Application of multilevel-multitracer transport experiments for the investigation of hydraulic and hydrogeochemical aquifer properties

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Abstract A multilevel-multitracer experimental technique for the investigation of parameters controlling non-reactive and reactive transport processes in groundwater, where non-reactive and reactive tracers are injected simultaneously, was applied in a highly heterogeneous porous aquifer. The focus was on surface sorption and retardation at different transport scales. Within the experiments it was observed that the field-scale retardation factor increases with transport distance. This macrokinetic sorption behaviour can be explained as a consequence of physical and chemical aquifer heterogeneities. Also, based on results from laboratory investigations, the effective diameter of the aquifer material grains was estimated from the field-scale retardation factors. The effective diameter can be used to predict the retardation of dissolved groundwater contaminants sorbing onto mineral surfaces, for example.

INTRODUCTION

Many industrial sites with contaminated groundwater are located in highly heterogeneous alluvial environments. For risk assessment and for the planning of aquifer remediation activities at such sites, reliable model simulations of the contaminant transport in groundwater are needed. Within a highly heterogeneous environment, such predictions and simulations require a characterization of the residual non-aqueous phase liquids (NAPL) contamination as well as a detailed knowledge of the aquifer parameters controlling the spreading of the solutes. Since the transport simulations very often have to be performed for transport scales of tens to several hundreds of metres, where ergodicity (e.g. Dagan, 1989) mostly cannot be assumed, a possible scale dependence of the transport parameters has to be considered. The scale dependence of e.g. dispersivity values is well-known and investigated (e.g. Gelhar & Axness, 1983; Gelhar et al., 1985; Dagan, 1989). But parameters describing reactive transport processes can also be scale dependent. For example, Miralles-Wilhelm & Gelhar (1996) have postulated that sorption macrokinetics, indicated by a retardation factor dependent on transport distance (or travel time), may arise from aquifer physical and chemical heterogeneities.

This paper presents the application of a forced gradient multilevel-multitracer technique for the direct investigation of non-reactive and reactive transport processes and the scale dependence of aquifer transport parameters in a highly heterogeneous porous aquifer at the "Horkheimer Insel" test site (Teutsch & Kobus, 1990). The focus was on surface sorption. An objective of the experiments was to obtain an
insight into the sorption process at field scale, to provide a database for model validation purposes and to investigate the scale dependence of the effective field-scale retardation factor. Also, based on results from laboratory investigations, it was possible to estimate the effective diameter of the aquifer material grains using the measured field-scale retardation factors. The estimated effective grain diameter can, for example, be used to predict the retarded transport of surface sorbing contaminants at the field-scale.

MULTILEVEL-MULTITRACER EXPERIMENTAL TECHNIQUE

The forced gradient multilevel-multitracer experimental technique can be performed either in a convergent or a divergent groundwater flow field. The forced gradient approach allows well-defined experimental conditions to be obtained and the tracer test duration to be reduced relative to natural-gradient tracer experiments. In the divergent approach, groundwater is injected into a monitoring well at a constant rate, and, after a quasi-steady-state flow field is established, the tracer mass is added instantaneously and mixed within the injection well along the entire length of the water column. Surrounding wells are then used to measure tracer breakthrough curves. In the convergent approach, groundwater is pumped out of a well, the tracer is injected instantaneously into surrounding groundwater wells, and multilevel breakthrough curves are measured within the pumping well itself. Effective transport parameters are then obtained from the evaluation of the measured breakthrough curves.

\[
\begin{align*}
\lim_{x,y \to \infty} c(x,y,z,t) &= 0 \\
\frac{\partial x}{\partial t} &= M/Q \cdot c(t)
\end{align*}
\]

Fig. 1 Differential multilevel-multitracer experimental approach for the investigation of effective transport parameters at field scale.
If reactive transport is to be investigated, at least two tracers, a non-reactive and one or more reactive, are injected simultaneously at the same location into the aquifer. Since all the tracers experience the same hydraulic conductivity field, the relative difference in their transport behaviour is only a "statement" of the reactive aquifer transport processes. Figure 1 shows the principle of this differential multitracer testing approach. The reactive tracer is chosen with respect to the reactive transport process investigated. Then, the parameter characterizing the reactive transport process can be deduced from the relative retardation of the reactive tracer with respect to the non-reactive tracer, if the relationship between the retardation factor and the process parameter(s) is known.

To obtain a high temporal and spatial (three-dimensional) resolution, on-line multilevel measuring equipment can be used, e.g. multilevel fibre optic fluorimeters for fluorescent tracers (Ptak & Schmid, 1996), ion selective probes for salt tracers, or gas diffusion membranes with a mass spectrometer or an electron capture detector for dissolved gas tracers.

The multitracer approach has been recently applied for e.g. the estimation of the effective surface of residual NAPLs using interfacial tracers (the tracer adsorbs at the NAPL-water interface) and for the estimation of the residual NAPL saturation using partitioning tracers (the tracer partitions into the NAPL) (e.g. Wilson & Mackay, 1995; Nelson & Brusseau, 1996; Hayden & Linnemeyer, 1997; Saripalli et al., 1997). Only a few field-scale applications of the multitracer approach have been reported up to now, and further research with respect to tracer selection, field application and evaluation is needed.

In the experiments presented here, fluorescein and rhodamine WT were used simultaneously as non-reactive and reactive tracers. Using rhodamine WT as a reactive tracer, sorption on to mineral surfaces can be investigated, which is relevant for example for the transport of polar/ionizable groundwater contaminants, e.g. some pesticides. Since surface sorption is the dominant reactive transport process, the field experiments described here are interfacial tracer tests, where the interface between the aquifer material and groundwater is investigated.

It should be noted that compared to the multitracer experiments reported up to now, the multilevel design employed here enables three-dimensional investigations (detection of preferential flow paths, localization (vertical position) of a NAPL sources, etc.), which is important e.g. for the design of remediation installations.

EXAMPLES OF APPLICATION OF THE MULTITRACER EXPERIMENTAL TECHNIQUE AT DIFFERENT SCALES

Three multitracer experiments with a convergent groundwater flow field were performed at the "Horkheimer Insel" test site, which is located in Germany in the Neckar valley, about 70 km north of Stuttgart. The heterogeneous aquifer at the test site is formed by a 2.5-4 m thick sequence of poorly sorted alluvial sand and gravel deposits of Holocene age, with a mean hydraulic conductivity of 0.012 m s⁻¹ and a variance $\sigma_{\ln K}^2$ of 2.34.

The field experiments are described in detail in Ptak & Schmid (1996) and Kleiner (1997). Three different transport distances between the tracer injection and
To estimate the rhodamine WT retardation factors from the multilevel breakthrough curves, temporal moments equations were applied. The $n$th temporal moment is defined as (e.g. Kreft & Zuber, 1978):

$$M_n = \int_0^\infty t^n c(r,t) \, dt$$

(1)

where $t$ (s) is the time, $c$ (kg m$^{-3}$) the concentration and $r$ (m) is the transport distance. Then the arrival time of the centre of mass is given by the first normalized moment, $m_{1,1} = M_1 / M_{0,1}$. Using the first normalized moment a mean effective transport velocity can be defined, $\bar{v}_{\text{eff}} = r / m_{1,1}$.

Assuming that fluorescein is an ideal tracer, an effective field scale retardation factor $R$ (-) can be defined for each set of two corresponding breakthrough curves:

$$R = \frac{\bar{v}_{\text{eff}} \text{ fluorescein}}{\bar{v}_{\text{eff}} \text{ rhodamine WT}} = \frac{m_{1,1} \text{ rhodamine WT}}{m_{1,1} \text{ fluorescein}}$$

(2)

The values of $R$ are in the range 1.27 to 1.40 for TT9, and between 1.26 and 1.37 for TT10, when individual multilevel breakthrough curves are compared. This variability indicates the heterogeneity of the aquifer. The arithmetically averaged retardation factors (Cvetkovic & Shapiro, 1990) are 1.35 for TT9 and 1.32 for TT10. For TT11 which has the largest transport scale investigated, an effective retardation factor $R$ of 2.17 is obtained.

### Table 1 Experimental parameters.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TT9</th>
<th>TT10</th>
<th>TT11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport distance (m)</td>
<td>8.9</td>
<td>12.8</td>
<td>32.7</td>
</tr>
<tr>
<td>Pumping rate (l s$^{-1}$)</td>
<td>3.02</td>
<td>3.02</td>
<td>3.3</td>
</tr>
<tr>
<td>Fluorescein injected (g)</td>
<td>10</td>
<td>20</td>
<td>102</td>
</tr>
<tr>
<td>Rhodamine WT injected (g)</td>
<td>8</td>
<td>16</td>
<td>102</td>
</tr>
<tr>
<td>Multilevel measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Vertical resolution (m)</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Temporal resolution (min)</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

observation wells were used in order to examine the scale dependence of the effective field-scale retardation factor. Table 1 summarizes the experimental parameters.

To test the sorption properties of the two tracers, fluorescein and rhodamine WT, laboratory batch experiments were performed using aquifer material from the test site (Strobel, 1996). Since aquifer sediments are a heterogeneous mixture of different lithocomponents with different grain size fractions, sorption isotherms were measured for the individual lithocomponents as well as for the individual grain size fractions of aquifer material samples of about 5 cm thickness. In the batch experiments, no significant sorption of fluorescein could be observed for the concentrations encountered during the field experiments. Rhodamine WT is known to be sorbed onto mineral surfaces (e.g. Sabatini & Austin, 1991) and in the batch experiments, rhodamine WT sorption equilibrium concentrations $c_{eq}$ were achieved almost immediately (after about 30 min maximum), which is typical for surface sorption; no significant kinetic behaviour was observed at the time scale of the field tracer experiments (7-14 days).

Assuming that fluorescein is an ideal tracer, an effective field scale retardation factor $R$ (-) can be defined for each set of two corresponding breakthrough curves:

$$R = \frac{v_{\text{eff}} \text{ fluorescein}}{v_{\text{eff}} \text{ rhodamine WT}} = \frac{m_{1,1} \text{ rhodamine WT}}{m_{1,1} \text{ fluorescein}}$$

The values of $R$ are in the range 1.27 to 1.40 for TT9, and between 1.26 and 1.37 for TT10, when individual multilevel breakthrough curves are compared. This variability indicates the heterogeneity of the aquifer. The arithmetically averaged retardation factors (Cvetkovic & Shapiro, 1990) are 1.35 for TT9 and 1.32 for TT10. For TT11 which has the largest transport scale investigated, an effective retardation factor $R$ of 2.17 is obtained.
COMPARISON OF RETARDATION FACTORS MEASURED AT DIFFERENT SCALES

The measurements clearly indicate a scale dependence of the effective retardation factor. At the field scale, the effective retardation factor increases with travel distance. This macrokinetic behaviour is observed, even though the sorption process within the batch experiments is practically instantaneous (maximum equilibration time of about 30 min and therefore a high Damköhler number, i.e. the ratio of the hydrodynamic residence time and the characteristic time of the sorption process), without any significant sorption kinetics at the time scale of the tracer experiments (7–14 days).

In the small scale tracer experiments (TT9 and TT10), in the heterogeneous aquifer most of the tracer mass is transported in highly conductive preferential pathways, since the horizontal correlation length of the hydraulic conductivity field at the test site is of the order of 10 m (Ptak & Teutsch, 1994), which is about the transport distance of the two experiments. Therefore, the probability of connected preferential pathways between the pumping and injection wells is relatively high for the small transport distances. In the intermediate transport distance tracer experiment (TT11), the probability for discontinuities in the high conductivity preferential transport zones increases, since the horizontal correlation length of about 10 m is smaller compared to the transport distance of 32.7 m. The tracer therefore has to also pass low conductivity aquifer zones, which are generally composed of finer grained materials than the high conductivity zones.

From the batch experiments using rhodamine WT, the following relationship between sorption capacity and grain size, based on a Freundlich isotherm model, was established:

\[
K_{Di} = \frac{1}{n_i} K_{Fr_i} c_\text{eq}^{n_i-1} = 0.85 \cdot 0.132 \cdot d_i^{-1.0} c_\text{eq}^{0.85-1} \tag{3}
\]

where \(K_{Di} \, (\text{kg}^{-1})\) is the distribution coefficient at sorption equilibrium, \(K_{Fr_i} \, (\text{kg}^{-1})\) is the Freundlich coefficient, \(c_\text{eq} \, (\mu\text{g l}^{-1})\) is the equilibrium concentration, \(n_i (-)\) is the Freundlich exponent of a grain size fraction \(i\), and \(d_i \, (\text{mm})\) is the representative diameter of \(i\). It can also be shown that it is not necessary to regard the lithological composition (quartz, Jurassic and Triassic limestones, Keuper and Bunter sandstones, calcite) as an aquifer property controlling the surface sorption of rhodamine WT. Then, if surface sorption is controlling the reactive transport process, following equation (3), higher sorption capacities are obtained within the lower conductivity aquifer zones with a higher specific surface. Since the tracer is hydrodynamically mixed into lower conductivity zones, as the transport distance becomes larger compared to the hydraulic conductivity correlation length, the effective retardation factor increases with travel distance.

Diffusion processes are not significant at the time scale of the tracer experiments, which follows from the comparison of characteristic time scales and from parameter studies. It can therefore be concluded that the observed breakthrough tailing, the retardation of rhodamine WT as well as the observed macrokinetic sorption behaviour result from the physical and chemical aquifer heterogeneities only.
Figure 2 shows the measured effective field scale retardation factors $R$ and summarizes the explanation for the scale dependence of $R$.

**INVESTIGATION OF THE EFFECTIVE AQUIFER MATERIAL GRAIN DIAMETERS**

Using equation (3), the effective field-scale retardation factors $R$ observed in the tracer experiments can be expressed as:

$$R = 1 + \frac{\rho_b}{\theta} K_{\text{D,eff}}$$

with:

$$K_{\text{D,eff}} = 0.85 \cdot 0.132 \cdot d_{\text{eff}}^{-1.0} \cdot c_{\text{eq}}^{0.85-1}$$  \hspace{1cm} (4)$$

where $\rho_b$ (kg m$^{-3}$) is the bulk density of the aquifer material and $\theta$ (-) is the porosity. Then, from equation (4), the effective diameter $d_{\text{eff}}$ (mm) of the aquifer material grains within the tracer transport paths can be estimated. The relationship between the retardation factor and the effective grain diameter is shown in Fig. 3.

It is seen in Fig. 3 that for the concentrations encountered within the tracer experiments the retardation factor does not strongly depend on the equilibrium concentration, which is due to the Freundlich exponent close to one. If in a first evaluation step the weak concentration dependence is neglected, the measured field-scale retardation factors yield effective grain diameters of about 3 mm for the small scale experiments TT9 and TT10, and of about 0.9 mm for the larger scale experiment TT11. The decrease of the effective grain diameter with transport distance is in accordance with the discussion of the macrokinetic sorption behaviour presented above, which states that for the longer transport distance the tracer has also to pass aquifer zones with a relatively low hydraulic conductivity, which are composed of finer grains.

The estimated effective aquifer material grain diameter can be used for example to predict the retardation of groundwater contaminants sorbing to the surface of aquifer material grains. Usually it is difficult to obtain field data on the transport of such contaminants as it is generally impossible to use the contaminants directly for field transport experiments due to environmental regulations. However, if the relationship of the distribution coefficient and the grain size is known for a specific surface sorbing contaminant (e.g. from laboratory measurements), the retardation factor can easily be predicted from the effective grain diameter, and its scale dependence can be taken into account.

**SUMMARY AND CONCLUSIONS**

A multilevel-multitracer experimental technique allowing the investigation of aquifer physical and chemical properties was applied in a highly heterogeneous porous aquifer at the “Horkheimer Insel” test site in order to investigate surface sorption at different transport scales. It was observed that the effective field-scale retardation factor increases with transport distance. The experimental findings suggest that the
Multilevel-multitracer transport experiments for the investigation of aquifer properties

**D = I**

- Dirac-Pulse
- Pumping and multilevel monitoring well
- Coarse gravel
- Sand
- Reactive Tracer
- Non-reactive Tracer

**D > I**

- Dirac-Pulse
- Pumping and multilevel monitoring well
- Coarse gravel
- Sand
- Reactive Tracer
- Non-reactive Tracer

**Experimental retardation factors**

![Graph showing experimental retardation factors](image)

- Ptak and Schmid (1996)
- Kleiner (1997)

**Instantaneous Surface Sorption**

Reactive Tracer: $K_{D_{Gravel}} < K_{D_{Sand}}$

**Fig. 2** Scale dependence of effective field scale retardation factors.
field-scale macrokinetic sorption behaviour is caused by aquifer physical and chemical heterogeneities.

From the field-scale retardation factors effective diameters of the aquifer material grains were estimated, which can, for example, be used to predict the retardation of dissolved groundwater contaminants sorbing onto mineral surfaces.

It is obvious, that the modelling approach needed for predictions of reactive transport under conditions such as at the "Horkheimer Insel" test site should account for the macrokinetic sorption behaviour, and, if necessary, also for concentration dependent distribution coefficients, i.e. nonlinear sorption isotherms. It should also be applicable for near-source transport problems, which is relevant e.g. for the planning of aquifer remediation activities, and it should account for the remaining parameter uncertainty. This can be achieved using for example a flexible three-dimensional Monte Carlo type numerical stochastic transport model described in Ptak (1997).

REFERENCES


Strobel, H. (1996) Sorption eines reaktiven Tracers (rhodamin WT) in heterogenem Aquifermaterial vom Testfeld "Horkheimer Neckarinsel\" (Sorption of a reactive tracer (rhodamine WT) in a heterogeneous aquifer material from the "Horkheimer Insel" test site). Diplomarbeit, Geologisches Institut, Universität Tübingen, Germany.
