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Fundamentals, Risk Assessment and Legislation

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Edited by

Alexander J.B. Zehnder
Swiss Federal Institute for Environmental Science and Technology (EAWAG)

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Authors

Allen, James F.; Squire, Sanders & Dempsey, Counsellors at Law, Palác Adria, Jungmannova 31/36, CZ-110 00 Prague 1, Czech Republic

Angst, Werner; Swiss Federal Institute for Environmental Science and Technology EAWAG, CH-8600 Dübendorf, Switzerland

Bachmann, André; Jena Umwelttechnik GmbH, Postfach 26, D-07727 Jena, Germany

Behra, Philippe; Institut de Mécanique des Fluides, Université Louis Pasteur, URA 854 CNRS, F-67000 Strasbourg, France

Blum, Winfried E.H.; University of Agricultural Sciences, Department of Soil Science, A-1180 Wien, Austria

Bosma, Tom; Limnological Research Center, Swiss Federal Institute for Environmental Science and Technology EAWAG, CH-8600 Dübendorf, Switzerland

Connor, Kevin; Squire, Sanders & Dempsey, Counsellors at Law, Palác Adria, Jungmannova 31/36, CZ-110 00 Prague 1, Czech Republic

Denu, Jeanine A.; School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA

Geckeis, Horst; Kernforschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik, D- 67021 Karlsruhe, Germany

Ghoshal, Subhasis; Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-3890, USA

Goltz, Mark; Department of Civil Engineering, Stanford University, Stanford, California 94305-4020, USA

Hopkins, Gary D.; Western Region Hazardous Substance Research Center, Stanford University, Stanford, California 94305-4020, USA

Isnard, Pascal; Rhône-Poulenc Industrialisation, Centre de Décines, F-69153 Décines Charpieu Cedex, France

Kamely, Daphne; Assistant Deputy Undersecretary of Defence for Environmental Security Technology DUSD/ET, Washington, DC 20301-3400, USA

Kim, Jae-Il; Kernforschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik, D-67021 Karlsruhe, Germany

Kozusnik, Rudolf; Squire, Sanders & Dempsey, Counsellors at Law, Palác Adria, Jungmannova 31/36, CZ-110 00 Prague 1, Czech Republic

Liptáková, Darina; KAP Environmental Service, Stupska 15, CZ-19800 Prague 9, Czech Republic

Lühr, Hans-Peter; Institute for Water Polluting Substances (IWS), Technical University Berlin, Hardenbergplatz, D-10623 Berlin, Germany

Luthy, Richard G.; Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-3890, USA

McCarty, Perry L.; Western Region Hazardous Substance Research Center, Stanford University, Stanford, California 94305-4020, USA

Moldan, Bedřich; Centre for Environmental Scholarship, Prague, Charles University, CZ-116 36 Praha 6, Czech Republic

Mosé, Robert; Institut de Mécanique des Fluides, Université Louis Pasteur, F-67083 Strasbourg Cedex, France

Mrkos, Jan; Fond národního majetku CR, Rasimovo nabrezi 42, CZ-12061 Prague 2, Czech Republic

Nakles, David D.; Remediation Technologies, Pittsburg, PA 15238, USA

Notenboom, Jos; Laboratory of Ecotoxicology, National Institute of Public Health and Environmental Protection, NL-3720 BA Bilthoven, The Netherlands

Poetzsch, Emmo; Umweltschutz Nord GmbH & Co, Industriepark 6, D-27777 Ganderkesee, Germany

Ramaswami, Anuradha; Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-3890, USA

Rijnaarts, Huub; Institute of Environmental Sciences, TNO Environment & Energy Research, Schoemakerstraat 97, 2600 JA Delft, The Netherlands

Růžička, Jiri; Ministersvo zivotního prostredi, Vrsovická 65, Udbor ekologickych skod, CZ-10010 Prague 10, Czech Republic

Ryckbost, Donatienne; University of Gent, Seminarie voor Milieurecht, B-9000 Gent, Belgium

Schneider, Gerhart; United Nations Environment Programme, Water & Lithosphere, P.O. Box 30552, Nairobi, Kenya

Schulz-Berendt, Volker; Umweltschutz Nord GmbH & Co, Industriepark 6, D-27777 Ganderkesee, Germany

Schwarzenbach, René; Swiss Federal Institute for Environmental Science and Technology EAWAG, CH-8600 Dübendorf, Switzerland

Shoemaker, Christine A.; School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA

Stauffer, Fritz; Institute of Hydromechanics and Water Resources Management, ETH Zurich, CH-8093 Zurich, Switzerland

Vogel, Timothy; Rhône-Poulenc Industrialisation, Centre de Décines, F-69153 Décines Charpieu Cedex, France

Whiffen, Gregory J.; School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA

Zehnder, Alexander J.B.; Swiss Federal Institute for Environmental Science and Technology EAWAG, CH-8600 Dübendorf, Switzerland

Zilliox, Lothaire; Institut de Mécanique des Fluides, Université Louis Pasteur, URA 854 CNRS, F-67000 Strasbourg

Preface

SCOPE, the Scientific Committee on Problems of the Environment, was established by the International Council of Scientific Unions (ICSU) in 1969 as an international, non-governmental, non-profit organisation with the mandate to

- advance knowledge of the influence of humans on their environment, as well as the effects of these environmental changes upon people, their health and their welfare-with particular attention to those influences and effects which are either global or shared by several nations;
- to serve as a non-governmental, interdisciplinary and international council of scientists and as a source of advice for the benefit of governments and intergovernmental and non-governmental bodies with respect to environmental problems.

SCOPE has been established because critical environmental concerns call for a thorough evaluation of the issues at stake, an assessment of their consequences at global and regional levels and the formulation of possible solutions.

Through its activities SCOPE identifies available knowledge, then synthesizing it to point out where gaps and uncertainties exist, and to recommend where efforts should be concentrated to develop explanations and solutions.

SCOPE aims at the dissemination of information to as large a forum as possible and to communicate it in a readily understandable form for practitioners in the scientific community and also for policy planners and decision makers, industry managers, engineers, technicians, teachers, and the public at large. It is only through such action that sound policies can be adopted to prevent, mitigate or adapt to the effects of an existing or potential environmental problem.

Groundwater pollution as a result of soil pollution has long been treated as a minor problem, either because the necessary analytics were not available or because the extent of the pollution has been largely underestimated. Only the Love Canal incident in the late 70s in the USA and soon after Lekkerkerk in the Netherlands has world-wide sensibilized authorities and scientists for groundwater and soil pollution. In 1987, SCOPE decided that an expert group should deal specifically with this problem, taking into account the special needs of the different regions on our globe.

This workshop and symposium in Český Krumlov, is one of a series. The first workshop took place in Stanford, California USA, the second in Bangkok, Thailand, and the third in San José, Costa Rica. More are planned, one in Beijing, China and the other in Adelaide, Australia. This is the fourth; it will specifically focus on soil and groundwater pollution in Central and Eastern Europe. It is the first workshop and symposium which takes, besides scientific, clearly legal and risk issues into account. These issues are necessary for a successful implementation of protection and remedial measures.

The aim of the workshop and symposium is to bring together scientists, engineers, lawyers, people from authorities and private enterprises to discuss new developments in legislation and in remediation and prevention measures against soil and groundwater pollution, and to make recommendations for future developments in technology, science and regulations.

We would like to thank the United Nations Environment Programme (UNEP) for sponsoring the workshop and symposium, the city of Český Krumlov and its Mayor Mr. Jan Vondrouš for their hospitality, and KAP Environmental Consultants and Engineers for all local arrangements. They made it possible for all of us to meet here in this beautiful city.

Český Krumlov, June 6, 1994

Christine A. Shoemaker
Alexander J.B. Zehnder

Welcome by the Representative of UNEP

It is a great pleasure for me to address you on behalf of the United Nations Environment Programme (UNEP), Nairobi, Kenya. I want to use this opportunity to highlight the background which led to UNEP supporting the project «Groundwater Contamination»:

Although the knowledge about ground water increased tremendously in recent times (especially with regard to modeling the movement of pollutants in aquifers), there are still many practical questions regarding groundwater protection and rehabilitation unresolved. Surprisingly, practical success has not been achieved to the same extent as knowledge of chemical and physical aspects of groundwater pollution increased.

We at UNEP believe that activities related to groundwater protection (as well as any other effective «environment protection measures») require close co-operation of experts from many different fields. UNEP has taken a strong interest in facilitating this necessary exchange of views beyond the borders of a specific discipline. Successful groundwater management can only be achieved in co-operation of people with natural sciences background (such as hydrologists, hydrogeologists, modelers, and so forth), and those who are experts in agricultural and industrial pollution. Of course, the experts' knowledge will have to be made available to political and administrative decision-makers. Thus, the workshop would have a twofold purpose: Firstly, to facilitate exchange between scientists from different fields, allowing us to identify gaps in knowledge which may prevent us from a successful groundwater resources management. Secondly, to provide an exchange between scientists and «users of scientific knowledge», such as representatives of environmental protection agencies, legal experts and administrators from Eastern Europe. We may also come to conclusions of some socio-economic obstacles (economic constraints/costs) of using the knowledge already available. All this is to be done with a very specific focus on the concrete situation in Eastern Europe. The participation at this workshop has shown us that we have at least achieved the representation of many different experts here!

An assumption of this project was that problems of groundwater pollution, as well as the state of knowledge what to do about it, are different in various regions of the world. The only other workshop held so far with UNEP involvement (in San José/ Costa Rica) focused on Latin America. Whereas basic problems such as pollution of ground water through industrial chemicals, oilspills, nitrogen fertilizers, saltwater intrusion, waterlogging irrigation, land subsidence due to groundwater withdrawal (damaging buildings and infrastructure) occur more or less everywhere, their extent and specific importance differ in various parts of the world. Therefore, the «regional structure» of the project.

This workshop focuses on groundwater pollution in Eastern Europe, which, I believe faces many specific and urgent environmental problems in this field. Immediately to mind come problems related to lowering of groundwater tables in order to allow (underground and open-pit) mining, the chemical pollution left behind by huge industrial conglomerates, and (last, but not least) the question who should pay for all that. Main target of this workshop is to get a clear idea on specific needs of this region (taking into account local capabilities/ institutions already in place), to publish the papers presented here in a volume of workshop proceedings, and possibly to initiate action. Therefore we are pleased about the very broad participation of people with different backgrounds at this workshop, and we hope on fruitful results.

Gerhart Schneider
UNEP, Nairobi, Kenya

I. Summaries and Recommendations

Fundamentals: Reactions, Transport and Modeling

Report of the workshop discussion by Tom N.P. Bosma, Huub H.M. Rijnaarts, Fritz Stauffer, and Timothy M. Vogel

The discussion in the session was based on the statement papers of the participants. The most important conclusions from the papers and the discussion are summarized below.

Reactions

Ideally, the study of the fundamentals of chemical reactions leads to the formulation of quantitative structure activity relationships (QSAR) that can be used to predict degradation rates and transformation pathways of pollutants. QSAR's have been proven to be applicable to abiotic and biotic reactions in well-defined systems, even when variability in environmental factors such as pH, redox and temperature are taken into account. However, QSAR's may fail in more complex environments because the rate limiting mechanisms may change when shifting from microscopic to macroscopic scales. This not only affects reaction *rates* but also reaction *pathways*. Reactivity is not always taken into account in the consideration of pollutant behavior and impact and, thus, may lead to serious problems because sometimes more toxic compounds may be formed from the parent compounds.

Reactions often involve biological reactions which - in most cases - are a prerequisite for the complete mineralization of organic pollutants. Microorganisms are very flexible in their metabolism and are able to rapidly adapt to new types of compounds. A lot of information concerning adaptation mechanisms is available already and could be applied successfully in bioremediation strategies.

Transport

The transport of pollutants depends on their speciation, their binding to the solid matrix, and their association with mobile colloids. The risk associated with the mobility of a pollutant depends on the type of contaminant. The transport of a very small fraction ($<<0.1\%$) of an extremely hazardous substance bound to colloids (e.g. radio nuclides / dioxins), normally considered «negligible», may pose a significant environmental risk. The lack of adequate methods to measure and assess colloid-chemical interactions greatly limits our ability to quantify colloidal and colloid-facilitated transport in soil and ground water. In addition, bacteria can be considered as living colloids. Thus, their transport may also increase the mobility of pollutants.

Modeling

An important advantage of modeling is that a rigorous expression of conceptual thinking is required. A sensitivity analysis can be performed with models in order to identify the most important parameters governing the fate of chemicals in soil and ground water. Models might be valuable tools for forecasting. However, different spatial scales (micro-, macro-, and field) require different equations, each having their own appropriate, scale-dependent parameters. These scale-dependent parameters cannot always be easily determined. For example, tremendous problems in modeling pollutant behavior are due to spatial variability of hydraulic conductivity, porosity, and microbial populations.

Biodegradable pollutants can penetrate into pores that cannot be entered by microorganisms. This leads to mass transfer limitation of the biodegradation process that slows down the progress in bioremediation and limits final achievable pollutant levels. Mass transfer limitation may also be manifest at larger scales e.g. due to the existence of preferential flow paths with little microbial activity next to larger regions with almost no flow but high microbial activity. Thus, the existence of mass transfer limitations to biodegradation also results in a scale-dependency of the parameters involved.

The relevance of the processes considered at the microscale must be carefully reconsidered during scaling-up. Forecasts based on modeling must always be critically evaluated with regard to these uncertainties.

Benefits of Fundamental Investigations

Fundamental investigations may reveal processes that determine pollutant behavior in soil and ground water and which can potentially be incorporated in models. Thus, understanding the fundamentals may lead to a better forecast of the fate of compounds, i.e. an improvement of their risk assessment. Better forecasting not only means a more accurate prediction matching real world pollutant behavior, but also a better quantification of the large uncertainty that is inherent to pollutant behavior. A better understanding of the fundamentals also gives the basis for optimizing treatment methods for polluted soil and ground water.

Research Needs

Prerequisites to develop adequate risk assessments and treatment technologies are:

- The assessment of colloid-chemical interactions in soil and groundwater materials to quantify possible colloid-facilitated transport
- The assessment of uncertainty of parameters and variables relating to the fate of pollutants in soil and ground water, and their incorporation in models
- The possibility to quantify the bioavailable pollutant mass which itself requires:
- The development of analytical procedures allowing the quantification of the total pollutant mass in soil or aquifer material.

Application Needs

- The assessment of the danger posed by both polluted and cleaned soil should involve (eco)toxicological testing, in addition to the classical chemical analysis.
- The existing knowledge about the versatility of microorganisms to adapt to new kinds of chemicals needs to be implemented in bioremediation technologies.

Field and Case Study Work Group

Mark N. Goltz

To guide discussion, the group examining case studies divided their inquiries into three general areas: (1) state-of-the-art, (2) problems/issues, and (3) recommendations. This report will summarize the discussions in each of these areas.

State-of-the-Art

The group agreed that there is a need for better predictive capabilities when designing hazardous waste site remediations. Currently, design is based on empirical, pilot test results. Thus, design is site specific, and a design at one site is not readily transferable to other sites. With better knowledge of fundamental mechanisms and processes, it may be possible to develop basic design rules and engineering criteria that can be used to design hazardous waste site treatment facilities. This will allow for better operational control and better prediction of performance.

As examples of gaps in our knowledge, it was noted that although we currently have some predictive capabilities regarding the fate and transport of single compounds in the subsurface, there is very little knowledge to help us predict the fate of mixtures (which, of course, are commonly present at hazardous waste sites).

With regard to our remedial capabilities, it was noted that currently we are unable to deal with «bound» contaminants - that is, the fraction of contaminants that are «irreversibly» sorbed to aquifer solids or that have such slow desorption rates as to essentially make them permanently bound. This fraction may not be available for biodegradation and is not amenable to pump-and-treat remediation. This precludes cleanup to background levels, which leads to a discussion of «how clean is clean.» Presently in the U.S., there is no set cleanup criteria for soil quality, and each site is dealt with individually during the risk assessment step in the remedial action process. In Europe, the Holland list has been used in the past, with its A, B, and C levels, in conjunction with the principle of multifunctionality, to set soil cleanup standards. Unfortunately, as came out in a discussion of the entire workshop group, both the U.S. and European methodologies have proved inadequate in setting cleanup criteria.

Problems / Issues

A problem was noted regarding transitioning hazardous waste treatment technologies from the laboratory to commercial use. Possible solutions involved partnering between universities (with their expertise in science and fundamentals) and industry (with their experience in application of technologies), although this particular combination may not be as applicable in Eastern Europe as in the West. Also mentioned was the need to have «intermediate-scale» demonstrations of technology, at field scales on the order of meters, to help transition between the laboratory and full-scale commercialization.

There was a long discussion on how to prioritize environmental restoration projects. It was pointed out that in the U.S. there is little prioritization, with everyone trying to comply as best they can with a host of environmental laws. Particularly in Eastern Europe, with its extensive environmental problems and limited resources, such an approach is inappropriate. The problems of the Czech Republic were discussed. Problem areas ranged from air pollution, to low level radioactive waste, to strip mines, to organics at military installations. Apparently some data are available regarding the extent of contamination at many of these sites, particularly military facilities. The risk assessment group looked further at how to prioritize projects to deal with these problems.

Problems regarding transfer of technology were also discussed. It was pointed out that technology transfer from the west to the east cannot be accomplished in a vacuum, but must take into account the abilities and knowledge of local workers. There was consensus that it was desirable for local workers to implement remediation. This has two immediate benefits-helping the local economy and building up the local capacity for dealing with environmental restoration. It was felt that there were extensive science and engineering capabilities in the Czech Republic, however retraining is needed so that these capabilities can be applied to environmental problems. Who should pay for the retraining was an item of further discussion.

Other issues regarding technology transfer involved the questions of high cost versus low cost technologies and conventional versus innovative technologies. The ideal technology would be low cost, innovative, usable by local workers and, of course, effective. Concern was expressed that vendors, particularly of innovative technologies, may propose ineffective solutions. The idea of certifying technology, using a quasi-government organization modeled after the Kuwait Institute of Science and Research, was discussed. Also discussed was the use of government/industry joint ventures to help develop and implement innovative technologies.

Recommendations

- Expedite the transition of technologies from research to commercialization through the use of «intermediate-scale» demonstrations and innovative partnerships (e.g. university/industry or government research center/industry).
- Set soil quality cleanup standards, perhaps using an operational test (e.g. water extraction). Base standards on rational criteria, accounting for economic realities.
- Make the best use of the existing environmental data that is available.
- Retrain engineers and scientists so they can apply their knowledge to environmental problems.
- Better «advertise» problems that impact an effective and timely response. This will help with solicitation of aid from the international community, in such areas as retraining and technology transfer.
- Establish an organization to certify remediation technologies and use innovative partnerships (e.g. government/industry) to help develop and implement technologies.

Report on Risk Assessment and Legislation

Christine A. Shoemaker, Jos Notenboom, and Donatienne Ryckbost

The discussion during the conference on risk assessment and its relationships with legislation focused on three aspects: risk assessment as a management tool and its (scientific) backgrounds; implementation of risk philosophy in legislation, and legislative aspects of soil protection and remediation.

Risk Assessment

Risk Assessment is a stepwise process by which scientific and environmental information from many sources is integrated in order to estimate possible harmful effects of contamination and other types of pertubation. It is a tool based on sound scientific principles with the objective to make information available for environmental management in order to identify problems, establish priorities, and provide a basis for regulatory actions.

Pollution prevention and control is extremely important because clean-up becomes increasingly costly. US programs move therefore more and more towards that direction (begin of pipe, reduction of waste, use of less polluting materials).

Assessment endpoints (the value to be considered at risk in a risk analysis) for ecological risk assessment are much more complex and difficult to asign then when risks for human health are assessed. For the assessment of actual ecological risks of contaminated sites a proper definition of assessment endpoints is necessary and the analysis of exposure and effect profiles need location specific input data. Mostly this information is not available or inappropriate and general assumptions should be made which result in an assessment of potential risks rather than actual risks. Potential risk estimates can be used for ranking situations in order to set priorities.

modeling can be very helpful in quantifying risk and the significant effects of uncertainty. Sensitivity analysis involves the systematic change in parameter values input to a model to determine the difference in model prediction. For example one can use a model to predict the amount of pesticide reaching ground water for differing values of one or a combination of parameters, such as the sorption rate or depth to ground water. In this way a quantification of the uncertainty in groundwater concentration at a site can be related to the already quantified uncertainty in model parameters based on literature and site studies.

General, thoroughly elaborated and internationally approved guidelines (computer assisted) for contaminated site investigation and risk assessment can be very helpful but need probably to be adjusted for regional purposes. It is helpful to have a well specified procedure for risk analysis so that its implementation can be mandated and so that studies can be planned and conducted in an efficient manner. The US Hazard Assessment System (HRS) is the primary example of a clearly specific procedure for risk assessment. However, there are some difficulties with the HRS and it would need to be modified to be used in Central and Eastern Europe.

To facilitate cost-benefit analysis and priority setting, it is important that risk assessment includes a range of risks. For example in the US, human health risk analysis focuses on avoiding a risk greater than one in a million (10^{-6}) of a person being harmed by contamination. However, in areas where remediation funds are severely limited, costs associated with a range of risks (e.g., 10^{-4}, 10^{-5}, etc.) should be assessed. If funds are not available to remediate sites to the level of 10^{-6} risk, it is better to clean many sites to a less stringent risk requirement, rather than remediate only a handful of sites to a 10^{-6} risk level and then leave the other sites untreated due to lack of funds. By knowing the costs associated with environmental benefits (as measured by a range of risk factors) priorities for ground water and soil remediation can be set.

It is the responsibility of the risk assessor to make uncertainties visible. Policy makers should be aware of the assumptions and uncertainties, and take them into account in their decision. Uncertainty analysis can help applied environmental researchers to direct their investigations on those fields where the largest reductions can be realized.

Risk Assessment is often done by private environmental firms that report to governmental officials. It is essential that consultants have been adequately educated in environmental risk assessment. It is also essential that governmental officials have been adequately educated in environmental sciences otherwise funds allocated for groundwater quality protection and remediation could be wasted. Education programs must therefore be developed in environmental sciences, engineering and risk assessment.

Risk Assessment and Legislation

Risk Assessment is applied for estimating risks for man and environment in particular for the regulation of new and existing chemicals. Little experience exists with Risk Assessment of contaminated sites in order to prioritize and define clean-up objectives. Clean-up goals based on risk decisions might be more realistic and feasible (financially, technically and socially) than when fixed target values are the only guidance. It is stressed that risk managers should integrate knowledge on risks with social constraints in order to make cost benefit decisions.

General environmental quality criteria are necessary for pollution prevention and control. Such criteria can be modified depending the conditions on a specific site and used as guidance for decisions on clean-up operations. This might be more effective than when decisions depend entirely on a risks assessment on a site by site basis.

Legislation

The pollution of the soil and ground water caused by contaminated sites is considered as a severe environmental problem. Many countries are developing policies and programmes to deal with land contamination and groundwater problems. There is a common need for strategies to deal with and treat contaminated sites including a comprehensve legislation.

In the Flemish approach a distinction is made between historic (before approval of the law) and new pollution (after approval of the law). Many countries identify and register polluted soils in order to have a data base for policy decisions and which also can function as an instrument to protect and inform potential buyers of polluted land.

The decision making process includes several steps. In Flanders remediation criteria of new pollution may differ in accordance to the use of the land. In the case of historical pollution these criteria depend on the risks for man and environment and on the ranking of the government. Remediation objectives take financial resources into account. With respect to the financial implications it is the question who is under the obligation to carry out the clean-up and thus to prefinance it. Next there is the final allocation of the costs to the liable party. There is a possible exception of innocent land owner.

In relation to the transfer of property there is a need to protect the buyer of polluted land and to inform him. For industrial sites a soil pollution investigation and a possible clean-up can be asked as a prerequisisite.

II. Statements

IIa Fundamentals: Physical, Chemical and Biological Processes

Modeling Subsurface Processes

Fritz Stauffer

Models in General

Generally a model of a complex real system of processes is every description or representation of them. Compared to the real system, represented, e.g., by a laboratory experiment, a field experiment or a natural field system, a model is always simplified and abstract. With increasing complexity a model should theoretically describe a natural process more and more correctly. Each model is characterised by its concepts, its specific conditions and its parameters. Most important kinds of models are conceptual models, analogy models (e.g. capillary models, or scale models), mathematical models, including statistical and stochastic models.

Mathematical Models

Generally a **mathematical model** may be any relationship between variables and /or parameters of a system. Examples are Darcy's law, Fick's law, Fourier's law etc., or balance equations (balance of fluid mass, pollutant mass, momentum, heat, etc.) formulated for an integral domain or a small control volume based on a continuum approach. Each mathematical description contains variables (e.g., fluid pressure, hydraulic head, fluid velocity, water content, chemical species concentration, fluid temperature, etc.) and parameters (e.g. hydraulic conductivity, transmissivity, porosity, coefficient of molecular diffusion, mass density, dispersion coefficient, equilibrium constants, rate constants, etc.). Mathematical models can be simple equations up to complex coupled systems of non-linear algebraic equations and/or partial differential equations. **Deterministic models** are formulated for given geometrical domains, balance equations, parameters, initial and boundary conditions. **Stochastic models** consider the spatial and/or temporal variability and uncertainty of the parameters, initial and boundary conditions. Generally on the one hand there is the **mathematical formulation** of a problem. On the other hand there is the **solution** of the mathematical problem. A broad spectrum of **analytical solution** techniques is available to provide exact or approximate solutions for a series of special cases (e.g. simplified geometry, constant parameters). **Numerical solution** techniques (finite difference method, finite element methods, random walk method, etc.) are more general and provide approximate solutions. The use of numerical techniques may be strongly related to the capacity and CPU performance of computers. A numerical **simulation** is a numerical experiment for specific conditions using a mathematical model. A typical **hierarchical procedure** for the formulation of mathematical models is a) the formulation of the process at the **microscopic scale** (pore scale), b) the formulation at the **macroscopic scale** (averaging over many pores), and c) the formulation at the **field scale** by averaging over many lenses, layers (e.g. vertically integrated aquifer models), etc. At each step only the relevant processes and parameters of the previous one should be considered. Each model is thus represented by its characteristic scales. It's important to relate e.g., field measurements, to the corresponding scale of the model and vice versa. The **test** of mathematical models involves the comparison of simulation results with analytical solutions of simplified systems, with data of well documented laboratory and/or field experiments or observations.

Need for Mathematical Models

The purpose of mathematical models is not only to provide instruments in order to **forecast** or **estimate** processes in a real system, but also to **relate sub-processes and concepts**, e.g. found in laboratory, and to **transfer concepts** from one system to another. Models thus represent also important research tools in natural science. An important application of mathematical models is their use in the **parameter identification** based on measured data of a real system (inverse modeling, parameter optimisation). Models are also valuable tools in the investigation of the **sensitivity** of a system. The chosen **level of complexity** of a model depends on the specific needs and purpose of its use.

Examples of the practical use of subsurface water models are:

- **Development and management of water resources systems** (well system for water supply, artificial groundwater recharge, thermal use of ground water, groundwater management, water quality control, groundwater protection zones, etc.).
- Assessment of the **impact of constructions** on groundwater flow and groundwater quality (industrial plants, power plants, dams, tunnels, deposits, etc.).
- Assessment of the **impact of accidents or technical system failures** on subsurface water quality and the **risk assessment** for subsurface water systems.
- Impact of the **inadequate use of substances** of various kinds in the environment (e.g. in agriculture).
- Development and evaluation of **remediation techniques** or measures for polluted soil water and ground water.
- Development and evaluation of subsurface **monitoring** systems.

Modeling Spatial Variability and Uncertainty of Parameters

Considerable problems in the formulation and application of subsurface water models are present in the treatment of the uncertainty of the parameters values (e.g. hydraulic conductivity), the initial and boundary conditions, or even in the formulation of the relevant processes itself. The uncertainty of the parameters may be on the one hand due to measurement errors inherent in a specific evaluation method. On the other hand it is due to the strong **spatial variability** of many parameters (e.g. hydraulic conductivity) which never can be known in detail everywhere. Ways out of the dilemma are e.g., to introduce **stochastic concepts** considering the subsoil as one of many stochastic realisations. A common approach is to formulate **effective parameters** thus replacing the real system by a homogeneous model and to estimate the **uncertainty** of variables and parameters (confidence intervals). A series of **analytical approximate expressions** have been developed to estimate effective flow and pollutant transport parameters based on the knowledge of geostatistical parameters (probability density functions, variance, correlation lengths, etc.). Alternative procedures are the use of **Monte Carlo techniques** by generating space-dependent (or also time-dependent) parameter values (e.g., hydraulic conductivity) of numerical models in a stochastic manner, and the subsequent solution of the corresponding deterministic numerical system. Also the use of a stochastic generation of facies elements with specific structural properties is increasingly used. Further perspectives are the consideration of measurement data in the stochastic generation process (**conditioned stochastic simulation**), e.g., by taking borehole data or geophysical information into account.

Modeling Complex Physical, Chemical and Biological Processes

Beside the spatial variability of parameters which affects any subsurface flow and transport system, the **modeling of complex physical, chemical and biological processes** in the subsurface poses a series of important problems concerning a) the concept, b) the mathematical formulation, and c) the subsequent numerical solution techniques. From a geometrical point of view one may consider in general a **multi-porosity** matrix of the porous medium (single, dual porosity e.g. in structured, or fractured media) thus constructing different compartments within the porous medium, and the formulation of the related flow and transport processes. These processes may be:

- **Multi-phase flow** in porous media (unsaturated flow, two-phase flow, e.g., water-air, multi-phase flow, e.g., water-air-hydrocarbon) with phase transfer processes (volatilisation, condensation, etc.) and **particle transport** (e.g. colloids) and the various mutual physical interactions and characteristics (phase content characteristics, phase conductivity, capillary effects, hysteresis phenomena etc.).
- **Multi-species reactive transport** in each phase of the porous medium with the formulation of the prevailing chemical reactions (local thermodynamic equilibrium, kinetic processes) of a variety of chemical species (homogeneous reactions, heterogeneous reactions, i.e., sorption processes, solution/dissolution).
- **Biochemical transformation** in porous media by various biological species, based on the supply of substrate, and the sorption and the **transport of microorganisms** in the porous medium.

In general, all these **processes are coupled**, posing subsequent coupling problems in modeling (e.g. formulation of rates between different compartments of the porous medium, or the sequence of prevailing chemical transformations, or inhibition effects in bacterial growth). Many gaps exist in the knowledge and mathematical formulation of the relevant processes and in the identification of the related **parameters** (chemical equilibrium and kinetic rate «constants» and their dependence on the «milieu» e.g. chemical milieu like pH, temperature etc.) within the porous medium, and more general, the mutual interdependence of various parameters.

The Radionuclide Migration Facilitated by Complexation and Colloid Formation in Subsoil Aquifer Systems

Jae-Il Kim

The radioecological significance of individual radionuclides, as environmental contaminants in subsoil aquifer systems, is controlled by their geochemical reactions which produce two different identities of chemical species, namely mobile and immobile species. How the immobilisation reactions of a given radionuclide are in competition with its mobilisation reactions is, for obvious reasons, regulated by the chemical nature of the radionuclide concerned as well as by the geochemical conditions of a given aquifer system. Of various geochemical reactions which may enhance the mobilisation process, two important geochemical reactions are discussed briefly in this statement paper in order to outline their general importance for the assessment of the long term aquatic behaviour of radionuclides.

The colloid generation and complexation of radionuclides are important geochemical reactions that may produce mobile species of the nuclides concerned in a given aquifer system. For obvious reasons, the aquatic species of radionuclides, which undergo more or less repulsive interactions with various mineral surfaces, may be mobile with nearly the same migration velocity as water. The formation of mobile species depends primarily on the chemical oxidation state of a given radionuclide. Under natural aquatic conditions, radionuclides can be distributed in seven different oxidation states, from one to seven, for example,

M(I) for Cs^+; M(II) for Sr^{2+}, Ra^{2+}; M(III) for REE (Eu^{3+}), Am^{3+}; M(IV) for U^{4+},

Np^{4+}, Pu^{4+}; M(V) for NpO_2^+, PuO_2^+; M(VI) for UO_2^{2+}, PuO_2^{2+}; M(VII) for TcO_4^-.

The monovalent cation, like Cs^+, does not undergo complexation and thus remains as a cation, whereas the divalent element, like Sr^{2+}, is weak towards complexation and, as a result, remains to a great extent also as a cation in aquifer systems. The two cationic radionuclides are reactive for much of mineral surfaces and sorbed on them mostly through ion exchange and/or mineralization processes. The former is reversible and the latter irreversible. Whatever the processes are involved, the mono- and divalent cations are scarcely migrational for a long distance of aquifer system.

The tri- and tetravalent cations, like Am^{3+} and Pu^{4+}, tend strongly towards hydrolysis or complexation, because of their higher electric charges. Such a tendency is stronger for the tetravalent than trivalent metal ion. The two ions are turned up as either colloidal or anionic species through sorption on aquatic colloids or complexation with carbonate anion or/and humic acid, respectively. Whenever the resulting species are involved in a reversible process, they are mobile only for a limited distance, whereas, once the species are produced by irreversible process, they may be migrational and thus will be of radioecological importance.

The rest oxidation states, namely penta-, hexa- and heptavalent, are so highly charged that they produce chemical spallation of water molecules and thus become the oxoion, either the dioxo-cations, like MO_2^+ and MO_2^{2+}, or the tetraoxo-anion, like MO_4^-. The MO_2^+ ion is, due to the structure of the ion with two oxygens, more stable than, for example, the Cs^+ ion in aqueous solution and can be migrational in various aquifer sytems. The MO_2^{2+} ion is chemically as reactive as the M^{3+} ion and, because of two oxygens associated with charge polarization, its hydrolysis or complexation strength appears to be rather strong. This ion undergoes easily colloid generation or formation of anionic complexes and thus becomes migrational. The MO_4^- ion is, under normal conditions, the most stable anionic species and, therefore, very migrational. However, the oxidation states of M(V), M(VI) and M(VII) are unstable against a strong redox front of deep aquifer systems and sensitive to reduction to the ions of tri- or tetravalent state. The reduction can be caused by various processes, such as reaction facilitated by strong complexation, e. g. with carbonate ion or humic acid, surface redox reaction generated, e. g. by $Fe^{2+} \rightarrow Fe^{3+} + e^-$, microbial effects, e. g. Tc(VII) → Tc(IV), etc. The reduction products are either M(IV) or M(III), which can be stabilised in ground water as either complexed anions or «pseudocolloids» through their sorption on aquatic colloids. Depending on the chemical stability of thus produced species, they can be mobile in a given aquifer system.

Following the simplified discussion made above, the radionuclides of possibly mobile oxidation state are tri- and tetravalent ones, which might be distributed either in immobile solid phase through co-precipitation and thereafter mineralization or in mobile aquatic phase as colloids and/or anionic complex species. Of important anionic complexes, carbonates and humates of M(III) and M(IV) are ubiquitous in every deep aquatic system, as speciated in various ground waters. They are also present as colloid-borne species in many ground waters. The migration behaviour of such potentially mobile species in different aquifer systems is one of the important research areas in connection with the radioecological assessment of environmentally contaminated radionuclides.

Transport of Bacteria in Ground Water

Huub H.M. Rijnaarts

Importance of Bacterial Transport for Soil and Groundwater Remediation.
Many soil sites and aquifers that are contaminated with organic chemicals can be remediated by stimulating the growth and activity of a part of the indigenous microbial population. In some cases, bioremediation may be improved by introducing special microorganisms into the soil or aquifer. This may reduce adaptation times, enhance bioconversion rates, or prevent the build-up of undesired intermediates or dead-end products. Microbial transport is important for bioremediation for three reasons. i) Bacteria can only be succesfully introduced into an aquifer when their transport and attachment behaviour is understood and can be controlled. ii) A widespread dispersal of indigenous or added microorganisms during or after application must be prevented to avoid microbial contamination of the aquifer. iii) Mobile microorganisms may take part in a colloid-facilitated transport of non-degraded or non-degradable contaminants and may thus contribute to an undesired dispersal of pollutants.

Statement 1

A control of microbial attachment and transport is required for successful and safe bioremediation of soil and ground water.

Interactions Between Microorganisms and Solid Surfaces.
Recently, the interactions between bacteria and solid surfaces and their effects on bacterial transport in model-porous media have been systematically investigated (1, 2, 3, 4, 5, 6, 7). The results and consequences for soil and groundwater bioremediation are briefly discussed below.

Bacteria and most solids are negatively charged at pH 7. A high repulsive barrier exists between cells and solid due to long-range electrostatic interactions. This barrier cannot be overcome by whole cells. Nevertheless, bacteria can attach by means of cell-surface macromolecules that penetrate this electrostatic barrier. This attachment is generally irreversible under the condition of low shear as in ground water. At high ionic strength (0.1 M), adhesion is completely controlled by the interactions between the solid phase and cell-surface macromolecules (steric interactions). These interactions can either inhibit or promote attachment depending on the type of cell-coating and the properties of the solid phase. Upon lowering the ionic strength, the location of the barrier shifts to greater cell-solid separations and the number of cell surface macromolecules that can reach the solid surface reduces. At a critical ionic strength, most of the macromolecules cannot reach the solid surface and a transition from sterically controlled adhesion to electrostatically inhibited deposition occurs. This critical ionic strength is mainly determined by the length of the cell-surface macromolecules. For most bacteria, this critical ionic strength falls between 0.03 M and 0.003 M. Most ground waters also have an ionic strength in this range.

Statement 2

Appropriate description and prediction of bacterial adhesion and transport in ground water requires an assessment of both the electrostatic and the steric interactions between bacteria and solids.

Effect of Interactions on Bacterial Transport.

The cell-solid interactions strongly influence bacterial transport in coarse grain porous media. This may be quantified in terms of an initial penetration distance, i.e., the length of a porous medium required to remove 99% of the cells fed to the system. Depths of penetration may be as high as 50 m at low ionic strength (0.001 M). At high ionic strength (0.1 M), this penetration depth varies between about 0.25 m and 20 m depending on the type of cell-coating.

In addition to cell-solid interactions, the interactions between attached cells and newly depositing cells influence bacterial transport. A strong cell-cell repulsion results in a great area blocked per attached cell which in turn leads to a low maximum fraction of surface covered with cells. It also prevents clogging of the pores between the media grains; the cells can be freely transported down-gradient after surface saturation. A low cell-cell repulsion causes multilayer adhesion and, eventually, pore-clogging. Cell-cell repulsion is partly of an electrostatic nature and can therefore be increased by reducing the ionic strength. At ionic strengths typical for ground water, this repulsion appears to be strong enough to prevent multilayer adhesion and poreclogging for most (but not all) bacteria.

Statement 3

A great diversity in transportability exists among different bacterial species mainly due to differences in structure and chemical composition of the cell-coating. The effect of these cell-surface properties must be accounted for in describing and predicting microbial transport.

Statement 4

During the development of bacterial strains for bioremediation purposes one should not only focus on the activity towards the degradation of pollutants but also on the cell surface properties that control the transport and attachment behaviour of the organisms.

Modeling Bacterial Transport in Porous Media.

Two types of models are often used to describe the transport of micron-size particles and microorganisms in porous media: i) the Deep Bed Filtration Model and ii) Convection-Dispersion models, developed for solute transport. Recently, it was demonstrated that a synthesis of both models is required to appropriately describe microbial transport in porous media (1, 2). In this approach the convection-dispersion model is extended with a deposition rate term. This term contains two colloid-chemical parameters: the collision-efficiency, which represents cell-solid interactions and the blocking factor, which accounts for cell-cell interactions. These parameters can be determined by applying the deep bed filtration model to experimental column breakthrough data.

Statement 5

Testing the applicability of the convection-dispersion model, extended with the collision-blocking deposition rate term, to microbial transport in natural porous media is a high priority topic for future bioremediation research.

References

1. **Rijnaarts, H. H. M., E. J. Bouwer, W. Norde, J. Lyklema and A. J. B. Zehnder.** Bacterial deposition in porous media related to the clean-bed collision efficiency and substratum-blocking by attached cells. Environ. Sci. Technol.: submitted for publication.
2. **Rijnaarts, H. H. M., E. J. Bouwer, W. Norde, J. Lyklema and A. J. B. Zehnder.** Bacterial deposition in porous media: effects of type of cell-coating, substratum hydrophobicity and ionic strength. Environ. Sci. Technol.: submitted for publication.
3. **Rijnaarts, H. H. M., W. Norde, E. J. Bouwer, J. Lyklema and A. J. B. Zehnder.** Reversibility and mechanism of bacterial adhesion. Colloids Surf. B: Biointerf.: In press.
4. **Rijnaarts, H. H. M., W. Norde, E. J. Bouwer, J. Lyklema and A. J. B. Zehnder.** 1993. Bacterial adhesion under static and dynamic conditions. Appl. Environ. Microbiol. **59**:3255-3265.
5. **Rijnaarts, H. H. M., W. Norde, J. Lyklema and A. J. B. Zehnder.** The isoelectric point of bacteria as an indicator for the presence of cell surface polymers that inhibit adhesion. Colloids Surf. B: Biointerf.: submitted for publication.
6. **Rijnaarts, H. H. M., W. Norde, J. Lyklema and A. J. B. Zehnder.** Steric and DLVO interactions in bacterial adhesion. Environ. Sci. Technol.: submitted for publication.
7. **Rijnaarts, H. M. M.** 1994. Interactions between Bacteria and Solid Surfaces in Relation to Bacterial Transport in Porous Media. Ph. D. Thesis, Wageningen Agricultural University, The Netherlands.

Chemical Reactions of Organics

Werner Angst and René P. Schwarzenbach

Abiotic (chemical) reactions of organic pollutants in soils and aquifers are important for several reasons. On the one hand, unlike microbial degradation, chemical transformation of a given pollutant does never lead to the mineralization of the compound. In fact, numerous reactions, particularly redox reactions of organic pollutants, may lead to products that are of considerable (eco)toxicological concern (Macalady et al., 1986). On the other hand, in certain cases, products may be formed that are more easily biodegraded, or that may undergo reactions with soil constituents to form so-called «bound residues» (Bollag, 1992). Furthermore, in heavily contaminated subsurface environments, chemical reactions involving organic pollutants may have a significant impact on biogeochemical processes, in that species are formed that may influence microbial activity (Heijman et al., 1994). Therefore, knowledge on the mechanisms and rates of chemical reactions of organic pollutants in the subsurface are of great interest, both for assessing the risks and hazards associated with pollution of soils and aquifers by organic compounds, as well as for in-situ, on-site or off-site remediations of contaminated sites.

The most important chemical transformations of organic pollutants in soils and aquifers can be grouped into two major types of processes: Reactions with nucleophiles (including β-elimination reactions) and redox reactions. Reactions with nucleophiles, particularly hydrolysis, have been investigated extensively in homogeneous aqueous solution, and quantitative structure-reactivity relationships for prediction of reaction rates have been established for various compound classes (Schwarzenbach et al., 1993; Chapter 12). Much less data is, however, available on surface catalyzed reactions. It has been demonstrated (Torrents and Stone, 1991) that certain mineral surfaces (e.g., FeOOH, TiO_2) may significantly enhance the hydrolysis of organic compounds that are capable of forming bidentate complexes with metal centers. The present knowledge about such catalysis does, however, not allow to derive general concepts for describing the kinetics of such surface mediated reactions. Obviously, as is the case with any heterogeneous reaction in complex systems such as subsurface environments, it is very difficult (if not impossible) to quantify the relevant reactive surface sites. Furthermore, it also has to be taken into account that a given organic compound competes for such sites with many other water constituents (see, e.g., Torrents and Stone, 1993 a and b).

Compared to the reactions with nucleophiles, an even more difficult situation is encountered in the case of abiotic redox reactions of organic pollutants. Such reactions include a.o. the oxidation of phenols and anilines, reductive dehalogenation of polyhalogenated alkanes, and the reduction of nitroaromatic and azo compounds (for more details and for a description of other reactions see Macalady et al., 1986). Although over the past five years, research in this area has been significantly intensified, one is presently still quite far away from a profound understanding of all the factors that control the rates of redox reactions of organic pollutants in the subsurface. In the following, it is attempted to review briefly the present state of the art of knowledge in this field, and to illustrate the intrinsic difficulties that one has to cope with when trying to develop general concepts for quantification of redox processes involving organic pollutants.

To date, the majority of studies investigating the kinetics of abiotic redox reactions of organic pollutants have been confined to determinations of initial transformation rates in homogeneous and heterogeneous aqueous batch systems. Some illustrative examples include the oxidation of phenols (Stone, 1987; Ulrich and Stone, 1989) and anilines (Laha and Luthy, 1990) by manganese oxides, the reduction of nitroaromatic compounds by reduced constituents of natural organic matter in the presence of hydrogen sulfide (Dunnivant et al., 1992), by an iron porphyrin (Schwarzenbach et al., 1990), by metallic iron (Agrawal and Tratnyek, 1994), by ferrous iron adsorbed to iron oxide surfaces (Klausen et al., 1994), and in anoxic soil and sediment slurries (Wahid et al., 1980; Adkya et al. 1981; Wolfe et al., 1986; Delgado and Wolfe, 1992), the reduction of azo compounds in anoxic sediment slurries (Weber and Wolfe, 1987), as well as reductive dehalogenation reactions of C_1- and C_2- compounds by transition metal complexes (Li and Wackett, 1993; Marks et al. 1989).

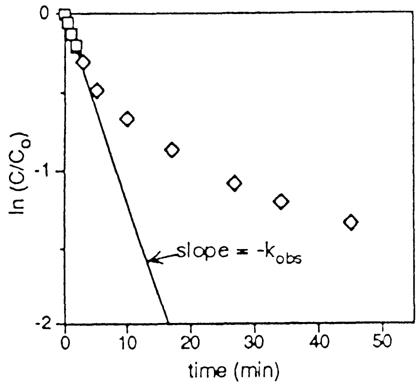

Figure 1
Reduction of nitrobenzene (NB) in aqueous suspensions containing 200 mg L^{-1} magnetite and 1.5 mM Fe^{2+} at pH 7. Plot of ln (C/C_0) versus time. C and C_0 are the concentrations of NB at time zero and t, respectively. The initial pseudo-first order rate constant, k_{obs}, is obtained by a linear least-squares fit of ln (C/C_0) = - k_{obs}•t, using only the first few data points.

Figure 1 shows the picture very often obtained when measuring the oxidation or reduction kinetics of organic compounds in heterogeneous batch systems. As is evident from this example, the reaction rate decreases significantly with time indicating that the most reactive species present (i.e., the species that determine the initial reaction rate) are exhausted quite fast. Hence, apparent first-order rate constants derived from initial rates in batch experiments are, although very valuable from other points of view, usually not very representative for typical situations encountered in the subsurface. Therefore, future research in this field should be directed more to studies using experimental systems that mimic better environmental situations (e.g., column systems) where, very often, a given environment is exposed to pollutants over much longer time periods during which steady-state conditions may establish. One recent example is the work of Heijman et al. (1994) who investigated the reduction kinetics of ten monosubstituted nitrobenzenes in aquifer columns under iron reducing conditions. They found that all compounds were reduced at the same rate, and they postulated that the rate of reduction was determined by the rate of regeneration of reactive iron(II) species by iron reducing microorganisms present in the aquifer material (Fig. 2).

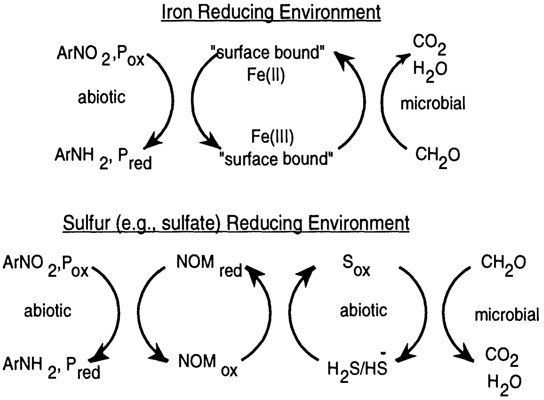

Figure 2
Coupling of abiotic and biological processes (for details see Heijman et al. (1994) and Dunnivant et al. (1992)).

When comparing the relative reduction rates of ten substituted nitrobenzenes determined in three different systems (Fig. 3), another difficulty encountered when trying to predict rates of redox reactions in the environment becomes evident. As can be seen, in one system, (Fig. 3a) the relative rates at which the compounds were reduced span a range of four orders of magnitude, in the second system (Fig. 3b), only a factor of one hundred difference was found, while in the last case discussed above (Fig. 3c), all compounds were reduced at virtually the same rate. These differences are found because, in the different systems, a different reaction or different reactions step(s) (i.e., actual electron transfer (case (a)), formation of the precursor complex (case (b)), or regeneration of reactive species (case (c)) are rate limiting. Consequently, even within a given environment, different members of a series of structurally related compounds (such as the substituted nitrobenzenes) may react by different pathways. For example, in sulfate reducing environments, very reactive compounds (i.e., compounds with a high one-electron reduction potential) may be reduced abiotically by NOM constituents, while the less reactive compounds (i.e., compounds exhibiting a very negative one-electron reduction potential) may undergo microbially mediated reduction. Finally, this example illustrates also the difficulty that one may have to distinguish whether a pollutant is transformed abiotically, whether the reaction is mediated by microorganisms, or whether both abiotic and strictly biological processes are important. In this context, one should, however, raise the question, whether it is always meaningful to separate transformation reactions of organic pollutants into strictly abiotic and biological processes, when considering that the dynamics of natural reactants may be intimately coupled to microbial processes. This often somewhat arbitrary separation is probably also one of the major reasons, why, in this field, the present collaboration between chemists and microbiologists is still rather poor.

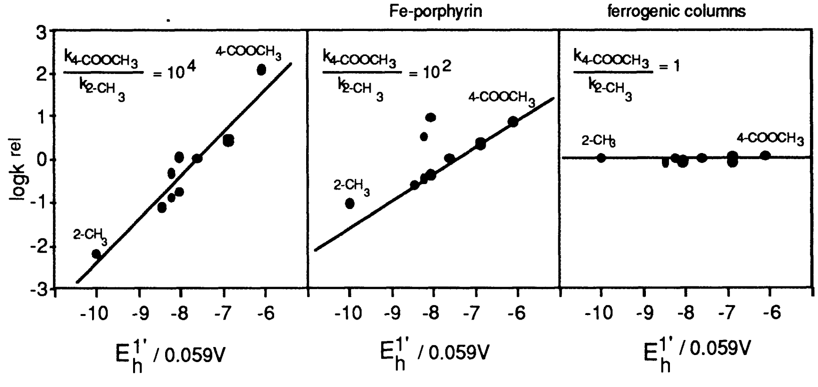

Figure 3

Comparison of the relative reduction rates of ten monosubstituted nitrobenzenes (nitrobenzene; 2-, 3-, 4-methylnitrobenzene; 2-, 3-, 4-chloronitrobenzene; 2-, 3-, 4-acetylnitrobenzene; the rates are relative to the reduction rate of 4-chloronitrobenzene) (a) in aqueous solution containing hydrogen sulfide and natural organic matter (Dunnivant et al., 1992), (b) in aqueous solution containing cysteine and an iron porphyrin (Schwarzenbach et al., 1990), and (c) in an aquifer column under iron reducing conditions (Heijman et al., 1994). The relative rates are plotted against the one-electron reduction potentials of the compounds.

References

Agrawal, A., & Tratnyek, P. G. (1994). Abiotic remediation of nitro-aromatic groundwater contaminants by zero-valent iron. *Extended abstract, ACS, San Diego, CA., 34*(1), 492-494.

Bollag, J.-M., Myers, C. J., & Minard, R. D. (1992). Biological and chemical interactions of pesticides with soil organic matter. *The Science of the Total Environment, 123/124,* 205-217.

Delgado, M. C., & Wolfe, N. L. (1992). Structure-activity relationships for the reduction of p-substituted nitrobenzenes in anaerobic sediments. ACS-Meeting. *Extended abstracts, San Francisco, CA.*

Dunnivant, F. M., Schwarzenbach, R. P., & Macalady, D. (1992). Reduction of substituted nitrobenzenes in aqueous solutions containing natural organic matter. *Environ. Sci. Technol., 26(*11), 2133-2141.

Heijman, C.G., Grieder, E., Holliger, Ch., and Schwarzenbach, R.P. (1994). «Reduction of nitroaromatic compounds coupled to microbial iron reduction in laboratory aquifer columns». Submitted to *Environ. Sci. Technol.*

Klausen, J. W., Tröber, S., Haderlein, S., & Schwarzenbach, R. P. (1994). Reduction of substituted nitrobenzenes in aqueous mineral (hydr)oxide suspensions containing dissolved iron(II). *To be submitted to Environ. Sci. Technol.*

Laha, S., & Luthy, R. G. (1990). Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environ. Sci. Technol., 24*(3), 363-373.

Li, S., & Wackett, L. P. (1993). Reductive dehalogenation by cytochrome P450 cam: substrate binding and catalysis. *Biochemistry, 32*(37), 9355-9361.

Macalady, D. L., Tratnyek, P. G., & Grundl, T. J. (1986). Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems: a critical review. *J. Cont. Hydr., 1,* 1-28.

Marks, T. S., Allpress, J. D., & Maule, A. (1989). Dehalogenation of lindane by a variety of porphyrins and corrins. *Appl. Environ. Microbiol., 55,* 1258-1261.

Schwarzenbach, R. P., Stierli, R., Lanz, K., & Zeyer, J. (1990). Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. *Environ. Sci. Technol., 24*(10), 1566-1574.

Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. 1993. Environmental Organic Chemistry (textbook), Chapter 12, Wiley, New York, 700 pages.

Stone, A. T. (1987). Reductive dissolution of manganese (III/IV) oxides by substituted phenols. *Environ. Sci. Technol., 21,* 979-988.

Torrents, A., & Stone, A. T. (1991). Hydrolysis of phenyl picolinate at the mineral/water interface. *Environ. Sci. Technol., 25*(143-149).

Torrents, A., & Stone, A. T. (1993a). Catalysis of picolinate ester hydrolysis at the oxide/water interface: inhibition by coadsorbed species. *Environ. Sci. Technol., 27*(6), 1060-1067.

Torrents, A., & Stone, A. T. (1993b). Catalysis of picolinate ester hydrolysis at the oxide/water interface: inhibition by adsorbed natural organic matter. *Environ. Sci. Technol., 27*(12), 2381-2386.

Ulrich, H.-J., & Stone, A. T. (1989). Oxidation of chlorophenols adsorbed to manganese oxide surfaces. *Environ. Sci. Technol., 23,* 421-428.

Wahid, P. A., Ramakrishna, C., & Sethunathan, N. (1980). Instantaneous degradation of parathion in anaerobic soils. *J. Environ. Qual., 9,* 127-130.

Weber, E. J., & Wolfe, N. L. (1987). Kinetics studies of the reduction of aromatic azo compounds in anaerobic sediment/water systems. *Environ. Toxicol. Chem., 6,* 911-919.

Wolfe, N. L., Kitchens, B. E., Macalady, D. L., & Grundl, T. J. (1986). Physical and chemical factors that influence the anaerobic degradation of methyl parathion in sediment systems. *Environ. Toxicol. Chem., 5,* 1019-1026.

Reductive Dehalogenation

Timothy M. Vogel

Reductive dehalogenation is widely accepted as a major degradative mechanism for highly chlorinated compounds in the environment. Observations of this phenomenon range over types of environmental niches, microorganisms and halogenated compounds. The occurrence of this biologically-mediated degradative or transformation process is credited in many cases as the cause for the natural or enhanced removal of potentially toxic compounds from the environment, even though some intermediates or metabolites might be more toxic for mammals. As a result of the potential benefit of controlling the reductive dehalogenation process, many different approaches to understanding and isolating the responsible microorganisms or biochemical agents have been explored. These results could be categorized under several different hypotheses. For example, the reductive dehalogenation might be enzyme controlled or not. The implications are not the same for the bioremediation of «contaminated» soil. Indeed, the very definition of «contaminated» can change the types of microorganisms that would exist at these sites.

Enzyme Issue

I. Halogenated Compound is Directly Coupled to Energy Production

The reductive dehalogenation of highly halogenated compounds can be an energy producing redox reaction as calculated at standard state conditions. The use of this energy for the benefit of the microorganisms would, therefore, probably be related to the use of the halogenated compound as an acceptor of electron(s), where the donor of electrons would either be an entirely different (and chemically more reduced) compound or the dehalogenated metabolite from the initial compound.

Ia. Entirely New Enzyme

One possibility is the development of an entirely new enzyme with little resemblance to other enzymes and an affinity for the halogenated compound and not other more traditional electron acceptors. This enzyme would be highly specific and probably would result from considerable mutational changes from its ancestors. The occurrence of this enzyme might be relatively rare and not necessarily be well represented in nature. Of course, a RNA genetic probe would help in determining if similar microorganisms exist in nature.

Ib. Retooled Enzyme

Another possibility is the occurrence of an enzyme that has changed little relative to its former non reductive dehalogenation type. This type of enzyme would be less specific than that described above and would still likely be able to use the original more traditional electron acceptor(s) for energy production. Clearly, less genetic mutation would be required to produce these changes relative to the totally specific enzyme described above.

In both cases (Ia and Ib), the driving force behind the development of these enzymes is the sufficient concentration of chlorinated compound to drive the mutation, selection, etc. processes. This concentration is not known for halogenated compounds, but could possibly be roughly estimated using calculated energy yields at non standard state chlorinated compound concentrations in the environment. This assumes that microbial species differences are less important than thermodynamic considerations for determining the lower limits of chlorinated compound concentrations.

II. «Fortuitous» Involvement of Enzyme Providing no Direct Energy

Enzymes could also mediate reductive dehalogenation without any connection to energy production. The occurrence of enzymes participating in other biochemical activities and also capable of mediating reductive dehalogenation reactions is difficult to differentiate from the activity described below (the non-enzymatic activity) since the participation of the protein structure has not always been established. This type of activity has been observed more often with oxidative type reactions and not reductive dehalogenations.

Hence, questions regarding the participation of the protein structure in controlling the reaction either in a negative or a positive sense have not been fully explored. If the responsible agent for the reductive dehalogenation is a metal-organic complex, then the surrounding protein might actually sterically hinder the reaction.

Non-Enzyme Issue

III. Dehalogenation by Cellular Components is Uncontrolled Redox Reaction

Another aspect of reductive dehalogenation is the apparent catalyses of this reaction by reduced components of the microbial cell without any direct method for recovering energy. The idea that these halogenated compounds act as electron sinks could in addition reduce the energy gained from electron donors by acting somewhat like electron transfer decouplers. Yet, the observation of this reaction in anaerobic («electron acceptor starved»?) conditions could be justified as a benefit ecologically by aiding in the general flow of electrons. Neither of these possibilities have been extensively studied.

IIIa. Metal-organic Compounds

Considerable research has, however, been conducted regarding the reaction between metal-organic complexes found in anaerobes and halogenated organic compounds. These studies generally wish to imply that metal organics are responsible for the reductive dehalogenations observed in anaerobic microbial communities and that these reactions are for the most part controlled by chemistry and not by proteins. The results have shown a general lack of specificity although not a lack of relativity between rates based on the reduction potential of the metal organic, the oxidation potential of the halogenated compound and its structure. The metal organics, of course, need an outside electron donor to re-reduce the metal after the reaction. In microorganisms, this would ultimately come from the electron donor.

III.b. Non-metal Organic Compounds

The reductive dehalogenation reaction can potentially be mediated by other reduced components in the microbial cell, such as quinones or reduced sulfur groups.

IV. Bioremediation

As described above, one of the motivations behind the search and discovery of microorganisms capable of using halogenated compounds as electron acceptors coupled to cellular energy production is their ultimate use for the degradation of these compounds in polluted soil. Similarly, investigations regarding the potential cometabolic or fortuitous reductive dehalogenation aim to influence natural microbial communities in a manner that would result in effective bioremediation of soils contaminated by halogenated compounds.

The difference between these two approaches could be categorized by their potential use for bioremediation. The use of selected microorganisms that use the halogenated compound(s) as a sole sink for electrons would be limited to concentrations above the minimum to sustain the population. In addition, methods for delivering the microorganisms to the location of the contamination would be needed on both macro- and microscales. An advantage would be the known kinetics and metabolic pathways for both estimating the time required and the potential risk of toxic metabolites. The second approach would lead to the manipulation of the soil chemistry in order to enhance the activity of indigenous microorganisms capable of «catalyzing» the reductive dehalogenation. The potential minimum concentration would be zero as the microorganisms would not be dependent on these compounds for their carbon and energy. The addition of microorganisms would be avoided and they would hopefully be very near the contaminant. Unfortunately, the control of indigenous microorganisms is not trivial and prediction of treatment times and potential metabolites would be more difficult.

Another possibility is the adaptation of indigenous microorganisms for the reductive dehalogenation of the contaminants in the soil. The concentration of these contaminants must be high enough to present a selective pressure, but not too high to inactivate the indigenous population. The occurrence of an adapted population at a contaminated site has not been well established for many halogenated compounds even in cases where reductive dehalogenation reactions have been observed.

Practically, in almost all cases, the addition of an electron donor is necessary in order to maintain anaerobic conditions and to provide the source of electrons for the reductive dehalogenation process. Indeed, several remediation processes have been initiated solely by the addition of the electron donor (e.g. benzoate) and nutrients. Therefore, some degree of optimism is maintained by researchers and practioners of reductive dehalogenation as result of the increase in knowledge and applicability of this process for the remediation of contaminated soils.

References:

Mohn, W.W. and Tiedje, J.M. 1992. Microbial reductive dehalogenation. *Microbial Reviews*, 56:482-507.

Vogel, T.M., Criddle, C.S. and McCarty, P.L. 1987. Transformations of halogenated aliphatic compounds. *Environmental Science and Technology*, 21:722-736.

Perspective and Limits in Biodegradation

Alexander J.B. Zehnder

Introduction

The increasing negative impact of polluted soils on the groundwater quality and incidences like Love Canal made soil protection a political issue. As a result, engineers and scientists started to investigate the possibilities for the clean-up of polluted soils and ground water and to predict the fate of chemicals in aquifers. Among others, also the question was raised about the potential of microorganisms to remove pollutants. It was and still is surprising how little is known about microbial processes in ground water and in a complex soil matrix. In contrast to aquatic systems the aquifer is highly heterogenic with respect to the spatial distribution of substrates, nutrients, and micro-organisms but also with respect to various phases and interfaces. This heterogeneity may considerably influence the bioavailability of a pollutant to micro-organisms.

The final fate of a pollutant depends on whether it is degraded or not. Consequently, it is important to know if micro-organisms present in the aquifer are able to degrade a given compound or have the capacity to eventually «learn» to degrade such a chemical. To obtain a satisfactory answer to the question of adaptation, information is needed about the influence of environmental conditions (pH, redox, surfaces, presence of other organisms, etc.) on specific microbially mediated reactions.

For quantitative predictions on the fate of pollutants it is necessary to possess kinetic data on the breakdown of a given compound or class of compounds obtained under different conditions (temperature, pH, redox, presence of other substrates and organisms, etc.). A kinetic parameter that has both environmental and toxicological importance is the threshold. The threshold of a chemical is the concentration below which it is not degraded anymore.

In the following the three topics interface/bioavailability, adaptation, and threshold will be discussed in the light of (i) their importance to obtain basic information on the biological, in particular microbial, processes in aquifers, (ii) what specific questions should be asked and investigated, (iii) the spin-offs that might be expected for other research areas and disciplines, and where applicable, (iv) the manner in which results from this research may be used to help to formulate rational environmental policies and/or more effective control strategies. At the end five theses are formulated.

Microbial Activities at Interfaces, Solid Surfaces and the Question of Bioavailability

Soils and sediments consist largely of particles of variable sizes. These particles are responsible for the presence of large areas of interfaces in particular solid/water. It has been shown that over 99% of the microbial activities in aquifers was found in connection with solid surfaces (Van Loosdrecht et al., 1990). It is therefore not exaggerated to state that microbial processes in aquifers take almost exclusively place on the surface of particles. In microbiology it is common practice to study microbial processes in homogeneous, aqueous systems. Solid surfaces are excluded whenever possible. During quantitative investigations, e.g. in a chemostat, all precautions are taken to prevent surface growth. As a consequence most mathematical models in microbiology can only be applied to homogeneously dispersed systems. Only recently models for non-homogeneous and non-dispersed systems, in particular for biofilms, have been developed.

For a thorough understanding of aquifer microbiology, the effect of the presence of a solid surface on the behaviour and metabolism of microbes must be systematically elucidated, however. The most basic questions which have first to be answered are: how do bacteria adhere to surfaces and how do bacteria attach to surfaces? Once these questions have been answered satisfactorily, the main topic can be tackled, which is: physiological, biochemical and genetic mechanisms triggering adhesion and attachment.

Much research has been done on microbial adhesion. A clearcut unifying theory based on molecular and atomic interactions is lacking yet. But it becomes increasingly evident that the DLVO-theory in combination with theories of steric colloid stability (SCS) and interfacial tension (IT) can adequately describe the physical-chemical process of microbial adhesion to particles (Rijnaarts, 1994). Once micro-organisms adhere, they may actively anchor to the surface using various sorts of polymeric extrusions (e.g. polysaccharides) or appendages (e.g. pili and fibrils). The medical literature contains a considerable amount of information about the mechanism of attachment of pathogenic and non-pathogenic micro-organisms to tissues, teeth, implants, etc. While much is known about how micro-organisms attach, our knowledge about the mechanisms triggering adhesion and attachment is almost absent. Data are needed about the effect of environmental parameters on physiological processes in micro-organisms and the subsequent expression of specific surface structures such as polysaccharides, etc. These surface structures may also influence the surface properties such as hydrophobicity or electrical charge. Solely when adequate informations about these regulations are available, we might begin to understand why micro-organisms, in particular bacteria, adhere and attach to particles in the environment and what physiological effect (if any) might be induced by the presence of surfaces and interfaces.

Adsorption of a chemical to soil and sediment matrix will lower its concentration in the bulk liquid. Adsorption will have two effects on biodegradation. Either, the degradation rate is reduced or in case of a toxic substance, its lower concentration may increase microbial activities (Bosma, this volume). Adsorption does not only take place at the surface of a particle. Natural particles commonly contain cavities, fissures, etc. which are too small for micro-organisms to penetrate but large enough for molecules to be reached by diffusion. Chemicals in these small pores have first to desorb and to diffuse to the micro-organisms before they can be degraded. As a consequence, biodegradation is limited by desorption and intraparticle mass transfer. Though a compound may be present at considerable concentrations in the aquifer materials, it is hardly or not at all available for microbes in the field. Besides being adsorbed in small pores, it can be sealed in particles by inorganic precipitates or be dissolved in an organic phase barely in contact with its surrounding water (e.g. in oil). Therefore, biodegradation is most often controlled in the field by availability and accessibility, rather than the ability of microbes to convert a certain chemical.

Microbial Adaptation

Soil is an ever changing environment, temperatures can vary from minus 50° C to over plus 50° C, and there is a continuum of water activities and redox conditions. Depending on the state of the environment these conditions can alter drastically, e.g. during day-night cycles, rainfalls, droughts, etc. In flooded soils redox conditions may even vary diurnally. All these, for surface soils typical continuous changes demand a tremendous adaptive capacity of the micro-organism living there. Aquifers are continuously inoculated by surface micro-organisms which bring their adaptive capacities to the water saturated parts of the soil.

About 50 years ago, man started to vary an additional factor by bringing into the environment alien compounds (xenobiotics) to which soil micro-organisms never have been exposed before. It became quickly apparent that micro-organisms can adapt to a large number of such compounds and are even able to transform or mineralize them. Compounds thought to be recalcitrant some fifteen years ago, suddenly are found to be biodegradable. One might hypothesize that either researchers learned to create the right conditions for the micro-organisms, which is probably true for some cases, or some microbes «learned» to degrade specific compounds. For this «learning» of microbes biologists have found some evidence. Three mechanisms have been described. The first is the activation of a genetic information already present in the organism (cryptic genes). The second involves an alteration in the substrate specificity of an enzyme as a result of a gene mutation induced by mutagenic agents. In this case the altered enzyme can now also attack structurally related molecules. The last mechanism consists of a recombination of pieces of pathways from different micro-organisms encoded on specific DNA fragments into one micro-organism. This recombination allows the final recipient to carry out biochemical reactions which it could absolutely not do before. All three mechanisms may occur in nature concomitantly or in any combination (Van der Meer et al. 1992).

At the moment we are very far from understanding these processes, especially the natural recombination. A thorough understanding of the adaptation reactions would supply us with information about the ultimate metabolic potential of a given microbial community and would allow to assess the chance for an aquifer for «self-purification». Based on this knowledge, one could decide whether a specific pollution is harmful and should be treated biologically or not.

Information from microbial adaptation research is necessary for a realistic formulation of environmental legislation because (i) these data offer the fundamental insights not only into the prospects but also the limits of micro-organisms to remove pollutants from the groundwater environment, and (ii) as a result of this knowledge, the sensitiveness of a given environment to anthropogenic influence (physical treatment, chemicals, input of alien micro-organisms, etc.) as well as the chances of recovery by adequate treatment or protection measures can be assessed.

The Threshold Concentration and Kinetics of Biodegradation

Once we are aware that a compound is biodegradable it is important to know the rate at which this process takes place and the minimum concentration which can be attained by the action of micro-organisms. Biodegradation kinetics, formation of metabolites, and the threshold concentration are controlled by physical, chemical, and biological parameters of the environment.

The most important physical parameters are: temperature, water activity, presence of surfaces and the concentration of compounds at the interfaces, mass transport limitation, degree of inhomogeneity, etc. The chemical environment is composed of other chemicals and their stimulatory or inhibitory (toxic) effects, specific nutrients, pH, availability of certain electron acceptors (redox), etc. Other organisms and their mutualistic, synergistic or antagonistic effects are the biological factors. During the process of biodegradation of organic chemicals, intermediary products may be formed which resist further microbial attack. These metabolites may even be more toxic than the mother compound. In almost all cases, the metabolites are much more soluble and thus also more mobile in aquifers because of their lower hydrophobicity. The change in hydrophobicity is the result of the elimination of non-polar groups or the addition of some polar functions to the molecule. By changing some environmental parameters the release of certain metabolites can be prevented.

A solid amount of information is available for a selected amount of compounds with regard to their biodegradation kinetics in the environment. We are also learning more and more about the quantitative influence of environmental parameters on these kinetics. However, concerning the threshold, our information is quite limited. A selected amount of publications deals with specific aspects of this phenomenon but the biological rational behind the threshold is in most cases not known (Rittmann and Sáez, 1993). Therefore, qualitative and quantitative information about the factors affecting it is lacking; e.g. how does the presence of a surface affect the threshold, what is the influence of a secondary substrate or the adsorption of the substrate itself, can the presence of certain organisms lower the threshold, etc? But it is also important to know whether a threshold for adaptation exists, or with other words, is there a concentration limit below which organisms will not adapt to new chemicals anymore? Answers to these kind of questions are essential if polluted aquifers have to be cleaned-up or if the harmfulness of a contamination has first to be assessed.

Theses

1. Microbial processes and factors affecting them are rarely considered in fate models.
2. Biodegradation is in the first instance controlled by the physical and chemical environment.

3. Fate models which consider only macroscopic processes have limited prediction values.
4. Chemodynamics of organic compounds are controlled by their «speciation».
5. Concentrations of chemicals extracted with solvents from aquifer material are hardly measures for their bioavailability and as consequence their ecotoxicity.

References

Rijnaarts, H.H.M. 1994. Interaction Between Bacteria and Solid Surfaces in Relation to Bacterial Transport in porous media. Thesis Wageningen Agricultural University, The Netherlands.

Rittmann, B.E. and Sáez, P.R. 1993. Modeling Biological Processes Involved in Degradation of Hazardous Organic Substrates. In: J.M. Levin and M. Gealt, Eds. *Biotreatment of Industrial and Hazardous Wastes*. McGraw-Hill Book Co., New York, p.p. 113-136

Van der Meer, J.R., de Vos, W.M., Harayama, S., and Zehnder A.J.B. 1992. Molecular Mechanisms of Genetic Adaptation to Xenobiotic Compounds. *Microbiol. Rev. 56*, 677-694.

Van Loosdrecht, M.C.M., Norde, W. , Lyklema, J., and Zehnder, A.J.B. (1990), Influence of Interfaces on Microbial Activity. *Microbiol. Rev. 54*, 75-87.

IIb Field and Case Studies

Bioslurry Treatment of NAPL-Contaminated Soil

Richard G. Luthy, Subhasis Ghoshal, Anuradha Ramaswami, and David V. Nakles

Soil Contamination and NAPLs

Industrial processes related to petroleum refining, coal coking, coal gasification and wood processing result in the production of liquid fuels and waste by-products, including motor fuels, coal tar, creosote and heavy oils. These organic-phase liquids are often sparingly soluble in water, and in the context of soil and sediment contamination are termed non-aqueous phase liquids or NAPLs. NAPLs such as fuel oil, creosote, gasoline and coal tar are multi-component mixtures that are composed of a broad range of hydrophobic organic compounds (HOCs). When NAPLs are released to the subsurface environment (e.g., from oil spills or leaking storage tanks), they function as long-term sources of HOCs, resulting in persistent soil and water pollution problems.

Remediation Limitations

Recent research efforts have focused on *in-situ* remediation of NAPL contaminated sites. Proposed treatment technologies include steam injection (Hunt et al., 1988), water flushing (Gellar and Hunt, 1993), enhanced solubilization by solvents and surfactants (Villaume, 1991; Luthy et al., 1992; Edwards et al., 1994) and bioremedation (Muraka, 1990). *In-situ* water-based remediation technologies, including water flushing and bioremediation, are found to be limited by the slow rate of release of organic solutes from NAPL to water and the significant complications arising from heterogeneities in the subsurface environment. Enhanced flushing by dissolution with surfactants and solvents may not overcome all the mass transfer difficulties, and may pose additional problems because of the volume of chemicals required, and the risks associated with the unpredictable migration of NAPL-solvent or NAPL-surfactant solutions (Fountain, 1992). Consequently, excavation from the subsurface, followed by *ex-situ* treatment of NAPLs and NAPL-contaminated soils, may be proposed, although often impractical (EPA, 1993).

In some instances, both technical and economic constraints favor in-place bioslurry stabilization of impounded surface soils or sediments contaminated with NAPL hydrocarbons. In this technique, it is envisioned that the upper portion of the soil or sediment (e.g., that containing heavy oils or tars) be treated in-place in well-mixed slurry bioreactors. The objective of bioslurry treatment is to process the top layer of material producing cleansed material that may be left in place. This treatment would eliminate direct exposure of contaminants to people, while helping to prevent the release of contaminants to surficial waters, thereby reducing health and ecological risk. Bioslurry treatment is not practical for decontaminating HOCs from dense NAPLs (DNAPLs) deep in the subsurface.

Bioslurry Treatment Process

Bioslurry treatment is analogous to conventional aerobic digestion of municipal and industrial sludges. Bioslurry treatment is designed to relieve factors commonly limiting microbial growth and activity in sediments and sludges (i.e., principally, the availability of oxygen and inorganic nutrients) and to correct for the heterogeneity of contaminants found in these matrices by providing thorough mixing. To achieve these goals, the wastes are suspended in a slurry form and mixed to maximize oxygen transfer rates and contact between contaminants and biomasss, and to improve desorption rates from the solid phase. Bioslurry treatment may be implemented in aboveground tanks (*ex-situ*), or in surface impoundments and contained water bodies (*in-situ*) (RETEC, 1994).

Aerobic treatment in batch biological slurry treatment systems has been used to treat oily hydrocarbon sludges (e.g., Huesemann et al., 1993). A principal goal of mixing and aeration is to supply oxygen as the electron acceptor in sufficient amounts throughout the slurry matrix. Mixing can be provided by aeration alone, which is possible for slow solids content wastes, e.g., <5%, or by aeration and mechanical mixing. For slurry systems with solid phases of relatively high specific gravity, such as sediments and soils, dredging systems are usually required to maintain the solids in a suspended condition. Aeration can be provided by floating or submerged aerators, or by compressors, spargers, and diffusers. VOC emission monitoring and/or control may be required with wastes high in VOCs.

Figure 1 shows a schematic of a plan view of an *in-situ* bioslurry treatment process that has been proposed for contaminated sediments (RETEC, 1994). The treatment cell is confined by Z-section sheet pile. A whole site would be treated either placing dredged materials into the cell or by constructing multiple cells as work progresses from cell to cell. The schematic shows submersible mixers and a floating dredge with a mounted aerator. The dredge digs into the zone of contaminated sediment. The dredge is anchored in a four-point cable traversing system. This configuration allows the floating dredge to reach sediments and macerate debris. The vertical depth of treatment is limited by the capabilities of the dredge. If contamination extends below the dredging depth, then a treatment objective would be to create a clean cap within the cell to prevent contaminant release from sediment to surficial water.

Research Needs

Slurry biotreatment of soils and sediments, either *ex-situ* or in-place, may emerge as a feasible and cost-effective method for management of soils and sediments contaminated with NAPL hydrocarbons. Slurry systems employ mixing to: (i) create a more homogeneous environment, (ii) facilitate mass transfer of HOCs from the NAPL to the aqueous phase, and (iii) provide adequate transfer of oxygen and nutrients to maintain viable microbial populations. Nonetheless, pilot-scale treatability studies with hydrocarbon-contaminated soils in slurry reactors indicate limited biotransformation of HOCs associated with the solid matrix, and suggest that mass transfer phenomena may pose a limiting constraint on biotransformation rates and end points (GRI, 1992; RETEC, 1994). Those studies indicate that an integrated assessment of physical, chemical and biological phenomena is required for development of viable biotreatment technologies for NAPL-contaminated soils.

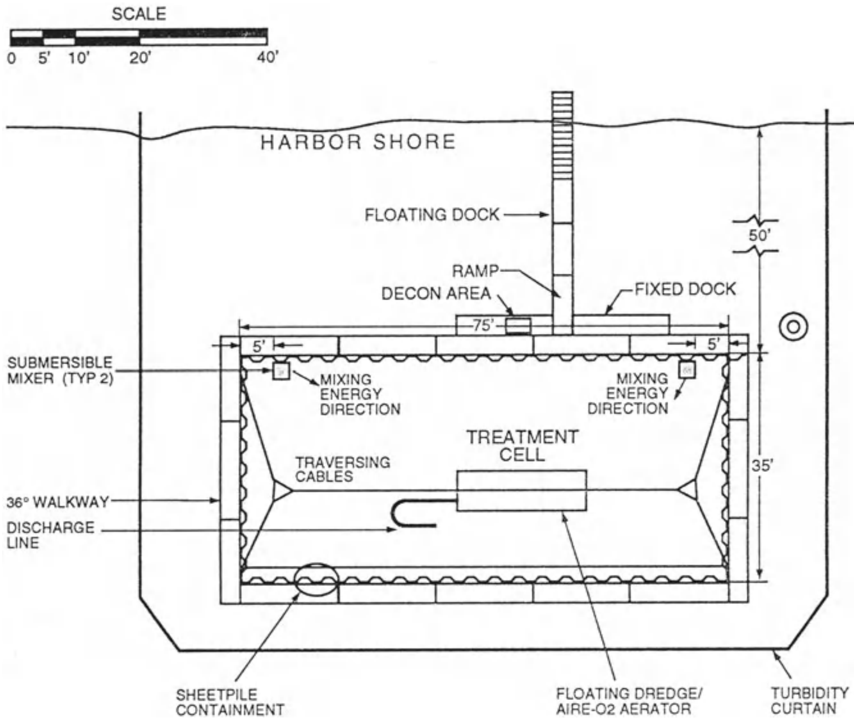

Figure 1
Schematic representation showing a plan-view of an *in-situ* bioslurry treatment process for contaminated sediments (RETEC, 1994).

Research is needed to develop phenomenological models and to conduct controlled laboratoy and field-scale experiments leading to quantitative analysis of physicochemical and biokinetic parameters controlling biotransformation rates of NAPL-derived HOCs.

The biotransformation of NAPL-derived hydrophobic organic compounds in sediments is a complex process resulting from a sequence of several physical, chemical and biological phenomena. The grain-scale phenomena are illustrated in Figure 2, which shows a multi-phase system composed of solid, NAPL, water and a microbial biofilm. The overall rate of biotransformation is controlled by the slowest of either the mass transfer or the biokinetic phenomena. To adress these issues, research is needed in the following areas:

- An analysis of physicochemical mass transfer phenomena affecting the «bioavailability» of hydrophobic-NAPL solutes in surface-dominated systems,
- An assessment of biokinetic factors affecting the functioning of the microbial populations and the potential rates and end points for degradation of hydrophobic-NAPL solutes, and
- Development of an integrated modeling framework that couples mass transfer processes with biokinetic phenomena to describe the overall rate of biotransformation of NAPLs in slurry bioreactor systems.

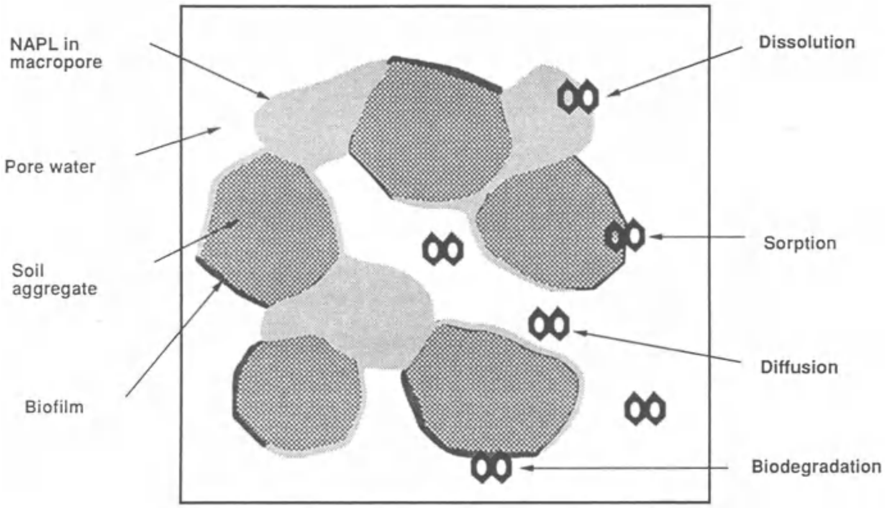

Figure 2
Schematic of grain-scale processes affecting biotransformation of NAPL from soil or sediment in bioslurry systems.

Laboratory scale research and process modeling are in progress at Carnegie Melon on these topics (Luthy et al., 1994). Model results, in conjunction with both laboratory and field data, will help provide quantitative criteria for the determination of rate-limiting phenomena in NAPL-water slurry systems. Such results are necessary for engineering and economic evaluation of *in-situ* slurry bioreactors.

It is also important to assess the potential for release of NAPL-bound HOCs that may persist after bioslurry treatment. Soil quality criteria for remediation goals need to be developed in recognition of technological feasibility and health/ecological risks based on expected land use, and allowance for source control.

References

Edwards, D.A.; Liu, Z.; Luthy, R.G. (1994), Surfactant Solubilization of Organic Compounds in Soil Aqueous Systems,*J. Environ. Eng., 120 (1),* 5-22.

EPA Publication 9234.2-25, (1993), *Guidance for Evaluating the Technical Impracticability of Ground Water Restoration,* U.S. EPA, Washington, D.C.

Fountain, J.C. (1992), In *Detection and Restoration of DNAPLs in Groundwater at Hazardous Waste Sites*, Technical Publication, Water Environment Federation: Alexandria, VA.

Geller, J.T.; Hunt, J.R. (1993), Mass Transfer from Nonaqueous Phase Organic Liquids in Water-saturated Porous Media, *Water Resour. Res., 29(4)*, 33-45.

GRI: Morgan, D.J.; Battaglia, A.; Hall, B.J.; Vernieri, L.A.; Cushey, M.A. (1992), *The GRI Accelerated Biotreatability Protocol for Assessing Conventional Biological Treatment of Soils: Development and Evaluation Using Soils from Manufactured Gas Plant Sites*; Gas Research Institute: Chicago, IL, GRI-92/0499.

Huesemann, M.H.; Moore, K.O.; Johnson, R.N. (1993), The Fate of BDAT Polynuclear Aromatic Compounds During Biotreatment of Refinery API Soil Separator Sludge. *Environ. Progress, 12(1)*, 30.

Hunt, J.R.; Sitar, N.; Udell, K.S. (1988), Nonaqueous Phase Liquid Transport and Cleanup. 2. Experimental Studies, *Water Resour. Res., 24(8)*, 1247-1258.

Luthy, R.G.; Dzombak, D.A.; Peters, C.A.; Ali, M.A.; Roy, S.B. (1992), *Solvent Extraction for Remediation of Manufactured Gas Plant Sites*, Final Report, EPRITR-101845, Project 3072; Carnegie Mellon University, Pittsburgh, PA.

Luthy, R.G.; Dzombak, D.A.; Peters, C.A.; Roy, S.B.; Ramaswami, A.; Nakles, D.V.; Nott, B.R. (1994), «Remediating Tar-Contaminated Soils at Manufactured Gas Plant Sites», *Environ. Sci. Technol. 28*:266-276.

Muraka, I. (1990), *Manufactured Gas Plant Site Investigations, EPRI Journal.*

RETEC (1994), Harbor Sediments: *In Situ Bioslurry Treatment Demonstration Work Plan*, Remediation Technologies, Inc.: Austin, TX, 3-0844/341.

Villaume, J.F. (1994), «Recovery of Dense Nonaqueous Liquids by *In-Situ* Flushing», Proceedings of the Technology Transfer Seminar, Electric Power Research Institute/ Gas Research Institute, Atlanta, GA.

Field Studies: Elicitation of Fate and Transport Processes and Application to Full-scale Remediation

Mark N. Goltz

Introduction

Although laboratory studies and studies of uncontrolled releases are essential elements in our quest to understand the fate and transport of organic contaminants in the subsurface, both types of studies have inherent limitations. Laboratory studies, though well controlled, do not recreate the complexity and variability of natural systems. Studies of uncontrolled releases, by definition, do not have the experimental controls (for instance, knowledge of the location of contaminant source in time and space) necessary to quantitatively elicit fate and transport processes. Thus, controlled field experiments are vital links, bridging the gap between laboratory and application, and helping us to understand fate and transport processes in natural systems, as well as helping us bring theory to bear on remediation of uncontrolled releases.

In this review, controlled field experiments which have been conducted over the past decade at Canadian Forces Base (CFB) Borden, Ontario and Moffett Naval Air Station (NAS), Mountain View, CA to elicit physical, chemical, and biological processes which affect fate and transport of organic compounds in ground water will be discussed. CFB Borden and Moffett NAS were chosen for this review as experiments at these two sites arguably comprise the most extensive series of field scale studies involving controlled introduction of organic compounds into the subsurface ever conducted.

CFB Borden Field Site

The first controlled release of organic compounds at CFB Borden was reported by Sutton and Barker (1985). The natural gradient experiment involved the injection of an inorganic chloride tracer and four organics (butyric acid, phenol, p-chlorophenol, and dimethyl phthalate) into an unconfined aquifer. Transport of the contaminants was monitored for 60 days. It was found that the organic plumes migrated at essentially the same rate as the chloride, indicating that sorption of the organics to the aquifer solids was not an important transport mechanism. Reduction of the relative concentrations of the organics appeared to be due to biodegradation, as the extent of reduction was directly related to literature estimates of biodegradability of the four compounds.

From 1982 to 1985, a large-scale field experiment on natural gradient transport of solutes was conducted by researchers from Stanford University and the University of Waterloo at CFB Borden. A well-defined initial pulse of inorganic tracers (chloride and bromide) and halogenated organic compounds (bromoform, carbon tetrachloride, o-dichloro-benzene, hexachloroethane, and tetrachloroethylene), was injected into the aquifer. Fate and transport of the contaminants were monitored over a three year period, as the plumes traveled tens of meters. Transport of all the organic compounds appeared to be affected by sorption. Hexachloroethane, bromoform, and o-dichlorobenzene also biotransformed. Since publication of the experimental results in 1986 (Mackay et al., 1986; Freyberg, 1986; Roberts et al., 1986; Curtis et al., 1986; Sudicky, 1986) extensive analyses have been conducted on the data in order to gain insight into the processes that affected contaminant fate and transport (e.g. Ball and Roberts, 1991; Goltz and Roberts, 1988; Farrell et al., 1994).

Three natural gradient experiments were conducted by University of Waterloo researchers from 1988 to 1990 to study anaerobic biodegradation of BTEX compounds (benzene, toluene, ethylbenzene, and o-, p-, and m-xylene) under denitrifying conditions. Slugs of BTEX and a bromide tracer were injected into the aquifer. For two of the experiments, nitrate was also added. It was found that when nitrate was not present, all the compounds except toluene were recalcitrant. In the presence of nitrate, toluene, xylene, and ethylbenzene biodegraded, though the xylene isomers and ethylbenzene biodegraded to a lesser degree. Benzene was recalcitrant under all conditions studied (Barbaro et al., 1992).

As natural gradient experiments take a longtime to complete (and are, therefore, expensive) Mackay et al. (1994) conducted a forced-gradient test at CFB Borden in 1989. Using four of the five organics that had been studied in the Stanford-Waterloo natural gradient experiment, Mackay and his coworkers concluded that forced-gradient tests, while not equivalent to natural gradient tests, can be useful in providing information on contaminant fate and transport in the field. In particular, sorption estimates obtained from the forced-gradient test were similiar to estimates obtained in the laboratory and from the natural gradient experiment.

More recently, University of Waterloo researchers have begun studying fate and transport of dense nonaqueous phase liquids (DNAPLs). Surrounded by a double walled sheet-pile cell, 230.9 L of tetrachloroethylene (PCE) was introduced into the Borden aquifer below the water table. After 28 days, the cell was excavated, to see how the PCE moved in the natural sand aquifer. PCE pools were revealed, as well as variable distributions of residual PCE ranging from 1% to 38% of pore space (Kueper et al., 1993). Two similar, though smaller scale experiments, were conducted at CFB Borden in the unsaturated zone. Each experiment involved the release of 6 L of PCE, with excavation 1 day later (Poulsen and Kueper, 1992).

Over the years, the Borden field site has provided invaluable data. Using understanding gained from the controlled experiments which were conducted there, practitioners are now better able to apply technology to remediate uncontrolled hazardous waste sites.

Moffett NAS Field Site

Three studies have been conducted at Moffett NAS to evaluate the capacity of indigenous microorganisms to aerobically and anaerobically cometabolically degrade chlorinated aliphatic hydrocarbons (CAHs). The Moffett studies were conducted in a shallow confined aquifer, at scales of several meters. An injection/extraction well pair was used, to obtain approximately one-dimensional transport of contaminant. After studying the physical mechanisms of transport using a bromide tracer, CAHs were injected into the aquifer to study retardation, as well as to see if CAH biodegradation would occur naturally. This was followed by the active biodegradation studies, which involved injection of primary substrates and electron acceptors into the aquifer, in order to evaluate degradability of the various CAHs (McCarty and Semprini, 1993).

One study evaluated methanotrophs, which use methane as a primary substrate and cometabolically transform CAHs with methane monooxygenase. Pulses of methane and oxygen were introduced into the aquifer, and degradation of vinyl chloride, trans- and cis-dichloroethylene (DCE), and trichloroethylene (TCE) was monitored. It was found that degradation occurred within one day's travel distance of the injection well. The transformation levels achieved were: vinyl chloride, 95%; cis-DCE, 50%; trans-DCE, 90%; and TCE, 20%. Details of these methanotrophic studies may be found in Roberts et al. (1990) and Semprini et al. (1990).

In an attempt to achieve higher transformation levels of TCE, a second study was conducted to stimulate phenol utilizers, in which toluene oxygenase is used as the cometabolizing enzyme. Pulsing phenol and oxygen into the aquifer, transformation levels of over 90% were achieved for TCE and cis-DCE (Hopkins et al., 1993a and 1993b).

A third study investigated cometabolic anaerobic degradation of carbon tetrachloride. Acetate was introduced into the Moffett aquifer. Nitrate was already present in the aquifer to serve as an electron acceptor. Approximately 95% degradation of carbon tetrachloride was observed, with chloroform being produced as an intermediate degradation product (Semprini et al., 1991).

The Moffett Field results presented above have potential applications to the nation's efforts to remediate hazardous waste sites contaminated with CAHs. TCE is found at numerous hazardous waste sites, and, based on the Moffett results, appears to be susceptible to cometabolic degradation by microorganisms which utilize phenol as a primary substrate. As a next step, a full-scale demonstration of this technology to aerobically, cometabolically biodegrade TCE is being planned.

Conclusions

Controlled field studies are an important intermediate between the laboratory and full-scale application. The work described above at CFB Borden and Moffett NAS is a good example of how field studies can provide important information, unattainable in either the laboratory or by studying uncontrolled releases.

References

Ball, W.P. and P.V. Roberts. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. *Environmental Science and Technology, 25:*1237-1249.

Barbaro, J.R., J.F. Barker, L.A. Lemon, and C.I. Mayfield. 1992. Biotransformation of BTEX under anaerobic, denitrifying conditions: field and laboratory observations. 1992. *Journal of Contaminant Hydrology, 11:* 245-272.

Curtis, G.P., P.V. Roberts, and M. Reinhard. 1986. A natural gradient experiment on solute transport in a sand aquifer. 4. Sorption of organic solutes and its influence on mobility. *Water Resources Research, 22:* 2059-2067.

Farrell, D.A., A.D. Woodbury, E.A. Sudicky, and M.O. Rivett. 1994. Stochastic and deterministic analysis of dispersion in unsteady flow at the Borden tracer-test site, Ontario, Canada. *Journal of Contaminant Hydrology, 15:*159-185.

Freyberg, D.L. 1986. A natural gradient experiment on solute transport in a sand aquifer. 1. Spatial moments and the advection and dispersion of nonreactive tracers. *Water Resources Research, 22:* 2031-2046.

Goltz, M.N. and P.V. Roberts. 1988. Interpreting organic solute transport data from a field experiment using physical nonequilibrium models. *Journal of Contaminant Hydrology, 1:*77-93.

Hopkins, G.D., J. Munakata, L. Semprini, and P.L. McCarty. 1993a. Trichloroethylene concentration effects on pilot field-scale in-situ groundwater bioremediation by phenol-oxidizing microorganisms. *Environmental Science and Technology, 27:* 2542-2547.

Hopkins, G.D., L. Semprini, and P.L. McCarty. 1993b. Microcosm and in situ field studies of enhanced biotransformation of trichloroethylene by phenol-utilizing microorganisms. *Applied and Environmental Microbiology, 59:*2277-2285.

Kueper, B.H., D. Redman, R.C. Starr, S. Reitsma, and M. Mah. 1993. A field experiment to study the behavior of tetrachloroethylene below the water table: spatial distribution of residual and pooled DNAPL. *Ground Water, 31:* 756-766.

Mackay, D.M., G. Bianchi-Mosquera, A.A. Kopania, and H. Kianjah. 1994. A forced gradient experiment on solute transport in the Borden aquifer. 1. Experimental methods and moment analyses of results. *Water Resources Research, 30:* 369-383.

Mackay, D.M., D.L. Freyberg, and P.V. Roberts. 1986. A natural gradient experiment on solute transport in a sand aquifer. 1. Approach and overview of plume movement. *Water Resources Research, 22:* 2017-2029.

McCarty, P.L. and L. Semprini. 1993. Ground-water treatment for chlorinated solvents. In *Handbook of Bioremediation,* R.D. Norris et al., eds. Lewis Publishers, Boca Raton, pp. 87-116.

Poulsen, M.M. and B.H. Kueper. 1992. A field experiment to study the behavior of tetrachloroethylene in unsaturated porous media. *Environmental Science and Technology, 26:* 889-895.

Roberts, P.V., M.N. Goltz, and D.M. Mackay. 1986. A natural gradient experiment on solute transport in a sand aquifer. 3. Retardation estimates and mass balances for organic solutes. *Water Resources Research, 22:* 2047-2058.

Roberts, P.V., G.D. Hopkins, D.M. Mackay, and L. Semprini. 1990. A field evaluation of in-situ biodegradation of chlorinated ethenes. Part 1. Methodology and field site characterization. *Ground Water, 28:* 591-604.

Semprini, L., G.D. Hopkins, D.B. Janssen, M. Lang, P.V. Roberts, and P.L. McCarty. 1991. In-situ biotransformation of carbon tetrachloride under anoxic conditions. *U.S. Environmental Protection Agency Report EPA/2-90/060,* R.S. Kerr Environmental Research Laboratory, Ada, OK.

Semprini, L., P.V. Roberts, G.D. Hopkins, and P.L. McCarty. 1990. A field evaluation of in-situ biodegradation of chlorinated ethenes. Part 2. Results of biostimulation and biotransformation experiments. *Ground Water, 28:* 715-727.

Sudicky, E.A. 1986. A natural gradient experiment on solute transport in a sand aquifer. Spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research, 22:* 2069-2082.

Sutton, P.A. and J.F. Barker. 1985. Migration and attenuation of selected organics in a sand aquifer - a natural gradient experiment. *Ground Water, 23:* 10-16.

Bioremediation in Practice: Problems and Results

Volker Schulz-Berendt, and Emmo Poetzsch

Over the last ten years biological treatment methods have been developed to regenerate soil with microbial aid based on natural processes. The main use of this method is the optimization and acceleration of these processes. Large-scale technical applications of such microbiological clean-up methods are used particularly in the field of contamination by mineral oil, polycyclic aromatic hydrocarbons (PAH) and chlorinated hydrocarbons. The product, which is clean soil, can be re-used in many sectors such as horticulture, recultivation, sound insulation walls or refuse tip covering.

Optimizing the microbial environment is essential for maximizing the degradation rates. These steps are performed initially and routinely through the course of each project to make corrections to maximize the degradation rates of each contaminant of concern. Soil properties directly and indirectly affecting the microbial environment (e.g. particle size distribution, nutrient balance, pH, moisture content) are carefully evaluated.

Large-scale experience in soil bioremediation today exists in the fields:

1. On-site remediation of soil contaminated with petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) in amounts of some hundred thousands of tons.
2. Off-site treatment of TPH and PAH contaminated soil as well as volatile compounds like aromatic (BTEX) and chlorinated pollutants (perchloroethylene, trichloroethylene, dichloromethane). In Germany a capacity of about 500.000 t/a is installed today.
3. *In-situ* treatment of sites contaminated with TPH, BTEX and chlorinated compounds at areas of some ten thousand square meters and a depth of about 10 to 15 m.

Homogeneity is a critical element in a successful bioremediation project. Therefore, on-site or off-site techniques are the preferred methods for biological soil treatment.

Soil classification and sorting plays an important role in remediation activities. The first step is to screen the soil to remove large pieces of material including foreign debris. A vibrating grizzly accomplishes this task in the mixing unit. Clay particles and any clumps of soil are broken apart in the mixing unit.

If necessary the soil mixer is totally sealed and the conveyor will have specially designed VOC controls. A vacuum is provided to both the mixer and conveyor through a manifold system that leads to a bio-air-filtration system. For the biological breakdown of the pollutants closed systems are used to maintain the conditions for microbial activity. This may be a tent for on-site treatment or any other enclosure that prevents rain water from penetrating the soil as well as volatile compounds to be released to the environment.

New developments include the design and construction of more technical systems like fermentation units for soil or sludge treatment. With these technologies degregation rates can be enhanced so that the treatment period is shortened to some weeks or even days. By the reactor treatment bioavailabiltity is enhanced so that in many cases the measured concentrations of pollutants rise before degradation leads to a decrease of the contaminant. But these techniques are very costly and therefore they should be used only in some special cases.

Biological soil remediation has developed from simple land farming to a sophisticated technology. At the same time, the large scale use of biological breakdown processes expanded from simple applications, like the degradation of petroleum hydrocarbons, to more complicated substances like aromatic or chlorinated compounds. In the most cases, it is not the lack of enzymatic potential for degradation of the contaminant that limits the biological breakdown but other properties like solubility or volatility. Therefore, technical efforts are necessary to make the pollutants available for microorganisms or their extracellular enzymes. Because of the more complicated metabolic pathways of the degradation, its processes must be controlled to insure that no harmful metabolites accumulate in soil.

In addition to this, the emission of compounds must be reduced to a minimum so that environment protection does not cause any environmental burden at other compartments of nature.

There are technical solutions to these problems but their realization eliminates the economical advantages of bioremediation as compared with other technologies. Because of the dimension of environmental problems, especially in Eastern Europe, such high-standard remediations will not be payable in many cases. Therefore, we have to keep in mind that bioremediation can be a simple and cheap way to improve the condition of nature damaged by human activities, provided space and time are available.

Demonstration of On-site Innovative Technologies: Case Studies in Soil and Groundwater Remediation

Daphne Kamely

The United States Department of Defense is responsible for restoring a significant number of domestic military sites contaminated by soil and groundwater pollutants. With the end of the Cold War, the Department is downsizing and remediation of formerly used defense sites and military bases that have been or are scheduled to be closed has become a priority. Many of the Defense Department's pollution problems are not unique to the Federal government. For example, soil and groundwater contamination by fuels, solvents, metals, acids, chemicals and low-level radioactive waste are problems common both to military sites and industrial properties. A mechanism being executed by the Department of Defense to create jobs, as well as to clean up contaminated sites, is to «convert» uniquely military technologies to address the public and private sectors' common environmental needs. Technologies that were developed and tested in conjunction with weapon systems' acquisition during the Cold War are, today, being adapted and demonstrated by the Department to monitor, treat and/or prevent environmental pollution. Once these «dual use» technologies are implemented and commercialized, they are expected to be more effective than conventional remediation techniques and provide significant cost savings for the Department of Defense and industry.

In order to protect the public health and the environment at military sites, and to enhance dual use technologies and defense conversion efforts in the United States, the Department of Defense has established the Environmental Security Technology Certification Program. Through the demonstration and validation of innovative technologies, this newly established program is expected to facilitate environmental remediation and compliance. It is also intended to minimize waste generation by reducing or eliminating pollution at the source and by substituting less toxic materials for the currently used toxic agents. In addition to demonstrating and validating innovative environmental technologies, the program will also encourage education and training that results in a skilled environmental workforce.

The Environmental Security Technology Certification Program focuses on technologies that are sufficiently mature to be demonstrated, validated and implemented at military sites, and then commercialized for domestic and international market use. In July 1991, a collaborative partnership was established among Federal, State, and local agencies, the goals of which are to: (a) Demonstrate cost-effective, innovative technologies on Federal facilities; (b) Streamline the approaches among the agencies; and (c) Avoid duplication among Federal and State entities. A Federal advisory committee, entitled the «Demonstrate On-Site Innovative Technologies for Environmental Restoration and Waste Management (DOIT) Committee», organized in December 1992, is the mechanism through which this partnership functions. The DOIT Committee consists of representatives from the United States Departments of Defense, the Interior and Energy, the Environmental Protection Agency and the National Governors Association. In January 1994, it recommended 14 demonstration sites and 20 demonstration projects to be conducted at those sites (Figure 1). These recommendations are being evaluated and matched with technologies available to each of the participating Federal agencies, and will be executed in order of priority.

Figure 1
DOIT Committee recommended regional innovative demonstration projects.

[1] Brooks AFB is headquartes for all AFCEE Bioventing and Intrinsic Bioremediation Projects;

[2] While outside the West, Jefferson Proving Ground can serve as a test bed for technologies applicable in western states.

Several technologies recommended by the DOIT Committee for demonstration apply directly to soil and groundwater remediation, and will be included among other case studies discussed in this symposium.

The first case study describes supercritical water oxidation which can be applied to chlorinated solvents and radioactive wastes with a destruction efficiency of over 99.99%. Effluents from the supercritical water oxidation treatment process are relatively benign, for example, carbon dioxide and water. Furthermore, the treatment unit can be designed as a full containment process with no release to the atmosphere. Initially, this technology will be applied to mixed wastes in Federal and private sector waste treatment facilities. Once the procedure is fully implemented, cost savings are estimated at $100 million annually.

The second case study involves plasma arc technology for thermal destruction of hazardous wastes. This technology can be used for the destruction of heavy metals, organic solvent contaminated soils, metal finishing sludges, pyrotechnic sludges, asbestos, and medical waste and the demilitarization of storage batteries. The treatment process eliminates the waste and liquid or gas side streams. Effluents of the process are a vitrified solid residue, carbon dioxide and water vapor. The process has a high energy transfer efficiency and minimal demand for air compared to fossil fuel incinerators. High temperatures accelerate the reaction rate and the energy efficiency of plasma arc torches consistently reaches between 85% and 93%. The faster and more complete reaction kinetics of plasma arc energy sharply reduces processing time and operating costs.

The third case study involved the use of a radio frequency induced, thermal decontamination *in-situ* process to remove volatile organic compounds from soil. The *in-situ* system is composed of a radio frequency energy deposition electrode array; a radio frequency power generation, transmission, monitoring, and control system; a vapor barrier and containment system; and a gas and liquid condensate system. Radio frequency energy heats the soil above 150° C, vaporizing contaminants and moisture. The vapor barrier directs the off gases to an appropriate treatment system. Contaminant removal by this method exceeds 95% without the need to remove contaminated soil. The contaminants are recovered in a relatively concentrated form without dilution by air or combustion gases.

A groundwater treatment process was selected as the fourth case study. This technology uses supercritical fluids as solvents to extract organic solvents from waste water and contaminated sludges and soils. Carbon dioxide is the supercritical fluid solvent of choice for aqueous solutions. The process separates more than 99% of the organics from the waste feed. Following phase separation of the solvent, organics and treated water, the solvent is vaporized and reutilized as fresh solvent. The organics are drawn off from the separator and are either disposed of or reused.

The fifth case study involves the enzymatic decomposition of energetic materials. It applies to waste stream treatment and the bioremediation of soils contaminated with energetic materials, such as nitrate esters. Various enzymes, isolated from both plant and animal microorganisms, are applied to the energetic materials, decomposing them into innocuous products, such as carbon dioxide, water and ammonia. *Aspergillus fumigatus* is used to metabolize the nitrogen released during aqueous hydrolysis of nitrocellulose. A batch process is used to select the strain of the biodegrading microorganism, and bioreactors are employed to optimize and scale up the enzyme producing process. Once the process is optimized and scaled up, the resulting enzymatic decomposition can be applied to the bioremediation of soils, sediments, and settling ponds, as well as for management of waste streams generated from industrial production facilities.

These case studies have provided only a sampling of the many innovative, alternative technologies being considered to combat soil and groundwater pollution under the Department of Defense Environmental Security Technology Certification Program. These technologies hold great promise in restoring contaminated military sites and industrial properties in the United States as well as in Central and Eastern European countries. Through international collaboration in research, development and demonstration of innovative environmental technologies, cooperative programs can be developed to monitor, treat and prevent pollution common to our countries. Increasing global environmental awareness and increasing competition for funding make it essential that we avoid duplication of effort in addressing environmental challenges common to our respective governments. In the spirit of East/West cooperation born of the aftermath of the Cold War let us pursue efficient, cost-effective and improved solutions to shared environmental challenges under an umbrella of cooperative innovative technology programs.

IIc Risk Assessment and Legislation

Groundwater Protection

Lothaire Zilliox and Robert Mosé

Concern for the preservation and management control of the water resources in river valleys are dependent on sound knowledge of the biological, geochemical and hydraulic equilibria which determine the socio-economic future of the basin. The human activities pursued in the valleys and the adjoining plains obviously have important repercussions on these equilibria.

The multiplication of the risks associated with human developmental activities has caused pollution of the natural environment which is encountered both in surface waters as well as in soils (media active in the transfer of pollutants) and the waters of very vulnerable ground water (absence of impermeable protective layers, outcrops, exchanges with watercourses).

The delayed appearance - often by several years - of subsoil contamination like the filter concept imputed to the alluvial sediments are suggestive of a security which is only apparent as far as the actual protection of ground water is concerned. Consequently, it no longer suffices to consider the capacity of the soil and subsoil to transport a water flux but it is necessary to take into account the capacity of the soil covers and substrates (sediments) to select the elements (contaminants in suspension and/or solution) transported by the water, to disperse them, even to transform them or also to bind them.

The introduction of a water contaminant into a ground water may be the result of:

- direct discharges into a well, a gravel pit;
- «leaching» of a dump or disposal site by rainwater;
- spreading in soils and plant covers, followed by percolation downwards;
- infiltration from a watercourse feeding the ground water;
- leaks from reservoirs or buried pipelines.

When local accidental contamination occurs in each of these given situations, the conditions of heterogeneous circulation in the medium are usually not known and are difficult to account for quantitatively in most cases.

It is absolutely necessary that groundwater protection be preventive in nature at level of the hydrological basin. Prevention should be based on the vulnerability criteria grouped under the headings:

- natural hydrodynamic and hydrogeological characteristics,
- human, agricultural or industrial environment,
- nature and mode of operation of water extraction works.

From this point of view it is useful to recall **the situation of an alluvial ground water in an interactive environment** :

- **Between rivers** at the surface and the underground **water** exchanges occur which vary in quantity depending on the area, the season, the hydraulicity of the rivers and the relative positions of the groundwater surface and the bed of the watercourse.
- **The sediments in contact with the ground water are not inert** to the passage of pollutants. Thus the sediments of the watercourses and the fine particles (clays and silts) of the aquifer react with toxic contaminants such as traces of heavy metals or pesticides. Laboratory experiments have shown that under certain conditions (for example a change in the water composition) a micropollutant such as mercury can be remobilized after being bound and transported by the water with the attendant risk of reaching a drinking water catchment site downstream.

Hence it appears that the sediments are able to store micro-pollutants (which is fortunate for groundwater protection) up to a certain threshold (most often unknown) but that other elements which alter the composition of the water can cause the accumulated substances to be displaced from these sediments which then pollute the ground water.

This emphasizes the importance of the prevention of both urban(1) and industrial discharges and the use of certain products in agriculture (nitrogenous fertilizers, pesticides,..).

- **What distinguishes the problems of pollution** of underground water from those of surface waters is, in the first instance, the time scale. In the case of a river in which the speed of flow of the water is of the order of km/hour, the time for the replacement of the volume contained in its bed is, on average, a few days, maximally a few weeks.

In the aquifer where the underground water circulates at speeds of the order of km/year, the indicator for the time of replacement of the volume contained in the reservoir is expressed in decades, even in centuries.

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(1) The «domestic» part of the pollution which results from the growth of towns and the concentration of zones of suburban development, both unplanned and even chaotic, is surely an indicator of our collective and individual negligence.

As a result of its rapid flow, the pollution of a watercourse (the effects of which are most often visible) is likely to be rapidly detected. On the other hand, the detection of the pollution of underground water (circulating very slowly and almost invisibly) may be delayed for several years or more. It thus follows that the «reaction times» are of the same order for cleaning up the pollution.

After stopping the pollution at source and implementing cleaning up procedures, the original quality of the river water will be regenerated after a relatively short delay.

To reduce the pollution in the aquifer reservoir will require decades. In extreme cases the situation may even become irreversible. This observation emphasizes the paramount need to protect the underground water resources and to pay attention right from the start to any deterioration in their quality, how ever slight !

In order to devise adequate protection strategies, use should be made of projections using models in accordance with an iterative process which integrates step-wise :

- questions asked by water management
- on-site experimental research
- possibilities of numerical and mathematical solutions
- the adequacy of technical management and economic choice.

Of undoubted economic value in agricultural and industrial development, the quality of ground water must be guaranteed against human activities which might inflict harm on the functioning of the ecosystems and on the life of populations in the medium and long term.

Among the threats which **adversely affect** underground waters (in addition to the known contamination due to chlorides, nitrates and sulfates) the use of pesticides, the exploitation of alluvial deposits and the isolation of the underground water compartment should be mentioned. *A* **growing danger** is taking shape to-day in the form of multiple «Altlasten» (also called historic dumps): these are residues and wastes buried long ago and whose effects are gradually becoming apparent and dangerously affecting the quality of the water catchment areas !

This situation - revealed in all industrialized countries by negative effects on the quality of drinking water and on the cost of its preparation - should to act as an incentive to increase the concerted actions of scientists, managers and decision makers with regard to the conservation of water quality in an economic context where the management of waters can no longer be dissociated from town and country planning (land management is an essential point).

As regards the characterization of transfer sites of pollutants towards the ground water, a distinction should be made between two types of «biogeochemical barriers» (potential screens being the subject of much scientific research);

- either dry (at the surface) or inundated soils, with or without plant cover, presenting very varied water conditions,
- or sediments, deposits obstructing watercourses, ponds, gravel pits,... in a state of maximal water saturation.

The present state of knowledge as to their *in situ* structure and their role as active media in the transfer of pollutants is still inadequate.

In order to make underground water a priority source of supply for the most demanding uses and to guarantee its quality in its «natural reservoir», it will be very important to **pay particular attention to the preferential supply areas of the ground water** (areas liable to flooding, alluvial cones in rivers, canals,...) and to devise strategies of preventive protection in particular by means of projections using models. A scientific approach using (on different scales) computer-controlled experimental physical models should make it possible by dynamic simulation to provide partial answers regarding:

- the spreading mechanism of various pollutants which should lead to an improvement in the efficiency of the measures of intervention and clean-up;
- the main parameters governing the spreading of the pollutant, parameters which need to be assessed on-site;
- the validity of the theoretical models presently available and their applicability.

Modeling, considered as that «art» which usually requires the isolation of as independent a part as possible of reality and the selection of only the essential processes and magnitudes by the choice of a space-time scale, indeed implies a «construction» both sufficiently complex to take into account a maximum of facts and simple enough to be able to be treated «mathematically»; the operation results in fact in calculations whose «economic cost» should not be neglected, either in the case of a deterministic mathematical model or in that of a stochastic model.

That ultimately the criterion of a good model is an optimization criterion in regard to the desired objective is to-day a notion widely shared. But when the essential problem of the adequacy of the model to represent correctly the actual situation which it is supposed to represent is examined, opinions very often diverge

It is for this reason that thinking and attitudes in relation to «aims and realities», «constraints and uncertainties» and «needs and limits» of modeling begin to evolve, irrespective of whether the construction approach is «physical-explanatory» (starting from experiments) or «mathematical-predictive» (resulting in calculations).

Both types of modeling may be implicated in one and the same problem. Actual or simulated experiments should lead to results. The comparison of the two types of data should reveal the validity of the models (the numerical simulations complement the experimental measurements).

Thus «thought about and managed», the modeling should be useful for the two reasons:

- as an aid to the researcher to «reason» about the phenomena as interdisciplinary agent and to «construct» a «finalized» projection compatible with the reality (even if it lacks properties judged to be irrelevant as a function of the choice of objectives, levels of observation or also of constraints on the means : availability of data, the exhaustiveness of the calculations...);
- as an aid to the decision maker by making available a practical tool designed, depending on the case, to reveal the mechanisms of change in a given case of pollution, to take measures to control the pollution or also to consider the town and country planning and the management of natural resources (including water and soils in particular) by minimizing the risks of pollution.

Finally doesn't the «useful model» go hand in hand with a «hierarchical representation» of the components of pollutant transfer and their analysis: the construction of a hierarchy of mechanisms, a hierarchy of methods but a hierarchy also as a function of management and questions to be answered?

Crucial Needs for Environmental Risk Assessment (ChemRisk®)

Remediation as Good as Possible, but Only as far as Really Necessary

André Bachmann

Summary

In view of the high number of contaminated sites with immense potential risks for man and the environment, a special method for the chemical risk assessment, ChemRisk®, is presented, which can be applied to technically support the actions needed and to clearly derive their priorities within an economically feasible frame. Its goal is to achieve an optimal effect to protect human health as well as the ecosystem as a whole with the financial means available. The aim is to show how with this process a substantial portion of the remediation costs can be saved without negative effects on human health or the environment.

1. Introduction

The constantly increasing requirements for the protection and the preservation of our environment as well as for the averting of human risks in view of immense environmental contaminations from accidents and spills, war effects, the irresponsible handling of dangerous materials, or environmental sins due to lack of knowledge, urgently need a scientifically based and economically acceptable process for the assessment and remediation of contaminations and other environmental damage.

Alone for the new German states it is estimated that over 200 billion DM are necessary to reach the environmental quality standard of West Germany. Approximately one fourth of all East German industrial sites are suspected of having ecological contaminations, of these about every eighth suspected site requires quick action.

For the economically feasible accomplishment of these huge tasks, ChemRisk® - a special type of chemical risk assessment - is an appropriate instrument that has been continually further developed on a scientific basis during the past years. In all cases, be they small or large, simple or complex, highly hazardous to the environment or less hazardous, the optimal solution should be found through an assessment that aims at minimizing the impairment of the entire ecosystem. The solution should be environmentally compatible, be technically and technologically optimal, be acceptable to the public, and, mainly, be financially feasible.

ChemRisk® provides an objective and well-balanced interpretation of all scientific and technical information in view of possible environmental risks. It answers the question of how clean a site really should be to be accepted as «clean»; and it provides the chance to remediate contaminated sites in an economically feasible manner.

2. Methodology of ChemRisk®

It is the aim of the assessment of contaminations to investigate objectively and according to scientific-technical standards the risks for man and the environment caused by the contaminants. Based on this evaluation, a decision can be made as to whether a site needs to be remediated and how much residual contamination may remain on the site after the remediation.

ChemRisk® is not a fixed model, but a logical and transparent process from the scientific-technical point of view, which can be adapted to each case. Since the remediation of contaminations includes a variety of problems, different specialists from the areas of environmental chemistry, toxicology, soil sciences, engineering, etc. are needed for the application of ChemRisk®.

The methodic frame here presented is based on experiences in the USA and further developed in various applications in Switzerland, Germany, Spain, and the Ukraine. Especially for the requirements of soil remediation the following four elements of the chemical risk assessment are important :

1. **Hazard Identification**
   Identification of the contaminants present (type, form, quantity, distribution) and assessment of the hazard potential of these materials
2. **Toxicological Assessment of the Contaminants**
   Assessment of the contaminants present regarding their toxicological characteristics for the various assimilation pathways (oral, dermal, inhalatory) and their dose-response relationship
3. **Exposure Assessment**
   Quantitative evaluation of the contaminant dose observed or expected under the given conditions.
4. **Risk Characterization**
   Description of the expected health hazards due to exposure, assessment of the maximum permissible exposure for the contaminants present, and definition of remediative goals (how clean is clean?)

The **first step** comprises mainly a compilation of the data available from investigations of contaminations and from the literature regarding the contaminants present, as well as their physical, chemical, and toxicological properties. The contaminants relevant in each case are identified based on the quantities and concentrations found, their toxicity and their environmental behaviour.

In a **second step** the relevant contaminants are subjected to a more detailed toxicological study. The toxicological effects for the various assimilation pathways are assessed. Depending on the contaminant and its effect (acute toxicity, chronic toxicity, cancerogenity, etc.) the adverse effect in relation to the assimilated dose can be evaluated. It is of special importance that, for example, there is no lower dose (the so-called threshold value) for carcinogenic products for which no effects are expected. For these materials it is often necessary to extrapolate data from animal tests to assess a dose-response relationship. For all other contaminants a threshold value can be derived.

The exposure assessment poses the following question in the **third step**: «Which human exposure is observed at the time or is expected under the existing conditions ?» The on-site contaminant behaviour is of central importance here. Based on literature data or in own laboratory tests every contaminant is assessed regarding its movement (outgasing, wash-out, plant uptake, etc.) and fate (degradation, redox reaction, etc.). With the help of movement and fate pathways (e.g. soil - ground water - drinking water - man) the concentrations of each contaminant are assessed, which are expected at the various exposure sites (e.g. drinking water pumping station). Depending on the case, contaminant transport models are used to assess the movement of contaminants for various media (soil, air, water). Subsequently, the contaminant assimilation for an exposed person, for example through consumption of drinking water, can be assessed. In many cases exposure is composed of various assimilation pathways (eating, drinking, breathing, dermal contact). Figure 1 shows a hypothetical example of the exposure assessment for the drinking water pathway.

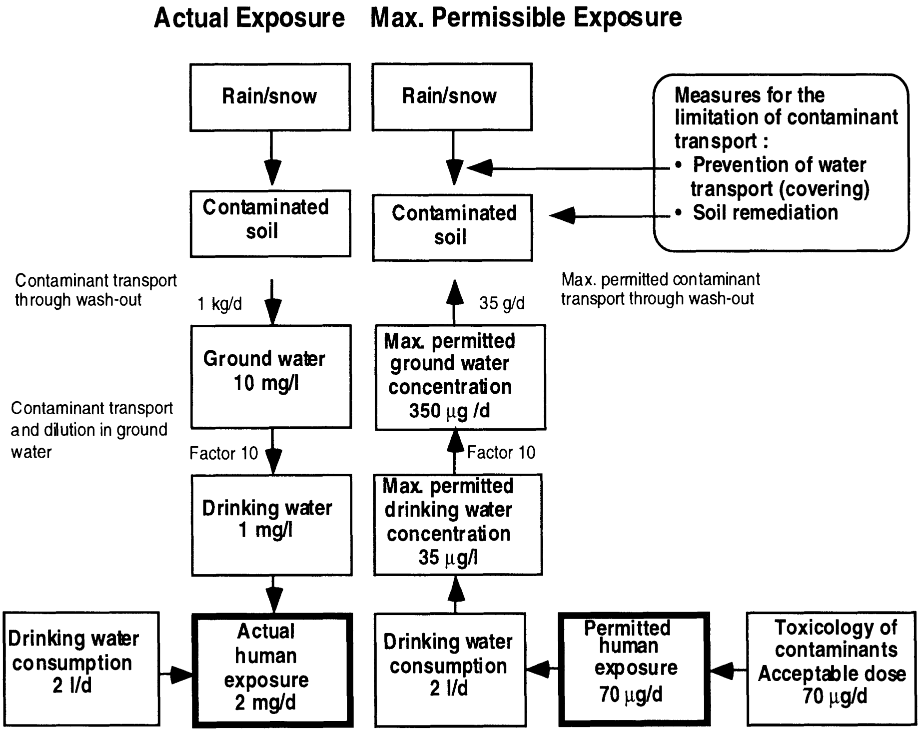

Figure 1

Example of a simplified exposure analysis with ChemRisk® for the movement pathway soil - ground water - drinking water. The actual exposure (left) is compared with the permissible exposure (right) based on toxicological data. Using the permitted exposure, the remediation goal can be calculated backwards (maximum movement 35 grammes per day). (Example for a person with a body weight of 70 kg).

In many cases the hazard can be located in a single movement pathway (e.g. soil - soil gas - indoor air). Figure 1 shows in a simplified way the human exposure to contaminants in soil through drinking water. The actual exposure is compared with the maximum permissible exposure based on the daily consumption of drinking water. Since the actual exposure is higher than the tolerable value, action is needed. In this hypothetical example, it is possible, by calculating backwards, to assess the maximum tolerable movement of contaminants from the soil into the ground water of 35 grammes per day. Which technical measures will permit a reduction of the emissions and therefore remove the human hazard is the concern of the subsequent remediative investigation.

The **fourth and last step** aims at assessing and describing the hazards. Based on all data and calculations an assessment is made of the actual hazards to man and the environment at present and in the future. This means that for each contaminant as well as for the totality of contaminants the expected assimilation of contaminants is compared with the maximum tolerable dose, and their possible effects are evaluated. Based on the tolerable dose, standards for the permissible assimilation of each single contaminant can be defined. In this way it is known for each relevant contaminant in which concentration it may appear at the site of exposure (e.g. drinking water pumping station), without posing a hazard to the health of exposed persons.

Then, the maximum permissible concentrations are compared with the existing regulatory standards and critically assessed. Many standards in the area of drinking water, for example, often are not toxicologically-based maximum concentrations but rather preventive values. The existing preventive values sometimes are not based on single compounds but contain a more or less clearly defined group of substances (e.g. phenol index). There are preventive values only for few organic contaminants, therefore there are no applicable values for many contaminated sites (e.g. chemical plants) for the relevant contaminants (e.g. nitroaromatics, aromatic amines, etc.). For these substances it is possible to define the corresponding toxicologically based values with the help of ChemRisk®. Therefore, it is necessary to evaluate, together with the authorities, whether in certain cases the preventive values, as for example for ground water, are applicable or whether, - based on the contaminant palette -, the corresponding values should be defined. Especially by less sensitive uses (e.g. within industrial zones) an application of preventive values is not appropriate.

3. Practical Process

The application of ChemRisk® in the total process of contamination assessments and remediations is shown in Figure 2 and will now be explained. The entire contamination investigation is planned based on ChemRisk®. The assessor of the contamination needs to know which information he will need for the risk assessment before he can start with the investigation. If during the risk assessment it becomes obvious that data are lacking, additional costs and delays are preprogrammed for the client. In real life, unfortunately, it happens often that contaminated sites are tackled by a contamination processor who does not realize which questions will need to be answered at a later time. He then has a task of assessing a hazard based on borings and analyses data without being able to figure out the contaminant behaviour and the contaminant transport.

When ChemRisk® is included in the planning phase, the availability of important data is secured and, if need be, other data can be determined without major trouble (e.g. storage of specially preserved or processed samples). The additional financial expense for this professional procedure usually helps save a multiple of the required extra expense of the investigation in view of remediative or corrective measures. Figure 2 shows a comparison between the traditional and the professional process with ChemRisk® and the resulting total costs of remediation.

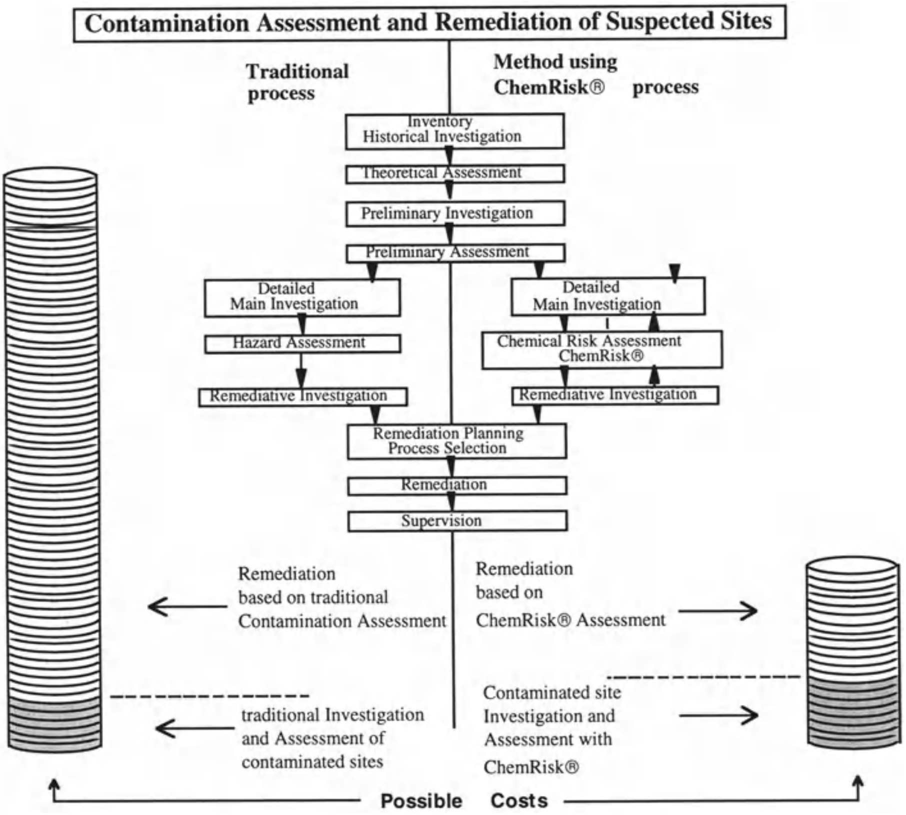

Figure 2
Comparison of the process flow and the possible costs of the assessment and remediation of contaminations at suspected sites according to the traditional method and with the use of ChemRisk®.

As opposed to the traditional hazard assessment, it is the goal of ChemRisk® to assess the actual hazard potential for man and the environment.
Our laws only contain reference values for the contamination of soil and subsoil but no defined standards. This may not be considered a gap. It would be an extremely complex task, probably even wishful thinking, to believe that it will be possible some day to assess the potential environmental hazard of a contaminated site with the help of a handy table.

The requirements of the data base are considerably higher for ChemRisk® than for a traditional hazard assessment. The financial costs are therefore higher for the main investigation. It is especially necessary for ChemRisk® to have a solid data base regarding the local behaviour and transport of the contaminants. Important fundamentals are :

- **Local geological and hydrogeological properties**
  e.g. soil structure, soil chemistry, groundwater flows, etc.
- **Contaminant characterization**
  e.g. specification of the metals : Cr, Hg, As, Zn, etc.
- **Partitioning of chemicals**
  e.g. adsorption on soil matrix : metals, dioxins, PAHs, etc.
- **Fate of chemicals**
  e.g. time for biological degradation or chemical transformation : reduction of chromium-VI to chromium-III
- **Movement and transport of chemicals**
  e.g. calculation of the time needed for benzo(a)pyren movement from soil into ground water

Only when the chemical behaviour is sufficiently known, is it possible to assess the present and future exposure of man and the environment, as shown in point 2, and to derive the health hazards. As an example we will here use the mobility of contaminants in subsoil. Many sites of electroplating companies have been assessed based on the total contents of chromium without considering the mobility of the chromium compounds present (differenciation between chromium-III and chromium-VI). Chromium-III is hardly mobile and relatively little toxic, while chromium-VI is very mobile and much more relevant from the toxicological point of view. This means that specifying the chromium is more complex that the assessment of the total contents. When the entire chromium contamination consists of the relatively harmless form chromium-III, maybe no hazard exists and therefore no remediative measures are needed.

4. Remediative Investigation and Remediative Planning With ChemRisk®

The remediative investigation aims at evaluation measures with which the hazards for humans and animals can be eliminated. Depending on the use, there are various possibilities for the reduction of hazards :

- Remediative measures (e.g. soil and/or groundwater remediation)
- Securing measures (e.g. superficial covering)
- Use limitations (e.g. agricultural use of top soil)

This shows that the reduction of hazards from contaminated sites does not have one simple solution, but that various combinations must be evaluated. The movement of contaminants into ground water, as shown in *Figure 1* for example, can be limited by soil remediation, a superficial covering as protection from rain, or by a combination of the two. The extent of soil remediation, the remediative values for soil, water and air or the permeability of the covering are calculated based on the above described environmental behaviour and transport of the contaminants with ChemRisk®. As can be seen, the application of ChemRisk® is not limited to the chemical risk assessment but it is also a means for the remediation planning.

ChemRisk® offers the possibility of planning optimally the costs of a remediation without reducing the safety of man and the environment.

5. Cost-benefit Assessment

An objective, scientific-technically based chemical risk assessment must guarantee that no contaminated or suspected sites are remediated unnecessarily, but also that the client will not have post-treatment liabilities from insufficient remediations.

The experiences with the application of this method have shown that the increased expenses for the chemical risk assessment, e.g. through the use of ChemRisk®, save a multiple of these costs in the remediation or other protective measures without reducing the safety of man and the environment. The *Table* shows selected projects where ChemRisk® was used.

Table: Costs Savings Through Application of ChemRisk® in Selected Projects

Selected Projects	**Cost Savings** millions DM	**Cost of ChemRisk®** millions DM
chemical risk assessment and remediation concept for an industrial site	800	2.5
remediation of a contaminated site	150	2.5
environmental assessment for property transaction	80	0.08
disposal of 1,000 tons of contaminated asphalt	1.8	0.09
remediation of an industrial site	4	0.08
backfilling of 80,000 tons of contaminated soil	7	0.04

6. Conclusions

The special method of chemical risk assessment, ChemRisk®, has proven to be a very practical method with a good theoretical foundation and ease of practical application to place the remediation of contaminated sites under the present conditions on a cost-effective ground. It permits solutions which fulfill the following criteria :

- ecologically sound
- technically and technologically optimal
- politically acceptable
- economically feasible.

ChemRisk® differentiates itself essentially from the traditional processes for the assessment of risks from contaminated sites through:

- the description of the complex interactions of the different contaminants with the media in question (soil, water, air). The client disposes of a rich interdisciplinary know-how and extensive experience;
- specific partial remediation corresponding to the biological, chemical, hydro-geological, and toxicological overall situation;
- use of laboratory scale pilot tests to optimize the remediative processes and minimize costs;
- consequent integration of the future use of a site for the definition of remediation goals.

The ChemRisk® method is not a standard process, but a specific way of thinking and acting, which in most cases saves considerable costs in the remediation of contaminated sites. [1]

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1)The Chemical Risk Assessment was developed by the Food and Drug Administration, but only for «food additives». General applications concerning the environment were initiated by the «Paradigm of the National Academy of Science: Risk Assessment in the federal government, National Adacemy Press, 1983». D. Paustenbach (ChemRisk® /McLaren/Hart) has been a pioneer in its application to hazardous waste sites. The first serious and published application regarding contaminated sites was the case Times Beach, by R. Kimborough et al., J. Toxicol. Environ. Health *14*, 47-93, 1984. ChemRisk® is used and accepted by EPA. MBT Environmental Europe adapted it to meet European needs. Related Literature: D. Paustenbach (ed.): The Risk Assessment of Environmental Hazards (a Textbook of Case Studies, John Wiley & Sons 1989, 1155 pp.

Assessment of Ecological Risks of Soil and Groundwater Pollution

Jos Notenboom

Introduction

This paper deals with the impact of pollution on the ecological properties of soil and ground water and the assessment of risks. Ecological risk assessment is a tool to structure and compile scientific information for environmental management in order to identify problems, establish priorities, and provide a basis for regulatory actions. After introducing some fundamentals of ecological risk assessment the derivation of soil quality criteria and the risks for groundwater ecosystems is emphasized.

Ecological Risk Assessment

Ecological risk assessment evaluates ecological effects caused by human activities, like the release of chemicals, habitat destruction, draining of wetlands, etc. The term «stressor» is applied to describe any chemical, physical, or biological entity that can induce adverse effects on individuals, populations, communities, or ecosystems. Contrary to human health assessment ecological risk assessment **can** consider effects beyond those on individuals of a single species and may examine a population, community, or entire ecosystems. Another peculiarity of ecological risk assessment is that there is no single set of ecological values to be protected that can be generally applied. Mostly ecological effects cannot be related to one single stressor and there is an increasing awareness that chemical stressors and nonchemical stressors should be considered in combination.

Ecological risk assessment consists of several steps. After problem formulation and establishing goals, breadth, and focus of the assessment, the analysis phase should focus on exposure profiles and effects of the stressor on identified ecological receptors. Next risk characterization integrates exposure and effect profiles. Ecological risk analysis can be performed at several hierarchical levels and risks can be expressed as a qualitative or quantitative estimate, depending on the available data. Risks should be discussed also in relation to ecological significance and uncertainty. Recently several documents appeared thoroughly treating the fundamentals of ecological risk assessment and its application in environmental management (US-EPA, 1992; Suter, 1993). For assessment of contaminated sites and establishing remediation objectives in Canada the concept was elaborated by EVS (1992).

Considering chemical stressors the distinction should be made between the assessment of potential risks of new and existing chemicals, and actual risks of contaminated sites. Potential risk assessment results in a ranking of relative risks of situations or substances. Such analyses are mostly based solely on laboratory toxicity data and some general assumptions how this information can be extrapolated to ecosystem protection levels. For the assessment of actual risks well defined ecological endpoints are necessary and the analysis of exposure and effect profiles need location specific input data.

Exposure Assessment

Exposure analysis evaluates the interaction of the stressor with the ecological component. An exposure profile quantifies the magnitude and spatial and temporal distributions of exposure within the formulated problem of the risk analysis. For chemical stressors fate and transport models often are used that rely on physical and chemical characteristics of the chemical coupled with the characteristics of the ecosystem. Such models could be combined with monitoring data.

Particularly in the terrestrial environment exposure assessment should be preceded by the determination of significant routes of exposure (inhalation, food uptake, soil/litter contact, pore-water uptake). Between these routes pollutant fate and transport, and ecological receptors may differ considerably. A key concept is that of bioavailability, that part of the contaminant that is available for uptake and could interact with biological processes.

For soil dwelling biota the most common simplification of bioavailability is that organisms are significantly exposed only to chemicals dissolved in the pore water. Partition models are used to calculate the relevant pore water concentrations. For lipophilic organic compounds it is often assumed that pore water concentrations are a function of the organic matter content of the soil or sediment (van Gestel & Ma, 1988). Many aquifers are poor in organic matter and sorption to organic particles plays probably a less important role in bioavailability than in soils.

Effect Assessment

During ecological response analysis, the relationship between the stressor and the magnitude of ecological effects invoked is quantified, and cause-and-effect relationships are evaluated. In addition, extrapolations from measurement endpoints to assessment endpoints are conducted. The result of the analysis is a stressor-response profile which is used as input to risk characterization. Direct measurements of the assessment endpoints are often not possible and extrapolations should therefore be made from measured endpoints, which are mostly data derived from laboratory experiments. Extrapolations commonly used include those between species, between responses, between hierarchical levels, and from laboratory to field. When extrapolating between different laboratory and field settings, important considerations include differences in the physical environment and organism behavior that will alter exposure, interactions with other stressors, and interaction with other ecological components.

Toxic chemicals affect organisms before their impact is manifested at population, community, or ecosystem level. For extrapolations to population level a proper understanding of sublethal (growth, reproduction) effects after long-term exposure, the relative sensitivity of different life-stages, and population dynamics is necessary. In extrapolations to community and ecosystem levels considerations should be made on interspecies interactions (e.g., competition), trophic-level relationships (e.g., predation), resource utilization, and spatial scales of stressors and receptors. Ecological recovery is an important aspect in the evaluation of the impact of pollution on ecosystem level. However, it is difficult to predict and depends on the existence of a nearby source of organisms, life history and dispersal strategies of the organisms, and the physical environmental quality following exposure to the stressor (van Straalen, 1993).

Risk Characterization

During risk characterization the likelihood of adverse effects occurring as a result of exposure to a stressor is evaluated. Although several integration approaches are possible comparison of single effect and (predicted or measured) environmental concentration is the one most commonly applied. Others are the comparison of distributions of effects and exposure and the application of simulation modeling. The method chosen strongly depends on the situation the risk analysis is applied for. For the screening of potential risks of new chemical substances a simple exposure-effect comparison is often considered sufficient, while the estimation of risks of environmental pollution for an endangered species need more sophisticated population modeling and the integration of various stressors.

As risk estimate for chemical stressors commonly the quotient of the exposure value and the effect value is used. If this quotient is ≥1 an adverse effect is likely to occur (Barnthouse *et al.*, 1986). Uncertainties are usually accounted for by using safety factors to adjust effect values. Although commonly used and accepted, particularly for assessing potential risks, the quotient method is the least probalistic method. Greater insight into the magnitude of the effects expected at various levels of exposure can be obtained by evaluating the full stressor-response curve instead of a single point and by considering the frequency, timing, and duration of the exposure.

Uncertainties in the assessment may be due to uncertainties in the exposure and effect component and result from stochasticity (natural variability), error, or ignorance (Suter, 1993). Uncertainties related to ignorance can be reduced by application of current methodologies (operational uncertainties). This is not possible when uncertainties are related to fundamental problems. Considering the problem of extrapolating soil ecotoxicity data to derive soil quality criteria van Straalen (1993) distinguished fundamental uncertainties related to: genetic variation and adaptation to stress factors, potential for ecological recovery, combination effects of chemical mixtures, and the modulation of toxicity by environmental factors. In these fields actual scientific knowledge is insufficient to reduce uncertainties.

Soil Quality Criteria

In the Netherlands soil quality criteria are derived from generally established risk levels for man and ecosystem. For ecosystems no specific targets are distinguished in order to derive risk values (concentration of a chemical in the environment). The assessment is based on the general assumption that when the structure of an ecosystem (abundance and diversity of species) is protected also its functions are safeguarded. This implies that ecological risks increase when the number of species which is affected by toxic substances increases.

For the derivation of ecological risk levels the method proposed by van Straalen and Denneman (1989) is used for refined risk assessment. As input for this extrapolation method laboratory toxicity data is taken, preferably NOEC-values (No Observed Effect Concentration, the highest concentration tested which caused no significant negative effect on the tested species). The method estimates a log-logistic relation between contaminant concentration and the percentage of protected species. The 5 and 50 percentiles of this distribution are taken as risk levels. This is mainly a political choice. The serious contamination risk concentration (SCC) is the concentration of a toxic chemical not affecting more than 50 % of the species, the maximum permissible risk concentration (MPC) does not affect more than 5 % of the species (Denneman, 1993).

The method is adjusted when microbial ecotoxicological process parameters appear more sensitive than structural parameters, when indications exist that rare or endangered species are not sufficiently protected, and when bioaccumulation and biomagnification may cause serious risks for species higher in food-chains. Since soil characteristics have influence on the bioavailability of toxicants risk concentrations are related to organic matter and clay content of the soil (Denneman, 1993).

Operational uncertainties of this method are associated with the structural lack of sufficient terrestrial ecotoxicity data, selection of appropriate input data, correction methods for soil properties (e.g., clay, organic matter), lack of data on actual risk levels, and relevance of laboratory data for field situations. Fundamental uncertainties have to do with the question if the function of an ecosystem is sufficiently protected when its structure is maintained, and insufficient knowledge about effects of combinations of stressors, and the incomplete understanding of the impact of soil properties on bioavailability.

Risks for Groundwater Ecosystems

Groundwater reservoirs are not only transport and storage systems but they are ecological systems as well. Energy and carbon sources of these ecosystems are the organic matter deposited during sediment genesis, and the organic substances leaching and infiltrating from soils and surface waters into aquifers. The quality and quantity of organic matter coming from soils and surface waters depend on natural factors and may be influenced also by anthropogenic activities. Zones of enhanced bioactivity in the subsurface environment are the transitional zones between soil/ground water and surface water/ground water (Stanford & Simons, 1992).

Subsurface microorganisms are able to metabolize organic substrates and on their turn serve as a resource for higher organisms. Groundwater organisms have developed innovative biological solutions as a response to the strong selective pressure imposed by the oligotrophic and hypoxic nature of their environment. Groundwater ecosystems are worth to protect because their unique biological diversity and the ability of biological degradation of natural and xenobiotic substances.

Groundwater ecology is a very young subdiscipline of ecology. Information on structure and functioning of groundwater communities is just limited available and still of incidental nature. Information on the impact of pollution on groundwater communities is scarce and ecological considerations play hardly any significant role in management decisions concerning groundwater quantity and quality.

The last five years, however, interest in this field is growing. Illustrative is the fact that US-EPA in collaboration with other US organizations has organized international groundwater ecology conferences in 1992 and 1994 (Stanford & Simons, 1992). A strategic plan for groundwater ecology within US-EPA is actually in discussion and the appearance of the first scientific textbook on groundwater ecology is foreseen in 1994 (Gibert *et al.,* in press).

The groundwater environment is threatened at different ways. Overexploitation may cause water table lowering and in coastal areas the intrusion of marine waters. Groundwater contamination originates from point or diffuse sources and is in general preceded by soil, surface water, or sediment pollution. With respect to the possible impact on groundwater ecosystems three categories of pollutants are distinguished: inorganic and organic toxic substances, nitrogen and phosphorous compounds (nutrients), and organic matter from sewage, manure, etc. Relatively best investigated is the impact of organic matter on aquifer communities.

A simple risk based approach applied for deriving environmentally safe concentrations of pesticides in ground water shows for some compounds risk values lower than actual drinking water EC directives (0.1 µg/l). This suggests that drinking water standards alone do not guarantee full protection of the ecological integrity of ground water. Little difference seems to exist in acute toxicity of selected substances between surface water and groundwater organisms. So, this provides the opportunity to base preliminary risk estimates for groundwater ecosystems on the vast amount of aquatic toxicity data. Theoretically, however, there are good reasons to assume that populations of ground water adapted organisms and their communities are much more vulnerable for environmental pollution than their acute sensitivity for toxicants might suggest (Notenboom, *et al.* in press). Moreover, recovery after pollution is probably much more difficult in ground water (patchy resources, low migration potential) than in surface ecosystems.

Fundamental uncertainties in estimating ecological risks of groundwater pollutants are important. Basic information on the occurrence, environmental requirements, functioning, food-web interactions, and ecotoxicology of groundwater biota is very scarce. When such information becomes available, a general framework for biomonitoring and assessment of ecological risks of groundwater contamination may emerge.

Conclusions

Ecological risk analysis forms a well established and useful instrument to integrate ecological and environmental information as a basis for management decisions. The concept includes all levels of biological hierarchy and complexity. When applied to soil pollution problems mostly a rather narrow interpretation of the concept is used consisting of a simple comparison of single effect value and environmental concentration. This approach seems successful for establishing general environmental quality criteria on the basis of an assessment of potential risks of situations and substances (e.g., Dutch clean-up criteria; van den Berg *et al.*, 1993).

For the assessment of actual risks of contaminated sites more sophisticated methods and site-specific environmental information are necessary. Moreover, actual risk assessment should be coupled with well defined ecological assessment endpoints. Fundamental uncertainties, dealing with the bioavailability of pollutants, combinations of stressors, and ecological responses at higher level of complexity make that explicit quantitative risk measures are hardly achievable yet.

The impact of pollution on structural and functional ecological properties of groundwater aquifers is hardly recognized in environmental sciences and policy as a serious problem. However, the conviction is growing that groundwater ecology should play a role in groundwater management when sustainability is a goal (1992 and 1994 International Groundwater Ecology Conferences; Stanford & Simons, 1992). Groundwater ecology in this context widely interpreted as the ecology of phreatic, deep and karst aquifers, and of terrestrial systems closely hydrologically connected to ground water, e.g., wetlands. The framework of ecological risk assessment seems appropriate to integrate ecology, hydrology, environmental chemistry for this goal.

For assessing the ecological risks of groundwater pollutants a step-wise approach is proposed. Starting with a preliminary assessment, based assumptions derived from aquatic ecotoxicology and applying safety factors. Working to a refined assessment which incorporates information on specific adaptations of groundwater organisms and communities to their environment and integrates information on fate and transport (models) of pollutants in ground water.

References

Barnthouse, L.W., G.W. Suter II, S.M. Bartell, J.J. Beauchamp, R.H. Gardner, E. Linder, R.V. O'Neill & A.E. Rosen, 1986. User's manual for ecological risk assessment. Publication no. 2679, ORNL-6251. Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Denneman, C., 1993. What is ecological risk? Risk based environmental quality objectives-Proc. National Conference on Ecological Risk Asessment from Theory to Practice. October 6,7 & 8, 1993. World Congress Centre, Melbourne, Victoria, Australia.

EVS, 1992. A framework for ecological risk assessment at contaminated sites in Canada. Report for Environment Canada, prepared by EVS Consultants, North Vancouver. EVS project no. 3/047-37.

Gibert. J., J., D.L. Danielopol & J. Stanford, in press. «Groundwater Ecology». Academic Press.

Notenboom. J., S. Plénet & M.-J. Turquin, in press. Groundwater contamination and its impact on groundwater animals and ecosystems. In: Gibert. J., J., D.L. Danielopol & J. Stanford (eds.). Groundwater Ecology. Academic Press.

Stanford, J. A., & J.J. Simons, 1992. «Proceedings of the First International Conference on Ground Water Ecology». American Water Resources Association, Bethesda, Maryland.

Suter, G.W., 1993. «Ecological risk assessment». Lewis Publishers, Boca Raton etc.

US-EPA, 1992. Framework for ecological risk assessment. Risk Assessment Forum U.S. Environmental Protection Agency, Washington. EPA/630/R-92/001.

van den Berg, R., C.A.J. Denneman & J.M. Roels, 1993. Risk assessment of contaminated soil: proposals for adjusted, toxicologically based Dutch clean-up criteria. In: F. Arendt, G.J. Annokkée, R. Bosman & W.J. van den Brink (eds.). Contaminated Soil '93, Berlin. Kluwer Academic Press.

van Gestel, C.A.M. & W.-Ch. Ma, 1988. Toxicity and bioaccumulation of chlorophenols in earthworms, in relation to bioavailability in soil. Ecotox. Environ. Safety 15: 289-297.

van Straalen, N.M., 1993. Open problems in the derivation of soil quality criteria from ecotoxicity experiments. In: F. Arendt, G.J. Annokkée, R. Bosman & W.J. van den Brink (eds.). Contaminated Soil '93, Berlin. Kluwer Academic Press.

van Straalen, N.M. & C.A.J. Denneman, 1989. Ecotoxicological evaluation of soil quality criteria. Ecotox. Environ. Safety 18: 241-251.

Soil Protection Concept of the Council of Europe

Winfried E.H. Blum

Based on an enlarged concept of soil, including also porous sediments and other permeable rock materials, together with underground water which these contain, the competitive use of the six main functions of soil are identified as the main problem of soil protection.

Three of these functions can be defined as ecological ones, three others are rather linked to human activities.

The three ecological functions are:

- Biomass production
- Filtering-, buffering and transforming action for the protection of the environment in general and the ground water and the food chain from pollution.
- Soil as a biological habitat and gene reserve. The three functions directly linked to human activities are: Soil as a spatial base for technical and industrial structures and socio-economic activities, e.g. housing construction, industrial development, transport systems as well as space for sports, recreation activities and dumping of refuse, and others. - Soil as a source of raw materials, supplying water, clays, sand, gravel, minerals, and others. - Soil as part of landscapes and cultural heritage, forming part of our environment and cultural development, concealing palaeontological and archeological treasures as a testimony to the history of earth and mankind.

Between these six main functions, three different types of intensive competition exist:

- exclusive competition between ecological and socio-economic or industrial functions;
- competition through intensive influences in the form of heavy loads from the functions directly linked to human activities and the ecological functions, e.g. pollution of soils from industrial production, traffic and others;
- competition between the ecological functions themselves.

Therefore, sustainable land use as a base of soil protection can be defined as a spatial, local and/or regional harmonization of all six soil uses, avoiding or minimizing irreversible ones.

Looking into the actual status of soil degradation three main passways can be distinguished: diffuse influences of atmospheric origin, influences by aquatic transport and specific influences of terrestrial origin.

A classification of problems in order of urgency allows to distinguish between irreversible and reversible damages, based on a time concept which defines impacts and/or damages, without possibility of repair within a hundred years (three human generations) as irreversible, those which can be repaired or healed by nature itself in a shorter time as reversible.

On such a base, a concept of soil protection and remediation was developed, distinguishing between the definition of the main goals, e.g. minimization of irreversible soil losses, minimization of irreversible or reversible impacts, and remediation of reversibly damaged soils.

Guiding principles within this concept were: system oriented procedures, the principle of precaution, the principle of plausibility and the principle of national or international cooperation and coordination.

Within the definition of procedures, four stages can be identified:

- Analysis of the actual state of soil problems, including assessment of causes and impacts,
- Monitoring of soil changes with time,
- Controlling of adverse influences on soils by introduction of regulative or preventive measures, and
- Remediation of soil damages in case of reversibility.

Looking into the actual status of soil protection in Europe, it can be seen that the countries are quite differently advanced in the four stages of procedure outlined above.

At the moment, the Council of Europe is preparing a comprehensive report entitled «The European Soil Resource» describing the current status of soil degradation, causes, impacts, and need for action.

References

Blum, W.E.H., 1988. Problems of soil conservation. – Nature and Environment Series No. 39, 62 pp., Strasbourg.

Blum, W.E.H., 1990. Soil pollution by heavy metals – causes, processes, impacts and need for future actions. – Information document - 6th European Ministerial Conference of the Environment, 42 pp., Brussels, 11-12 October.

Blum, W.E.H., 1990. The Challenge of soil protection in Europe. - Environmental Conservation **17,** 72-74, 1990.

Blum, W.E.H. 1993. Soil Protection concept of the Council of Europe and integrated soil research. - In: Soil & Environment, Vol. 1, H.J.P. Eijsackers and T. Hamers (eds): Integrated soil and sediment research: A basis for proper protection, 37-47, Kluwer Academic Publishers, Dordrecht.

Blum, W.E.H., 1994. Sustainable land management with regard to socioeconomic and environmental soil functions - a holistic approach. - In: R.C. Wood and J. Dumansky (eds.): Proceedings of the International Workshop on Sustainable Land Management for the 21st Century. Volume 2: Plenary Papers, 115-124. The Organizing Committee. International Workshop on Sustainable Land Management. Agricultural Institute of Canada, Ottawa.

III. Reports

IIIa Legal Aspects

Environmental Measures Reflecting Political Changes in the Czech Republic

Bedřich Moldan

Immediately after the 1989 «velvet revolution» the newly created Czech Ministry of Environment published its «Blue Book» with the first ever official and full report on environmental situation in the Czech Republic. The tone of this book is rather pessimistic because the data published here show that the scope of environmental pollution in the Czech Republic has been truly enormous.

The recent Report on the State of Environment by the same Ministry gives a more encouraging picture. Especially in the air pollution the situation is getting better. The emissions of major pollutants are steadily decreasing as well as the extent of the water pollution even if the latter to a lesser degree. The contamination of food has also decreased. Certainly the overall situation is not at all good and the improvements are only marginal till now. But we may hope that the worrisome trends of the recent past have been changed.

Unfortunately, the virtually only reason for the current modest environmental improvement is the economic slow-down connected with the economic transformation. In fact, given the two-digit decline in the economic and particularly industrial output between years 1989 and 1993 a more positive environmental impact could be expected. There are several reasons why this could not be realized.

Firstly, the generally disastrous consequences of the environmental policy of the Communist regime were even worse during the last years before its collapse because of rapid economic decline. Therefore, the «ecological investments» were almost totally abandoned. The impact of this neglect is still visibly present.

Secondly, the remaining polluting industries are tolerated partly because of social concerns and also because of revenues they bring especially in the exports.

Thirdly, the new dynamic entrepreneurs both domestic and foreign are very clever to explore any loopholes in existing laws. This legislation is still to a large extent of the Communistic origin and that means inadequate for the new free market situation.

Fourthly, the institutional situation in respect to the environmental law enforcement is neither stabilized nor adequate even if it is rapidly improving. The appropriate institutions are not yet optimally designed, they are understaffed, the officials are insufficiently educated and the technical support is inadequate. This is bad, but understandable in the period of the deep and rapid changes encompassing virtually all kinds of institutions in the society.

Fifthly, and perhaps most important, is the diminished attention paid to the environmental problems by the public at present. Immediately after the fall of Communism the enthusiasm for the environment was indeed great. But the expected improvement has not appeared and many people have been frustrated. Moreover, with the newly acquired freedom people are allowed – and sometimes even forced – to take their own individual lives more seriously and responsibly. That means they are more focusing on immediate, mostly economic tasks. The result is a tendency to postpone everything else including environment even if they knew rather well how bad the situation is.

However serious are these obstacles to rapid improvement of the environmental situation in the Czech Republic they are rather well recognized and addressed. It will undoubtedly take a time before the situation will improve substantially. But it definitely may be stated that a solid foundation for a real change was already laid. In the period from 1990 to the first half of 1994 more than 60 legal norms (laws, decrees, etc.) were passed. Some of the acts are truly modern and progressive ones, like the Environmental Impact Assessment Act No. 244/92 Sb, where the principles of prevention and precaution are anchored. It also enables large-scale public participation. Some of the laws have applied a phased approach so that deadlines for specific compliances are set well in advance. The most important laws are already fully enforced and are starting to bring measurable benefits.

Most of the existing legislative is of the «control and command» type, i.e. it relies on norms, standards, and limits. On the contrary, the contemporary view favors more the economic instruments, in particular those that are market-based. The present work on environmental policy is focused on such instruments.

The democratic transformation of the society is essentially finished. From the point of view of environment it brought several important improvements. There is growing public participation in decision-making processes including environmental decisions. Concerned citizens and especially NGOs are participating in many ways in developmental decisions, in preparation of legislature, in monitoring environmental performance of industry and business. Environmental information is plentiful and easily accessible. There are many ongoing activities to improve environmental education which is still far from being satisfactory.

The economic transformation which defined property rights and brought transparent tax system and other economic rules is clearly one of the most important prerequisites for any successful environmental policy. It is certainly well known that the market has its failures and that market forces are not environmental panacea. However, the establishment of the foundation to the market system alone already contributed by environmental benefits simply by elimination of some of the gross distortions of the old regime. One example is the rapid decline of the overconsumption of fertilizers and pesticides which had been heavily subsidized. Therefore they are much more expensive now. The health of the landscape and wildlife has improved instantly.

One of the most important questions now being intensively discussed is the issue of mobilizing financial resources for environmental improvement. It was already said that the new direction of environmental policy is more focusing on economic instruments based on well-known principles like the polluter-pays-principle or full cost pricing. Several environmental charges are already in place and new measures are planned to create a comprehensive system. Also, the ecological tax reform (basically revenue-neutral) is being considered.

The environmental investments in the Czech Republic (in billions of Kč) are given in Table 1 (according to the documents of the Ministry of Environment).

Table 1: Environmental investments in the Czech Republic.

Year	National Budget	Other sources	State Fund	Total	% GDP
1990	3.31	2.74	-	6.05	1.06
1991	7.82	1.56	-	9.38	1.31
1992	10.80	6.15	1.5	18.45	2.3
1993	8.62	-	2.9	-	-
1994 (preliminary)	10.81	-	3.5	-	-

The investments from «other sources» mean predominantly private sector or partly state-owned companies like ČEZ (Czech Energy Industries). The direct influence of existing laws is envisaged here namely of the Clean Air Act.

An important source of finance is the State Environmental Fund. It was created by law (Act on the State Environmental Fund of the Czech Republic No. 388/91 Sb.). It is administrated by a state agency under the Ministry of Environment. The source of income to the Fund are pollution charges. Table 2 (according to the Environmental Yearbook of the Czech Republic, 1992) shows the proportion of different charges.

Table 2 Distribution of the charges between waste and the environmental compartments water, soil and air (in millions of Kč).

	Water	Soil	Air	Waste
Pollution charges	1026.7	208.6	782.8	48.1
Total income	1320.0	208.6	845.8	48.1

Currently, the Fund is moving from subsidies as the main form of financing to new measures particularly loans bearing no interest or interest up to 10%. There is an ongoing discussion on the best use of the Fund's resources and its relationship with other financial sources. Also, the role of National Budget is being discussed. Our policy is generally focusing on mobilizing domestic financial resources. Loans from abroad or other foreign sources are seen only as a complementary measure of lesser importance.

The Transfer of the State Property

Jan Mrkos

The transfer of the state property to the Czech or foreign legal or natural persons in the privatization process is regulated by Law No. 92/1991 of Legal Code as per the amended provisions. According to Article 15 of this Law, in addition to the ownership rights to the privatized property also other rights and obligations connected with the privatized property are being transferred to the acquirer (transferee). Within the area of obligations transferred to the acquirer there are also ecological obligations. In Law No. 171/1991 of Legal Code as per amended provisions, it is stipulated in Article 18 that the property of the National Property Fund of the Czech Rep. (hereafter FNP CR) can be, in compliance with the government decision, used for reimbursement of costs for removal of damage to the environment caused by hitherto activities of the corporations until the date of accomplishment of the privatization project.

To reconcile the ecological obligations of the plants in the privatization process, two principal resolutions of the Czech government have been passed. The resolution No. 455 of 24 June 1992 and No. 123 of 17 March 1993 which has replaced the previous resolution. In resolution No. 123 the government stipulates that with the privatization projects approved by 16 March 1993 resolution No. 455 will apply. However resolution No. 455 was not used, but for some rare exceptions, because no legislative amendments to the relevant legal directives to ensure procedures in compliance with this resolution have been made. That is why with some of the highly binding requirements resulting from the privatization projects approved before 16 March 1993, after a positive standpoint of the Executive Committee of the FNP CR, an application for Award of Exception from the government resolution No. 123 was filed with the Government of the Czech Republic through the Privatization Ministry of the Czech Republic, MSNMP CR. The MSNMP CR is preparing a binding resolution on the basis of FNP CR proposal for the process of reconciliation and evaluation of these applications. The «rules» for solving the ecological obligations in privatization process have been approved through the currently valid resolution of the Czech government No. 123/93. The conditions of submission and approval of the application for closure of «Agreement on reimbursement for costs of removal of ecological irregularities» (hereafter Agreement) are specified in the government resolution No. 568/93.

According to these two resolutions the FNP CR will in these cases, if requested by the acquirer (transferee) and approved by the Czech government, close an «Agreement» with the acquirer (transferee) in which the FNP CR will pledge to reimburse the costs of removal of ecological irregularities originated before the «privatization». The acquirer (transferee) must submit the application for closure of the «Contract» to the FNP CR at latest by the date of completion of the decision-making process on the privatization project (completion of the decision-making process means the closure of a purchase contract or a contract for property transfer and property hand-over and take-over procedures, or as the case may be, establishment of a joint-stock company and transfer of at least 67% of the shares to the new owner). Together with this application it is necessary to submit also so-called ecological audit and a standpoint of the relevant regional department of the Ministry of Ecology of the Czech Republic. This application is together with a standpoint of the FNP CR in case of the affirmative standpoint of the FNP CR (the applicant is being notified about a rejection standpoint directly) being passed on to the government of the Czech Republic for decision. In case of affirmative standpoint of the Czech government the FNP CR will close an «Agreement» with the acquirer (transferee).

Ecological irregularities for which a reimbursement from the FNP CR can be provided based on the «Agreement» are exclusively and only the following ones:

- pollution of ground waters
- pollution of soil
- existence of harmful waste dump sites

It is absolutely not possible to reimburse active investment projects from the Agreement (e.g., erection of water treatment plants, projects of gas introduction, etc.).

In compliance with the government resolution the expert guarantee and inspection at removal of ecological irregularities are ensured by specialist regional departments of the Ministry of Ecology according to the «Methodological Directive for Procedures of the Czech Environmental Inspection for Solution of Ecological Obligations of Corporations during Privatization» of 21 January 1994.

With respect to expected high financial demands from the acquirers (transferees) for reimbursements for ecological damage, the FNP CR secured, through the form of competitive examination process, organizations that will for it and according to its task specification conduct so-called supervision in selected cases. This will proceed from inspection of corrective measures procedure to evaluation at decontamination work termination. In addition there has been an obligation of the acquirer (transferee), proposed to be incorporated in the prepared amended resolution of the Czech government No. 568/93, to ensure after finishing the research of ecological damage its evaluation by «Risk analysis» as a necessary precondition for reimbursement for costs of ecological projects from the FNP CR budget.

Management of Environmental Liabilities in the Czech Republic

James F. Allen, Rudolf Kozusnik, and Kevin Connor

As the Czech Republic gears up for the second wave of its large-scale privatization program, the country's business and legal infrastructure is increasingly stable and predictable. Many aspects of Czech commercial and financial law are familiar to Western investors because they were drawn from free-market models.

With a handful of issues, however, some uncertainty remains. One set of questions concerns environmental liability, namely, how to divide responsibility for pollution cleanup costs between the government and future owners of the privatized properties. These questions obviously are of great concern to Western investors, particularly because of the cost of remedying environmental contamination at some sites can be substantial and, if paid by the privatized company, can affect the feasibility of the company's operations.

The Czech Republic's fundamental approach to these issues dates back to the early stages of the privatization process. Essentially, the driving principle behind the government's outlook is outlined in the Commercial Code and Large-Scale Privatization Act of 1991. In a broad sense, these laws make clear that the privatized company inherits the liabilities associated with the purchased property. (A shareholder's risk, however, is limited to the value of his investment. See Czech Commercial Code §154(1).)

What are «Liabilities»?

It has been suggested that future costs expended to clean up historic contamination are not «Liabilities» of the state-owned enterprise. Even if this is true, nothing prevents the Czech government from adopting a US «Superfund» law in the future. This aside, consider some relevant points.

While privatization takes numerous forms, a common technique of Western investment in Czech firms is to purchase shares of a joint stock company from the National Property Fund («NPF»). A basis exists in Czech law for the new company's being exposed to future cleanup liability, which in turn could significantly affect the real values of the shares to be purchased by the Western investor. For example, the Czech Civil Code imposes an obligation «to behave so as avert damage to personal health and property, and to nature and the environment.» (Civil Code §415.) This generally is interpreted to mean that one must refrain from causing such damage.

On the other hand, the Act on the Environment could be read to impose a cleanup duty on anyone who discovers a threat to the environment, whether or not the discoverer caused it: «Everyone who learns about a threat to the environmental damage is obliged to take such measures that are within his or her powers to eliminate the threat or minimize its consequences and to report the facts without delay to the state administrative authorities.» (Act on the Environment §19.)

Accordingly, current Czech legislation offers no clear comfort that the Western investor will not some day be held liable for conditions on the investor's property that were caused by past operations.

Consequently, no-one - least of all the Czech government - will assure an investor in a newly privatized Czech company that the new company did not inherit the potential responsibility to clean up decades of environmental neglect, both on and off the premisses. Compound this fact with US business' understandable paranoia from its 13 years of bad experience with the US Superfund Law, and the reasons why potential environmental liabilitites have become so important in these transactions become obvious.

Government Indemnifications

Although the Czech government maintains the position that all environmental liabilities transfer to a privatized company, it has recognized that this unquantifiable risk is a disincentive to investing. Ad hoc decisions in both specific privatization transactions and specific governmental resolutions have addressed the issue of responsibility for pre-privatization environmental contamination. (See, for example, Resolutions of the Czech Government No. 694 [Dec. 9, 1992], No. 455 [June 24, 1992], and No. 123 [March 17, 1993].) Pursuant to these decisions and resolutions, the Czech government has promised to reimburse investors for costs associated with cleaning up pollution that resulted from the operation of state-owned enterprises.

Without belaboring the details of each turn in the road, the scheme that evolved incorporated these elements:

1. All «liabilities» of the state-owned company, including environmental liabilities, are transferred to the new company. The price of the shares may **not** be reduced to account for potential environmental cleanup costs.
2. In the privatization process, a detailed environmental audit of the facility must be performed. In theory, the company to be privatized does this; in practice, one of the new investors often will do or supplement the audit. The audit is supposed to determine cleanup and compliance costs.
3. In the share purchase agreement, or in an independent document, the NPF will agree to reimburse cleanup costs, normally to a cap, for a limited time, provided the cleanup is done according to a plan duly approved and incorporated into an order issued by the Czech Inspectorate for the Environment («CIE»).
4. The NPF may also agree to indemnify the company for cleanup costs of contamination not identified in the environmental audit.

In theory, the company will select a contractor through a limited tender, complete the cleanup, and get its costs reimbursed from the NPF. In practice, there could be problems. First, because a detailed site investigation is often not completed at the time of sale, cleanup costs cannot be estimated accurately. As a result, no one knows the relationship of the cleanup costs to (1) the size of the company, (2) the sale price, (3) the cap on the government's indemnity, or (4) the ability of the company to pay. The Western investor's tendency is to rush, fearing that the chance to get the government to pay for the cleanup is fleeting, and so, to push to get going. Without these pressures, the parties would tend to negotiate cleanups having standards and time schedules commensurate with actual health risk and the ability of the company to pay. Instead, the tendency is to make hurried commitments - before all the facts are in, and while the government money is available.

Second, the cost control issue is difficult. Three basic entities are involved once the cleanup stage is reached: the privatized company, the NPF, and the CIE - each with its own agenda. (Other entities that are usually involved are the territorial department of the Ministry of Environment, the appropriate district environmental officials, and the appropriate branch of the local health service.) Typically, the company is looking for a prompt cleanup, with costs under the reimbursement cap and a clean break with the past through a release or acknowledgement from the government. Presumably, the CIE wants a cleanup to meet certain standards, regardless of cost, and the NPF wants to protect itself from unreasonable (above cap) costs. Negatiotions are often bilateral, however, to merge these different agendas into a common goal is difficult.

A third (and related) problem is the age-old «how clean is clean?» question. The CIE has published a «Methodological Instruction», under which the CIE may apply uniform Dutch «A, B, C» guidelines for soil and groundwater cleanup. These Western standards can be unrealistic targets, and often are overly stringent when viewed in light of actual health risk. However, the Dutch standards - which even the Dutch do not apply to the exclusion of other, risk based criteria - provide at least a «bright line» test to indicate no cleanup is needed. Czech written policy is not completely inflexible. Annex 2 to the Methodological Instruction states: «Top cleanup technology is applied to serious contamination of soil and underground water only after it is ascertained that the contaminant is migratory and poses a threat to the surrounding environment.» Going further, a CIE draft instruction concerning settlement of environmental liabilities states: «In making decisions concerning the necessity to clean up the contamination, it will be necessary to inspect and consider the degree of urgency of the cleanup and distinguish such urgent cases where a threat of further contamination or defilement of important natural resources, or danger to the human health exists. Definition of target parameters for the decontamination shall be in conformity with these criteria, taking into account the prospective use of the affected area.»

So, the CIE seems to be willing to consider risk-based cleanup targets, even if they are higher than the Dutch «C» standards. In any event, at this early stage, it is difficult to tell how consistent the CIE will be in setting cleanup targets. As yet, the CIE lacks experience with soil and groundwater cleanups, and so, may tend to be either overly conservative or erratic in its decision-making.

Fourth, some investors have raised the specter of the «empty pot» - that is, notwithstanding the NPF's promise to reimburse the cleanup costs, they fear that after long-term cleanups, either the NPF will have been dissolved or its funds will be gone, so it cannot honor its promise to reimburse. The Czech government has expressly reassured investors that it considers the NPF's obligations to be the Czech government's, and as such, will be backed up by the government. Also, there is comfort in the treaties between the governments of the United States and Czech Republic normalizing commercial relations and agreeing against expropriation of property. (The Agreement on Trade Relations Between Czechoslovakia and the United States (April 12, 1990), the Investment Incentive Agreement Between the Government of the United States of America and the Government of Czech and Slovak Federative Republic (Oct. 18, 1990), and the Treaty Between the United States of America and the Czech and Slovak Federal Republic Concerning the Reciprocal Encouragement and Protection of Investment (signed Oct. 22, 1991). In view of these agreements and the clear political posture of the current Czech government to move to a free-market economy, it would be not only contrary to these treaties, but also damaging to the external commercial relations of the Czech Republic, to abrogate agreements willy-nilly on the technicality that the NPF does not speak for the Czech government. Moreover, the NPF is now specifically authorized by the Czech Large-Scale Privatization Act (§18) to enter into cleanup cost reimbursement agreements.

These potential problem areas will no doubt get sorted out as the government's policy stabilizes and both the agencies and the private sector gain experience with them.

On a broader scale, however, the pressure to allocate liabilities for historical contamination may divert scarce resources from more pressing matters. When viewed from the perspective of relative risk to public health, most historical contamination (unless affecting drinking water supplies) ranks low on the severity list, usually well below the problems caused by excessive air and water pollution from active operations.

A possible way to avoid this misallocation of resources would be for the Czech government flatly to accept responsibility for all pre-privatization contamination. This approach would allow the CIE and the company to focus on upgrading current pollution controls. The government could decide which sites should have the highest priority for cleanup and address them at its own pace. This approach, however, will not now be adopted.

Although, as indicated above, the existing Czech method of allocating liabilities has its faults, it works well in at least one sense. Given the level of Western investment in the Czech Republic, it would be difficult to assert that the government's environmental policy is a serious deterrent to investment. The procedure for negotiating the various agreements, site investigation, cleanup, and reimbursement of costs is cumbersome, but with experience and careful planning, it should get smoother.

Also, The Czech government could address the question of priorities within the existing system. If it sets reasonable, risk-based cleanup targets and time schedules to achieve them, the Czech government will promote cost-effective cleanups. This should leave more resources to invest in active operations and pollution controls. And if the government sets reasonable compliance requirements on active operations, substantial progress in pollution reduction can be made relatively quickly.

Indeed, the Czech Republic might set a record for moving in the shortest possible time from a socialist economy, where pollution controls were not a priority, to a market economy with sophisticated and effective environmental regulation.

Legal Framework for Soil Remediation in Flanders (Belgium)

Donatienne Ryckbost

The Flemish Council is expected to approve a new draft Decree on Soil Cleanup for Flanders (Belgium) in the near future. The text was initially drafted by the Interuniversity Commission for the Revision of Environmental Law in the Flemish Region, under Professor Hubert Bocken. This was an independent commission. The text was adopted, with minor amendments, by the Government on 22 June 1994. The amendments were made in the light of statutory consultations with the Conseil d'Etat, the Social and Economic Council (SERV) and the Environment and Nature Council (MINA-Raad)[1]. A vote in the Flemish Council is expected soon and it is understood that the Government hopes to have the law in effect by the beginning of 1995.

1. The Current Legal Framework

Belgium, like other countries, may face serious environmental damage from contaminated land. The soil has become so heavily polluted that soil rehabilitation is necessary. The current legal framework in Belgium does not allow for a systematic set of remedies to facilitate remediation. However, in certain circumstances, public authorities can use a large number of existing rules to adopt certain measures. These existing rules are laid out in article 21, §2c of the decree of 2 July 1981 on waste.

In the Flemish Region, the OVAM (Flemish Public Waste Company) has a major role in the cleanup activities. The general rules governing waste disposal in the Flemish Region can be found in article 21, §2c. Pursuant these general rules, OVAM acquired powers which gave it discretion to determine when and how contaminated land should be rehabilitated. If the operator of a site, after having been properly held liable by OVAM or by the Ministry of the Flemish Community, had omitted to take the necessary measures or to carry out the necessary works within the imposed period of time, OVAM could officially eliminate waste, and clean-up both the polluted soil and the closed industrial installations containing a risk for the environment. The operator bore the cost of this clean-up. Article 21, §2c was abrogated when the waste decree was modified in the recent past[2].

According to the former art. 21, §2c, the sole criterion for the imposition of cleanup measures was that the pollution of the soils had to contain a risk to the environment and to public health (it was unclear whether the "and" constituted a cumulative condition). Hence, the official cleanup by OVAM did not depend on the presence of waste in the sense of the decree on waste.

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[1] Gedr. St. V1.R., 1993-1994, nr. 587/1

[2] Decree of 20 April 1994 to the decree of 2 July 1981 on waste, B.S., 29 April 1994

Beyond Article 21, §2c, there were no further general legal criteria for determining the cases in which a clean-up should be carried out. Neither the soil and groundwater quality requirements in Vlarem II (Flemish Regulation on the Environmental Permit II) nor the few extant technical standards provided substantive guidance. Therefore, other than a vague requirement that it be careful and employ standards of fair management, OVAM was fairly unconstrained in its implementation of the policy. In practice, OVAM based its behavior on the standards of other countries, e.g. the cleanup standards (Key Soil Remediation) of the Dutch Law on Soil Remediation.

Central to the entire process was the determination of whether the soil and groundwater pollution constituted a serious threat. This was determined through a risk assessment. The risk assessment took into account such factors as: the nature and the concentration of the substances, the possibility of their spreading, the risk of exposure to man, plants or animals and water winnings, the characteristics and the use of soil, and the local pollution situation. Key variables considered when determining the nature and the concentration of the polluting substances were their specific characteristics such as toxicity, vapour pressure, solubility, mobility, accumulation, and corrosivity. Key variables considered when determining the possibility of the pollutant spreading included the types of soil, the local conditions and the geological and the hydrological situation. Key variables considered when determining the risk of exposure to man, plants or animals and water winnings were the future use of the soil and the possibility of contact between the polluting substances and man, plants or animals. More specific goals for the risk assessment were laid out in Vlarem II. These varied as a function of the soil or ground water use.

Article 21, §2c was not without problems. While it authorized OVAM to conduct clean-ups on the sites of those it found liable, there was no guidance at to when to consider the situation serious enough that liability should be found. Similarly, many thought OVAM had too much choice over the measures employed. Problems like this led to extensive criticism of the law.

OVAM is not the only authority with clean-up responsibilities. Local authorities (the governors and mayors) and the civil protection administration also have the power (and responsibility) to take remedial action in certain pollution incidents. Art. 54 of the decree of 2 July 1981 grants the governor and the mayor the power to take the necessary remedial action whenever waste is illegally handled or disposed of. Similarly, the Royal Decree of 23 June 1971 requires the civil protection administration to take, on its own initiative, remedial action in case of a major pollution incident. In the event of incidents of less importance, its intervention, or that of the local fire brigade, may be requested by local authorities. Art. 85 of the Act of 24 December 1976 is relevant in this case. The article also imposes on the state or the city the obligation to recover the expenses of the cleanup from the owner of the polluting substances. Fault is not required, as it is a case of strict liability.

Other regulations also empower publicauthorities to take some remedial action in cases of soil pollution. These include Art. 133 and 135 of the new Municipal Law, art. 128 of the Provincial Law, and art. 31 paragraph 3 of the Flemish decree on the groundwater protection of 24 June 1984. In certain circumstances the courts may also require soil rehabilitation measures.

2. The New Waste Decree and the Transition Regulation

The legislation on waste and soil remediation is presently rapidly evolving. On 20 April 1994 the Flemish Council approved the decree on prevention and management of waste[3]. The decree modifies the decree on waste of 2 July 1981 and has come into effect on 7 May 1994. It confirms the authority of OVAM on soil remediation. Art. 39, 7° stipulates that OVAM is authorised to identify, inventory and examine polluted soils which constitute a risk to the environment and to public health, and to take remedial action in conformity with the stipulations of the decree. The much-discussed art. 21, §2c was, however, not retained in the new decree. Nevertheless, a transition regulation is adopted under which OVAM can continue all initialised cleanup actions. Art. 14, 3 stipulates that the measures for the official cleanup of polluted soils and closed industrial installations in virtue of (the former) art. 21, §2c of the decree of 2 July 1981 on the management of waste, of which the execution has begun before the date the decree came into effect, are to be completed and that the costs are to be recovered in conformity with the regulations applied before this decree came into effect.

3. The Future Decree on Soil Remediation

The new Flemish draft decree relating to soil cleanup which has been elaborated in the context of the activities of the Interuniversity Commission for the Restatement of Environmental Law in the Flemish Region, is intended to replace article 21, §2c of the decree of 2 July 1981, which is thought to be too vague for current requirements. It includes provisions for: the separate handling of new and historical pollution, identification of the pollution, the constitution of a register of polluted soils, the imposition of restrictions on the use of soil and the protection of the buyer of polluted property, mandatory soil cleanup examinations upon transfer of ownership of sites containing listed potentially contaminating plants or activities. Of utmost importance was the administrative process according to which decisions are to be made with respect to when and to what extent the soil is to be cleaned. Much attention has been paid to the financial implications of the operation and the allocation of liability.

Key Issues of the Flemish Draft Decree Relating to Soil Cleanup

The key issues of the Flemish draft decree on soil cleanup can be summarised as follows. The draft decree aims for a co-ordinated approach of soil pollution and makes a fundamental difference between pollution occurring after the decree has come into effect and historical pollution arisen before this date.

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[3] B.S., 29.04.1994.

First of all the draft decree organises the identification and registration of polluted soils. The authorities will proceed with a systematic examination of polluted areas at the occasion of transfer of property or the closure of certain institutions and activities which may cause pollution and which are listed by the Flemish Government. They can also gather more coincidental information as a result of some investigations of the soil quality. The information on soil pollution will lead to the constitution of a register of polluted soils under the administration of OVAM (The Flemish Public Waste Company). This register can serve as a data base for policy decisions and can also function as an instrument to protect and inform potential buyers of polluted soils. If soil pollution is discovered, it may be necessary to take precautionary actions and safeguarding measures awaiting the actual execution of cleanup operations. The authorities have the power to impose restrictions with respect to the use of seriously polluted soils awaiting cleanup. These restrictions will also be made public in the register of polluted soils.

The draft decree also elaborates an administrative process according to which decisions are to be taken with respect to when (remediation criteria) and to what extent (remediation objectives) the soil is to be cleaned. The cleanup of new pollution is, according to the draft decree, required whenever the soil remediation conditions to be set by the Flemish Government, have been exceeded. With respect to historical pollution, the decree is based on a recognition that the means for an overall soil cleanup will be insufficient in the near future. It states as a general principle that measures for soil remediation must be taken whenever the historical pollution constitutes a «serious threat». At the suggestion of OVAM the Flemish government will draw up a priority list of the historically polluted soils that need to be remediated. However, as long as no soil remediation standards have been set up, the criterion of soil pollution constituting a serious threat also holds for new cases of pollution. The draft decree defines soil pollution posing a serious threat in terms of actual or potential contact between polluting substances or organisms and human beings, plants or animals, where this contact will certainly or probably have damaging consequences for the health of any of these three, and also where the pollution may have a negative effect on water collection. Criteria for evaluating the seriousness of the threat include soil characteristics, type and concentration of the pollutants, the possibility that they may spread, the functions of the soil and the risk of exposure.

The draft decree includes target levels for cleanup. The aim of soil remediation as set forth in the new decree is to achieve a level of soil quality where no adverse effects are observed. All cleanups – of new pollution as well as of historical pollution – must aim to reach the background levels in comparable, unpolluted soils. However, the decree wishes to offer sufficient flexibility to take account of developing technology and environmental evolution and the specific data of each separate case. Hence, no theoretical choice is made between the elimination or the treatment, the masking or immobilisation of polluting substances. The decree tries to achieve a balance between the ecological and economic considerations by a reference to the state-of-the-art of the available technology. Any cleanup should be carried out by using the best available technology which is not unreasonably expensive in comparison with the expected results for man and environment. Furthermore, restrictions on the use of the polluted soil and aftercare measures can be imposed.

Separated from the establishment of ultimate liability, the draft decree specifies which parties will be responsible for carrying out and pre-financing cleanups where they are necessary, some of whom may subsequently seek to recover costs from the original polluter. In the draft decree a cleanup obligation rests with the site operator where a plant or activity requiring licence or notification under the Decree of 28 June 1985 on Environmental Permits is present on the site (where the pollution entered the soil), and with the site owner in all other cases unless the owner can demonstrate that a third party has actual control over the site, in which case that third party is responsible for cleanup. The situation is, however, different when historical pollution is concerned. In historical pollution cases, the same parties are under a primary obligation to cleanup. As the polluted soil is identified by the Flemish government, the obligation for the cleanup will only exist when the operator, the owner or the third party which has actual control over the site is urged by OVAM to carry out the cleanup.

The administrative procedure incorporates sufficient guarantees for a correct and efficient cleanup and expressly stipulates that the inventory of the pollution as well as the scientific remediation investigation are to be carried out by or under the control of certified experts. OVAM will supervise the cleanup operations. Finally, financial guarantees for the execution of the cleanup activities must be provided for by the operator.

The draft decree expressly stipulates that the party who is obliged to carry out the clean-up must also prefinance it. This does not mean that he must eventually bear the costs. He can try to recover the expenses from the liable person. The party causing the pollution will be strictly liable for investigation, cleanup and associated expenses, whereas for historical pollution, liability will be established in accordance with the liability rules applicable as before 6 May 1994 (date before the coming into force of the modifications of decree on prevention and management of waste which abrogated art. 21, §2c).

The draft decree foresees a special rule for the situation of the innocent owner/ possessor who acquired contaminated land without knowing it was polluted. The operator, the owner and the controller can escape his obligation to clean-up (and the obligation to pre-finance) if all of three requirements are met: (1) the contamination was not caused by that person; (2) the person was neither aware nor should have been aware of the pollution at the time he became operator, owner or controller; and no listed plant of activity was established or conducted on the land since 1 January 1993. In these cases OVAM can take over the cleanup and officially carry out the works.

In historical pollution cases, the parties which are under a primary obligation to clean-up will be exempted if they did not cause the pollution and were neither aware nor should have been aware of its presence when they acquired or started using the site. A person who acquired historically polluted soil before 1993 despite being aware or having reason to be aware of the pollution, can still escape responsibility to clean-up if he can show that he did not cause the pollution and has used the ground solely as a private residence since the purchase. In the case of liability also, the draft decree introduces a more favourable rule for the «innocent owner/ possessor». The draft decree furthermore contains an ample set of rules aiming at informing the buyer of (eventually polluted) land of the situation of the soil.

The register of polluted soils is the basis of a universal system of soil quality disclosure, under which all transfers of sites, whether or not they contained listed plants or activities, will have to be accompanied by a soil certificate from OVAM, obtained by the vendor, revealed to the purchaser and included in the transfer agreement. Failure to do this will render the sell null and avoid. The soil certificate must also appear in all deeds ruling the transfer of land, including private deeds. Any transfer under living persons of the property right to land falls under the draft decree. This rule will entail an additional burden for OVAM's administrative services as well as for the instrumenting officer, but it also offers information and protection for the buyer.

Furthermore, a systematical examination and possibly a further cleanup is imposed for the transfer of land bearing installations which can cause soil pollution and when closing these installations. Hence, an additional clean-up moment is introduced and it is avoided that the transfer to an insolvent party or a closure takes place in order to escape the obligation of cleanup.

A preliminary soil examination is compulsory at the vendor's (transferor's) expense for the transfer of sites which contain listed plants or activities and at the user's expense upon closure or cessation of such activities. Such examinations must be done under the supervision of a soil cleanup specialist, for the purpose of which it is understood that the government will establish a certification scheme. In case of transfers, a new examination is not required if an examination has been conducted less than two years earlier and no further potentially contaminating activities have since taken place.

Where preliminary examination, a register of the contaminated soil or pre-decree examinations suggest either that new (post-decree) contamination has occurred or that there is a serious threat from historic pollution, the Flemish Public Waste Company (OVAM), can order the transferor to conduct an «in-depth» soil examination within 60 days of the notification of transfer. When the cleanup standards to be set by the Flemish Government have been exceeded or a serious threat is present, the transfer will not be allowed to proceed unless the transferor: (a) draws a project for soil cleanup, (b) makes a formal commitment to OVAM to clean-up the soil and (c) provides financial guarantees to underwrite completion of the work.

Current Stage of the German Legislation on Soil Protection

Hans-Peter Lühr

Since several years a Soil Protection Act (SPA) has been discussed. This act should contain the basic indications and standards for investigation, assessment and remediation of contaminated sites in order to provide legal certainty for investors and owners of these sites. Currently only a draft from the ministry of environment is available, which defines standards for handling the soil and the contaminated sites specifically in the Federal Republic of Germany.

The SPA-draft contains precautionary regulations aimed at avoiding new contamination of soils as well as treating existing contaminated sites, which are dangerous for human health and the environment. Both aspects of the regulations - the precautionary soil protection and the remediation of contaminated sites - are judged equally important.

The SPA-draft contains the following essential measures:

- The responsible authority is required to register those sites which are suspected of being contaminated. If there are sufficient indications of contamination, an investigation must be ordered.
- The responsible authority assesses the sites, using the results of the investigations to determine whether the human health or the environment is under acute danger caused by the contaminated site.
- Based on this assessment the authority must decide if the suspected site is a contaminated site; either further measures must be undertaken or it can be discharged from the register.
- The responsible person for a contamination site, or his successor, as well as the owner of the site is obliged to remediate the contaminated site. In doing this, the current and future use of the site is to be considered.
- The responsible authority can demand a remediation plan from the responsible person or company. This plan must contain the assessment of the danger, the current and future use of the site, the requirements of the remediation measures as well as the time schedule for the realisation of the measures.

Strategy for the Assessment

The following principles (Fig. 1) have been accepted in the Federal Republic of Germany:

1. Each area can become a suspicious site by reason of a detected or supposed contamination.
2. An assessed suspicious site becomes a contaminated site, if certain levels are exceeded.

3. The assessment takes place for different protection goals. These are
   - Human Health
   - Ecology (flora, fauna, ground water, biotope, etc.)
   - Construction

   Further, one has to differentiate with respect to the behavior of the chemicals: along which pathways and resulting from what types of use can they reach the various protection goals.

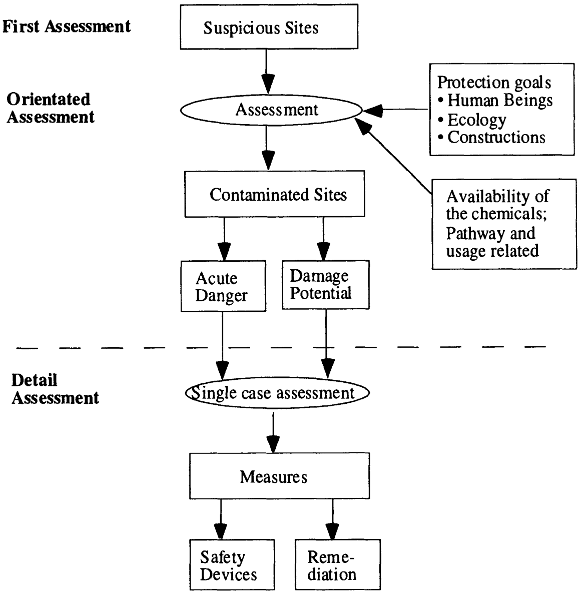


Figure 1 Procedure to treat suspicious sites.

These assessments are worked out on different information levels. First the assessment is carried out by that information (**First Assessment**), based on documents without any field investigations. Then the so-called **Orientating Assessment** is to be carried out, for which field investigations are needed. This assessment is necessary to compare the large number of suspicious sites and set up a priority list.

4. The primary aim in assessing the suspicious sites is to determine those sites from which a real and acute danger is emitted directly to the protection goal «Human Health» and those sites which present «only» a damage potential.

As to the protection goal «Human Health» the direct contact between human being and chemical(s) by pulmonary, oral or cutaneous intake is to be assessed (Fig. 2) as well as the indirect path by intake of drinking water, of food and of air. If the result will be **a real and acute danger** along one of the paths, then this danger must be removed.

A damage potential is «only» a potential which can lead to an injury to the protection goal «Human Health» or others. Those sites are first to be secured and/or to observe more intensively so that one can act immediately, if a transition from damage potential to acute danger takes place.

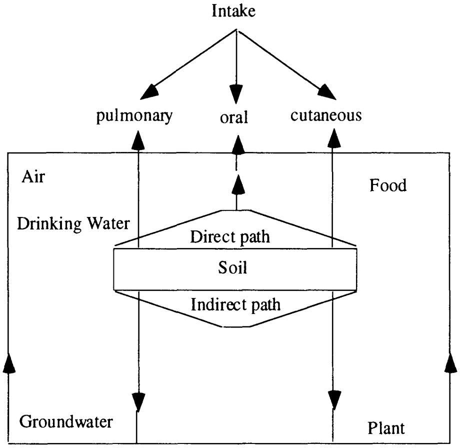


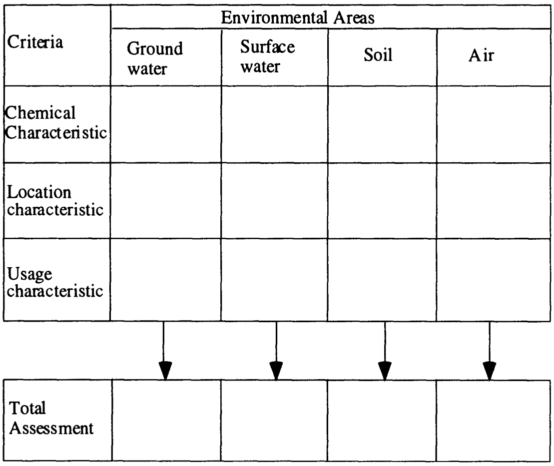
Figure 2
Paths of contaminations from soil to human beings

5. For this comparative assessment on both levels - First Assessment and Orientating Assessment - various formalized «Assessing Models» are available in the Federal Republic. A unique federal model does not exist up to now. Considering how far the situation is advanced such is hardly not to be expected.
6. The contamination sites thus detected, in which there are real and acute dangers, are investigated and treated as individual cases on an in-depth and detailed way (**Detail Assessment**). This assessment is to be used in determining the measures to be used for the remediation of the contaminated site.
7. A remediation of contaminated sites, which are detected as having a damage potential will take place as needed in connection with the future use of the sites, for example if foundation work must be done to erect buildings.

Standards for Assessment

Real danger, that is the damage potential of a contaminated site, depends on the quantity of hazardous chemicals which reaches the protection goal along various paths, such as ground water, soil and air. The conditions at the location and of the usage on contaminated site and its surroundings, determine the character and the range by which the hazardous chemicals are set free, dissipated and affect the surroundings.

The respective danger or damage potential of a contaminated site can be described as a function of three independent criteria, the chemical characteristic, the location characteristic and the usage chracteristic. The assessment can be described in a matrix (Fig. 3). The total assessment is the sum of the three criteria. In principle the assessment is to be worked out for all three criteria and the four environmental areas. In practice however, the biggest difficulties are involved in working out the criterium chemical chracteristic. Normally the path or the environmental area «Ground water» is the most important part.



Criteria	Environmental Areas			
	Ground water	Surface water	Soil	Air
Chemical Characteristic				
Location characteristic				
Usage characteristic				
Total Assessment				

Figure 3 Matrix tfor assessment

The chemical characteristics of a site are assessed based on the inventory established of a contamination site and the situation around it.

The damages and effects which stem from the chemicals are very different. For this situation, lists of hazardous chemicals have been established. They mainly contain values, which are derived toxicologically.

As for the location characteristic, especially the spreading of the chemicals by the ground water is of major importance. Regarding the usage characteristic, the sensitivity of the usages surrounding the contaminated site is to be assessed.

To assess the chemical situation a so-called «Three Area System» (TAS) can be used as a basis to define the decisions clearly (Fig. 4).

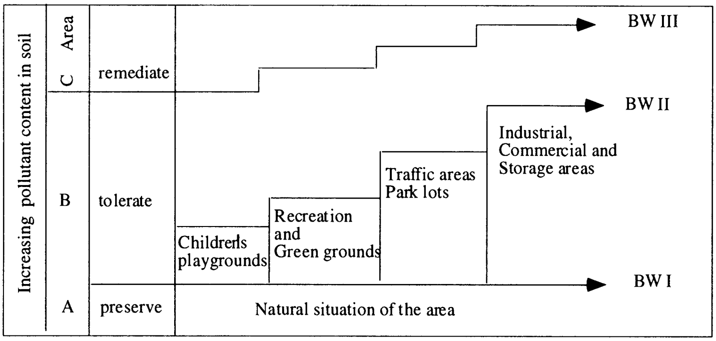


Figure 4 «Three Area System (TAS)»

The value BW III, the so-called «Acting Value», is that limit where the authority has to act, if this value is met or exceeded. This value must be standardized throughout the Federal Republic.

The value BW II, the so-called «Remediation Value», will be defined individually with a safe distance to the Acting Value. This value describes the tolerable level of a residual concentration of a particular chemical in order to use the soil, or describes the point where the pumping of the contaminated ground water can be stopped. This is the duty of the responsible authority, which has to enact the remediation directive individually for the specific case.

The value BW I, the so-called «Reference Value», is the local or regional background value for the soil and the ground water. This value is important, because the Remediation Value cannot be fixed below this value (principle of proportionality). These values must be elaborated by the regional authorities in order to characterize the natural chemical situation of groundwater areas and soil regions.

Summary

By using the strategy - at first, only remediation for sites which possess a real and acute danger - the problem of the contaminated sites can be more readily dealt with along the time axis. Thus the enormous estimated costs can be cut down with regard to the real situation.

Risk Assessment from a Business Company View-point

Pascal Isnard and Timothy M. Vogel

In order to evaluate the risk due to the use of chemicals, several concepts need to be employed whether in a qualitative or quantitative manner. Among these concepts are two which are used extensively in discussions of chemical risk assessment: the exposure of a potentially sensitive object (or organism) to the chemical and the sensitivity of that object (or organism) to the chemical. Although often dealt with as completely separate concepts, there is a connection which is in reality quite important. The sensitivity of an object (or organism) to a chemical is usually dependent on the exposure path. For example, an organism could be extremely sensitive to a chemical in the gas phase (e.g, significant lung effects) while not at all sensitive to the chemical in the liquid phase (e.g., insignificant skin effects). Given these concepts, the actual determinations of the probability of exposure to new chemicals (where no field data is available) and their effects on different organisms and objects are extremely difficult and lead to the proposals of several logical approaches. The one that is described more or less in this paper is that derived from the European Commission (Directive 93/67/EEC) and ECETOC report #51.

The approach here is rather direct conceptually. The chemical is evaluated for whether it is «dangerous» to the environment and whether exposure is possible. If the responses to both are affirmative, then independent calculations of the predicted environmental concentration (PEC) and the predicted no-effect concentration (PNEC) are performed (see figure 1). These two values are compared and if PEC is less than PNEC, the risk is considered limited.

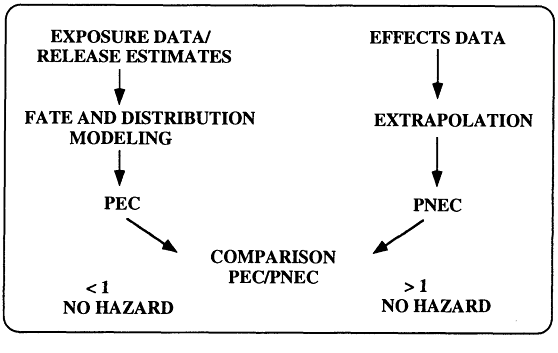


Figure 1
The PEC and the PNEC values are compared and if PEC is less than PNEC, the risk is considered limited.

Decisions regarding further testing and modeling are related to the mass of the chemical to be produced per year (see flow sheet - figure 2). Essentially, better data is required when more of the chemical will be produced or when the PEC:PNEC ratio is larger.

The extreme case being when over 100 tonnes will be produced and the initial PEC:PNEC ratio is greater than 1000.

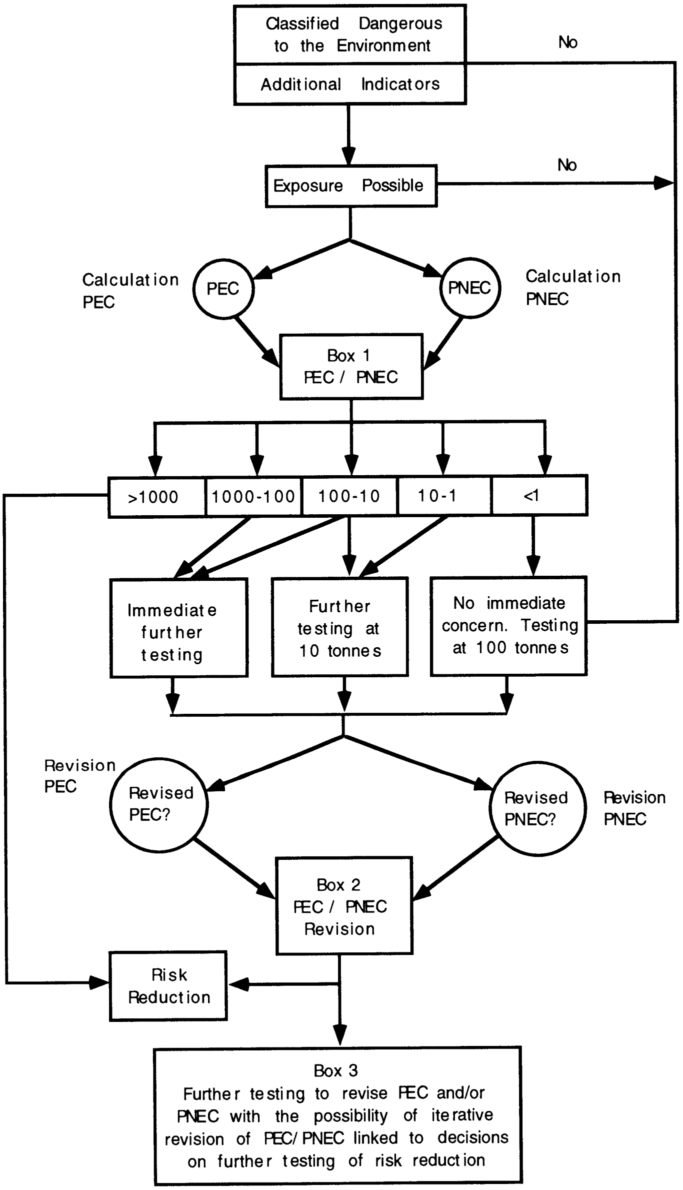


Figure 2 Decision scheme for aquatic risk charcterization.

For existing chemicals, both the concepts behind the calculation of the PEC and PNEC values begin to change. Already, the processes that control the fate of chemicals and their effects on the environment have had time to act even if knowledge about which processes are the most important is lacking. Measurements of compound concentrations and potential ecological effects are now theoretically possible. The problems related to existing chemicals are the accuracy and sensitivity of analytical techniques for discerning both background chemical concentrations and, even more difficult, ecological impact.

In both cases, new and existing chemicals, the errors in measurements and calculations of the processes that control a chemical's fate in the environment lead to dramatically large ranges in predicted fate (Mackay and Vogel, 1986). In addition, most ecological data results from laboratory studies that are not necessarily perfect predictors of ecological effects in the environment (see figure 1, step extrapolation for PNEC). Thus, in practice, the predictions of PEC and PNEC are wrought with uncertainty resulting from the limit of the natural spatial variability of the PEC and the extrapolation errors of the PNEC that lead to a distribution of their potential values. The concern is related to the probability that PEC is greater than the PNEC (figure 3). Unfortunately, rarely does sufficient data exist to evaluate the probability distribution of the two calculations.

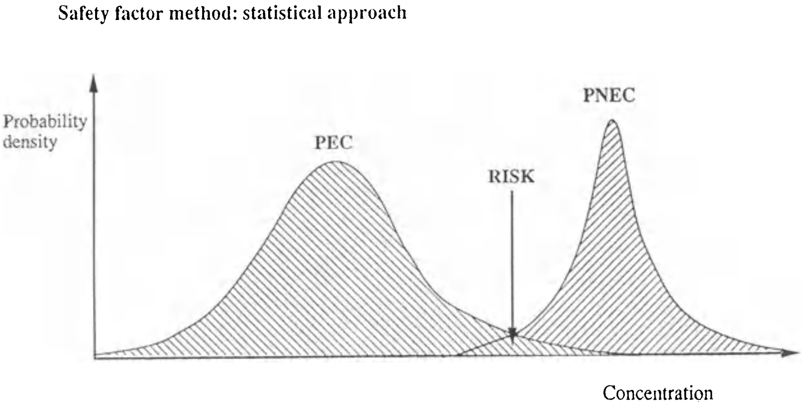


Figure 3 Distribution of potential and no-effect exposure levels.

Fortunately, an approach has been developed that while simplifying the work involved allows for the possibility of determining the PEC:PNEC ratio relatively simply and allows for further testing and calculations if the results are marginal. This is the approach demonstrated in figure 2. The PEC is divided into PEC (initial) and PEC (regional or local) and is often related to the release of chemicals via sewage treatment plants. Therefore, except in cases of obvious exceptions, the performance of sewage treatment plants can be evaluated by a combination of laboratory and modeling work. Laboratory work includes biodegradation tests and abiotic processes, such as hydrolysis, volatilization, and sorption.

The PNEC is based upon an initial series of short-term toxicity data (e.g., in aquatic environments this would be fish, daphnia, algae, etc.). These are often the same results used at the beginning of the flowsheet (figure 2) for deciding if the chemical should enter this approach (i.e., «dangerous for the environment»). Then for further extrapolation of the single-species short-term toxicity data to the full-scale ecosystem, several assumptions are promoted:

1. «ecosystem sensitivity depends on the most sensitive species»; and
2. «protecting community structure protects community function».

Given even these guidelines, the extrapolations proposed are generally conservative, leading to concentrations that have no effect without guaranteeing that higher concentrations will have an effect.

In summary, the difficulty is assessing whether a risk exists, or worse, will exist based on simplified laboratory and modeling work restricts the accuracy of such predictions. An approach has been proposed to attempt to evaluate the potential risks with a conservative yet realistic approach. Scientific criticism of this approach is easily produced while significant improvement is difficult.

References:

European Commission (Directive 93/67/EEC). Risk Assessment of Notified New Substances. Technical Guidance Document, Brussels 1993.

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, ECETOC report #51. European Chemical Industry Ecology and Toxicology Centre, Brussels.

Mackay, D.M. and **Vogel**, T.M. 1986. Ground water contamination by organic chemicals: Uncertainties in assessing impact. pp. 52-59. In: Proceedings of Second Canadian/American Conference on Hydrogeology, Banff, Alberta, Canada, B.Hitchon and M.R. Trudell (eds), National Water Well Association.

IIIb Priorities, Risk Assessment and Case Studies

The Introduction of Risk Analysis in Environmental Protection

Jiri Růžička

There is a wide range of human activities connected with negative potentially effects on human health and the environment. In such a case we need to deal with the field of risk analysis. In this we classify the stage of risk evaluation and the stage of risk review and control supported already by some concrete technical measures.

In the field of environmental protection we encounter the following main aspects of risk analysis:

a) Risks resulting from the potential sources of accidental pollution of the environment as the basis for evaluation of the optimum technical or other type of prevention.

b) Evaluation of emission of harmful substances from a number of points of view (protection of human health, other living organisms, technical facilities, etc.). An integral aspect of the overall risk evaluation is also the contamination of a given rock environment for its surroundings.

Hereafter I will deal mainly with this last category which is signified aspect in evaluating contaminated sites. This essentially means to evaluate the contaminants in earth, in soil, air, and in ground waters which if left untreated would lead to pollution of the surroundings. At the present time, the estimated cost of treating the known contaminated sites is 30 to 50 billion Czech Crowns. This shows that in establishing the targets for decontamination measures, it will not be possible to adapt uniform directives, for all cases nor to follow the idea of decontaminating the rock environment to the level of natural background. Here the risk analysis is instrumental in allocating financial resources in an appropriate way.

The stages of risk analysis performance are as follows:

- identification of the pollution and its evaluation, especially with respect to intended use of the evaluated land
- determination of the decontamination concept, i.e., reduction or total removal of the risk, carrying-out the decontamination and verification of the attained result
- if need be, review of the risk associated with the residual contamination of the rock environment after completed decontamination.

The risk analysis of the polluted environment can also be carried out as a preliminary estimate based on available documentation. In more complicated cases of extensive contamination, one can proceed from the results of more detailed research supplemented by determination of migration rates of the substances, together with an attempt to quantify the effects on the individual subjects. To be able to quantify the risk, it is necessary to know the characteristics of the individual contaminants (toxicity, biodegradation, physical and chemical qualities, etc.) and also their behaviour under the conditions of the given rock environment, stability of the water environment, etc. There is a number of technical and legal problems connected with the application of the risk analysis to treating contaminated sites. In some cases, it may be practical, depending on the circumstances, to deal with the issue in the usual way by applying directives set up for the specific case.

According to the result of the risk analysis, it will be possible to classify the decontamination cases in the following way:

- Decontamination will not be necessary, or it will only be necessary in more distant future
- Decontamination will be necessary only for part of the site and for the rest, the previous procedure will apply

With the decisions not to decontaminate or to decontaminate only partially, a problem is raised concerning monitoring of the remaining contamination, its continuous control, and especially the transfer of legal liability associated with its existence to the new land owners.

Regarding the concrete elaboration of the risk analysis, research work can make a decisive contribution. Current research on the rock environment, more attention is paid to the technical performance than to the need of determining the extent of the contamination as completely as possible. The basic deficiencies in this kind of work can be summarised as follows:

a) The research is being carried out without regard for the existence of contamination sources on the surface and without identification of surfaces suspected of contamination. In most cases there is hardly any basic information on the potential sources of contamination and on the temporal behaviour of their effects.

b) The research does not point out the relevant spatial factors involved in the breakdown contamination.

c) The research is often oriented toward those subsoil and bedrock characteristics, which are of marginal importance regarding the spreading of the contamination. On the other hand there is a lack of documentation concerning their ability to migrate.

d) The research seldom mentions what areas of subjects can be harmed by the seepage of contaminants from the contaminated site.

Further, the research work in our country is currently oriented toward the standard decontamination procedures, often without further documentation which would enable decisions based on other possibilities. This often that a company performing the research work will recommend such decontamination methods which can be performed by the company.

The initial risk analysis of subsoil and rock pollution in our country, appears to be mainly an attempt to estimate the danger to the surroundings. If we dismiss those cases in which the risk analysis is being exchanged for a commentary on the result of often incomplete research, then the main factual shortcomings of this analysis are as follows:

- there is no accurate and concrete documentation on the further utilisation of the decontaminated land, often because the future development after privatisation is not certain. In some cases there is no information on the possibilities of further pollution from the soil itself or whether there is an additional pollution source bringing in different problems into the research, or the planning.
- Procedures for removal of contaminated sites which were created before privatisation.

Geochemical Processes in Ground Water of the Aquifer along the River Danube

Darina Liptáková

Here the chemical and biochemical changes in the quality of ground water in the Danube bank's aquifer during the period of 1955-1991 are discussed. Special emphasis is given to the thermodynamic conditions particularly the redox potential E_h during the period from 1987 to 1991. The Danube is a well oxygenated river in which organic contaminants are removed and relatively clean water infiltrates into the aquifer. During the last few decencies, water quality has degraded and the groundwater composition is affected negatively in some places, particularily during flooding events.

For our study, we chose the Danube flood plane. Ground water in this area has been used as drinking water without any additional treatment (except chlorination) for 15-20 years. Water quality corresponds here to Czechoslovak Standards for drinking water.

The physico-chemical and (bio)chemical changes were followed in the stream and in the ground water originating from surface water after its infiltration through the river sediments.

The hydrogeochemical system of the Danube quaternary gravel-sand deposits was extraordinarily stable. Ca, Mg and HCO_3^- ions dominate and create a high buffer capacity in the aquifer. According to the measured values of E_h and pH, a distinction could be made between the oxic and anoxic zone of the subsurface system. Biologically catalyzed oxido-reduction processes seem to play an important role in the aquifer.

A flood occurred in the river Danube between August 1st to August 9th 1991 (Fig. 1). From August 27th to October 8th 1991 the qualitative changes in the ground water of the riverine zone were monitored in weekly intervals. Cl^- ions indicated changes in groundwater quality before changes in hydraulic pressure could be observed (Fig. 2).

Statistically significant changes of oxygen concentration, non polar extractable matter (NPEM), and in E_h values occurred throughout the aquifer investigated. Concentration of dissolved oxygen dropped to the average value of 1.1 $mg.l^{-1}$ (Fig. 3), values of NPEM were increased at depth of approximately 30 meters up to the value of 0.15 $mg.l^{-1}$. The limit for drinking water of 0.05 $mg.l^{-1}$ was surpassed 17 times (Fig. 4).

The values of pollutants like PCB exceeded the limits according to the Czechoslovak Standard for drinking water in several locations (Table). They were measured between August 27th and October 8th 1991 in the ground waters of the riverine Danube zone. Most measurements were close to the highest limit of Czechoslovak Standards for drinking water (limit 50 $ng.l^{-1}$). At the same time, also the concentrations of chlorinated hydrocarbons, such as tetrachloromethane and perchloroethylene passed the limits set for drinking water.

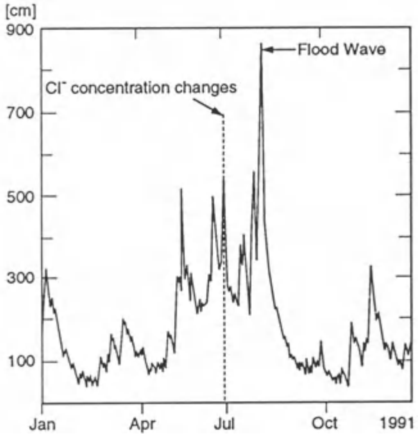


Figure 1
Time dependence of Danube surface water level January - December 1991

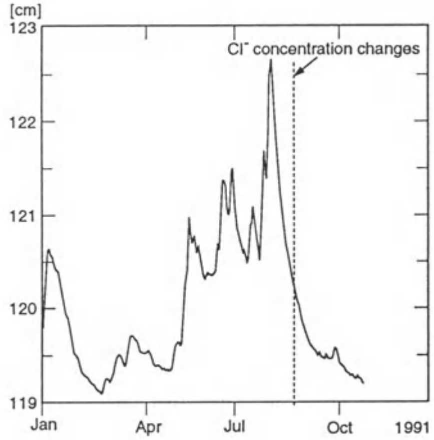


Figure 2
Time dependence of groundwater level - Dobrohošt site January - December 1991

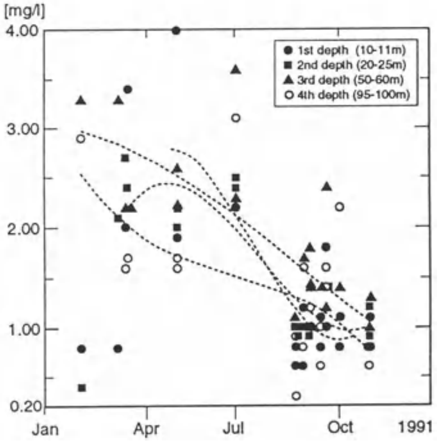


Figure 3
Dissolved oxygen

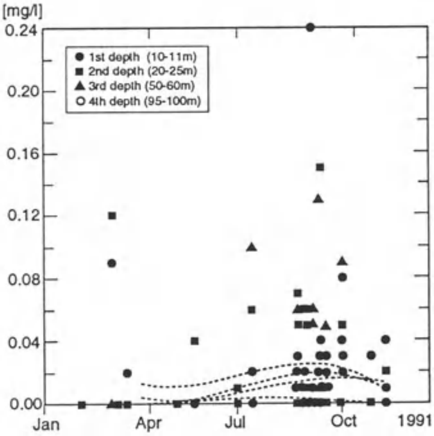


Figure 4
Non polar extractable matter NPEM

Table: PCB concentrations (ng l^{-1}) at different wells.

Well	Time period		
	27.8.91 - 31.8.91	1.9.91 - 9.9.91	9.9.91 -2 4.9.91
P - 4	80	38	38
Kalinkovo # 4			66
HGP-6	46	50; 35	
Hamuliakovo # 8		50; 985; 30	78; 37
P1-XII	45		
CHCH 5	49; 49	92; 43	49; 55 42; 58
CHCH 10	43; 42		

Increased infiltration velocities, resulted in a more intense vertical mixing. Elevated concentrations of iron (0.80 - 1.02 mg.l^{-1}), (Fig. 5) and negative E_h values (-0.01 V to -0.0016 V) at Dobrohost indicated significant physico-chemical changes in the aquifer (Fig. 6). In many places the Eh dropped below 0 V. The lowest values measured were between -0.102 and -0.299 V (Fig. 7). Such low E_h values are typical for anaerobic conditions with strong reduction processes as sulphidogenesis or methanogenesis.

The flood on the Danube river lasted only one week. After about 70 days, the composition returned back to what it was before the flooding event.

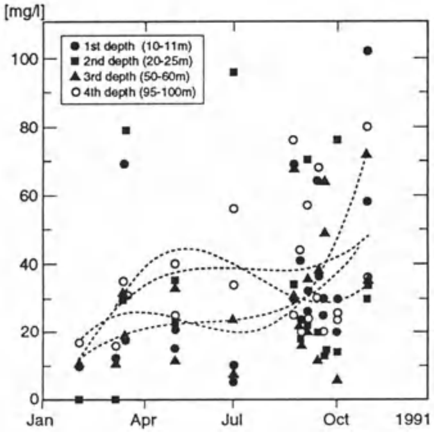


Figure 5 Iron

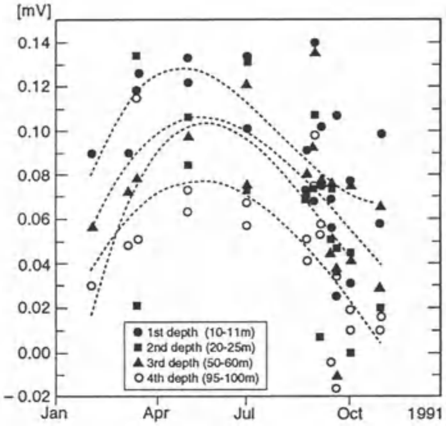


Figure 6 Calculated Eh values

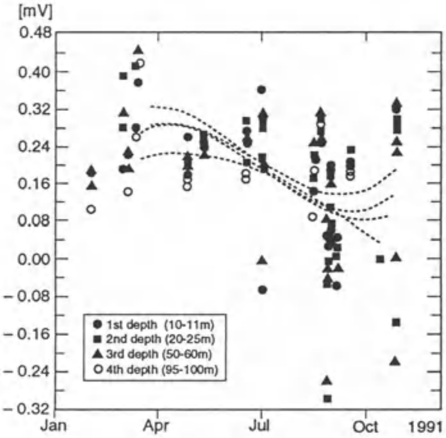


Figure 7 Measured Eh values

References

Hucko, P. et al. 1991. Monitoring of water quality in riverine zone of the Danube river with flood situation on Danube. Research Report of Water Research Institute, Bratislava.

Liptáková, D. 1993. Geochemical and anthropogenic factors determining composition of ground waters in riverine zone of the Danube river. Slovak Academy of Sciences, Bratislava.

Liptáková, D. 1992. Impacts of Danube sediments to ground water. In: Journal Czech Geological Survey and Ministry of the Environment of Czech Republic, ed. F. Reichmann, Prague, p. 24-34.

Liptáková, D.; Zajícová, H. 1991. Stabilization of hydrogeochemical system of ground waters with modification of artificial lake Hrušov for alternative ecological solution. Research report for Federal Ministry of Environment, Prague.

Liptáková, D. 1992. An analysis of processes creating chemical changes of infiltrated waters from the Danube river. In: Journal Geological Investigations, Vol. 34, No 11, Prague.

Field Studies: Elicitation of Fate and Transport Processes and Application to Full-scale Remediation

Mark N. Goltz, Gary D. Hopkins, and Perry L. McCarty

Introduction

In this presentation, field experiments which were conducted at Canadian Forces Base (CFB) Borden, Ontario, Canada, and Moffett Naval Air Station (NAS), California, will be used as case studies to demonstrate: (1) how field experiments can be used to elicit physical, chemical, and biological processes which affect contaminant fate and transport in ground water, (2) how field experimental results may be used to explain and predict contaminant behavior during hazardous waste site remediation, and (3) how full-scale hazardous waste site remediations can be designed based upon results of field experiments.

CFB Borden Field Experiment

From 1982 to 1985 a large-scale field experiment on natural gradient transport of solutes was conducted by researchers at Stanford University and the University of Waterloo at CFB Borden. By extensive monitoring of a well-defined initial pulse of inorganic tracers and halogenated organic compounds, insights were gained into the physical, chemical, and biological processes that affected contaminant fate and transport (Mackay et al., 1986). This presentation will focus on the processes affecting sorption of the organic compounds. Though not discussed in this presentation, there have also been extensive analyses conducted on other processes which may have governed contaminant transport during the experiment (e.g. Ball and Roberts, 1991; Freyberg, 1986; Rajaram and Gelhar, 1991; Sudicky, 1986).

Transport of contaminants at CFB Borden was monitored with a dense, three dimensional array of more than 4000 sampling points. Two types of sampling were conducted. Spatial data were obtained from synoptic or «snapshot» sampling sessions, each of which measured the three-dimensional spatial distribution of solute at a particular point in time. Temporal data (breakthrough curves) were obtained by measuring the solute concentration at a relatively high sampling frequency at a few preselected sampling points. Details of the experimental design and implementation may be found in Mackay et al. (1986).

The local equilibrium model, which has been traditionally used to describe transport of sorbing contaminants, assumes instantaneous equilibration between contaminant in the dissolved and sorbed phases. This assumption leads to the prediction that for sorbing contaminant transport, the zeroth moment of each contaminant plume (mass in solution) should be constant over time (Goltz and Roberts, 1987). The local equilibrium model also predicts that the velocity of each plume should be constant (Goltz and Roberts, 1987) and that the breakthrough curves should be relatively symmetric (Van Genuchten and Wierenga, 1976). By analyzing synoptic data from the Borden experiment, Roberts et al. (1986) demonstrated that sorbing contaminant plumes exhibited both a decrease in mass and velocity over the course of the experiment. Analysis of the temporal data showed that while the inorganic tracers had relatively symmetric breakthrough curves, the sorbing organics exhibited extensive tailing. Goltz and Roberts (1988) showed that a model which incorporated rate-limited sorption could explain the observed deviations from ideal equilibrium contaminant transport.

Rate-limited sorption, which is a possible explanation for the transport behavior observed at the Borden field experiment, has implications far beyond the bounds of the experimental site. A study sponsored by the U.S. Environmental Protection Agency found that during pump-and-treat hazardous waste site remediations, contaminant concentrations tended to level off after an initial rapid decline, only very slowly reaching clean-up levels (tailing). In addition, it was found that when the pump system was turned off, contaminant concentrations «rebounded» to higher levels (U.S. EPA, 1989). Both of these phenomena (rebound and tailing) may be explained using the same rate-limited sorption model which was used to describe the plume behavior at CFB Borden (Keely, 1989). Models which incorporate rate-limited sorption are currently being used to predict contaminant behavior during hazardous waste site remediations, as well as being used to help optimize pump-and-treat remediations (Goltz and Oxley, 1991; Haggerty and Gorelick, 1994; Miller and Rabideau, 1993).

Moffett NAS Field Experiment

Two studies have been conducted at Moffett NAS to evaluate the capacity of indigenous microorganisms to aerobically cometabolically degrade chlorinated aliphatic hydrocarbons (CAHs) (McCarty and Semprini, 1993). One study evaluated methanotrophs, which use methane as a primary substrate and cometabolically transform CAHs with methane monooxygenase. The second study examined phenol utilizers, in which toluene oxygenase is used as the cometabolizing enzyme. In both studies, the test zone, which consisted of a 7 m length of a confined aquifer between an injection and extraction well, was first saturated with the CAH contaminant or contaminants of interest. Oxygen and pulses of the primary substrate (methane or phenol) were then added to the extracted (contaminated) ground water prior to injection into the aquifer through the injection well. An automated, on-line data acquisition system was used to monitor CAH, primary substrate, and oxygen levels in the test zone. Details of these studies may be found in Semprini et al. (1990), and Hopkins et al. (1993a and 1993b). The rest of this presentation will focus on the ability of phenol utilizers to degrade TCE.

Figure 1 shows a vertical cross section of the test zone used for the study of TCE degradation by phenol utilizing microorganisms. Groundwater travel times from the injection well were approximately 4, 12, and 30 hours to the SSE1, SSE2, and SSE3 monitoring wells, respectively. Figure 2 plots normalized TCE concentration versus time at the three monitoring wells. In Figure 2, the phenol time-averaged injection concentration is 12.5 mg/L. TCE injection concentration was increased from 62 to 1000 mg/L over the 1000 hour period (see the top of Figure 2 for injection concentration at various times).

As may be seen, as long as the TCE concentration was less than 500 mg/L, TCE removal exceeded 90% by SSE3 (about one day travel time). An increase of TCE injection concentration to 1000 mg/L resulted in a decrease in removal efficiency to less than 80%. Figure 3 shows, however, that by increasing time-averaged phenol concentrations from 12.5 mg/L to 25 mg/L, TCE removals of 90% could be attained, even while injecting 1000 mg/L of TCE (Hopkins et al., 1993a).

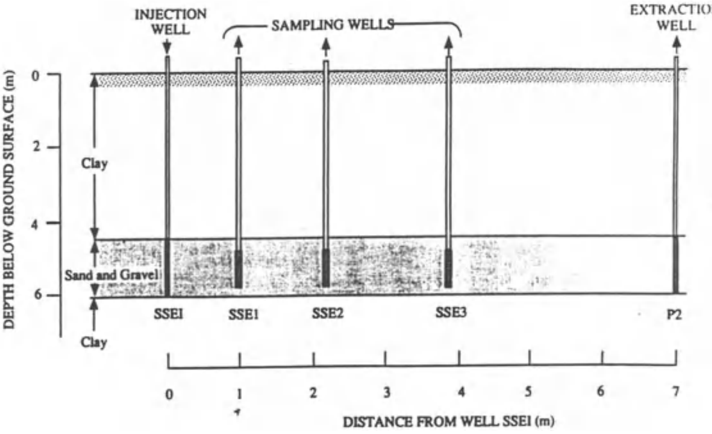


Figure 1 Vertical cross section of the Moffett NAS experimental site (Hopkins et al., 1993b).

Application of Moffett Field Results to a Full-scale Remediation

The Moffett Field results presented above have potential applications to the nation's efforts to remediate hazardous waste sites contaminated with CAHs. TCE is found at numerous hazardous waste sites, and, based on the Moffett results, appears to be susceptible to cometabolic degradation by microorganisms which utilize phenol as a primary substrate. As a next step, a full-scale demonstration of this technology to aerobically, cometabolically biodegrade TCE is being planned. An engineering question that must be answered prior to full-scale implementation of this technology is how best to mix the primary substrate, the oxygen source, and TCE, and subsequently get the mixture to the microorganisms.

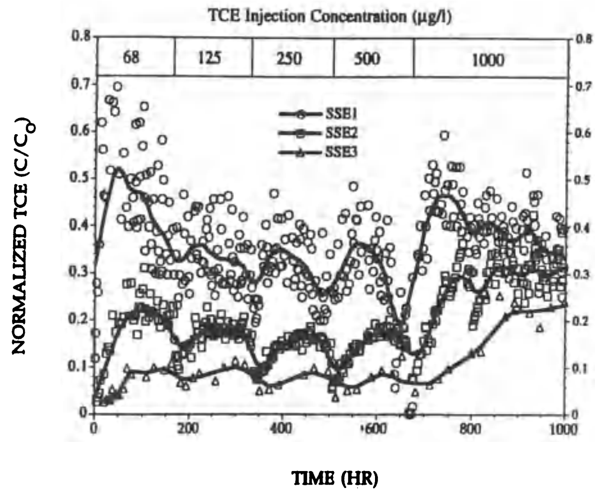


Figure 2
Normalized TCE concentration with time at 3 monitoring locations. Increasing TCE injection concentrations, constant phenol injection concentration (12.5 mg/L). (Hopkins et al., 1993a).

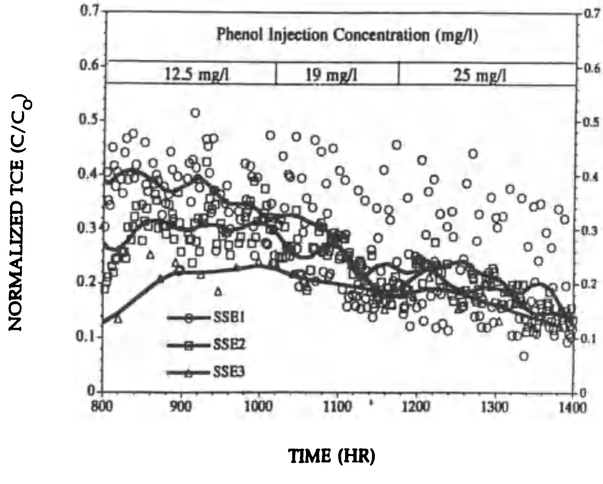


Figure 3
Normalized TCE concentration with time at 3 monitoring locations. Increasing phenol injection concentrations, constant TCE injection concentration (1000 mg/L). (Hopkins et al., 1993a).

At Moffett Field, mixing of these three components was accomplished above ground, with the mixture then introduced into the subsurface through an injection well. In a full-scale demonstration, the TCE will, of course, already be in the ground water. A major objective of the technology demonstration will be to investigate how a primary substrate and an oxygen source can be efficiently mixed and transported to indigenous microorganisms, in order to promote cometabolic degradation of TCE. For the demonstration, it is anticipated that a subsurface recirculation system, similar to that described by Herrling (1991) and McCarty and Semprini (1993), will be used. The remediation system, shown in Figure 4, will consist of two wells, each, screened at two depths. In operation, a submersible pump installed between the two screens would draw TCE contaminated water into the well at one screened interval. The primary substrate and oxygen will then be introduced into the water through feed lines, and the water, which now contains TCE, primary substrate, and oxygen, will be discharged into the aquifer from the second screened interval. In essence, an *in-situ* treatment zone will be created in the aquifer, around the discharge screens. Based on the Moffett Field results, this treatment zone is expected to cover an area within approximately one day's groundwater travel distance out from the well.

To help design the full-scale demonstration, preliminary modeling studies using a model which incorporates rate-limited sorption have been conducted. As may be seen in Figure 5, which compares contaminant concentrations at an extraction well for systems with and without *in-situ* biodegradation, significant reductions in contaminant concentration can be achieved by the bioremediation.

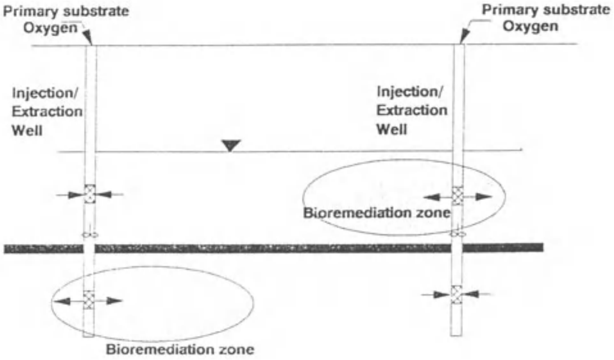


Figure 4 Dual recirculation well system concept for *in-situ* bioremediation

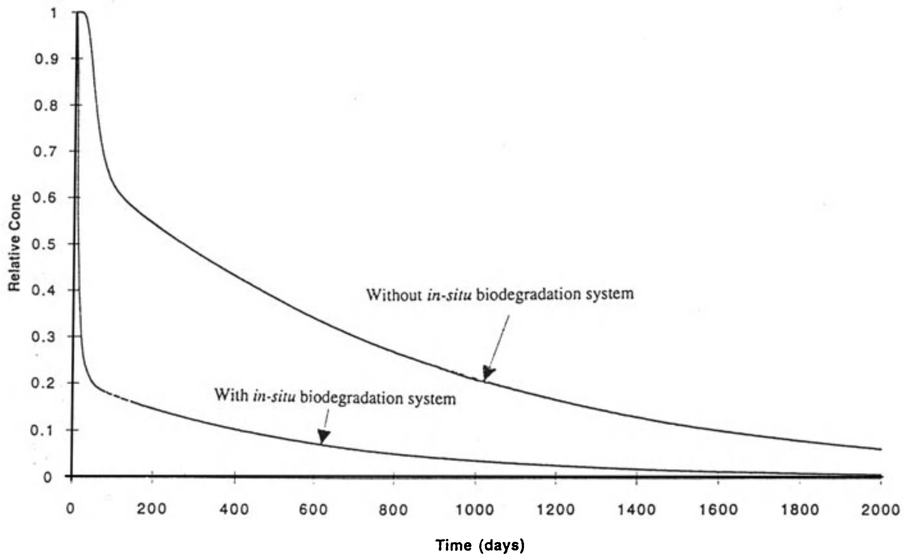


Figure 5 Simulated contaminant concentration at an extraction well for systems with and without bio degradation.

References

Ball, W.P. and P.V. Roberts. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. *Environmental Science and Technology, 25:*1237-1249.

Freyberg, D.L. 1986. A natural gradient experiment on solute transport in a sand aquifer. 1. Spatial moments and the advection and dispersion of nonreactive tracers. *Water Resources Research, 22:* 2031-2046.

Goltz, M.N. and M.E. Oxley. 1991. Analytical modeling of aquifer decontamination by pumping when transport is affected by rate-limited sorption. *Water Resources Research, 27:* 547-556.

Goltz, M.N. and P.V. Roberts. 1987. Using the method of moments to analyze three-dimensional diffusion-limited solute transport from temporal and spatial perspectives. *Water Resources Research, 23:*1575-1585.

Goltz, M.N. and P.V. Roberts. 1988. Interpreting organic solute transport data from a field experiment using physical nonequilibrium models. *Journal of Contaminant Hydrology, 1:*77-93.

Haggerty, R. and S.M. Gorelick. 1994. Design of multiple contaminant remediation: sensitivity to rate-limited mass transfer. *Water Resources Research, 30:* 435-446.

Herrling, B. 1991. Hydraulic circulation system for *in situ* bioreclamation and/or *in situ* remediation of strippable contamination. In *On-Site Bioreclamation,* R.E. Hinchee and R.F. Olfenbuttel, eds. Butterworth-Heinemann, Boston, pp. 173-175.

Hopkins, G.D., J. Munakata, L. Semprini, and P.L. McCarty. 1993a. Trichloroethylene concentration effects on pilot field-scale *in-situ* groundwater bioremediation by phenol-oxidizing microorganisms. *Environmental Science and Technology, 27:* 2542-2547.

Hopkins, G.D., L. Semprini, and P.L. McCarty. 1993b. Microcosm and *in situ* field studies of enhanced biotransformation of trichloroethylene by phenol-utilizing microorganisms. *Applied and Environmental Microbiology, 59:*2277-2285.

Keely, J.F. 1989. Performance evaluations of pump-and-treat remediations. *U.S. Environmental Protection Agency Report EPA/540/4-89/005,* R.S. Kerr Environmental Research Laboratory, Ada, OK.

Mackay, D.M., D.L. Freyberg, and P.V. Roberts. 1986. A natural gradient experiment on solute transport in a sand aquifer. 1. Approach and overview of plume movement. *Water Resources Research, 22:* 2017-2029.

McCarty, P.L. and L. Semprini. 1993. Ground-water treatment for chlorinated solvents. In *Handbook of Bioremediation,* R.D. Norris et al., eds. Lewis Publishers, Boca Raton, pp. 87-116.

Miller, C.T. and A.J. Rabideau. 1993. Development of split-operator Petrov-Galerkin methods to simulate transport and diffusion problems. *Water Resources Research, 29:* 2227-2240.

Rajaram, H. and L.W. Gelhar. 1991. Three-dimensional spatial moments analysis of the Borden tracer test. *Water Resources Research, 27:* 1239-1251.

Roberts, P.V., M.N. Goltz, and D.M. Mackay. 1986. A natural gradient experiment on solute transport in a sand aquifer. 3. Retardation estimates and mass balances for organic solutes. *Water Resources Research, 22:* 2047-2058.

Semprini, L., P.V. Roberts, G.D. Hopkins, and P.L. McCarty. 1990. A field evaluation of *in-situ* biodegradation of chlorinated ethenes. Part 2. Results of biostimulation and biotransformation experiments. *Ground Water, 28:* 715-727.

Sudicky, E.A. 1986. A natural gradient experiment on solute transport in a sand aquifer. Spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research, 22:* 2069-2082.

U.S. EPA. 1989. Evaluation of ground-water extraction remedies. *U.S. Environmental Protection Agency Report EPA/540/2-89/054,* Office of Emergency and Remedial Response, Washington, DC.

van Genuchten, M.Th. and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media. 1. Analytical solutions. *Soil Science Society of America Journal, 40:*473-480.

Prediction of Pollutant Transport in the Subsoil

Fritz Stauffer

Abstract

Modeling results of pollutant transport in the subsoil are presented for three studies. The first example shows the influence of heterogeneities in the hydraulic parameters of aquifers on the solute transport in ground water by using a stochastic simulation technique. The second example deals with the transport of aqueous solutions infiltrating into the subsurface and propagating in the capillary and the groundwater zones. The third study shows modeling results of the transport and biochemical transformation of organic and inorganic compounds in saturated soil columns.

Stochastic Modeling of Solute Transport in Heterogeneous Aquifers

The propagation of contaminant plumes in gravel aquifers is highly dominated by the heterogeneities of the hydraulic parameters, i.e., the hydraulic conductivity. The description of heterogeneities in natural gravel deposits in North-Eastern Switzerland (Rhine valley near Zurich) yielded statistical information on the coherent sedimentary structures of such aquifers. Unweathered outcrops in several gravel pits were investigated. Distinct sedimentary structures appearing as lenses and layers can be identified. Fig. 1 shows an example of detected sedimentary structures at the Hüntwangen pit.

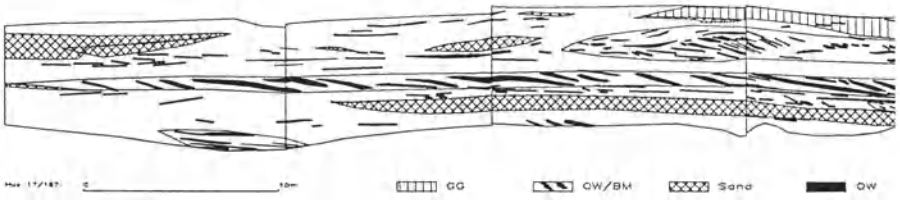


Figure 1 Sedimentary structures of natural gravel formations at the Hüntwangen pit (vertical section)

The observed sedimentary structures in fig. 1 were classified as grey gravel lenses (GG), open framework gravel lenses (OW), open framework/bimodal gravel-couplets (OW/BM), sand lenses (SA), brown gravel (BG), and alternate brown/grey gravel layers. The last two types are represented by the white background in fig. 1. GG is a sandy gravel with little silt; BG is a sandy and silty gravel; OW is a poorly graded coarse gravel practically without sand or silt; in BM gravel coarse sand is lacking. BG and GG represent a kind of background gravel where the lens type structures are imbedded.

OW/BM layers in the couplets are often inclined. A typical length scale of lenses is of the order of 1m for OW, 11m for OW/BM, and 5m for sand lenses.

The variability of the hydraulic properties of the different structures (hydraulic conductivity and porosity) was determined in the laboratory on the basis of disturbed and undisturbed samples. The data revealed large differences in hydraulic conductivity K between distinct structural elements (order of magnitude of K(mm/s): OW:100, SA:0.3, GG:0.1, BG:0.02). The probability density function of K could be approximated by two clearly separated lognormal distributions. On the other hand only a weak variability is present within single structural elements. A geostatistical analysis (indicator variograms) of the structural elements showed that these are essentially randomly located within the natural deposit (Jussel et al., 1994a).

The statistical information obtained was used to numerically generate distinct realisations of synthetic block size aquifers according to a Monte Carlo method. The lenses are approximated by an ellipse in the plan view and a power function in the cross section. The generated aquifers have the same statistical properties with respect to the hydraulic parameters as the investigated deposits. The generation process may be conditioned by the information of borehole data and/or of geophysical investigations in vertical profiles (Huggenberger et al., 1994). Numerical experiments of saturated flow and transport of conservative tracers were performed. For this reason a three-dimensional finite element flow model and a corresponding random walk transport model were developed. Ten unconditioned, stochastic, numerical transport experiments with synthetic gravel aquifers allowed the estimation of effective parameters as the effective hydraulic conductivity, the mean flow and tracer velocity and the effective macrodispersivity (e.g., apparent longitudinal macrodispersivity, fig. 2) of the investigated formation.

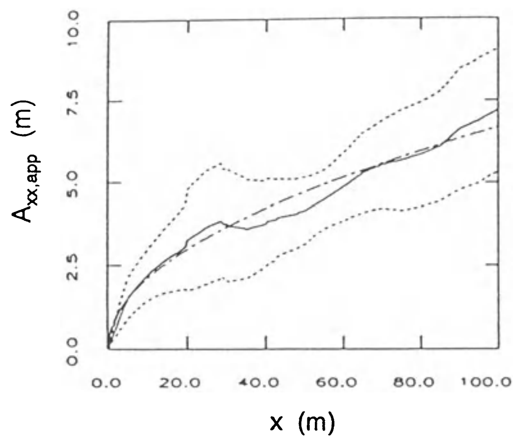


Figure 2

Stochastic simulation: Apparent longitudinal macrodispersivity values $A_{xx,app}$ of the tracer cloud (solid line) over flow distance x in numerically generated gravel aquifers, with 95% confidence interval (dotted line) and fitted empirical square root function (dashed-dotted line)

These estimated values were compared with estimates from stochastic theories. The simulated effective hydraulic conductivity values correspond well with Dagan's theory (Dagan, 1989). Deviations are apparent in the effective macrodispersivity values and their dependence on the transport distance. It is expected that the reason for the discrepancies mainly lies in the existence of the coherent sedimentary structures which cannot be completely described by a single covariance function of the logarithm of hydraulic conductivity (Jussel et al., 1994b).

Modeling of Solute Transport in Saturated-unsaturated Heterogeneous Soils

The infiltration of aqueous solutions into the subsurface initiates a solute propagation in the capillary domain towards the groundwater table and a subsequent transport in the groundwater zone. The processes involved are the non-steady water flow under unsaturated and saturated conditions including prevailing capillary effects (i.e., hysteresis effects) in the soil water characteristics, and the non-steady solute transport in both the unsaturated and the saturated zones. A two-dimensional experimental and numerical study was performed in order to investigate the relevant flow and tracer transport processes of non-reactive aqueous solutions and to test a mathematical-numerical simulation model (Stauffer and Dracos, 1986). The flow and transport in the laboratory experiment was induced by the local infiltration of a NaCl solution at constant rate through the surface of a layered sand packing (fig. 3). The parameters needed in the simulation were all determined with the help of independent experiments. The hydraulic conductivity values were 24mm/s in the fine layer, and 0.73mm/s in the coarse layer. The initial water distribution was obtained by lowering the water table from the top to a fixed outflow level and was given by a static profile. The infiltration rate was 0.08mm/s per unit surface area.

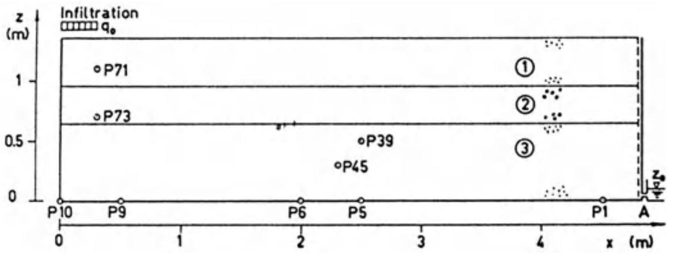


Figure 3
Infiltration experiment in sand box: lay-out; 1: fine layer, 2: coarse layer, 3: fine layer.

The non-steady two-dimensional mathematical model of the unsaturated flow is based on the Richards equation and is numerically integrated by the finite element method with a finite difference discretization in time. The non-steady tracer transport model accounts for the advective solute transport neglecting molecular diffusion, local dispersion, and chemical reactions using a particle tracking technique. The layering of the sand packing as well as hysteresis effects in the water content characteristics were taken into account. The measured and simulated relative solute concentrations over time at the outflow of the box are shown in fig. 4, together with measured relative concentrations at local stations.

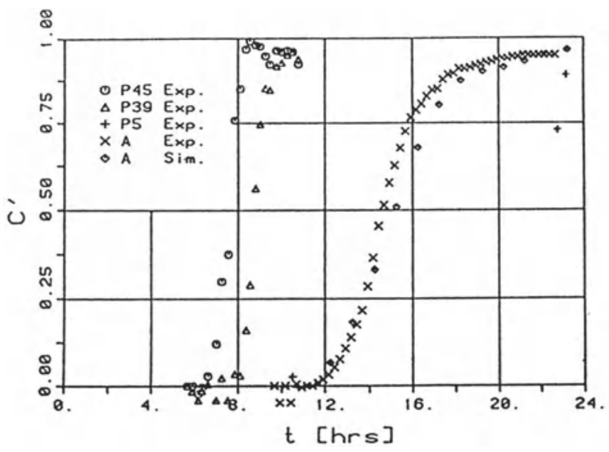


Figure 4
Infiltration experiment in sand box: Measured and simulated relative solute concentration C' over time t at the outflow; measured relative concentration at local stations.

The results show that the integral breakthrough curve of the solute is well explained by the model by only considering advection. It can be concluded that local dispersion only plays a minor role in the overall solute transport of the experiment.

Modeling of Groundwater Pollutant Transport With Biotransformation

Organic and inorganic compounds infiltrating into ground water may be subject to redox reactions catalyzed by bacteria. These bacteria tend to form conglomerates and to adsorb to the solid matrix. Assuming a biofilm concept, the processes in and near the biofilm, such as the supply of the substrates to the bacteria or the detachment of biofilm parts by shear force, are controlling factors for the microbial activity. A one-dimensional model for the transport of dissolved substances in groundwater-biofilm systems has been developed by Zysset et al. (1994a). This model conceptualises the microscopic transport processes by using a penetration factor approach to describe a diffusion limitation within the biofilm. As biological processes, the growth, the energy maintenance and the decay of the bacterial population are explicitly accounted for. The model consists of mass balance equations for the adhering bacteria, for the limiting substrate, and for the suspended bacteria thus describing a coupled kinetic transport system. The necessary biochemical parameters are the kinetic rate constants for bacterial growth, for decay, for bacterial adsorption and for bacterial energy maintenance, a parameter characterising the diffusion limitation of the substrate within the biofilm, and a stoichiometric coefficient. The model is formulated for one-dimensional flow fields and is numerically solved using an operator splitting technique. It uses the finite element method for calculating the transport part. The kinetic model part is numerically solved by a predictor-corrector scheme (Zysset et al., 1994a).

The model is able to reproduce the transport and the transformation of nitrate and sulfate in laboratory column experiments of von Gunten and Zobrist (1993) in which these substances served as dissolved electron acceptors in bacterially mediated redox reactions in connection with lactate. These experiments were designed to be a material model of a system where river water contaminated with organic compounds infiltrates into ground water. For this purpose, columns were filled with aquifer material. A synthetic river water containing an organic electron donor (lactate), inorganic electron acceptors and various trace elements were then pumped through these columns at a constant flow rate. The experiments were started by inoculating the columns with a small amount of corresponding bacteria. Nitrate reducing bacteria in the columns transform the inflowing nitrate to gaseous nitrogen and other nitrogen compounds. Sulfate on the other hand is reduced to sulfide. These bacteria simultaneously oxidise lactate. Apart from the bacteriologically mediated reduction, no other chemical reactions acted on nitrate or sulafate. We simulated the non-steady development of the nitrate and sulfate profile. Based on experimental observations of von Gunten and Zobrist (1993), we assumed that the growth of the nitrate and of the sulfate reducing bacteria is limited by the supply of one dissolved substrate, namely the nitrate and the sulfate, respectively. The simulated and the observed nitrate profiles are compared in Figure 5 (Zysset et al., 1994b).

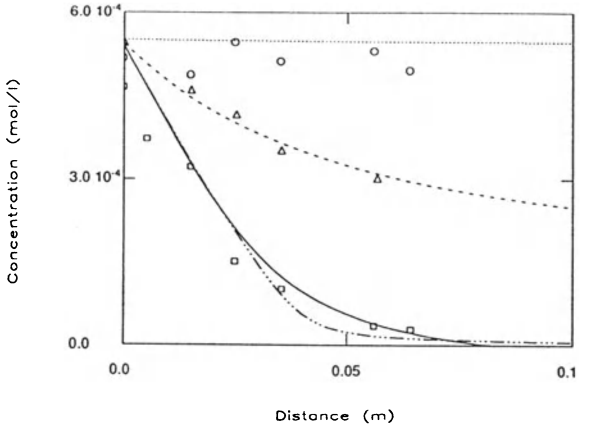


Figure 5
Pollutant transport-biotransformation system: Observed and simulated nitrate profiles at different time values (O: t = 0.2 d, Δ: t = 7d, □: t = 14 d in laboratory column (experimental data by von Gunten and Zobrist, 1993).

The figure shows a successful calibration of the nitrate reduction model. Based on the parameters obtained, the model was able to successfully predict the nitrate profile in an other column experiment (Zysset et al., 1994b). The sulfate profile could be simulated in a similar manner.

References

Dagan G. 1989. Flow and transport in heterogeneous formations. Springer.

Huggenberger P., M. Rauber, and F. Stauffer. 1994. Integration of geophysical and sedimentological information in the stochastic description of inhomogeneities in fluvial gravel deposits. Proc. IAHR Symposium on Transport and Reactive Processes in Aquifers, ed. by T. Dracos and F. Stauffer, p. 177-182, Balkema, Rotterdam.

Jussel P., F. Stauffer, and T. Dracos. 1994a. Transport modelling in heterogeneous aquifers: 1. Statistical description and numerical generation of gravel deposits. Water Resour. Res., in press.

Jussel P., F. Stauffer, and T. Dracos. 1994b. Transport modelling in heterogeneous aquifers: 2. Three-dimensional transport model and stochastic numerical tracer experiments. Water Resour. Res., in press.

Stauffer F., and T. Dracos. 1986. Experimental and numerical study of water and solute infiltration in layered porous media. J. Hydrology, 84, 9-34.

von Gunten U., and J. Zobrist. 1993. Biogeochemical changes in groundwater-infiltration systems: Column studies. Geochim. Cosmochim. Acta, 57:3895-3906.

Zysset A, F. Stauffer, and T. Dracos. 1994a. Modelling of chemically reactive groundwater transport. Water Resour. Res., in press.

Zysset A., F. Stauffer, and T. Dracos. 1994b. Modelling of reactive transport governed by biodegradation. Accepted for publ. in Water Resour. Res.

Optimizing Groundwater Remediation Including Weighted Feedback for Incorporating Model Uncertainty

Christine A. Shoemaker, Gregory J. Whiffen, and Jeanine A. Denu

Abstract

The «Nonlinear Weighted Feedback Method» for addressing uncertainty has been presented by the authors in Water Resources Research in September 1993. This paper will present extensions of this method to more complex problems in groundwater remediation. The examples consider

a) a much larger range of uncertainty in parameter values,

b) multiple types of uncertainty, and

c) the use of feedback in conjunction with parameter updating and re-optimization. The numerical results indicate weighted feedback generates an exceptionally robust strategy over a very wide range of error and uncertainty.

Introduction

Groundwater remediation is very expensive because of the cost of well construction, treatment for contaminant removal, and energy cost for pumping contaminated water out of the ground. Environmental consultants frequently use mathematical models flow and contaminant transport to evaluate the benefits of alternative schemes for well location and pumping rates. By simulating each scheme with the model the cost and impact on contaminant concentration can be evaluated. However, for a complex site there can be an enormous number of alternative schemes that are possible and hence trial and error simulation is not feasible for all alternatives. A feedback law is an algorithm for modifying system control as a function of the difference between predicted and observed conditions. In our analysis, the feedback law generated by a constrained Differential Dynamic Programming algorithms with penalty functions is used as a basis of feedback laws.

Whiffen and Shoemaker (1993) introduce the «weighted nonlinear feedback» method for control of groundwater remediation under uncertainty. It is the purpose of this paper to summarize extensions of this earlier work. Full detail about the extensions, including figures for numerical results can be found in Whiffen, Denu, and Shoemaker (1994 in preparation). This research has grown out of related work by our group including Chang et al. (1992) and Culver and Shoemaker (1992 and 1993).

Optimal Control Problem Formulation

Optimal policies were calculated to solve the following constrained optimal control problem,

$$J = \min_{u_t} \sum_{t=1}^{N} g^t(x_t, u_t) \qquad \textit{Cost} \qquad (1)$$

where x_t is a state vector of dimension n containing the head and concentration at each active node of the finite element mesh at time step t, u_t is a control vector of dimension m containing the pumping rates at each potential remediation well at time t, and $g^t(x_t, u_t)$ is the cost incurred at time t due to state x_t and control u_t. The total number of decision time periods is N. The cost function can be any nonlinear twice differentable function of x_t and u_t. The minimization is constrained by the finite element model's prediction of the state of the aquifer at a future time step given the control and state at the current time step,

$$x_{t+1} = T^t(x_t, u_t) \qquad t = (1,2,\ldots,N\text{-}1) \qquad \textit{Transition Function} \qquad (2)$$

where the function T is composed of matrices generated by the finite element model for each time step t. The initial state of the aquifer before any remediation is

$$x_{t=1} = x_o \qquad \textit{Initial Condition} \qquad (3)$$

Further constraints were added to ensure only extraction is allowed at each withdrawal site (this is optional), to ensure total pumping at each time step does not exceed waste removal treatment capacity U_{max}, and to ensure a water quality standard $C_{standard}$ is met at all observation wells by the final time step, $t = N$:

$$u_t \leq 0 \qquad t = (1,2,\ldots,N) \qquad \textit{Extraction only} \qquad (4)$$

$$-\sum_{Wells\ i} u_t(i) \leq U_{max} \qquad t = (1,2,\ldots,N) \qquad \textit{Treatment Capacity} \qquad (5)$$

$$c(x_{t=N}) \leq C_{standard} \qquad t = N \qquad \textit{Drinking Standard} \qquad (6)$$

The function $c(x_{t=N})$ represents the concentration at each observation well at the final time step, N. The constrained optimal control problem, (1) through (6), can be approximated by an unconstrained optimal control problem by introducing a penalty function into the objective function.

Differential Dynamic Feedback Laws

Once optimal policies are established for estimated parameter values, feedback laws can be generated using the optimal solution. DDP generates a feedback law during each iteration and uses this feedback law to establish an improved policy. The feedback law generated by DDP will always result in the optimal policy when applied if the system dynamics are linear and the objective to be minimized is quadratic in x and u. The form of the feedback law generated by DDP is

$$u_t^{act} - \bar{u}_t = \delta u_t = \beta_t \delta x_t + \alpha_t, \qquad \text{where } \delta x_t = x_t - \bar{x}_t \tag{7}$$

The term u_t^{act} is the policy that is implemented under feedback and $\bar{u}_t$ is the optimal policy. The term $\delta x_t = x_t - \bar{x}_t$ is the vector difference between the current observed state x_t after applying (7) from time step 1 to t-1, and the predicted state $\bar{x}_t$. The term β_t is an mxn matrix and a_t is an m-vector which are both functions of the first and second derivatives of $T^{t'}$, $g^{t'}$, and $Y^{t'}$ with respect to $x_{t'}$ and $u_{t'}$ where $t' \varepsilon \{t, t+1, ..., N\}$. At the optimum α_t is zero for all t. For a description of the DDP algorithm including the calculation of β_t and α_t appearing in (7) see Whiffen and Shoemaker (1993).

Modeling Uncertainty

In our previous analysis we developed feedback policies that are robust under a range of uncertainty. In particular, in Whiffen and Shoemaker (1993) we associated with 10 possible weights on 270 aquifer realizations, drawn from 9 probability distributions. Based on this analysis a feedback law (#9) was selected.

In our current analysis we test feedback law (#9) against more difficult error conditions: error in initial concentration (not previously considered) and a much wider range of error in hydraulic conductivity error in bias and standard deviation. Conductivitiy uncertainty was modeled by generating inhomogeneous isotropic conductivity fields from a long-normal distribution using the spectral method. The correlation distance was chosen as 100 meters.

Uncertainty in initial pollution conditions was modeled by generating «excess» pollution, which is randomly added to the initial, assumed contamination distribution. Excess pollution was modeled in three ways:

a) normally distributed,

b) concentrated clumps, and

c) small, distributed clumps,

The earlier Whiffen and Shoemaker (1993) paper did not consider uncertainty in initial pollution distribution.

Numerical Results

The numerical results indicate that the feedback policy performs much better than the deterministic policy without feedback. The figures describing these results are in Whiffen, Denu, and Shoemaker (in preparation). These figures show that the performance index (which includes cost functions and constraint violations) increases rapidly for the no feedback policy with increases in all types of error considered (bias and standard deviation in conductivity; the three types of error in initial contamination concentrations). By contrast the feedback policy performs well over the entire range of error, with relatively small increases in the performance index as error increases. It should be recalled that the feedback law used here was selected based on a realatively small range of error considered in Whiffen and Shoemaker (1993) however, it performed very well on a wide range of error.

Conclusions

There is a great deal of parameter uncertainty in charaterizing aquifers and this affects the way in which we should approach the use of models to design aquifer remediation programs. Our numerical results indicate that Nonlinear Weighted Feedback is an effective way to generate pumping strategies that will be robust in the face of large errors in the mean and variance of both hydraulic conductivity and initial concentration distribution. In all the cases we tested we found that the feedback did remarkably well in minimizing the increase in performance index due to increases in error.

References

Chang, L.-C., C.A. Shoemaker, and P.L.-F. Liu. 1992. Application of a constrained optimal control algorithm to groundwater remediation. Water Resour. Res. **28** (12), 3157-3173

Culver, T. and C.A. Shoemaker. 1992. Dynamic optimal control for groundwater remediation with flexible management periods. Water Resour. Res. **28** (3), 629-641.

Culver, T. and C.A. Shoemaker. 1993. Optimal control for groundwater remediation by differential dynamic programming with quasi-Newton approximations. Water Resour.Res. **29** (4), 821-831.

Whiffen, G.J. and C.A. Shoemaker. 1993. Nonlinear weighted feedback control of groundwater remediation under uncertainty. Water Resour. Res. **29** (9), 3277-3289.

Whiffen, G.J. , J.A. Denu, and C.A. Shoemaker. 1994. A test of nonlinear weighted feedback control of groundwater remediation under uncertainty. Water Resour. Res. in preparation.

Geochemical Problems in Nuclear Waste Disposal

Horst Geckeis, Jae-Il Kim

1. Introduction:

The worldwide use of nuclear energy generates yearly considerable amounts of fission products and transuranium elements. The heat producing high level waste will be deposited in deep geological formations (Kim, 1993). Nuclides relevant for long-term safety assessment are transuranium elements and long-lived fission products like Tc-99, I-129 etc.. The safety of high level waste disposal in geological formations is determined by the effectiveness of individual barriers isolating radioactive waste from the biosphere. A distinction is made among the following barriers:

- the **engineered** barrier, which consists of the packaging material and the waste form itself;
- the **geotechnical** barrier, which consists of the backfill materials, being used to fill the remaining cavities in the repository;
- the **geological** barrier, which consists of the geological formations surrounding the repository.

Fig. 1 illustrates the production and decay of radionuclides within 10^7 years after discharge from a light water reactor (Lewi et al., 1990). Their radiotoxicity is expressed as ALI (annual limit on intake by workers, normalized to 1 GWe · year) and given for direct storage and disposal after fuel reprocessing.

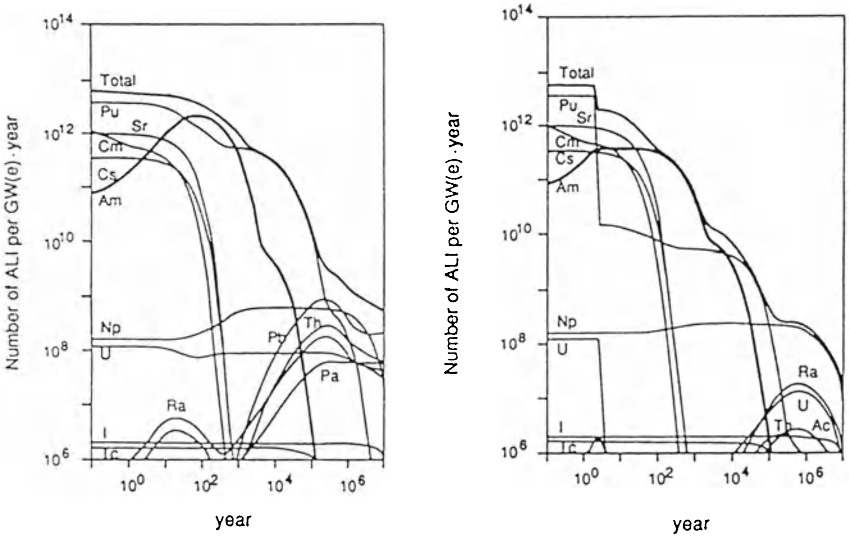
The amounts of Pu and U are reduced by two orders of magnitude after fuel reprocessing. But in both cases the main contribution to the radiotoxicity, after the decay of most fission products, comes from transuranium elements. The effectiveness of the barriers must be guaranteed over a period of many thousands of years until the radiotoxicity of the waste has dropped to a level comparable to that of an uranium mine.

Localized safety problems involved in each repository site are under intensive investigation in many countries. This includes the chemical and migrational behavior of actinoids and fission products in the near field as well as in the far field of the repository. The latter is represented by the geological surrounding of the disposal site including aquifer systems. The present paper describes the processes leading to a release of radionuclides from the nuclear repository and retardation processes focusing on the migration behavior of transuranium elements in natural aquifer systems.

2a. Chemical Interactions of Radionuclides in the Near Field of a Nuclear Repository

For obvious reasons water represents the main transport medium for radionuclides. Therefore, the dissolution of the waste form - either highly active glass or spent fuel -

will be the first step of mobilizing actinoids and fission products. The dissolution behavior is influenced by the chemical medium of the given ground water penetrating into the repository, temperature and radiation effects. The possible chemical and geochemical processes occurring in a nuclear repository are visualized in fig. 2.



Decay after discharge from LWR without reprocessing

Decay after discharge from LWR with reprocessing

Figure 1
Radioactivities of various elements normalized to ALI (annual limits on intake by workers), generated from the production of 1 GWe • year in a light water reactor and their decay processes.

The solubility of actinoids will be influenced by the presence of carbonate or other aquatic complexing anions in ground water. Radiolysis is considered to generate oxidizing conditions and to decrease pH-values in brine solutions. This creates a rather aggressive medium which might effectively increase the solubility of radionuclides, especially of transuranium elements. Under alpha radiolysis conditions, transuranium ions are oxidized to Pu(VI) (Büppelmann et al., 1988), Np(VI) (Fukusawa et al., to be published) and Am(V) (Magirius, 1985). The dissolution behavior of vitrified waste is considerably accelerated in brines containing Mg, due to formation of Mg-silicates and simultaneous decrease of pH (Lutze and Grambow, 1992). Formation of polynuclear species is known for transuranium elements and can as well lead to a higher solubility and mobility of these nuclides.

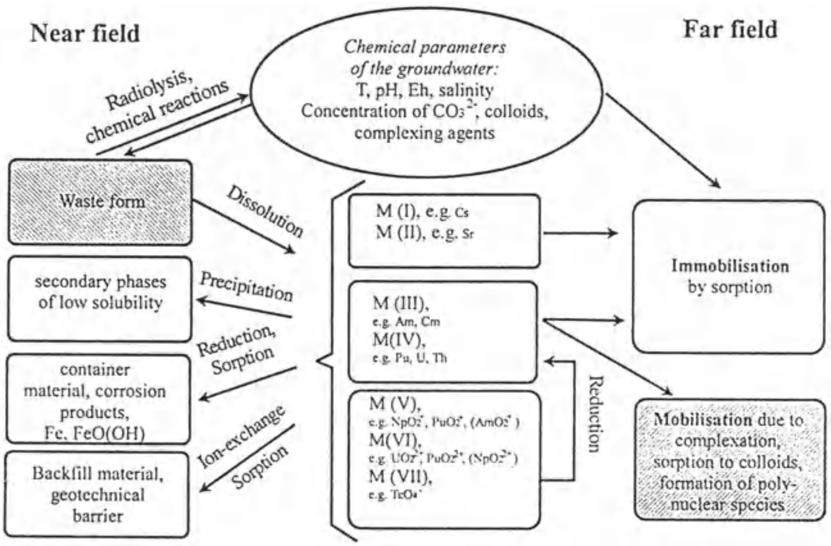


Figure 2
Possible chemical interactions of radionuclides in the near and far field of a nuclear repository.

Processes that may lower the solubility of actinoids and other radionuclides in the near field are:

a) Formation of secondary solid phases, which have been observed in the case of glass dissolution in brines. Powellites, coffinite and cerianite are assumed to act as host phases for radionuclides, thus immobilizing them (Lutze and Grambow, 1992). Schoepite is found to be generated as a secondary phase in the case of spent UO_2 fuel dissolution, which is possibly to control the solubility of at least uranium in solution.

b) Reduction and/or sorption of radionuclides by container corrosion products. A prerequisite for the dissolution of nuclear waste is the failure of container materials and the subsequent entrance of ground water. Corrosion of container materials, which consist mainly of iron, will always produce hydrated iron oxides and additionally generate a reducing medium. Hydrated iron oxides are known for their adsorptive properties due to their large surface. The reducing medium might transfer fairly soluble radionuclides to oxidation states of which their solubility under given conditions is much lower: e.g. Pu(V) ---> Pu(IV), Pu(III); Np(V) to Np(IV) and Tc(VII) to Tc(IV). Fig. 3 shows the dissolution behavior of radionuclides in the presence of iron in saline solution, which is in contact with spent fuel. The concentration of Cs appears very high demonstrating the high mobility of this nuclide in the considered system.

c) Sorption of radionuclides onto backfill material. Besides container corrosion materials many more surfaces can be made available in the near field of the repository, which will sorb radionuclides thus immobilizing them. Such an effect can be enhanced by the construction of so-called «intelligent» or «geotechnical» barriers. Use of hydroxy apatite or bentonite is discussed as a backfill material, both of which have pronounced sorption properties.

Up to now, most of the individual processes mentioned above are not fully understood for all relevant nuclides. Hence, the development of geochemical models for the migration behavior of radionuclides is always affected by large uncertainties. Problems arise from the lack of well verified thermodynamic data for radionuclides under near field conditions (e.g. high concentrated brine solutions, high temperature, and multicomponent systems).

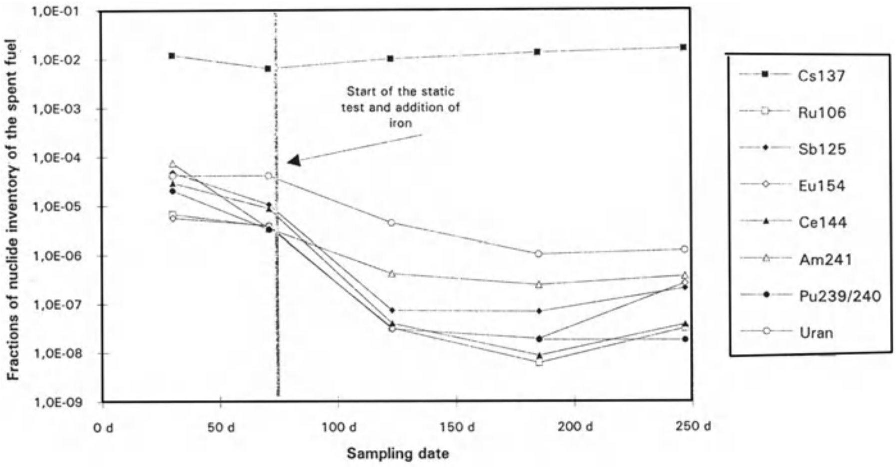


Figure 3
The behavior of radionuclides in the presence of iron powder in 5 M NaCl-solution. The solution is in contact with a spent fuel pellet under anaerobic conditions. After two washing steps, where the solution has been totally exchanged, iron powder was added. During the subsequent static test the dissolved radionuclides accumulated in solution.

2b. Chemical Interactions of Radionuclides in the Far Field of a Nuclear Repository

Due to the importance of transuranium elements as possible long-term environmental contaminants, their chemical behavior in natural aquifer systems has been investigated with particular attention. If radionuclide species migrate from the near field, the geochemical conditions in the surrounding aquifer system determine their chemistry as follows:

- The solubility for all transuranium ions with oxidation states +3, except pentavalent actinyl ions, remains far below 10^{-6} mol/l. This is due to the neutral medium (pH = 4-9) of natural ground waters, which favors hydrolysis of highly charged transuranium ions. Additionally, sorption of these species occurs on nearly every mineral surface.

- Of special importance is the presence of complexing anions in natural water, e.g. carbonate, humate/fulvate ions. They are able to stabilize highly charged cations in solution and prevent their retention in the geosphere, as can be derived from the analysis of actinide homologues in various ground waters. Fig. 4 shows the dependence of naturally occuring trace element concentrations of oxidation states > 3+ on the DOC (=dissolved organic carbon) concentration (Kim et al., 1987). As DOC in these ground waters consists of humic and fulvic acids, the complexation of trace metal ions is evident and results in a strong correlation of dissolved trace metal ions with the DOC concentration.

- All natural ground waters contain colloids, originating from degradation of organic material, weathering of minerals, microorganisms or hydrolysis of metal ions. The concentration of colloidal particulates in ground water varies, depending on geochemical nature, from 10^8 to 10^{17} particles per liter. Their size ranges from < 30 nm to 450 µm. Beside the formation of so called «real colloids», where hydrolyzed radionuclides aggregate to polynuclear species, the sorption of actinoid ions to natural colloids («pseudocolloids») appears to be of cardinal importance for the migration behavior of these elements. Experiments reveal that a large fraction of transuranium ions spiked to natural groundwater samples can be separated from solution by ultrafiltration (fig.5) (Kim et al., 1989). In fig. 5 the «solubility» of $Am(OH)_3$ is shown in two different ground waters. Gohy 2122 is saline and the generation of large sized colloids is supressed by high ionic strength. But even there it can be seen that more than 68 % of Am in solution is sorbed on small colloids with diameter < 5 nm. The dissolved Am species in the groundwater sample Gohy-1061 with low salinity and high content of natural colloids are found to be exclusively pseudocolloids. These results indicate the relevance of pseudocolloid formation of transuranium ions, especially when ground water contains colloidal humic substances.

- Due to the wide Eh and pH range of ground waters, the complex redox chemistry must be considered, which strongly determines the geochemical behavior of actinoids. Pu can be expected to exist as tetra-, penta- and hexavalent ions under groundwater conditions. The pentavalent species might be the most stable, due to its stability towards hydrolysis, in contrast to the tetra- and hexavalent ions. But according to different geochemical conditions of groundwater systems, the stability of the oxidation state may change.

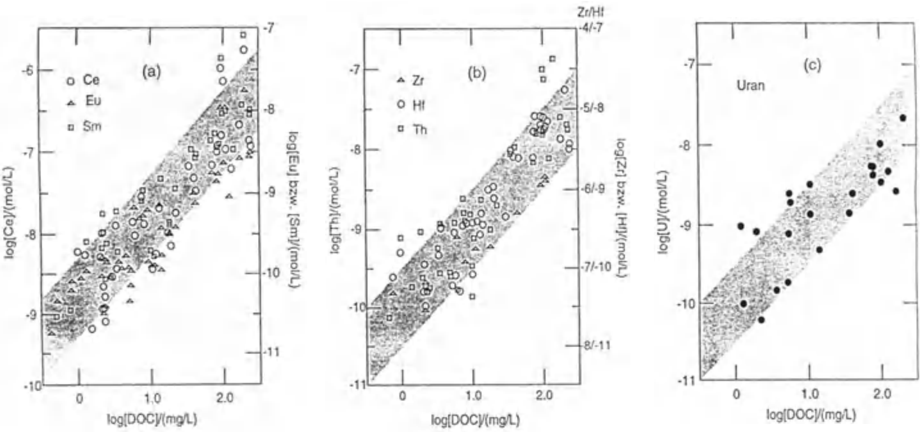


Figure 4

Natural concentrations of trace elements of oxidation states III (a), IV (b) and IV/VI in ground waters (originating from the planned German repository site Gorleben) as a function of the DOC (dissolved organic carbon) concentrations. DOC is composed of humic/fulvic acids.

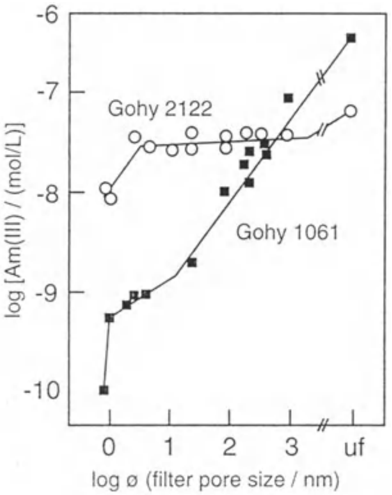


Figure 5

Solubilities of Am-241 hydroxide in ground waters containing humic colloids (originating from the planned German repository site Gorleben: Gohy-1061 is non-saline, Gohy-2122 contains 2.5 M NaCl), as determined after ultrafiltration through various sizes of pores from unfiltered (uf) down to 1 nm (Kim et al., 1989).

3. Conclusions

Safety considerations on nuclear energy must include the long-term safety aspects of nuclear waste disposal as a back-end of the fuel cycle. It is assumed that fission products and transuranium elements may undergo immobilization either in the near field or in the far field of a nuclear waste repository in deep geological sites. The evaluation of migrational trace concentrations of radionuclides and relevant pathways requires better understanding of their geochemical behavior. Research has to be concentrated on the quantification of geochemical processes in the surrounding of a nuclear repository to allow more comprehensive understanding and, moreover, to facilitate geochemical modeling of the radionuclide migration. Laboratory designed experiments cannot match all details of the reality, therefore experiments have to be carried out in systems which are as close as possible to reality. This requires the development and application of sensitive analytical methods to get straightforward information about the chemical species of nuclides generated in natural systems even at lowest concentrations.

References

Kim, J.I. 1993: The Chemical Behavior of Transuranium Elements and Barrier Functions in Natural Groundwaters. Mat. Res. Soc. Symp. Proc. **294**, 3-21.

Lewi, J., Izabel, C., Kaluzny, Y. 1990: Safety Assessment of Radioactive Repositories, OECD, Paris.

Büppelmann, K., Kim, J.I., Lierse, Ch. 1988: The Redox-behaviour of Plutonium in Saline Solutions Under Radiolysis Effects. Radiochim. Acta **44/45**, 65.

Fukusawa, K., Lierse, Ch., Kim, J.I. to be published.

Magirius, S., Carnall, W.T., Kim, J.I. 1985: Radiolytic Oxidation of AM(III) to AM(V) in NaCl Solution. Radiochim, Acta **38,** 29.

Lutze, W., Grambow, B. 1992: The Effect of Glass Corrosion on Near Field pH. Radiochim. Acta **58/59**, 3.

Kim, J.I., Buckau, G., Zhuang, W. 1987: Humic Colloid Generation of Transuranic Elements in Groundwater and Their Migration Behaviour. Mat. Res. Soc. Symp. Proc. **84**, 747.

Kim, J.I., Buckau, G., Rommel, H., Sohnius, B. 1989: The Migration Behaviour of Transuranium Elements in Gorleben Aquifer Systems: Colloid Generation and Retention Process. Mat. Res. Soc. Symp. Proc. **127**, 849.

Chemical Reactions of Organics

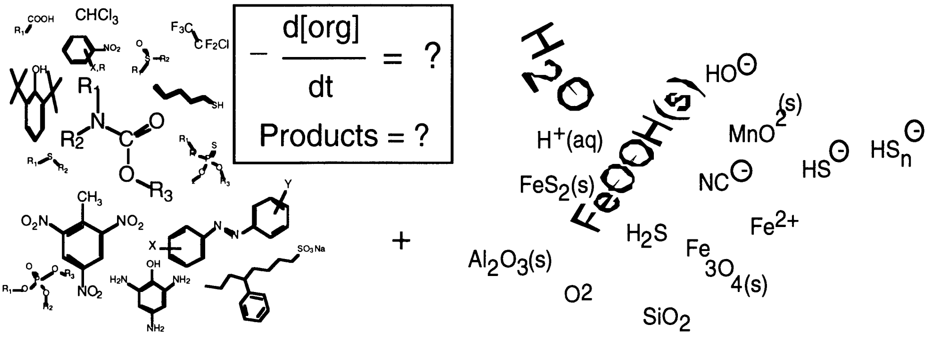
Werner Angst and René P. Schwarzenbach

Abiotic (chemical) reactions of organic pollutants in soils and aquifers are important for several reasons. On the one hand, unlike microbial degradation, chemical transformations of a given pollutant does never lead to the mineralization of the compound. In fact, numerous reactions, particularly redox reactions of organic pollutants, may lead to products that are of considerable (eco)toxical concern (Macalady et al., 1986). On the other hand, in certain cases, products may be formed that are more easily biodegraded, or that may undergo reactions with soil constituents to form so-called «bound residues» (Bollag, 1992). Furthermore, in heavily contaminated subsurface environments, chemical reactions involving organic pollutants may have a significant impact on biogeochemical processes, in that species are formed that influence microbial activity (Heijman et al., 1994). Therefore, knowledge on the mechanisms and rates of chemical reactions of organic pollutants in the subsurface are of great interest, both for assessing the risks and hazards associated with pollution of soils and aquifers by organic compounds, as well as for *in-situ*, on-site or off-site remediations of contaminated sites.

The most important chemical transformations of organic pollutants in soils and aquifers can be grouped into two major types of processes: **reactions with nucleophiles** (including elimination reactions) and **redox reactions**. Reactions with nucleophiles, particularly hydrolysis, have been investigated extensively in homogeneous aqueous solution, and quantitative structure-reactivity relationships for prediction of reaction rates have been established for various classes of compounds (Schwarzenbach et al. 1993; Chapter 12). Much less data is, however, available on surface catalyzed reactions. It has been demonstrated (Torrents and Stone, 1991) that certain mineral surfaces (e.g. FeOOH, TiO_2) may significantly enhance the hydrolysis of organic compounds that are capable of forming bidentate complexes with metal centres. The present knowledge about such catalysis does, however, not allow to derive general concepts for describing the kinetics of such surface mediated reactions. Obviously, as is the case with any heterogeneous reaction in complex systems such as subsurface environments, it is very difficult (if not impossible) to quantify the relevant reactive surface sites. Furthermore, it also has to be taken into account that a given organic compound competes for such sites with many other water constituents (see, e.g. Torrents and Stone, 1993 a and b).

An even more complicated situation is encountered in the case of redox reactions. Such reactions include e.g. the oxidation of phenols (e.g. Ulrich and Stone, 1989) and anilines (Laha and Luthy, 1990), reductive dehalogenation of polyhalogenated alkanes (e.g. Li and Wackett, 1993), reduction of nitroaromatic compounds (Schwarzenbach et al., 1990; Agrawal and Tratnyek, 1994) as well as azo compounds (Weber and Wolfe, 1987).

In this paper, a few general statements illustrated by some examples will be made to demonsrate the problems and difficulties encountered when trying to assess the pathways and kinetics of chemical reactions of organic pollutants in the environment.



The problem(s):

A given organic compound may undergo various different reactions. Each reaction exhibits different activation energy (T-dependency)

- The relative importance of a given reaction depends on the «concentrations» of the reactants (solutes, solid surface sites) and on temperature.
- Example 1: the hydrolysis half-lives of some carboxylic acid esters as a function of pH at 25°C (Fig. 1).
- At different temperatures there may be different product distributions.

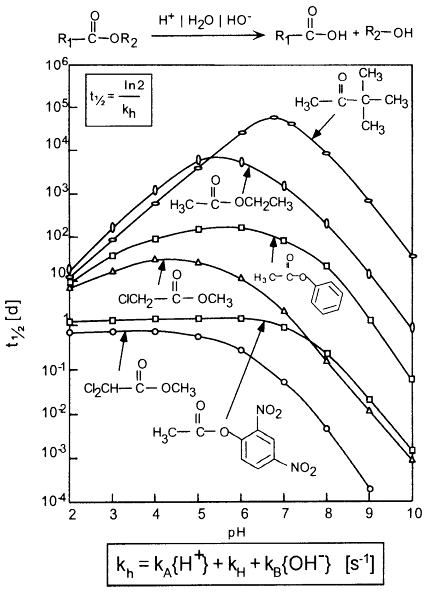
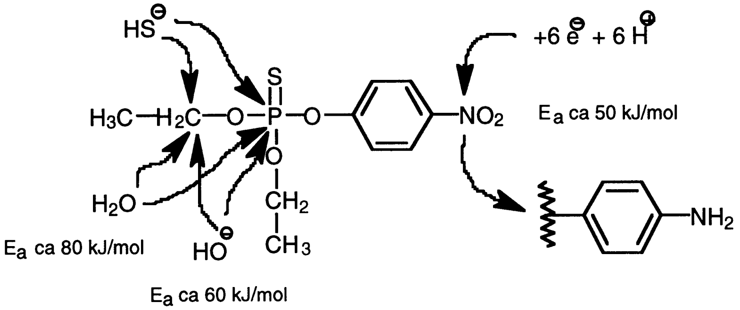


Figure 1
The hydrolysis half-lives of some carboxylic acid esters as a function of pH at 25°C

Example 2: Reaction pathways of parathione



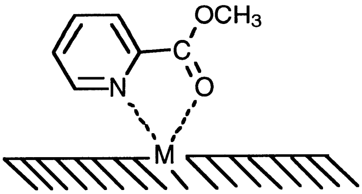
t› (distilled water, pH 7, 25°C) = 89 days

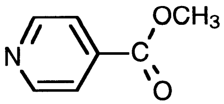
t› (anaerobic soils, sediments, pH 7-8, 20-25°C) = seconds to minutes

> The relative importance of a given reaction may be influenced by competitive effects.

Example:

surface catalyzed hydrolysis of methyl picolinate; competition with phosphate.





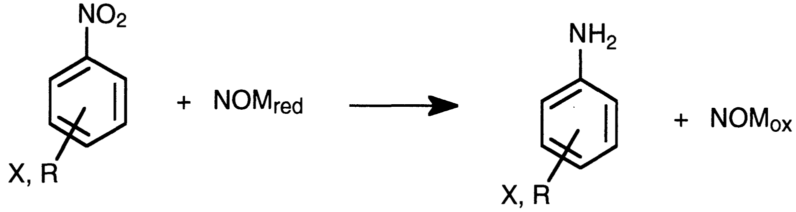
no surface catalysis observed

Surface catalysis observed, but decreases with increasing concentrations of phosphate in solution.

> Reaction rates of «structurally closely related» compounds may vary by orders of magnitude due to
>
> - Electronic and steric effects of substituents (1)
> - Different reaction mechanisms (2)
> - Catalysis (see example above)

Examples:

(1) Reduction of substituted nitrobenzenes by reduced NOM species



The reaction constants cover a range of several orders of magnitude. A correlation can be made. Under the conditions used (NOM, 5mM H_2S, pH 7.5) the half-lives of the compounds vary from ten hours to about 15 years (Fig. 2).

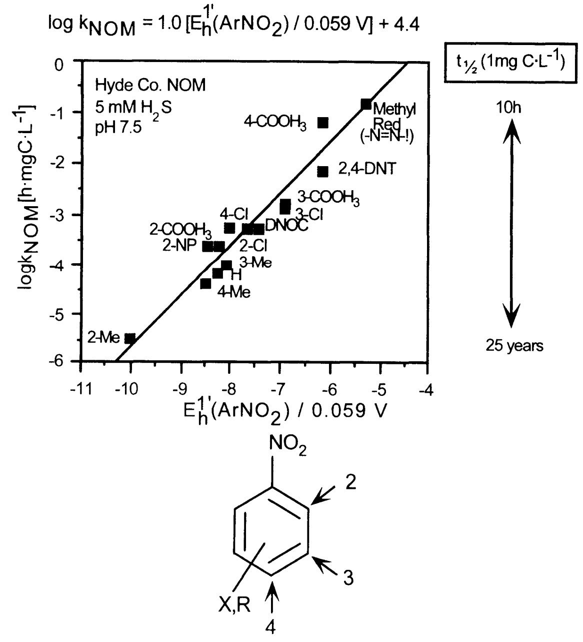
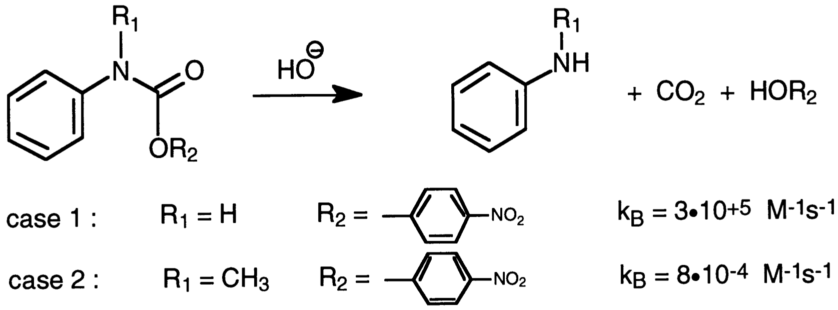


Figure 2
The half-lives of the compounds under the conditions used (NOM, 5mM H_2S, pH 7.5).

(2) Base catalyzed hydrolysis of a series of carbamates:



Although in both cases the carbamate function is hydrolyzed by a base catalyzed reaction, due to different reaction mechanisms, the observed hydrolysis constants differ by several orders of magnitude!

These examples raise then the question: What is «structurally closely related»?

For a given type of reaction, the relative reaction rates within a series of «structurally closely related» compounds may vary significantly between

- different (environmental) systems
- different rate determining step(s)
- different «speciation» of the compounds

Example: Reduction of substituted nitrobenzenes in three different environments (Fig. 3)

The first part of the figure shows a plot of log k_{NOM} versus $[E(ArNO_2)/0.059\ V]$ for monosubstituted nitrobenzenes in aqueous solutions of Hyde County NOM at pH 7.5 and 5 mM H_2S. The regression line log $k_{NOM} = 1.0[E(ArNO_2)/0.059\ V] + 4.4$ is the result of a linear least-squares fit (adapted from Dunnivant et al., 1992). The second part of fig. 3 shows a plot of log k_{FeP} versus $[E(ArNO_2)/0.059\ V]$ for the same monosubstituted nitrobenzenes. Note that the slope is only ca 0.5 in this regression indicating that the formation of a precursor complex is a rate limiting step in the transfer of the first electron.

The diagram in the third part of fig. 3 shows the reduction of the same nitrobenzenes in a laboratory column system containing aquifer materials from the banks of a river-ground water site. For a given sediment column and equal conditions the apparent zero-order rate constants, k_{obs}, are virtually all the same. This finding indicates that neither precursor complex formation nor electron transfer between reductants and substrates was rate limiting.

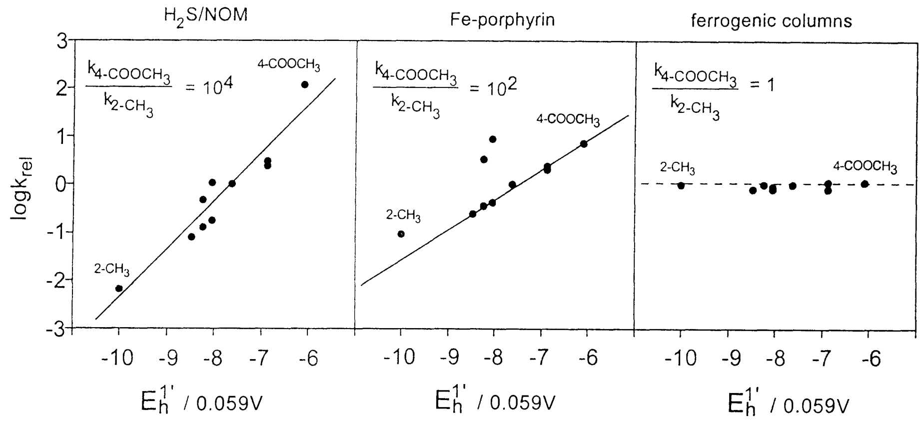


Figure 3
Reduction of substituted nitrobenzenes in three different environments.

Particularly for redox reactions of organic pollutants it is often difficult

- to assess whether a reaction occurs purely abiotically, whether it is catalyzed by microorganisms, or whether abiotic and biological processes play a role.
- to identify and to quantify the natural electron donor(s) or acceptor(s) involved in the reaction.
- to derive appropriate rate laws (especially in heterogeneous systems)

The natural reactants may be intimately coupled to microbial processes (fig. 4). An apparent abiotic process is governed by the conversion of organic material (indicated as CH_2O) to CO_2. This can be even more complex in sulfate reducing environments.

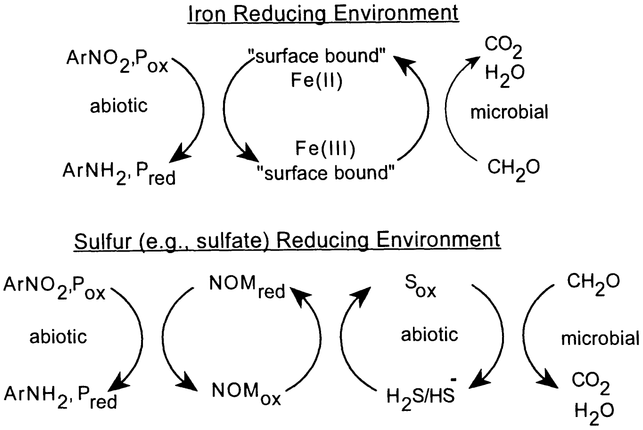


Figure 4 The natural reactants coupled to microbial processes.

Even within a series of structurally closely related compounds, the relative importance of abiotic vs. biological transformation may vary significantly. Chemically very reactive compounds tend to react with their environment (hydrolysis, reaction with nucleophiles) before microorganisms can degrade them. Because the growth of the organisms and the development of the degradative systems takes some time, the probability of biological transformation (which works very well with chemically nonreactive compounds) increases with decreasing reactivity.

References

Agrawal, A., & Tratnyek, P. G. (1994). Abiotic remediation of nitro-aromatic groundwater contaminants by zero-valent iron. *Extended abstract, ACS, San Diego, CA., 34,* 492-494.

Bollag, J.-M., Myers, C. J., & Minard, R. D. (1992). Biological and chemical interactions of pesticides with soil organic matter. *The Science of the Total Environment, 123/124,* 205-217.

Dunnivant, F. M., Schwarzenbach, R. P. & Macalady, D. L. (1992). Reduction of Substituted Nitrobenzenes in Aqueous solutions Containing natural Organic Matter. *Environ. Sci. Technol., 26,* 2133-2141.

Heijman, C. G., Grieder, E., Holliger, Ch., & Schwarzenbach, R. P. (1994). Reduction of nitroaromatic compounds coupled to microbial iron reduction in laboratory aquifer colums. Submitted to *Environ. Sci. Technol.*

Laha, S., & Luthy, R. G. (1990). Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environ. Sci. Technol., 24,* 363-373.

Li, S., & Wackett, L. P. (1993). Reductive dehalogenation by cytochrome P 450cam: substrate binding and catalysis. *Biochemistry, 32,* 9355-9361.

Macalady, D. L., Tratnyek, P. G., & Grundl, T. J. (1986). Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems: a critical rewiew. *J. Cont. Hydr., 1,* 1-28.

Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (1993). Environmental Organic Chemistry (textbook), Chapter 12, Wiley, New York, 700 pages.

Schwarzenbach, R. P., Stierli, R., Lanz, K., & Zeyer, J. (1990). Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. *Environ. Sci. Technol., 24,* 1566-1574.

Torrents, A., & Stone, A. T. (1991). Hydrolysis of phenyl picolinate at the mineral/water interface. *Environ. Sci. Technol., 25,* 143-149.

Torrents, A., & Stone, A. T. (1993a). Catalysis of picolinate ester hydrolysis at the oxide/water interface: inhibition by coadsorbed species. *Environ. Sci. Technol., 27,* 1060-1067.

Torrents, A., & Stone, A. T. (1993b).). Catalysis of picolinate ester hydrolysis at the oxide/water interface: inhibition by adsorbed organic matter. *Environ. Sci. Technol., 27,* 2381-2386.

Ulrich, H.-J., & Stone, A. T. (1989). Oxidation of chlorophenols adsorbed to manganese oxide surfaces. *Environ. Sci. Technol., 23,* 421-428.

Weber, E. J., & Wolfe, N. L. (1987). Kinetic studies of the reduction of aromatic azo compounds in anaerobic sediment/water systems. *Environ. Toxicol. Chem., 6,* 911-919.

Evaluation of Mass Transfer and Biodegradation of Naphthalene from Coal Tar in Slurry Treatment Systems

Subhasis Goshal, Anuradha Ramaswami, and Richard G. Luthy

Introduction

Coaltar is a byproduct of coal gasification processes, and is often associated with subsurface contamination at many former manufactured gas plant (MGP) sites (Luthy et al., 1994). Coal tar is a multi-component, nonaqueous phase liquid (NAPL) having aromatic compounds including various polycyclic aromatic hydrocarbons (PAHs). The immobilized coal tar may serve as a long-term source of soil and ground water contamination due to the slow dissolution of PAH compounds and other solutes.

Several bench scale studies on biodegradation of PAHs from contaminated MGP-site soils (Nakles et al., 1991; Morgan et al., 1992; Erickson et al., 1993) have hypothesized that mass transfer limitations may cause the PAHs to be unavailable to microorganisms in the aqueous bulk phase, and thereby limit biodegradation of PAHs from contaminated MPG-site soils. The work reported here focuses on quantitative evaluation of the rate limiting processes governing biodegradation of naphthalene, a PAH compound often in greatest abundance in coal tar. Independent measurements of rates of naphthalene dissolution and biodegradation have been made to identify the rate limiting process.

Conceptual Model Development

Several factors may influence the overall rate of biotransformation of PAH compounds released from coal tar. These factors include physico-chemical phenomena related to dissolution and mass transfer of PAH compounds from the organic phase to the bulk aqueous phase, and biokinetic phenomena pertaining to the intrinsic microbial degradation rates. Using lumped mass transfer and biokinetic rate constants, a two-step dissolution-degradation model has been developed that describes these concurrent processes. The dissolution degradation model describes the effect of mass transfer on biodegradation in slurry batch systems. The dynamic changes in aqueous phase PAH concentration, C_t $[M/L^3]$, is described as:

$$\frac{\partial C_{(t)}}{\partial t} = k_l a \left[C_{eq(t)} - C_{(t)} \right] - k_{bio} C_{(t)} \qquad (1)$$

where the first term on the right hand side represents the rate of input of PAH to water due to dissolution from coal tar, and the second term represents the rate of removal of bulk aqueous phase PAH due to biodegradation. The biodegradation rate is expressed as a pseudo first or biokinetic coefficient, k_{bio} $[1/T]$, derived from the Monod or Michaelis-Menten models for conditions of low substrate concentration and stable microbial populations (e.g., Seagren et al., 1993). The dissolution rate is represented by a lumped mass transfer rate coefficient, k_la $[1/T]$, that incorporates the specific surface area for mass transfer, a $[L^2/L^3]$, and a linear driving force term that represents the departure of the aqueous concentration, C_t, from the equilibrium concentration, $C_{eq,t}$.

The aqueous phase concentration of a PAH compound in equilibrium with coal tar-NAPL is predicted by Raoult's law as:

$$C_{so} = \chi_{PAH} \ * \ C^{PAH}_{\text{pure liquid}} \tag{2}$$

where C_{so} is the equilibrium aqueous phase concentration of a tar-derived PAH compound, χ_{PAH} is the mole or mass fraction of the PAH compound in coal tar, and $C^{PAH}_{\text{pure liquid}}$ is the solubility of the pure subcooled liquid compound in water. Since most coal tar constituents are essentially insoluble in water, the PAH mole fraction in coal tar and the equilibrium aqueous phase PAH concentration should decrease as cumulatively increasing quantities of the PAH compound are solubilized and then degraded by microbes. Using Raoult's law, the change in equilibrium aqueous phase PAH concentration, $C_{eq(t)}$, is given by:

$$C_{eq(t)} = F_{PAH(t)} \ * \ C_{so} \tag{3}$$

where C_{so} is the initial solubility of a tar-derived PAH compound in water and $F_{PAH(t)}$ is the fraction of that PAH compound remaining in coal tar at time, t. Equations 1 through 3 may be used to describe coupled mass transfer and biokinetic phenomena occurring in slurry tar-water systems.

The overall rate of biotransformation of a PAH compound like naphthalene is controlled by the slower of either mass transfer or degradation processes. It can be shown that when $k_la >> k_{bio}$, i.e, when mass transfer occurs much faster than biodegradation, the aqueous phase concentration of naphthalenein the reactor is close to equilibrium such that $C_{(t)} \simeq C_{eq(t)}$. Assuming zero growth of microorganisms, and neglecting the utilization of naphthalene for cell biomass and possible accumulation of intermediate degradation products, the rate of mineralization of naphthalene is given as:

$$\frac{\partial C_{CO_2}}{\partial t} = k_{bio}\, C_{(t)} \simeq k_{bio}\, C_{eq(t)} \quad \text{for} \quad k_{bio} << k_la \tag{4}$$

where the left hand side of Equation 4 represents the increment of PAH mass converted to CO_2 per unit time, per unit aqueous volume in the reactor.

Conversely, when $k_l a << k_{bio}$, i.e, when mass transfer occurs much slower than biodegradation, analysis of Equation 1 shows that the aqueous phase naphthalene concentration in the reactor is small compared to the equilibrium concentration and the slope of the biomineralization curve is given by:

$$\frac{\partial C_{CO_2}}{\partial t} = k_l a \; C_{eq(t)} \quad \text{for} \quad k_l a << k_{bio} \tag{5}$$

Equation 5 represents a system in which the overall biotransformation rate is controlled by mass transfer processes. For such a condition, the slope of the biomineralization curve is directly related to the mass transfer rate coefficient, $k_l a$.

The ratio of the mass transfer rate coefficient to the kinetic coefficient is a quantitative criterion that can be used to identify whether mass transfer phenomena or biological processes pose a limiting constraint on biotransformation rates. This ratio can be expressed as dimensionless Damkohler number, Da,

$$Da = k_{bio}/k_l a \tag{6}$$

which indicates mass transfer control for values much greater than unity and biokinetic control for values much less than unity. Depending on the values of the Damkohler number, the rate of mineralization may also be predicted from Equations 5 and 6.

The value of the Damkohler number may be computed from estimations of mass transfer and biodegradation rate constants. Values of intrinsic biodegradation rates for different PAH compounds may be obtained from literature. For example, estimates of naphthalene degradation rate constant range from approximately 1/day (Mihelcic and Luthy, 1991) to 25/day (Guerin and Boyd, 1992).

Mass transfer coefficients for transport from the surface of spherical bodies to the bulk aqueous phase may be estimated from several correlations available in the chemical engineering literature (Levins and Glastonbury, 1972). A limiting value of the lumped mass transfer coefficient for a PAH compound released from the surface of coal tar-imbibed particles, or globules of coal tar, in a gently mixed aqueous medium may be approximated by:

$$k_l a = k_{aq} * a \simeq n_p \, 4pr^2 \, * \, \frac{D_{m;aq}}{r} \simeq n_p \, 4pr \, D_{m,aq} \tag{7}$$

where a is the surface area per unit volume for mass transfer, and is related to the spherical surface area, $4pr^2$, of the particle or globule in contact with water and the number density of particles or globules per unit volume of water, n_p. $D_{m,aq}$ is the diffusion coefficient of the PAH compound in water. Thus, a lower bound estimate of the Damkohler number in minimally mixed slurry may be estimated as:

$$Da \simeq \frac{k_{bio}}{4pn_p r\, D_{m;aq}} \qquad (8)$$

Experimental Techniques

Coal tar used in these experiments was obtained from a former manufactured gas plant site located in Stroudsburg, PA. The coal tar was primarily a mixture of polycyclic aromatic hydrocarbons with naphthalene as the most abundant PAH compound (2.2% w/w). Radiolabeled ^{14}C naphthalene was added to the coal tar. The radiolabeled coal tar was imbibed into microporous silica beads (mean dia $\simeq$ 250 *mm*, average pore dia = 140 Å, PQ Corporation, PA) to model coal tar entrapped in microporous media. The coal tar-containing microporous media was used for the mass transfer and biodegradation experiments. Mass transfer and biodegradation experiments were also conducted with globules of coal tar containing radiolabeled naphthalene. The globules of coal tar were produced by carefully expressing the coal tar through syringe needle immersed in water.

Mass Transfer Experiments: Mass transfer tests were carried out in batch and flow-through systems. In batch tests, the coal tar, present either as globules or imbibed within the silica beads, was contacted with water and the aqueous phase naphthalene concentration was measured at equilibrium. The measured equilibrium aqueous phase naphthalene concentration was compared with that predicted from Raoult's law in Equation 2.

The dissolution of naphthalene from coal tar was studied in gently stirred flow-through reactors. The outflow of water created a driving force for further dissolution, and by varying the flow-rate, experiments were conducted at different residence times. The aqueous phase concentration of naphthalene in the reactor was monitored periodically by measuring the ^{14}C activity of the effluent. At the end of each flow-through test, the pump was turned off and the contents of the reactor vessel were allowed to re-equilibrate. The equilibrium aqueous phase concentration measured at the end of the test period was compared to that predicted by Equation 3 to verify the utility of Raoult's law in predicting dynamic changes in equilibrium concentration (Luthy et al., 1993).

Biomineralization Experiments: Experiments were carried out under aerobic conditions in 250 mL biometer flasks fitted with a side tube. The side tube and the flask were sealed with neoprene stoppers covered with aluminium foil and the biometers were shaken in a gyratory shaker. In slurry tests, five grams of silica beads were imbibed with 1 mL of coal tar spiked with radiolabeled ^{14}C naphthalene, and added to each biometer along with 50 mL of autoclaved nutrient media. Tests with coal tar globules were done with a single globule of 0.7 mL coal tar and 50 mL of nutrient media. The contents of the biometers were mixed by mounting the biometers on a gyratory shaker. Biometers were inoculated with 2 mL of an actively growing bacterial culture of naphthalene-degrading organisms containing approximately 5×10^7 cfu/mL, as determined by naphthalene plate counts. Sterile controls containing mercuric chloride were used to assess any abiotic mineralization. Radiolabeled CO_2 from biomineralization of naphthalene was trapped in the NaOH contained in the side arms of the biometers. The NaOH was sampled periodically, and the activity of the $^{14}CO_2$ in the NaOH was measured with a Beckmann LS 5000TD scintillation counter with automatic quench compensation. At the end of both mass transfer and biodegradation experiments, the residual radioactivity in the silica beads and in the supernatant was measured to check for mass balance of the radiolabeled naphthalene. Recovery of ^{14}C from the systems ranged from 85% to 105% with an average of 93%.

Results

Mass Transfer Experiments: Batch tests were conducted to measure the initial aqueous phase solubility of PAH compounds from coal tar. Results from these tests matched well with the theoretical predictions from Raoult's law in Equation 2, indicating an initial equilibrium aqueous phase naphthalene solubulity of 4 *mg/L* for the Stroudsburg tar. Typical examples of the data obtained from these experiments are displayed in Figure 1a and 1b. Concentration profiles, showing effluent and equilibrium concentrations, are plotted as a function of pumping time for coal tar imbibed in microporous media and coal tar globules.

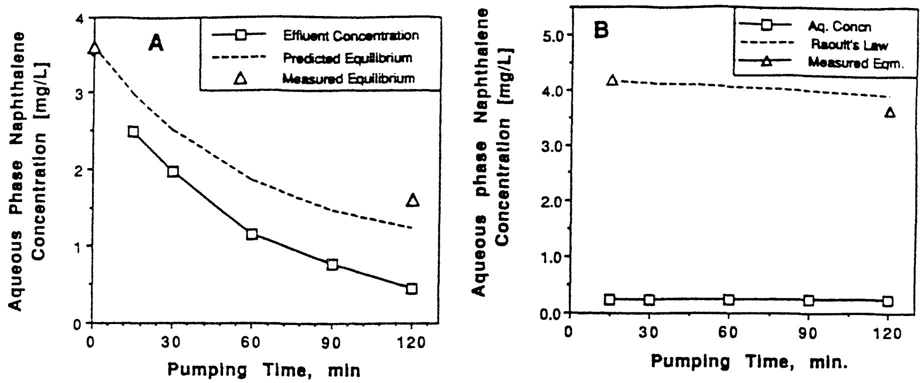


Figure 1

Aqueous phase naphthalene concentration in flow through stirred tank reactors. (A) Slurry system with coal tar imbibed in 0.25 mm dia microporous silica beads. Residence time = 1 minute. Measured $k_l a \simeq$ 6000/day - 500/day. (B) System with single 11 mm dia coal tar globule. Residence time = 5 min. $k_l a \simeq$ 1.8/day.

For the system where coal tar was imbibed into microporous silica, the lumped mass transfer coefficents derived from measured aqueous concentrations decreased with time from about 6000/day to 500/day. These values were within the range of a theoretical prediction of about 3000/day given by Equation 7. The variation in mass transfer rates with time was observed upon «aging» of coal tar in water, was believed to be a result of interfacial film formation in tar-water systems (Luthy et al., 1993).

A mass transfer rate coefficient equal to 1.8/day was obtained from flow through tests with a 0.7 ml coal tar globule. For both liquid globules and silica beads, the measured mass transfer coefficients were found to be within the range of that predicted by Equation 7, accounting for the fluid mechanic energy input from gentle hydrodynamic mixing due to pumping (Levins and Glastonbury, 1972).

Biomineralization Tests: Naphthalene biomineralization tests were conducted with coal tar imbibed in microporous media and with 0.7 ml coal tar globules suspended in water. The mineralization profiles for these experiments are displayed in Figure 2a and 2b. The system comprised of small microporous silica particles exhibits a significantly greater initial biomineralization rate (13/day) compared to that containing the coal tar globule (1.3/day).

For small media, predicted values of the Damkohler number lie in the range of 0.001 to 0.01, assuming biokinetic rate constants of 1/day to 25/day, reported in literature. These values of the Damkohler number indicate biokinetic control. The k_{bio} of 13/day estimated from the mineralization profile, and the average mass transfer coefficient, $k_l a$ of 3000/day determined from the flow-through tests, result in a Damkohler number equal to 0.004. Thus, both experimental data and theoretical predictions indicate that the biotreatment system composed of small particles in a coal tar slurry system is limited by kinetic factors. The rate of naphthalene mineralization approached a limiting value in the latter stages of this experiment. At the point where biomineralization activity ceased, about 10% to 15% of the initial mass of naphthalene remained in the coal tar. In the experiments with coal tar globules, approximately 70% of the naphthalene was mineralized in a 110 day period, and at the end of this period, only 5% of the initial mass of naphthalene remained the coal tar globule.

For biomineralization of naphthalene from a 0.7 ml coal tar globule (Figure 2b), both theoretical predictions and experimental determinations yield a Damkohler number greater than 1, suggesting that mass transfer may limit the biotransformation of naphthalene from large coal tar blobs. This also indicates that the value of the mass transfer coefficient should be related to the slope of the experimental biomineralization data in Figure 2b through Equation 5. Applying Equation 5 to the slope of the mineralization curve in Figure 2b, a value of approximately 1.3/day was obtained for the mass transfer coefficient, $k_l a$. This value of $k_l a$ matches well with a value of approximately 1.8/day obtained in the companion flow-through mass transfer test.

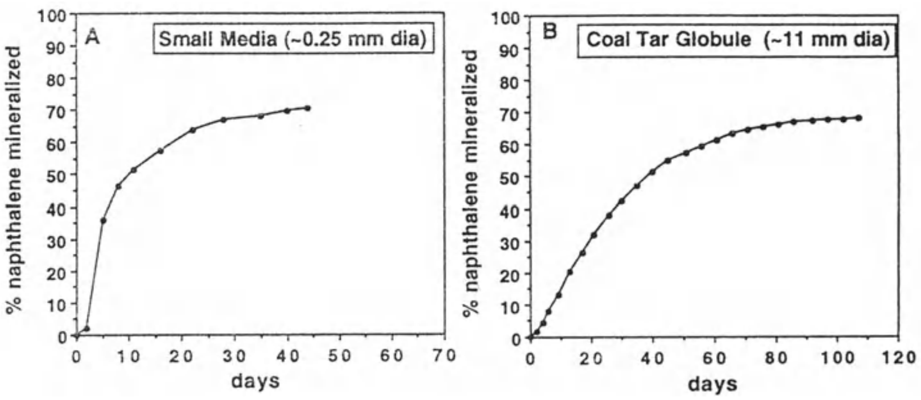


Figure 2
Naphthalene mineralization profiles. (A) Slurry system with coal tar imbibed in 0.25 mm dia microporous silica beads. Mineralization in this system is biokinetic limited (Damkohler number less than 1). (B) System with a single 11 mm dia coal tar globule. Mineralization in this system is mass transfer-limited (Damkohler number larger than 1).

Conclusions

Independent mass transfer and biomineralization experiments indicate that biotransformation of naphthalene from coal tar in slurry systems may be limited by either mass transfer or biokinetic phenomena, depending on the size dimension and number density of the coal tar globules or particles. A simple dissolution degradation model adequately described the general behavior of different coal tar-water systems. The Damkohler number was found to be useful indicator for identifying rate-limiting phenomena in different tar-water systems. Values of the Damkohler number obtained from the biomineralization and mass transfer experiments matched well with theoretical estimates, and provided a quantitative criterion to distinguish between systems that are mass treansfer limited from those thar are biokinetic limited.

In future tests, the utility of the mathematical framework will be assessed by varying physical parameters of the tar-water systems. The experimental and mathematical framework will also be expanded to accomodate conditions of active bacterial growth.

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References

Erickson, D.C.; Loehr, R.C.; Neuhauser, E.F. 1993: PAH Loss During Bioremediation of Manufacturted Gas Plant Site Soils. Water Research. 27:911-919.

Guerin, W.F.; Boyd, A.S. 1992: Differential Bioavailability of Soil-sorbed Naphthalene to Two Bacterial Species. Appl. Environ. Microbiol. 58:1142-1152.

Levins, D.M.; Glastonbury, J.R. 1972: Interfacial Films in Coal Tar Nonaqueous-phase Liquid-water Systems. Trans. Inst. Chem. Eng. Sci., 1972, 50:132-145.

Luthy, R.G.; Ramaswami, A., Ghoshal, S.; Merkel, W. 1993: Environ Sci. Technol., 27:2914-2918.

Luthy, R.G.; Dzombak, D.A.; Peters, C.A., Roy, S.B.; Ramaswami A.; Nakles, D.V.; Nott, B.R. 1994: Remediating Tar-Contaminated Soils at Manufactured Gas Plant Sites. Environ. Sci. Technol.. 28:266-276.

Mihelcic, J.R.; Luthy, R.G. 1991: Sorption and Microbial Degradation of Napthalene in Soil-water Suspensions Under Denitrification Conditions. Environ. Sci. Technol., 25:169-177.

Morgan, D.J.; Battaglia, A.; Hall, B.J.; Vernieri, L.A.; Cushney, M.A. 1992: The GRI Accelerated Biotreatability Protocol for Assessing Conventional Biological Treatment of Soils: Development and Evaluation using Soils from Manufactured Gas Plant Sites; Gas Research Institute: Chicago, IL, GRI-92/0499.

Nakles, D.V.; Linz, D.G.; Murarka, I.P. 1991: «Bioremediation of MGP Soils: Limitations and Potentials», Paper presented at EPRI Technology Transfer Seminar on Management of Manufactured Gas Plant Sites, Atlanta, GA, April 2-3.

Seagren, E.A.; Rittman, B.E.; Valochhi, J.A. 1993: Quantitative Evaluation of Flushing and Biodegradation for Enhancing in Situ Dissolution of Nonaqueous-phase Liquids. J. Contam. Hydrol. 12(1/2):103-132.

Rate Limiting Steps in Bioremediation

Tom N.P. Bosma

Introduction

Organic pollutants can be removed from soil by means of biological treatment. A major problem in the application of these treatments is the efficiency of biodegradation in soil. The bulk of the pollution can often be removed but certain residual amounts remain unaltered (19, 22). In addition, biodegradation rates are often much slower than expected on the basis of laboratory trials. The kinetics of microbial growth alone are not sufficient to explain the slow biological removal rates in soil and the occurrence of residual amounts after bioremediation. The present paper will give a summary of factors that potentially result in a reduced biotransformation rate in soil, or in other words, reduce the bioavailability of the pollutants. First, a short discussion of the problem of bioavailability is presented. Then, several factors that may reduce the bioavailability of pollutants are discussed.

Bioavailability

The notion of a reduced bioavailability in soil is often used to explain the retarded biodegradation of organic pollutants in soil. A problem is that bioavailability is ill-defined. The notion implies that part of the pollution may be bioavailable whereas the remaining fraction is not. However, there is no sense in asking whether a pollutant is bioavailable or not. A gradient exists between unavailable and fully available and it depends on the properties of the system under consideration, i.e. the properties of pollutants, soil, and microbial population, to which extent a pollutant is available for biodegradation. Bioavailability is defined here as *the potential flux of pollutant to the microbes in a given system.* The purpose of bioremediation is to maximize the availability of pollutants for biodegradation and hence, to maximize the flux of pollutants to the microbes. In order to establish a flux, there must be a concentration gradient between the bulk soil concentration and the concentration at the microbial cell surface which results from biodegradation (Fig. 1).

The flux is then governed by the concentration gradient as driving force and by the «permeability» of the soil matrix for the pollutant under consideration. Both aspects are discussed in the following sections.

The Concentration Gradient: Bound Residue Formation and Dissolution Kinetics

The concentration gradient between bulk soil and microbes can be affected by other processes than biodegradation. The incorporation of pollutants in organic matter and precipitation due to a low solubility both lead to decreased bulk concentrations and hence, a smaller concentration gradient. Pollutants like substituted phenols, benzoic acids, and anilines are very similar to natural organic compounds and can be incorporated in humus-like structures (3). Natural inorganic materials (e.g. clay, iron oxides) and enzymes (peroxidases, phenol monooxygenases) can catalyze the coupling of these compounds to organic matter. The process of coupling - known as bound residue formation - results in a decrease of the bulk concentration of the pollutants and hence, reduces their bioavailability. Chemicals which are thus incorporated in organic matter loose their original chemical and biological activity. It is therefore proposed to stimulate the formation of bound residues as a biological remediation technique (2). However, macromolecular components of dissolved organic matter may form mobile colloids under circumstances which may lead to a remobilization of the pollutants (11). Moreover, the involved coupling reactions can also yield by far more hazardous products than the substrates such as polychlorodibenzodioxins and -dibenzofurans (12, 18). A last disadvantage of this technique is the retardation of biodegradation due to the decrease of the concentration gradient between the bulk soil and the degrading microorganisms.

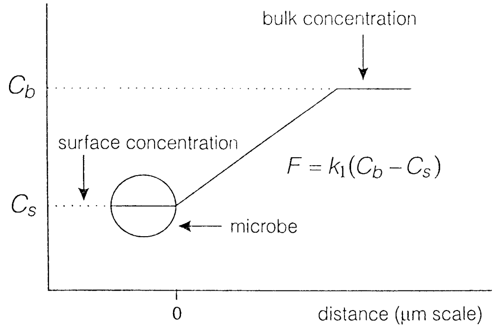

Figure 1
Schematic representation of the concentration gradient of a pollutant from bulk soil to a microbial cell. The flux (*F*) resulting from the gradient as driving force is determined by the permeability of the soil as represented by a permeability factor (k_1).

Since hydrophobic pollutants are generally not equally dispersed in soil, they tend to stick together at high concentrations and form droplets. In other cases pollutants were simply deposited in pure form. Coal-tar at manufactured gas plant sites provides an extreme example of this situation (10). Such pollutants must dissolve before uptake via the porous soil can take place. Hence, the kinetics of dissolution also affects the flux of pollutants to the degrading microbes. Dissolution rates may be enhanced by the addition of surfactants.

The Concentration Gradient: Reduction of the Cell Surface Concentration by Biodegradation

Biodegradation results in a decrease of the cell surface concentration and thereby maintains a flux from the bulk soil to the degrading microorganisms. The biodegradation of organic pollutants is the result of the expression of the appropriate information on the genome of the microorganisms involved. Generally biotransformation pathways will only evolve when (i) the overall reaction is energetically favorable and (ii) when the highest energy barrier in the reaction pathway can be overcome by the enzymes that serve as catalysts. This section first discusses mechanisms leading to the acquisition of the appropriate genetic information and then discusses some energetic aspects of biodegradation.

Acquisition of Genetic Material

The degradation of an organic compound involves the activity of different enzymes. The persistence of certain chemicals during bioremediation may result from a lack of appropriate genetic information. The acquisition of the capability to degrade xenobiotic compounds can result from a redistribution of metabolic capacities already present within the microbial population in combination with small changes in the properties of enzymes involved in the initial steps of transformation (20). Sometimes long acclimation times occur before biodegradation is observed, indicating the need for the evolution of biodegradative pathways (4, 5). Bioaugmentation may be a means to shorten acclimation times considerably. It involves the addition of non-indigenous bacteria to a soil to supply additional genetic information that the indigenous population can adopt and use (15). The indigenous bacteria may take up the foreign genetic material by making direct contact with the non-indigenous donor cells (conjugation). Alternatively, they can take it up as free DNA from the soil, after its release from the introduced cells (transformation).

Energetic Considerations

The biodegradability of pollutants depends on the thermodynamics of the overall reaction and on the kinetics of the rate-limiting step in the enzymatic pathway involved. The rate-limiting step in the transformation pathway is often the step involving the highest activation energy needed to initiate the reaction.

The biological mineralization of most organic pollutants is thermodynamically favorable under aerobic and anaerobic conditions as typified by high negative values of the Gibbs energy change (DG) of the reaction (16). The process of reductive dehalogenation is also thermodynamically favorable when it is coupled to the oxidation of organic substances (7, 21). So, there seems to be no thermodynamic reason for a reduced biodegradation rate of organic pollutants in soil. However, reactions which are thermodynamically favorable appear not always to proceed in environmental samples. Reductive dechlorination of monochlorobenzene for example was never observed although the DG of this reaction is of the same order of magnitude as for the other chlorinated benzenes which are readily reduced (1, 6, 7, 8). An explanation may be that the energy barrier involved in one of the first steps of the reaction is so high that the overall reaction cannot proceed anymore. This is feasible in the case of chlorinated benzenes because the stability of the molecules highly increases with decreasing numbers of chlorine substituents.

Soil «Permeability»: the Effect of Mass Transfer on Observed Biodegradation Rate

The average distance between bacteria in a soil can be estimated at about 25-60 mm which is 25-60 times the average diameter of a microbe. The majority of bacteria lives in pores with sizes of 0.8-3 mm (9, 13). When pollutants enter a soil they will first contaminate the macropore system with relatively few bacteria. Then, they diffuse into smaller pores where biotransformation may take place. Finally, they may enter extremely small pores (<< 1 mm) due to incomplete degradation and slow diffusion after long exposure of a soil to pollution. Thus, the mass transfer to the microbes plays an important role during bioremediation, because the rediffusion rate from these highly tortuous pores can be more than ten orders of magnitude slower than in aqueous environments (4). For normal bioremediation conditions one can assume that the kinetics of pollutant uptake are fully dominated by diffusion kinetics. This explains why first order kinetics generally are sufficient to explain biodegradation rates in soil (Fig. 1). Bioremediation strategies should aim at maximizing the «permeability» of the soil for the pollutant. Pulverization has been shown to be an effective way to enhance the desorption and mineralization rates of organic pollutants (14, 17). However, this method is not appropriate for *in-situ* remediation set-ups.

The occurrence of relatively high residual amounts of pollutants can also be explained by mass transfer limitation (4). It was mathematically demonstrated that the residual concentration of pollutant in soil is inversely proportional to the soil permeability factor k_1. So, maximizing the mobility of pollutants in contaminated soil results not only in increased biodegradation rates but also in decreased residual concentrations.

Conclusions

Mass transfer becomes the dominant rate-limiting step in bioremediation once microbes developed the ability to degrade organic pollutants. Increasing the permeability of the soil by pulverization seems to be the only way to relieve this limitation in an *ex-situ* treatment. It is imaginable to remove the mobile fraction in a relatively short time via a biological *in situ* treatment, leaving the residual «immobilized» fraction trapped inside soil aggregates where they are biologically inactive. The pollutants that are slowly released from the soil aggregates should be monitored in an «after-care» phase so that additional remediation action can be undertaken if necessary.

References

1. **Beurskens, J. E. M., C. G. C. Dekker, H. Van den Heuvel, M. Swart, J. De Wolf, and J. Dolfing.** 1994. Dechlorination of chlorinated benzenes by an anaerobic consortium that selectively mediates the thermodynamic most favorable reactions. Environ. Sci. Technol. **28:**701-706.

2. **Bollag, J.-M.** 1991. Enzymatic binding of pesticide degradation products to soil organic matter and their possible release. Pestic. Transf. Prod. **459:**122-132.

3. **Bollag, J. M., and M. J. Loll.** 1983. Incorporation of xenobiotics into soil humus. Experientia **39:**1221-1231.

4. **Bosma, T. N. P.** 1994. Simulation of subsurface biotransformation, PhD-thesis, Agricultural University Wageningen, The Netherlands.

5. **Bosma, T. N. P., R. A. G. Te Welscher, J. G. M. M. Smeenk, G. Schraa, and A. J. B. Zehnder.** Biotransformation of organic contaminants in sediment columns and a dune infiltration area. submitted to Ground Water

6. **Bosma, T. N. P., J. R. Van der Meer, G. Schraa, M. E. Tros, and A. J. B. Zehnder.** 1988. Reductive dechlorination of all trichloro- and dichlorobenzene isomers. FEMS Microbiol. Ecol. **53:**223-229.

7. **Dolfing, J., and B. K. Harrison.** 1992. Gibbs free energy of formation of halogenated aromatic compounds and their potential role as electron acceptors in anaerobic environments. Environ. Sci. Technol. **26:**2213-2218.

8. **Holliger, C., G. Schraa, A. J. M. Stams, and A. J. B. Zehnder.** 1992. Enrichment and properties of an anaerobic mixed culture reductively dechlorinating 1,2,3-trichlorobenzene to 1,3-dichlorobenzene. Appl. Environ. Microbiol. **58:**1636-1644.

9. **Kilbertus, G.** 1980. Etude des microhabitats contenus dans les agrégats du sol. Leur relation avec la biomasse bactérienne et la taille des procaryotes présents. Rev. Ecol. Biol. Sol **17:**543-557.

10 **Luthy, R. G., D. A. Dzombak, C. A. Peters, S. B. Roy, A. Ramaswami, D. V. Nakles, and B. R. Nott.** 1994. Remediating tar-contaminated soils at manufactured gas plant sites, technological challenges. Environ. Sci. Technol. **28 (in press).**

11. **McCarthy, J. F., and J. M. Zachara.** 1989. Subsurface transport of contaminants. Environ. Sci. Technol. **23:**496-502.

12. **Öberg, L. G., B. Glas, S. E. Swanson, C. Rappe, and K. G. Paul.** 1990. Peroxidase-catalyzed oxidation of chlorophenols to polychlorinated dibenzo-para-dioxins and dibenzofurans. Arch. Environ. Contam. Toxicol. **19:**930-938.

13. **Postma, J., and J. A. Van Veen.** 1990. Habitable pore space and population dynamics of *Rhizobium leguminosarum* biovar *trifolii* introduced into soil. Microb. Ecol. **19:**149-161.

14. **Rijnaarts, H. H. M., A. Bachmann, J. C. Jumelet, and A. J. B. Zehnder.** 1990. Effect of desorption and intraparticle mass transfer on the aerobic biomineralization of a-hexachlorocyclohexane in a contaminated calcareous soil. Environ. Sci. Technol. **24:**1349-1354.

15. **Rittmann, B. E., B. F. Smets, and D. A. Stahl.** 1990. The role of genes in biological processes. 1. Environ. Sci. Technol. **24:**23-29.

16. **Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden.** 1993. Environmental organic chemistry. John Wiley & Sons, New York / Chichester / Brisbane / Toronto / Singapore.

17. **Steinberg, S. M., J. J. Pignatello, and B. L. Sawhney.** 1987. Persistence of 1,2-dibromoethane in soils: Entrapment in intraparticle micropores. Environ. Sci. Technol. **21:**1201-1208.

18. **Svenson, A., L. O. Kjeller, and C. Rappe.** 1989. Enzyme-Mediated Formation of 2,3,7,8-Substituted chlorinated dibenzodioxins and dibenzofurans. Environ. Sci. Technol. **23:**900-902.

19. **Valo, R. J., and M. S. Salkinoja-Salonen.** 1986. Bioreclamation of chlorophenol-contaminated soil by composting. Appl. Microbiol. Biotechnol. **25:**68-75.

20. **Van der Meer, J. R., W. M. De Vos, S. Harayama, and A. J. B. Zehnder.** 1992. Molecular mechanisms of genetic adaptation to xenobiotic compounds. Microbiol. Rev. **56:**677-694.

21. **Vogel, T. M., C. S. Criddle, and P. L. McCarty.** 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. **21:**722-736.

22. **Wang, X., and R. Bartha.** 1990. Effects of bioremediation on residues, activity and toxicity in soil contaminated by fuel spills. Soil Biol. Biochem. **22:**501-505.

Behaviour of Metals

Philippe Behra

1. Introduction

The extension and intensification of human activities are at the origin of the increase in contaminant dispersion in natural media. The different pathways of dispersion are (i) aerosols, smokes or atmospheric depositions in the atmosphere, (ii) the infiltration from waste disposals, from manure or pesticide spreading, (iii) the run-off from waste disposals, or direct discharge in surface or subsurface waters, and (iv) accidents during transports or handling of chemicals. These pollution sources are a threat to ground waters which constitute a very large portion of our drinking water resources.

The new challenge for people dealing with groundwater contaminants is the prediction of the transport of organic or inorganic pollutants in the subsurface domain and in groundwater aquifers (Dagan, 1989). Since the solid phase is in large excess with respect to the gas or liquid phases, the chemistry of the groundwater system mainly depends on its composition. We have to consider that (i) the water is both a vector or a scavenger of solutes or particulate matter, and a reagent; (ii) the solid phase on the one hand is the skeleton through which water flows, and on the other hand can react with components of the liquid phase; and (iii) an aquifer is a heterogeneous system with regard to physical and chemical parameters. Therefore, we need information concerning the properties of such a complex system to predict the movement of pollutants which becomes a difficult task.

Concerning the chemistry of the system, the mechanisms which play the main role in the transport of contaminants such as metals are the complexation in the aqueous phase, the precipitation/dissolution processes, the sorption, the flocculation/peptisation processes, the scavenging of contaminants combined with the precipitation/dissolution of oxides, the sorption of organic matter, and/or the flocculation/peptisation of colloids (Stumm and Morgan, 1981). Moreover, the presence of microorganisms plays a very important role in the accumulation and transformation of chemicals in the environment. They also control many redox reactions in either oxic or anoxic conditions if nutrients are not limiting (Bidoglio and Stumm, 1994).

2. Methodology for Mechanism Identification

The knowledge of physical, chemical and geochemical mechanisms which control the behaviour of contaminant transport is the first step to design models which may be useful to forecast the fate of pollutants. Experimental laboratory, field approaches and modeling are necessary and complementary.

2.1 Laboratory Investigation

2.1.1. *Batch Reactor System* is used to study equilibrium and kinetic processes which occur between the different compounds present in the liquid, solid or gaseous phases. One way is to look at well defined systems with surface models and synthetic solutions, the other one is to use natural samples such as sediments, soils or natural waters. By keeping constant parameters and temperature in the system and by changing total concentration of one solute we obtain the so-called isotherm curves: (i) the linear isotherm curve the slope of which is the distribution coefficient; (ii) the non-linear isotherm which may be described by Freundlich or Langmuir type relationship (Schweich and Sardin, 1981; Bürgisser *et al.*, 1993; Morel and Hering, 1993; Schwarzenbach *et al.*, 1993). The physico-chemical properties of surfaces and solutes can be studied by changing pH, ionic strength, ligand concentration or redox conditions. The main disadvantage of the batch reactor approach is coming from the necessity of the separation between the liquid and solid phases to determine the concentration of the solute. The difference between the total concentration and the liquid concentration of the solute is not necessarily equal to the solute concentration on the solid phase which is present in the system. Such interpretation is too often a source of errors due to adsorption on batch walls, precipitation, co-precipitation or separation techniques especially at very low concentrations.

2.1.2. *Flow-Through Reactors Approach*, which may be a recycling or an open system, is an alternative to batch reactor studies. The first one can replace batch reactor system (Nitsche, 1991). Indeed, no additional mixing device such as external stirring rod which may destroy or change the physico-chemical properties of the solid phase is necessary. The open flow-through reactor method is usually used to study the transport of solutes through a porous medium packed column. Both methods are comparable to the liquid-solid chromatography approach. The main advantages are: (i) there is a immobile solid phase which mass is constant and through which a solution the volume of which may be very important circulates; (ii) the porous medium can have a structure comparable to an aquifer sample; (iii) the flow velocities which are imposed to the moving solution may be chosen in the same order of magnitude as those of real systems; (iv) the products of reactions, *e.g.* from chemical reactions, desorption, dissolution, biodegradation, are removed from the system. This point is particularly important when products are interacting with reactants by accelerating or inhibiting the studied reactions. In other words, many advantages are in favour of the use of flow-through reactors, and the development of the chromatographic theory has to help the investigation and identification of processes (Schweich & Sardin, 1981; Borkovec *et al.*, 1991; Bürgisser *et al.*, 1993): from breakthrough curves, it is possible to very easily determine the isotherms if the local equilibrium assumption is observed, or to titrate a solid surface even if the site density and the specific surface area are low (Bürgisser, 1994). With column experiments, it is also possible to study either purely chemical kinetics or purely diffusive kinetics into and through the solid matrix (Nicoud and Schweich, 1989; Sardin *et al.*, 1991).

However, a discrepancy is often observed between batch and flow-through reactors because local equilibrium cannot be assumed in the latter reactors. Dead end pores, double porosity or internal diffusion, difference in the site accessibility due to local heterogeneities are at the origin of such observations.

2.2 Field Study

At that scale, it is necessary to have a network of wells or piezometers in order to control the variations in the hydrodynamics and chemical composition of ground waters. Since we are blind with respect to subsurface knowledge, it is important to have many investigation points and to know the geology, the hydrology and the hydrogeology of the system. Each core extracted during boring should be used to investigate the physico-chemical properties of field in order to draw up a map of the field properties which will be necessary to the modeller.

3. Physico-chemical Processes

The basic physico-chemical mechanisms which control the transport of metals are the same than those of the major compounds which are present in the aqueous phase. The main difference is due to the fact that metals are very often at very low concentrations and in turn their behaviour is influenced by the environmental factors. The distribution of metals between the liquid and solid phases mainly depends on the chemical composition of the liquid and solid phases. Several processes may explain the retention onto or the leaching of metals from solid surfaces in aquifers. We will summarise some important mechanisms.

3.1 Precipitation and Dissolution

Precipitation and dissolution mechanisms play a very important role in the fate of metals at the interface between the surface and ground waters. They are very often associated to redox processes. Sediments are generally in anoxic conditions where we can observe a redox cycle of Mn and Fe. In reducing conditions, Fe(III) oxides are reduced and dissolved. If sulphurs or carbonates are in excess, Fe(II) may precipitate as pyrite or siderite, respectively. When the conditions are again oxidising (after few meters), Fe(II) is re-oxidized. New Fe(III) oxide phase appears. These redox, transport and precipitation-dissolution sequences are very important with respect to metal transport. Indeed, if they are adsorbed on solid phases, they will be first desorbed due to dissolution of iron oxide, then precipitated as metal sulphides or carbonates, or scavenged on small colloids before new adsorption or co-precipitation.

3.2 Ionic Exchange

The following reaction describes ionic exchange between metal cations (M^{z+} et B^{w+}):

$$wM^{z+} + zB_s^{w+} = wM_s^{z+} + zB^{w+} \qquad (1)$$

In that case, M^{z+} which is present in the aqueous phase is exchanged against B^{w+} which is adsorbed on the solid phase (B_s^{w+} with the index s when the cation is on sorbate). The selectivity coefficient is defined as:

$$K_{M^{z+}/B^{w+}} = \frac{\{M_s^{z+}\}^w \, [B^{w+}]^z}{[M^{z+}]^w \, \{B_s^{w+}\}^z} \tag{2}$$

On the other hand, we assume electroneutrality at the surface:

$$N_E = z \, \{M_s^{z+}\} + w \, \{B_s^{w+}\} \tag{3}$$

where N_E is the ionic exchange capacity of the solid.

Ionic exchanges between metals mainly occur when clay minerals are present, *i.e.* in soils, because of the source of the negative surface charge. On the other hand, this process does not involve all metals (Bolt, 1982).

3.3 Surface Complexation Model

The main constituents of the solid phase in aquifer system are mainly quartz, feldspars, clays and traces of Fe, Mn, Al (hydr)oxides. These oxides and other natural solids which are present in aquatic systems have ionised surface functional groups (–OH, –COOH, –NH_2, or –OPO_3H_2, –SH). In the presence of water, such a surface (≡S-OH) behaves as weak acid:

$$\equiv S\text{-}OH_2^+ = \equiv S\text{-}OH + H^+; \qquad K_{a1}^s = \frac{\{\equiv S\text{-}OH\} \, [H^+]}{\{\equiv S\text{-}OH_2^+\}} \tag{4}$$

$$\equiv S\text{-}OH = \equiv S\text{-}O^- + H^+; \qquad K_{a2}^s = \frac{\{\equiv S\text{-}O^-\} \, [H^+]}{\{\equiv S\text{-}OH\}} \tag{5}$$

These surfaces are positively charged at low pH, and negatively charged at high pH. A reaction of complexation at the surface may occur where free metal ion, M^{z+}, is exchanged against protons (Stumm and Morgan, 1981):

$$M^{z+} + n\,(\equiv S\text{-}OH) = (\equiv S\text{-}O)_n M^{(z-n)+} + nH^+ \tag{6}$$

where n = 1 or 2, and the intrinsic constants are:

$$^*\beta^s_n = \frac{\{(\equiv S\text{-}O)_n M^{(z-n)+}\}\,[H^+]^n}{[M^{z+}]\,\{\equiv S\text{-}OH\}^n} \tag{7}$$

The advantage of such a model is to account for the pH-dependence of metals. On the other hand, the role of the speciation both in solution and at the solid-liquid interface appears in the fate of metals in ground waters. The adsorption properties of metals at the surfaces depend on the physico-chemical properties of the surface, and on the properties of co-ordination of each metal. We can use the difference between hard and soft acids to often forecast the behaviour of metals with respect to surfaces and even living or non-living organic matter. Correlations between surface complexation constants and hydrolysis constants can be done. They are called Linear Free Energy Relationships (LFERs). For example, on silica and on iron oxides, the sequence of adsorption is Fe(III), Hg, Pb, Cu, Cd from the stronger metal adsorbed to the weaker (Morel and Hering, 1993). On the other hand, we do not have to forget the role of transition metals as metal oxides or redox catalysts.

The difference between ionic exchange model and surface complexation model is due to the energy of bonds and the origin of the charge. In the first one, bonds are weak and mainly electrostatic, whereas in the second one covalent bonds are formed between free cations and oxygen atoms of surface functional group (case of inner sphere surface complexes).

3.4 Surface Precipitation Model

In the presence of iron oxides, metal carbonates and at high cation-sorbent ratios, the adsorption may be controlled by surface precipitation, in which the sorption of new free cations at the surface involves the formation of a new solid metal hydroxide at the surface. At low sorbate concentrations, surface complexation is the predominant sorption mechanism. As concentration increases, surface sites become saturated and surface precipitation becomes predominant and gives rise to the formation of a solid solution (Morel and Hering, 1993). This process may occur at high concentrations but also when the pH is high with respect to the solubility product of the metal hydroxide.

4. Comparisons Between Experiments and Modeling

A shuttle between laboratory investigations, field studies and modeling appears to be the keystone of scale investigations and process knowledge.

4.1 Redox Processes at the Surface and Groundwater Interface

A very well known field site is the one close to Glattfelden in northern Switzerland (Zobrist *et al.*, 1976; Hoehn *et al.*, 1983; Schwarzenbach *et al.*, 1983; von Gunten *et al.*, 1991; von Gunten and Lienert, 1993). Significant seasonal variations in organic or inorganic compounds have been observed. The change in concentrations can be assumed to be controlled by temperature which in turn plays a role in the biogeochemical reactions occurring during the infiltration of water between surface and ground waters. Fig. 1 summarises the different interactions and reactions which involve organic matter, iron and manganese either as oxides or dissolved species, *i.e.* the redox cycling of Fe and Mn. The overall system also involves the redox cycling of sulphur and nitrogen. The concentrations of Fe and Mn have been measured at the test site. To better understand what happens, Matsunaga *et al.* (1993) have done some column experiments on the one hand, and modeling calculations on the other hand.

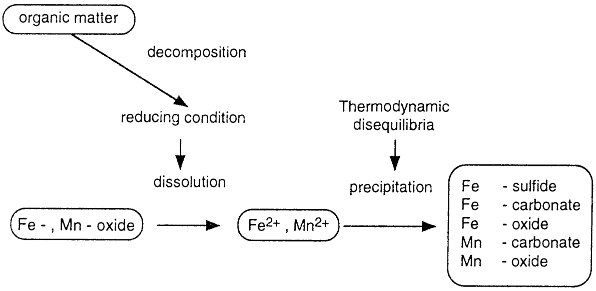

Figure 1
Schematic picture of reactions involving organic matter, Fe and Mn in river-recharged ground water at Glattfelden (after Matsunaga et al., 1993)

Fig. 2 sums up the redox sequences from the oxygen consumption to the reduction of organic matter. Mn and Fe appear as important intermediates in such redox reactions. Metal oxides are first reduced, then both metals are present in the aqueous phase prior to re-precipitate as sulphur or carbonate oxides depending on the sulphate reduction or carbonate concentration. In the system, pH is more or less constant. The calculations from a model coupling chemistry and transport may help the interpretation. In turn, we may estimate rate constants. Going back to the field, Karametaxas (1991) observed a similar behaviour of Fe and Mn in the water of river-recharged ground water at Glattfelden: first a peak of Mn and Fe, then a decrease in concentration of both elements.

Other experiments have been carried out in the same way. The redox sequence is generally the same, and such a conclusion may be applied to infiltration flow path from soil surface to unconfined aquifer (Postma *et al.*, 1991), from river to aquifer (Schulte-Ebbert *et al.*, 1991; von Gunten and Zobrist, 1992, 1993), or from lake to sediments

(Davison, 1985). But at a larger scale, the system appears to be heterogeneous and the models used for such studies cannot take into account the correct description of the spatial variations. Moreover, the rate constants are too often unknown. In steady-state conditions, these rate constants may be estimated. If the system is neither at equilibrium nor at steady-state, laboratory experiments are a good way to estimate them.

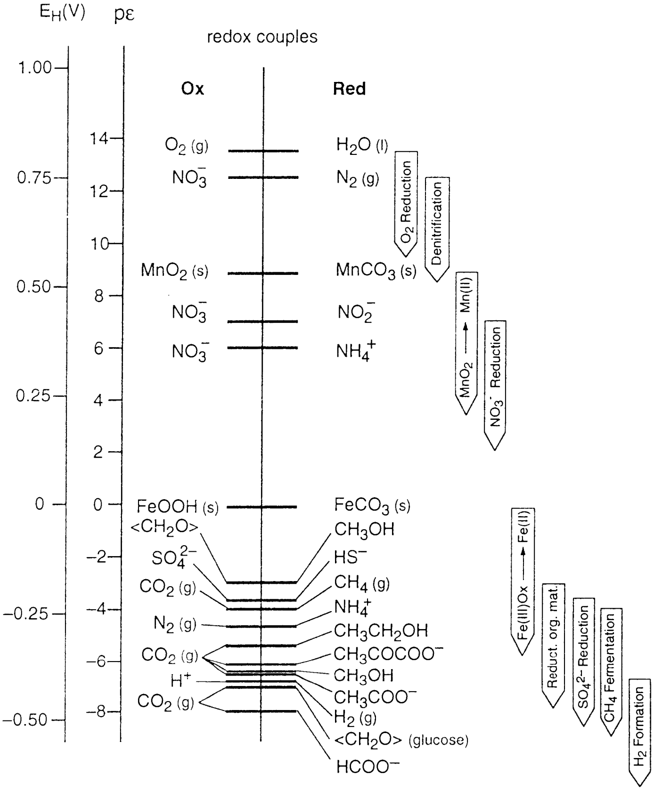

Figure 2

Sequence of microbial mediated redox processes which may occur in lake, sediments or at the interface between surface and ground waters (at pH 7). Given conditions:

[HCO_3^-]10^{-3}M, [S]$_{tot}$$10^{-3}$M, ([$NO_3^-$]+[$NO_2^-$]+[$NH_4^+$]+[$NH_3$])$10^{-3}$M and [$N_2$]$_{aq}$ $5 \cdot 10^{-4}$M

Fe and Mn concentrations are determined from solubility products of metal oxides (after Sigg et al., 1994)

4.2. Field Experiment and Modeling

The experiments of Valocchi *et al.* (1981) are often used to compare field test and simulation of breakthroughs of cations. Water of low ionic strength has been injected into an aquifer. Concentrations of several ions, Na^+, K^+, Mg^{2+} and Cl^-, have been monitored at a well located 16 m away from the injection point. In this simple case, no important reaction occurs in the aqueous phase. Changes in the concentration of Na^+, Mg^{2+} and Ca^{2+} are due to cation exchange. For the simulation, cation exchange capacity is determined from soil samples and selectivity coefficients are from literature. Chloride ion is used as a tracer, and its breakthrough to estimate the dispersivity and the average linear velocity between the two wells. The computed results are in very good agreement with the experimental data (Valocchi *et al.*, 1981; Behra *et al.*, 1990).

Such a comparison exemplifies the possible agreement between multi-component transport modeling and field test. But, there are unfortunately not so many « ideal » field experiments which can be *a posteriori* simulated. In other words, the forecast of contaminants is not obvious at field scale when chemical or physico-chemical processes are involved.

4.3. Thought About Scale in Multi-component Modeling

Different kinds of model can be used to account for the behaviour of contaminants in natural media (Bidoglio and Stumm, 1994). A first way which is still too often used depicts the exchanges between the solid and liquid phases by empirical approaches using Henry (linear relationship with distribution coefficient), Langmuir, Freundlich or BET (Brunauer, Emmett and Teller) relationships determined from batch or flow-through reactors. The main weakness of this concept is that these types of relationships are only usable in particular conditions which fit very well the experiments. Indeed, they describe macroscopic and global behaviour of pollutants. A second way which has been developed in the last fifteen years consists in coupling mass action law to mass transfer equations. The advantage of such an approach is evident since there is a set of intrinsic constants. It has been successfully applied to laboratory experiments and good agreement between simulations and experimental data has been obtained in various conditions (Valocchi *et al.*, 1981; Sardin *et al.*, 1986; Krebs *et al.*, 1987; Behra *et al.*, 1990).

5. Conclusions

Important questions and remarks are: (i) To very well describe the behaviour of pollutants in aquatic systems, do we need a very fine description of mechanisms which occur at a molecular level? (ii) As we pointed out above, is it possible to lump together mass transfer equations which are valid at macroscopic scale, and concepts which take into account processes at atomic or molecular scale? Such a problem specially arises in the case of redox or dissolution/precipitation processes which are rate limited. (iii) Do we need better approaches or better concepts and theories? Is transition from microscale to field scale feasible? Finally, can we get effective parameters which would be useful at large scale?

The last question is a key point to go further in the knowledge of up-scaling. One way seems to open since Schäfer (1992) who introduced a stochastic approach for the distribution of parameters into a coupled numerical transport model to estimate the effective parameters. If the use of distribution coefficient is still questionable, it would be worth thinking in this direction which looks very promising.

As discussed above, laboratory, field experiments and modeling have to be complementary. From well-controlled laboratory experiments and sophisticated modeling, it is possible on the one hand to qualitatively predict the behaviour of contaminants such as metals owing to the knowledge of the different mechanisms of sorption, degradation or transformation, and on the other hand to give notice of what has to be done or not to be done when the ground waters are contaminated by toxic substances.

References

Behra Ph., A. Zysset, L. Sigg and F. Stauffer. 1990. Modelling of pollutant transport in groundwater: Chemistry as a key factor, *EAWAG-News* 28/29, 6-11.

Bidoglio G. and W. Stumm. 1994. *Chemistry of Aquatic Systems: Local and Global Perspectives*, Kluwer Academic Pub., Dordrecht.

Bolt G. H. 1982. *Soil Chemistry B. Physico Chemical Models*, Elsevier, Amsterdam.

Borkovec M., B. Buchter, H. Sticher, Ph. Behra and M. Sardin. 1991. Chromatographic methods and transport of chemicals in soils, *Chimia* 45, 221-227.

Bürgisser Ch.S. 1994. *Transportverhalten von nicht-linear sorbierenden Stoffen in chromatographischen Säulen am Beispiel der Adsorption an Cristobalit*, Ph.D. Thesis, ETH, Zürich.

Bürgisser Ch.S., M. Cerník, M. Borkovec and H. Sticher. 1993. Determination of nonlinear isotherms from column experiments: An alternative to batch studies, *Environ. Sci. Technol.* 27 (5), 943-948.

Dagan G. 1989. *Flow and Transport in Porous Formations*, Springer, New York.

Davison W. 1985. Conceptual Models for Transport at a Redox Boundary in *Chemical Processes in Lakes*, ed. W. Stumm, Wiley & Sons, New York, 31-53.

Hoehn E., J. Zobrist and R.P. Schwarzenbach. 1983. Infiltration von Flussmasser ins Grundwasser -Hydrogeologische und hydrochemische Untersuchungen im Glattal, *Gas-Wasser-Abwasser* 63, 401-410.

Karametaxas G. 1991. *Redox-Prozesse bei der Infiltration von Flusswasser*, Ph.D. Thesis, Bern University.

Krebs R., M. Sardin and D. Schweich. 1987. Mineral dissolution, precipitation, and ion exchange in surfactant flooding, *AIChE J.* 33, 1371-1378.

Matsunaga T., G. Karametaxas, H.R. von Gunten and P.C. Lichtner. 1993. Redox chemistry of iron and manganese minerals in river-recharged aquifers: A model interpretation of a column experiment, *Geochim. Cosmochim. Acta* 57, 1691-1704.

Morel F.M.M. and J.G. Hering. 1993. *Principles and Applications of Aquatic Chemistry*, Wiley, New York, 2nd edition.

Nicoud R.-M. and D. Schweich. 1989. Solute transport in porous media with solid - liquid mass transfer limitations: Application to ion exchange, *Water Resour. Res.* 25, 1071-1082.

Nitsche C. 1991. Verfahren und Vorrichtungen zur Erfassung von System - zuständen im Boden - und Grundwasserbereich auf der Grundlage von Bodenwasserproben, TH Darmstadt, Wasserbau - Mitteilungen der TH, Nr. 31.

Postma D., C. Boesen, H. Kristiansen and F. Larsen. 1991. Nitrate Reduction in an unconfined sandy aquifer: Water Chemistry, reduction processes, and geochemical modeling, *Water Resour. Res.* 27 (8), 2027-2045.

Sardin M., R. Krebs and D. Schweich. 1986 . Transient mass-transport in the presence of non-linear physico-chemical interaction laws: Progressive modelling and appropriate experimental procedures, *Geoderma* 38, 115-130.

Sardin M., D. Schweich, F.J. Leis and Th. van Genuchten. 1991. Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review, *Water Resourc. Res.* 27, 2287-2307.

Schäfer W. 1993. *Numerische Modellierung mikrobiell beeinflußter Stofftransportvorgänge im Grundwasser*, Ph.D. Thesis, Stuttgart University, Schriftenreihe gwf Wasser-Abwasser, vol.23, R.Oldenbourg Verlag, Munich.

Schulte-Ebbert U., R. Hollerung, U. Willme and B. Kaczmarczyk. 1991. *Verhalten von Schwermetallen unter wechselnden Redoxbedingungen im Grundwasser*, Schriftenreihe des Instituts für Wasserforschung der Dortmunder Stadtwerke AG, Nr. 43.

Schwarzenbach R.P., W. Giger, E. Hoehn and J.K. Schneider. 1983. Behavior of organic compounds during infiltration of river water to groundwater. Field studies, *Environ. Sci. Technol.* 17, 472-479.

Schwarzenbach R.P., Ph.M. Gschwend and D.M. Imboden. 1993. *Environmental Organic Chemistry*, Wiley, New York.

Schweich D. and M. Sardin. 1981. Adsorption, partition, ion exchange and chemical reaction in batch reactors or in columns: A review, *J. Hydrol.* 50, 1-33.

Sigg L., W. Stumm and Ph. Behra. 1994. *Chimie des Milieux Aquatiques*, Masson, Paris, 2nd edition.

Stumm W. and J.J. Morgan. 1981. *Aquatic Chemistry*, Wiley, New York, 2nd edition.

Valocchi A.J., R.L. Street and P.W. Roberts. 198). Transport of ion exchanging solutes in groundwater: Chromatographic theory and fields simulation, *Water Resour. Res.* 17 (5), 1517-1527.

von Gunten H.R., G. Karametaxas, U. Krähenbühl, M. Kuslys, R. Giovanoli, E. Hoehn and R. Keil. 1991. Seasonal biogeochemical cycles in riverborne groundwater, *Geochim. Cosmochim. Acta* 55, 3597-3609.

von Gunten H.R. and Ch. Lienert. 1993. Decreased metal concentrations in groundwater caused by controls of phosphate emissions, *Nature* 364, 220-222.

von Gunten U. and J. Zobrist. 1992. Redoxprozesse in Grundwasser - Infiltrations Systemen : Experimentelle Simulation in Kolonnen, *Vom Wasser* 78, 259-271.

von Gunten U. and J. Zobrist. 1993. Biochemical changes in groundwater - infiltration systems: Column studies, *Geochem. Cosmochim. Acta* 57, 3895-3906.

Zobrist J., J.S. Davis and H.R. Hegi. 1976. Charakterisierung des chemischen Zustandes des Flusses Glatt, *Gas-Wasser-Abwasser* 56, 97-114.