Biodegradation **15:** 453–465, 2004.

Evaluation of exploration and monitoring methods for verification of natural attenuation using the virtual aquifer approach

Dirk Schäfer[1]*, Bastian Schlenz & Andreas Dahmke
*Christian-Albrechts-Universität zu Kiel, Institut für Geowissenschaften, Angewandte Geologie Olshausenstraße 40 - 60, D-24098 Kiel, Germany (*author for correspondence: e-mail: dschaefer@gpi.uni-kiel.de)*

Accepted 1 December 2003

Key words: geostatistics, monitoring, natural attenuation, virtual aquifer

Abstract

Though natural attenuation (NA) is increasingly considered as a remediation technology, the methods for proper identification and quantification of NA are still under discussion. Here the “Virtual Aquifer” approach is used to demonstrate problems which may arise during measurement of concentrations in observation wells and for interpolation of locally measured concentrations in contaminated heterogeneous aquifers. The misinterpretation of measured concentrations complicates the identification and quantification of natural attenuation processes. The “Virtual Aquifer” approach accepts the plume simulated with a numerical model for a heterogeneous aquifer as “virtual reality”. This virtual plume is investigated in the model with conventional methods like observations wells. The results of the investigation can be compared to the virtual “reality”, evaluating the monitoring method. Locally determined concentrations are interpolated using various interpolation methods and different monitoring set-ups. The interpolation results are compared to the simulated plume to evaluate the quality of interpolation. This evaluation is not possible in nature, since concentrations in a heterogeneous aquifer are never known in detail.

Introduction

In the last years natural attenuation processes are increasingly considered as alternative remediation technique for porous aquifers contaminated with microbially degradable substances. Rules and laws how to verify natural attenuation in aquifers, like the “lines of evidence” (US EPA), are already available or under construction.

It is well known that aquifer parameters as conductivity, porosity or chemical composition are heterogeneously distributed. The effects of these heterogeneities on flow fields, contaminant transport (Sudicky 1986; Vereecken et al. 2000) and degradation rates (Berglund et al. 2001; Schäfer 1992) have already been investigated, but their consequences on the measurement and verification of natural attenuation processes still have to be discussed. Unfortunately it is nearly impossible to investigate this effect directly on site, since the properties of the aquifer cannot be determined in detail without destroying it.

One way of gathering information on heterogeneously distributed parameters is through collection of many data points, for example by installing a large number of multi-level sampling wells, as has been done at the Borden (Woodbury & Sudicky 1991), Cape Cod, Columbus (Boggs et al. 1992) or Krauthausen site (Vereecken et al. 2000). But even this extensive sampling method cannot measure heterogeneous structures on a scale smaller than the distance of the wells or larger than the test site. Moreover, for practical purposes this approach is far too expensive.

Another approach is the outcrop analogue model that has been developed for crude oil extraction (Flint & Bryant 1993) and transferred to aquifers (Koltermann & Gorelick 1996; Siegenthaler & Hugenberger 1993; Webb & Anderson 1996). In the outcrop analogue project the unsaturated zone of a specific sedimentological system (e.g. braided river, meandering river) is investigated. In an outcrop the 2-dimensional (vertical & horizontal) parameter distribution of e.g. hydraulic conductivity is mapped in detail. The final aim is a characterisation of spatial parameter distributions depending on the sedimentological genesis of the aquifer. The determined structures can be transferred to the saturated zone since the geological genesis of saturated and unsaturated soil is similar. Due to aerobic conditions in the unsaturated zone this method is not suited for redox sensitive parameters. Based on this sedimentological and hydrological information, numerical models can be used to simulate and understand the complex transport processes in this specific aquifer (Bersezio et al. 1999; Weissmann et al. 1999).

The "Virtual Aquifers"-approach uses virtual realities to investigate the influence of heterogeneities on the detection and verification of natural attenuation processes. Virtual realities are used in other application areas to simulate complex processes in systems which are hard to parameterise. Well known examples are the simulation of car crash tests or the simulation of traffic for town planning. Here a concept is presented for the use of virtual realities to evaluate exploration, monitoring and remediation strategies for contaminated aquifer systems.

The idea of "Virtual Aquifers" is to construct a synthetic heterogeneous aquifer only in the virtual reality of a computer based simulation program. The statistical properties required for generation of a heterogeneous conductivity distribution are taken from well investigated sites but also from outcrops. Statistical properties of the spatial distribution of other parameters like the Fe(III)- or C_{org}-content are not yet known and have to be determined. By modifying these stochastic parameters new test sites can be generated in the computer at low cost. This generated data set does not describe an existing known natural aquifer, but it is similar to reality. In contrast to real aquifers the virtual aquifer has the advantage that its hydraulic and geochemical properties are exactly known at every point. Numerical models can be used without additional assumptions to simulate reactive transport processes of contaminants in this virtual aquifer resulting in concentration distributions which are similar to those in real aquifer systems. The resulting plumes can be used to test, visualise and monetarise different remediation and monitoring strategies.

In this article an aquifer with heterogeneous conductivity distribution is generated and natural attenuation processes of an organic contaminant are calculated. The resulting plume is investigated with the model using various observation wells at different pumping rates. The comparison of simulated plume concentrations with the virtual monitoring result shows the uncertainty of present investigation methods in aquifers. Hence, the first part of the investigation aims on the reliability of concentration measurements by pumping in observation wells and intrinsic uncertainties of present monitoring methods for determination of concentrations in aquifers.

In a second step local concentrations are interpolated using different interpolations methods and assuming varying numbers of observation wells. The comparison of the interpolation with the simulated plume shows the suitability of interpolation methods and the influence of position and number of observation wells on the interpolation result. This points out the uncertainty of approaches for regionalisation and characterisation of a contaminant plume.

Methods

Generation of a virtual aquifer

The calculation of reactive transport processes concerning natural attenuation are performed with the numerical model TBC (Transport, Biochemistry and Chemistry). A detailed description of the model can be found elsewhere (Schäfer et al. 1998a), here only some relevant aspects are discussed.

According to the Borden test site the generated virtual aquifer consists of 5 layers with 1 m thickness each. Every layer is 120 m long in flow direction with a width of 40 m, discretised in 240 × 80 cells of 0.50 × 0.50 m. A ground water recharge of 300 mm/a is assumed. Two constant head boundaries with a head difference of 45 cm cause a gradient of 3.7‰, other boundaries are impermeable. The porosity is assumed to be constant in the whole domain (33%) resulting in an average pore velocity of 0.09 m/d. For simplification stationary flow is assumed.

The conductivity is heterogeneously distributed, the parameters are chosen according to the Borden test site (Woodbury & Sudicky 1991) to ensure, that they are in a reasonable order of magnitude (Table 1). However, the model does not intend to be a site model for the Borden test site. The random conductivity distributions of the 5 layers (Figure 1) are generated independently using the field generation tool (Frenzel 1995) provided with the PMWIN user interface (Chiang & Kinzelbach 2000) for MODFLOW. Vertical conductivities are assumed to be 1/10 of the horizontal values. Since mixing due to heterogeneous permeability distribution is explicitly considered in the model,

Table 1. Flow and transport parameters of the Borden test site (Woodbury & Sudicky 1991)

Parameter	Value
Average horizontal conductivity k_{fh}	9.3E-5 m/s
Standard deviation σ of $\log_{10}$ normal k_{fh} distribution	0.21 (m/s)
Horizontal correlation length ($\lambda_X = \lambda_Y$)	5.14 m
Vertical conductivity k_{fv}	$= k_{fh}/10$
Porosity	0.33

comparatively small dispersivities of 0.36 m longitudinal, 0.03 m transversal and 0.0003 m transversal vertical are chosen with a molecular diffusion coefficient of 7.4E-5 m^2/d, according to the Borden site (Sudicky 1986).

A homogeneously distributed LNAPL contamination with a size of 10 × 2.5 m^2 is assumed at the water table (in the top layer) of the aquifer. For simplification we suppose that the contaminant is present in immobile residual saturation. The contamination consists of only one substance with a maximum solubility $C_{saturation}$ of 50 mmol/l. The dissolution of the NAPL into the mobile pore water ($C_{dissolved}$) follows a gradient law:

$$\frac{\partial C_{dissolved}}{\partial t} = v_{dissolve} \cdot (C_{saturation} - C_{dissolved}).$$

The dissolution velocity constant $v_{dissolve}$ is set to 1 d^{-1}, such that the maximum solubility is obtained along the flow path through the contaminated area. The rate constant is assumed to be constant during the simulation time, effects like e.g. decreasing NAPL surface are neglected.

The dissolved contaminant is transported downgradient via advective and diffusive transport mechanisms. The numerical model TBC uses a node-centred finite volume approach for simulation of transport therefore concentrations are displayed above and below every layer (Figure 1).

Initially the aquifer is aerobic with oxygen concentrations of 0.3 mmol/l. Nitrate with 2.0 mmol/l and sulphate with 1.0 mmol/l serve as additional electron acceptors for microbial degradation processes. These three mobile oxidants are transported with their initial concentrations from the inflow boundary (left hand side) and due to groundwater recharge into the simulated aquifer. The soil contains a homogeneously distributed Fe(III)-mineral (1 mmol/kg) that can be reduced to Fe(II) in order to oxidise organic contaminant.

For simulation of microbial reactions three different bacteria groups are assumed: aerobic facultative denitrifying, sulphate reducing and Fe(III) reducing. Growth of each bacteria group (X) is simulated by double Monod-kinetics (Monod 1942; Schäfer et al. 1998b):

$$\frac{\partial X}{\partial t} = v_{max} \cdot X \cdot \frac{OC}{(MC_{OC} + OC)} \cdot \frac{Ox}{(MC_{Ox} + Ox)}.$$

Microbial growth is controlled by a maximum growth velocity v_{max} and two Monod-terms regarding organic carbon (OC) and the electron acceptor (Ox) consumed. Micro-organisms grow exponentially with maximum velocity if both Monod-terms are 1, i.e. organic carbon and electron acceptor are available in high concentrations, larger than their specific Monod-concentration (MC). If the concentration of organic carbon or electron acceptor is low, its Monod-term becomes nearly zero reducing or preventing microbial growth and degradation.

Aerobic and facultative denitrifying bacteria can grow by consuming oxygen or nitrate as electron acceptors which is simulated by summing up two Monod-equations for oxygen and nitrate. An inhibition term controls which electron acceptor is preferred by the micro-organisms. If oxygen concentrations are high, denitrification is inhibited. With the help of the same inhibition term sulphate- and Fe(III)-reduction is prevented if oxygen is present, since the required bacteria groups are anaerobic.

Decay of bacteria is simulated by a constant decay rate. Total growth of microorganisms is the sum of all growth terms and the decay term.

If bacteria grow, they consume organic carbon and electron acceptors. For calculation of stoichiometric demand of electron acceptors it is assumed that the contaminant consists of toluene. The consumption of toluene and electron acceptor is directly coupled to microbial growth.

$$C_6H_5CH_3 + 9O_2 + 3H_2O \rightarrow 7H_2CO_3,$$

$$\begin{aligned} 5C_6H_5CH_3 &+ 36NO_3^- + 36H^+ \rightarrow 35H_2CO_3 \\ &+ 3H_2O + 18N_{2(g)}, \end{aligned}$$

$$\begin{aligned} 2C_6H_5CH_3 &+ 9SO_4^{2-} + 18H^+ + 6H_2O \\ &\rightarrow 14H_2CO_3 + 9H_2S, \end{aligned}$$

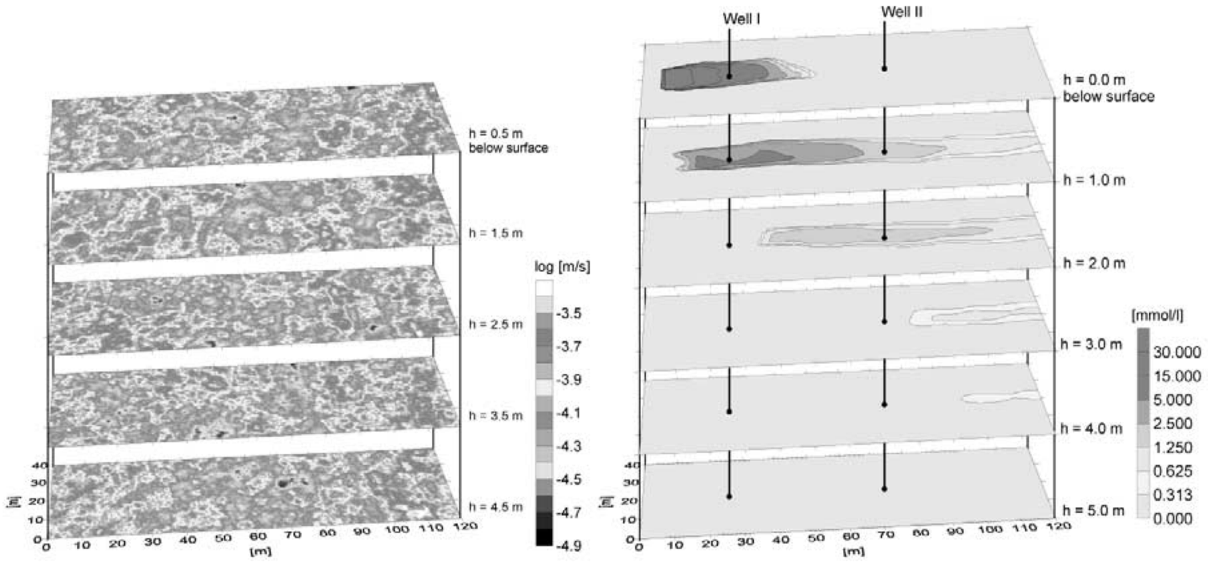

Figure 1. Assumed permeability distribution and resulting contaminant plume after 1800 d with observation wells assumed for sampling.

$$\begin{aligned} C_6H_5CH_3 \;+\; & 36Fe(OH)_3 + 72H^+ \\ \rightarrow\; & 7H_2CO_3 + 87H_2O + 36Fe^{2+}. \end{aligned}$$

The parameters required to describe the kinetic growth of the three different groups of micro organisms are taken from a field investigation on microbial in situ remediation (Table 2).

Microbially catalyzed reactions also change the chemical composition of the groundwater e.g. due to production of carbonate and sulphide. If the inorganic composition of groundwater is to be used to estimate microbial degradation, chemical reactions have to be considered. In this example a simplified geochemistry is simulated, consisting of a calcium-carbonate equilibrium system and precipitation of iron sulphide.

The calculation is performed for a simulation time of 1800 days (~5 y). The plume approaches a steady state after about 1600 days.

Plume investigation with observation wells

The stationary contaminant plume is monitored after a simulated time span of 1800 d. Two observation wells are placed in the virtual aquifer 10 and 55 m downstream of the contaminated area. Screenings are assumed from −0.50 to −1.50 m and −3.50 to −4.50 m below water table, additionally full screened wells are simulated. The observation wells are pumped with different pumping rates (2 and 10 l/min) and the measured concentrations are forecast by the model. For a pumping rate of 10 l/min additionally an increased vertical conductivity is assumed within the observation well to simulate the effect of a vertical flux in the sand filter of the well.

The model neglects further (bio-) chemical reactions of the sample as soon as the water is pumped from the well. This corresponds to a proper conservation of the sample in nature.

Comparison of interpolation methods

If local concentrations have been measured, they need to be interpolated to obtain spatial information. For simplification only the second layer below top of the simulated aquifer is investigated and only contaminant concentrations after 1000 d of simulation time are considered. The assumed observation wells are screened in the second layer and local concentrations are used for interpolation, i.e. mixing effects or measurement errors are neglected. An irregular configuration of observation wells is assumed as shown in Figure 4. The positions of the wells were chosen knowing size and shape of the simulated plume, such that maximum concentrations and the boundary of the plume are well marked. A good interpolation method should be able to obtain a reliable result with such an ideal data base, though only few data points are available. Note, that it is impossible to place observation wells in this way in reality, since the plume is never sufficiently known.

Table 2. Parameters for simulation of microbial degradation

	Max. growth velocity (d^{-1})	Decay rate (d^{-1})	Monod constant contaminant (mmol/l)	Monod constant electron acceptor (mmol/l)
Aerobic	2	0.2	0.50	0.01
+ denitrifying	2		0.50	0.01
Sulphate reductive	2	0.2	0.50	0.05
Fe(III) reductive	2	0.2	0.50	0.05

The local contaminant concentrations are spatially interpolated and displayed using the interpolation software SURFER®. Five different interpolation methods are used:

a) Triangulation (linear interpolation).
b) Kriging (SURFER® default parameters; linear variogram, no nugget effect, anisotropy ratio = 1).
c) Kriging (same as before, but anisotropy ratio = 3.5).
d) Inverse distance (SURFER® default parameters; power = 2, anisotropy ratio = 1).
e) Modified Shepard (SURFER® default parameters; anisotropy ratio = 1).

The interpolation results are compared to the simulated contaminant plume. Two criteria are considered: size and shape of the plume as well as the spatial integral of the concentrations. Size and shape of the contaminant plume are compared by means of a simple optical comparison, since more objective criteria for comparison of plumes (e.g. visual recognition technologies) first have to be adapted to geological problems. The spatial integral of concentrations is calculated by an extended trapezoidal rule using SURFER®, obviously erroneous interpolation results like negative concentrations are set to zero before calculation. The spatial integral corresponds to the contaminant mass stored in the plume. This is an objective but quite rough criteria for assessment of degradation processes.

Influence of the number of observation wells on the interpolation result

The quality of interpolation results does not only depend on the applied interpolation algorithm, but also on the number of measurement points available and on the position where they are set. The virtual observation wells are now set without knowledge of the plume and in a regular array. In order to estimate the effect of an increasing number of observation wells on the interpolation results the virtual aquifer is monitored with 3 different set ups of wells (see Figure 5). Each virtual observation well is screened in 5 depths corresponding to the layers of the model. Additionally wells screened over the total aquifer depth are investigated.

For the multilevel wells an ideal concentration measurement is assumed without mixing or measurement errors. In the full screened wells concentrations are flux-averaged over depth. For interpolation of concentrations the Kriging method with an anisotropy factor of 3.5 was used, because it provided best results of the interpolation methods investigated. The resulting interpolated concentrations were compared to the simulated "real" concentrations as described above.

Results

Generated virtual aquifer

The mechanisms and parameters for transport and degradation were chosen such that the generated virtual aquifer shows a typical redox sequence as observed in natural aquifers. Figure 2 shows the concentrations of a selected set of substances in the second layer below the water table 1800 days after contamination of the aquifer. Dissolved contaminant spreads downstream of the NAPL-source, moving into lower layers due to groundwater recharge (Figure 1). Within the plume oxygen and nitrate have been completely consumed by aerobic and denitrifying micro-organisms, now degradation occurs only within the diffusive zone at the boundary of the plume where contaminant and oxygen or nitrate are found at the same time. As expected from the redox sequence denitrification occurs slightly deeper inside of the plume. Sulphate reduction can only be observed under anaerobic conditions inside the plume, it occurs in the diffusive zone where sulphate and contaminant are available.

In the example Fe(III)-reduction takes place nearly within the whole plume, since iron minerals and contaminant are present and the major part of the plume is anaerobic. Fe(III)-reduction is assumed to be slow since in nature it is limited by microbial availability of the minerals. A significant increase of Fe^{2+} concentrations as a degradation product of Fe(III)-reduction is not observable due to high sulphide concentrations and precipitation of iron sulphide.

Of course the simulation result depends on the assumed conductivity distribution and the chosen geochemical parameters, but with regard to our present knowledge the concentrations obtained from the numerical model seem to be quite similar to real sites contaminated with microbially degradable contaminants like e.g. BTEX.

Reliability of concentration measurements by pumping in observation wells

Figures 3 shows the contaminant concentrations simulated for a measurement in the two observation wells over time for two different pumping rates. The observation well 10 m downstream of the contaminant source and with an assumed screening from -0.50 to -1.50 m is placed nearly in the centre of the plume, hence high concentrations are measured immediately. Contaminant concentrations increase over time, since higher contaminated water is drawn through permeable areas from the contaminant source. Later concentrations decrease due to mixing with clean water. For higher pumping rates these effects evolve faster. If a distinct vertical flux through the sand filter of the observation well is not prevented, severe mixing has to be expected. If the observation well is screened from -2.50 to -3.50 m, the centre of the plume is above the screening. Initial measured concentrations are zero, but increase over time because contaminated water is drawn from the plume downwards. This process evolves faster at high pumping rates and especially if a vertical flux through the sand filter of the observation well is assumed. The full screened observation well shows average concentrations with slightly decreasing trend due to mixing with clean ground water.

In the observation well 55 m downstream of the source the upper screening is in a higher contaminated area, but concentrations decrease with start of pumping due to mixing. This is accelerated if a vertical flux through the sand filter occurs. In the lower screening low concentrations are present, but they increase with pumping, because more contaminated water is drawn from the plume. Again the full screened observation well shows average concentrations.

The measurements in the virtual observation wells are well understandable, since the location of the plume in relation to the screening is known. This is not the case at real sites, usually the detailed location of the plume is unknown and aim of the investigation. The common procedure e.g. following the German DVWK directives (DVWK 1992, 1997) for taking water samples is to start pumping at a pumping rate >1 l/min (if possible) and taking a single water sample as soon as stable conditions are achieved. Stable conditions are usually expected after at least single exchange of the water within the observation well (including sand filter) or they are indicated by a constant value for electrical conductivity, temperature, pH or oxygen content of the pumped groundwater. With regard to the simulation, concentrations change even after a long time of pumping, they are affected by mixing and one single sample taken after an arbitrary time of pumping is only an insufficient information on the local concentration.

These effects have been investigated for an ideal three dimensional plume of a non reactive tracer in an isoptropic homogeneous aquifer (Martin-Hayden & Robbins 1997), but they are much more pronounced in heterogeneous aquifers with reactive contaminants. Mixing effects are usually not taken into account for site investigation, leading to an under- or overestimation of concentrations. A simple recommendation to become aware of mixing effects would be taking several samples during pumping time, at least when the observation well is investigated for the first time. Changing concentrations indicate a distinct mixing within the sampling well.

Comparison of interpolation methods

In comparison to the "real" concentrations linear interpolation adequately reproduces the shape of the plume (Figure 4), its maximum concentrations and the total contaminant mass of the plume (Table 3). The method can be used for interpolation only and delivers no data outside of the outer observation wells. In the example all outer wells are placed outside of the plume and signalise clean water. If this information is not available the plume is cut off and the interpolation method produces erroneous results.

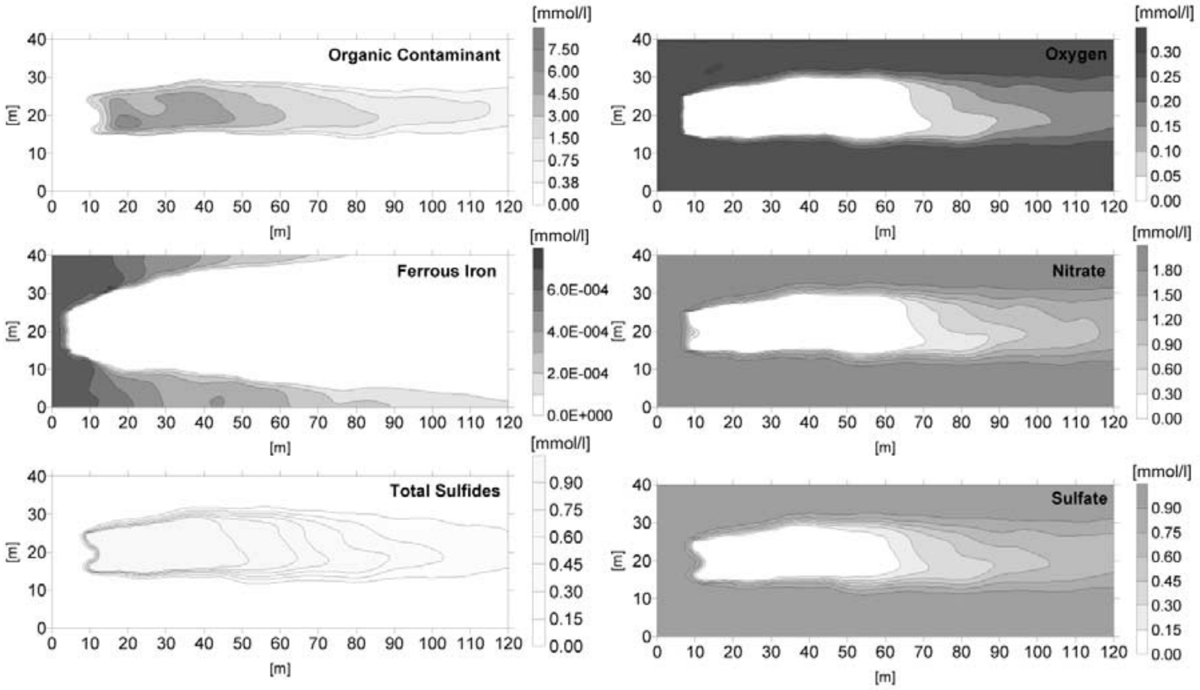

Figure 2. Selected set of dissolved concentrations, simulated for the second layer below water table after 1800 d of simulation time.

Table 3. Contaminant mass in layer 2 calculated from interpolated concentration distributions in relation to "real" mass

"real mass"	Triangulation	Kriging (standard)	Kriging (with anisotropy)	Inverse distance	Modified Shepard
100.0%	103.4%	99.3%	107.9%	209.2%	119.0%

The Kriging method is suited for data inter- and extrapolation. It is often used in Geology since it generates cohesive structures even for small data sets. The standard Kriging method well estimates the mass of the contaminant plume, but shape and concentration distribution within the plume are inadequate, since the method tends to generate round lenses. The accuracy of the interpolated plume can be increased by applying an anisotropy ratio to the weighting of data points. Since transport is directed in flow direction, more oval structures should be expected. This is considered in Figure 4, where an anisotropy ratio of 3.5 is assumed in flow direction. The introduction of this additional knowledge enhances shape and concentration distribution of the plume, but erroneously increases the contaminant mass.

The conventional inverse distance least square method is not suited for interpolation of concentrations in this aquifer. Neither shape nor mass of the contaminant plume are acceptable. The modified Shepard's method is an inverse distance weighted method, too, but the use of local least squares reduces the "bull's-eye" appearance of the conventional inverse distance method. Size and shape of the interpolated plume agree well to the "real" plume, though the area with high concentrations is slightly overestimated. This results in an overestimation of the contaminant mass. The application of an anisotropy factor of 3.5 in flow direction does not significantly enhance the interpolation result (without figure), the overestimated calculated mass only decreases for 0.1%.

Shape of the interpolated plume, interpolated concentrations and contaminant mass within the plume

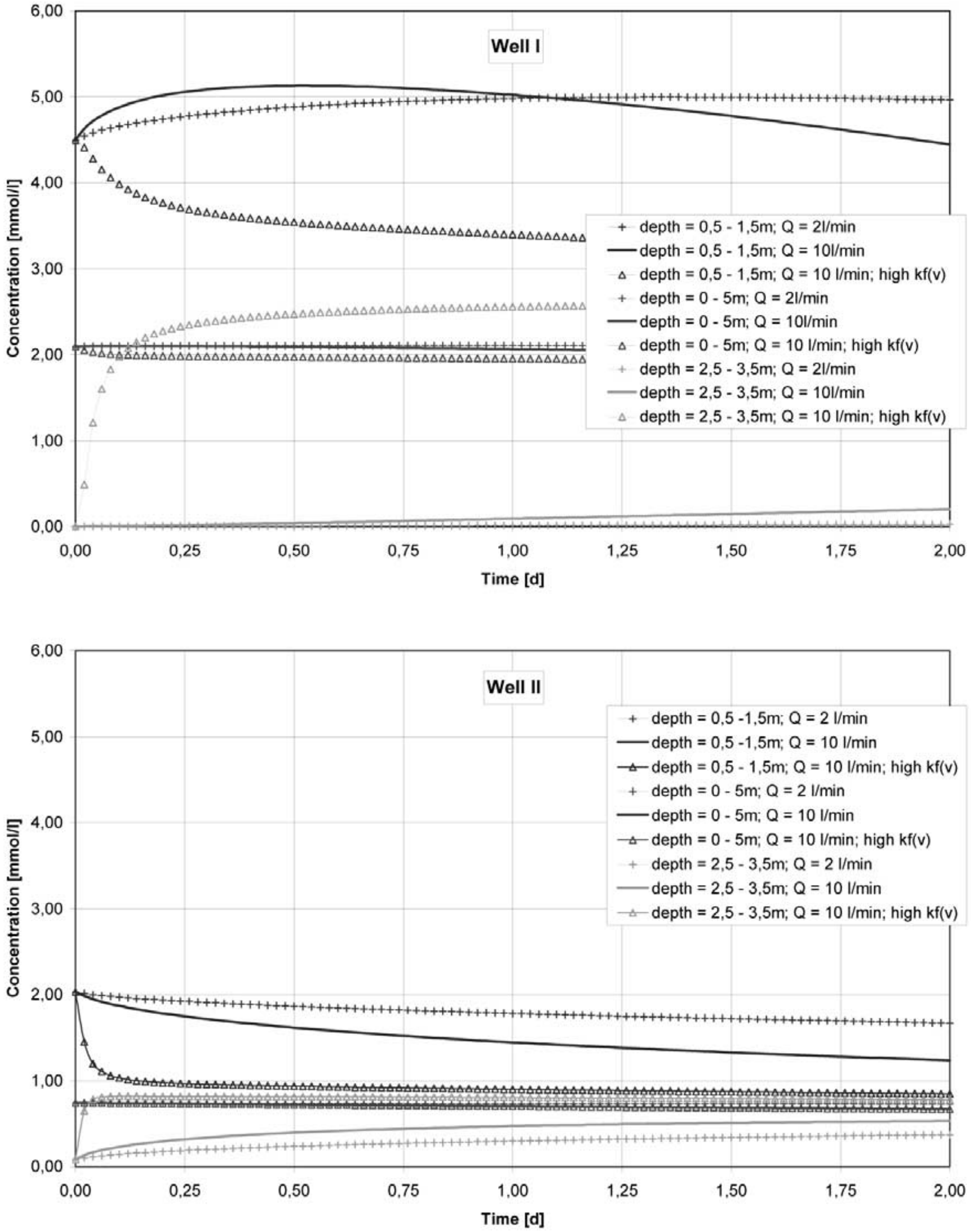

Figure 3. Contaminant concentrations in two virtual observation wells, each screened 1 m or 3 m below water table and over whole aquifer depth, using pumping rates of 2 and 10 l/min. High kf(v) means, an increased vertical permeability is assumed in the cells of the well to simulate the effect of a sand filter.

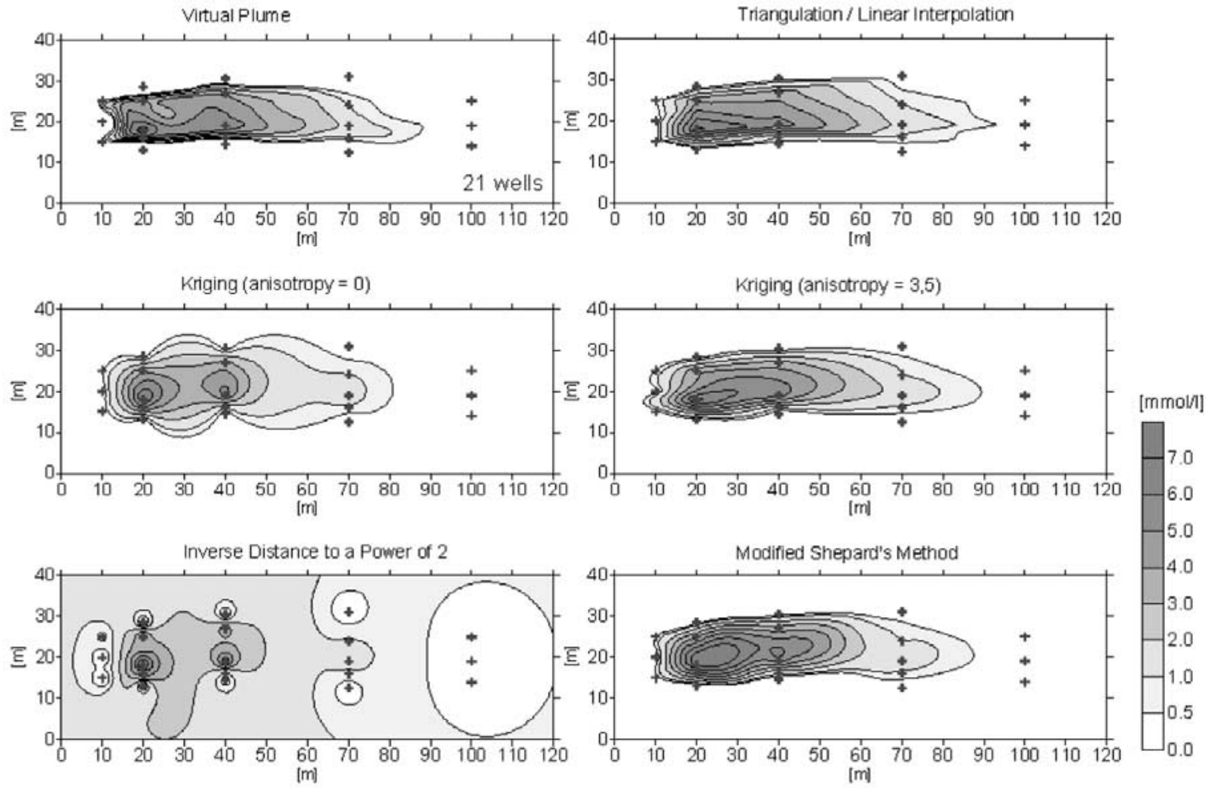

Figure 4. "real" contaminant concentrations in the second layer after 1000 d simulation time monitored with 21 observation wells and concentration distributions interpolated with different interpolation methods.

change depending on the interpolation method, even if the data set is chosen with knowledge of the plume. For our investigation linear interpolation, Kriging (with anisotropy factor 3.5) and Shepard's Method provided best interpolation results, but these methods may fail in other cases. Since the determination of natural attenuation processes is based on interpolated concentrations and calculated masses a reliable method for interpolation has to be found.

Influence of the number of observation wells on the interpolation result

As expected the quality of interpolation increases with the number of multilevel observation wells. In particular the shape of the plume and the concentration distribution becomes more realistic for all interpolation methods. With an increasing number of data points the interpolation results of different methods become more similar. The calculated contaminant mass does not necessarily follow this trend (Table 4). Except for the modified Shepard's method all interpolation methods underestimate the mass with up to −10% if 55 observation wells are assumed, while the mass is calculated with ± 5% for 35 wells.

Table 4. Contaminant mass in layer 2 calculated from interpolated concentration distributions, depending on the number of observation wells and the interpolation method (100% = "real" contaminant mass)

Number of wells	Linear interpolation	Kriging	Modified Shepard
24	116.3%	122.4%	143.4%
35	93.6%	98.3%	108.9%
55	90.1%	93.6%	100.6%

The main reason for this behaviour seems to be that from 35 to 55 observation wells only a refinement of data points in X-direction is performed. This describes the plume in more detail, but does not help to determine the boundary of the plume transverse to the flow direction. Calculation of the contaminant mass is most sensitive to the exact determination of this boundary.

The interpolation quality also increases with the number of full screened observation wells. The contaminant mass in the plume is interpolated with 158.8% for 24 wells, 108.7% for 35 wells and 112.1% for 55 wells. As described above the refinement to 55 wells does not lead to a better mass detection. The shape of the plume is detected in more detail though the measured maximum concentration is with 4.1 mmol/l about a factor of 12 smaller than in virtual reality (49.9 mmol/l) due to mixing. With measured concentrations much smaller than the real concentrations, this type of plume monitoring is not suited to determine if a critical value is exceeded. Additionally with such underestimated concentrations the realistic modelling and assessment of all concentration dependent processes like adsorption, microbial degradation and chemical reactions is very difficult.

In the previous investigation with different interpolation methods only 21 observation wells were used resulting in a quite reliable interpolation of shape and mass of the plume. Since the observation wells were set with knowledge of the plume the interpolation result is much better than while 24 wells are set in a regular grid (Figure 5), but even the expenses for 55 wells do not lead to a much better result. This shows that placing the observation wells in an intelligent way can save money and still leads to reliable results. Unfortunately this is a very complex problem in nature, but the model exercise gives hints where wells should be positioned. Interpolation methods show the most reliable results, if the boundary of the plume is determined as exactly as possible. This means observation points should not only be positioned within the plume but mainly next to the boundary, in particular transverse to the flow direction. The information where the plume has ended, thus zero contaminant concentration is measured, is as valuable for interpolation as detection of the contamination. Since microbial degradation is usually limited by transversal diffusion of dissolved electron acceptors into the plume measurements in this highly active area help to determine the concentration gradient, mass flux of electron acceptors into the plume and potential microbial degradation. In a stationary plume it is possible to place observation wells next to the boundary of the plume, but in moving, growing or shrinking plumes the wells cannot follow the plume boundary. However, directly downstream of the contaminant source movement of the plume is usually small and detection of the boundary should be possible.

Conclusions

The virtual aquifer approach was used to illustrate the uncertainties of plume exploration and monitoring in groundwater. Though only one single example of a comparably small aquifer is presented and though some processes like NAPL-distribution and -dissolution are considerably simplified, some general problems can be identified. These findings are transferable to real sites, but the extent of the problems may depend on the unknown parameter distribution of the real aquifer. Up to now we can only point out these problems without having any solution for them.

Even if measurement errors are neglected and the measurement is performed according to common guidelines, determination of concentrations with pumping wells is problematic due to mixing. Full screened observation wells only provide average concentrations over the aquifer depth. For a three dimensional plume this measurement does not reproduce the real concentrations, hence the assessment of all concentration dependent processes (e.g. adsorption, degradation) is very difficult. The efficiency of other sampling methods like passive sampling systems or emission pumping tests can be investigated in the future.

For interpolation of measured concentrations various methods are used. For a small but well positioned set of observation wells triangulation was successful, though it is only suited for interpolation, not for extrapolation. The result of the Kriging method could be severely increased by assuming an anisotropy ratio to the weighting of data points in flow direction. The assumption on an anisotropy seems to be reasonable for most transport phenomena in groundwater, since they are in general directed processes. However, the optimal value of the anisotropy factor remains unknown without knowledge of the plume. Perhaps there is a relationship between plume extension and optimal anisotropy ratio, what can be investigated with the virtual aquifer approach in future.

The quality of the interpolation result increases with the number of observation points and the results of different interpolation methods become more similar. Though up to 55 multilevel wells were assumed, a threshold error in the calculated mass remains. The error should decrease with more wells, but 55 multilevel wells are already very expensive for a standard application of this size. A better interpolation result can be obtained by optimal placement of observation wells. Interpolation methods show the most reliable results,

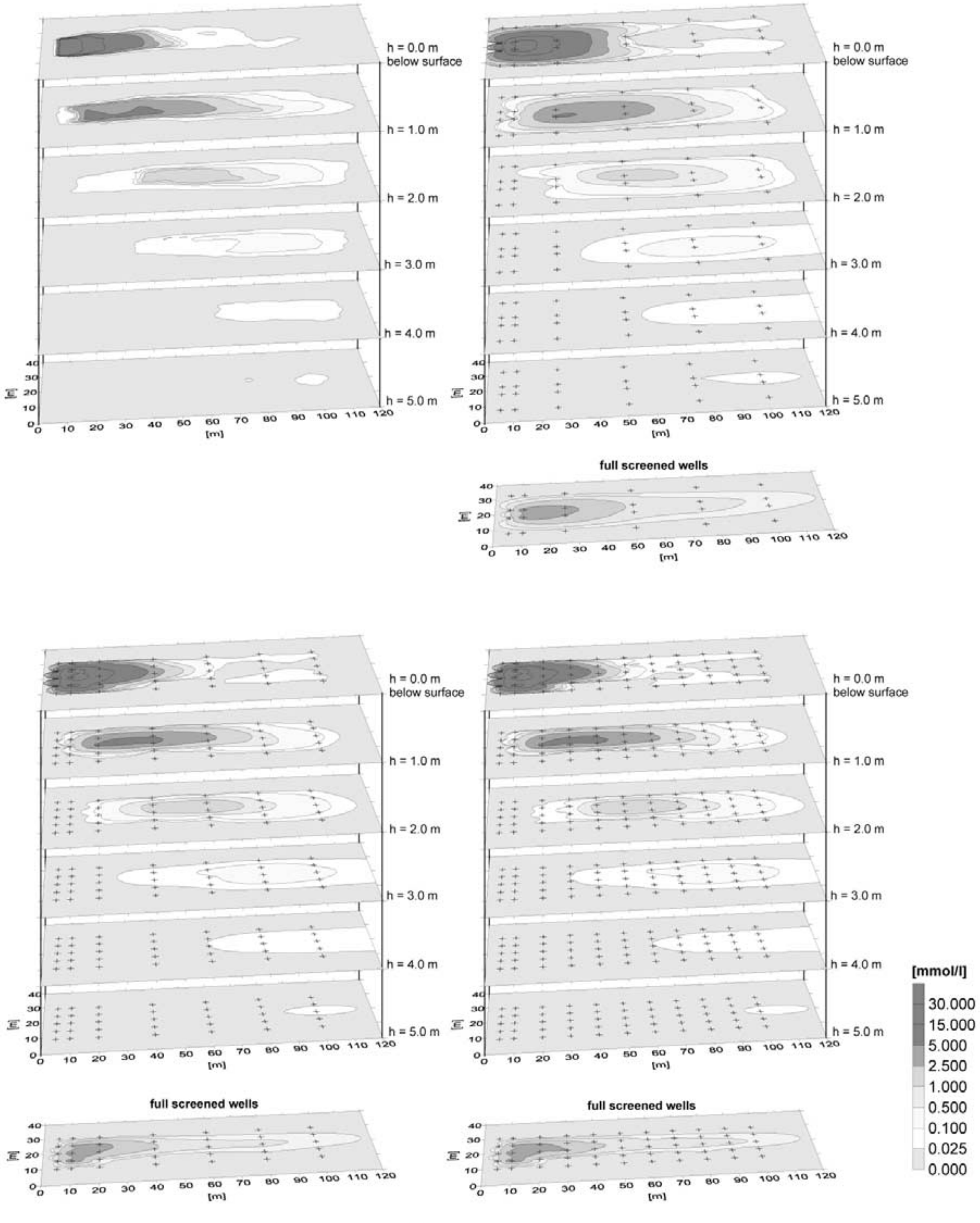

Figure 5. "real" contaminant concentrations after 1000 d of simulation time and interpolated concentration distributions using Kriging method (anisotropy = 3.5) assuming 24, 35 or 55 multilevel or full screened observation wells.

if the boundary of the plume is determined as exactly as possible. The virtual aquifers approach could be used to test intelligent search algorithms to find this boundary if the plume is not known as it is in nature. If water is pumped in this area with high concentration gradients the mixing effect should be severe, hence passive sampling systems should provide more reliable results.

The simulated concentrations and the derived statements concerning monitoring and interpolation severely depend on the heterogeneity of the aquifer. The investigated virtual aquifer is comparably homogeneous, the problems discussed should complicate with increasing heterogeneity. The different effects of sampling, interpolation method and placement of observation wells were investigated independently. If these effects superimpose, the resulting plume can pretend completely absurd conditions, like degradation of a nonreactive tracer as discussed by Martin-Hayden & Robbins (1997).

Reliable determination of concentrations is indispensable for evaluation of natural attenuation, since sorption and most degradation processes depend on concentrations. A precise definition of plume extensions is also required to investigate the spreading, shrinking or steady state of a plume, what is an assessment criterion for natural attenuation. For reasonable application of natural attenuation an improvement of present observation and monitoring methods will be required.

The significance of the virtual aquifer approach depends on a realistic description of natural aquifers. Unrealistic input parameters for the generated virtual aquifer result in arbitrary simulated plumes, leading to insignificant conclusions on exploration and monitoring. The spatial distribution of conductivity has already been investigated, but there is still a lot of research required to understand conductivity structures in aquifers in detail. Much less is known about other parameters like the spatial distribution of minerals (e.g. calcite, Fe(III), Mn(IV)), organic carbon, and the correlation of these distributions with conductivity. Methods to map and describe such heterogeneities, which can be observed on various scales, still have to be found. For the generation of random distributions proper statistical approaches and parameters are required to describe such rough parameter changes on different scales. The presently assumed lognormal distribution does not seem to be suited to describe such structures, because it produces smooth transitions from large to small values. For calculation of reactive transport in such generated heterogeneous structures with rough parameter changes specialized numerical models will be required.

Acknowledgements

The authors would like to thank the reviewers for their constructive comments. The project "Virtueller Aquifer (VA) – Computergestützte Bewertung von Erkundungs-, Sanierungs- und Monitoringstrategien im Hinblick auf das "Natural Attenuation" (NA) und "Enhanced Natural Attenuation" (ENA) – Potential kontaminierter Böden und Grundwässer" is a cooperation of the Universities Kiel and Tübingen. It is funded by the BMBF (02WN0389) since January 2003.

References

Berglund S, Cvetkovic V & Haggerty R (2001) Natural attenuation in heterogeneous aquifers: combined effect of biodegradation and rate-limited mass transfer. Proceedings: Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution, 471–478

Bersezio R, Bini A & Guidici M (1999) Effects of sedimentary heterogeneity on groundwater flow in a quarternary proglacial delta environment: joining facies analysis and numerical modelling. Sediment. Geol. 129: 327-344

Boggs MJ, Young SC, Beard LM, Gelhar LW, Rehfeld KR & Adams EE (1992) Field study of dispersion in a heterogeneous aquifer: 1. Overview and site description. Water Resour. Res. 28(12): 3281–3291

Chiang W-H & Kinzelbach W (2000) 3D-Groundwater Modeling with PMWIN: A Simulation System for Modeling Groundwater Flow and Pollution. Springer-Verlag, Berlin, Heidelberg

DVWK (1992) Entnahme und Untersuchungsumfang von Grundwasserproben: DK 556.32.001.5 Grundwasseruntersuchung, DK 543.3.053 Probenahme, pp. 36. Deutscher Verband für Wasserwirtschaft und Kulturbau e.V.

DVWK (1997) Tiefenorientierte Probenahme aus Grundwassermessstellen, pp. 35. Deutscher Verband für Wasserwirtschaft und Kulturbau e.V.

Flint SS & Bryant ID (1993) Quantitative clastic reservoir geological modelling; problems and perspectives. Proceedings: The gelogical modelling of hydrocarbon reservoirs and outcrop analogues, 3–20

Frenzel H (1995) A Field Generator Based on Meija's Algorithm. Institute for Environmental Physics, University of Heidelberg

Koltermann CE & Gorelick S (1996) Heterogeneity in sedimentary deposits: a review of structure-imitating, process-imitating and descriptive approaches. Water Resour. Res. 32(9): 2617–2658

Martin-Hayden JM & Robbins GA (1997) Plume distortion and apparent attenuation due to concentration averaging in monitoring wells. Ground Water 35(2): 339–346

Monod J (1942) Recherches sur la croissance des cultures bacteriennes. In: Bordet J (Ed) Actualites Scientifiques et Industrielles, Vol 911 (pp 70–78). Hermann et Cie, Paris

Schäfer D, Schäfer W & Kinzelbach W (1998a) Simulation of reactive processes related to biodegradation in aquifers: 1. Structure of the three-dimensional reactive transport model. J. Cont. Hydr. 31: 167–186

Schäfer D, Schäfer W & Thullner M (1998b) TBC – a novel numerical model for simulation of Transport, Biochemistry and Chemistry in aquifers. Math. Geol. 2: 79–93

Schäfer W (1992) Numerische Modellierung mikrobiell beeinflußter Stofftransportvorgänge im Grundwasser. R. Oldenbourg Verlag, München

Siegenthaler C & Hugenberger P (1993) Pleistocene Rhine gravel: deposits of a braided river system with dominant pool preservation. In: Best J & Bristow C (Eds) Braided Rivers, Vol 75 (pp 47–162). Geological Society Special Publication

Sudicky EA (1986) A natural gradient experiment on solute transport in sand aquifer: spacial variability of hydraulic conductivity and its role in the dispersion process. Water Resour. Res. 22(13): 2069–2082

Vereecken H, Döring U, Hardelauf H, Jaeckel U, Hashagen U, Neuendorf O, Schwarze H & Seidemann R (2000) Analysis of solute transport in a heterogeneous aquifer: the Krauthausen field experiment. J. Cont. Hydr. 45: 329–358

Webb EK & Anderson MP (1996) Simulation of preferential flow in three-dimensional, heterogeneous conductivity fields with realistic internal architecture. Water Resour. Res. 32(3): 533–545

Weissmann GS, Carle SF & Fogg GE (1999) Three dimensional hydrofacies modeling based on soil surveys and transition probability geostatistics. Water Resour. Res. 35(6): 1761–1770

Woodbury AD & Sudicky EA (1991) The geostatistical characteristics of the Borden aquifer. Water Resour. Res. 27(4): 533–546