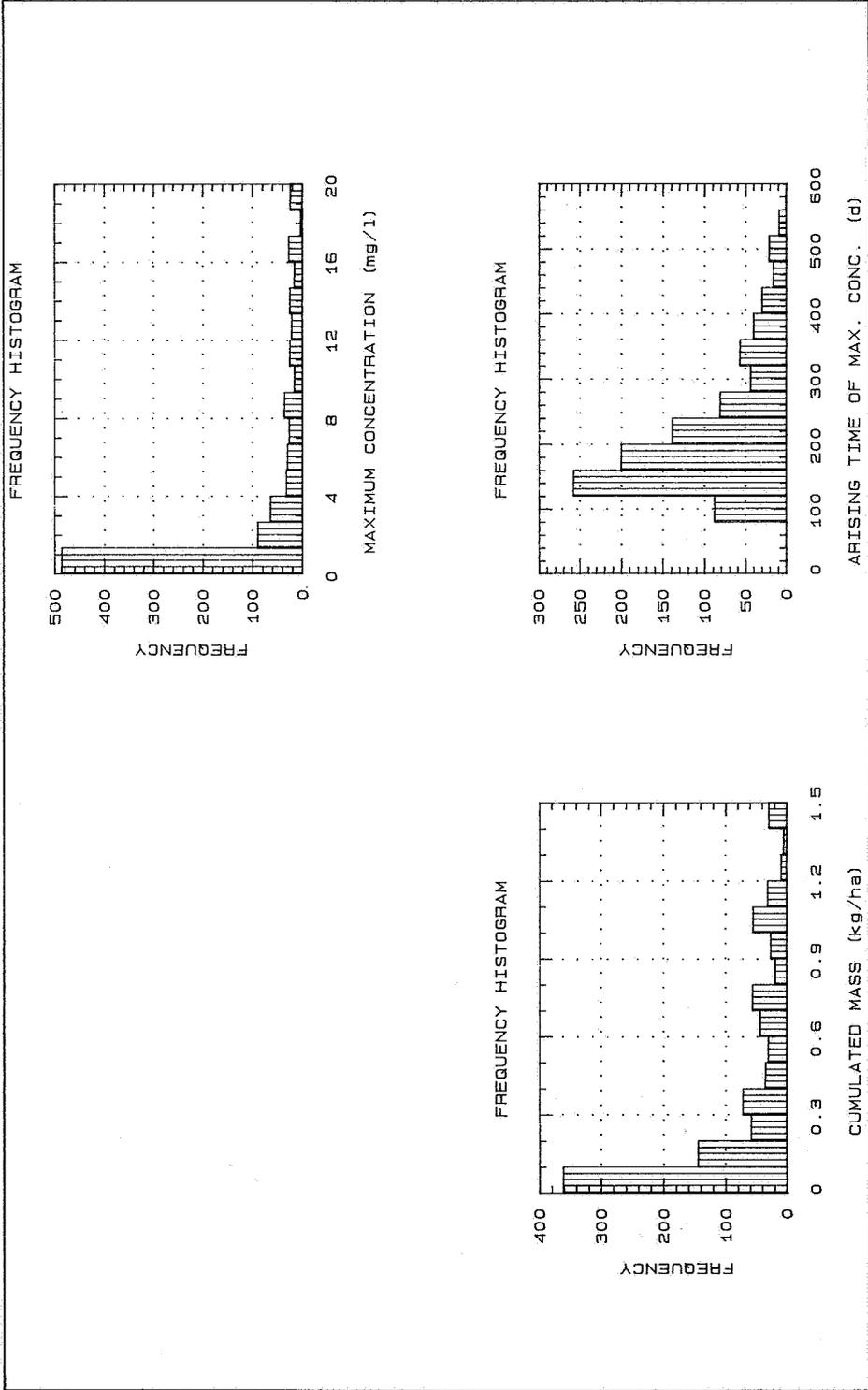


Figure 4. Effect of the three distributions of parameters

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