Distr.
LIMITED
E/ESCWA/ENR/2000/WG.3/18
13 November 2000
ORIGINAL: ENGLISH

ESCWA UNEP BGR (MEW)

ECONOMIC AND SOCIAL COMMISSION FOR WESTERN ASIA

Expert Group Meeting on Implications of Groundwater Rehabilitation
for Water Resources Protection and Conservation
Beirut, 14–17 November 2000

SOLUTE TRANSPORT MODELS: AN IMPORTANT TOOL FOR STUDIES ON GROUNDWATER PROTECTION OR REMEDIATION

00-0691

Solute Transport Models: An Important Tool for Studies on Groundwater Protection or Remediation

K. Schelkes (BGR) & W. Schäfer (Uni Heidelberg)
Contributions from: W. Duijnisveld, G. Franken, G. Schmidt (BGR), W. Schneider (TU-HH)

1. Introduction

Numerical groundwater models have been used to solve geohydraulic and hydrogeological problems for about twenty years. In the beginning, simple flow models were used to determine zones influenced by groundwater withdrawal and the drawdown of the water table depending on the pumping rate. The increasing capacity of computers and the increasing knowledge of processes in the groundwater regime permitted the progressive addition of the complexities (of the hydrogeological structure, as well as of the fluid components and phases). The discretisation steps were made smaller and smaller. and more and more processes, for example, transport and reaction of substances, were included in the models. Relatively complex models with very fine grids can now be solved within an acceptable time on a PC. The use of flow models for groundwater management is state-of-the-art, whereas the use of transport and reaction models is still growing. Research is being conducted on many of the problems related to this kind of model.

Transport models are used for many groundwater-related problems. Transport models, for example, can be used to interpret the data from chemical analyses of groundwater in terms of the transport history of the analysed substance. Important transport parameters, like dispersivity, and confidence intervals can be determined by varying the parameter values in the models. The model results can be used to determine whether modifications should be made in a monitoring network, e.g., locations for additional observation boreholes.

The behaviour of a solute plume can be predicted, e.g., its spreading and reactions of the solutes with the matrix. Models that take into account withdrawal of water or infiltration are generally more complex than the simple models mentioned in the previous paragraph. Such models are used to investigate the intrusion of salt water from the sea in coastal areas or from deep aquifers in inland areas. The effects of the hypothetical or actual input of a contaminant on groundwater quality can be derived directly from such transport calculations. Information about the short-term behaviour in the area around a contaminated site can be obtained and predictions can be made regarding the long-term safety of a waste disposal site for chemical or radioactive waste.

Transport models are prerequisite for all activities for groundwater protection and remediation. The effectiveness of pump-and-treat remediation, the benefit of the chemicals used for treatment, and the usefulness of reactive walls, e.g., when the funnel and gate method is used, can be calculated and evaluated. The remediation system can be designed on the basis of scenarios, which can be easily varied by changes in the parameter values and in the design concept. Examples for the pump-and-treat method are changes in the length of time for pumping and treating the contaminated water, as well as the choice of the chemical additive. Examples for the funnel-and-gate method are the length and depth of the funnel and the choice of the absorbing material in the gate. The possibility of bioremediation should also be considered. Transport models can be used not only to study ecological aspects, but also economic aspects, i.e., the cost of remediation can also be derived from the model results.

Transport models can also be used to determine the boundaries of groundwater protection zones. Even if parts of an aquifer system are contaminated, a strategy can be developed for the sustainable use of the uncontaminated groundwater resources, taking into account not only the location and kind of contamination, but also any remediation activities. It is also important for these models to take natural attenuation into consideration, which under certain circumstances is a good alternative or supplement to technical methods.

The basic equations and various methods used in transport modelling are discussed in the following chapters, from the simple modeling method of particle tracking to multi-component reactive transport. Some examples of analytical and numerical models are presented. Emphasis will be on reactive transport models, which are being developed in many places and which seem to be the most powerful and promising tools in the field of groundwater remediation.

2. Groundwater flow and particle tracking

The following chapters will not give a complete representation of the features and processes that have to be taken into account if solute transport in groundwater is to be modeled. They are meant only to give an impression of the different kinds of transport problems and a mathematical description of some of these. The variety of problems is very large. Sometimes simplifications can be used to make the calculations of the transport behaviour much easier, e.g., by using analytical solutions or particle tracking. Often the problem can be solved only by using suitable numerical models. Some of the problems are so difficult to solve that much research still has to be carried out on them.

The spreading of solutes in the groundwater depends on many conditions, e.g., the groundwater velocity field, kind of solutes, type of aquifer, minerals in the rock matrix, and the kind of source and rate of input. Generally, all the transport calculations are based on the advective flow field, which can be calculated from the flow equation, a combination of Darcy's law with the continuity equation. The simplest three-dimensional form of the flow equation for calculating advective flow in a porous medium containing an incompressible fluid of constant density, e.g., water, is given by

$$\frac{\partial}{\partial x}\left(k_f^x \frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial x}\left(k_f^y \frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(k_f^z \frac{\partial h}{\partial z}\right)=S_S\frac{\partial h}{\partial t}+Q \ ,$$

where

k_f^x, k_f^y, k_f^z	are the hydraulic conductivity components in a Cartesian co-ordinate system,
h	is the hydraulic head,
S_s	is the specific storage coefficient,
Q	is the sources and sinks in the system.

The flow components q_x, q_y, q_z of the Darcy velocity are

$$q_x=-k_f^x\frac{\partial h}{\partial x},\ q_y=-k_f^y\frac{\partial h}{\partial y},\ q_z=-k_f^z\frac{\partial h}{\partial z}\ ,$$

It is important to keep in mind that not the so-called Darcy velocity but the pore velocity $\vec{v}$, which is the quotient of the Darcy velocity $\vec{q}$ and the effective porosity n_e, is the velocity used for solute transport.

The simplest way to obtain a generalized picture of the transport of a solute in a flow field calculated from the continuity equation is by particle tracking. Only advection is assumed. In general, particle tracking provides the main spreading direction of a contaminant plume. It also provides travel times from a contaminant source to, for instance, a well. It is often the first step in transport modelling, for example, for the safety analysis of a potential repository for radioactive waste.

An example of early model calculations at the Gorleben site in Germany, based on the GSMO flow model developed by G. Schmidt, yield groundwater flow paths based on particle tracking (Fig. 1). These paths start from points at the base of the aquifer at a depth of 200 – 250 m at the top of a salt dome and end in possible recharge areas. Different travel times are shown in Figure 1 for a model that includes (incl.) the influence of the cap rock of the salt dome and one that excludes (excl.) this influence. The particle tracking identifies the main flow direction and discharge area of the groundwater that would be contaminated if the salt barrier fails between the repository area in the salt dome and the overlying aquifer system. But, in most cases, this is only a conservative estimate. For a more realistic estimate, important additional processes have to be considered.

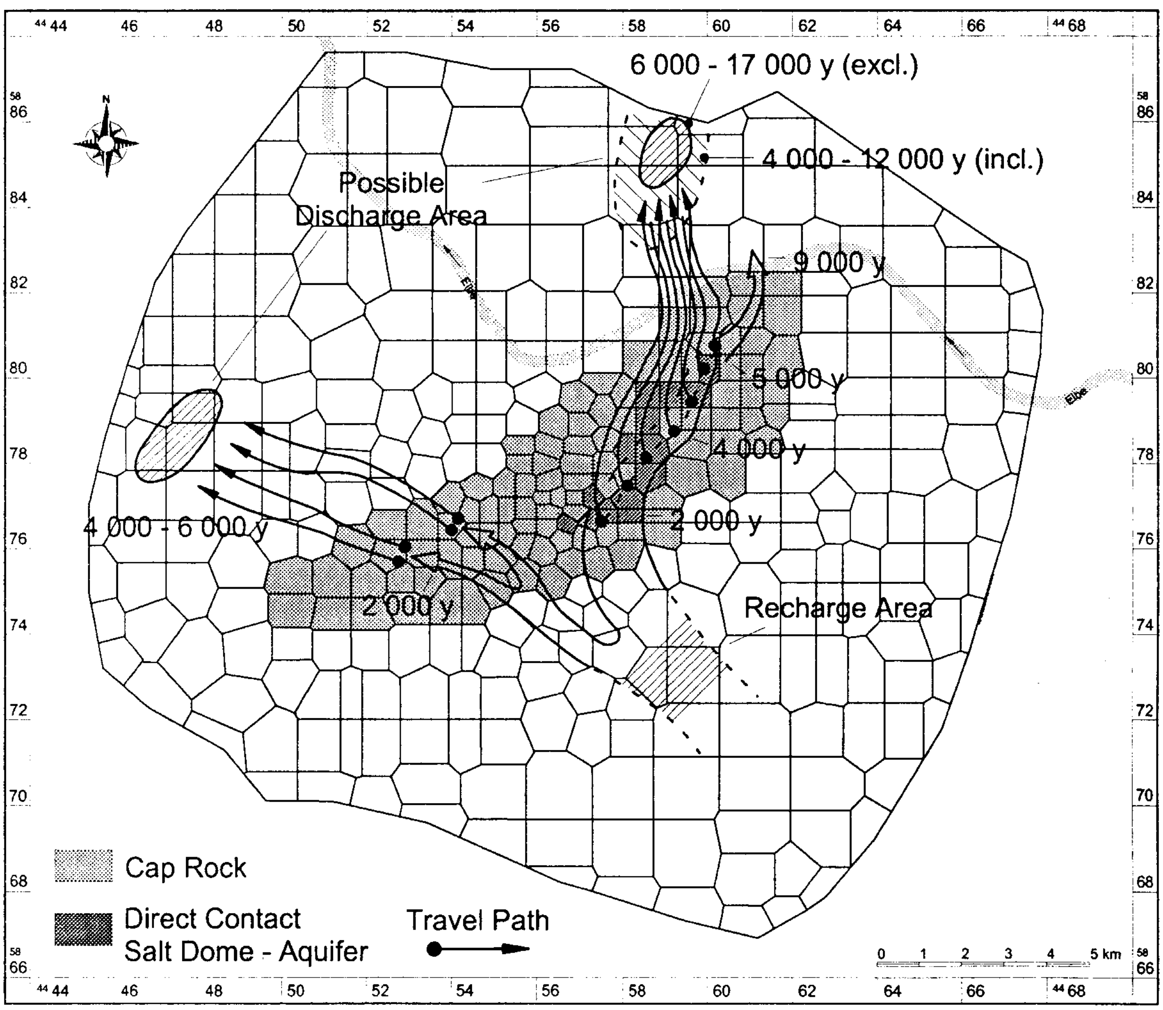


Figure 1: Example of calculated groundwater flow paths with travel times in an area above the Gorleben salt dome

Another example using flow paths is given in Chapter 4.

3. Advective-dispersive transport

In addition to advection, solute transport depends on various features and processes in the groundwater system, for example, mixing processes. One mixing process is diffusion, which decreases solute concentration differences. It is a second-order process and described by Fick's second law. The dispersion is also a second-order process; it represents the spreading of the solute in the groundwater and depends on the structure of the rock matrix. It is scale-dependent and generally becomes larger as the scale of observation is increased. One known form of the transport equation is

$$\frac{\partial c}{\partial t} = -v\nabla c + \nabla\left(\overline{D}\nabla c\right) + \frac{P}{n_e} + \frac{Q}{n_e}\left(c_z - c\right),$$

where
c is the concentration,
P is sinks and sources that are independent of groundwater flow,
$\overline{D}$ is the dispersion tensor (which includes both diffusion and dispersion), and
c_z is solute concentration in the water entering the system.

Analytical transport models based on this equation provide the easiest possibility for calculating solute transport in groundwater. Many simplifications in geometry, flow conditions and material properties have to be made before these models can be used. Some such simplified assumptions are:

- homogeneity of the medium (constant material properties and in fractured media: isotropy in the fracture and the matrix),
- simplified initial and boundary conditions (e.g., fixed concentration at infinity, point or line sources),
- laminar and steady-state flow,
- constant density and viscosity of the fluid (no influence of temperature and concentration),
- incompressibility,
- chemical and thermodynamic equilibrium,
- constant molecular diffusion and dispersion coefficients.

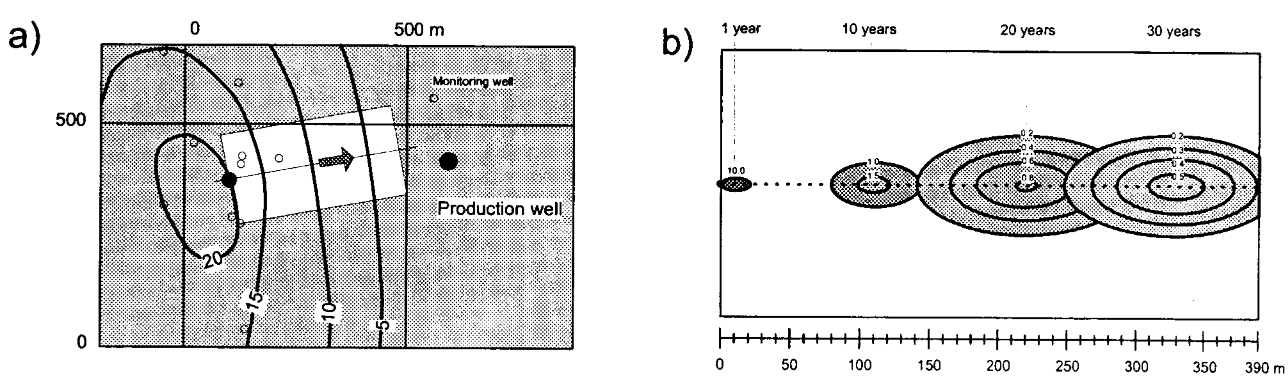


Figure 2: Transport and spreading of a contaminant from an industrial site after instantaneous injection; a) site map, b) time-dependent behaviour of the contaminant

An industrial site near Limassol in Cyprus was contaminated by an accidental input of polychlorobiphenyl (PCB). On a large scale, the aquifer could be assumed to be homogeneous.

The hydraulic head distribution downstream from the industrial site indicated a flow regime with relatively constant flow velocity and flow direction (Fig. 2a). An analytical 2-D solution for instantaneous injection was used to obtain an estimate of the transport velocity and spreading of PCB from this site. Under the given assumptions (e.g., neglecting reactions) it was shown that the centre of the contaminant will move about 330 m in 30 years, spreading more than 140 m in the direction of flow and 70 m laterally (Fig. 2b).

Another important process is matrix diffusion, especially in fractured media. Exchange takes place between the mobile and immobile fluid phases of the flow system during matrix diffusion. To take this into account, a double porosity model is can be used, in which the transport equation is replaced by two transport equations coupled by an exchange term. in. Another possibility to take matrix diffusion into account is to include it in an adsorption term in the transport equation.

Only advection and dispersion are relevant for an ideal tracer. Many programs take advection and dispersion into account. Most of these programs use finite element, finite difference or integrated finite difference methods. To overcome numerical problems in these methods, e.g., numerical dispersivity, special methods have been developed. Examples of such methods are the method of characteristics (e.g., in the MOC code, Konikow, 1978) or the "random-walk" methods (e.g., the early "random-walk " transport model developed by Prickett et al.,1981).

The Prickett-Longquist model was used to investigate the effect of artificial recharge on the groundwater quality in the Larnaca District on Cyprus. In this area, the shallow sandy and gravely aquifer is used predominantly for irrigation. Owing to intensive pumping of groundwater, the quality of this aquifer has increasingly deteriorated due to intrusion of salt water from the sea and the salt lakes and possibly also from deeper groundwater occurrences. The model calculations were carried out for the hydrogeological studies to determine possibilities for improving groundwater quality by artificial recharge. As a simplification, the density of the water was assumed to be constant even if in reality the density changes with salt content (see Chapter 5). For these simulations, infiltration of clarified sewage water was assumed. The model simulates various aspects of the changes in the groundwater flow and of the spreading of contaminants caused by artificial recharge.

The groundwater heads calculated in the transient flow calibration are close to those in the observation wells. In addition, the calculated concentration isolines indicating the seawater intrusion are generally close to the corresponding hydro-chemical analyses (Fig. 3a).

The envisaged injection of clarified sewage water of 1.1 million m^3/year into the aquifer will provide a hydraulic barrier against seawater intrusion. But it also raises the water table, which causes a slight increase in pollution of the groundwater. The calculated rise in the groundwater table amounts up to 3 m, and a hydraulic quasi steady-state situation is reached after approximately five years. Assuming continuous groundwater production, some seawater intrusion is still be expected at that time, but may have ceased after another ten years. The total area of contaminated groundwater will have increased. However, the maximum TDS values in the groundwater will be reduced from those of seawater to those of clarified sewage water, which is assumed to be about 600 mg TDS/L (Fig. 3b).

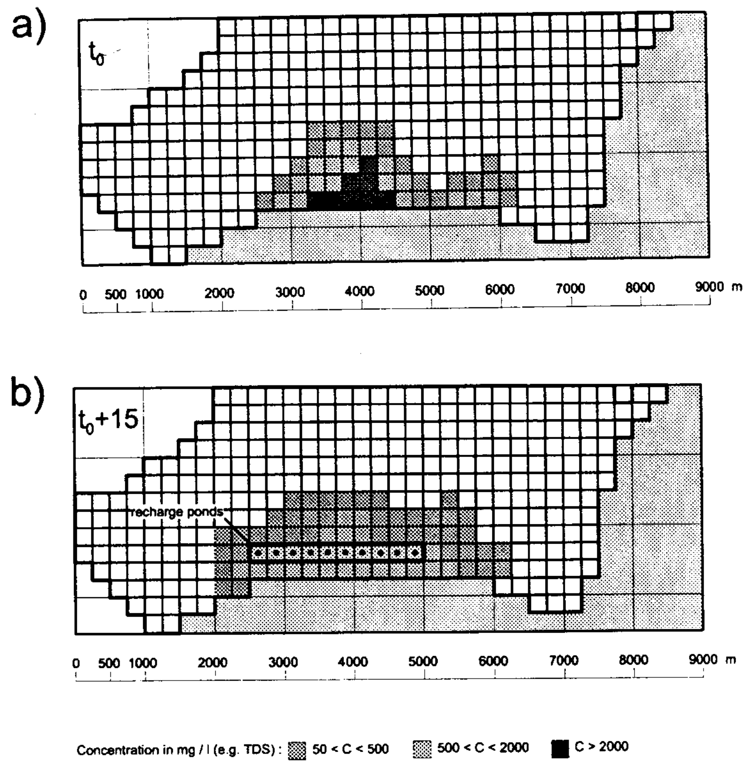


Figure 3: Seawater intrusion and artificial recharge in the Larnaca district
a) Seawater intrusion after 20 years of pumping 1.8 million m^3/year,
b) Influence of artificial recharge after 15 years (1.1 million m3/year of clarified sewage water)

4. Reactive transport

Most of the solutes in an aquifer react with other solutes in the water and also with the rock matrix. Adsorption, desorption, complexing, precipitation and degradation often strongly affect the transport and distribution of solutes in the groundwater. The neglect of chemical reactions in the interpretation of solute transport can result in a totally wrong prediction of the behaviour and inappropriate remediation measures. In such cases, transport models must be coupled with reaction models.

If sorption is much faster than advection and dispersion, equilibrium between adsorbed and dissolved species in the groundwater can be assumed. Equilibrium isotherms are used to describe the sorption process. In simple cases, a linear isotherm term and a retardation factor are added to the transport equation (k_d concept). This leads, e.g., for example, to the well known equation with a retardation coefficient R. This retardation coefficient is the only difference from the ordinary transport equation.

$$R \cdot \frac{\partial c}{\partial t} = -\vec{v}\nabla c + \nabla\left(\overline{D}\nabla c\right) + \frac{P}{n_e} + \frac{Q}{n_e}\left(c_z - c\right),$$

Nonlinear adsorption isotherms can also be used, e.g., the Freundlich isotherm or the Langmuir isotherm. Both result in nonlinearities in the transport equation and require iterative solution methods.

Changes in concentrations are often proportional to the concentration itself. Examples are radioactive decay, for which a linear term has to be added to the transport equation, the decay of micro-organisms in groundwater, and the degradation of organic substances.

In most groundwater models, e.g., MT3D (Zheng, 1990) and ASM (Chiang et al., 1998), advective-dispersive transport and degradation of solutes can be modelled in a simple manner (e.g., first-order degradation). Such models can provide a rough picture of the behaviour of a solute plume, e.g., nitrate reduction during transport.

In general, many chemical parameters influence the transport of a solute, e.g., during denitrification. If a number of solutes are present in the groundwater system which all interact with each other, a multi-component model has to be developed. The general form for the equation for solute transport in such a system is given by n transport equations coupled by sink and source terms:

$$\frac{\partial c_i}{\partial t} = -\rho_i \nabla c_i + \nabla\left(\overline{D}\nabla c_i\right) + \frac{P_i}{\theta_i} + \frac{Q_i}{\theta_i}\left(c_{z,i} - c_i\right) + \frac{1}{\theta_i}\sum_{j=1}^{n} S_{ij}\left(c_1 \mathrm{K}\ c_n\right),$$

where
i is the species index,
n is the total number of species,
θ_i is the specific volumeof the phases in which the species are present (e.g., the pore water or the aquifer matrix), and
S_{ij} is the source or sink term for the reaction of the respective species pair.

The reaction system is homogeneous if all reactions occur in only one phase e.g., the groundwater. If there are also interactions with the aquifer solids, the reaction system is called heterogeneous. Sometimes it can be assumed that the reaction processes are faster than the transport rate, e.g., some dissolution and degradation reactions (see above). In this case, an equilibrium system can be assumed and sink and source terms implicitly follow from the new chemical equilibrium. To model such a system, reactive transport models with sources/sink terms for the solutes were coupled with thermodynamical models, e.g., PHREEQE, EQ3, and MINTEQ. Such a situation is described, for example, by Engesgaard and Kipp (1992) for denitrification in an aquifer in Denmark with a sharp denitrification front.

But mostly, the reaction rate is slower than the advective transport rate. Then the kinetics of the reaction has to be taken into account and kinetic multi-species reaction models have to be used.

4.1 Neutralisation of acid input

The Fuhrberger Feld aquifer in northern Germany, which is used for the water supply of the city of Hannover, is an example of a complex, multicomponent system (Franken, 2000; Franken et al., 2000). The neutralisation of acid input into this aquifer was modeled using the MINTRAN program (Walter et al., 1994), in which a transport model is coupled with the MINTEQA2 program based on MINTEQ. Kinetic models for sulfate reduction and weathering were added to the MINTRAN program,

The impact of acid rain in the forested areas is observed within the uppermost groundwater zone of the Fuhrberger Feld aquifer. The major buffering processes in the groundwater are weathering, sulfate reduction and cation exchange. Modelling of the buffering confirms that the neutralization of acidity can be explained mainly by the last two processes. The question was what is the maximum distance the acidification front travels and can it influence the quality of the pumped water.

The modeling of neutralization in this aquifer shows that sulfate reduction together with a small contribution of weathering are sufficient to neutralize the acid input into groundwater within a residence time of 14 yrs. This would correspond to a maximum distance of about 1200 m that the acids would travel in the groundwater. The present acidification front has traveled about 600 m. The difference is due to neutralization by cation exchange (Fig. 4). However, variability in the properties of the sediment and in the solute concentrations in the groundwater leads to uncertainties in the predicted neutralization rates.

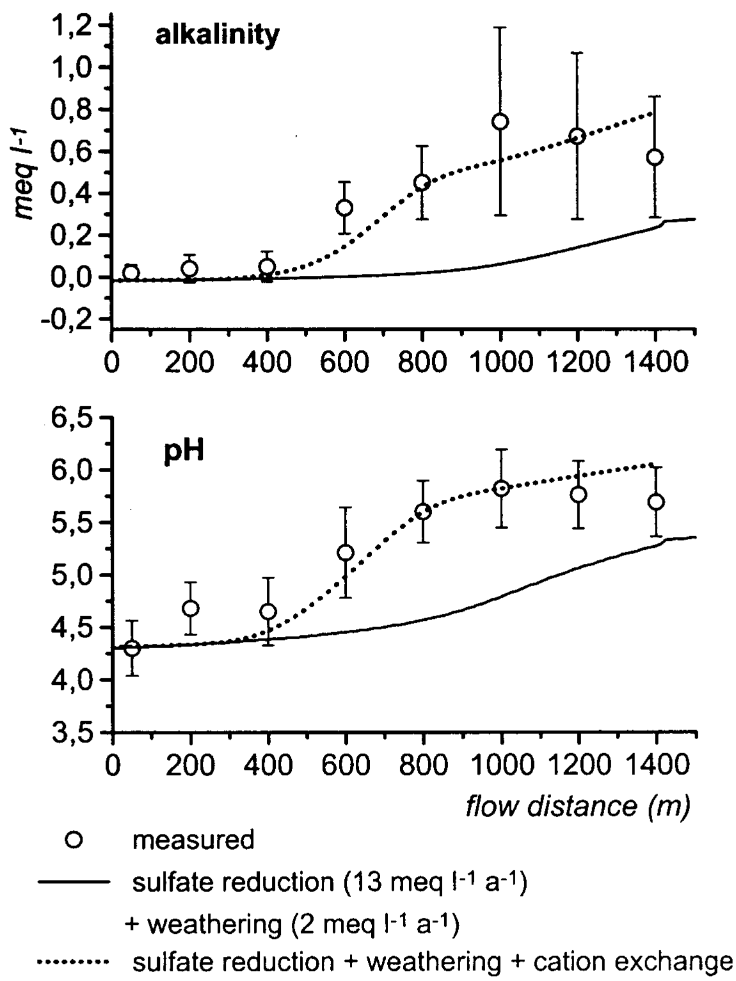


Figure 4: Alkalinity and pH as functions of flow distance: measured values, curves calculated using mean rates for weathering and sulfate reduction, and curves calculated using mean rates for weathering, sulfate reduction and cation exchange.

4.2 Remediation strategies for the Georgswerder landfill

The Georgswerder landfill begun in the sixties is about 5 km south of the center of Hamburg. The waste is underlain by marine clayey sediments. Although the permeability of this layer is very low and its adsorption capacity is high, contaminants, mainly benzene and volatile chlorinated hydrocarbons leaked through this layer into the underlying aquifer at an increasing rate over the years. To reduce the input of contaminants into the groundwater, the landfill was sealed at the surface. Thereafter, the water level within the waste slowly lowered. An investigation was then begun of the transport behaviour of the contaminants to estimate the long-term risk of groundwater contamination from the dump and preparation of am optimum remediation plan both ecologically and economically.

To fulfil these aims, data on kind and rate of solute transport was obtain in the laboratory and field. Representative solute transport parameters were derived from these experiments for the hydrogeological units underlying the dump, namely the clayey marsh sediments and the sandy aquifer.

Initial cross-sectional model calculations were carried out to analyze the flow in the area around the disposal site. The inflow of water from the dump and the associated input of benzene through the clayey layer into the aquifer was reconstructed for 25 years with the simplified assumptions of a steady-state flow field and a fixed water level in the waste. Together with simulations carried out by a second modelling group, these results were the basis for a more realistic model using the Processing Modflow (PM) program with the MODFLOW module for the flow model and the MT3D module for the simplified reactive transport calculations.

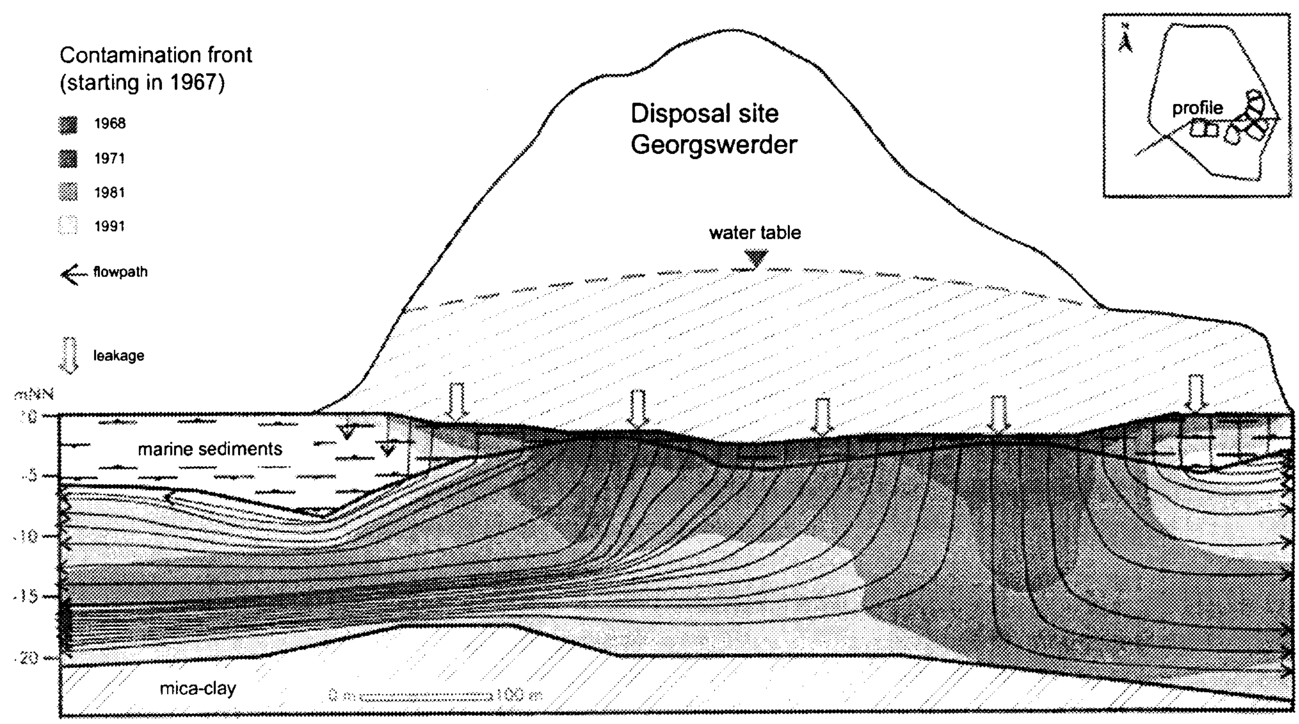
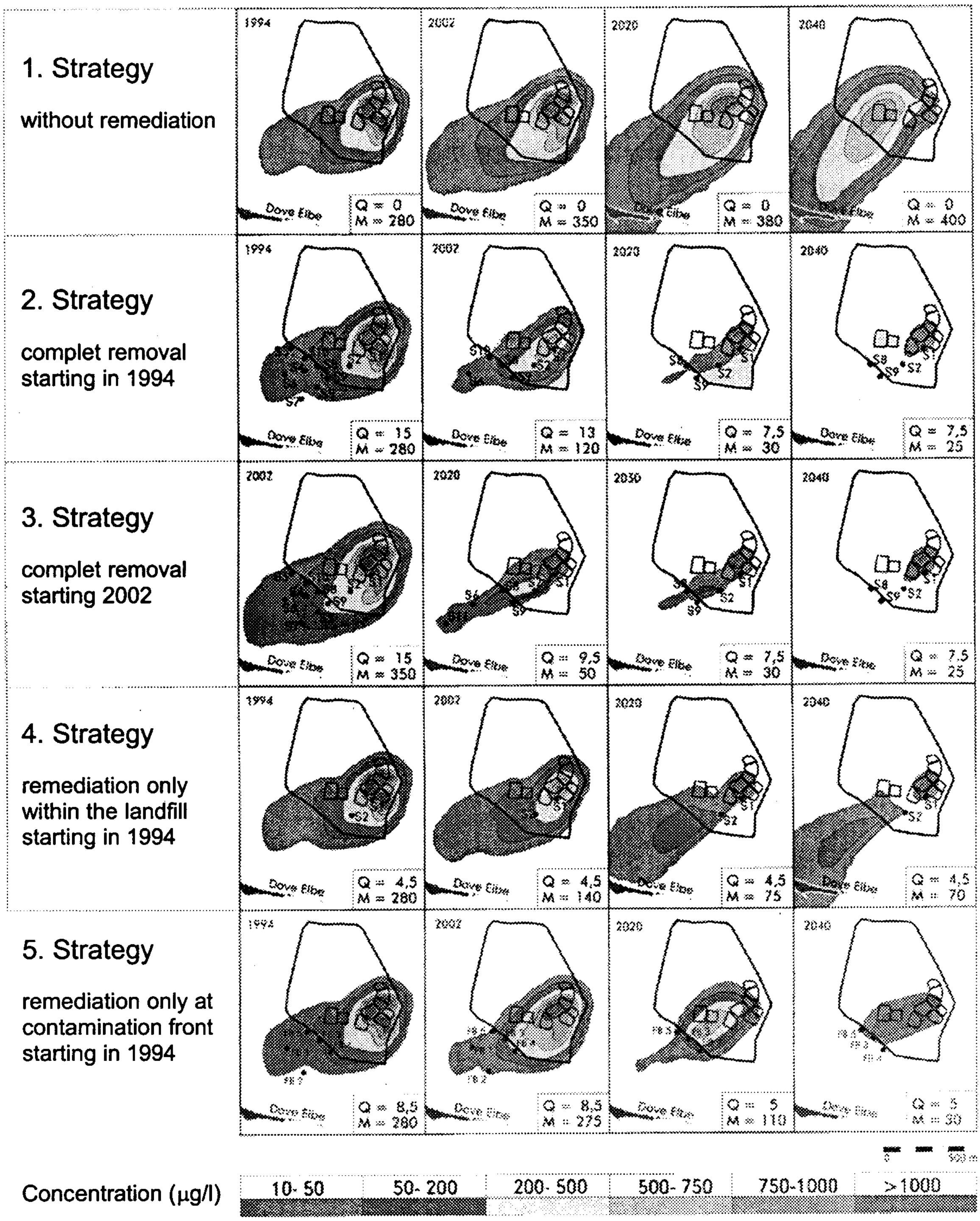


Figure 5: Schematic cross-section of the flow and transport system around the Georgswerder landfill



Q	pumping rate [m^3 / h]
M	mass of contaminants [kg]
S1,...,S11	locations of assumed wells
FB1,...,FB5	locations of remediation wells

Figure 6: Comparison of the effects of different remediation strategies on the transport of volatile chlorinated hydrocarbons between 1994 and 2040

The model showed that the groundwater movement under the landfill is strongly influenced by the water flowing from the landfill. This occurs especially in areas where the clayey layer is relatively thin. The contaminated water flows more or less radially from one of the areas of entry into the aquifer, but with different flow velocities in the different directions (Fig. 4). The flow system was simulated for the time from 1967 to 1992. The measured and calculated solute concentrations showed good agreement, demonstrating the usefulness of the model for prediction.

Five scenarios with different remediation strategies were modeled for a prediction until 2040:
- No remediation, i.e.,, no contaminated groundwater will be withdrawn for treatment;
- Complete removal of the contaminants as rapidly as possible, starting in 1994 (determination of the optimum sites of the remediation wells, including the contaminated water outside the dump);
- Complete removal of the contaminants as rapidly as possible, but starting in 2002 (determination of the optimum sites of the remediation wells, including the contaminated water outside the dump);
- Remediation starting in 1994 only within the landfill (accepting low level contamination outside the main contaminated area);
- Remediation starting in 1994 only at the contamination front.

The efficiencies of the five remediation strategies on limiting the spreading of benzene and volatile chlorinated hydrocarbons in the groundwater up to the year 2040 was demonstrated with the model (Fig. 5). The results provided the basis for a decision on the best strategy for the remediation in terms of both economic and ecological aspects. They decided to use the strategy with remediation starting in 1994 at the contamination front. That was also the least expensive solution for this problem. This decision shows the value of the transport modelling, because no one had taken such a solution into account before the model calculations were carried out.

4.3 Bioremediation

Another multi-species reaction model applied in the next examples is the TBC program (Transport-Biochemistry-Chemistry) developed by Schäfer et al. (1998a). It includes, in addition to saturated groundwater flow and advective-dispersive transport (based on a model developed by Therrien and Sudicky, 1996), three kinds of reactions: microbially mediated reactions, chemical equilibrium, and kinetically controlled chemical reactions. The reaction equations are programmed in a very general way, providing a general structure of reaction types that can be adapted to the reaction system of the observed processes. TBC is flexible and can be adapted to an individual situation without changes in the program code (Schäfer et al., 1998b)

In complex situations, various steps must be taken using different models to find a solution for the remediation of contaminated groundwater. This is shown in the following example (Thullner and Schäfer, 1999).

In situ bioremediation is a promising possibility to clean up aquifers contaminated with biodegradable chemicals. Oxygenated water can be injected to enhance microbial degradation of contaminants. Groundwater simulation models are key tools for a rigorous interpretation of the data, for quantifying reactive transport processes, and for evaluating the efficiency of bioremediation. The following example of bioremediation also gives an impression of how a remediation facility can be designed.

An aquifer below an abandoned chemical plant in Hamburg, Germany, is heavily contaminated with chlorinated aromatic compounds, mainly chlorobenzenes. Preliminary evaluation indicated that normal pump-and-treat remediation of the site would be inefficient, due to adsorption of the contaminants by the rock matrix and possible presence of DNAPL (dense non-aqueous-phase liquids) in the aquifer. Other preliminary studies indicated that benzenes with a low degree of chlorination, which account for the bulk of the contamination in the aquifer, can be degraded by aerobic bacteria. Thus, in situ bioremediation using dissolved oxygen as an oxidant was proposed as an alternative to pump-and-treat remediation. A pilot study was conducted on a 30 x 55 m test plot to assess the feasibility of bioremediation at this site.

For several years, the regional groundwater flow was towards a drinking water well field about 1.5 km south of the contaminated site. In 1990 these wells were shut down, and the regional groundwater flow changed from south to north. A preliminary study to optimize decontamination well locations and pumping rates was carried out using the PAT analytical flow model (Kinzelbach and Rausch, 1990). A configuration with two central injection wells and six surrounding extraction wells along with a total injection and extraction rate of 43 m^3/h proved to be the optimal solution under the given constraints (Kinzelbach et al., 1990). Figure 7 shows the calculated flow paths for this well scheme for one direction of groundwater flow. When compared with the flow pattern for other directions of groundwater flow in the test site aquifer, it is seen that the flow pattern is fairly insensitive to variations in the regional groundwater flow. On the basis of the modeling, the test site was equipped with two injection wells, six extraction wells, ten fully screened observation wells, and eight multilevel observation wells.

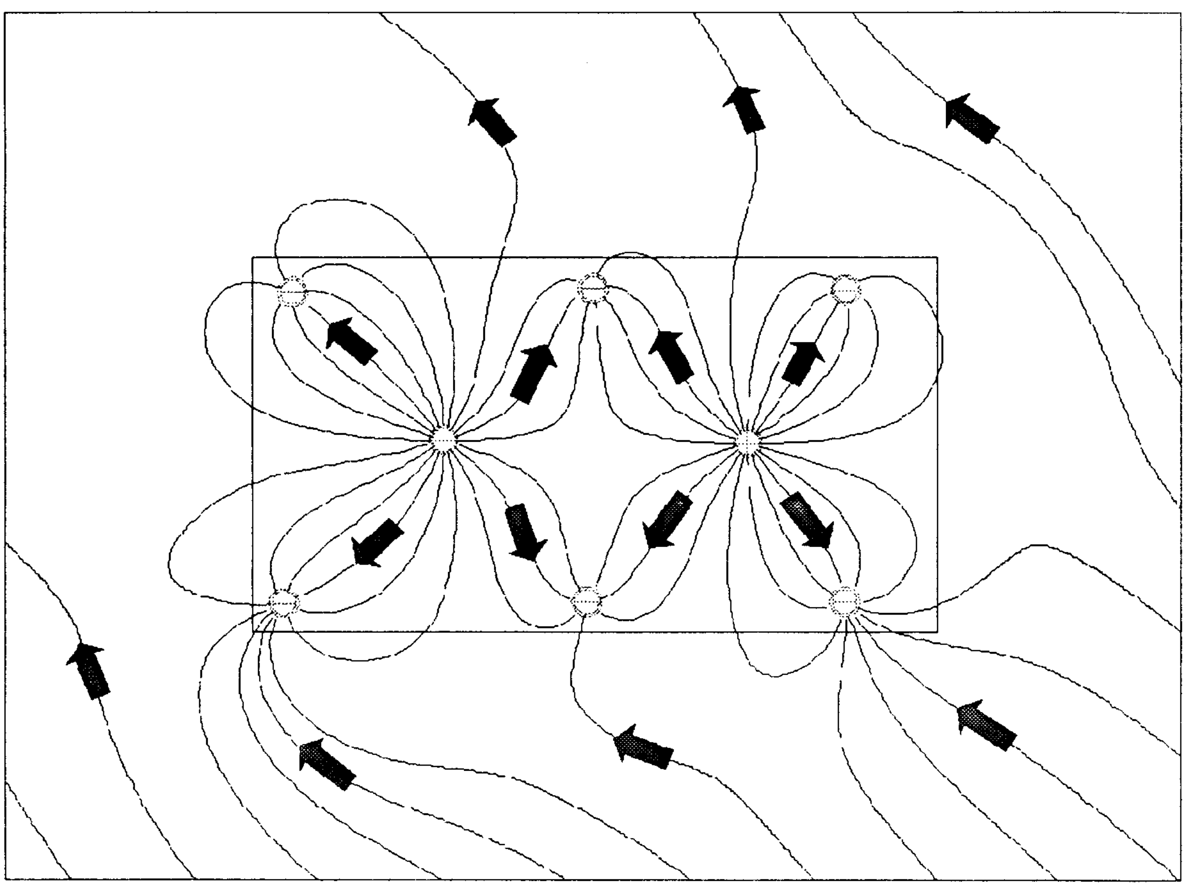


Figure 7: Calculated flow paths for one direction of groundwater flow

In the next step a tracer test with quasi instantaneous injection of different nonreactive tracers in both injection wells was conducted to verify the hydraulic functioning of the remediation well configuration. Results of this tracer test were also used to calculate the hydraulic parameter values used for the reactive transport modeling. The recovery of more than 80 % of the initial tracer material after 36 days showed that a closed hydraulic circulation system was indeed achieved.

The tracer test was evaluated using a three-dimensional "random–walk" transport model (Kinzelbach et al., 1993) based on the USGS MODFLOW model (McDonald and Harbaugh, 1988). Comparison of measured and simulated uranine concentrations in a extraction well and a multilevel sampling well showed good agreement between simulated and observed arrival times (Fig. 8). A, The main objective of the tracer test, identification of the effective mean parameters and the general flow field of the aquifer, was achieved if some discrepancy between measured and calculated breakthrough curves is accepted..

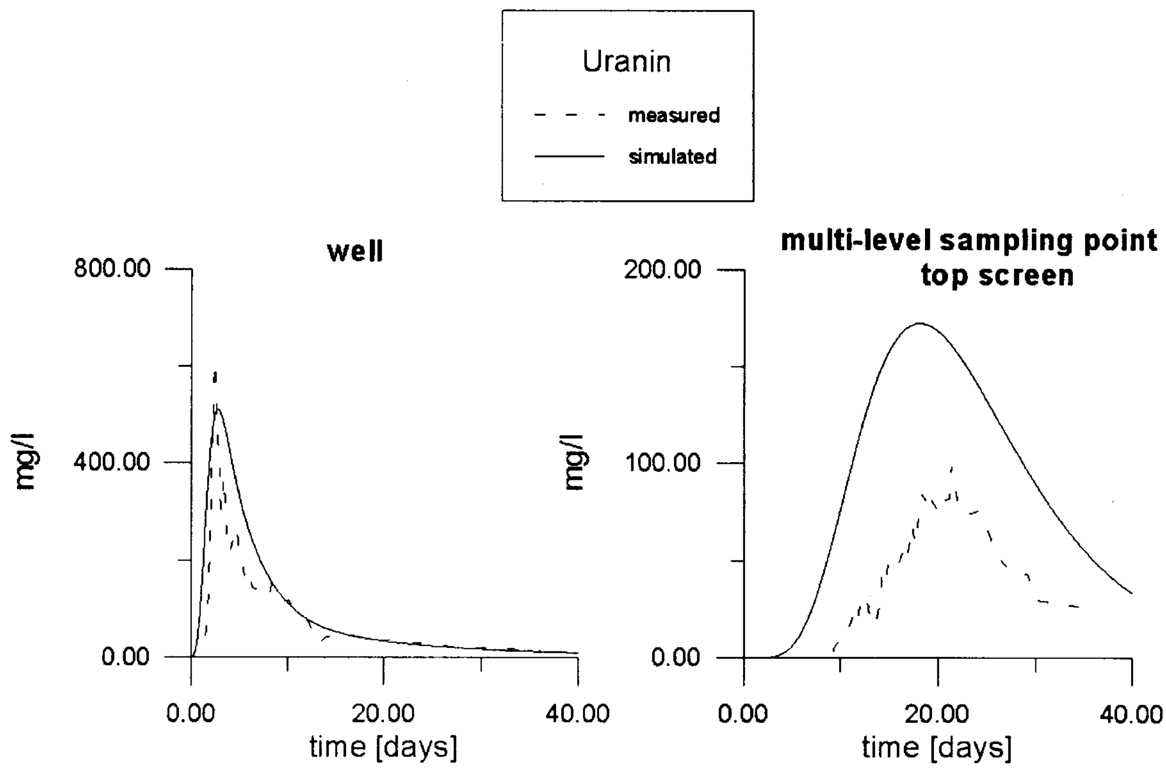


Figure 8: Comparison of measured and simulated uranine concentrations in well 201 and multilevel sampling well 501

To test the effect of bioremediation, water saturated with oxygen using pure oxygen was injected for 433 days. The three dimensional TBC reactive transport model was used to identify transport and reactive processes and oxygen-consuming processes. The model calculations showed that a significant portion of the injected oxygen either oxidized inorganic species in the aquifer instead of the contaminants or was extracted again at the extraction wells. The predominant process was probably oxidation of pyrite to sulfate, followed by oxidation of ferrous iron and ammonia. Contaminant degradation consumed only about 2 % of the oxygen, an unacceptably low efficiency of the in situ bioremediation measure. The results of the pilot study clearly suggested that in situ bioremediation is not an appropriate clean-up method for this specific aquifer. Since pump-and-treat remediation is also unpromising, a practicable solution may be to surround the contaminant source by slurry walls.

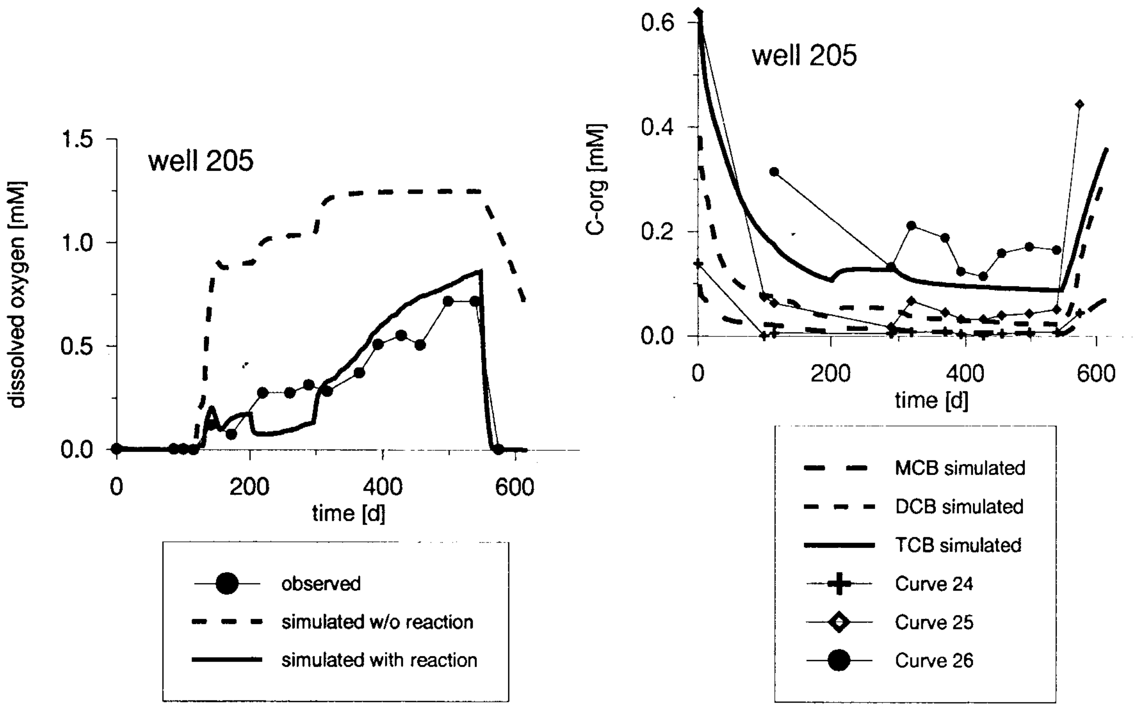


Figure 9: Comparison of measures and calculated data

4.3 Natural attenuation

It has been known for many years that decontamination of groundwater can occur naturally in aquifers. Much work has been done in the last few years to investigate this effect of natural attenuation. To take natural attenuation into consideration as one element in a decontamination strategy, it is important to know the processes and to observe the time-dependent behaviour of the contaminant plume in the aquifer as part of risk management. The aim of risk management is to avoid unnecessary decontamination procedures and to minimize the cost of the groundwater remediation. If the monitoring of the contaminant distribution shows that natural attenuation is not sufficient, additional remediation procedures have to be used.

Aquifer contamination with mineral oil products is a widespread environmental problem. There is clear evidence that many mineral oil products, like benzene, toluene and xylene (BTX), are often microbial degraded in soils and aquifers. The numerous field studies on the fate of BTX compounds in aquifers suggest, for example, that the degradation of these compounds in aquifers (also called intrinsic bioremediation or natural attenuation) can be expected to be rather efficient. Consequently, natural degradation should be taken into consideration in risk analysis and contaminant transport predictions. Otherwise the hazardous potential of these compounds might be overestimated.

The ground below a xylene production unit of an abandoned refinery in Germany was contaminated with various mineral oil products. The contaminated aquifer, saturated thickness between 14 and 16 m, consists of calcite-rich Quaternary fluvial sand. After detection of the underground contamination, the soil above the groundwater table was excavated and treated off-site. The area was refilled with uncontaminated sand. Unfortunately, the groundwater table at that time was relatively high and an appreciable amount of contaminants still remained below the groundwater table. These contaminants produced a plume of aromatic hydrocarbons in the groundwater (Fig. 10). Groundwater sampling yielded strong evidence for in situ microbial degradation of xylene. Three abstraction wells were installed downstream from the contaminated area to prevent further contaminant spreading.

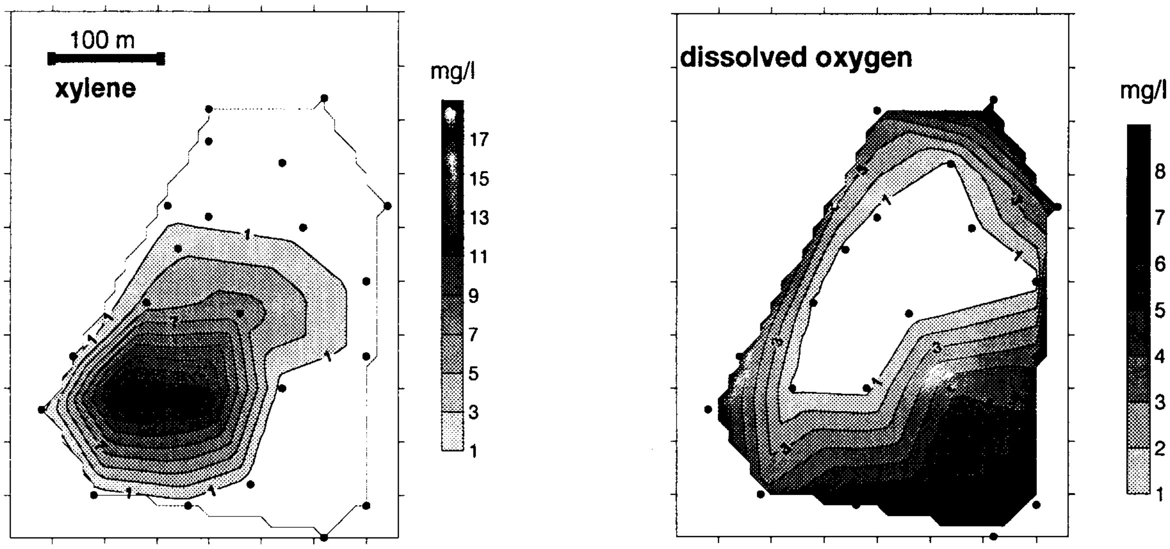


Figure 10: Concentrations of xylene and oxygen in groundwater in August 1990. The dots in the figures denote positions of the groundwater sampling points.

The TBC program, mentioned above, was used to to quantify the proportion of microbially degraded xylene to the amount removed in the wells. It was shown that microbial degradation accounted for about one-third of the total xylene removal. A further objective of the model simulation was to predict the spreading of the xylene under the natural regional flow conditions, i.e., without the three abstraction wells while retaining the parameters of the biochemical model.

Although the pump-and-treat remediation was supplemented by in situ degradation of the xylene, its efficiency was low (Fig. 11). The simulation results suggest, however, that the expected in situ degradation would be sufficient to limit the extent of the xylene plume to a distance of less then 1000 m downstream from the contaminated area (see Fig. 12). Therefore, natural bioremediation is a realistic alternative to pump-and-treat remediation in this case. This is also reflected by the fact that the scenario simulating the in situ xylene degradation rate under natural flow conditions (1.5 kg xylene/d) equals the xylene extraction rate actually achieved by the three remediation wells.

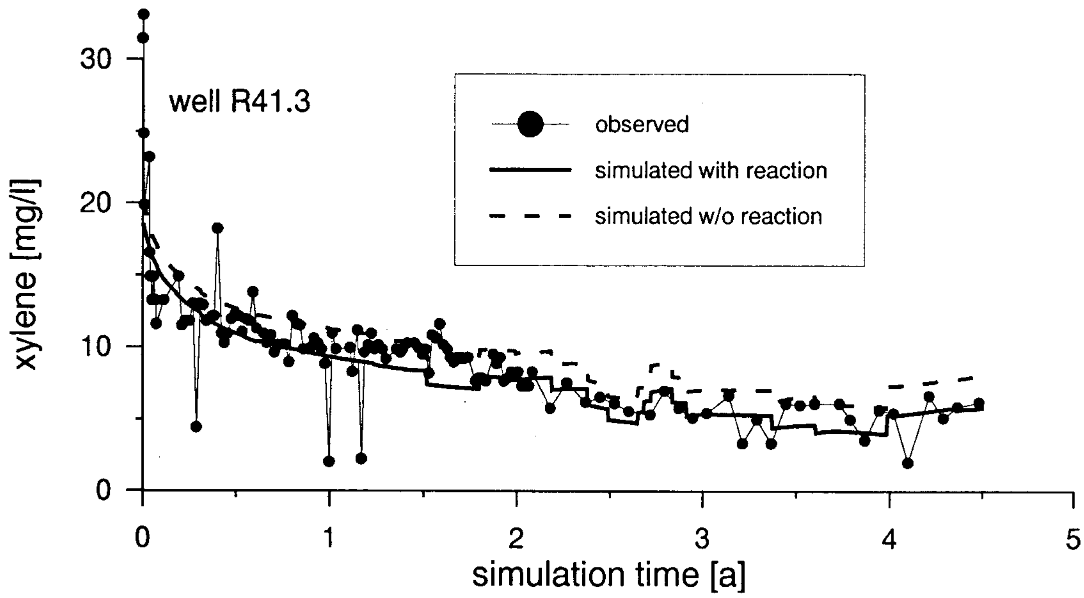


Figure 11: Measured and simulated xylene concentrations in the one of the three abstraction wells. The concentration curves exhibit the typical trend of pump-and-treat remediation schemes showing a pronounced decrease in concentration during the first weeks of the operations and only very gradually decreasing concentration at later times.

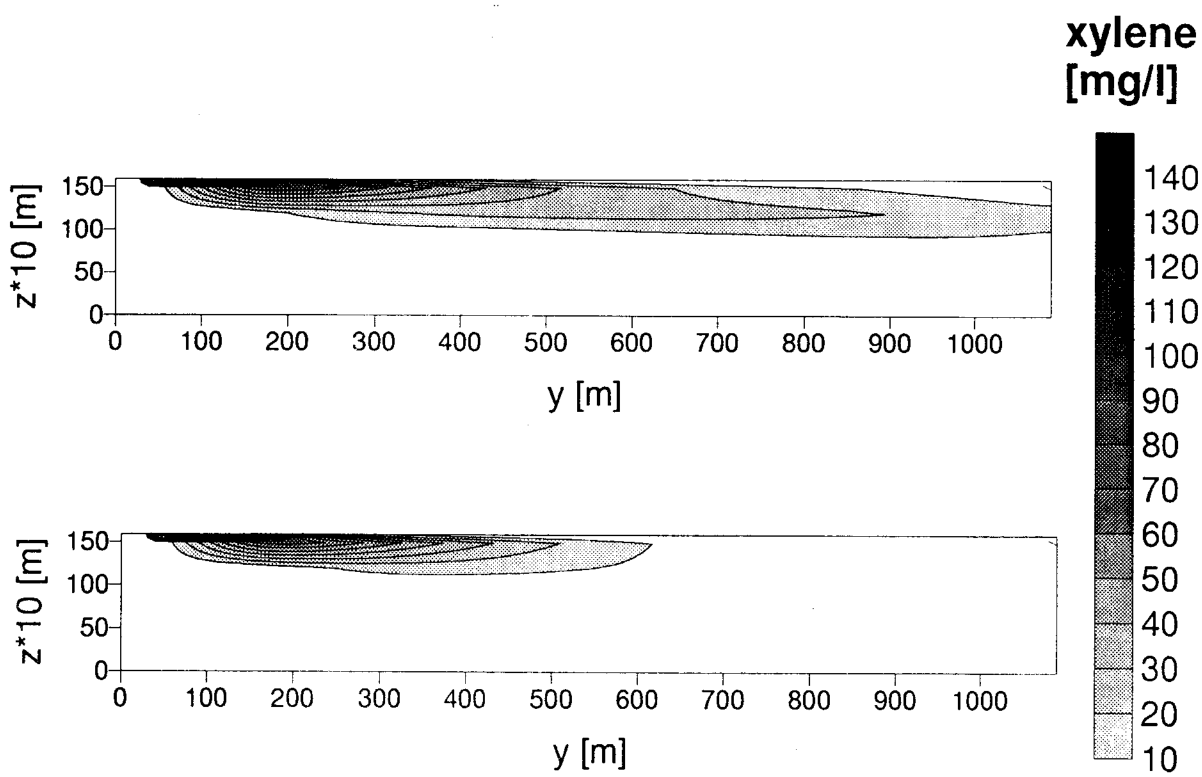


Figure 12: Simulated xylene distribution for a cross section in the direction of flow for two scenarios. While in the non-reactive case (top of figure) xylene had migrated beyond the boundary of the model domain at the end of the simulated time (24 years), in the reactive case (bottom of figure)it is remained in a quasi-steady-state plume .

In the case presented here, the authorities decided in 1996 to allow a cessation of the remediation activities and to rely on the degradation potential of the aquifer. The xylene concentrations continue to be continuously monitored, but, owing to the low groundwater flow velocities, it will still take several years until the measured data can be used to evaluate the model predictions. In any case, the groundwater quality will always be deteriorated by the xylene contamination, because even for very efficient xylene degradation, e.g., the iron concentration in the groundwater will rise well beyond the threshold values for drinking water (in Germany: 0.2 mg/L total iron). The decision of the authorities is nevertheless corroborated by the findings of the study presented in this section.

5. Density-dependent transport and salt water intrusion

It is known that fresh water is obtained in many countries in western Asia from coastal aquifers which supply water for the often urbanized areas on the coast and large areas in the hinterlands. Agricultural and urban development has increased demand for water in the past twenty years. Especially due to the arid climate, salt water intrusion has become a matter of crucial importance. The fresh water/saline water interface has been advancing inland. The calculation of the movement the freshwater/saltwater boundary is also a transport problem, but with one important difference.

In all of the above equations above, it was assumed that the density of the water does not change with solute content. But in situations like salt water intrusion, this assumption is not correct. The density of the water has to be taken into account. The continuity equation and the transport equation are therefore coupled via the density and viscosity of the water. Simplifications are possible in some of these problems. However, if only an approximate solution is of interest, and the water density is not too high, e.g., intrusion of water with a density less than that of sea water, transport calculations with the simplifying assumption of constant density can provide a sufficient picture of the situation. An example is given in Chapter 3. Another, but more correct simplification is, for example, the sharp-interface approach for the fresh/salt water boundary in coastal areas. But often these problems can be realistically solved only with the help of complex numerical models using a system of coupled partial differential equations.

Various geohydraulic simulation programs are available for planning sustainable withdrawal from coastal aquifers. They permit an assessment of scenarios with different well locations or artificial recharge. Mostly finite difference or finite element models, like HST3D, SUTRA, FEFLOW, and SALTFLOW, are used, sometimes other models, e.g., based on the method of characteristics (MOCDENSE). An overview is given in ESCWA, 1999.

But it is often useful to simplify the system, e.g., assuming a sharp interface between freshwater and saltwater. This means that in coastal aquifers freshwater and saltwater often behave like immiscible fluids. Although fresh water and salt water are miscible, in many situations they act like immiscible fluids separated by a relatively thin transition zone. This can be approximated by an abrupt change of density at the interface between the two volumes of water. The freshwater forms a pillow (or lens), variable in thickness and underlain by the denser saltwater. Together with some additional assumptions, this situation can be approximated by the sharp-interface approach (e.g., Huyacorn and Pinder, 1983)

One example of the programs that have been developed using this approach is the program SIM_COAST. It was developed to simulate the time-dependent behaviour of coastal aquifer systems in porous rock in cross-sectional models (Brunke and Schelkes, 1998). It was used, for instance, to investigate groundwater recharge from water behind a dam across Wadi Ham near Fujayrah in the United Arab Emirates. The effect of overexploitation could clearly be observed in the model results (Fig. 13a). Saltwater intruded far into the aquifer. Although the dam across the wadi discernibly affects the groundwater system, the resulting artificial recharge is not enough to prevent sea water from intruding the coastal aquifer. Simulation results of several abstraction/infiltration scenarios showed that seawater may be expected to cease intruding or even retreat as shown in Figure 13b.

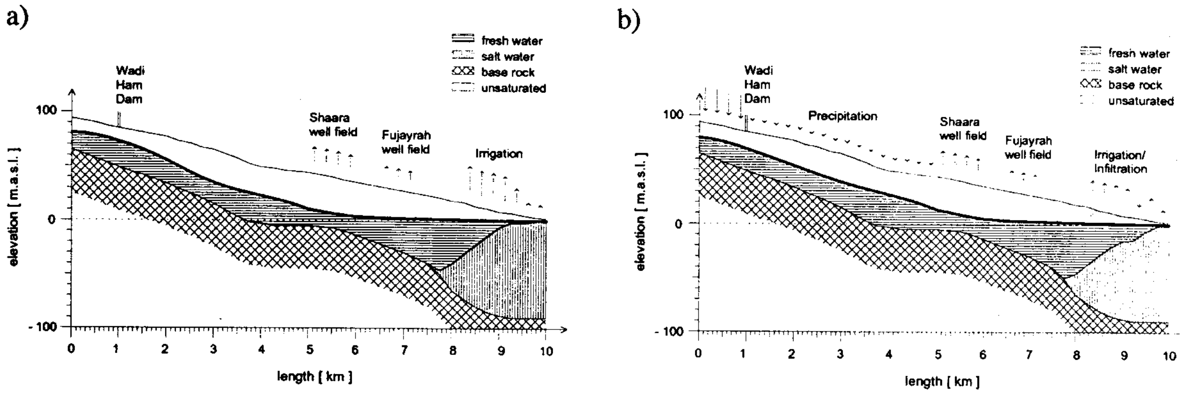


Figure 13: a) Situation at the end of 1996 after a flood;
b) Predicted situation in 2010 with reduced abstraction and additional infiltration

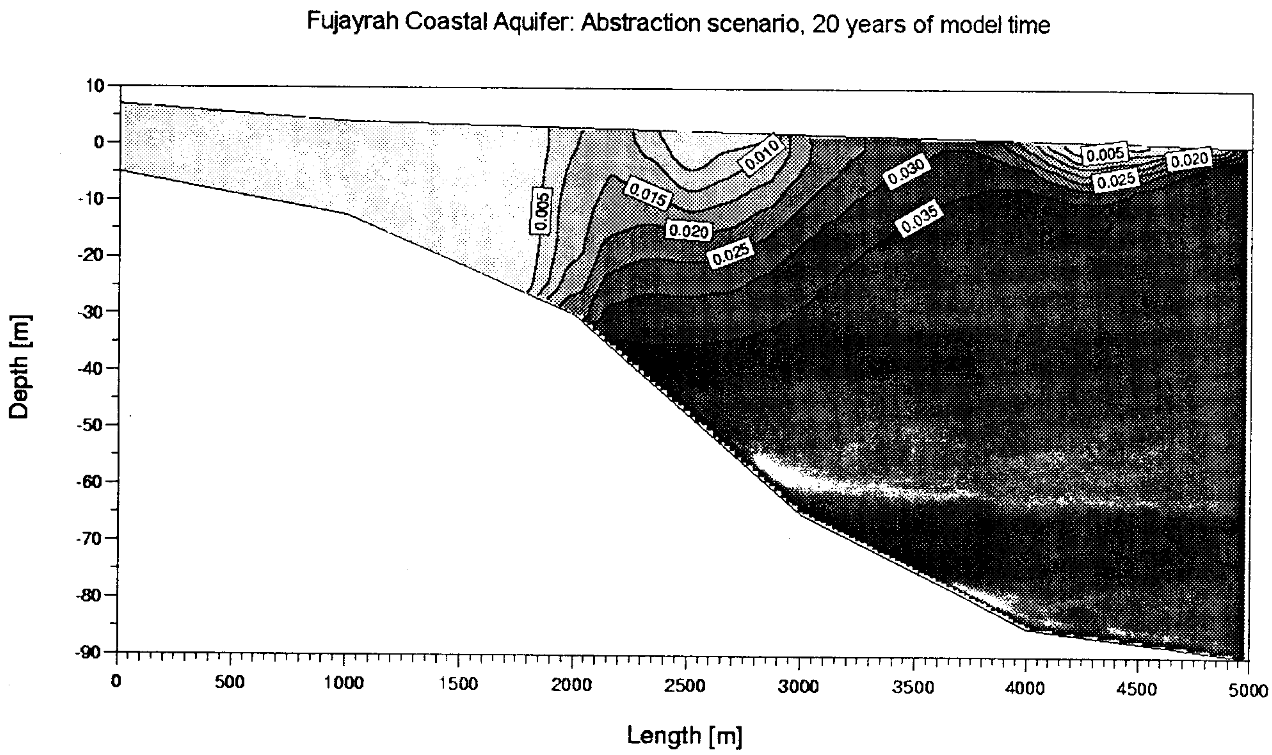


Figure 14: Distribution of salt concentration after 20 years of groundwater abstraction (salt concentration in kg/kg) as simulated using the SUTRA model of the Fujayrah area.

A comparative study was carried out for the same area using the two-dimensional SUTRA code (Voss, 1984), which is based on a system of partial differential equations with variable groundwater density. In order to save computation time, the modeled part of the cross section was shortened to 5 km of the coastal plain, because only in this part of the aquifer is interaction between fresh and salt water expected. If a relatively sharp interface was to be achieved with the grid used for the modeling, anisotropy and a practically vanishing transversal dispersivity had to be assumed. The general trend in the results compared well with the SIM_COAST results. Figure 14 shows the effect of seawater intrusion.

6. Conclusions

The problems that have to be solved in remediation or protection of groundwater resources are highly variable. Differences exist in almost all of the involved disciplines: in the hydrogeology (e.g., rock types, heterogeneities, porous structure and permeabilities), in the hydrochemistry (e.g., solute content and hydrochemical parameters), in the microbiology, and in the mineralogy. This situation explains the difficulty to find general solutions. Each of the remediation problems has to be solved in a unique manner.

Therefore, it is very important to start with the development of a comprehensive conceptual model. This model has to take into account all the knowledge in the existing data base of hydrogeological and hydrochemical data. Uncertainties have to be identified, and possible simplifications in developing a protection or remediation strategy have to be discussed. The enlargement of the data base that could follow this first analysis should be problem- and goal- oriented to minimize additional costs.

As part of the conceptual model, scenarios for protection or remediation have to be identified. In these scenarios, the various technical remediation methods (e.g., soil excavation, pump and treat, funnel and gate) as well as natural attenuation have to be taken into consideration and evaluated before a decision can be made about which protection or remediation procedure should be used.

In almost all steps of this evaluation, flow and transport models are a useful tool. They can help characterise the system, identify gaps in the data and locations for additional wells; they can deal with uncertainties, compare different scenarios, and indicate the best remediation or protection procedure under the given circumstances. There are many programs available, from simple flow models using particle tracking and analytical models to multi-species, multi-phase transport models and variable density models coupled with reaction models. The choice of the right model(s) for a given purpose is also a very important aspect of the development of the conceptual model.

It was only possible to discuss a small number of models here. They were adapted to various situations and fulfilled various purposes. These examples should only provide an initial impression of the use of such models. For the evaluation of easier problems, described in Chapters 2 and 3, as well as problems involving simple reactions, a number of very powerful verified programs can be used.

It is more difficult in the area of complex reactive processes. Although some excellent programs are available for this kind of complex reactive transport problem, most such programs are still under development. The more complex the problem is, the more this is the case. For the calculation of systems of n coupled transport equations, systems of multiphase flow (which means more than one mobile phase (water, gas, oil)) and density-dependent flow, much research is yet necessary. Combinations of these processes are also possible, e.g., transport of n interacting species in a density-dependent flow system, or other influences, e.g., temperature effects, may have to be taken into account.

But, in many of the cases that have to be considered, simplifications make it possible to use analytical solutions, one-phase models, simplified multi-component or density-dependent models. Although it is often possible to identify appropriate remediation procedures, the problems and results of modelling remediation of groundwater in complex systems as well as experience with remediation procedures indicate that groundwater protection is much better and cheaper than remediation. In any case, transport models can help to identify the right protection measures.

References

Thomas A. Prickett, Thomas G. Naymik, and Carl G. Lonnquist, 1981: A “random-walk” solute transport model for selected groundwater quality evaluations, Illinois State Water Survey, Champaign, Bulletin 65.

G. Schmidt et al., 1988: Groundwater Model Investigation on the Kiti Aquifer. Republic of Cyprus and Federal Republic of Germany, Technical Cooperation Project on Pedology, Hydrochemistry and Non-metallic Mineral Resources, Project report no. 11, BGR archive no. 103.554, Hannover.

Kinzelbach, W. and R. Rausch, 1990. Pathlines and Traveltimes Model "PAT"; Kassel, Germany

Kinzelbach, W., A. Voss and W. Schäfer. 1990. Hydraulische Auslegung einer in-situ Sanierungsmaßnahme in der gesättigten Zone auf dem ehemaligen Werksgelände der Fa. Boehringer; Dekonta GmbH, Hamburg, Germany

Kinzelbach, W., D. Schäfer and W. Schäfer, 1993. "Auswertung der im Vorführtestfeld durchgeführten Tracerversuche"; University of Kassel, Germany.

McDonald, M.C. and A. W. Harbaugh, 1988. "MODFLOW, A modular three-dimensional finite difference ground-water flow model"; *Techniques of Water-Resources Investigations of the U.S.G.S,* Book 6, Chapter A1, pp 576.

Schäfer, D., W. Schäfer and W. Kinzelbach, 1998. "Simulation of Reactive Processes Related to Biodegradation in Aquifers: 1. Structure of the 3D Reactive Transport Model"; *J. Contaminant Hydrol.*, 31(1–2): 167–186.

Therrien, R. and Sudicky, E.A., 1996. Three-dimensional analysis of variably-saturated flow and solute transport in discretely fractured porous media, *J. Contaminant Hydrol.*, 23(1–2): 1–45.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N., 1980. PHREEQE – a computer program for geochemical calculations. U.S. Geological Survey.

Thullner, M. and Schäfer, W., 1999. Modeling of a Field Experiment on Bioremediation of Chlorobenzenes in Groundwater. *Bioremediation Journal.,* 3(3):247–267.

Franken, G., Duijnisveld, W.H.M., Böttcher, J. Molson, J.W., Mayer, K.U. and Frind, E.O., 2000. Processes neutralizing athmospheric acidification in a sandy aquifer in northern Germany. In: Groundwater Research, Rosbjerg et al. (eds.), Balkema, p.

Franken, G., 2000. Neutralisation saurer Einträge in einem Aquifer aus basenarmen Sanden – Feldstudie und Modellierung. Geol. JB, Sonderhefte, SC 1, 161 S., Hannover

Walter A.L., Frind E.O., Blowes D.W., Ptacek C.J. & Molson J.W. 1994. Modeling multicomponent reactive transport in groundwater: 1. Model development and evaluation. *Water Resources Research* 30: 3137–3148

Voss, C.I.: 1984: Saturated-unsaturated transport (SUTRA), USGS Water Resource Investigations 84–4369.

Konikow, L.W., Bredehoeft, J.D., 1978: Computer Model of Two-dimensional Solute Transport and Dispersion in Ground Water. Book 7, ch C2. U.S. Geological Survey.

Sanford,W.E., and Konikow, L.F., 1989. A two-constituent solute transport model for groundwater having variable density. Holcomb Research Institute. TNO-QGV Institute. Golden, CO: IGWMC-FOS36.

Huyacorn, P.S., Pinder, G.F., 1983: Computational Methods in Subsurface Flow. Academic Press, Orlando, Florida.

Frind, E. and Molson, J., 1994: Saltflow 2.0 users guide, Waterloo Center for Groundater Research, Canada.

Diersch, H-J, 1994: FEFLOW Users Manual Version 4.2, WASY GmbH, Berlin, Germany.

ESCWA, 1999. Groundwater Quality Control and Conservation in the ESCWA Region. E/ESCWA/ENR/1999/1, New York

Chiang, W.-H., Kinzelbach, W. and Rausch, R., 1998. Aquifer Simulation Model for Windows – Groundwater Flow and Transport Modeling, an Integrated Program. Borntraeger, Stuttgart, Germany