PROSPECTIVE TERRESTRIAL ENVIRONMENT AND GROUNDWATER POLLUTION RESEARCH CONFERENCE

Göteborg, 15-18 November 1998

Prospective terrestrial environment and groundwater pollution research conference

Göteborg, 15-18 november 1998

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Summary of recommendations

GPoll (Groundwater Pollution) is a long-term programme, initiated by European Science Foundation in Strasbourg, aiming at promoting multi-national, inter-disciplinary research on pollution of groundwater by chemical substances, radionuclides and by excess nutrients (http://www.esf.org/esf.org/GPoll). The Swedish Foundation for Strategic Environmental Research - MISTRA - supports strategic environmental research with a long-term perspective directed towards solving major environmental problems (http://www.MISTRA-RESEARCH.se). The research supported by MISTRA is to be organised in the form of a number of broad-based inter- and multidisciplinary programmes, so called MISTRA programmes. One of MISTRA's four scienticfic committees, the committee for strategic terrestrial environment and groundwater research, especially addresses groundwater pollution issues.

This report gives the outcome of a conference identifying to the GPoll steering committee, the MISTRA committee and the scientific community the most urgent and important research tasks for preventing further terrestrial environment and groundwater pollution and for restoring already caused pollution. The most important recommendations are listed below:

1. Inter- and multidisciplinary collaboration between hydrology, biology, geology and chemistry together with experts in modelling should be promoted through both national and international scientific programs, workshops and fellowships.

2. New sampling strategies should be developed, particularly for hard rock. Methods for analysis and detection should be standardised, especially for organic pollutants. Accurate determination of very low concentrations of pollutants must be advanced. Methods for molecular subterranean microbial diagnostics need development. We should increase our understanding of the relevance of low concentrations of pollutants and how they interact with suspended matter, humic substanses and colloids in groundwater.

3. The relevance of up-scaled (or down-scaled) media properties and biogeochemical processes needs to be investigated with regard to their use in quantitative models. Transport processes in groundwater must be investigated with emphasis on the coupling of flow and biogeochemical processes, their reaction dynamics and kinetics. The importance of sludge and sediment transport with groundwater also needs to be investigated. Modelling of process integration is important, as is a posterior analysis of models. Predictive models must be optimised with respect to available subsurface data quantity and quality.

4. When groundwater becomes polluted, techniques for delivering remedies to the contaminated site, without causing additional problems elsewhere, require novel approaches. Methods must be refined to analyse and trace the fate of microorganisms used for biodegradation. The biological potential for natural attenuation ("self cleaning") should be studied under field conditions. All these approaches require basic research on subsurface processes. The GPoll aims:

   - analysis and detection
   - physical transport
   - chemical transformation and immobilisation
   - biotransformation

   should be in focus

5. An European groundwater pollution database containing pertinent physical, chemical, biological and geological data should be built.

Göteborg den 7 December 1998

Karsten Pedersen
chairman of ESF scientific program GPoll
chairman of the MISTRA committee for terrestrial ecosystems and
groundwater strategic research

The following table is an attempt to put the conference recommendations in a broader perspective.

RESEARCH AREA	BASIC RESEARCH	APPLIED RESEARCH	EXPERIMENTAL DEVELOPMENT	ENGINEERING PRACTICE
Analysis and Detection	- accurate determination of flow concentrations of organic pollutants - metal speciation - molecular microbial diagnostics - methodology for pollution plume detection	- adequacy of sampling with respect to natural conditions and immobilisation - methods of coupling and analysis of different long-term series	- cheaper analytical methods - quicker analytical methods - more relibile analytical methods	- standardisation
Physical Transport	- relevance of scale and heterogeneity - transport related media characterisation and parametrisation - coupling and dynamics of flow and mass transport related processes - models: improved conceptualisation, process integration, parametrisation and prediction uncertainty quantification	- sensitivity analysis of factors involved - model testing	- model development and testing - search for cost-effective models	- methodology and solutions for engineering practice
Chemical Transformation and Immobilisation	- processes in unsaturated conditions - mineral matrix related immobilisation - retardation coefficients definition	- soil protection layer impact on aquifer vulnerability - dissolution processes from landfills	- barrier design development	- barrier design recommendations (pollutant and conditions specific)
Biotransformation	- biotransformation of inorganics - biotransformation of organics - biotransformation in saturated and unsaturated porous environments	- impact of biotransformation products - case specific biotransformation - biotransformation speed-up	- biotranformation techniques - biotransformation technologies	- biotransformation of ore wastes (sulphates, heavy metals and organic pollutants)
Impact on Organisms and Ecosystems	priority of other ESF programmes	Priority of other ESF programmes	priority of other ESF programmes	priority of other ESF programmes
Remediation Activities and Measures	- microbial response - black box system	- pollutant adapted remedial measures - case specific remedial measures	- cheaper techniques - more effective techniqes - success rate evaluation methods	- Industrial remediation techniques - Industrial remediation technology
Prevention	- controlling factors - communication	- pollution assessment methods - intervention capacity	- refinement of monitoring - intervention procedures - land use planning	- pollution risk assessment - monitoring standardisation - pollution deterrence

1 European initiatives for groundwater pollution research

1.1 The European Science Foundation scientific program on groundwater pollution

A clean and safe source of drinking water is regarded by the United Nations as a fundamental human right. Many European countries depend on groundwater for drinking water supplies. As this water becomes increasingly polluted, they are faced with two options: Develop increasingly complex and expensive methods of cleaning the water, or risk the consequences to human health of drinking polluted water. Groundwater pollution is, of course, also of concern in environmental terms. Most of the groundwater participates in the hydrological cycle although the residence time may vary from months to centuries. A schematic representation of the hydrological cycle in Europe is given in Figure 1.

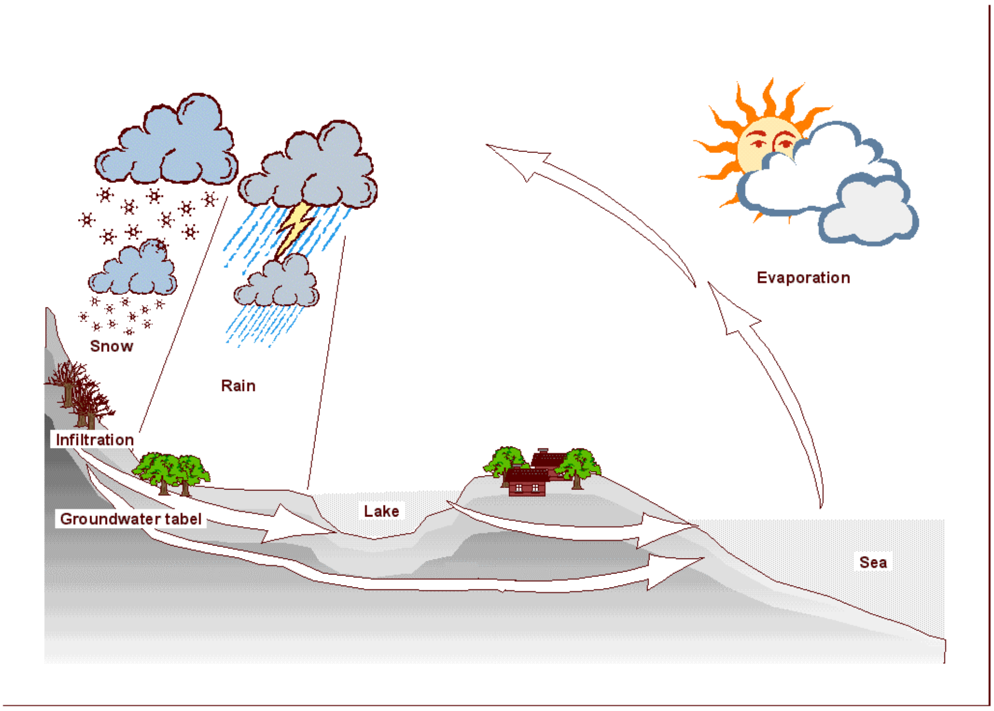

Figure 1: *The hydrological cycle is driven by the sun and gravitation. Not more than 10% of the precipitation over Europa fall directly to lakes and rivers, a part (10-40%) is captured by the vegetation as interception whereas the main part of the rain and snow infiltrate into the ground. Runoff from surface water systems is generally transported much faster than the transport of water through the ground. Residence times of water in the ground can be from days to hundreds of years and longer. That is why groundwater in many cases reacts slowly on pollution.*

GPoll (Groundwater Pollution) is a long-term scientific programme, initiated by European Science Foundation (ESF) in Strasbourg, aiming at promoting multi-national, inter-disciplinary research on pollution of groundwater by chemical substances, radionuclides and by excess nutrients. It focuses on pollution in groundwater systems because of their significance for human and environmental health. The research has urgency because of the sharp increases in the incidence of pollution-related disorders and the increasingly conspicuous damage caused by pollution to natural ecosystems. The processes causing groundwater pollution often only become apparent over the long term. Hence, the programme includes planning for long-term research and monitoring programmes.

The programme is subdivided into seven parts:

- Analysis and detection
- Physical transport
- Chemical transformation and immobilisation
- Biotransformation
- Impact on organisms and ecosystems
- Remedial measures
- Prevention

The emphasis in the programme is on fundamental and strategic research that has potential for use in maintaining clean water supplies. Determining whether prevention of a specified kind of pollution is urgent, requires research on the fate and impact of the pollutant, or mixture of pollutants, and on the remedial measures required to degrade, immobilise or contain them. European collaboration provides added value, partly because pollution is international, and also because environmental problems require interdisciplinary research. No single country can provide all of the necessary expertise and therefore international co-operation is essential between centres of excellence in different subject areas. The aim is to encourage the best scientists from widely different disciplines to engage in environmental research, and to co-operate internationally.

1.2 Mistra

The Swedish Foundation for Strategic Environmental Research - MISTRA - was established in January 1994 with a capital of SEK 2.5 billion, deriving from the former Employee Investment Funds. MISTRA´s funds are held in form of Swedish and foreign shares and securities and are managed by well-established asset managers. The capital is now, 1998, close to SEK 4 billion. The income earned on the capital is used to support strategic environmental research. MISTRA´s budget for activities in 1998 amounts to SEK 300 million.

Article 1 of MISTRA´s statutes provides the basis for MISTRA´s activities: "The Foundation shall promote the development of strong research environments of the highest international class with importance for Sweden´s future competitiveness. The research shall be of importance for finding solutions to important environmental problems and for a sustainable development of society. Opportunities for achieving industrial applications shall be taken advantage of."

MISTRA supports strategic environmental research with a long-term perspective directed towards solving major environmental problems. The research should meet the highest scientific standards and be guided by a vision of an environmentally sounder society. It should promote sustainable use of resources, radically reduced environmental impacts, or essential new knowledge about environmental problems and their relative significance contributes to Sweden's competitiveness. It must have clear and measurable objectives, enabling it to be effectively evaluated. The research supported is to be organised in the form of, on one hand, a number of broad-based inter- and multidisciplinary programmes, so called MISTRA porammes. They should create strong research environments, linked into national and international networks, promote the recruitment, training and mobility of researchers. They should also involve the participation of industry, public agencies and other stakeholders, and have effective management structures that ensure integration and cross-pollination between projects. On the other hand, so called MISTRA projects should encourage and bring to light new ideas and subjects areas, promote the work of young researchers, and serve as a complement to MISTRA programmes.

2 Sources and classes of groundwater pollutants

Pollution enters the groundwater system from different sources. A convenient way to distinguish these sources is:

- **Diffuse pollution** input from different sources including the atmosphere and from agricultural use of fertilisers and crop protecting chemicals.

- **Local pollution** from point sources including industrial sites and waste dumps.

- **Subsurface infrastructure pollution** including sources like storage facilities, tunnels and pipelines.

The priority pollutants to be considered are:

- Agrochemicals including fertilizers and pesticides

- Hormones and antibiotics

- Fuels and other solvents

- Metals including radionuclides

- Microorganisms and viruses

The fate of the pollution in the groundwater system determines to a large extent the quality of the groundwater resources used by man and surface ecosystems. Our current knowledge of the subsurface processes that occur in the groundwater is insufficient to predict the fate of most pollutants. One of the purposes the ESF scientific program GPoll was to identify a research agenda to ensure the sustainable use of groundwater supplies. The suggestions for research are derived from a schematic representation as shown in Figure 2. It addresses processes in the subsurface based on input of water, input of pollutants, geochemical properties of the subsurface, and biogeochemical activities therein.

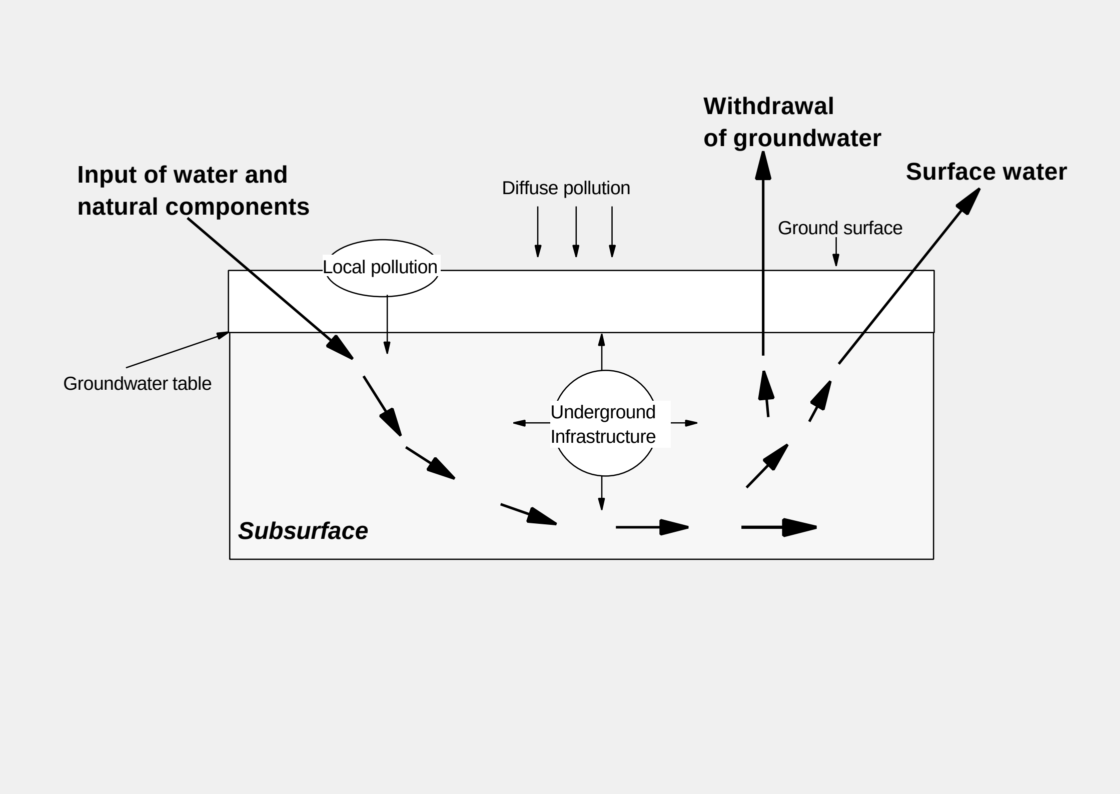

Figure 2: *Input of water from the surface to the subsurface generates groundwater. Groundwater may receive pollutants from three principally different sources. More then 50-70% of the drinking water in Europe is drawn from the subsurface. The quality of such drinking water reflects the many different processes and possible pollutants groundwater meets during its flow underground.*

3 The conference

At the first GPoll steering committee meeting mid May 1998 it was decided that a conference should be organised that focussed on urgent groundwater pollution research issues. The MISTRA committee delegates agreed on the need of this conference at their first meeting, end of May 1998. This report gives the outcome of that conference identifying to the GPoll steering committee and to scientific community the most urgent and important research tasks for preventing further terrestrial environment and groundwater pollution and for restoring already caused pollution. It was regarded especially important to identify urgent areas of research that presently lack sufficient attention from the scientific and public communities. This task required that documents were prepared in advance of the conference, summarising opinions in various fields of expertise. They are compiled in this conference volume (section 7). The GPoll steering committee meet directly after the conference to set the topics for 1999 call for fellowships and workshops, according to the outcome of the conference.

The conference program included working groups that in three sessions should treat the different aims of GPoll according to the program given next.

4 Conference progamme

Saturday 14th Nov 1998

During the afternoon	Arrival of most participants	
20:00 hrs	*Dinner*	

Sunday 15th Nov 1998

10:00 - 10:30 hrs	*Coffee*	
10:30 - 11:00 hrs	**Introductory remarks** Presentation of conference delegates, (K. Pedersen)	
11:00 - 13:00 hrs	**Analysis and detection; Physical transport.** Conference room 1, Chairman: M.Veselic	
	Miran Veselic	Physical transport in pollution spreading and control
	Katarina Abrahamsson	Occurrence and analytical aspects of petroleum in crystalline bedrock
13:00 - 14:30 hrs	*Lunch*	
14:30 - 17:30 hrs	**Analysis and detection; Physical transport.** Conference room 1, *Chairman:* M. Veselic	
	Jerker Jarsjö	Groundwater pollution: Modelling flow and transport processes at the field scale
	Sonja Lojen	Environmental isotopes in groundwater pollution investigations
15:00 - 15:30 hrs	*Coffee*	
	Joao Paulo Lobo-Ferriera	Flow and transport of miscible tracers in the vadose zone
17:30 hrs	*Dinner*	
19:45 - 20:45 hrs	Visit to worlds largest maritime museum (optional), http://www.gmtc.se/eng/shipmuseum.htm	

Monday 16th Nov 1998

08:30 - 12:30 hrs	**Chemical transformation and immobilisation; Biotransformation.** Conference room 1, *Chairman:* B. Svensson	
10:00 - 10:30 hrs	*Coffee*	
	Bo Svensson	Biotransformation of organic

		pollutants of relevance for contaminated soil and groundwater.
	Eckart Bedbur	Natural and artificial barriers as a tool for remediation of contaminated groundwater.
	Walter Gläßer	Pollution of the environment by heavy metals from copper shale mining in Central Germany: dispersion, transport and immobilisation
	M. Isenbeck-Schröter	Occurrence and transport of contaminants in groundwater: two examples to show site- and milieu-specific aspects
	Bo B. Lind	Long-term changes of groundwater quality due to atmospheric deposition and remediation activities
	Horst D. Schulz	Models for the combination of transport and geochemical reactions in groundwater
12:30 - 14:00 hrs	*Lunch*	
14:00 - 18:00 hrs	**Impact on organisms and ecosystems; remedial measures; Prevention.** Conference room 1, *Chairman:* Wim Harder	
	Wim Harder	Processes in the subsurface: from black box towards understanding
	Göran Bengtsson	Adaptation and habitation - key processes in sustainability and remediation
	Thomas Nilsson	Environmental Quality Criteria for Sweden
	Karsten Pedersen	Microbial processes in hard rock aquifers and their potential influence on hydrocarbon pollution and radionuclide migration
	Ute Rößner	*In-situ* bioremediation of contaminated aquifers - scale up investigations
	Mirja Salkinoja-Salonen	Microbial activity in cold climate
16:00 - 16:30 hrs	*Coffee*	
18:15 - 19:15 hrs	Visit to The East Indiaman Götheborg Adventure (optional) Http://w1.317.telia.com/?u31703617/index_eng.htm	
19:30 hrs	*Dinner*	

Tuesday 17th Nov 1998

08:30 - 12:30 hrs	**Split up in working parties**
10:00 - 10:30 hrs	*Coffee*
	Analysis and detection; Physical transport: Room E36 Katariana Abrahamsson Sonja Lojen Joao Paulo C. Lobo-Ferriera Miran Veselic *(group leader, reporter)*

Tuesday 17th Nov 1998
Continue

	Chemical transformation and immobilisation; Biotransformation: Room E37 Bert Allard Eckert Bedbur Walter Gläßer Margot Isenbeck-Schröter Bo Lind Horst Schulz Bo Svensson *(group leader, reporter)*
	Impact on organisms and ecosystems; Remedial measures; Prevention: Room E38 Göran Bengtsson Jan de Bont Wim Harder *(group leader, reporter)* Thomas Nilsson Karsten Pedersen Ute Rößner Mirja Salkinoja-Salonen
12:30 - 14:00 hrs	*Lunch*
14:00 - 15:30 hrs	**Working parties continue**
15:30 - 16:00 hrs	*Coffee*
16:00 - 17:00 hrs	**Working parties continue**
18:00 hrs	*Dinner*

Wednesday 18th Nov 1998

08:30 - 11:00 hrs	**Report from working groups.** Conference room 8 *Chairman K. Pedersen*
08:30 - 09:15 hrs	**Impact on organisms and ecosystems; Remedial measures; Prevention.** *Wim Harder*
09:15 - 10:00 hrs	**Analysis and detection; Physical transport.** *Miran Veselic*
10.00 - 10:30 hrs	*Coffee*
10:30 - 11:15 hrs	**Chemical transformation and immobilisation.** *Bo Svensson*
11:15 - 12:00 hrs	**Concluding discussion**
12:00 - 13:30 hrs	*Lunch*

5 Conference participants

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6 Report from the working groups

Three inter-disciplinary working groups were put together with the task to particularly penetrate two or three of the aims of GPoll (1.1) and to identify important research areas that GPoll and MISTRA should support.

The groups were:

Working group 1:	Analysis and detection, physical transport
Working group 2:	Chemical transformation and immobilisation, biotransformation
Working group 3:	Impact on organisms and ecosystems, remedial measures, prevention.

6.1 Working group 1

6.1.1 Analysis and Detection

Uncontrolled use of organic compounds lead to the occurrence of a new generation of pollutants in the surface and groundwater, such as antibiotics, hormones, halogenated compounds and hydrocarbons (see 7.2) etc. To be able to reliably investigate this kind of pollution at low concentrations, new methodologies need to be developed. **Representative sampling** is the basis of any accurate determination of concentration or transformation of these compounds (see 7.4). Interaction of pollutants with solid surfaces is of special concern for their distribution in the subsurface environment. Due to the lack of standardisation of analytical methodology, misleading results can be obtained.

To assess the impact of **metals** on the environment, special attention should be paid to their **speciation** (see 7.7).

Molecular microbial diagnostics needs intensive further development if we want to know who is doing what in the ongoing subsurface microbial processes and which are the dominant organisms.

To detect an existing pollution, the limits and the direction of its spreading and the location and extension of its source, sensitive, accurate, quick and cheaper methods have to be developed.

***Table 1** Priority list of research needs with respect to analysis and detection*

1 Standardisation of analysis and detection, especially for organic pollutants.

2 Develop sampling strategies, particularly for hard rock.

3 Accurate determination of very low concentrations of pollutants.

4 Increase our understanding of the relevance of low concentrations.

5 Interaction between pollutants and suspended matter in groundwater.

6.1.2 Physical Transport

The relevance of **scale and heterogeneity** to the conceptualisation and parametrisation of porous media and to an appropriate **up-scaling** and **down-scaling** of its models must be further researched by means of the appropriate physical models of these media as well as *in-situ* to be fully understood (see 7.3).

To properly understand and forecast pollution propagation, porous **media characterisation and parameterisation** must be made with respect to the mass transport. Media characterisation with this respect is still uncertain in very heterogeneous (fractured and karstic) rocks. Rock parameter acquisition, relevance and representativeness have still to be improved at the general level.

Flow and mass transport, governing pollution propagation in the groundwater, are dependent on physical, chemical and biological processes (see 7.1). An appropriate **coupling of** these **processes** must be achieved as well as a better understanding of process and/or reaction dynamics (see 7.10). Further, the role of suspended matter transported in groundwater as a pollution carrier must be investigated and incorporated.

***Table 2** Priority list of research needs with respect to physical transport*

- Characterisation of media for appropriate up-scaling and down-scaling.
- Investigation of transport processes with empasis on the coupling of processes, their reaction dynamics and kinetics.
- The importance of sludge and sediment transport with groundwater.
- Modelling of process integration.
- A posterior analysis of models.
- Optimisation coupling tools.

6.2 Working group 2

6.2.1 Chemical Transformation and Immobilisation

Pollution of groundwater is the result of a redistribution of elements or components leading to unacceptable concentration levels. A detailed understanding of the transport is therefore needed for the analysis and prediction of a particular case of groundwater pollution (See the priorities of working group 1, Table 2).

The physical transport of pollutants in subterranean systems to the groundwater, e.g. from a point source or a diffuse source (Figure 2), is directly dependent on the speciation, i.e the chemical state of the particular element or compound. The speciation and any change of it is determined by the over-all biogeosphere processes that govern the hydrochemistry and the transport route. Parameters of particular importance are pH, the redox potential, particularly the presence of redox sensitive elements (Fe, S, As, Se as well as O, N) and the presence of complexing ligands.

The transport of a trace metal depends on the speciation of the solution which is continuously determined by the composition of the aqueous phase (see 7.8 and 7.14). Of particular importance is the formation of stable complexes with organic acids (notably humic substances and other polycarboxylic acids). The trace component is distributed between a stationary solid phase, mobile suspended solid phases and the mobile aquatic phase through adsorption / desorption processes.The suspended solid phase is either a stable mineral or organic / biologic matter of a size in the colloidal range or a precipitate that is formed when a sparingly soluble system exceeds the solubility limit. The kinetics of the distribution is governed by a fairly rapid adsorption, a slow diffusion into the pores and a slow, coupled desorption/ diffusion process. Advection is moving the whole package of water with suspended particulate matter, which is undergoing sedimentation / filtration during the water route.

The adsorption / desorption reflects the complex coupled interactions between the matrix of the solid, colloidal matter forming a surface layer. This will involve e.g. a negatively charged clay phase interacting with a positively charged oxide surface, organic matter (negatively charged at pH above pK_a) and the dissolved trace constituent (organic as well as inorganic).

Research areas to address enabling an understanding of the mobilisation and immobilisation mechanisms are therefore:

- Thorough studies of **the speciation of target element** and compounds require detailed knowledge on the hydrochemical factors. Thus, dynamics in the proton concentration as well as the concentration of redox active compounds have to be known.

- The mobilisation and immobilisation of metals and organic compounds by **the carrier function of humic substances and other colloids**. The formation and disintegration of colloids and the presence of more stable particles and aggregates and their velocity in the groundwater flow should be investigated. This is important because of the sorption interaction between these structures and particles with elements, organic and inorganic compounds. The compounds may be subjected to enhanced transport velocities by being sorbed in this manner. Substances with low water solubility may be sorbed or bound to humic substances or other colloids. Humic materials may accelerate the transport rate of the contaminant. The role of moderate or high organic matter content in groundwater should be studied in order to quantify carryover of secondary contaminants.

6.2.2 Biotransformation

Organic compounds mainly of anthropogenic origin make up a wide spectrum of pollutants identified in soil and groundwater. They belong to almost all varieties of substituted and unsubstituted aliphatic and aromatic compounds. Biotransformation of such compounds, either intrisic or facilitated, is one way of preventing the polluting compounds from reaching target organisms which would react on their toxicity or resulting in water not accepted for use for drinking or irrigation (see 7.5). Thus, efforts are taken to study and utilise biotransformation in order to remediate soils and groundwaters. There are several cases reported, where successful biotransformation of polluted areas have occurred. A challenge is to study and decide if a polluted area should be left for **natural attenuation** or if it should be subjected to more active **remediation measures**. The primary source of pollution should always be tracked and eliminated if possible.

The chemical structure of an organic pollutant giving its physical properties will form the background for its aptitude to be degraded. Organic pollutants of anthropogenic origin i.e. new compounds synthesised by man as well as petroleum products of different refinery grades are in analogy with their naturally formed cousins dependent on a row of parameters among which are:

- Ability to function as a substrate i.e. as carbon and/or energy source or as electron acceptor.

- Suitability for co-metabolic transformation.

- Toxicity to microorganisms.
- Solubility in water – concentration levels.
- Sorbtion features.

Upon these compound specific properties microorganisms able to transform the compound will need nutrients and electron donors or acceptors and a suitable physical-chemical environment e.g. appropriate pH and redox conditions. A combination of the above features will govern the fate of a certain compound or group of compounds in relation to biotransformation. This means that the kinetics and thus the degree of persistence of a compound will be determined by these properties. In order to assess the extent of biotransformation of a compound or a mixture of compounds polluting a groundwater basin a row of parameters have to be studied:

- **Mobility and transport** as mediated by different phases, i.e. dissolved in water and/or attached to different colloids and particles. This means that a handle on the hydrology dynamics is necessary (see 6.1.2). This would likely mean that a thorough modelling of the hydrological regime over time and space at different scales is needed to arrive at the transport velocities for a compound in a particular aquifer.

- Appropriate **analytical chemical tools** to follow the extent of transformation and distribution in the basin area are needed (see 6.1.1). The occurrence of intermediates released into the environment also calls for such tools. Due to different matrix characteristics, demands for modification or development of methods may be raised, which may also be the case for possible intermediates.

- **The availability of nutrients, electron donors and/or acceptors**, i.e. the input and/or replenishment of these components (via chemical or (micro) biological routes) should be addressed in order to understand the dynamics of transformation rates and patterns (see 7.6 for example). This will strongly link to the chemical transformations and physical conditions set by the matrix medium. Thus, weathering rates and exchange of redox active compounds with each other may pose constraints on the biotransformation rates.

- Organic compounds and metals may become fixed in the matrix, which renders them inaccessible to further transformation reaction or mineralisation. Such fixation is not necessarily stable. **Conditions affecting its reversibility** need to be studied.

- Basic knowledge of **the underlying microbiology** is essential in order to interpret the patterns observed in the field and in supporting laboratory studies. Therefore, the regulation of the physiology of single microorganisms and the interaction among them are important to study.

Investigations along the lines above may call for **studies at different scales** i.e. in time and space as well as in the form of different levels of complexity of the system. Thus, field, macro- and microcosm and stratified laboratory studies. The interpretation and integration of reinforced studies into the field reality is a challenge, which should be addressed by modelling efforts. Interdisciplinary strategies should be included in the protocols for this type of research.

6.2.3 An Interdisciplinary Approach

The complexity of natural systems requires **interdisciplinary research** as well as a combination of different scales of investigations. If parameters obtained from simplified systems like e.g. batch experiments do not match field observations, *they should not be used to generate models*. The complexity of the field situation should be scaled down to experimental set-ups in order to define parameters matching the system dominating processes. The field investigations as well as the experiments have to be designed in close co-operation of different scientific groups as e.g. geologists, geochemists, biologists and modellers. This target can be achieved by an appropriate funding of interdisciplinary research activities:

- Vulnerability of aquifers to **disturbance of steady state conditions** in the biogeochemical balance.

- Changes in **the input-output situation** as e.g. variation in the water table may instabilise the geochemical steady state conditions and lead to severe damages, for instance pyrite oxidation. This is reflected in changes in pH and/or pE, leading to changes in the ion content as well as the mobility of pollutants. The factors determining the vulnerability of the system towards such disturbances, e.g. reduction-oxidation capacity or the buffer capacity, are poorly understood and are in need of research effort.

- Effects of **changing land use** on groundwater quality.

- Harvesting boreal forests by **clear cutting often damages groundwater quality** e.g. by increasing the groundwater contents of aluminum and other undesireable ions and also organic substances. Similar problems are linked to other **changes of land use**. The processes linking the biogeochemical groundwater system with deposition, hydrological regime and the living ecosystem are not sufficiently known to give the scientific community tools for predicting or avoiding groundwater damage (see 7.9).

6.3 Working group 3

This working group rapidly concluded that the three aims to be discussed, impact on organims and ecosystems, remedial measures and prevention, only could be addressed with appropriate basic knowledge about subsurface processes. The report of this group, therefore, came to constitute the frame within which the research priorities of working groups 1 and 2 fit very well.

6.3.1 Processes in the Subsurface

The basic approach taken was to consider processes in a small-scale representative cell (scaled down box) taken from the subsurface system (see 7.11). This approach allows us to consider a multitude of cases ranging from heavily polluted point sources to processes related to diffuse pollution and covering both well understood reaction mechanisms and descriptive rate measurements. The aspects to be addressed are summarised in Figure 3.

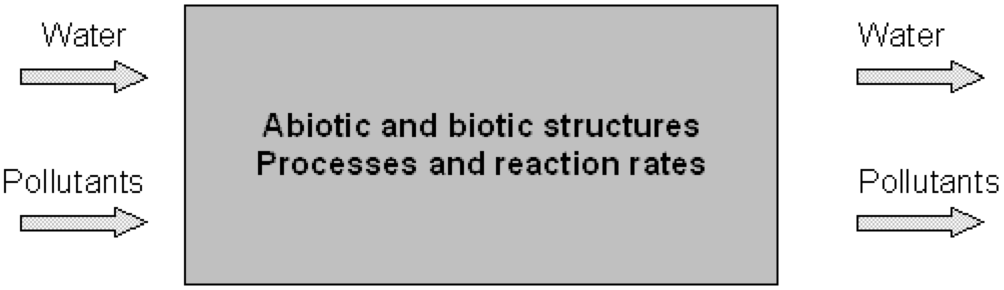

Figure 3. *The small scale box for study of subsurface processes*

The processes in this small grey box are governed by the input parameters water and polluting chemicals, the characteristics of the abiotic matrix, and the microbial activity (see 7.13). We have particularly considered the biological agents in this small scale box, and in addition to the development of molecular diagnostics to determine the nature of the dominant organisms, feel the need for an appropriate physiological characterization of the microbiological potential relevant to the prevailing micro-environmental status. In particular attention should be paid to the generally low temperature of the subsurface environment (see 7.15), the often oligotrophic nature of the organisms involved, and the distribution of pollutants between the aqueous and solid phases in the system. The small scale boxes may be considered as suitable experimental systems that can provide relevant information at the laboratory scale. They may take the shape of aquifer microcosms e.g. sediment columns.

If sufficient information of representative cells of the subsurface system has been generated, the next challenge is to upscale the processes in both time and space. The quality of upscaling is strongly dependent on the understanding of the small-scale processes and the scale-dependent heterogeneity of the system.

We strongly recommend to build and manage, similar to the existing PANGAEA database in the marine sciences, a European GPoll database which should contain information about the geological, geophysical, hydrological and biogeochemical properties of the subsurface, about the behaviour and toxicity of pollutants, about ongoing research and available results.

The present conference convincingly demonstrated to the participants the usefulness of interactions between scientists from different disciplines in addressing complex environmental problems. A similar interdisciplinary research effort is required to improve the existing knowledge base.

Table 3 *Priority list of research needs with respect to subsurface processes*

1. Encourage inter- and multidisciplinary collaboration in hydrobiogeochemistry through workshops and fellowships.

2. Development and use of suitable laboratory systems (small scale boxes) to study processes under relevant boundary conditions.

3. Development and use of molecular diagnostic techniques for the characterization of the biological agents.

4. Studies of the biological potential, natural attenuation, under field conditions.

5. Build and manage an European Gpoll database containing pertinent physical, chemical and biological data.

7 Contributed presentations

7.1 Physical transport in pollution spreading and control; Miran Veselic

7.1.1 Pollution spreading

Pollutant immission into the groundwater at the pollution source may be direct or indirect. When direct, a pollutant is injected directly into the saturated zone of the aquifer. When indirect, it is disposed within the aquifer's unsaturated zone, within the adjacent aquitards (low permeability rock bodies) or to the land surface above the aquifer. With indirect pollutant disposal, a concentrated pollution inflow affects the aquifer much faster than a disperse one. Again, with indirect pollutant immission, surface disposal, activating the soil's filtration and biological decay potentials, retains and reduces the pollutant propagation additionally.

Spreading of water pollution from the source shall be regarded as a transport of mass or energy through the subterranean water retaining porous medium. The 'mass' of some substance (similar for the energy) is being moved by water through the saturated or unsaturated porous medium. The mechanisms affecting the pollutant transport in such a medium are advective, dispersive and diffusive fluxes, solid-fluid interactions, various chemical reactions and decay phenomena, which can be regarded as source-sink phenomena for the pollutant. And as far as the biological pollution is considered, the above list of mechanisms has to be enlarged by the biological processes, defining the endurance of a given species or pollutant within the groundwater environment.

7.1.2 Physical transport in terrestrial environments

7.1.2.1 Flow and mass transport in porous media

Traditionally, the water flow rate was calculated by Darcy's law and the mass transport by the advection-dispersion equation. The Darcy's law can be applied when the flow is laminar and the media homogeneous. In a heterogeneous medium, even with a known permeability distribution, it does not determine the mean permeability nor provide exact results for the local flow rate, velocity or water particle residence time variations. With a wide water particle residence time distribution, the minimum observed residence times may be much shorter than calculated.

The advection-dispersion equation gives good description of the solute transport in a homogenous porous media, if the fact that the coefficient of mechanical dispersion is flow velocity dependent is taken into account. It is important to note that the involved dispersion coefficients have to be experimentally determined by the non-sorbing tracers.

In the highly heterogeneous, fractured porous media the advection-dispersion equation does not give correct description of the solute transport, since the flow in fractured rocks is taking place in channels and in fractures. With a few extremely conductive channels, i.e. with a wide channel conductivity distribution, the high conductivity pathways may lead to channelling over long distances. If, within an observed distance, the channels intersect very often, a Fickian type dispersion will result and an adequate advection-dispersion model may be applied. If, on the contrary, the channels intersect very seldom, the flow situation approaches to that of parallel independent tubes. In the latter case, the solute residence time will be shorter and the dispersion smaller than given by the advection-dispersion model.

For the solutes, interacting either chemically or physically with the solid matter in the rocks, the residence time distribution can be very much different from that of the water. A porous medium can be divided into three flow domains: the mobile (gravitationally flowing) water, the stagnant water (in micropores) and the solid matter (matrix). Flow residence times of the flowing water can be approximated as a quotient of flux and of effective porosity. In fractured and karstified rocks, the latter is generally several orders of magnitude smaller than the total porosity. The solutes penetrate the stagnant water by molecular diffusion. If, due to small matrix blocks and long residence time, all of the matrix porosity (stagnant water) is accessible, than the solutes residence time will be determined by the total porosity and will be much greater than that of the water. If, due to the large blocks (long diffusion distances) and relatively short water residence time, most of the matrix porosity may not be involved, than the solutes residence time will be substantially that of the water. Partial matrix penetration of the solutes, occurring with the intermediate cases, will result in a large residence time distribution and break curve dispersion.

The solute retardation is proportional to the square of the flow-wetted surface, which is the contact surface of the flow domain to the matrix (block) domain. The magnitude of this surface has a dominating influence on the residence times of sorbing tracers regardless of the transport model applied. Unfortunately, correct determination of this surface is not easy. For flow through pores of the intergranular media, it can be deduced from grain size distribution data. For flow through fractures, it can be derived from their density, length and fraction of their effective opening (generally a few percent of the fracture area). For flow through channels, it can be deduced from the data on channel density, lengths and widths.

To give an insight into the nature of fluid flow, mass transport and particle sorption, our past discussion focused on the pollutants that perfectly dissolve and mix (dilute) in the water and which, do not change the water flow properties and its water-rock interactions. Even here, we had to distinguish between the sorbing and the non-sorbing species. Actually, several types of vastly different fluid flow to pollutant mass transport relations exist, giving birth to different types of pollution propagation. We can distinguish between the following pollutant mass transport types:

a) Soluble and well mixing (diluting) species that do not change water flow and rock wettability properties; advection, dispersion, diffusion and retardation (sorption, decay) mechanisms are involved; examples: radioactive tracers, various salts

b) Soluble and well mixing (diluting) species that change water flow and rock wettability properties; advection, dispersion, diffusion mechanisms are involved but little retardation; example: detergents and other surfactants

c) Soluble, but poorly mixing cases due to a change in the water density and flow properties; advection, dispersion, diffusion and retardation (cooling) mechanisms are involved; examples: hot water, salty marine water

d) Nonsoluble but well mixing species that do not change water flow and rock wettability properties; advection, dispersion, and retardation (dying, decay) mechanisms are involved but no diffusion; examples: bacteria, viruses, colloids, suspended matter

e) Poorly soluble but nonmixing fluids creating multiphase flow conditions; advection, dispersion and retardation (sorption, oxidation, decay) are active within the pollutant phase flow domain, solution at the phase boundary and advection, dispersion, diffusion and retardation of dissolved species in the water flow domain; examples: various non-aqueous phase liquids (NAPL) with light (LNAPL) and dense (DNAPL) varieties

Mass transport mechanisms with respect to the water flow are practically identical for the above enumerated types a) through d) - they all adhere to the single phase mixing flow conditions of which our past discussion was representative. Type b) is changing only the water flow properties, which may lead to better channelling and less dispersion. With type c) poor mixing becomes important with low gradient and velocity flows; yet it is very obvious with hot springs in fractured aquifers. Finally and obviously, concerning type d), suspended matter in general (bacteria and viruses involved) can not be moved by diffusion. We shall not enumerate here all possible retardation mechanisms, which may differ considerably from species to species and from case to case. The retardation effects, however, may differ characteristically between the enumerated types of pollution propagation.

Flow and mass transport conditions of the above type e) are quite different from the previously observed. The movement of the polluting fluid is governed by the same laws and influenced by the same porous media properties as previously elaborated for the single-phase fluid flow. However, as its density, viscosity, relative rock wettability and saturation are different from that of the aquifer water, its flowing velocity is very different from that of the adjacent water. Generally, such polluting fluid bodies move relatively slowly. Due to this, the dissolution of various species at the water-polluting fluid interface is generally the governing groundwater polluting mechanism. Then the resulting type of mass transfer becomes the already discussed type a) of the mixing flow conditions.

The unsaturated flow domain shows many particular features as far as the pollutant transport is considered. The fluid flow is mostly vertical, the pore saturation is seldom complete and therefore the flow retarded, capillarity and water retention play an important role, as do the sorption processes, bacterial activity and oxidation (especially in the soil horizon). All this is resulting in the well observed and known fact that most of pollution deactivation takes place in the unsaturated zone.

The mass transport in the unsaturated fractured media is influenced by the specifics of the unsaturated flow in such media and by their mass transport related properties. The pore surface area and, especially, the flow-wetted area of such rocks are much smaller than those of the rocks with intergranular porosity. Pollutant fixation will therefore be much smaller. Due to the nature of such rocks, especially when carbonate rocks are considered, the surface covering soils are thinner and the infiltration flows are faster, all this giving less time for pollutant decay. As already pointed out when discussing the unsaturated flow, the matrix porosity flow is preponderant within the unsaturated zone. Therefore, greater matrix porosity within the unsaturated zone will lead to a greater pollutant fixation potential. With such rocks, weathering can provide for some additional matrix porosity within the unsaturated zone.

7.1.2.2 Flow and mass transport related models of porous media

With the stochastic models set appart, three types of conceptually different, more or less deterministic models are used to model fluid flow and mass transport within the porous rocks. Remark more or less refers here to the way in which the porous media are being described within a given type or subtype of such models, whose basic characteristics are as followed:

1. Continuum or equivalent continuum models - Porous rocks are represented as a spacial replication of a representative elementary volume (REV) and in such a way statistically homogenized. With a continuum model, the dispersion-advection equation is applied for such media. With an equivalent continuum model, the fractured rock masses are assimilated to the equivalent porous media and the fluid flow within such media is modelled. Variables are defined by their average values rather than by their distribution.

2. Discrete flow models - With these models, fluid flow in the discontinuities or channels is explicitly modelled. To do this, the governing flow equations are either derived for the individual discontinuities or channels or as the mass flow equations for the complete discontinuity or channel network. In the first case, the variables are defined for the individual discontinuities. In the second case, the discontinuity (or channel) network variables are defined either for the individual, clearly distinguishable discontinuity (channel) sets, or stochastically, with an equivalent random probability distribution function.
3. Double and triple porosity models - Rock matrix and the discontinuity (channel) network are considered here as two distinct but overlapping continua, modelled with different but hydraulically coupled models. Rock matrix is modelled with an equivalent continuum model and the discontinuity network is generally modelled in the same way.

Discrete flow models were an attempt to overcome the problems posed by the REV definition and the resulting drawbacks of the computational results of these models.

Field experience has evidenced that flow and mass transport through such porous media are scale dependent. For flow distances being orders of magnitude bigger than the adequate REV, the advection-dispersion model looks adequate. For flow distances ranging from one tenth to some orders of REV, the fracture or channel network flow models seem appropriate. For flow distances shorter than some orders of REV, the channel flow model seems the most suitable. The above statements reveal that the flow and transport behaviour are relative scale and not absolute scale dependent. The appropriate flow and transport model selection will therefore depend on an adequate description of the intrinsic structural and flow features of the porous media.

In case of fractured media, it seems that by the discrete flow models it is possible to avoid the necessity of a REV definition and to predict the large scale transport behaviour of such media on the basis of its small scale definition. But, as far as known to the author, discrete flow models were tested only within the low permeable fractured rocks. They still have to be verified for the highly permeable and karstic rocks that constitute the aquifers, interesting from the point of view of water resources. For such aquifers the double or triple porosity models have been generally applied when the simple continuity model failed to furnish adequate results.

The described conceptual models were derived to model the fluid flow within the saturated media. Most of them are also used to model the fluid flow within the unsaturated media. Yet, it shall be pointed out on the conceptual level that in the unsaturated fractured porous media, the fluid flow is restricted to microfractures and avoiding macro-fractures before sufficient saturation is achieved. For this reason, when single continuum, double porosity or any other model is applied to the unsaturated fractured media, the saturation dependant changes in the active fracture (network) distribution and the involved fracture (network) parameters has to be taken into account. It is rather doubtful that the channel network models are the most appropriate ones for that type of job, since the channel distribution certainly reflects the distribution of the largest conduits and hence of macropores.

Finally, when modelling the fractured rock masses subjected to the strongly varying pressure fields (close to the underground or surface excavations and to the large pressure changes surrounding deep wells), the hydromechanical coupling, allowing for the stress related fracture network deformations, must be taken into account. This requires the coupling of the fracture flow models with the elasto-plastic mechanical models of the fractured rock mass.

7.1.3 Pollution control

To control the water pollution once it occurred from a pollution source, one has to be able to simulate the processes that govern the pollution transfer at least qualitatively. A throughout quantitative simulation of the pollutant transfer is the desired ultimate tool of a perfect pollution control. The resulting computing models should enable engineers and planners to predict the distribution of a given pollutant within an aquifer as a function of its rock and flow characteristics, of the pollutant chemical and biological stability, of the pollutants' input area and of the time elapsed between the pollutant immission and the observed distribution period.

7.1.4 Research deficits and objectives

The ultimate groundwater pollution research objective is to provide reliable groundwater pollution prognostics, needed for physical planning and pollution control. A concerted research, involving basic and applied research as well as experimental development and, study of the current engineering practices is further needed to achieve this objective. Basic research should yield understanding, formulation and parametrization of the involved mechanisms and processes. Applied research should provide environment and pollution type specific transport models. Experimental development should made them more case specific. And finally, study of engineering practices should provide us with draw backs feed back.

7.2 Occurrence and analytical aspects of petroleum in crystalline bedrock; Katarina Abrahamsson

7.2.1 Introduction

The technique of storing petroleum products in large underground bedrock cavities has been used for a long time in many countries, both for military and civilian purposes. Only in Sweden, there are around 100 facilities of which some have been emptied and others are still in use. The walls of the caverns are usually left bare for economic reasons, and therefore the stored products are in direct contact with a large bedrock surface during decades. It is most feasible that petroleum products could contaminate the rock surrounding the storage cavities during all phases of the operation, during filling, storage, emptying and after decommissioning.

7.2.2 Description of the caverns and their operation

The storage caverns could be surrounded by either a fixed or a movable groundwater bed. During the excavations, groundwater is pumped out of the caverns and thereby the surrounding rock is drained. In caverns with a fixed groundwater bed the petroleum products are filled into the emptied cavern, while caverns with movable beds are first refilled with water before loading of the petroleum. In both cases, it is probable that during the loading phase, petroleum products can flow out of the cavity, at least in some fractures.

During storage, the system is pumped so that the cavities are under-pressurised. In a movable bed facility, the pressure level is often regulated by a tube connecting the lower part of the cavern with a tank that has an overflow at a certain level. In this way an almost constant pressure level will be secured over the entire operation. Still, it can be expected that the groundwater pressure above the caverns give only limited isolation of the product within the caverns.

After the petroleum products have been pumped away, the caverns will be filled with water up to the level of overflow, thus, the pressure in the caverns will remain the same. Also, an additional method to minimise the movement of product in the surrounding rock could include lowering the water level by means of active pumping, which will result in a reduction of the pressure within the cavity. In this way the movement of water will be towards the cavern, which will increase the probability that the product which remains in the rock will return to the cavern.

After decommissioning, the pumping of the facilities will cease and the water level in the cavern as well as the groundwater level will rise. This will re-saturate the surrounding rock, which may lead to changes in flow directions and flow rates for fractures. In this way, product that was previously immobilised may again become mobile.

Extensive studies of the penetration of petroleum products have been performed in highly porous matrices such as sand stones, but little is known about crystalline rock which constitutes the rock surrounding the petroleum storage facilities in Sweden.

7.2.3 Mobility of petroleum products

The massive rock is very seldom homogeneous. Consequently, petroleum products could be found in larger “pockets “, in fractures both macroscopic and microscopic, as well as in the pores of the rock. The mobility of the petroleum is also governed by the physico-chemical properties of the individual compounds that constitute the product. Of special concern is of course the compounds with the largest water solubility, such as low molecular weight alkanes and aromatic compounds.

From an environmental perspective several questions arise after decommissioning when all activities have ceased, especially

1. How much of petroleum is left in the crystalline rock ?

2. Will leaching of petroleum products from the crystalline rock to water containing fractures be of environmental concern for extended period of time?

3. Which is the rate of anaerobic degradation of petroleum products in bedrock?

7.2.3.1 Analytical procedures

In order to be able to answer these questions, adequate analytical methods have to be developed for both groundwater and the rock itself. The very complex nature of petroleum makes it difficult to accurately assess the amount of petroleum found in different matrices. Therefore, the choice is always to try to evaluate which compounds, or group of compounds that should be measured. For the most common compounds in petroleum, there are methods available for their determination in water. However, methods for the determination of petroleum in crystalline rock are scarce.

7.2.3.2 Groundwater

Access to groundwater is usually not to complicated, since a number of holes have usually been drilled during the exploration of the site. Also, if the operation area is close to villages, samples could be taken in wells used for drinking water. If, however, samples are collected in drilled holes, the diameter of the hole is usually rather small, approximately 5 cm, which makes sampling more complicated. Water could be pumped, but care must be taken to avoid contamination from the pumps, and usually teflon tubing is needed. Specially designed samplers, with small outer diameters could be used. However, the small diameter inevitable leads to small sampling volumes, which could be a problem if the expected concentrations are in the nmol l^{-1} range or lower.

Pre-concentration of water samples is a necessity, and is easily performed with liquid-liquid extraction, or solid phase extraction. Solid phase micro extraction could be a technique to make pre-concentration easier in the field, and it could be an extremely useful technique for monitoring of contaminants for longer period of times in integrated water samples.

The most common analytical technique is chromatography, especially capillary gas chromatography - mass spectrometry (GC-MS), which is a powerful analytical tool for quantitative measurements of organic componds in complex matrices.

7.2.3.3 Crystalline rock

Access to relevant rock samples is more complicated and more costly than for water. Since the rock is so heterogeneous, the chances of finding the area, which is contaminated, are very small. During coring, special care must be taken, since it is extremely easy to contaminate the sample from the drill rigg, and also, there is a large risk to contaminate the cores due to passage through petroleum-filled fracture zones. Therefore, the use of a so called triple-tube corer is preferable.

Traditionally the occurrence of petroleum in crystalline samples has relied on UV fluorescence, which restrict the choice of measurable components to fluorescent molecules. More reliable are methods that determine individual compounds, mostly performed with chromatography. Potential methods for pre-concentration of analytes include liquid-liquid extraction, pyrolysis or supercritical extraction, which all have been used for analysis of pourus matrixes such as soil, ash or sedimentary rock. These techniques would need the sample to be crushed prior to the extraction, and there would still be insecurities regarding the total amount of components in the sample that have been extracted. The crushing of the rock also increase the risk for contamination, and losses due to heat. Another way, which we have used successfully, is digestion of the rock prior to extraction.

Preparation of reference material is an additional complication, and we have experienced discrimination between substances when *in vitro* samples have been prepared, for instance when petroleum has migrated into evacuated bedrock.

The determinations are again preferable made with GC-MS.

7.2.3.4 Degradation products

The detection and quantification of anaerobic degradation products in groundwater can provide details about the status of the microbial degradation processes involved in rock associated with storage caverns. This could give us a tool to a more rapid, and less costly, way of increasing our knowledge at a specific site, about the level of, and rate of degradation of petroleum. Therefore, efforts should be made to develop analytical methods in order to be able to identify indicators of microbial degradation in anaerobic rock environments. Low-molecular-weight organic acids could be a first approach as described by Cozzarelli *et al*. (1994).

7.2.4 References

Cozzarelli I.M.; Baedecker M.J.; Eganhouse R.P. and Goerlitz D.F. 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater. *Geochimica et Cosmochimica Acta* **58** (2) pp 863-877.

7.3 Groundwater pollution: modelling flow and transport processes at the field scale; Jerker Jarsjö , Georgia Destouni and Vladimir Cvetkovic

7.3.1 Abstract

The understanding and quantification of field scale flow and transport processes is important for predicting spatial and temporal changes of groundwater quality. Here, we discuss the modelling of physical transport of pollutants, by which we mean general transport aspects that are independent of the biogeochemical properties and transformations of specific pollutants; in a general modelling formulation, different biogeochemical properties may be handled as different parameterisation cases. Due to the inaccessibility and heterogeneity of the subsurface environment, relevant models for subsurface water quality changes are by necessity statistical. The key to reliable statistical modelling of dissolved pollutant movement is a description of coupled hydraulic and biogeochemical processes that accounts for the effects of subsurface heterogeneity in the transition from the scale of local measurements to the field or regional scale of model prediction. A particular issue of interest in future research is the *characterisation* of subsurface properties and existing contaminant plumes from the local to the regional scale. Such characterisation is necessary for developing relevant *quantitative models* of pollutant transport which account for coupled flow and biogeochemical processes under conditions of heterogeneity and provide descriptions of transport based on the statistical information that can realistically be extracted from the subsurface. An important research challenge is how to develop and implement these models such that they both account for the most dominant processes and are sufficiently simple and transparent to be *reproduced* by independent experts within a reasonable time frame, and be useful within a risk assessment and decision-making framework. With regard to non-aqueous phase liquid (NAPL) flow and transport, the research front lags behind that of solute transport and needs to be advanced in terms of quantitative approaches to account for inherent fluctuations and prediction uncertainties in heterogeneous subsurface systems.

7.3.2 Introduction/ the pollution problem

Groundwater composition change is a result of interactions between natural material flows and anthropogenic fluxes of trace metals, organics, nutrients, and radioactive and toxic substances. Understanding and quantification of the field scale flow and transport processes is important for the prediction of the spatial and temporal changes in groundwater quality, regardless of which specific groundwater pollutant is being considered. In turn, such predictions constitute the basis for practical decisions regarding remediation, protection and control measures.

Different pollutants interact in different ways with the environment. However, the fate of each pollutant is largely affected by the properties of the subsurface. The subsurface is generally spatially heterogeneous, implying that both physical and biogeochemical properties often vary highly and irregularly over a wide range of scales. In addition, there is temporal variability, for instance in temperature and groundwater recharge.

From the viewpoint of physical transport modelling, groundwater pollutants may be divided into two main categories, namely:

1. Pollutants that are easily dissolved in water

2. Non-aqueous phase liquid (NAPL) pollutants, characterised by low water solubilities.

Both category (1) and (2) may sorb onto the solid phase and react in different ways with the surrounding medium. However, whether various reactions and decay processes are of importance for a specific pollution problem is again not dependent on the pollutant properties alone, but also on the properties of the porous/fractured medium and the time scale(s) relevant for the pollution problem. For instance, a decaying substance may be considered to be inert if the loss of mass due to decay is small over the relevant time scale(s) of a specific pollution problem.

Hence, one important step towards the understanding and quantification of a specific groundwater pollution problem is to identify and quantify the processes, properties and time scales relevant for that problem. In some cases, the solution of a pollution problem may even lie in changing these properties in a favourable way. For instance, one remediation measure for the cleanup of NAPLs, such as chlorinated hydrocarbons, is flooding with alcohol-surfactant-solvent solutions. This implies considerably increased NAPL solubility in the water phase and changes in the interfacial properties, such that the originally immobile NAPL may be removed by pumping and treating the surrounding groundwater.

7.3.3 Current knowledge

Pollutants in the subsurface are transported by the water movement, and are retarded and/or transformed by physical and biogeochemical processes. Key retention/transformation processes for dissolved contaminants may be summarised as follows: chemical sorption-desorption (e.g., adsorption, ion exchange), diffusive mass transfer into and from immobile (stagnant) water (e.g., intra-aggregate porosity, low conductivity lenses), and degradation in form of biodegradation (by microbial populations), irreversible sorption, or decay. In most cases, several of these processes act simultaneously, with critical factors being the rates of reactions and their (ir)reversibility. Chemical sorption is generally fast and reversible (equilibrium) but may be non-linear for high concentration levels. Diffusive mass transfer is a relatively slow and linear process, most appropriately described as non-equilibrium and reversible. Degradation is a non-equilibrium and irreversible process that may be described as linear or non-linear, depending on the type of degradation considered.

Key features of aquifers are *heterogeneity* and *inaccessibility*. Complex thermomechanical and chemical forces have shaped the subsurface properties over geologic time. The result of these long-term processes is heterogeneity on scales that may range from centimetres to kilometres. Subsurface heterogeneity often exhibits more or less distinct structural features (e.g., soil horizons, macropores, fractures and fracture zones, faults, lithofacies, lenses). However, even within seemingly uniform structural components (say a soil horizon, a fracture zone, or a sand aquifer), subsurface properties are characterised by random variations.

Spatial variability in the hydraulic properties of soils and aquifers has been extensively documented over the past three decades. Furthermore, mounting evidence from field and laboratory investigations indicates that parameters which directly or indirectly affect reactions (e.g., specific surface area, pH, organic content, mineral composition, microbial density), as well as directly measured reaction parameters (e.g., the distribution coefficient, sorption capacity) also vary randomly in space. Some cross-correlation between the reaction and hydraulic parameters (such as hydraulic conductivity, porosity) is plausible, although currently available field and laboratory data are inconclusive about the exact nature of such correlation. Such spatial variability and possible cross-correlation between hydraulic and biogeochemical properties may greatly affect the fate of pollutants in the subsurface and needs to be accounted for in all pollutant transport problems (see, e.g., Dagan and Neuman, 1997).

The presence of NAPLs in the subsurface implies partial blocking of the natural water flow paths. Many investigations have addressed relations that govern unsaturated NAPL flow in porous media. Thereby, considerable knowledge has been gained regarding this blocking effect on water flow (caused by the presence of the NAPL), as well as regarding the flow of the separate non-aqueous liquid phase in porous media (see, e.g., Kueper and Frind, 1992). However, there are relatively few investigations that have addressed unsaturated NAPL flow in porous media under conditions similar to those prevailing in the field with spatially variable properties, or unsaturated NAPL flow in fractured media. Porous medium type of relations for unsaturated flow, for instance, have been applied to fractured media, even though these type of relations generally rely on experimentally determined parameters that may be very difficult or impossible to acquire for fractured media. Since the pore geometry of a fractured medium differs considerably from the pore geometry of a porous medium, it is plausible that alternative representations may turn out to be more appropriate for fractured medium applications. Due to the general lack of experimental data, the few alternative models that have been developed have so far not been thoroughly evaluated. Moreover, the research front with regard to NAPL flow and transport in heterogeneous media lags behind that of solute transport in terms of possible approaches to account for inherent fluctuations and prediction uncertainties in heterogeneous subsurface systems.

7.3.4 Ongoing research, examples

Examples of ongoing, general research areas that involve modelling of the physical transport of pollutants in the subsurface and may be both relevant and important for different groundwater pollution problems are:

- spatial-temporal upscaling of the quantitative pollutant transport description, from laboratory to field or catchment scales
- quantitative coupling of pollutant fluxes through different geohydrological and/or biogeochemical subsurface systems, such as unsaturated soils and underlying aquifers
- quantitative coupling of relevant biogeochemical and physical transport processes for different groundwater pollution problems, such as heavy metals leaching from mining wastes, or nutrients leaching from agricultural areas
- quantitative aquifer and contaminant plume characterisation
- multiphase flow and transport, e.g., NAPL flow and transport in aquifers, or two-phase flow in fractured rock
- quantification of rapid flow and pollutant transport through preferential pathways, such as macropores, clay fractures or rock fractures
- solute retention in fractured rock
- evaluation of prediction uncertainties for risk-assessment
- setting the pollutant transport modelling in a decision making framework
- coupling pollutant transport modelling with economic modelling

7.3.5 Prospective research

A particular issue of interest in future research is *characterisation* of subsurface properties from the local to the regional scale, as well as of existing contaminant plumes in the subsurface. Specific open questions in this context can be formulated as:

- What are the most effective testing methods and strategies?
- How can the biogeochemical properties/parameters be estimated on the field scale?
- What is he relevance of chemical and microbiological parameters obtained in the laboratory for field scale predictive modelling?
- To what extent can geophysical methods be used in characterisation?
- How practical are partitioning tracers for plume characterisation?
- How can we most effectively evaluate the extent of natural attenuation of existing plumes?

Due to aquifer inaccessibility and relatively high costs of data acquisition, few field measurements are usually available for the characterisation of subsurface transport properties. Moreover, movement of pollutants can in most cases be monitored at relatively few locations, even though the spatial distribution of a contaminant plume is, as a rule, highly irregular and uncertain. Thus, there is a need to develop *quantitative methods* (models) for predicting the fate of pollutants in the subsurface, which:

- account for coupled flow and biogeochemical processes under conditions of heterogeneity, and
- provide descriptions of transport based on statistical information that can realistically be extracted from the subsurface.

Modelling of groundwater pollutant transport constitutes an integral part of risk assessment, that is itself a part of a decision-making framework. The key issue for predictive modelling in the context of risk assessment is *reproducibility*. Most current models that can cope with the complexities of subsurface pollutant transport are numerical and are becoming increasingly intricate and cumbersome. As a result, modelling exercises for predictive purposes are becoming increasingly exclusive, making it impossible to independently check or reproduce the modelling results. Thus an important challenge is how to develop and implement models for physical transport that:

- on the one side, account for the most dominant processes
- on the other side, are sufficiently simple and transparent, such that transport calculations can be reproduced by independent experts within a reasonable time frame, and be useful within a risk assessment and decision-making framework.

With regard to modelling of NAPL flow and transport, the presence of NAPLs in the subsurface implies partial blocking of the natural water flow and constitutes an additional degree of complexity affecting the NAPL spreading with the groundwater. This is in contrast to transport and spreading of dissolved substances, which in most cases do not affect the natural water flow paths. Although the effect of this partial blocking on flow is relatively well known on a laboratory scale, the implications for NAPL transport on the field scale constitutes an open research area. There is a need to:

- investigate whether stochastic approaches that have proved useful for quantifying reactive solute transport in heterogeneous subsurface systems can also be applied to describe NAPL flow and transport at the field scale, and
- quantify associated prediction uncertainties.

7.3.6 References

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7.4 Environmental isotopes in groundwater pollution investigations; Sonja Lojen and Milena Horvat

7.4.1 Abstract

Environmental isotopes are used as natural tracers for water tracing, as well as for study of the transport and reaction pathways of dissolved compounds, giving information about their origin, possible precursors from which they were formed and their interactions and transformations. They are rarely studied on an exclusive basis, but should be incorporated into interdisciplinary research on the chemical and biological transformation and immobilisation of the pollutant of interest.

7.4.2 The problem

Groundwater pollution has become a world-wide problem due to the many forms of domestic, agricultural and industrial use of freshwater, involving both point- and non-point sources of various organic or inorganic pollutants. In some regions, water scarcity is even more acute due to climatic conditions or anthropogenically induced changes in the hydrological regimes of groundwater. The vulnerability of groundwater depends generally on the hydrogeological conditions; in some cases such as karst areas, target distance limits of pollution can be extremely high and often unpredictable because of complicated hydrology. To estimate or to predict the transport pathways of pollutants, movement of the water mass in certain hydrological conditions through the aquifers must be known. Since the early 1960s, the employment of nuclear techniques for water resource assessment, development and management, has been promoted by the International Atomic Energy Agency (IAEA) in Vienna as one of the most promissing tools in the peaceful uses of the atom. In water resource investigations stable or radioactive environmental isotopes, i.e. naturally occurring and artificial isotopes, that are introduced into the (ground)water as tracers or pollutants are used. The application of environmental isotopes is a potentially powerful tool to study the physical transport and transformations of all pollutants that contain or are bond to compounds containing a particular environmental isotope.

Environmental stable isotopes that are of potential interest for groundwater pollution studies are:

- Isotopes composing the *water molecule* itself - ^{2}H, ^{18}O - are applied as conservative natural tracers for identification of the origin of water, determination of recharge areas, hydraulic connections between aquifers, aquifer leakage, mixing between different groundwater bodies or with surface waters, irrigation, salinisation, or for identification of palaeowaters. Since the isotopic composition of water is subject to change during evaporation, condensation, or interaction with the bedrock through geothermal activity, such processes undergone by the water can be identified, too.

- The stable isotopic composition of *constituents dissolved in the water* is used to explain their origin, the dynamics of the hydrological system, the migration of contaminants in the system and biogeochemical processes that are taking place in the system.

- The isotopic composition of *contaminants or other compounds* dissolved in water is used to identify their sources and processes they have eventually undergone.

Environmental radioactive isotopes are most commonly used in hydrology for age determination. However, they can provide essential information for estimating transport mechanisms, fissure flow, identification of recent recharge, palaeowaters or rock-water interactions.

The most important environmental isotopes that are useful in groundwater research are listed in the table below.

Isotope (substance)	Half-life (years)	Application
^{2}H, ^{18}O (H_2O)	stable	origin of water, identification of recharge areas, hydraulic connections, aquifer leakage, mixing of water, salinisation mechanisms, recycling of irrigation water, geothermal activity
^{3}H (H_2O)	12.43	identification of recent recharge, transport in the unsaturated zone
^{3}He, ^{4}He	stable	determination of retention time
^{11}B ($B(OH)_3^-$, $B(OH)_4^-$)	stable	identification of sewage effluents
^{13}C (DIC - dissolved inorganic carbon, CH_4, organic compounds)	stable	origin of carbon compounds, identification of palaeowaters, groundwater dynamics, identification of sources and origin of pollutants, biomarkers
^{14}C (DIC, organic compounds)	5730	groundwater dynamics, identification of palaeowaters
^{15}N, ^{18}O (NO_3^-, NH_4^+, N_2, N_2O)	stable	groundwater dynamics, identification of palaeowaters
^{34}S, ^{18}O (SO_4^{2-}, S^{2-}, organic compounds)	stable	identification of sources of pollution, acidification, salinisation, acid mine drainage, groundwater flow in geothermal systems
^{32}Si	100	dating shallow groundwater, weathering rates, exposure ages
^{36}Cl	306 000	dating, rock-water interaction
^{37}Cl (Cl^-, CFC)	stable	identification of sources of pollution, salinisation
^{39}Ar	269	dating
^{81}Kr	210 000	dating

^{85}Kr	10,8	transport mechanisms (fissure flow), delineation of protection zones
^{234}U	250 000	dating, rock-water interaction

When studying groundwater pollution and its dynamics, the pathway of water from precipitation, infiltration and recharge to the sampling point or well must be known. Many physical and chemical processes such as groundwater mixing, interaction with the host rock (leaching, dissolution), as well as biological activity, affect the isotopic fingerprints of water and dissolved compounds, so an understanding of processes that take part in groundwater is essential for an interdisciplinary approach to pollution investigations. Stable and selected radioactive isotopes provide invaluable information on dynamics within the water cycle, especially on the atmosphere-surface-groundwater continuum. The IAEA in collaboration with WMO (World Meteorological Organisation) therefore started a worldwide network of precipitation collection stations, which led to the establishment of GNIP (Global Network of Isotopes in Precipitation). Further, intensive tritium measurement programmes in river, lakes and ground waters at selected sites representative of different climate zones took place.

Isotopic characteristics of groundwater constituents which are formation specific reflect the properties of the solid medium, i.e. soil and rock with which the water has been or is in contact, and biogeochemical processes that took place in the water or in contact with soil or host rock. Carbon, nitrogen and sulphur are biogenic elements that are most commonly dissolved in groundwater in different ionic species. They can be derived from precipitation, from soil or from interaction with the host rock in the unsaturated or saturated zone. Their isotopic fingerprints provide information on their source, on the conditions of recharge, geological characteristics of the host rock, and biogeochemical reactions occurring in the groundwater pathway from the point of precipitation infiltration to the sampling point [1]. In the cases of dissolved carbon, definition of its sources is a prerequisite for any interpretation of ^{14}C ages.

Environmental radioactive isotopes are most commonly used for groundwater dating. Since each water molecule in a water body has an individual history, a single groundwater age does not exist, and the distribution of individual ages is generally not known. So only model ages of groundwaters based on hypothetical age distributions can be calculated. The most common sources of environmental radionuclides are production by cosmic rays, natural radioactive decay and activation processes in the subsurface, and anthropogenic production by reactor operation and weapons' testing. For dating of young waters (<50 years), ^{3}H is most commonly used. However, since its activity has recently dropped practically to pre-bomb levels, dating of very young (some years old) waters has become problematic. So alternative methods of age determination such as measurement of CFC concentrations in groundwaters are receiving more attention. Each isotopic method is applicable within a certain age range and has its limitations since processes other than ageing may affect the isotopic composition, such as underground production (important for ^{36}Cl, ^{37}Ar, ^{39}Ar), interactions of water with the host rock (affecting mostly ^{14}C and ^{36}Cl), and uncertainty about the input concentration which may be poorly known or may vary with time (^{3}H, ^{14}C, ^{36}Cl and ^{85}Kr)[2] . ^{3}He and ^{4}He, both stable isotopes, often accumulate in groundwaters as a result of subsurface production through β decay of tritium or degassing from the Earth's mantle (^{3}He), or from radioactive decay of rock minerals (^{4}He). Their concentration in groundwater can be several orders of magnitude above the values in samples that have reached equilibrium with the atmosphere during infiltration. So high He concentrations can under some circumstances be used for determination of the residence time of water in a particular rock formation.

For analysis of the stable isotopic composition of particular compounds and some radioactive isotopic concentrations of heavy metals in environmental samples, highly sophisticated equipment is needed, such as isotope-ratio mass spectrometers (IR-MS), compound-specific GC-IRMS, isotope-dilution MS, high-resolution mass spectrometers with thermal ionisation mode or ICP-MS, or accelerator mass spectrometers. Commercially available high-performance equipment has become user-friendly; however, its price often restricts the availability of some promising techniques to the scientific and applied sciences/technological community.

Ongoing research on environmental isotope hydrogeology or biogeochemistry is manifold, dealing with specific regional topics. The IAEA organises regular biannual symposia on isotope techniques in water resource development and management where recent developments are presented. Here some case studies are mentioned:

- Use of environmental isotopes in organic contaminant research in groundwater systems[3] where ^{13}C and ^{37}Cl were used as tracers to define the sources and transformations of perchlorethylene (PCE), trichlorethylene (TCE) and 1,1,1, trichlorethane (TCA).

- Study of the influence of sedimentary organic matter on dissolved fulvic acids in groundwater and their significance for groundwater dating with ^{14}C in dissolved organic matter[4], where the influence of ^{14}C-free sedimentary organic matter was found to falsify the groundwater age calculated by the ^{14}C content of dissolved fulvic acids.

- Use of δ^{18}O and δ^{15}N of nitrate to determine sources of nitrate in early spring runoff in forested catchments[5], where atmospheric deposition of nitrate and ammonia in the snowpack and soil derived nitrate were analysed; it was proven that the nitrate pulse in stream water during early melt derived largely from precipitation from previous months or years that is flushed from storage

- Isotopic study of controls on the geochemistry of sulphur in an aquifer (East Midlands, U.K.)[6], where 8 different sources of dissolved sulphate in the groundwater were defined using a combination of isotopic and chemical analyses of diagnostic indicators including Br, Cl, Sr, B, $\delta^{13}C$ and nitrate
- Use of $^{234}U/^{238}U$ and ^{36}Cl as tracers for determining mixing of groundwater between a confined and an unconfined aquifer [7]
- Tracing of nitrate deriving from military activity in karst areas using $\delta^{15}N$[8]
- Use of ^{15}N isotope dilution and direct gas measurement in nitrification/denitrification studies in swamp forest soils [9]

In any case, however, environmental isotopes cannot be used as tracers alone without an extended set of hydrogeochemical data.

In Slovenia, environmental stable isotopes are used in two fields of research dealing with groundwater: karst hydrology and the impact of urban, industrial and agricultural point- and non-point pollution sources on groundwater quality.

An interdisciplinary study on tracing mercury contamination within the classical karst in the area between the Idrija mine and the Bay of Trieste recently started, giving a good example of trans-boundary movement of contaminants where the source of pollution is located in Slovenia and the final target aquifers provide water resources for the Trieste area in Italy. The contaminated river, draining the mercury polluted area of Idrija (once the second largest Hg mine in the world, operating for almost 500 years), flows through the karst area and the current water supply in Trieste may occasionally, depending on hydrological conditions, be contaminated from the river through contaminated sediments.

In the framework of an interdisciplinary research project dealing with groundwater pollution in Slovenia, the hydrogeochemical parameters in vulnerability assessment as an approach to the regionalisation of groundwater vulnerability and possible restoration measures were studied. A case study was performed in NE Slovenia where sources of nitrate pollution were defined using the stable isotopic composition of dissolved nitrogen in the groundwater, combined with the spatial and temporal appearance of nitrates in wells. Two main sources of nitrates in the groundwater were defined, i.e. mineral fertilisers as a non-point source and point sources of nitrates deriving from septic tanks. Currently, a laboratory column experiment is in progress to determine the influence of the soil on the concentration and isotopic composition of nitrates in groundwater. It was found that the isotopic composition of dissolved nitrate under the same watering conditions depends mostly on the mineralogical characteristics of the soil. However, the research is not completed yet. The results obtained are used for development of a model forecasting the environmental effects on groundwater of the use of N fertilisers in the area.

As prospective research topics, age determination of young waters and tracing of dissolved contaminants and their transformations in the groundwaters using environmental isotopes or other tracers can be addressed. Since groundwater age is one of the crucial parameters in assessing the vulnerability of groundwater, more efforts in finding new reliable and easy-to-handle techniques for dating are needed. CFCs (which are entirely man-made compounds first produced in the 1930's and since then accumulating in the atmosphere) are suitable for dating of young waters where no results can be achieved with ^{3}H, or where the recharge temperature is uncertain or even unknown. Generally, there is no existing data base for CFC input functions for groundwater dating, such as exist for environmental isotopes of water in precipitation. For establishing a suitable CFC input function, a worldwide or at least regional European database is required. The use of environmental isotopes represents a supporting tool for tracing transport and reaction pathways of particular compounds, giving information about the origin, possible precursors from which a compound was formed and the reaction pathway of their interactions and transformations. So they are rarely studied on an exclusive basis, but should form part of interdisciplinary research on the chemical and biological transformation and immobilisation of the pollutant of interest.

7.4.3 References

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7.5 Biotransformation of organic pollutants of relevance for contaminated soil and groundwater; Bo H. Svensson

7.5.1 Introduction

Compounds occurring as pollutants in soils and groundwater basins and which may undergo biotransformation are found both among organic and inorganic compound groups addressed by the present workshop. Thus, speciations of metals and, the nitrogen in N-fertilisers may be acted upon by microorganisms in their dissimilative processes i.e. they take part in the redox reactions giving rise to beneficial energy transformations. This presentation will focus on the biotransformation of organic compounds regarded as pollutants.

Large quantities of a vast variety of organic compounds are produced and used in the society today. Many of these have been identified as vulnerable to organisms of different kinds including man. Both the production and the use of organic compounds may give rise to an introduction of them into soil and groundwater environments. They are toxic, carcinogenic and/or bioaccumulative. Some of them give taste and odour to water, which makes them unpalatable by humans. Biota in soil and groundwater may be effected directly in different ways, while other biota, including man, may be effected by such compounds as they are routed directly via water or indirectly via bioaccumulation.

The ways of contamination are linked to the production *per se* i.e. emissions via air and wastewater from the production units as well as disposal of any rest products formed. The production of a compound mostly give rise to direct and instantaneous contamination at a specific site or nearby water bodies. However, airborne plumes may pollute more distant areas. The utilisation of an organic compound as such or as a part of other products result in dispersed ways of distribution. The release of the compound into the environment may be retarded and/or slow. A delay may be due to the period of utilisation, i.e. the compound may not reach the environment until its containment become waste. A slow release may occur as result of time for transformation of the material of which the compound forms a part. When the material is used directly in contact with the soil or water compartments the compound may also be subjected to a release. About the same scenarios are applicable when the compound itself or its containment become a waste. Thus, depending on whether it will be incinerated, landfilled or passed through a wastewater treatment system, it may be subjected to direct or indirect release into soils and groundwater.

Organic compounds mainly of anthropogenic origin make up a wide flora of pollutants identified in soil and groundwater. They belong to almost all varieties of substituted and unsubstituted aliphatic and aromatic compounds. The source areas are found among chemical production sites, sites where e.g. solvents are used, refinaries and places for distribution, storage and utilisation of petrol products, sites for gasification of coal and coke production and deposits of industrial and municipal wastes. This means that there is a wide distribution of sites polluted with toxic organic compounds in most countries. Examples of different types of compounds and the possibility for their transformation and/or degradation will be presented.

Biotransformation, either intrisic or facilitated, is one way of preventing the polluting compounds from reaching target organisms which would react on their toxicity or resulting in water not accepted for use for drinking or irrigation. Thus, efforts are taken to study and utilise biotransformation in order to remediate soils and groundwaters. There are several cases reported, where successful biotransformation of polluted areas have occurred. A challenge is to study and decide if a polluted area should be left for natural remediation or if it should be subject to more active remediation measures. Special concern has to be taken to the primary source of pollution and the possibility to eliminate it.

7.5.2 Frames for biotransformation of organic pollutants

The chemical structure of an organic pollutant giving its physical properties will form the background for its aptitude to be degraded. Organic pollutants of anthropogenic origin i.e. new compounds synthesised by man as well as petroleum products of different refinary grades are in analogy with their naturally formed cousins dependent on a row of parameters among which are:

1) Ability to function as a substrate i.e. as carbon and/or energy source or as electron acceptor.
2) Access to electron donors and acceptors
3) Suitability for cometabolic transformation
4) Toxicity to microorganisms
5) Solubility in water – concentration levels
6) Sorbtion features

A combination of the above features for the compound in question will govern its fate in relation to biotransformation. This means that the kinetics and thus the degree of persistence of a compound will be determined by these properties.

During the last 20 years, studies of degradation of different anthropogenic compounds have led to a comprehensive knowledge on new metabolic pathways and their genetic regulation. Degradation reactions regarded as impossible have concomitantly been proven to occur. This was the case for anoxic transformation of several types of compounds e.g.: saturated alkanes, unsubstituted aromatics and those with functional groups composed of halogens or carbon and hydrogen. These were regarded as persistent under anoxic conditions, while the alkanes now are known to be degraded by sulphate reducers and benzene has been found to be susceptible to transformation as coupled to iron reduction. Concerted action of aerobic and anaerobic organisms in environments with different degrees of oxygen availability has been shown to enhance the degradation of aromatic pollutants. This should be valid also for aliphatic compounds.

The biological transformation of some more or less harmless compounds may lead to the formation of intermediates or products, which are more toxic than their parent molecule. The transformation may also lead to changes in the sorbtion characteristics of the compound as well as its water solubility and, thus, its mobility and transport features. Examples are: the formation of vinyl chloride during the transformation of tetra-, tri- and dichloroethenes which take place when these chlorinated ethenes occur as pollutants in groundwaters and landfills. Vinyl chloride is a potent cancerogenic compound. The vinyl chloride may be further dechlorinated to ethene and reduced to ethane depending on the conditions prevailing; the degradation of phthalic acid diesters proceed via their corresponding monoesters. The latter expose a carboxylic acid function, which render them more water soluble and thus more mobile than their mother compounds. The diesters are of low toxicity, while the monoesters are believed to have hormon activivity . The monoesters are further degraded both under oxic and anoxic conditions, but may especially under the latter circumstances persist enough to move away from their source e.g. they occur in leachates from landfills.

The biotransformation of a compound will be governed by the enzyme affinities of the microorganisms present in the polluted groundwater or soil system. Two thresholds are involved: one concentration level needed for an organism to recognise the compound as potential substrate and another threshold will form at the level down to which an organism is capable to take up the compound. The latter is mostly lower than the first, why environmental concentration levels are likely to occur between these two thresholds. These levels are coupled to the availability of the compound as regulated by its solubility in water and its sorbtion characteristica. Still other thresholds are to be accounted for: concentrations and degradations suitability of other components may interact with the preferences taken by the microbial population and mixotrophic utilisation and growth will also affect the potential for a certain compound to be degraded.

7.5.3 Ongoing research

Organic compound pollution in soil and groundwater as a result of e.g. oil spills and landfill leachates have been focussed on for several years. The first area has been addressed by several groups especially in the U.S., where the E.P.A. and the so called Superfunding been motors to develop this project area, while the second has been especially researched in Europe by the group of Thomas Christensen in Denmark. Through the years there has also been great efforts made to evaluate biotransformation of different pesticides in soil and groundwater. The sources differ among these areas: i.e. landfills and other deposits give rise to dynamic changes in their source strength and type of leachate release. This is due to the great variety of compounds present and the above mentioned release mechanisms. The degradation and transformation within a landfill or a mine waste deposit will give rise to a sequential development of the leachate quality and the quantity of pollutants. The behaviour and occurrence of organic pollutants in landfills has been less investigated. In Sweden, degradation studies of specific compound groups in relation to the development phases of landfills, which give rise to different leachates, has been addressed by my own laboratory. Recently, Cecilia Öman presented a thesis on emissions of organic compounds from Swedish landfills. On the contrary an oil spill is given in amount and quality and therefore its fate should be more predictable under the environmental conditions given.

Examples on biotransformation of organic pollutants occurring in groundwaters will be given from these areas.

7.5.4 Research areas to be visited

From our own studies and those by Öman and Christensen's group in Denmark, it is obvious that a comprehensive knowledge of landfills as sources for groundwater pollution by organic compounds need an interdisciplinary research effort including:

- Hydrology of the landfill source and its downstream water flows. Seasonal and interannual models are needed for predictions.
- Advanced analytical chemistry is needed to enable the establishment of the occurrence of organic chemicals of the wide range suspected to occur in the landfill and its pollution plume. The knowledge of the compound structure give many of the properties of the pollutant e.g. sorbtion and solubility characteristics and to some extent its degradation potential.
- Determination of the chemical and physical properties of the soil, rock and water environment subjected to the pollution. This will form the thermodynamic basis for an understanding of the actual degradation pattern observed as well as of the options available.
- Microbial and abiotic transformation and degradation capacities within the landfill as well as within the polluted soil and water bodies. This in conjunction with the points above is the basis for how extended the pollution will become in time and space.
- A system analyses including components describing the future of the source and its reflection in the emissions and pollution pictures should aid in decisions strategeis to be taken for each site.

Research concepts as above will give rise to knowledge of methodologies applicable to any type of organic pollution situations which may occur in soil and groundwater.

7.6 Natural and artificial barriers as a tool for remediation of contaminated groundwater; Bedbur, E. and Dahmke A.

At present "pump and treat" is the most commonly used method for groundwater and aquifer remediation. Due to the fact that the source of organic contaminants very often is a separate non-aqueous phase and due to natural heterogeneity in subsurface pump and treat commonly lacks from transport limitations. Therefore different remediation alternatives are currently under research and the so called "geochemical barrier"-concept seems to be one of the most promising to the plume of groundwater contamination (Morrison & Spangler, 1992).

In this context a "geochemical barrier" can be defined as a natural or artificial subsurface zone in which contaminants are to be immobilised or degraded under favourable E_H-pH-conditions abioticaly or by micro-organisms. If the spreading of the contaminants is significantly restricted by geochemical reactions in the aquifer without any technical means the so called "natural attenuation" or "intrinsic bioremediation" can be a very cost extensive method for various compounds.

A well known example for such naturally occurring degradation processes in aquifers is the oxidative (bio-)degradation of BTEX, whereby different oxidants from O_2 up to SO_4^{2-} are used (Baedecker et al, 1979). A recently published summarisation of plume lengths of different important organic components based on a statistically examination of literature data (Grathwohl et al., 1998) showed that transport of these contaminants is mostly limited by natural attenuation processes. Even plume lengths of inorganics like heavy metals are in most cases controlled by sorption or precipitation processes. Only for components, which are favourable degradable under reductive conditions such as chlorinated aliphatics, a long plume up to 14 km and more can be observed, because the microbial dehalogenation via different reductants like FeS_2 on their flow path leads to problematic recalcitrant products.

But despite of the large efforts in research there exists a bundle of open problems which restrict the use "natural attenuation" as a tool for plume treatment. The main points are:

First degradation processes of many contaminants and fate of their metabolic products is often unknown.

Second, the steady state behaviour of a plume in time and space is hardly detectable in a short and inexpensive examination period. Especially in aquifers with high hydraulic and geochemical heterogeneity.

In the future we see two strategies, a statistical approach or a more cost intensive site specific investigation program to overcome these problems.

The first approach is based on the plume length statistics coupled with parameters like contamination history, hydrogeological and geochemical conditions etc.. With this information a reaction volume can be defined within the aquifer, where the use of groundwater is restricted for a given time. Such statistical treatment, which is similar to approaches in the field of public health care, would be helpful for a lot of sites but could fail dramatically at specific sites. Therefore the estimation of the contamination probability has to be combined with a safety factor, which will lead on the other hand to an overestimation of the plume length in most cases. Additionally long term monitoring is necessary.

Because of these reasons natural attenuation is at the most sites based on site specific investigations, mainly groundwater analyses and sometimes transport modelling. Even transport reactions models like TBC (Schäfer, D. et al., 1998) are now available which allow theoretically the calculation of complex sorption and biodegradation processes in the subsurface. But the application of such programs is limited by calculation time and - more important - by the quality and quantity of available field data. For example comparison between the modelling results based on intensive investigation program and data from new wells at the german test site ("Testfeld Süd", Stuttgart) have shown important deviations. These deviations can clearly be explained by the geochemical and hydraulic heterogeneity of aquifer, which is only describable with a large and very extensive amount of observation wells. Under practical aspects such large amount of wells is unacceptable. Therefore we see an enormous need of the development of scale adapted investigation methods like reactive tracers.

If the spreading of contaminants is significantly restricted by biogeochemical reactions in the aquifer without applying any technical means, ^Natural Attenuation or Intrinsic Bioremediationp is regarded to be sufficient and a very cost extensive method. If this is not the case different technologies can be applied in order to modify and enhance natural geochemical barriers or to "create artificial geochemical barriers" in the subsurface. One approach is the injection of reactive liquids (e.g. H_2O_2, $FeCl_3$, $FeCl_2$ etc.) which are reacting with sediment components (especially Fe-phases) whereby *in-situ* sorption as well as oxidation or reduction zones can be built up. A rather new concept is also the injection of reactive colloids into the ground reaction. The most developed technology is the use of *in-situ* permeable "reactive walls" or "treatment walls" which are consisting of different types of reactive solids and are placed downstream the contaminant plume. Very often they are combined with impermeable walls ("funnel"), leading the contaminated plume to the permeable, reactive parts of the wall (^gatep). Because of its high costs effectiveness, *in-situ* reactors are being developed for various contaminants (BTEX, chlorinated solvents, heavy metals, NO_3^-).

So several large scale pilot plants of Fe^o reactive walls for the treatment of halogenated aliphatics in the groundwater have been running rather successful in North America. The reaction has proved to be pseudo first order with respect to the concentration of CAH and the reaction rate is proportional to the metal surface/solution volume in a wide range and decreasing at higher pH. Half lives of common CAH are in the range of hours (e.g. TCE 1 h×m²/mL), but some (c-DCE, CDA) are hardly degraded. Few research, however, has been done on the effect of high organic and inorganic groundwater constituents on the geochemical and hydraulic long- term reactivity and stability of a Fe^o-wall.

Therefore we have investigated recently the effect of dissolved inorganic groundwater constituents on the kinetics of TCE degradation by Fe^o in column and mainly batch experiments (TCE_m 20 mg/L, room temp., A_{fe}/V_{sol} = 0,071 m²/mL). In all experiments 1,2-DCE(cis) was the only chlorinated intermediate detected in solution with a maximum concentration (DCE_{max} = 0,5-0,7 % TCE_m) fairly independent of all of the inorganic parameters studied so far. TCE and subsequent DCE degradation was found to proceed faster only at high chloride concentrations (600 mg/L) with respect to our reference experiment (0_2-saturation, Milli-Q water). Nor low initial concentration of O_2 (0,13 mg/L) neither high concentration of NO_3^- (100 mg/L) had any effect on the dechlorination kinetics. High initial carbonate concentrations (600 mg/L HCO_3^-, 44,9 mg/L $CaCO_3$) resulted in decreasing TCE and DCE degradation rates due to the passivation of the iron surface by the formation of carbonate precipitates. Inhibition of the dechlorination reaction was also observed at high phosphate (C_m = 100 mg/L) and high sulfate (C_m = 2100 mg/L) concentrations.

Further batch experiments are performed to localise the effective concentration of the respective parameter for the inhibition of the dechlorination reaction. If we can reproduce our results in column experiments the decrease in reactivity most be taken into consideration for the design of permeable reactive Fe^o-walls.

This approach is not restricted to the above mentioned group of substances but can be transferred to other groundwater contaminants. In the case to handle diffuse contamination complex land use systems have to be understood and combined in an integrated strategy for the protection of groundwater.

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7.7 Pollution of the environment by heavy metals from copper shale mining in Central Germany: dispersion, transport and immobilisation; Peter Schreck and Walter Glaesser

7.7.1 Abstract

Even 8 years after mining and smelting was abandoned in the district of Mansfeld (Central Germany), smelting residues, in particular flue dust (“Theisen sludge”) from copper shale smelting, significantly contribute to the pollution of the environment. The extremely fine grained sediments are subject to erosion by wind and water. The most effective dissemination mechanisms are deflation (wind erosion), rain water „wash-off“ and leaching. Environmentally significant pollutants derived from Theisen sludge comprise metals (zinc, lead, copper, arsenic, cadmium), PAH and radionuclides (^{210}Pb, ^{210}Po). These pollutants can be found in lake and river sediments, in soils, in the surface water and in the groundwater of the former mining district. The most serious environmental hazards of Theisen sludge are (a) the pollution of the surface water and groundwater by harmful, soluble and bioavailable organic and inorganic compounds; (b) the mechanical erosion of metalliferous sediments in the mining area and their accumulation in the lakes of Mansfeld, a potential threat to wildlife and vegetation; (c) harm to human health by inhaling radioactive particles.

A large part of the pollutants derived from the mining waste is immobilised in the former mining area by natural processes such as precipitation, sedimentation and adsorption. Lakes and wetlands act as a trap for particulates and secondary enrichments of metalliferous sediments are common. In anoxic lake sediments dissolved metals are precipitated and immobilised as sulphides. Carbonaceous soil, mainly loess, limestone waste rock and slag buffer acidic leachates from flue dust weathering. This leads to the natural formation of less soluble heavy metal carbonates, hydroxides and oxides. In some places storage minerals directly precipitate from mine dump leachates (glaucocerinite) and immobilise dissolved metals such as zinc, copper and nickel. Lab scale experiments show that natural precipitation of storage minerals can be optimised and finally immobilises about all dissolved metals. This has to be verified by extended field experiments.

7.7.2 The pollution problem

Copper shale mining in Central Germany, a traditional mining area, dates back to the early 13th century. In the beginning of the industrial age, from 1880 to 1890, large-scale processing of copper shale was introduced in two major smelting works. By 1990, when mining and smelting in the German copper shale district was abandoned for economic reasons, 2.2 million tons of copper and 11,000 tons of silver had been recovered from about 109 million tons of copper shale ore (KNITZSCHKE [1995]). Apart from copper and silver the smelting of copper shale yielded about 30 metals of economic importance including zinc, lead, cadmium, tin, molybdenum, rhenium, germanium, indium and selenium. The latter group of metals were extracted from the flue dust scrubbed from the furnace top gas. For more than 70 years this heavy metal rich sludge (average 18% Zn, 14% Pb) was used as a raw material to produce Zn, Pb, Cd, Ge, Re, Se and other rare metals.

After the closure of a major metallurgical plant in 1978 and a lack of economically suitable alternatives for further treatment, the Theisen sludge, the former resource, turned into hazardous waste. By 1990, the final year of mining and smelting, more than 300,000 tons of Theisen sludge had been produced and deposited in basins and ponds on slag heaps and mining waste dumps close to the former copper shale smelting works in Eisleben and Helbra. The remaining amount of slag is 50 million tons in total, located at both sites. Initially most of the Theisen sludge storage basins were used to dewater metalliferous suspensions and slurries from scrubbing, hence no sealing was performed. As a result of dewatering, suspended flue dust infiltrated the fractured slag heaps and the lumpy mining waste and even today is subject to leaching.

Both slag and Theisen sludge dumps are situated in a densely populated area, about 2-4 km west of the town of Eisleben and about 45 km west of Halle. A recreational area extends between the two towns including the lakes of Mansfeld, the wine-growing area of Höhnstedt and several nature reserves. All pollutants derived from copper shale smelting affect the environment in the surroundings of the smelters in one way or another. Details are given in the following chapters.

7.7.3 Current knowledge

Today pollutants derived from Theisen sludge and related metalliferous sediments are spread to the environment by three mechanisms (Fig. 1):

- Deflation of dried sludge (dust) by the wind
- Erosion of the fine grained metalliferous sediments by heavy rain falls and torrential waters, removal by the surface water
- Leaching of pollutants from the sediments by precipitation and dispersion in the surface and the groundwater

7.7.4 Airborne dispersion of pollutants

Airborne dispersion (deflation) affects all unprotected fine-grained surficial sediments. Desiccation of the sludge results in the formation of mud cracks, several tens of centimetres deep. Proceeding from the mud cracks, precipitation and oxygen destroy the protective binding agent of the sediments, i.e. organic matter in Theisen sludge, and the remaining dust is easily scattered by the wind. This metalliferous dust is responsible for metal enrichments in soils close to unprotected Theisen sludge dumps. Marquardt (1997) sampled soil profiles below and along the southern flank of the Helbra slag heap, 0.5 - 1.5 km distant from a Theisen sludge storage basin on top of the heap. He observed distinctly increased contents in heavy metals in the upper 20 cm of the soil profiles, in particular in elevated terrain. The metal ratios in the enriched soil samples correspond to those in Theisen sludge, a proof for the airborne dispersion of metalliferous dust.

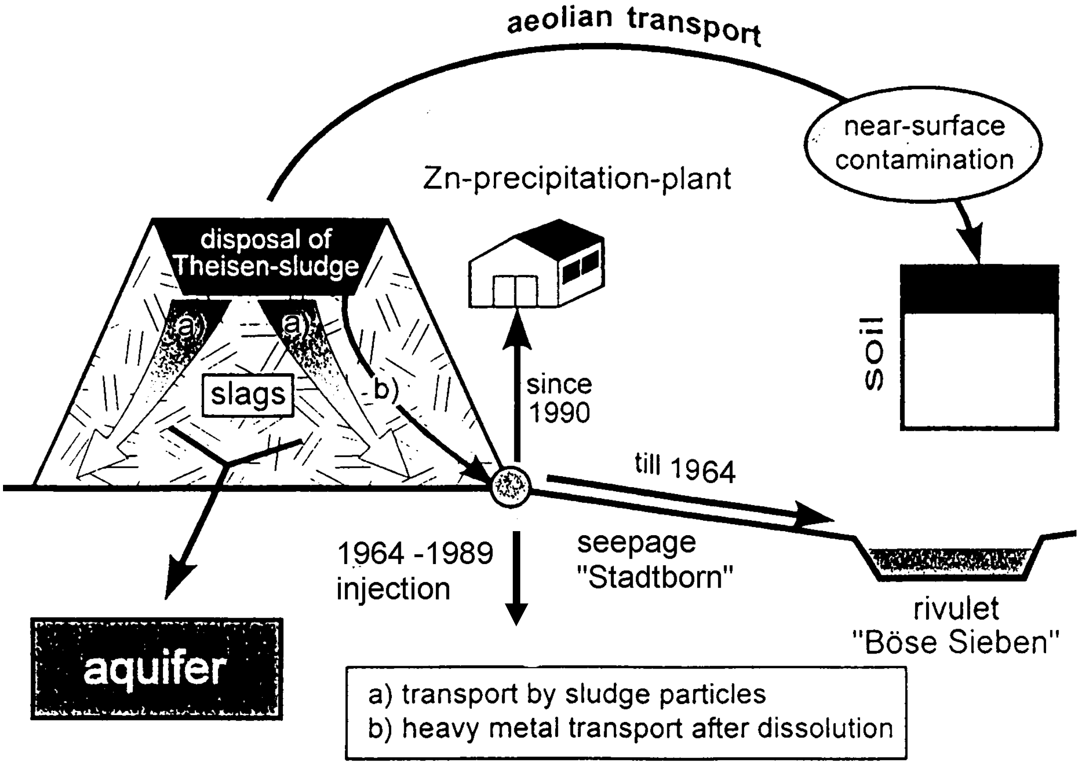

Figure 1: *Paths of pollutant migration by the weathering of Theisen sludge. Modified after Jahn et al. (1997)*

7.7.5 Mechanical erosion and dispersion of metalliferous sediments by the surface water

In the early years of the century furnace top gas scrubbing in Helbra suffered from various technical shortcomings and a lack of environmental awareness. Several times Theisen sludge storage basins leaked or spilled over and suspended flue dust was spread to the environment. In times of increased smelting activities, and lacking storage capacities, the flue dust suspension was passed into the mining waste and slag dumps (heap filtration) or even directly released to the surface water. Today we find about 30,000 tons of metalliferous sediments in the wetlands of the river Glume close to the former smelter. Lenticular intercalations of Theisen sludge in flood plain sediments are common in the river channel between Helbra and Eisleben. Even 15 km to the East, in the sediments of the lakes of Mansfeld, mineral compounds from Theisen sludge such as Sphalerite (ZnS) have been found (SCHRECK et al., 1998). The major mechanism for Theisen sludge dissemination and redeposition is erosion by torrential waters caused by isolated but heavy rainstorm events. This mechanism affects unprotected Theisen sludge dumps as well as redeposited metalliferous flood plain sediments.

7.7.6 Leaching of pollutants from Theisen sludge by precipitation

Flue dust and Theisen sludge, in particular when carbonised, are easily leached by water. This is the result of sulphide mineral oxidation generating soluble sulphates of zinc, copper and cadmium while lead sulphate is more resistant to leaching.

Most of the Theisen sludge deposits and flue dust accumulations set up on slag heaps are either unprotected or lightly covered by tarpaulins to avoid deflation. This measure does not prevent the leaching of the smelting residues by precipitation. Even after the relocation of most of the Theisen sludge from temporary dumps to the central deposit Pond 10, many thousand tons of metal-contaminated waste material and slag (“mixed material”) remained on site and are subject to leaching by precipitation.

7.7.7 Ongoing research

Several springs can be found at the base of the Helbra slag heap. This seepage is enriched in metals and organic pollutants leached from smelting residues by precipitation. At two locations, Stadtborn and Vietsbach, metal and sulphate concentrations far surpass the accepted environmental norms, making leachate treatment necessary (Tab. 1).

***Table 1:** Average zinc, copper and sulphate contents (1992-1997) in leachate-dominated water of the Stadtborn well*

mg/l	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**$^{1)}$
Zn	1.457	2.363	2.655	3.241	2.541	2.186
Cu	13,65	14,33	20,36	16,64	11,96	10,92
Sulphate	5.267	5.918	6.494	7.260	7.199	6.057

Data from Mansfeld Rohhütten GmbH i.L., Helbra, with permission (Analyst: Pfeiffer); $^{1)}$ *average first 6 months of the year*

The distinct increase in zinc and sulphate values between 1994 and 1996 is probably due to Theisen sludge relocation measures in Pond 9, situated above the Stadtborn well on the Helbra slag heap. Aeration and artificial wetting (dust prevention) accelerated sulphide oxidation and the subsequent leaching considerably. The gradual decrease in metals and sulphate after 1995 is a proof for the effectiveness of the relocation measures.

Around the Stadtborn well pebbles and leaves are coated by a greenish precipitate, the mineral glaucocerinite [Zn8-xAlx(OH)16][(SO4)x/2(H2O)9], first described by Witzke (1997). Glaucocerinite possesses a hybrid layer-lattice structure and may absorb additional metal cations such as Cu, Co and Ni. Mineral precipitation is triggered by changes in water temperature, oxygen content and redox potential. Lab scale experiments revealed, that the precipitation rate for glaucocerinite can be optimized by moderately increasing the pH-value and adding Al3+-ions (Fig. 2). Finally about 95% of the dissolved zinc was removed from the leachate by mineral precipitation.

Organic components released from the smelting residues can be used as geochemical tracers. The PAH content of Theisen sludge (Pond 9) is 1,030 mg/kg (Schreck [1997a]). Leachates from Theisen sludge deposits contain 1,736 ng/l PAH (Stadtborn, analyst Dermietzel, UFZ). The distribution pattern of the 16 EPA PAH’s in leachates from Theisen sludge shows typical enrichments in lighter PAH such as naphthalene (1), acenaphthene (3), phenanthrene (5) and fluoranthene (7) and only minor amounts of heavier PAH (Fig. 3). A similar distribution pattern, the “finger print” of Theisen sludge, can be found in the water of the lakes of Mansfeld. The lower percentage of naphthalene in lake water, about 15 kilometers away from the source, probably results from biological degradation.

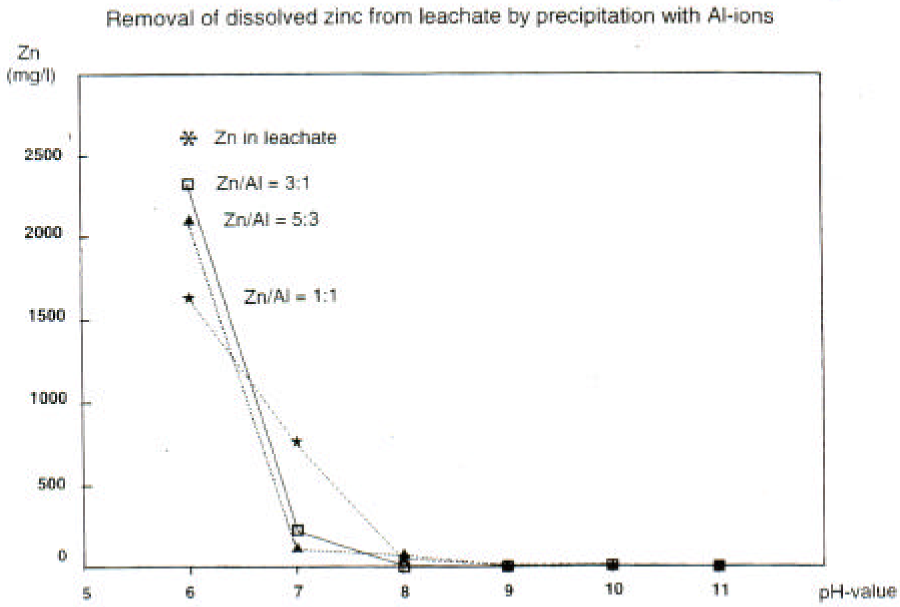

Figure 2: Precipitation of glaucocerinite and zinc-oxide from leachate

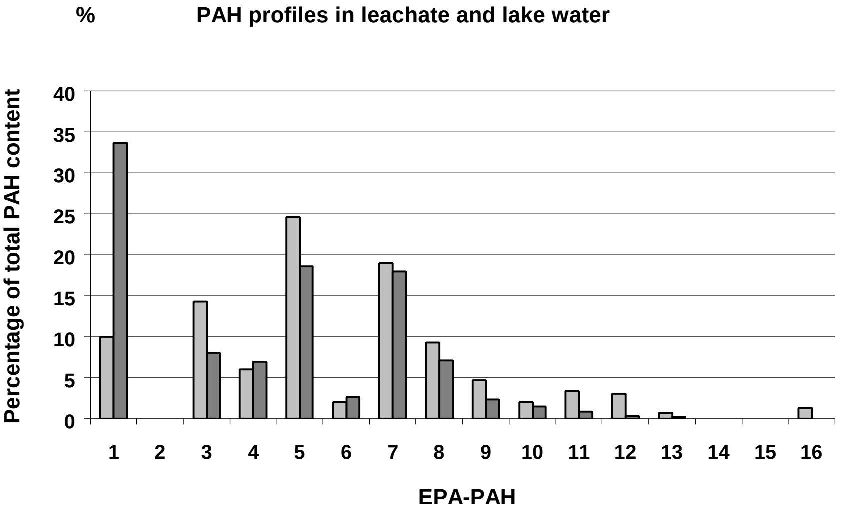

Figure 3: *PAH profiles in seepage from Theisen sludge (Stadtborn, dark grey, total PAH = 1.736 ng/l) and in lake water (light grey, total PAH = 301 ng/l).*

Numbers 1-16: EPA-PAH from naphthalene (1) to indeno(1,2,3-cd)pyrene (16).

Pollutants leached from the smelting residues by precipitation contaminate the shallow aquifer in the surrounding of the former smelters. In Helbra sixteen groundwater observation wells have been installed in three different aquifers. As an example, data from well 2 (shallow aquifer, 4.77m) and well 2A (deeper aquifer, 31.06m) are presented (Tab. 2). Compared with the deeper aquifer, the shallow aquifer is enriched by a factor of 700 times in zinc, 175 times in nitrate, about 10 times in sulphate and about 5 times in chloride. The level of pollution in the shallow groundwater sampled from more remote wells in discharge direction is much lower than the presented values.

Table 2: *Groundwater characteristics of two aquifers close to Pond 10 at Helbra. component*

Component (mg/l)	groundwater observation well 2 (depth 4.77m)	groundwater observation well 2A (depth 31.06m)
Zn	16.54	0.024
Pb	< 0.0008	< 0.0008
Cu	< 0.0003	< 0.0003
Cd	< 0.0003	< 0.0003
As	0.017	< 0.0003
SO_4	2,325	247
Cl	463	82
NO_3	96	0.55
pH	7.2	6.5

From Schreck (1997b). Analyses UFZ: AAS and IC (C. Böhnisch, A. Sawallisch)

7.7.8 Prospective Research and Conclusions

The environmental impact of flue dust (Theisen sludge) and related metalliferous residues from copper shale smelting was assessed in early 1990 and extensive redevelopment concepts for the region were developed (1991, 1994, 1997). At present, 8 years after smelting was abandoned in the Mansfeld mining district, only temporary measures to prevent environmental hazards were put into practise. These measures include the dismantelling of the technical installations, the relocation of Theisen sludge from different unprotected dumps to Pond 10, the continuation of leachate treatment and a small monitoring programme. Many of the recommended and necessary, but expensive measures such as the capping and sealing of contaminated areas, the relocation of metalliferous sludge from the wetlands and the technical improvement of the leachate treatment plant are still in the state of planning.

Today pollutants derived from smelting residues, in particular from Theisen sludge, can be found in the surface water and in the groundwater, in sedimentary sequences of the wetlands, in soils and even in the sediments of the lakes of Mansfeld. In recent years the district of Mansfeld has changed from a mining and industrial region to tourism and recreation. This new objective, together with the hope for job creation and prosperity, is based on a clean environment, unpolluted lakes and attractiveness for leisuretime activities. To keep this vision alive, it is high time to answer the remaining open questions on the environmental impact of selected heavy metals by a multidisciplinary research, covering ecotoxicology, microbiology, hydrology and pedol ogy.

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7.8 Occurrence and transport of contaminants in groundwater: two examples to show site- and milieu-specific aspects; Margot Isenbeck-Schröter

7.8.1 Abstract

To point out the necessity of including environmental factors into studies of groundwater contamination, two different examples are described. In the first example (pesticides) hydrolic, geographic and technological factors are combined to explain monitoring results. The second case shows, how geochemical conditions alter the mobility of a contaminant. The processes of interest are studied in laboratory experiments. Both examples can be transferred to deduce prospects of future research in the scope of groundwater contamination.

7.8.2 Introduction

The pollution of groundwater due to anthropogenic activities causes severe damages of aquifers used as drinking water supplies. Risk assessments normally include monitoring of the contaminant distribution by sampling and specific analysis as well as computer simulation in order to predict the plume spreading and/or to simulate possible remediation scenarios. Different transport processes have to be included into these models depending on the contaminant's nature as well as on the specific geochemical properties of the aquifer.

In the case of pesticides, site specific properties like climatic factors, soil properties and agricultural technics have to be combined with their use in order to minimize groundwater pollution (*Isenbeck-Schröter et al., 1997).* For other contaminants, the species distribution and/or the degradation behaviour of different contaminants is heavily affected by the geochemical conditions of the aquifer. In the case of different oxidation status, e.g. metals like chromium develop quite different mobilities and health risks. Therefore research is necessary to investigate specific transport behaviour.

7.8.2.1 Pollutants of concern, current knowledge and research activities

Whereas from the point of view of practical impact various organic contaminant groups are of concern (2,4,5,9), I want to give one example from these groups (pesticides (5)) from a literature study. Then I want to present some aspects of groundwater contamination by metals (7) dealing with redox species of chromium.

7.8.2.2 Pesticides

Since the early 1980s, considerable public attention has focused on the pollution of groundwater by pesticides (e.g. *Cohen et al., 1984).* In the EU, large-scale public debate on the subject of "pesticides and water" resulted initially from the discovery of isolated groundwater traces of these substances. This led to establishment of an EU drinking water limit for individual substances of 0.1 µg/l. The limit value of 0.1 µg/l is designed above all to indicate that the synthetic substances involved are considered not acceptable in drinking water. Their specific effects on health are not taken into account.

In the first decades of pesticide use, scientists and others assumed that soil prevented the passage of pesticides into groundwater. This view was based on the fact that pesticides were microbially degraded in upper soil layers and clung to soil particles for lengthy periods. Pesticide registration therefore also focused on the chemicals' behaviour in the soil. Users' primary concern was that pesticides should not harm crops. Application form, volume and frequency were thus often determined by the registration authorities. The discovery of pesticides in groundwater caused a considerable shift in perspective. All the EU-countries involved have altered their pesticide registration procedures. This development has led to an overall reduction in the number of products registered in the EU. Some pesticides were banned in a number of countries.

Supervision of such rules requires analytical methods capable of detecting any excess values. Over the last 25 years, improvements in apparatus have greatly refined environmental analysis, particularly of organic compounds. Above all the combination of gas chromatography with mass spectrometry offers a highly sensitive method of detecting synthetic organic compounds. Numerous pesticides can now be traced in water at levels well below 0.1 µg/l. However, when evaluating pesticide monitoring data, it should be remembered that even with sophisticated technology, ultratrace analysis still poses major problems. Pesticides form a very heterogeneous group of substances. They can be grouped by use (herbicides, fungicides, insecticides, etc.), or by chemical structure (triazines, phenylureas, carbamates, etc.). A large number of "positive" findings in ground, surface and drinking water have led to a ban on the herbicide atrazine in several EU countries.

A chemical's behaviour in the environment is in part determined by its structure, and illustrated in many laboratory and field studies. Knowledge of these studies as well as of substances' structure and physico-chemical characteristics is therefore of great importance for an assessment of their potential threat to water quality. These investigations enable scientists to estimate processes both of environmental transfer and transformation (*Schwarzenbach et al., 1993*). Investigation is required of the correlation between substances' specific characteristics and their occurrence in water.

Another important aspect of this discussion is the form, intensity and frequency of application. The available statistics usually differentiate only broadly, for example between "farming" and "other" uses. It would, however, be valuable to describe the actual form of use. The question arises of whether water pollution is related to a specific application strategy. Usage volumes can only be estimated from the sales figures, and in such cases have to be averaged out per local area.

Each region has its particular climatic, geological and morphological features. Each also has its own pattern of plant growth and human settlement. These may well contribute to the occurrence of pesticides in water. Unlike climate, geology or morphology, land use is readily alterable. Agriculture and settlement often determine how seriously a particular case of pollution is taken, and how the authorities react. Regional factors lead to widely varying pesticide problems within the EU. A major aspect to be borne in mind when interpreting monitoring data is the number and choice of sampling sites, as well as the sampling strategy.

Data discussed here are results of a literature study of pesticide residues in water in different EU countries (*Isenbeck-Schröter et al.1997*) and evaluated including the following aspects:

- How reliable are the different data presented for individual countries, given the monitoring strategies and data interpretation in the reports?

- To what extent do pesticides occur in groundwater, how does this correlate to regional agriculture and geography, and why?

Atrazine and its metabolites still are the most abundant pesticides in groundwater. This is because overall, the groundwater system reacts much more slowly to outward circumstances than does surface water. The first determining factor is the top soil layer. Dutch monitoring results show a close relationship between positive findings and the distance of the groundwater surface from the treated field. In the French groundwater study pronounced pesticide occurrence in groundwater was limited to free vulnerable aquifers. Thus the hydrogeological situation is one of the most important regional characteristics. Mid-term, the problem remains of contamination from substances no longer on the market or subject to restrictions. The problem of "inherited pollution" is illustrated by the rising atrazine levels seen in groundwater (in contrast to surface water) between 1992 and 1995. In addition, groundwater shows noticeable concentrations of atrazine's polar metabolites, which play a much smaller role in surface water. Farmers used atrazine over many years at high volumes, which is likely to have left behind a soil pool. The age of groundwater determines its impact as well. So a less pronounced application, e.g. according to Good Agricultural Practise, will lead to a decrease of concentration levels in several years.

It can be said in summary that the groundwater system is affected by a range of factors and processes. Pesticides´ characteristics, as well as climatic and geological features play a stronger role than in the case of surface water. The time scale of impact as well as of possible decrease in residues in most cases extends over decades.

The most important long-term method for reducing pesticide water pollution is the reduction and improvement of their use. Good Agricultural Practice now includes a number of further measures to the same end. GAP usage recommendations are based on the principles of integrated farming. For example: Pesticides should only be used when pests are present at above a given level, and application volumes should be kept to a minimum. Farmers should also take local soil conditions into account. The most important question is site-specific farming. Very exposed sites should not be used extensively, fertilizers and pesticides should not be applied. Another important aspect is precision dosing. Appropriate technology helps to reduce diffuse contamination, e.g. via wind drift. In combination with measures like crop rotation and agricultural de-intensification on exposed sites, this can lead to a considerable reduction in water pollution. Correct disposal of spray residues is also essential. Expert systems and other models now enable forecasting of a whole range of scenarios. Optimum application volumes can be calculated, as can the necessary size of pesticide-free zones. The example of bentazone shows that such forecasts can now support prediction of a particular substance's threat to water. These models can thus be used both for registration purposes and for designing pesticide monitoring programmes. The pesticide industry has for some time been developing a highly active substance type which can be applied at considerably lower volumes (multiples of 10 g/ha). First results for sulfonylurea herbicides suggest that this is a promising way to reduce usage. Another practical purpose is the reduction of biologically inactive isomers or analogues in the trade product.

Cases of water pollution led to a rapid increase in related research. A review of the recent literature shows the considerable body of knowledge now available on the subject of crop protection products and water. There are countless individual studies of substances' behaviour in water and soil. Field case-studies have also been published. The public pesticide debate has thus accelerated some positive developments. There remain numerous major gaps in our knowledge and understanding of the behaviour of pesticides and their metabo lites in the environment, and their impact on the ecological system.

Topics of relevant research include:

7.8.2.3 Metals

Species-specific transport behaviour of chromium

Chromium is a transition element existing in the valence states -II to +VI. At natural conditions +III and +VI are the most stable valence states in solution. In the trivalent form chromium behaves like a typical cation and acts amphoteric It tends to form complexes, hydroxo- and chloro-complexes being the most important ones. The hexavalent chromium forms oxoanions like chromate or dichromate. (*Richard & Bourg 1991*). The geochemical behaviour of chromate is similar to other oxoanions (*Zachara et al. 1987*), but in contrast to these chromate is a powerful oxidant. Trivalent chromium is an essential trace nutrient for animals and plants being involved in the glucose metabolism and amino- and nucleic acid synthesis (*Anderson 1989*). Chromium(III) is not acutely toxic to humans even at high dosage, whereas chromate is acutely toxic, mutagenic as well as carcinogenic with effects on bacteria, plants and animals (e.g. *Appenroth et al. 1996*). Naturally chromium occurs nearly exclusively in the form of Cr(III) species (*Richard & Bourg 1991*). Hexavalent chromium may be formed in nature by oxidation on manganese oxides in well-aired soils (*James & Bartlett 1983b*). Thus the most important source of Cr(VI) in the geosphere is industrial waste. Chromate concentrations of several 100 mg/l may appear in waste depositions coming from steelworks, chromium electroplating, wood treatment chemical manufacturing and leather *(Palmer & Wittbrodt 1991*).

The mobility differs significantly between the two valence states. The concentration of trivalent chromium is controlled by the solubility of Cr(III)hydroxides with lowest solubilities at neutral pH conditions (*Rai et al. 1987*). Cr(III)-organic complexes may raise the solubility (*James & Bartlett 1983a*). Chromates are well soluble and high concentrations may occur in water. Both chromium species are adsorbed on iron- and aluminium(hydr)oxides, organic substance and clay minerals (*Charlet & Manceau 1991*). The trend is that a decrease in pH results in an increase in Cr(VI) and a decrease in Cr(III) adsorption. Overall, the hexavalent chromium is the mobile form in the groundwater environment.

Thus the redox behaviour of chromium has distinct effects on its mobility and influences the environmental conditions in a significant way (*Palmer & Wittbrodt 1991*). In sediment-water-systems, chromate may be reduced by organic substance, by dissolved or solid ferric iron and by sulfide (*Kent et al. 1994, Wittbrodt & Palmer 1995*). The trivalent form then disappears from the solution due to precipitation of hydroxides and adsorption. The reduction rates increase with decreasing pH. A long term natural attenuation of chromium contaminations potentially may occur in anoxic soils or aquifers (*Waldmann 1995*). The reduction of chromate combined with hydroxide precipitation is practically used for Cr(VI)-waste water treatment (e.g. *Palmer & Wittbrodt 1991*). Although these redox processes play such an important role for practical purposes, the reactions themselves as well as the geochemical factors controlling these reactions are poorly understood.

In a laboratory investigation column experiments were performed in order to simulate the chromate transport in a sandy aquifer containing iron monosulphide characterized by sulphate reducing conditions and slight alkaline pH value (*Ebert, 1997*). In continuous flow experiments two columns were contaminated with 0.05 mmol/l and 0.5 mmol/l Cr(VI) respectively. The chromate was reduced in the columns and Cr(III) precipitated during the experiment. Fe(II) in the solid phase is the reaction partner at 0.05 mmol/l accompanied by S(-II) at 0.5 mmol/l. The iron(III) formed is precipitated while sulphur species are released into the pore water. The microbial activity is inhibited nearly complete at 0.5 mmol/l. A subsequent oxygen, nitrate and iron reduction is observed at 0.05 mmol/l Cr(VI) and consequently chromate is reduced by Fe(II) continuously. The redox reaction between Chromate and the solid phase affects all solutes. Cations and anions are adsorbed at (hydr)oxide surfaces previously formed and a desorption is observed when uncontaminated water was streamed through the columns. Overall, 0.58 mmol/kg is fixed on the 0.05mmol/l column while 2.54 mmol/kg chromium are fixed on the column operated with 0.5 mmol/l Cr(VI) . Different redox reaction kinetics must be the reason for the behaviour of chromate.

7.8.3 Conclusions and Prospects

Necessary research should focus on monitoring strategies on one hand and on species-specific studies on the other hand. This is true for a couple of different environmental chemicals which enter groundwater by diffuse pathways or as source-contamination. For both topics it is necessary to develop good sampling procedures and analytical technologies. Field studies have to be combined with laboratory experiments and modelling tools for a better understanding of processes.

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7.9 Long-term changes of groundwater quality due to atmospheric deposition and remediation activities; Bo B. Lind

7.9.1 Abstract

In areas with slow-weathering bedrock and thin soil cover the overall groundwater quality is gradually changing due to atmospheric deposition of pollutants. The picture may be further complicated by the spreading of soil conditioners such as wood ash over large areas. Long-term changes of groundwater quality should be studied in relation to the specific geological conditions within the discharge area. This can be done with a GIS modelling method, using trajectories through the catchment area.

7.9.2 Introduction

Acidification of soil and waters is one of the most severe environmental problems in many parts of the world with slow-weathering bedrock and thin soil cover. There is good evidence that the deposition of sulphur- and nitrogen- based acids, is affecting not only the surface waters but also the overall groundwater quality. The groundwater quality is gradually changing. This means increasing metal concentrations, falling pH and alkalinity and rising sulphate and nitrate concentrations. The groundwater is also becoming more and more aggressive to pipes and other installations.

One of the most serious effects of acidification is the depletion of valuable nutrients such as base cations, from the soil profile. In order to meet the threats from nutrient depletion and vegetation damages, the concept of eco-cycling of wood ash has been launched, e.g. by the Swedish forestry industry. There are several concepts of treating the wood ash but they all end up in spreading about 1-4 tonnes of granulated or compacted ash per hectare. Wood ash contains at least 30 different components. The majority are nutrients such as Ca (19 %), K (13 %), Mg (5.5 %) and P (1.3 %) (wood ash, Combustion plant, Kalmar Enegri, Lindahl & Claesson, 1996). However, there are also other, less desirable, components like Cu (200 ppm) B (750 ppm) and Al (2600 ppm) (Holmberg & Claesson, 1998). The long-term effect on groundwater quality from atmospheric deposition and from the spreading of ashes is an important issue to address. The groundwater is the basis for the water supply for more than half of the communities in Sweden. The groundwater also forms the basis for the quality of watercourses and lakes.

7.9.3 Current knowledge

The effects of long-range atmospheric deposition to lakes and rivers have been known since the middle of the 1960´s, but the effects on groundwater quality were not revealed until the 1980´s. The changes of groundwater quality can best be studied as trends in long-term datasets from public water supply plants or from the groundwater monitoring net. One of the first signs of effects on the groundwater was increasing hardness, due to both Ca and Mg, and increasing sulphate content. Around the year 1970 there is also a break point where the pH and alkalinity started to have negative trends. Since then much has been done to reduce the sulphur emissions all over the world and from the early 1980´s it is possible to see a trend of decreasing sulphate at many observed groundwater sites in Sweden (e.g. Lång & Villalba, 1998). However, the groundwater response has varied between different geological environments. Our understanding of the connection between groundwater quality and the geological environment is still very poor. There is an obvious need for further research in order to understand the dynamics of the overall groundwater response to the regional deposition of pollutants.

The effects of wood ash spreading on forest soils have been studied in a few experimental areas in Sweden for about 3-5 years (Egnell et.al 1998). Some effects on the soil-water and runoff have been reported, with increasing concentrations of e.g. sulfate, cloride and potassium. However, there is a general lack of knowledge about the long-term effects on the groundwater are not known.

We can conclude that long-term groundwater quality is changing due to the global spreading of pollutants, but there is a lack of knowledge about what the effects are in different geological environments. Moreover, the long-term effects on groundwater due to modern forestry, with increasing take out of bio-mass compensated by ashes or other fertilisers, are not well understood.

7.9.4 Ongoing research

Not much has been done to study the changes of groundwater quality in relationship to geological settings within discharge areas, although this has been acknowledge as a potentially severe problem (Hilding-Rydevik & Johansson, 1998). Data on groundwater quality may be available from the early 1960´s, from public water supply plants, like in Örby or Fåglaslätt, Western Sweden, Fig. 1-2. The effects of the diffuse pollution is visible as long-term trends in chemical variables. The groundwater quality response is varying between different areas and regions. At the same time most of the environmental considerations of modern forestry are concerned with water quality. One focus of the research is to describe and preferably predict the effects of land use and diffuse pollution on the groundwater.

However, a new method presents new opportunities. A practical modelling method using trajectories through a catchment area has been developed at Uppsala University (Tierfelder, 1998a). All relevant conditions in the catchment that could influence the qroundwater quality can be digitalised and entered into a GIS (Tierfelder 1998b). Based on the GIS information geohydrological groundwater trajectories can be calculated. The grid-cell contribution to the chemical composition of down-stream waters can be calculated for each individual cell. This is of major significance in determining the groundwater quality in relation to the geological environment.

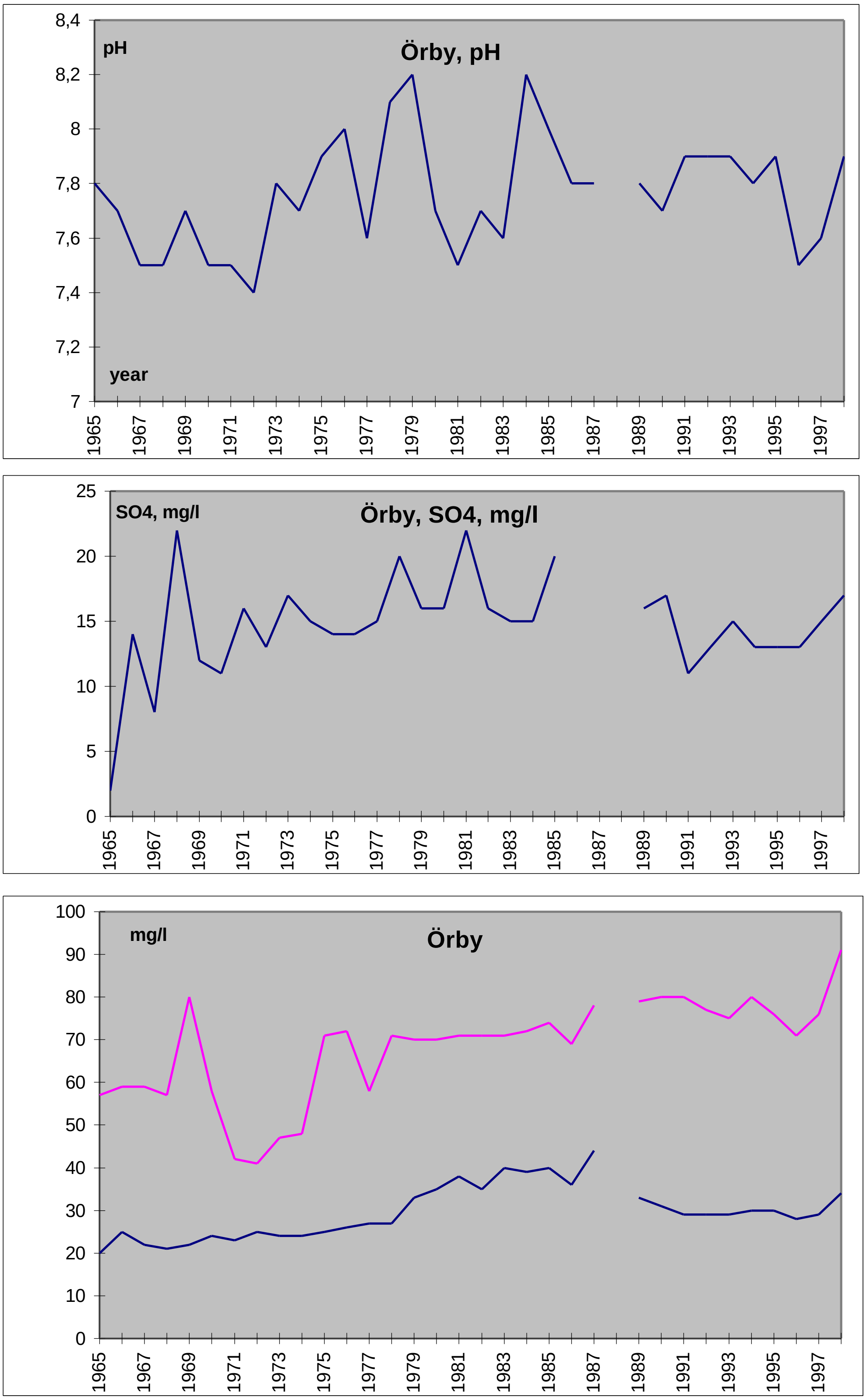
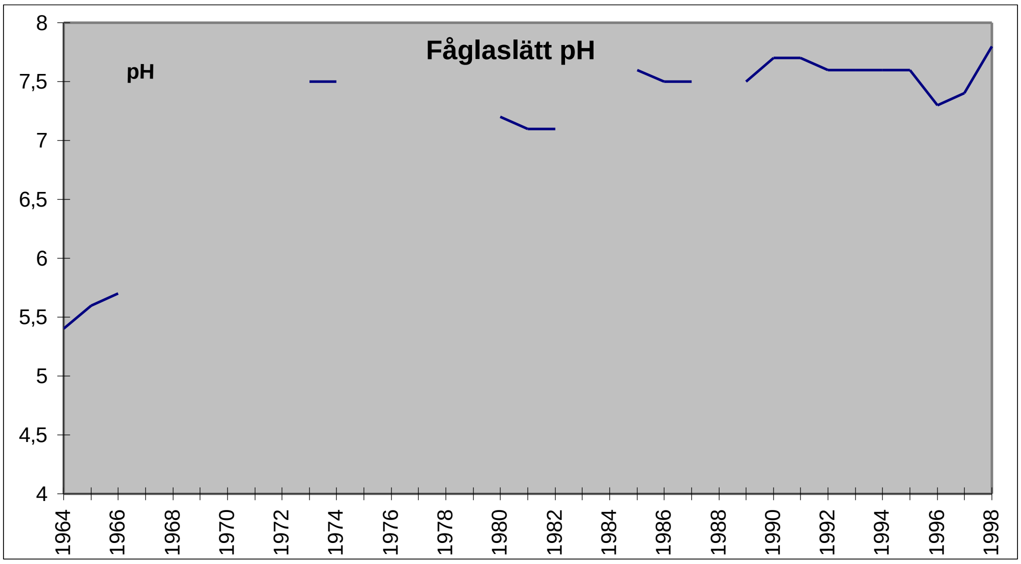
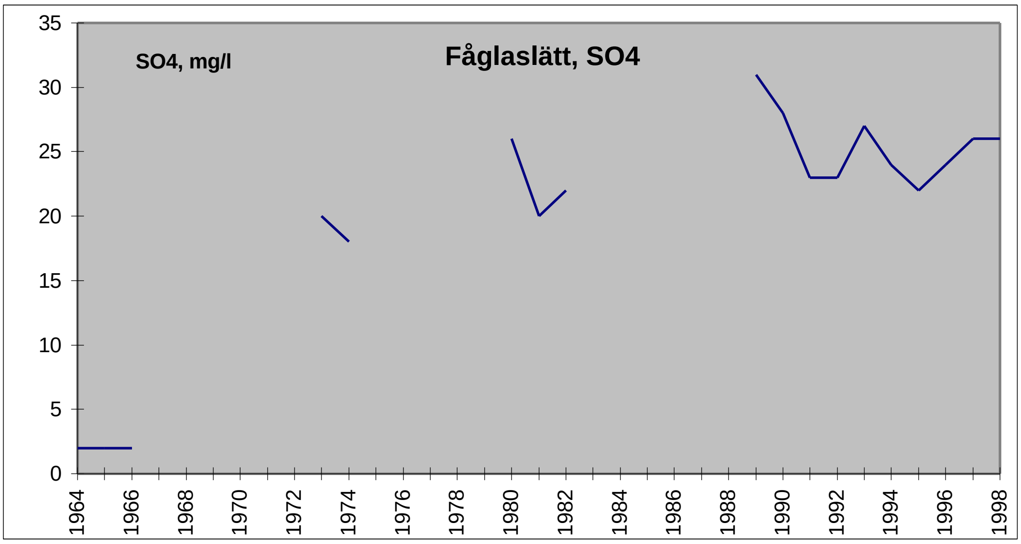


Figure 1. Groundwater quality at a water supply plant in a glaciofluvial deposit in Örby, Western Sweden.





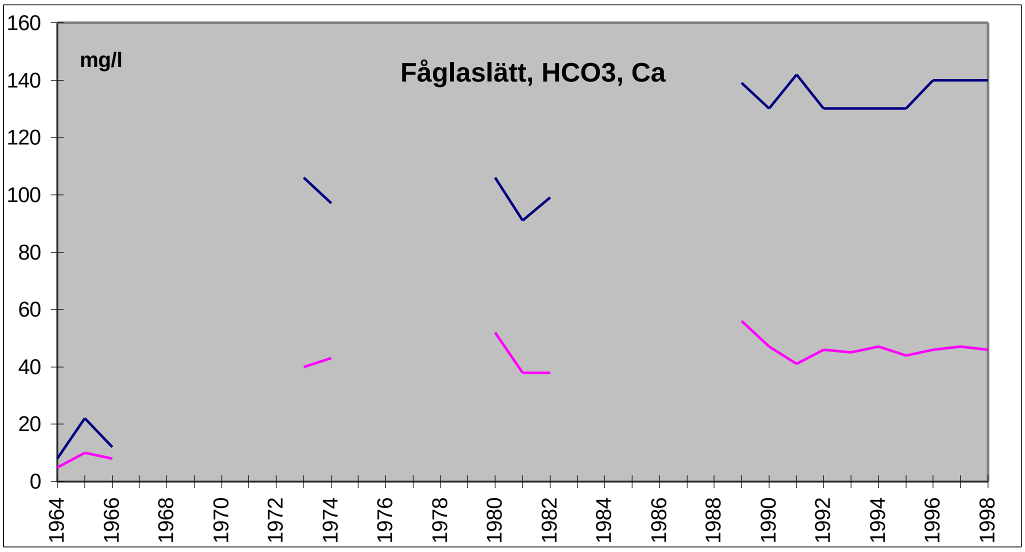


Figure 2. Groundwater quality at a water supply plant in a glaciofluvial deposit at Fåglaslätt, Western Sweden.

7.9.5 Prospective research

Although not very glamorous, long-term groundwater quality must be watched and evaluated in relation to the regional spreading of pollutants or the spreading of wood ash over large areas. Relevant research topics include:

- Heavy metals in shallow groundwater in ash treated areas.
- Variations in groundwater quality due to geological conditions and the identification of critical geological parameters.
- Overall trends of groundwater quality in different regions.
- It will be quite a job to normalise data from different series of analyses.

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7.10 Models for the combination of transport and geochemical reactions in groundwater; Horst D Schulz

7.10.1 Using adsorption/desorption with different isotherms and decay is not sufficient

For some of the organic pollutants in groundwater (aromatic hydrocarbons, halogenated compounds, pesticides) a transport/reaction modelling, which only takes adsorption/desorption processes with different isotherms and eventually a desintegration with a certain half-life into account, may only be adequate as long as a short time of prognosis and a limited travel distance in groundwater is acceptable. Therefore this model-concept should only be applied to modelling the behaviour of only one constituent, not looking at secondary reactions, neglecting interactions between different constituents and/or different phases and of cause conditional reactions and formation of metabolites.

Especially for inorganic pollutants (fertilisers, metals, radionuclides), for all types of redox-reactions, for biogeochemical processes and for dissolution/precipitation including the kinetics of such reactions, much more complex processes have to be incorporated into transport/reaction models. Microorganisms cannot only be treated as ”pollutants” but have to be regarded as an important – perhaps even the most important – part of the system pollutant/groundwater/aquifer.

7.10.2 Column experiments as a tool the understanding of processes and parameters

The biggest problem for such a way of transport/reaction modelling in groundwater is: how can we get all the different parameters which describe the different reactions and their kinetics sufficiently. Since many years it is quite clear, that batch experiments, where aquifer material is just put together with water containing a specific content of dissolved constituents and which is then stirred or shaken for a certain time, are not leading to a realistic understanding of a natural aquatic system. These K_d-values contain uncontrollable attributes and properties of the constituents and their reactions, they are influenced by other constituents of the aquatic phase and also of the solid phase, and they are not at all constant for different concentrations. The only advantage of these K_d-values is, that they are easy to measure and that it is also easy to calculate something like a R_d-coefficient, a retardation-coefficient from a K_d-value, which again easily can be used in a transport modelling in groundwater. But easy to measure and easy to model is a nice but not a sufficient argument for the description of a complex natural system.

On the other hand, field experiments under natural conditions are often too expensive and too time consuming. They leave the researcher quite often with a result, which shows between different analyzed points of the flow system already so many changes in the concentrations of different constituents, that again many parallel processes cannot be understood correctly. Also usually only one part of the system – the aquatic phase – can be analyzed, whereas the other sometimes more important part – the solid phase of the aquifer material - remains inaccessible.

The compromise between these both extremes is usually the column experiment with natural material under conditions as natural as possible (flow velocity, water quality, temperature, open or closed with respect to different gas phases, microbial activities). Column experiments under such conditions are also not at all a cheap solution of the problem. For their design and construction usually a high level of experience and of technical effort is necessary. In order to reach e.g. steady state situations or to find the results of changes in the aquatic phase sufficiently documented in the solid phase it may often be necessary to run column experiments over a time of one or two years without an interruption. But since at any time and at any point of the flow system it is possible to take samples of the aquatic phase and since at least at the end of the experiment it is possible to analyze also samples of the solid phase, usually all necessary information will be available about different reactions and about the reaction rates.

7.10.3 The technique of operator splitting as the way to complex transport/reaction models

Many scientists – especially from the mathematical sciences – have found many different solutions for the combination of physical transport and (bio)geochemical reactions in computer models. From my point of view a very elaborate, interesting and complete synopsis in the last years was given by Boudreau (1997). His book concentrates on the processes of early diagenesis mainly in younger marine sediments, but this covers nearly exactly the same group of problems as in groundwater and the same type of mathematical solutions for these problems. All these solutions are mathematically usually very intelligent, have long and impressive equations – and are far beyond, what a (bio)geochemist is usually able (or willing) to understand. But nevertheless often these solutions simplify the natural situation already to an extent, which in most cases where we start to understand some processes in natural aquatic systems is not acceptable for a (bio)geochemist.

Therefore a solution is preferred, which offers the implementation of a nearly unlimited variety of geochemical processes into a transport/reaction model although it is from a mathematical point of view a rather unintelligent type of model. This type divides up not only the path of flow into a number of discrete points or cells but also the time into discrete time-steps. For each time-step the physical part of the transport (usually advection, dispersion, diffusion) for all points or cells of the flow path is solved first as independent from all possible reactions. Then, following the physical part of the transport, the (bio)geochemical reactions are calculated and may contain all the ideas, which (bio)geochemists at a certain time may have developed and probably will develop in the future.

Boudreau (1997) describes this type of transport/rection model as ”operator splitting” and starts his very short notice with the words: ” *This is an apparently crazy idea that works rather well in practice*.” As far as I know, this technique was first used in groundwater by Schulz and Reardon (1983) with a combination of cation exchange processes and the calcite/carbonate equilibrium.

7.10.4 The model CoTReM (Column Transport and Reaction Model)

Since many years different types of such models with the technique of operator splitting have been developed in our group. They always concentrated mainly on the (bio)geochemical side of the combined problem of transport and reactions and were always designed for specific geochemical systems. The first more general version (CoTAM = Column Transport and Adsorption Model) of Hamer and Sieger (1994) still concentrated on a specific type of reactions (adsorption/desorption), but already contained a (not always correctly working) subroutine for most redox reactions in the different (bio)geochemical systems and used for the first time the geochemical model PHREEQE (Parkhurst et al., 1980) as a subroutine for calculating the species distribution and mineral precipitation/dissolution reactions. The updated version CoTReM (Landenberger, 1998) contains a new redox-subroutine and uses the new C++ version PHREEQC (Parkhurst, 1995) for precipitation/dissolution reactions.

The part of physical transport in all these model versions is one-dimensional (except the first ”nearly” two-dimensional, but unidirectional version of Schulz and Reardon, 1983). This restriction still is and will be necessary at least in the near future, because even a one-dimensional calculation which uses PHREEQC in each time-step and each cell of the flow path may need some few hours or in the worst cases days of calculation time on a modern Pentium®-PC. But since our group is more interested in the geochemical part of the problem, we do not see at the moment any reasons for designing a model version of a higher than one dimensionality. We would always prefer to calculate flow paths in a two- or even three-dimensional hydraulic model and than concentrate with the one-dimensional transport/reaction model on specific paths of geochemical interest.

The model CoTReM is available at *http://www.geochemie.uni-bremen.de/cotrem.html* together with a manual and some examples with input- and output files. These files demonstrate the different features of the model CoTReM using examples from the research of the marine part of the group. That means diffusion, bioturbation, bioirrigation as (bio)physical part of the model and different redox reactions with degradation of organic matter with different electron acceptors, dissolution/precipitation of different secondary minerals (calcite, pyrite, $Fe(OH)_{3,am.}$). Examples implementing advective transport in groundwater are in preparation.

7.10.5 (Redox-)Reaction fronts in marine sediments

The concentration profiles of porewater in marine sediments usually show very clearly the different biogeochemical reactions of early diagenesis. The physical transport in such sediments is - except in the upper one or two bioturbated decimetres – usually only governed by molecular diffusion. The primary biogeochemical reactions of the degradation of organic matter induce a complex series of secondary reactions (re-oxidations, mineral precipitation and dissolution), which are not at all totally understood. For most of especially the primary reactions it is well known, that they are microbially catalysed – although in some cases the acting microorganisms are not yet known. One very typical example for such a reaction was described by Niewöhner et al. (1998). They described the redox-reaction between sulfate and methane to sulfide and carbonate, which is documented in the measured porewater profile by a marked change in the diffusive gradients of the affected constituents. This narrow layer in the sediment with a thickness of only some few centimeters probably contains the still unknown bacteria (or the consortium of bacteria) which somehow take their energy from this reaction.

If such a system is in a steady state situation, than this layer of redox reaction will move upward with the sedimentation rate, always keeping a constant distance to the sediment surface. Changes in the methane flux from the deep or other changes of the boundary conditions will result in a non-steady state situation, changing gradients and the development towards a new steady state situation. In both cases – steady or non-steady state situation – a redox reaction front moving with a certain velocity through the sediment/porewater system is the characteristic feature.

7.10.6 Upscaling of processes and modelling: the concept of (redox-) reaction fronts

Especially for redox reaction many examples for similar fronts are known, which move through an aquifer with the certain velocity in the direction of groundwater flow. The velocity of such reaction fronts is governed by the flow velocity of the groundwater and by the concentrations of products and educts of the specific reaction in the aquatic phase of groundwater and as well in the solid phase of the aquifer. All characteristic parameters to describe the behaviour of such reaction fronts can be determined by the use of column experiments. The accuracy of these parameters is ”only” determined by the amount of acceptable or possible effort.

One of the most important problems of laboratory experiments and field scale transport/reaction processes is the ”upscaling” of the modelling. Already the physical part of the upscaling rises many problems (e.g. handling of the aquifer heterogeneities) and many researches of different groups are working on that. These problems of cause re-influence the biogeochemical part of the problem, but nevertheless the concept of (redox-) reaction fronts, their determination with adequate column experiments, and their modelling with the technique of operator splitting offers a promising approach to upscaling of transport/reaction models.

7.10.7 Prospective research

We are at the very beginning of a promising way. The final goal should be something like a computer model - preferably using the technique of operator splitting – on the one side and a somehow normalized column experiment on the other side, which leads to the necessary parameters. Both – model and column experiment – should be designed in a way that they fit together. Some of the most important scientific and practical questions on this way could be:

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7.11 Processes in the subsurface: from black box towards understanding; Wim Harder

7.11.1 Abstract

For the purpose of the present ESF-Gpoll Programme it is suggested to limit the scope of the research efforts to that part of the groundwater that participates in the hydrological cycle and has an average residence time of <200 years in the subsurface. One way to approach the fate of polluting chemicals in the groundwater that flows through the heterogeneous subsurface environment is to consider this environment as a large scale biogeochemical reactor (black box approach) which can be characterised by input/output fluxes of materials. A scale-down for subsequent scale up approach is appropriate in which the existing large body of geological, hydrological, chemical and (micro)biological data is used to describe the abiotic conditions and the biotic potential. In addition ex-situ and *in-situ* measurements are needed to adequately analyse the in- and output fluxes in the scaled-down black box; in particular new techniques to follow processes *in-situ* in real time must be developed to provide the necessary data. Apart from adequate data-management a multi-disciplinary effort in "hydrobiogeochemistry" is required to supply the necessary knowledge base for appropriate risk assessment and groundwater management.

7.11.2 Introduction

The purpose of the ESF/EERO Groundwater Pollution Research Programme (Gpoll) is to initiate and promote multinational and multi-disciplinary research on the fate in groundwater of toxic chemicals, radionuclides and excess nutrients. It focuses on pollution in groundwater systems because of their significance for maintaining clean water supplies for human and environmental health. Although it is now well-established that microbially-catalysed chemical processes occur of depths in excess of 1000m in the deep subsurface, it is proposed that the scope of the Gpoll Programme be limited to that part of the groundwater that participates in the hydrological cycle and has an average residence time in the subsurface of <200 years.

Human activities may introduce pollution into groundwater systems by either of the following pathways:

Each of these pathways results in a load on the subsurface ecosystem; the nature and extent, particularly with respect to concentration, however, may be quite different.

7.11.3 Diffuse pollution

Diffuse pollution generally leads to low concentrations of organic and inorganic pollutants. They reach the groundwater through percolation processes and communication with surface waters and constitute a load of potential electron-donors, electron-acceptors or nutrients for subsurface microbial life. A description of the fate of these compounds can best be made by considering the subsurface environment as a huge biogeochemical reactor, which can be characterised by input/output fluxes of materials. Appropriate scale-down of the heterogeneous large-scale black box to a series of communicating small-scale black boxes, taking into account the existing body of geological, hydrological, chemical and (micro)biological date, may then be used to provide a description of the abiotic conditions and biotic potential. Initially this is carried out for the small-scale black boxes and ideally should be validated by appropriate laboratory experiments. These could include microcalorimetry coupled to flux measurements in order to establish overall processes and should be followed up by characterising the dominant microbial populations using molecular diagnostic techniques. Subsequent physiological studies may then reveal the metabolic potential of the dominant organisms under the prevailing (micro)-environmental conditions. After this work has provided a description of the behaviour of the small-scale black box in response to realistic influx conditions, a more comprehensive picture may be obtained by joining the results of the individual parts together into a description of a system on a regional scale.

7.11.4 Local pollution

Local pollution resulting from industrial activities or waste dumps often leads to quite high concentrations of various pollutants in the neighbourhood of the source. In recent years research programmes and field experiments have been initiated in many countries to investigate the potential for intrinsic biodegradation of the subsurface ecosystem as a mechanism to reduce the risk of the pollutants that have entered the soil. In the Netherlands the so-called NOBIS programme has initiated a substantial research effort, often by way of a public-private partnership, to assess the bioremediation potential for sites contaminated with aromatic and chlorinated hydrocarbons. The results obtained so far have demonstrated that in the case of aromatic compounds that were present in anaerobic aquifers, toluene and ethylbenzene were biodegraded, while the degradation of benzene required small amounts of oxygen. Also in the case of chlorinated hydrocarbons the redox condition in the aquifer turned out to be a key factor in determining the potential for intrinsic biodegradation. Low redox conditions generally favour reductive dechlorination processes, while high redox conditions generally allow oxidative degradation. The redox condition in the field is determined by the organic load (i.e. age) of the sediment, the organic influx (naturally or artificially) and the amounts of the various election acceptors present in the sediment and in the groundwater. When degradable organic matter enters the subsurface, the available electron acceptors are used and become depleted in the order O_2, Mn(IV), NO_3^-, Fe(III), SO_4^{2-} and MCO_3^-.

Often, natural biodegradation processes appear capable of converting large amounts of chlorinated hydrocarbons without any external stimulus. When sufficient time and space is available, intrinsic bioremediation is then completely protective for man and the surrounding ecosystem. However, at other sites the natural biodegradation processes need to be enhanced, either by providing a suitable electron donor (occasionally also acceptor) or by putting in place a bio-active zone or bioscreen to prevent spreading of the plume. Detailed studies of the physiology of the organisms involved in the metabolism of the various compounds and the conditions for optimal activity has provided a knowledge base with predictive power. When the physio-chemical properties of the environment are known, a remediation protocol can now be put together which will lead to the required risk reduction with an adequate level of confidence.

7.11.5 Intensive exploitation and use of the subsurface

In densely populated countries available land space is becoming a problem. As a result the subsurface is increasingly used for large infra-structural constructions and the effect that these structures have on the subsurface environment are largely unknown. The same is true for large-scale storage of heat or cold and underground storage of natural gas, hydrogen or carbon dioxide. In particular hydrogen, which is an excellent electron donor for various groups of anaerobes (in combination with CO_2), may cause great disturbance in the sub-surface ecosystem and should not be stored underground except under well-controlled conditions.

7.11.6 Prospective research

A major issue for strategic research is to learn more about the various processes that occur in the subsurface. This applies both to processes in undisturbed systems and in systems that are subjected to low levels of pollutants that enter the subsurface by way of diffuse pollution. This type of research requires a multinational and multidisciplinary effort in "hydrobiogeochemistry" and should heavily lean on adequate datamanagement of the huge database that is already available. A "scale-down" for "scale-up approach" is suggested which should be supported by new techniques (to be developed) to provide *in-situ* process data in real time.

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7.12 Environmental quality criteria for Sweden; Thomas Nilsson

7.12.1 Abstract

The Swedish Environmental Protection Agency has during four years developed Environmental Quality Criteria for Sweden, which will be published in late 1998. Six different environments are treated in separate reports: 1) the forest landscape, 2) the agricultural landscape, 3) groundwater, 4) lakes and watercourses, 5) marine coastal waters and the sea, and, 6) highly contaminated land. The purpose of the Environmental Quality Criteria is to make it possible for regional authorities to assess the environmental status. The assessment is divided into two parts: 1) an assessment of the environmental status based on knowledge about effects on human health or natural ecosystems and biodiversity, and 2) an assessment of human impact, measured as divergence from a natural or background value. Parameters included, among others, are acidification, eutrophication, pesticides, other organic pollutants and metals.

7.13 Microbial processes in hard rock aquifers and their potential influence on hydrocarbon pollution and radionuclide migration; Karsten Pedersen

7.13.1 Abstract

Hard rock is used in many countries for storage of crude oil, diesel, gasoline, gas and other fuels. At closure, or by accident, hydrocarbons may enter the groundwater and treat drinking water sources for a very long time. Hard rock aquifers are very difficult to remediate which leaves natural degradation as the only realistic alternative for clean up. Most deep groundwater is anaerobic which implies that anaerobic degradation must occur or will the groundwater be contaminated for all future. Repositories for radioactive waste will also placed underground, often in hard rock environments. Research on microbial processes in deep environments aims at understanding the influence on repository performance and radionuclide migration. The knowledge gained will contribute to the understanding of how accidental releases of radionuclides can be remediated using microorganisms. It will also give insight in microbial processes that may increase radionuclide migration.

7.13.2 Introduction

7.13.2.1 Hydrocarbon pollution of hard rock aquifers

A stock pile of approximately two billion litres of fuel, mostly diesel and gasoline, were stored in Swedish underground vaults 30 to 40 years ago; back in the time of cold war and oil crises. The repositories were built 30 to 50 meters below ground level, mostly in granitic rock and they were generally unlined, except for the use of concrete to make the vault floors flat enough for driving trucks etc. One single repository could consist of up to six vaults, each with a volume of 10 000 m^3. More than 40 repositories were built. A changing world with an end of the cold war and a diversified production of oil has made these repositories nonessential. The Swedish stock pile of diesel and gasoline have now been sold out and the repositories are to be phased out, stripped of equipment and delivered back to nature. Before doing so, investigations were undertaken to ensure that the surrounding rock and groundwater were free from diesel or gasoline above the approved concentration limits. Groundwater from hard rock aquifers is commonly used as a source of drinking water and is therefore sensitive to hydrocarbon contamination. Preliminary investigations, however, indicated that large quantities of fuel remained in the rock matrix and in the groundwater conducting fractures surrounding the repositories. As consequence, a major research and development program was launched during 1996, with the main task to study in more detail, the distribution, transport and possible biodegradation of this fuel. Industry and military in Sweden have built and are still running another 60 vaults. Underground vaults for storage of petroleum products are common all over the world, making this research a global concern.

As long as storage is in use, it is pumped for groundwater which sustains a groundwater flow towards the vaults. Most hydrocarbon contaminants then move with the groundwater. They can be removed before disposal of the pumped groundwater. However, once storage is abandoned, groundwater flows will go back to the original flow directions and this creates a potential pollution problem. Remaining hydrocarbons may follow with the groundwater and make a potential contamination risk for drinking water sources downstream the storage. The paper by K. Abrahamsson in this volume treats detection and analysis of hydrocarbons in hard rock and groundwater.

Aerobic microbial degradation of many different hydrocarbons is known to occur but much less is known about anaerobic degradation. It is generally accepted that anaerobic degradation of hydrocarbons is a much slower process if occurring at all. Groundwater in hard rock aquifers is generally anaerobic and this raises some important questions. Will migrating hydrocarbons be degraded by microbes in anaerobic hard rock groundwater and at what rate?

7.13.2.2 Radionuclide migration in hard rock aquifers

Radioactive waste arises mainly from the production of nuclear power. Significant amounts of radioactive waste also come from research, hospitals, industry and military. Most countries plan to deposit their low, intermediate and high level nuclear wastes in repositories underground. The performance of such repositories is in focus for large national and international research programs with multidisciplinary approaches. The influence from microbial processes on repository performance is a growing research area in several countries. The knowledge gained through this research will be of high value for understanding how microbial remediation techniques should be applied on accidental releases of radionuclides.

7.13.3 Current knowledge

7.13.3.1 Hydrocarbon pollution of hard rock aquifers

Anaerobic degradation of various hydrocarbons has been demonstrated in laboratory experiments: Saturated hydrocarbons by sulphate reducing bacteria (SRB) (Aekersberg et al. 1991). Toluene and crude oil by SRB (Rabus and Widdel 1995b, Rabus et al. 1993, Rueter et al. 1994). Ethylbensen and toluene by denitrifying bacteria (Biegert and Fuchs 1995, Rabus and Widdel 1995a). Toluene, phenol, *p*-cresol and aromates by iron reducing bacteria (Lovley and Lonergan 1990, Lovley et al. 1994, 1996). Aliphatic and aromatic hydrocarbons by a *Pseudomonas* strain (Morikawa and Imanaka 1993). Some field studies have also been performed. Jet fuel degradation in underground vaults (Roffey et al. 1989), and degradation of benzene, toluene and xylene by mixed populations (Edwards and Gribic-Galic 1992, Edwards et al. 1992). All these publications suggest that anaerobic degradation of hydrocarbons is possible in hard rock aquifers, provided relevant electron acceptors are available.

7.13.3.2 Radionuclide migration in hard rock aquifers

The bulk part of radionuclides produced in a nuclear electric power reactor remains in the spent fuel elements, characterised as high level radioactive waste (HLW). Radioactivity will decay with time, but some long-lived radionuclides will make the HLW hazardous for a very long time. The spent fuel elements will be encapsulated in copper-steel canisters and placed in bentonite in deposition holes in tunnels at an envisaged depth of about 500 m. The amount of spent fuel in a canister and the distances between the canisters in the repository are chosen so that the peak temperature is reaching about 80 °C at the warmest location at the canister surface. The restriction in temperature is mainly there to guarantee the long time performance of the bentonite. The low solubility of the spent fuel matrix, the copper canister, the bentonite buffer and the depth of emplacement in stable host rock are the main barriers to protect man from the radionuclides.

In 1987, microbiology became a part of the Swedish scientific program for the safe disposal of HLW. The goal of the microbiology program is to understand how subterranean microbial processes will interact with the performance of a future HLW repository. Our research on microbial life in deep granitic rock aquifers (Pedersen 1996, 1997b) has been performed at seven sites at depths down to 1500 meter. The Stripa research mine in the middle of Sweden (Ekendahl and Pedersen 1994, Ekendahl et al. 1994, Pedersen and Ekendahl 1992a), the Äspö hard rock laboratory (HRL) situated on the south eastern coast of Sweden (Pedersen 1997a, Pedersen and Ekendahl 1990, 1992b, Pedersen et al. 1996a, 1997b, c) and on four sites in Finland. The Äspö HRL has been constructed as a part of the development of the Swedish concept for deep geological disposal of spent nuclear fuel and the work has been divided into three phases; the pre-investigation (1986-1990), the construction (1990-1995) and the operating (1995-) phases. Some work has also been performed in co-operation with other national or international research groups in Canada (Stroes-Gascoyne et al. 1997) and at the natural analogue sites Oklo in Gabon (Pedersen et al. 1996b) and Maqarin in Jordan (Pedersen et al. 1997a).

In general, it can be concluded that microbial processes will have a much larger influence than anticipated a decade ago on migration of radionuclides possibly escaping from various repositories and accidental releases (Pedersen 1997c, Pedersen and Karlsson 1995).

7.13.3.3 Hydrocarbon pollution of hard rock aquifers

A two years research project on analysis, detection and microbial degradation of diesel in crystalline rock and groundwater surrounding large underground vaults for long term storage of diesel has recently been completed. During these two years, we have detected degradation of alifatic hydrocarbons *in vitro* and *in situ* by sulphate and iron reducing bacteria. We are now in the planning phase for a more long-term project (4-5 years) that will go deeper into the problem.

7.13.3.4 Radionuclide migration in hard rock aquifers

Seven research tasks were identified by Pedersen (1996) that are of importance for the performance assessment of microorganisms in radioactive waste disposal. They were:

The reports by Pedersen and Karlsson (Pedersen and Karlsson 1995) and by Pedersen (Pedersen 1997c) summarise ongoing activities in the Swedish program for the above arrayed research tasks.

7.13.4 Prospective research

Anaerobic degradation of hydrocarbons in hard rock aquifers. At what rates and to what extent will anaerobic microbial degradation of hydrocarbons occur in hard rock aquifers? Can site specific constrains be identified?

The intra-terrestrial biosphere. Is there a deep intra-terrestrial biosphere and how does it sustain its life processes? What energy sources and fluxes of energy will be available for microorganisms in and around radioactive waste repositories?

Microbial reducing activity. Will bacterial oxygen consumption significantly contribute to oxygen removal from radioactive waste repositories? To what extent may bacterial production of reduced compounds such as organic material, methane, sulphide and ferrous iron contribute to keeping the repository host rock reduced?

Microbial influence on radionuclide migration. To what extent, if any, can bacterial dissolution of immobilised radionuclides and production of complexing agents increase radionuclide migration rates?

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7.14 *In-situ* bioremediation of contaminated aquifers - scale up investigations; Ute Rößner

7.14.1 Introduction

The paper presents our experiences in the field of *in-situ* remediation of contaminated aquifers, especially from the perspective of co-operative research work of engineering and geomicrobiology. One of the important requirements to investigate the possibility of *in-situ* bioremediation of contaminated aquifers is the sampling and preservation of relatively unchanged sediments and groundwater or porewater, respectively. Based on the sediment and groundwater samples the laboratory experiments can be planed. The first step of investigation should be the estimation of the population density and the potential metabolic activity of subsurface bacteria. These tests allow to define aquifer horizons of a potential microbial transformation of contaminants. The microbial transformation also depends on the availability of contaminants. After the geochemical and -microbial analysis of sediments it is important to investigate the kinetics of biotransformation as a function of aquifer conditions. These investigations should be performed as batch experiments to estimate the time dependency of the process. The simulation of the overall transport processes (time and local dependency) of contaminants are performed by one-dimensional column experiments. The scaling up investigations on one example of a large aquifer contamination in Germany are presented in the following paper.

7.14.2 Site characterization and concept of the remediation technology

Groundwater within the subsurface drainage area of the Berlin-Friedrichshagen waterworks (south-east of Berlin, Germany) is in part highly contaminated with ammonium due to former disposal of domestic and industrial sewage (coal gasification plant) on land and drainage from the non-sealed, sludge drying places of the Münchehofe waste water treatment plant (Figure 1). The contaminated aquifer has a volume of about 200 million m³ (1.5 km length, 3 km width and 45 m depth). The ammonium concentration in the groundwater spans a range of 10 to 90 mg/L NH_4-N. Nitrate was only measured beneath the former irrigation fields in the upper part of the aquifer.

The idea for an *in-situ* remediation technology is building up an oxidation zone by pumping oxygenated water into the deep aquifer. Ammonium dissolved in pore water and released by desorption from sediments has to be oxidized to nitrate. Nitrate as a product of nitrification moves like a tracer with no retardation out of the oxidation zone into the anoxic aquifer and has to be reduced (e.g. by organic or reduced sulfur compounds). Alternative technologies for remediation of this ammonium contamination are physical-chemical processes (e. g. degassing of ammonia (NH_3) at high pH value or ion exchange of ammonium). Increase of pH in the large volume of the contaminated aquifer is impossible. Ammonium is distributed between sediment and pore water with a distribution coefficient of 0.5 L/kg, which means 80 % of ammonium is associated with the sediment surface in a specific volume. Ion exchange requires the input of an additional cation (e. g. calcium) into the aquifer. Flushing the aquifer with water (free of ammonium) needs a minimum of five cycles of pore water exchange, which is not affordable.

Microbial nitrification of ammonium is used as a technology in waste water treatment. The nitrification rate depends on temperature, pH-value and oxygen supply. *On-site* technology has the problem of decreasing nitrification during winter time. An advantage of the aquifer as a reactor is the constant temperature of 12 °C. Because of the large volume of the aquifer and the low flow velocity of groundwater the required reaction rate of nitrification for an efficient *in-situ* remediation can be small. A major problem of *in-situ* nitrification is the oxygen input and transport through the aquifer. Mixing of oxygen with the groundwater in the subsurface is only possible with the process of dispersion. The build-up of a nitrification zone in the subsurface has been reported up to an ammonium concentration of 5 mg/L [2, 3] .

7.14.3 Sampling sediment and water

Bore-holes were drilled on the former sewage irrigated fields located in the northern part of the contaminated aquifer. Sediment from the aquifer was collected as core samples (1 m length, 0.1 m diameter). The sampler for sediments was rammed with a pile driver into the subsurface below the groundwater table. The sole of the bore-hole was sealed with a clay suspension (bentonite) to prevent the inflow of water used for bore-hole stabilization. This way the pore water of sediment cores was not changed. Sediment cores were immediately stored at a temperature of -18°C to keep the anoxic conditions. Drinking water from the Berlin-Friedrichshagen water works was used as water for laboratory experiments, because it is the planned infiltration water of the remediation technology. Water was stored at a temperature of 10°C.

7.14.4 Estimation of potential microbial activity

The total cell density of sediment was estimated with AODC (Acridine Orange Direct Count). The main bacterial groups were quantified with MPN (Most Probable Number). The potential metabolic activity of subsurface bacteria was estimated with an enzyme activity test (dehydrogenase activity). The sediment samples were taken from 5 different boreholes up to 50 m depth. All profiles showed similar results. The total cell density ranged from 5×10^8 to 10^9 cells/gdw independently from the depth of aquifer. The potential enzyme activity (dehydrogenase) was also measured with the same substrate utilization over the hole profile. Bacterial group of ammonia oxidizers (nitrification) were not detectable. Bacterial group capable of denitrification was estimated in a range of 10^4 to 10^6 cells/gdw. This results indicates the problem of developing a bacterial population capable of nitrification by oxygen infiltration.

7.14.5 Investigation on microbial transformation of contaminants

Batch reactors with sediment from different boreholes/depths and drinking water (provided as infiltration water) spiked with ammonium were incubated at room temperature (18-22°C) and at 10°C (the approximate aquifer temperature). After a lag phase of 7...15 days ammonium was completely oxidized to nitrate. Nitrite was only measured as an intermediate product up to 5 mg/L NO_2-N. Ammonium oxidation at 10°C required a longer lag phase of 40...50 days. The total time required for complete ammonium oxidation was 3 times longer at 10 °C than at room temperature. Nitrite was measured at low concentrations <0,5 mg/L NO_2-N.

In order to investigate ammonium oxidation at higher oxygen concentration (100...150 mg/L O_2)simulating the conditions of 30 m depth near the infiltration well screen a batch experiment under pressure was conducted. Water spiked with ammonium (15 mg/L NH_4-N) was saturated with oxygen up to 150 mg/L O_2 at a pressure of approximately 3 bars. Oxygen concentration was kept constant between 100 and 150 mg/LO_2. Oxygen loss was caused by pressure loss of the reactor. No ammonium oxidation was observed for about 100 days. After lowering the oxygen concentration on 40 mg/L O_2 we estimated a lag phase of 50 days for nitrification. Within 60 days ammonium was completely removed from water, but the concentration of nitrite and nitrate still increased. Additional 60 days were required to a complete oxidation of ammonium released from the sediment. Results of this test shows the inhibition of ammonium oxidation by an oxygen concentration of 100...150 mg/L O_2 At a concentration of 50 mg/L O_2 and a temperature of 10°C the same lag phase and reaction kinetics was observed than in previous batch experiments. Nitrification of ammonium dissolved in pore water and released from sediments contributes with 50 % respectively to the nitrate production.

7.14.6 Overall transport of contaminants

Based on the results of batch experiments a laboratory column experiment was designed to simulate the build-up of an oxidation zone and transport of oxygen, ammonium and nitrate through the aquifer. The reactor consisted of an stainless steel column (2 m length, 0.2 m diameter, 63 L volume) with sample ports (SP) of stainless steel filter tubing (7.5 cm length, 2 mm diameter, 0.2 mm holes) at five horizons

(0.0 m input; 0.1 m SP1; 0.45 m SP2; 1.0 m SP3; 1.55 m SP4; 1.9 m SP5 and 2.0 m output). Pore water of the contaminated sediment had an ammonium concentration of 7...15 mg/L NH_4-N and contained no nitrate and oxygen. Input water was saturated with oxygen up to 45 mg/L O_2. Water was pumped through the column with a flow rate of 1 Liter/day.

The concentration curves for different sample ports along the flow path were fitted with the one-dimensional transport model (Equation 1).

$$\overbrace{\Delta\left(v\,D\frac{\partial c}{\partial x}-Qc\right)}^{\text{inf lux – outflux}} = \overbrace{Rnw\Delta x\frac{\partial c}{\partial t}}^{\text{storage}} + \overbrace{v\,\Delta x\,l^{*}}^{\text{decay}}c + \overbrace{v\,\Delta x w^{*}}^{\text{source/ sin k}} \quad \text{in } (g_C/\text{day})$$

(1)

with D = dispersion coefficient in m_R^2/d; Q = flow rate in m_W^3/d, c = concentration in g_C/m_W^3; x = Cartesian coordinate in m_R; t = time in d; R = retardation coefficient dim.less; n = water filled porosity in m_W^3/m_R^3; ω = cross sectional area in m_R^2; $\lambda^* = \lambda \cdot n$, λ = first order decay rate in d^{-1}; $w^* = w \cdot \rho_b$, w = source/sink flux (zero order rate) in $g_C/kg_{DW}/d$, ρ_b = bulk density in kg_{DW}/m_R^3. Indices are R = room (space), W = water, C = compound (oxygen, ammonium, nitrate), DW = dry weight of sediment. The transport equation is solved by a finite-difference approximation. The number of elements and time steps amounts to 200 respectively.

The transport model was extended with the option of an oxygen consumption capacity and an ammonium desorption capacity. Measured oxygen concentration at different sample ports along the flow path was simulated with an oxygen consumption kinetics of 1 mg/kg/day. The consumption capacity of sediments in the column ranged between 100 and 150 mg/kg. Ammonium concentration along the flow path was simulated with a desorption rate of 0,05 mg/kg/day NH_4-N and a desorption capacity of 3,9 mg/kg NH_4-N. Kinetics of ammonium oxidation (nitrification) was controlled by desorption kinetics of ammonium. Therefore, nitrification and denitrification rate were set equal to the desorption rate. Nitrate concentration was simulated with a 45 day lag phase of nitrification corresponding to the results of batch tests.

7.14.7 Conclusions on perspective research work

This example of our research work shows some points for collaborating work of engineers, microbiologists, chemists and geologists to develop effective *in-situ* remediation strategies for contaminated aquifers. One of the most important questions is the distribution of contaminants between groundwater or porewater and the solid sediment matrix. The storage capacity has to be known to quantify the release of contaminants from sediments to the groundwater. The mass transfer rate of contaminants is very often determined by diffusion controlled desorption processes. If the concentration of contaminants on sediments is relatively high and we observe a slow kinetics of release it should be useful to investigate the mobilization and solubilization with surfactants or cosolvents. Investigations on different scales are very important. At the first step the principle microbial transformation processes has to be studied under defined conditions. On the second level the simulation of microbial transformation processes under real hydraulic flow conditions of the aquifer is very important to quantify the real mass transfer processes. *In-situ* remediation technology should be evaluated at the pilot scale to quantify the impact of natural heterogeneity of the aquifer on the transformation processes.

7.15 Microbial activity in cold climate; Mirja S. Salkinoja-Salonen, Mika A. Kähkönen, Christophe Wittmann, Rainer Peltola, Jukka

7.15.1 Abstract

Microbial activities in soils and ground water aquifers were studied at low temperature to gain understanding of the limitations put by temperature on the intrinsic remediation capacity of Finnish soils exposed to diffuse and point source pollution. The results show that the cold temperature had only a marginal effect on the microbial degradation reactions, Q_{10} near 0°C ranged from 2.0 to 2.8. Degradative activities towards many substrates were maximal in October and not in the warmer summer months. The activation energy (E_a) of degradation tended to be lower at substrate concentrations of <1 ppm than at 50 ppm. Biodegradative activity became zero at –7 $\pm 1^{o}$ C – value obtained by extrapolation, because such low temperature was not observed in any of the soil horizons druing the 365-d observation period. The degrader bacteria active at temperatures relevant to the annual average in soils were psychrotrophs and belonged to *Sphingomonas* and related α-proteobacterial genera, and to yet to describe genera of the actinomycetes and cytophaga groups.

7.15.2 Introduction

The average annual temperature in Finland is from 3.5ºC (north) to 6ºC (south). It is the northernmost industrialized country in the world. The main drinking water resource is groundwater (55%). The main industrial resource is forest, covering 66% of the land surface (Anon, 1998). The groundwater aquifers are mainly shallow (<30 m subsurface), generated under glacially formed eskers. The ground water is used young: the impact of the snow (pH 4) is in many aquifers observed as a drop of pH a few months after the snow has melted.

The surface soil is frozen many months a year. The groundwater recharge during winter is minimal. The forests are mainly coniferous, and the soil is podzolised and acid (pH 3 to 4.5) (Table 1). In the text below we attempt answering the question how and what kind of microbes (biochemical, taxonomic, ecological properties) will under these conditions – general in textbooks regarded as nonpermissive for microbial activity – transform the acid rain water to clean groundwater, and if or how the ambient temperature may limit their action in the cold season. The studies were conducted at the agricultural research farm in Helsinki, Viikki, at the forest station of Helsinki University, Hyytiälä, 200 km north of Helsinki and at the Kärkölä community (130 km north of Helsinki) groundwater resource (now closed), polluted since >25 years heavily with chlorinated phenols.

7.15.3 Descriptions of the study sites

Fig. 1 summarizes the results of 365 (1997-8) average daily temperature measurements of air and from the different layers of the podzol soil at Hyytiälä (30yr old scots pine canopy) and Mämmilampi (100 yr old Norway spruce canopy). The soil pH and contents of various inorganic anions and cations are measured on continuous basis in these forests at Hyytiälä station (Ilvesniemi & Pumpanen, 1997). The temperature profiles in Fig 1 may be considered typical of the Finnish situation. The temperature of soil is 0ºC or below (frozen) from November to April. The summer temperature at the depths of $\leq$ -10 cm reaches $\geq$12ºC for about 6 to 8 weeks per year (Kähkönen et al., 1998). Finnish conifer forest floor is acid (Table 1) because of the acids generated by the coniferous litter degradation and the acid bedrock. The humic and the eluvial layers of the soil are approx. 1 mM in respect to exchangeable protons (1 mmol l^{-1} of soil) while the deeper layers are ca. 0.5 mM.

Farm soils are limed to be less acid (pH 5.8 to 7). The Viikki farm in Helsinki belongs to the University and has been used for agricultural education for over 60 years. The samples were take after autumn ploughing to minimize the effect of vegetation. The forest soils from Viikki nature park were from near the Baltic Sea coastal line (<300 m), nonmanaged deciduous, mainly birch, forest.

The Kärkölä groundwater aquifer was contaminated by a large sawmill. The mill used a mixture of chlorophenols, 1 to 2 % of sodium salts of 2,3,4,6 tetrachlorophenol (80%), 2,4,6-trichlorophenol (10…15 %) and pentachlorophenol (5…10 %) for dip treatment of wood in outdoor basins. The aquifer adjacent (<500 m) to the mill was found to contain up to 190 mg of chlorophenols l^{-1} (Lampi et al., 1990).

7.15.4 Microbial activities in soil: methods

We measured many different activities from forest and farm soils during 4 different seasons in 1997-1998: *i*. the net flux of CO_2 from the pine forest floor soil cuvette as well as from *ii*. the freshly sampled, sliced soil in closed bottles; *iii*. twelve different enzymic activities measured at their *in-situ* pH within a few hours from sampling; *iv*. oxidation potential for methane and *v*. mineralization potential for selected xenobiotic compounds (pesticides and PAH-compounds) by radiorespirometry.

The soil cuvette (5 l) was automatically operated in the forest and the gas composition on-line autoanalysed (for a description, see Haataja & Vesala, 1997). The cuvette lid was normally open, but closed for 15 s at intervals of 10 min. During closure of the lid, the changes of concentrations of inflowing and outflowing O_2 and CO_2 to and from the cuvette were measured. Simultaneous to this net flow measurement, soil cores were sampled using a Westman corer (Westman, 1995), the six horizons separated on site (the illuvial layer as two parts) and the endogenous respiration measured without delay and no adjustment of the natural moisture, by the closed bottle method (5 g of soil & 120 ml of air per bottle). The CO_2 was monitored by gas chromatography (Kähkönen et al., 1998). It was insteresting to observe, that when the carbon dioxide evolution by the individual horizons were added up, the figure obtained was close to that obtained by measurement of the net flow rate using the soil cuvette. The results will be described in detail (Pumpanen et al., 1998).

The results cited above thus validated the authencity of mineralization assays where the soil strata were separately analysed. The mineralization potentials of the soil strata towards selected PAH compounds and pesticides were analysed by macro- and microradiorespirometry (Laine & Jorgensen, 1996; Kurola 1998, Peltola 1997). The hydrolytic enzymic activities were measured by kinetic fluorimetry *on-site*, using umbelliferyl-conjugated subtrates as described (Suominen et al., 1998).

7.15.5 Cold season microbial activities in soils: results

Examples of selected biochemical potentials of the forest soils potentials measured over 4 seasons are shown in Table 2. It shows that the total methane oxidation potential in the soil column was similar in July and in October (0.01 mmol CH_4 oxidized m^{-2} d^{-1}), although the soil had experienced temperatures from +9ºC to +13ºC in the weeks before sampling in July and +2ºC to +6ºC in October (Fig. 1). Potential activities of β-glucosidase and phosphatase (Table 2), β-xylosidase, cellobiosidase (not shown) were similar or higher in October than in July. These findings indicate, that the season for microbial biocatalytic maximum was not directly linked to temperature, but maybe more to the availability of substrate (litter fall in October).

As the potential activities were (see above) high in the cold season (Table 2), we carried out the actual measurements at several temperatures above and below 0ºC . Table 3 shows results of such measurements for the endogenous respiration in winter. The activities in December and January (i.e. at 0 °C soil temperature) were only little lower than at 4 to 5 °C in October, when most microbial activites were observed to be maximal in soil (Table 2). When the reaction rate *vs* ambient temperature was plotted, it cut the x-axis at -7 ±1ºC, indicating that this temperature probably the end point of soil mineralization processes. Such low temperature was not seen in any of the soil horizons on any of the 365 monitoring days, on either of the monitored sites (Mämmilampi and Hyytiälä). We thus conclude that the biomineralization of organic matter in these forests soils was not blocked by cold temperature in any season.

Table 3 also shows that Q_{10} of endogenous biomineralization in the forest soil ranged from 2.0 to 2.8 in the cold season (soil temp. of 0.1ºC to 5ºC). This is significantly lower than the Q_{10} of 8 calculated for soil organic matter decomposition by Kirschbaum (1995) at this temperature, and similar to that calculated at 20ºC (Kirschbaum 1995). Similarly weak temperature dependence (Q_{10} = 1.8) has also been observed in coastal sediments in Denmark (Thamdrup et al., 1998). The data also show that the apparent activation energy for biodegradation of xenobiotic compounds (Table 4) did not increase when ambient temperatures were low. Our data indicate the presence of temperature adapted microbial populations.

Mineralization of ^{14}C-labeled (1 to 4 rings) aromatic substrates were studied at different temperatures in agricultural and forest soils. The apparent activation energy was for < 2 ppm of substrate (simulating diffuse pollution) always lower than for higher concentrations (5 or 50 ppm, simulating point source pollution) (Table 4). Similar trends were observed for 2,4,5-trichlorophenol and for phenanthrene. This may indicate that the natural soil contained population was adapted to diffuse pollution. Some of the pollutants studied (benzene, pyrene, phenanthrene, pentachlorophenol) were measurably mineralized by the agricultural soils and by the fine root fraction of the forest soil, but not by the strata of forest soil from which the fine roots were removed by sieving. The findings indicated a role for the rhizosphere microorganisms as organic pollutant degraders.

The ultimate mineralization yield (i.e. $^{14}CO_2$) from ^{14}C–ringlabeled benzene was >70% at 20 ºC , but only 50% at +4 ºC. These yields were obtained within 2 weeks after spiking the ^{14}C-benzene; no further increase occurred upon the subsequent 12 weeks of incubation of the soils. When the soil spiked with ^{14}C benzene was incubated buried in the earth, from March to May, the ambient temperature increased from 0 °C to +15 °C and the $^{14}CO_2$ yield from 15% to 40% (Peltola, 1997). The nonmineralized benzene-carbon was in the soil not as benzene, indicating essentially complete reaction. The results suggest the soil microorganisms were more economical with their energy housekeeping at low (suboptimal?) temperature. They minimized the portion of substrate that was burned to $^{14}CO_2$ (for gaining ATP). Such regulatory mechanisms could represent one explanation to the well known fact, that more organic matter turns into humus in boreal climate than in warm climate, eg. tropics. This could also be interpreted to mean that more bound residue is generated from pollutants in the cold climate.

7.15.6 Organic matter and –pollutant degraders in the cold : who are they?

Chlorophenol degraders were isolated from the heavily polluted aquifer of Kärkölä community. Out of the 59 pure cultures isolated, 17 different taxa were identified. All grew at +8 °C and degraded 2,3,4,6-tetrachlorophenol at 1 ppm, some isolates releasing 60% of the stoichiometric amound of Cl^-. Some isolates also degraded 2,4,6-trichlorophenol (7 mg l^{-1}) and pentachlorophenol (2 mg l^{-1}) (Männistö et al., 1998). Many of the gram negative isolates tolerated >100 mg of chlorophenols l^{-1}, the gram positive isolates only 5 mg. Partial sequencing of 16SrDNA genes (450 bp) indicated similarity at >98% level with *Sphingomonas aromaticivorans* (99%) and *Sphingomonas sp* CF6 (99.3%), *Rhizomonas suberifaciens*^{T} (98.2%) and *Caulobacter sp* (98.0%). All of these are α-proteobacteria. Only one gram negative strain outside the α-proteobacteria was identified (*Pseudomonas amygdali*^{T}, 99.2%). Several of the gram positive strains were nocardioform actinomycetes (containing signature fatty acids 10-Me-C16:0 and 10-Me-C18:0), but not assignable to any of the present genera (Männistö et al., 1998).

One terrestrial of psychrotrophic actinomycete, degrading natural organic matter, was taxonomically fully investigated. The group represents a new genus, possessing a rare type of peptidoglycan (B2 β-). It contains a hitherto unknown fatty acid as a signature fatty acid (13…20%). This fatty acid coincides in retention time (GC, HP5) with 2-OH C14:0 but GC/MS data show it is not this hydroxy fatty acid (Mikkola, 1998). This new genus will be proposed the name *Frigoribacter*, to honour the ability of this species to only grow in chilled environment (Kämpfer et al., 1998). Although thousands of bacterial genera and species have been taxonomically described in the literature, very few of them optimally grow below +10 °C. Recently one such actinomycete was described, *Cryobacterium psychrophilum*, isolated from the Antarctica (Suzuki et al., 1997). It possesses a B-type of peptidoglycan but is phylogenetically unrelated to *Frigoribacter* from Finland. We conclude from our initial studies with the terrestial and ground water microbes that organisms preferrably or only growing in the cold, are found in ample amounts in these environments but represent an unexplored taxonomic habitat. Many more new taxa wait to be described and have their physiological and ecological skills described.

Bild saknas

Fig. 1. Average daily soil temperatures over a 365 day period in air and the different layers of the Mämmilampi spruce forest floor. ***Data of H. Ilvesniemi from: Kähkönen et al., 1998.***

Table 1. Podzol soil of Mämmilampi 100yr old Norway spruce canopy, Hyytiälä Finland. Measured October 1997.

Soil layer	*Depth to cm*	*TOC, mg g^{-1}*	*N_{tot}, mg g^{-1}*	*pH (H_2O)*	*pH (KCl)*
Humic	-4	450	12	4.4	2.9
Eluvial	-7	104	0.5	4.7	3.3
Illuvial up	-12	61	0.9	5.1	3.8
Illuvial low	-17	12	0.3	5.3	4.3
Ground soil	-23	10	0.1	4.9	4.4

Data from: Kähkönen et al., 1998.

Table 2. Cumulative microbial activities in forest floor of a 30 yr old pine canopy at Hyytiälä Forest Station. The potential activities were measured at substrate saturation separately from the different horizons (immediately after sampling) and integrated to the depth of –23cm (see Table 1). The methane oxidation potentials were measured at +7ºC and the enzyme activities at 30ºC.

	Potential activity, mmol m^{-2} h^{-1}					
Season	*CH_4 oxidation*	*Xylosidase*	*b-glucosidase*	*a-glucosidase*	*Chitinase*	*Phosphatase*
July´97	0.01	88	49	0.8	107	152
Oct´97	0.01	98	210	2.1	64	160
Dec ´97	0.046	15	50	0.5	21	90
Jan ´98	0.05					
Mar ´98	0.096	8	48	0.4	21	80

Data from: Wittmann, 1998, Kähkönen et al., 1998

Table 3. Response of soil organic matter mineralization rates to temperature in the winter months. The rates in the humic (0 to –4 cm layer of 30 yr old pine forest at Hyytiälä Station*.

Wintermonth / analysis parameter	*Oct '97*	*Dec '97*	*Jan '98*	*Oct ´98*
Average soil temperature ºC	+4.2	+0.4	+0.1	+4.8
Endog. Respiration, μg CO_2 g^{-1} h^{-1}	2.1	1.5	1.3	4.2
Q_{10} respiration rate $[ºC]^{-1}$		2.0	2.8	2.2
Extrapolated zero activity ºC	-7.5	-7.0	-7.6	-6.0

*data of M. Kähkönen, C. Wittmann, I. Tsitko, J. Kurola, H. Ilvesniemi & M.S. Salkinoja-Salonen.

Table 4. The apparent activation energies of phenanthrene mineralization by Finnish soils, calculated from Arrhenius plots. The ^{14}C-phenanthrene or ^{14}C-2,4,5-trichlorophenol was spiked into soil (0.2….50 ppm) and the response of rates of mineralization to temperature measured at –2.5ºC to +15ºC .

Soil type	*Sampling Depth*	*E_a (kJ) phenanthrene*			*E_a (kJ) 2,4,5-trichlorophenol*		
		50ppm	*5ppm*	*0.2ppm*	*50ppm*	*5ppm*	*1.8ppm*
Farm soil	0 to 20 cm	171	133	91	89	45	29
Farm	20 to 40 cm	94	83	124	75	48	50
Aspen forest, fine roots	0 to 5 cm	172	105	75	113	81	97

Aspen forest fine roots	5 to 10 cm	nd	nd	62	102	72	59
Average		145	107	88	95	62	59

nd; not determined. Data of´ J . Kurola, 1998

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