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Tracer tests for the investigation of heterogeneous porous media and stochastic modelling of flow and transport—a review of some recent developments

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Abstract

In heterogeneous porous aquifers, simulations and predictions of groundwater flow and solute (contaminant) transport require detailed knowledge of aquifer parameters and their spatial distribution. In most cases this information cannot easily be obtained at acceptable expenses. In general, subsurface investigation techniques are applied only at borehole locations, and the parameter values measured have to be regionalized in order to obtain continuous parameter fields. Geophysical measurements very often yield unsatisfactory results due to resolution, detection range and parameterisation problems. In such situations tracer tests offer the possibility to efficiently investigate the aquifer between the wells and to characterize the relevant aquifer properties based on effective parameter values. Tracer tests can be performed at laboratory and field-scales with depth integrated (two-dimensional) or multilevel (three-dimensional) set-ups, and under natural or forced hydraulic gradient conditions. Both non-reactive and reactive tracer compounds can be used. This contribution covers and gives examples on the following topics: depth integrated and three-dimensional natural and forced gradient tracer test methods together with their fields of application at different transport scales, novel tracer compounds and applications, high resolution multilevel–multitracer methods and high resolution multilevel–multitracer equipment, as well as approaches to evaluate tracer experiments and to quantify tracer transport. In this way the paper shows some recent trends in tracer based subsurface investigation and emphasizes the advantages and importance of modern tracer testing.

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Keywords: Groundwater; Solute transport; Subsurface investigation; Tracer testing; Stochastic modelling

1. Introduction

It is generally accepted that tracer testing is a very efficient and versatile multipurpose method to characterize subsurface properties and to investigate

the spreading of both non-reactive and reactive solutes in groundwater at the whole range of investigation scales, i.e. from the laboratory scale in the order of centimeters to the regional field-scale in the order of kilometers. Due to lacking information on subsurface transport behavior, tracer testing very often even becomes a prerequisite to obtain reliable groundwater transport model predictions. A typical example is the identification of the main transport path of contaminants

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(the so called contaminant plume centreline) within natural attenuation studies (e.g. Bockelmann et al., 2003).

There is principally a large variety of application possibilities: tracer test methods can be applied for classical subsurface investigation purposes yielding effective transport parameters (transport velocity, porosity, and dispersivity), which may describe non-reactive as well as reactive (contaminant) transport processes within an aquifer. Information on subsurface structure (preferential flow paths, and structural anisotropy) can be obtained as well. This information may for example be used to set up and calibrate deterministic flow and transport models. Tracer test methods have also been applied to identify contamination pathways, to test the connectivity of different aquifer layers, etc. (e.g. Käss, 1998).

Tracer tests provide a database (tracer breakthrough curves and their statistical moments respectively derived transport parameters) too, which can be applied for testing of forward transport predictions obtained from deterministic or stochastic model approaches, for the reduction of prediction uncertainty within stochastic modelling frameworks, or for the development and application of inverse stochastic flow and transport modelling methods.

Recent applications, employing novel tracer compounds and tracer test instrumentation, have focused for example on the characterization of subsurface contamination with residual NAPL phase, on the quantification of the biodegradation potential in case of subsurface contamination with organic contaminants, on the quantification of mineral (Fe^{3+}) phases in the context of feasibility studies for the implementation of natural attenuation protocols, on testing of reactive barriers for groundwater cleanup, on the delineation of wellhead protection zones etc.

Out of the numerous application possibilities, this paper focuses on a summary of examples of some recent developments in the field of tracer testing and tracer based subsurface investigation, emphasizing the advantages and importance of modern tracer testing. It does not aim at providing a complete overview of all possible tracer testing approaches and related methods (e.g. borehole dilution methods), set-ups and evaluation procedures, which would require the size of a textbook. The paper covers the following topics: depth integrated and multilevel natural

and forced gradient tracer test methods together with their advantages and disadvantages, their fields of application at different transport scales, difficulties encountered due to subsurface heterogeneity, novel tracer compounds and examples of their application, high resolution multilevel–multitracer methods and high resolution multilevel–multitracer equipment, as well as approaches to evaluate non-reactive and reactive tracer experiments and to quantify tracer transport. The focus of our tracer testing is mainly on applications in unconsolidated porous media at field-scale. However, for the testing and development of innovative tracer compounds, as well as for the investigation of (reactive) transport processes, the experiments have to be at first performed at laboratory scale. Therefore both applications at laboratory and field-scales will be shown in this paper.

2. Aquifer heterogeneity, scale hierarchy, and implications for tracer testing

Looking at Fig. 1, which shows an outcrop of a heterogeneous alluvial sand and gravel aquifer, it becomes evident that the aquifer properties, defined for ‘point scale’, i.e. for very small representative elementary volumes (REV's) compared to the investigated aquifer domain, are variable in space. This variability is observed for both physical (hydraulic conductivity and porosity) as well as for hydrogeochemical (e.g. sorption capacity) and microbiological aquifer properties.

It is not surprising that aquifer structural properties, such as size, position and amount of clay lenses, sand and gravel layers, and the resulting distribution of hydraulic conductivity, porosity and



Fig. 1. Outcrop of a heterogeneous alluvial sand and gravel aquifer (Klingbeil, 1998).

hydrogeochemical parameters significantly control groundwater flow and spreading of solutes (e.g. Dagan, 1989; Gelhar, 1993).

A typical manifestation of this physical aquifer heterogeneity is overall anisotropy of hydraulic conductivity, even though the local, point scale hydraulic conductivities are isotropic (e.g. Gelhar and Axness, 1983; Vert et al., 1999). Another well investigated effect of physical aquifer heterogeneity is macrodispersion (e.g. Dagan, 1989; Ptak and Teutsch, 1992; Gelhar, 1993). It has been observed in field tracer experiments, that dispersivities estimated at field-scale may be several orders of magnitude higher compared to laboratory-scale dispersivities (e.g. Gelhar, 1986; Dagan, 1989), and that they may increase with transport distance. The reason is that at field-scale, compared to mechanical dispersion at pore level, the differential advection due to the field-scale heterogeneities, i.e. preferential flow around low conductivity zones, tends to increase the spreading of a solute plume.

Chemical aquifer heterogeneity can be recognized at laboratory scale for example from different sorption properties for different lithological components and grain size fractions of aquifer material (Grathwohl and Kleinedam, 1995; Ptak and Strobel, 1998; Karapanagioti et al., 1999; Kleinedam et al., 1999; Rügner et al., 1999), and at field-scale for example from an enhanced spreading of solutes (e.g. Burr et al., 1994; Ptak and Schmid, 1996). Another effect of physical and chemical aquifer heterogeneities is the so called makrokinetic sorption behavior, which is characterized by an effective retardation factor increasing with time, even though the solute is locally at sorption equilibrium (Miralles-Wilhelm and Gelhar, 1996; Ptak and Kleiner, 1998). Teutsch et al. (1998) have shown, that in case of a chemically heterogeneous fluvial sand and gravel aquifer, the mean arrival time of a kinetically sorbing solute is controlled by sandy aquifer zones with a relatively medium hydraulic conductivity, and not necessarily by the high conductivity preferential flow paths formed by gravels. The effects of microbiological heterogeneities have been investigated for example by Miralles-Wilhelm et al. (1997). The authors have shown that in a heterogeneous aquifer the correlations of retardation and biodegradation parameters with hydraulic conductivity may significantly control

the field-scale dispersion process. The effective decay rate may be significantly reduced compared to the mean. It follows that subsurface heterogeneities have to be considered when tracer-based investigation strategies are developed, when measured data are evaluated and when model simulations using tracer data have to be performed.

If heterogeneity and its effects on spreading of solutes have to be investigated by tracer tests, it is necessary to consider at first the relations of the investigation scale (characterized by the size of the investigated aquifer domain), the scale of heterogeneity (characterized by the typical size of aquifer structural elements), and the detection scale of the investigation method (characterized by the size of the aquifer domain covered by the investigation method). A comprehensive discussion on scale problems is given e.g. by Dagan (1986), Neuman (1990), Teutsch et al. (1990), Di Federico and Neuman (1998), and Zlotnik et al. (2000).

In most cases the aquifer material may be treated as homogeneous, if the heterogeneity scale is much smaller compared to the investigation scale. On the other hand, heterogeneity becomes relevant, if the heterogeneity scale is in the order of the investigation scale. Homogeneity is assumed for instance in most laboratory column and/or tank experiments, where the heterogeneity scale is characterized by the (constant) grain size. Deterministic approaches are then applied to evaluate the measured data and to quantify aquifer parameters.

At a regional investigation scale, mostly in the order of kilometers, the strong near-source irregularities in solute spreading may tend to average out, if the characteristic heterogeneity scale becomes much smaller compared to the investigation scale. It may then become admissible to use constant effective aquifer parameters, defined for relatively large aquifer portions (e.g. transmissivities from large-scale pumping tests, constant macrodispersivities, effective retardation factors) for the quantification of flow and transport. This approach of defining parameters for 'large-scale REVs' is the fundamental principle of deterministic flow and transport modelling at a regional scale.

However, in many situations typical for hydrogeological practice, for instance planning of subsurface remediation activities, the investigation scale

required is in the order of tens to hundreds of meters. This near-source, intermediate scale will mostly correspond to only a few (or even a single or less) characteristic heterogeneity lengths. Here, a strongly irregular solute spreading and a scale dependence of effective transport parameters (for instance effective macrodispersivities increasing with transport distance) can be expected as a consequence of aquifer parameter variability. In such a situation, to resolve the heterogeneity structure, the detection scale of the investigation method should be smaller compared to the heterogeneity scale. Unfortunately, to obtain a characterization of aquifer parameter distributions detailed enough for a deterministic model, the costs of investigation would become prohibitively high. The reason is that in general the construction of expensive monitoring wells is required. Finally, due to the usually limited number of measurements available, a parameter uncertainty remains after investigation.

To illustrate the effects of aquifer heterogeneity and the problems of investigating and characterizing solute transport in groundwater at an intermediate investigation scale, where the heterogeneity scale is in the order of the transport distance, Fig. 2 shows the distribution of transport velocities estimated from a natural gradient tracer test (NGTT) with a transport

distance of up to about 60 m and depth integrated sampling (Ptak and Teutsch, 1994a). Due to aquifer heterogeneity, it was impossible to find one common transport parameter set for the entire ensemble of the measured breakthrough curves. For the illustration purpose, the transport velocities were therefore estimated for each individual measured breakthrough curve, assuming individual transport paths within the aquifer and the transport direction to be parallel to the line connecting the injection and the breakthrough curve monitoring wells (the resulting transport directions are within the range of possible direction estimates based on hydraulic head measurements). The transport velocities range from 6.2 to 18.0 m/d. This variety of values was measured at monitoring wells separated by a distance of only 12 m.

This example clearly shows that in heterogeneous aquifers site assessment and transport predictions based on parameter values obtained at a limited number of borehole locations may be highly uncertain. Due to the variability of aquifer parameters at the intermediate scale and the resulting irregular solute spread, the investigation results may highly depend on the number and position of monitoring wells.

Consequently, to overcome the difficulties in dealing with aquifer heterogeneity, improved or new tracer investigation and measurement techniques as well as data interpretation and flow and transport simulation methods are needed.

3. Tracer test techniques

Tracer testing is an integral investigation method as it allows to estimate effective parameters describing non-reactive and reactive transport processes within an aquifer or aquifer material (in case of laboratory experiments) between the tracer injection and sampling locations. Out of the numerous approaches for tracer testing in heterogeneous aquifers, two fundamentally different strategies can be recognized.

Firstly, the application of tracer tests at local scale and estimation of point scale (very small REV) subsurface parameters. This approach is employed mainly in small-scale laboratory (column and tank) experiments or in small-scale field investigations using for example the dipole flowmeter test tracer

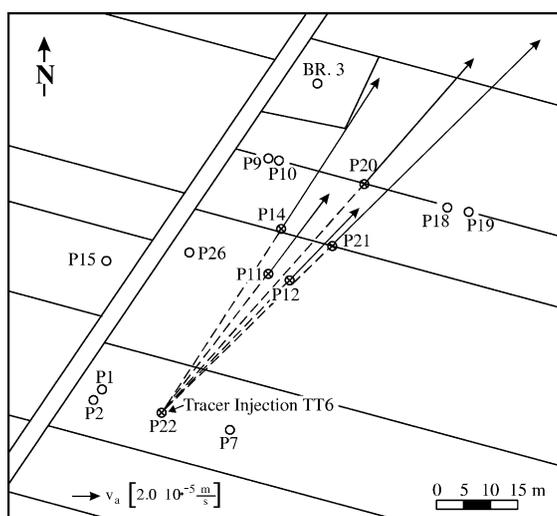


Fig. 2. Distribution of transport velocities in a heterogeneous porous aquifer (length of arrow indicates value of velocity; Ptak and Teutsch, 1994a).

combined with tracer injection and detection (Sutton et al., 2000). The resulting small-scale measurements are employed for example for gaining understanding of non-reactive and reactive transport processes, for testing of process based transport model code formulations, and for transport model predictions, which however, due to the remaining parameter uncertainty after investigation in case of heterogeneous aquifers, should be performed within a stochastic modelling framework. It should be mentioned that, considering aspects of hydrogeological practice, the efforts to obtain a sufficient database on local scale tracer transport can be expected too high for standard field-scale modelling purposes.

Secondly, the direct measurement of effective subsurface parameters at field-scale. This approach may be applied especially in many situations of hydrogeological practice, where the costs to obtain the amount of input data needed for stochastic simulations, the efforts with respect to the geostatistical data analysis, and the computation time become prohibitively high, or if some input parameters (for instance concentrations within the contaminant source zone) cannot be described using geostatistical methods. It may also be applied, if administrative authorities are not willing to accept stochastic variability of model predictions respective probabilistic model results. Of course, as mentioned above, the results can be used for more demanding tasks such as testing of forward transport predictions obtained from stochastic model approaches, for the reduction of prediction uncertainty within stochastic modelling frameworks, for the development and application of inverse stochastic flow and transport modelling methods etc. as well (e.g. Ezzedine and Rubin, 1996; Rubin et al., 1997; Woodbury and Rubin, 2000; Fernandez-Garcia et al., 2002).

Fig. 3 summarizes the approaches for using tracer test based data.

Principally, tracer tests can be performed under natural hydraulic gradient conditions in an undisturbed groundwater flow field, or under forced gradient conditions, induced by groundwater pumping or groundwater/tracer solute injection. In the experiments, tracer solution is injected into a well/laboratory column, and tracer breakthrough curves are measured in monitoring wells/at column outlets.

The detection scale is defined by the transport distance between the tracer injection and monitoring locations. Depending on the experimental set-up, depth integrated or multilevel breakthrough curves can be obtained in the field.

A variety of tracer compounds can be used. They can behave both non-reactive, i.e. as ideal tracers, and also reactive. Non-reactive, ideal tracers are used if the transport of solutes is investigated, which are not subject to degradation and/or interaction with the subsurface material. Depending on the site specific subsurface conditions, ideal tracers might be for example salt based tracers such as Chloride (e.g. NaCl), Bromide (e.g. NaBr), fluorescent tracers such as Fluoresceine, Eosine, Pyranine, Sodium–Naphthionate, Tinopal, radioactive tracers such as $^1\text{H}^3\text{HO}$, ^{82}Br if the decay is accounted for, dissolved gas tracers such as He or H_2 , environmental isotopes and chemicals, or particle tracers such as (natural, dyed, or fluorescent) spores, fluorescent microspheres, or other drift particles. Before selection of a conservative tracer compound laboratory testing should be performed to prove ideal or almost ideal tracer behavior. Of course, also aspects of environmental and administrative law have to be considered. Then, in most countries only a few compounds remain legal for injection in field experiments, mainly salt tracers and some fluorescent tracers. In Germany for example, it is practically impossible to use radioactive tracers and Rhodamine compounds (except Amidorhodamine G) within field experiments. If new tracers (especially the reactive tracers described below), not known yet to the administration, are planned for injection within field experiments, lengthy and tedious procedures to obtain permission for their use are required. It would be beyond the scope of this paper to summarize the physical and chemical properties of all (standard) tracers and the compound-specific analytical methods to estimate tracer concentrations. Comprehensive information, including aspects of the use of bacteria and phages as tracers, is given for instance in the textbook by Käss (1998). Reactive tracers will be treated in sections following below, focusing on some new developments.

Standard approaches for evaluation of the measured breakthrough curves (mainly in terms of transport velocities and dispersivities), based for

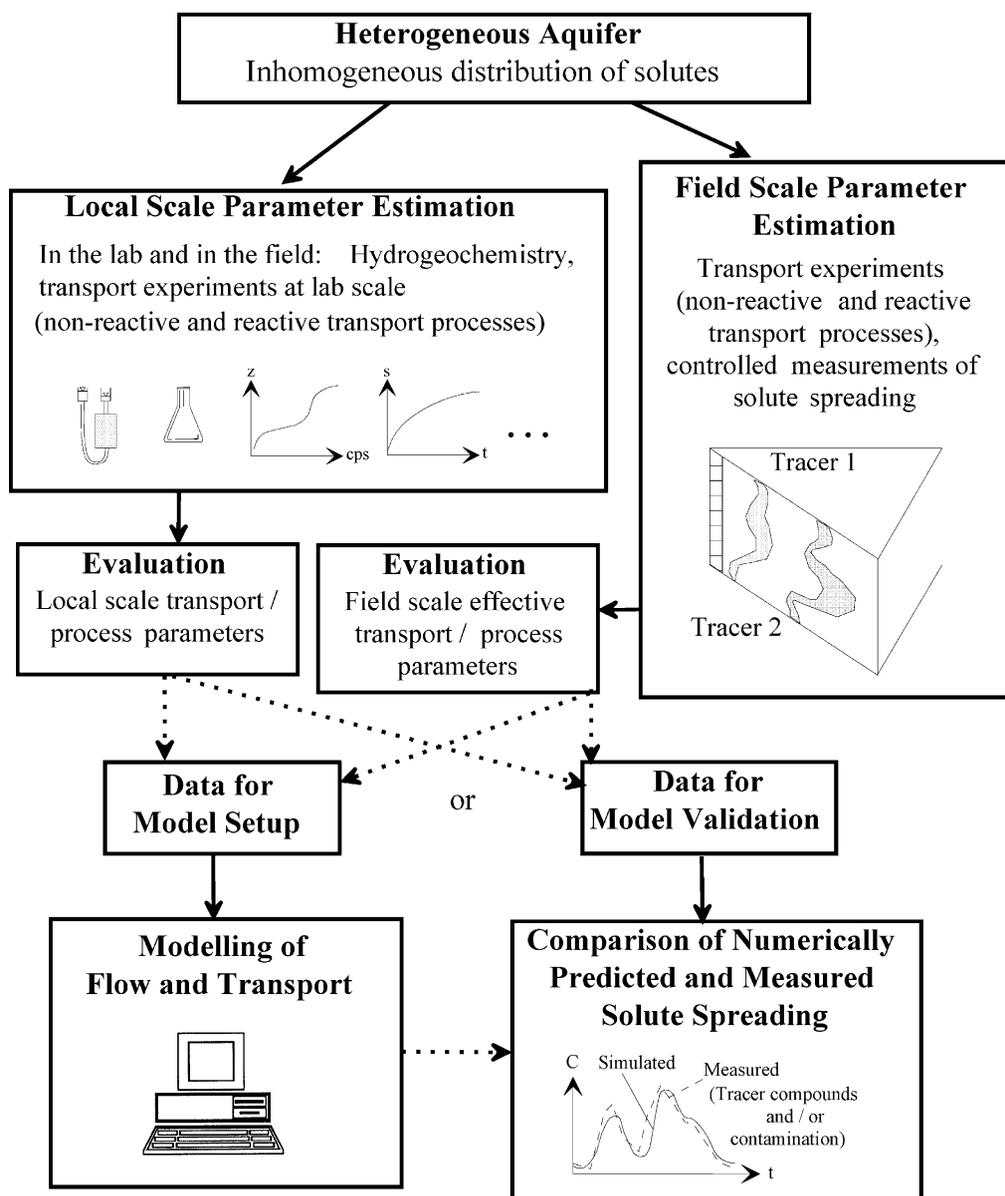


Fig. 3. Approaches for using tracer test based data.

example on fitting of analytical solutions of the transport equation, or on computing of concentration (temporal or spatial) moments (which can be related to transport parameters), or on inverse numerical modelling would be beyond the scope of this paper as well.

In most cases, information on tracer solute transport is available in terms of measured concentration time series, i.e. breakthrough curves, at monitoring locations. Procedures to obtain transport parameters from fitting analytical solutions of the transport equation to the breakthrough curves are

described for example in Fried (1975), Kreft and Zuber (1978), Sauty (1980), Fetter (1993) or Domenico and Schwartz (1990).

Evaluation approaches based on temporal moments of measured breakthrough curves are summarized for example in Kreft and Zuber (1978), Valocchi (1985), Ptak and Teutsch (1994a), Ptak (1995), and Ptak et al. (1996). A method of temporal moments to interpret solute transport with sorption and degradation is presented by Pang et al. (2003).

Spatial moments (e.g. Kreft and Zuber, 1978; Freyberg, 1986; Goltz and Roberts, 1987; Dagan, 1990; Garabedian et al., 1991; Rajaram and Gelhar, 1991; Adams and Gelhar, 1992) require the measurement of concentration values within a solute plume and the application of interpolation techniques. The difficulty to be managed is that due to the usually limited number of concentration measurement locations, especially in heterogeneous aquifers the computation of spatial moments cannot be performed reliably enough. It could be shown that in heterogeneous aquifers, even with an extremely dense monitoring network (e.g. Freyberg, 1986; Garabedian et al., 1991) the interpolation procedure can lead to bias in the moment (Barry and Sposito, 1990) and in the solute flux estimates.

3.1. Natural gradient tracer tests

In a NGTT at field-scale, the tracer solution is injected continuously, over a limited period, or pulse-like into the undisturbed groundwater flow field. Depth integrated or multilevel breakthrough curves are then measured in monitoring wells positioned in a downstream direction. A prerequisite for a successful experimental design is therefore knowledge about the approximate mean transport direction. Also, for planning of sampling activities, the approximate average transport velocity should be known in advance.

The investigation scale of NGTTs is not limited by principle, however the experimental efforts may become too high if the transport velocity is relatively small, and the transport distance to be investigated is relatively large. Furthermore, if the mean groundwater flow direction is shifting due to changes of boundary conditions, the evaluation of the measured breakthrough curves may become difficult. Another

disadvantage of the NGTT approach applied in heterogeneous aquifers is that a huge amount of monitoring wells may become necessary to reliably characterize the solute plume and its development.

An example of such extensive efforts needed for a small to medium investigation scale (5–50 m) is provided in Rügge et al. (1999). A continuous injection NGTT was carried out in the anaerobic part of a leachate plume downgradient of the Grindsted landfill in Denmark. Bromide and 18 xenobiotic compounds were injected over 195 days, with the aim of surveying the transport of a continuous plume. At each 5 m distance downgradient from the injection wells, between 4 and 12 monitoring wells were sampled over a period of 924 days. One result of the conducted moment analysis was, that bromide showed decreasing transport velocities over time. This was explained by the observed varying flow conditions and the heterogeneity of the sandy aquifer.

A series of well-known large-scale NGTTs was performed in USA and Canada. These include the experiments at Cape Cod, Massachusetts, at the Columbus site, Ohio, and at the Canadian Forces Base Borden, Ontario. All those experiments are based on extensive sampling networks, enabling some of the most detailed site characterizations reported in the literature.

At Cape Cod, the disposal of treated sewage produced a 2.5 mi long contaminant plume (composed of hydrocarbons, detergents, metals, nitrate and specific microbes) in the sand and gravel aquifer. This aquifer was investigated in detail by more than 1000 hydraulic conductivity measurements, derived from core material permeameter (Wolf, 1988; Wolf et al., 1991) and borehole flowmeter tests (Hess, 1989). During NGTTs involving both conservative and reactive tracers (Garabedian et al., 1991; LeBlanc et al., 1986, 1987, 1991), groundwater was sampled by more than 650 observation wells, each with sampling ports over 15 vertically different levels allowing an accurate definition of the 3D plume development. The extensive subsurface investigation program has provided a good basis for a reliable characterization of the spatial and temporal behavior of non-reactive and reactive solute plumes, and for the related investigation of non-reactive and reactive transport processes in the subsurface, of density and recharge effects, and of natural attenuation of

the sewage plume (e.g. Ezzedine and Rubin, 1997; Zhang et al., 1998; LeBlanc et al., 1999; LeBlanc, 2001; Moench et al., 2001; Davis et al., 2001a, b; Hess et al., 2002a, b; Shinga et al., 2003; Walter and Masterson, 2003). For example, in a multispecies reactive tracer test, Hess et al. (2002) studied the dispersive transport of Bromide and Nickel. The focus was on effects of spatially variable chemical conditions within the aquifer as well as on transverse and longitudinal dispersivities.

The Macrodispersion Experiment (MADE) site at the Columbus Air Force Base, Mississippi, is a typical example of an aquifer located in highly heterogeneous fluvial deposits. Tracer tests were performed aiming at the investigation of solute spreading under highly heterogeneous subsurface conditions. The aquifer has a saturated thickness of 10–12 m and consists mainly of unconsolidated sand and gravel materials. Characterization of the site employed 2451 permeability measurements (based on slug tests, grain size analysis, pumping tests, laboratory core testing, and flowmeter tests), surface and borehole geophysics, hydrofacies mapping, as well as water level measurement in more than 100 monitoring wells. Rehfeldt et al. (1992) concluded that data from flowmeter tests provide the most direct and successful measure of hydraulic conductivity (K). The variance of $\ln(K)$, $\sigma_{\ln K}^2$, is as high as 4.4. At first in 1986, a conservative tracer experiment was performed by a 48 h pulse injection of 10 m³ of groundwater containing Bromide and three organic tracers (pentafluorobenzoic acid, *o*-trifluoromethylbenzoic acid, and 2,6-difluorobenzoic acid). Over a 20-months period, seven sampling campaigns were performed to delineate the tracer plume at approximately 1–4 months intervals using an extensive 3D sampling well network (Boggs et al., 1992). The tracer plumes showed highly irregular, asymmetric, non-Gaussian patterns (Zheng and Gorelick, 2001; 2003), and it was concluded that solute transport at the MADE site appears to be dominated by preferential flow paths resulting from aquifer heterogeneity at decimeter and smaller scales, and that a large portion of the aquifer acts like a series of immobile reservoirs. Many other publications were released on modelling of flow and solute transport within the performed NGTTs (e.g. Adams and Gelhar, 1992; Harvey and Gorelick, 2000; Feehley et al., 2000). Zheng and Jiao (1998) reported the simulated

plume being more sensitive to the way the hydraulic conductivity field is interpolated from the measured data than to the dispersivity value. Their transport model with longitudinal dispersivities in the range of 1–5 m reasonably reproduced the observed plume to a certain concentration limit, but failed to reproduce the significant spreading of the tracer at diluted concentrations as observed in the field. This shows possible difficulties in modelling solute transport in highly heterogeneous aquifers. Such modelling requires a characterization and quantification of transport processes, aquifer parameters and aquifer structural properties at a high resolution. Here, specifically designed tracer tests can significantly help to improve the solute transport modelling efforts.

One of the most known field-scale NGTTs was conducted at the Borden experimental site between 1982 and 1984. 12 m³ of solution containing two inorganic tracers (Chloride and Bromide) and five organic compounds were injected as a pulse into the shallow, unconfined sandy aquifer. A very dense, three-dimensional array of monitoring points was used to record breakthrough curves and to monitor plume development. The experiments are discussed extensively in the literature (e.g. Mackay et al., 1986; Freyberg, 1986; Sudicky, 1986; Roberts et al., 1986; Sposito and Jury, 1988; Rajaram and Gelhar, 1991; Brusseau, 1992; Cvetkovic and Dagan, 1994; Burrell et al., 1994; Miralles-Wilhelm and Gelhar, 1996). Many of the publications focus on characterizing the spatial variability of the hydraulic conductivity field and on the spatial and temporal behavior of non-reactive tracer transport. Only a few of them focus on the transport of the reactive, organic solutes with a significant non-ideal transport behavior. Rate-limited sorption (Sposito and Jury, 1988; Cvetkovic and Dagan, 1994) and diffusive mass transfer (Goltz and Roberts, 1988; Thorbjarnarson and Mackay, 1994) were the first reasons thought to explain the non-ideal transport. Brusseau and Srivastava (1997) postulated a coupled effect of non-linear sorption and enhanced spreading caused by variable hydraulic conductivity and spatially variable sorption (especially for their negative correlation) to be a major cause of the enhanced longitudinal spreading, observed for the organic solute plumes in comparison to the conservative plumes.

A tracer study carried out in a heterogeneous aquifer closely located to Grenoble, France, focused on

characterizing dispersion as a function of the spatial structure of the hydraulic conductivity field (Courtois et al., 2000). A deterministic interpretation of field-scale NGTT data and a geostatistical analysis of the spatial structure of the hydraulic conductivity field, followed by a spatial moment analysis of stochastic particle trajectories, produced similar dispersivity values (reaching an asymptotic limit of 6 m after a 50 m travel distance, i.e. about ten correlation lengths).

A field-scale NGTT conducted at Krauthausen, Germany, involved three different conservative and reactive tracers: Bromide, Fluoresceine and Lithium (Vereecken et al., 2000). Bromide was used as conservative tracer, and Fluoresceine and Lithium were regarded as reactive tracers in the heterogeneous aquifer. In laboratory batch experiments and column tests a sorption behavior of Fluoresceine and Lithium according to a Freundlich isotherm was determined. The solute plume evolution was surveyed for 398 days for Bromide and 449 days for Fluoresceine and Lithium. A spatial moment analysis applied to the Bromide plume emphasized a longitudinal effective dispersivity of about 3.64 m, which is a bigger value than the one observed at the Borden site. This result corresponds with the higher heterogeneity and variance of $\ln(K)$ (0.84–1.08 compared to 0.29 at Borden).

The NGTT technique was also extensively applied to test analytical solutions from stochastic transport theory (e.g. Sudicky, 1986; Freyberg, 1986; Rehfeldt et al., 1989; Hess et al., 1992; Fiori, 1998), or to test numerical stochastic transport model predictions (e.g. Ptak and Teutsch, 1992).

An example of application of the multilevel NGTT method for direct investigation of transport behavior and effective transport parameters in a contaminated heterogeneous aquifer at a former gasworks site is described in Bösel et al. (2000) and Herfort and Ptak (2002). Here, the NGTT served in a multitracer version for the identification of main transport paths, for the investigation of transport velocities, and to obtain probability density functions (pdfs) of travel time, which are a prerequisite for the application of a new Lagrangian stochastic transport model called SMART (Finkel et al., 1997). In this multitracer NGTT, to maximize gain of information and to reduce the experimental effort, four different tracers (Fluoresceine, Eosine, Sodium–Naphthionate, and

Sodium–Bromide) were injected at four different locations. Bromide concentrations were analysed by ion chromatography (IC), and the concentrations of the fluorescent tracers were measured in parallel using a further developed fluorimetric separation method (Kleiner, 1997), where the concentrations of the individual tracers are determined from the evaluation of synchronous fluorescence scans (Behrens, 1982) employing pH shifting. This tracer testing proved to be essential for the evaluation of natural attenuation rates at field-scale and for the quantification of the natural attenuation potential at the investigated site (Bockelmann et al., 2003).

Possible fields of application, considering the advantages and disadvantages of the NGTT method, are summarized in Table 1. To overcome some of the disadvantages, it may be reasonable to perform tracer tests under forced gradient conditions.

3.2. Forced gradient tracer tests

Forced gradient tracer tests (FGTTs) can be performed in a convergent, in a divergent, in a dipole type groundwater flow field, or with a subsequent application of divergent and convergent flow conditions (push–pull tests). Due to the forced gradient, well-defined experimental conditions are obtained, the effects of natural gradient variations are minimized, and the tracer test duration is reduced compared with natural gradient tracer experiments.

In the divergent flow field approach, groundwater is injected into an injection well at a constant rate, and, after a quasi-steady-state flow field is established, the tracer mass is added continuously, over a limited period, or instantaneously, and mixed within the injection well across the entire length of the selected injection section. Surrounding monitoring wells are then used to measure depth integrated or multilevel tracer breakthrough curves. Measurements can be obtained in all directions using only a single tracer.

In the convergent flow field approach, groundwater is pumped out of a extraction well, the tracer is injected continuously, over a limited period, or instantaneously into surrounding wells, and breakthrough curves are measured usually at the extraction location. Using a flow separation technique (Ptak and Schmid, 1996; see also text below), it is also possible

Table 1

Tracer test techniques and possible application for subsurface investigations (+ corresponds to a suitable application, the numbers in brackets refer to comments/explanations in the bottom part of the table), considering the advantages and disadvantages of the NGTT and FGTT methods

	Natural gradient tracer tests (NGTT) ^{1,2,3}		Forced gradient tracer tests (FGTT) ^{6,7}	
	Depth integrated sampling	Multilevel sampling	Depth integrated sampling	Multilevel sampling
Investigation of main transport direction under natural conditions	+	+	– ⁸	– ⁸
Proof of postulated position of contaminant sources	+	+	– ⁸	– ⁸
Spatial distribution of tracer transport times (for stochastic transport modelling)	–	+	–	+
Investigation of spatial distribution of transport parameters	–	+	–	+
Investigation of aquifer structure, connectivity, detection of preferential flow paths and spreading zones	–	(+) ⁴	–	+
Validation of transport model predictions	+	+	+	+
Estimation of effective transport parameters describing non-reactive solute transport (non-reactive tracers)	+	+	+	+
Estimation of hydrogeochemical aquifer properties and effective transport parameters describing reactive solute transport (reactive tracers)	(+) ⁵	(+) ⁵	+	+
Applicability for differential multitracer investigations (simultaneous use of non-reactive and reactive tracers)	(+) ⁵	(+) ⁵	+	+

Advantages

Disadvantages

NGTT

Detection scale not limited in principle

1. Relatively long duration of experiment
2. Evaluation possibly difficult due to varying hydrogeological boundary conditions
3. Detection of tracer plume and calculation of mass balance problematic
4. Dense monitoring well network required
5. In most cases not suitable for use of reactive tracers due to the resulting long duration of experiment

(continued on next page)

Table 1 (Continued)

	Advantages	Disadvantages
FGTT	<p>Relatively short duration of experiment (especially with induced radially symmetric groundwater flow) Effects of hydraulic gradient variations effectively reduced</p> <p>Possibility to consider several transport directions using only one tracer compound (divergent flow pattern) Possibility to calculate mass balance (convergent, dipole type and push–pull flow patterns) Use of reactive tracer compounds manageable at affordable expenses</p>	<p>6. Detection scale limited</p> <p>7. Treatment of pumped groundwater sometimes necessary (convergent, dipole type and push–pull flow patterns)</p> <p>8. No natural groundwater flow during experiment</p>

to measure multilevel breakthrough curves within the pumping well itself. If different flow directions have to be considered, different tracers can be used.

In the dipole flow field approach (two-well or interwell test), groundwater is extracted from a well, and re-injected into another well. The tracer is introduced into the infiltration well, or an injection well within the dipole (pulse like, continuously, or pulse like with recirculation), and monitored at the extraction well and/or dedicated sampling locations between the wells. In a symmetrical set-up, the groundwater extraction and infiltration rates are the same. The nature of the dipole flow field may require relative long experimental times to obtain a satisfying tracer recovery. Tracer recovery may be improved in an asymmetrical set-up by increasing the extraction rate compared to the infiltration rate.

In the divergent and convergent flow field approach (single-well push–pull test), the tracer solution is injected into a well, sometimes followed by the injection of clean water to force the tracer out of the well, and then extracted from the same well.

The advantage of the aforementioned convergent, dipole type, and push–pull test approaches is the possibility of obtaining (high) tracer mass recovery rates.

To obtain a high temporal and (three-dimensional) spatial resolution, on-line measurement equipment

can be used, e.g. multilevel fiber optic fluorimeters for fluorescent tracers (Ptak and Schmid, 1996; see below), ion selective probes for salt tracers, or gas diffusion membranes with a mass spectrometer, or an electron capture detector for dissolved gas tracers. Effective transport parameters are then obtained from the evaluation of the measured breakthrough curves (see also Section 3). The detection scale of the forced gradient experiments can be easily controlled by the pumping or infiltration rates.

Chen et al. (1999), for example, used tracer tests in a radially convergent flow field to evaluate transverse dispersivity. Fernandez-Garcia et al. (2002) used convergent-flow tracer tests in an experimental tank to study the applicability of effective transport parameters based on an equivalent homogeneous aquifer assumption.

Other applications of the FGTT technique in a highly heterogeneous aquifer as a direct subsurface investigation method using non-reactive tracers are described in Ptak and Teutsch (1994a), Ptak (1995), and Ptak et al. (1996). FGTTs with both divergent and convergent flow fields were applied to investigate the aquifer structure by identifying preferential flow paths and estimating anisotropy of solute spreading, connectivity of layers, and spatial variability of effective transport parameters from multilevel breakthrough curves. As a result,

a significantly improved geological model of the subsurface could be obtained.

The interwell set-up was used for example by Nelson and Brusseau (1996), and Annable et al. (1998a, b) to detect non-aqueous phase liquids in an aquifer. The single-well push–pull technique was employed for instance by Istok et al. (1997) and Haggerty et al. (1998) for the in situ determination of microbial metabolic activities and reaction rate coefficients in groundwater.

Further forced gradient tracer tests and details on dipole type and push–pull FGTTs will be presented in Sections 3.5.2 and 3.5.3 below, dealing with reactive tracers.

As for the NGTT method, possible fields of application, considering the advantages and disadvantages of the FGTT method are summarized in Table 1. Table 1 is based on information from literature and on the authors' experience gathered during numerous tracer tests, and is intended to provide an overview and general suggestions for the application of the different tracer testing methods. Of course, depending on site specific conditions and aims of an experiment, other applications, combinations and set-ups are possible.

It should also be taken into account, that different tracer test types may yield different transport parameters such as longitudinal dispersivity. Tiedeman and Hsieh (2003) evaluated simulated forced gradient tracer tests in heterogeneous aquifers. Their results show that for the forced gradient tests, a radial flow test tends to yield the smallest longitudinal dispersivity, an equal strength two-well test tends to yield the largest longitudinal dispersivity, and an unequal strength two-well test tends to yield intermediate values due to the different aquifer portions sampled by the different experiments. Results also indicate that longitudinal dispersivity estimated from forced-gradient tests generally underestimates longitudinal dispersivity that characterizes solute dispersion under natural-gradient flow. The only exceptions are for equal and unequal strength two-well tests with large well separation distance conducted in aquifers with a low degree of heterogeneity.

To avoid difficulties based on different transport parameter values from different tracer test set-ups, a stochastic modelling approach can be used, suitable for the simulation of solute transport within

heterogeneous aquifers without the need to introduce macrodispersivity values or relations for the scale dependence of dispersivity (see Section 4).

The decision whether a Dirac pulse, finite pulse or a step tracer input function is applied depends mainly on practical considerations. For relative short transport distances and high transport velocities, it may become difficult to create a Dirac type input function, as the tracer injection time may become significant compared to the tracer transport time. Then a step input function might be a better approach. However, for relatively long transport distances a step input might yield prohibitively high experimental efforts and costs due to the amount of tracer solution needed and the time required for the continuous tracer solute injection. Then a Dirac pulse or finite pulse type tracer injection might be the better approach, even though a higher initial concentration of the tracer solution will be required to account for the concentration decrease during transport. A careful experimental design employing numerical transport simulations is suggested to find the optimal solution.

During the assessment of aquifer transport properties via both NGTT and FGTT, a number of factors (e.g. injection duration, flow rate, well-bore mixing and dilution effects, local distortion of the flow field around the injection well, tracer capture in the well bore) can cause the tracer input function to depart from the assumed theoretical injection profiles (Dirac pulse, finite pulse or step functions), which might lead to incorrect interpretation of the test. While injection duration and flow rates are usually under control, the other factors that are related to well and aquifer interactions are more difficult to deal with. Neglecting the influence of the actual injection conditions can lead to two types of error (Rentier et al., 2002): (i) the values of the fitted parameters can be far from reality, (ii) the identification of the main active transport processes can be strongly biased. For example, an observed extended tailing and attenuation of the tracer breakthrough curve could erroneously be attributed to a kinetic sorption process or the occurrence of a dual porosity effect, when actually they are the result of the delayed release of the tracer, captured in the well at the end of the injection. To overcome some of the aforementioned limitations, Brouyere (2000) and Rentier et al. (2002) proposed a new conceptual and numerical approach, which can be easily implemented

in any existing flow and transport simulator, allowing to model the injection conditions of a tracer in a well during field tracer tests.

3.3. Multitracer approach and DNA sequence based tracers

As described above in the section dealing with the application of the NGTT technique, to reduce experimental efforts and to maximize gain of information from the generally costly tracer experiments, multiple tracers can be used within one experiment (Bösel et al., 2000; Herfort and Ptak, 2002). Then, groundwater samples have to be analysed for multiple tracers. However, due to the physical and hydrogeochemical properties of the usually used fluorescent, gas or salt tracers, and the resulting limitations of the tracer analysis procedures, the maximum number of different tracer compounds that can be used in parallel would usually amount to about 8–10, and different analytical techniques such as fluorescence spectrometry, wet chemistry, ion chromatography and mass spectrometry would become necessary, requiring high experimental efforts. However, in the last years special tracing techniques involving synthetic DNA (deoxyribonucleic acid) molecules with individually coded information were developed (Aleström, 1995). With such new tracer compounds it becomes principally possible to perform multitracer experiments with a theoretically unlimited number of tracer injection locations.

DNA is constituted by a sequence of subunits called nucleotides, specific in size and internal order (Knippers, 2001). Every nucleotide is made up of nitrogenous bases (adenine-A, guanine-G, cytosine-C and thymine-T) and a sugar skeleton. Because the complementary cytosine (C) and guanine (G) are bound by three hydrogen bonds, compared to only two bonds for the other pairs adenine (A)–thymine (T), the percentage of GC is a measure of the stability of the molecule. In nature, mostly double stranded molecules occur, with nucleotides disposed on two opposite strands. Normally, the DNA is a very long molecule (1 mm) compared to its very small diameter (20×10^{-10} m). Therefore the rather fragile double strands of the DNA molecule can be easily broken apart.

Shorter or longer fragments of single stranded nucleotide sequences can be designed by chemical

synthesis. The difference compared to the natural single stranded DNA molecules consists in the molecule length (90 nucleotides for the presented field case study), which is several orders of magnitude shorter than the natural molecules.

As the DNA molecule is an anion, with a negative charge synthetically adapted to the requirements (Knippers, 2001), sorption of DNA molecules is dependent on the aquifer material type as well as physical and chemical properties of the groundwater. It has been proved that adsorption to clay minerals is several orders of magnitude higher than to sand grains. Adsorption to sand is directly related to pH, salt content and cationic valence (Lorenz and Wackernagel, 1987). More adsorption was monitored with increasing presence of bivalent cations Ca^{2+} and Mg^{2+} than of monovalent Na^+ . All studies point out a minimum of adsorption for neutral pH conditions (Lorenz and Wackernagel, 1987; Aardema et al., 1983). Adsorption was found to be fast compared to desorption (Lorenz and Wackernagel, 1987) and temperature independent. Degradation of DNA molecule seems to be enhanced by the presence of bacterial activity. Consequently, further research is needed with respect to adsorption and degradation of DNA molecules in the subsurface, depending on site specific physical and hydrogeochemical conditions.

The presence of DNA is proven by regular polymerase chain reaction analysis (PCR), a routine method commonly used in forensic medicine and biology. With new methods it is even possible to quantify the number of identical DNA molecules in one sample (quantitative PCR). Theoretically, the detection limit goes down to one molecule (Watson et al., 1992). In addition to a practically unlimited number of different DNA sequences, meaning different tracers, the extremely low detection limit represents another huge advantage of using synthetic single stranded DNA molecules for tracing purposes in groundwater, compared to traditional tracers. The synthetic DNA molecules are usually available in 1 ml ampoules, which contain 10^{16} – 10^{18} identical molecules. Even if adsorbed, degraded and diluted under subsurface transport conditions by a factor of 10^{14} – 10^{15} (which is much more than expected during standard hydrogeological applications), the tracers still remain easily detectable.

3.3.1. Examples of DNA tracer application

One of the first experiments designed to test the mobility and migration of DNA coded molecules within sandy aquifers was performed at the Morrepen-3 research site, closely located to Gardermoen Oslo airport in Norway (Sabir et al., 1999a, b). In a forced gradient steady state flow regime, a combination of Sodium–Chloride (NaCl) and a single stranded DNA tracer was injected into an unconfined sandy aquifer. The distance between the injection and pumping wells was 12 m. The migration of the solute plumes was investigated with 38 multilevel monitoring wells, out of which 35 were installed over a 5 m × 5 m area. The results of analyses showed an overlapping of the plumes, with a general trend of DNA molecules being detected farther away and at greater depths compared to the chloride anions. The reason was the high detection sensitivity of the PCR method (as low as only a few identical DNA molecules), compared to the chloride anions, with detection limits several orders of magnitude higher. The experiment demonstrated that specially designed DNA molecules can be recorded in a variety of depths and distances from the injection point and therefore be used for groundwater tracer testing purposes.

The possibility to encode a considerable amount of specific information creates the chance to generate a practically infinite number of different DNA tracers. Colleuille and Kitterod (1998) used five differently labelled DNA tracers to delineate preferential flowpaths and to prove contaminant source location.

The use of different DNA codes for several horizontally and vertically differentiated injection points and a subsequent injection of the different tracers can quantify solute transport in space and time. In a DNA tracer injection in fractured hard rocks performed within the Romeriksporten railway tunnel project in Norway (Sabir et al., 2000a, b), it was possible to determine the degree of connection between the excavation and a surface water body, as well as to estimate the travel time of water in the fractured rock.

A similar study (Sabir et al., 2000a, b) carried out at Holmedal, Sogn and Fjordane, Norway, proved the usefulness of such tracers in a study of connectivity between wells drilled in fractured rocks, together with a first assessment of groundwater velocity within fractures.

3.3.2. Development of a quantitative DNA tracing approach

In the previous studies, the investigations were performed in a qualitative manner only. Therefore, a quantitative approach is presently being developed, allowing the measurement of DNA breakthrough curves and the estimation of effective transport parameters. This research is performed at the Lauswiesen experimental site located closely to the city of Stuttgart (Fig. 4), where the topic of drinking water well protection zones is presently under investigation.

At the test site, a quite regular sequence of upper clay, followed by highly conductive (mean $K = 8.8 \times 10^{-3}$ m/s) quaternary sand and gravel deposits, is found. The saturated aquifer thickness is about 5 m. The groundwater has a neutral pH (7.0–7.2), a moderate content of bivalent cations (Ca^{2+} : 100–150 mg/l, Mg^{2+} : 20–30 mg/l), and a low microbiological activity. Therefore no significant adsorption and degradation of DNA molecules is expected.

3.3.2.1. Laboratory testing. To test the new DNA tracers and the newly applied technique to measure quantitative breakthrough curves, three laboratory column experiments using undisturbed core samples (50 cm length, 10 cm diameter) from the Lauswiesen test site were conducted in a first step. Sodium–Bromide was used as a conservative reference tracer. The flow rate was adjusted in a way to obtain a transport velocity within the columns of about 14.4 m/d, which is comparable to the transport velocities expected in the subsequent field tracer test. For all three tests the injected tracer volume was 40 ml, containing 2.79×10^9 (DNA tracer no. 1) respectively 2.64×10^{10} (DNA tracer no. 2) identical DNA molecules. The samples were analysed by ion chromatography (Bromide) and quantitative PCR (DNA tracers). Fig. 5 shows examples of measured DNA and Bromide breakthrough curves. One should note that the peak of the DNA breakthrough curve arrives earlier compared to Bromide. The higher transport velocity of the DNA tracer, compared to the conservative Bromide tracer, could be possibly explained by size exclusion effects and resulting selective flowpaths, with larger diameters and therefore higher transport velocities, detected by the DNA

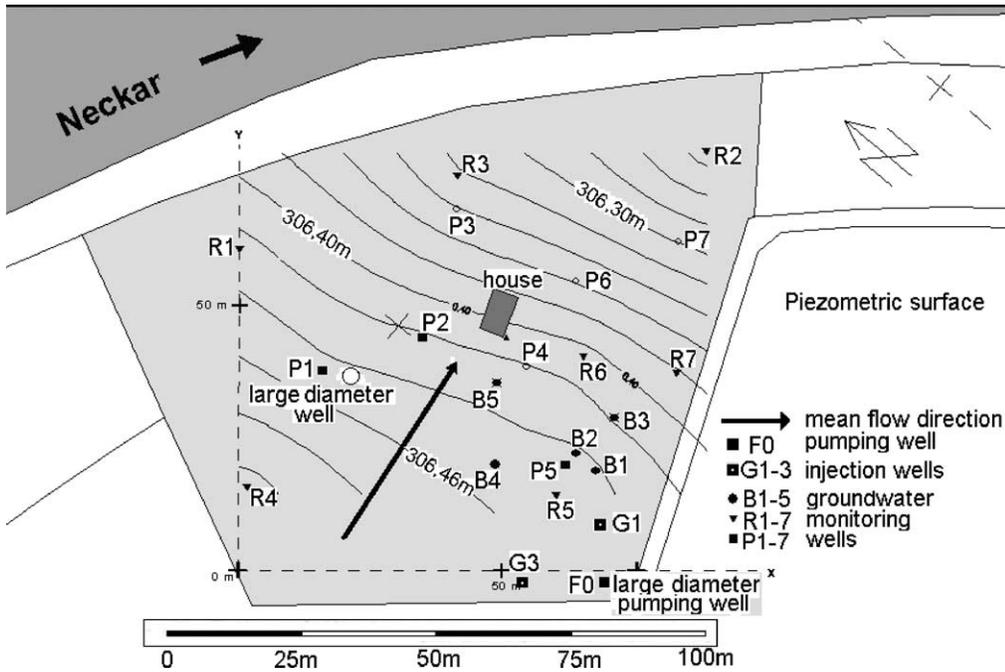


Fig. 4. The Lauswiesen experimental site and monitoring network.

tracers due to their relatively larger molecule size. The results are supported by previous studies (Sabir et al., 1999a, b).

3.3.2.2. *Field experiment.* To reproduce the flow situation of a drinking water well field, the first quantitative DNA field tracer experiment at the Lauswiesen site was run under convergent flow forced gradient conditions (set-up shown in Fig. 4; G1, G3: fully screened DNA injection wells; F0: pumping and DNA monitoring well; B1: additional DNA monitoring well). Due to the high aquifer heterogeneity (variance $\sigma_{\ln(K)}^2 = 2.97$, based on laboratory-scale sieve analyses), the tracer test was performed in a multilevel set-up (see below) with four sampling sections in vertical direction.

The two different DNA tracers (10^{16} single stranded molecules, 90 nucleotides each), tested in the laboratory experiments, were injected together with Sodium–Bromide and Sodium–Naphthionate as reference tracers at the two injection wells (G1, G3), which results in an overall transport scale of the experiment of about 10 m. Examples of breakthrough curves are shown in Fig. 6. Fig. 6 presents according

to our knowledge a first example of quantitatively measured DNA breakthrough curves at field-scale. It is seen, that at field-scale earlier peak concentration arrival times of the DNA tracer compared to Bromide are not necessarily observed. Other field-scale breakthrough curves, however, still indicate earlier peak concentration arrival times of the DNA tracers compared to Bromide. This supports the above-mentioned laboratory experiments, regarding the behavior of the used DNA tracer as a relatively long

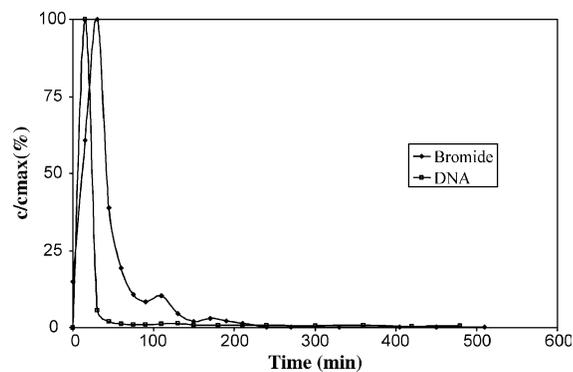


Fig. 5. Example of measured laboratory column breakthrough curves for Bromide and a DNA tracer.

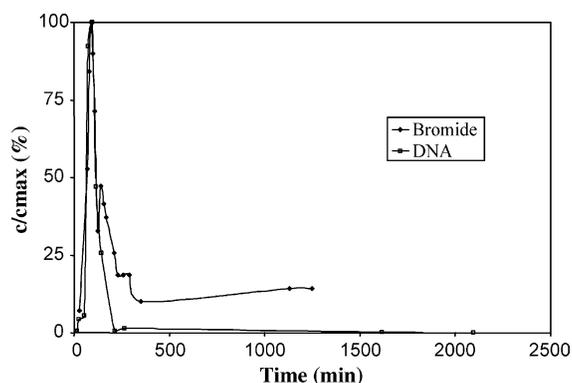


Fig. 6. Example of measured field-scale breakthrough curves for Bromide and a DNA tracer (tracer no. 2).

molecule, which is therefore possibly subject to the aforementioned pore size exclusion effects.

The first results of the field experiment show that it is feasible to measure DNA breakthrough curves in aquifer materials using quantitative PCR analysis. Due to the possibility of using practically an unlimited number of different DNA tracers with a very low detection limit within one multitracer experiment,

quantitative DNA tracing may become a powerful tool for (three-dimensional) subsurface investigation at a variety of transport scales. More detailed laboratory and field experiments directed towards a better understanding and quantification of transport, adsorption and degradation processes of the synthetic single stranded DNA molecules, depending on the soil type and hydrogeochemical conditions, will help to improve mass balance calculations, and applicability of the DNA tracer method.

3.4. High resolution multilevel multitracer sampling and concentration measuring equipment

At some field sites with a high degree of heterogeneity, a three-dimensional subsurface characterization may become necessary, i.e. the measurement of depth-differentiated multilevel breakthrough curves. Multilevel sampling systems (e.g. Ptak et al., 2000) may be installed for this purpose. However, especially at sites with deep aquifers and coarse aquifer material, monitoring well installation costs may become a limiting factor. To allow multilevel

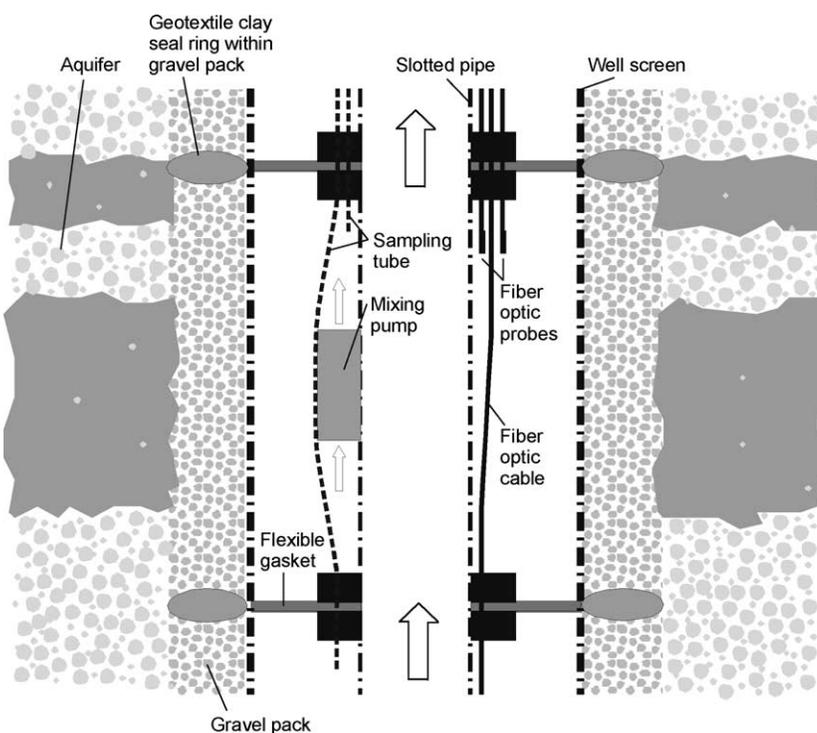


Fig. 7. Multilevel sampling within pumping wells (Ptak and Schmid, 1996).

groundwater sampling also within fully screened pumping wells, avoiding installation of additional costly monitoring wells when performing forced gradient transport experiments, a flow separation technique was introduced (Ptak and Schmid, 1996; Fig. 7) and further improved at the Lauswiesen experimental site for the application in large diameter pumping wells (Fig. 8).

In this multilevel set-up, the screen within a pumping well is divided into individual measuring sections using a slotted-wall multilevel packer (Fig. 7). Each section can be equipped for instance with fiberoptic probes for on-line in situ fluorescence spectrum measurements (for example if the transport velocity is relatively high, making round the clock frequent sampling necessary), and/or other probes yielding chemical and/or physical parameters. Mixing pumps can be provided in order to obtain parameter values representative for the entire section thickness. Additional groundwater sampling tubes allow taking (level integrated) multilevel groundwater samples.



Fig. 8. Multilevel sampler for large diameter pumping wells.

In order to avoid vertical flow within the gravel pack during the multilevel sampling procedure, geotextile clay seals (Ptak et al., 2000) can be installed within the gravel pack of the wells.

3.5. Multitracer forced gradient transport experiments for the investigation of physical and hydrogeochemical aquifer properties

If the FGTT approach is used to investigate reactive transport processes, at least two tracers, a non-reactive and one or more reactive, are injected simultaneously at the same location into the aquifer. Since all tracers experience the same (heterogeneous) hydraulic conductivity field, the relative difference in the transport behavior of the tracers (e.g. higher second order temporal moments of reactive tracer breakthrough curves compared to the non-reactive ones, relative retardation etc.) is only a statement of the reactive transport processes within the aquifer. Fig. 9 shows the principle of this differential multitracer testing approach in a multilevel version. The multilevel version allows in addition the investigation of three-dimensional structural properties such as preferential flow paths, connectivity, structural anisotropy etc.

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.

3.5.1. Application of multitracer forced gradient transport experiments for the investigation of subsurface structural properties, surface sorption, and scale effects

The above multitracer forced gradient technique was initially applied for the investigation of surface sorption, of effective field-scale retardation at transport distances of up to 33 m, and of scale effects related to reactive transport within three convergent groundwater flow experiments using a non-reactive (Fluoresceine) and a reactive, surface-sorbing fluorescent tracer (Rhodamine WT) (Ptak and Schmid, 1996; Ptak and Strobel, 1998; Ptak and Kleiner, 1998). Using Rhodamine WT as a reactive tracer, sorption onto mineral surfaces can be investigated,

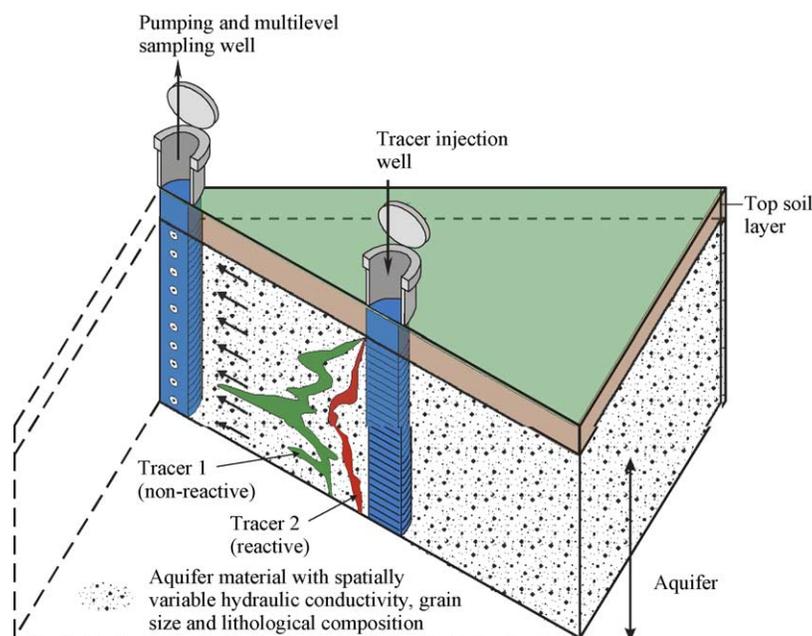


Fig. 9. Forced gradient multilevel–multitracer approach (Ptak and Kleiner, 1998).

which is relevant for example for the transport of polar/ionizable groundwater contaminants, e.g. some pesticides. Since surface sorption is the dominating reactive transport process, the field experiments described here are interfacial tracer tests, where the interface between the aquifer material and groundwater is investigated.

The multitracer experiments 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 and a variance $\sigma_{\ln(K)}^2$ of 2.34. The field experiments are described in detail in Ptak and Schmid (1996) and Kleiner (1997). Three different transport distances between tracer injection and observation wells were used in order to examine the scale dependence of the effective field-scale retardation factor. Table 2 summarizes the experimental parameters.

To test the sorption properties of the two tracers, Fluoresceine and Rhodamine WT, laboratory batch experiments were performed using aquifer material from the test site (Ptak and Strobel, 1998). 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 Fluoresceine could be observed for the concentrations encountered during the field experiments. On the other hand, Rhodamine WT is known to be sorbing onto mineral surfaces (e.g. Sabatini and Austin, 1991). In the batch experiments, Rhodamine WT sorption equilibrium concentrations c_{eq} were achieved very fast

Table 2
Experimental parameters

Experiment	TT9	TT10	TT11
Transport distance (m)	8.9	12.8	32.7
Pumping rate ($l s^{-1}$)	3.02	3.02	3.3
Fluoresceine injected (g)	10	20	102
Rhodamine WT injected (g)	8	16	102
Multilevel measurements	Yes	Yes	No
Vertical resolution (m)	0.3	0.3	–
Temporal resolution (min)	1	1	5

(after maximally about 30 min), which is typical for surface sorption, and no significant kinetic behavior was observed at the anticipated time scale of the field tracer experiments (7–14 days).

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 and Zuber, 1978):

$$M_{n,t} = \int_0^{\infty} t^n c(r,t) dt \quad (1)$$

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 center of mass is given by the first normalized moment, $\mu = M_{1,t}/M_{0,t}$. Using the first normalized moment a mean effective transport velocity can be defined, $\bar{v}_{\text{eff}} = r/\mu$. Assuming that Fluoresceine is an ideal tracer, an effective field-scale retardation factor R (–) can be defined for each set of two corresponding breakthrough curves:

$$R = \frac{\bar{v}_{\text{eff Fluoresceine}}}{\bar{v}_{\text{eff Rhodamine WT}}} = \frac{\mu_{\text{Rhodamine WT}}}{\mu_{\text{Fluoresceine}}} \quad (2)$$

The values of R are in the range between 1.27 and 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 (after Cvetkovic and Shapiro, 1990) are 1.35 for TT9 and 1.32 for TT10. For TT11 with the largest transport scale investigated, an effective retardation factor R of 2.17 is obtained.

3.5.1.1. Comparison of retardation factors measured at different scales, scale effects. The results obtained from the tracer tests show that for near-source investigations, where the solute travelled only a few correlation lengths of the subsurface structure, the scale dependence of non-reactive and reactive transport parameters has to be taken into account, even if the reactive process is at local equilibrium.

The scale dependence of e.g. macrodispersivity values is well-known and investigated (e.g. Gelhar and Axness, 1983; Dagan, 1989; Gelhar et al., 1992; Rajaram and Gelhar, 1995; Ptak and Teutsch, 1992; Ptak and Teutsch, 1994a).

The increase of field-scale retardation factors of organic compounds with time respective transport

distance was attributed to the relatively slow process of intraparticle diffusion (e.g. Roberts et al., 1986; Ball and Roberts, 1991). In the multitracer FGTTs discussed here, an increase of the effective field-scale retardation factor of the surface sorbing tracer (Rhodamine WT), also called macrokinetic sorption behavior (Miralles-Wilhelm and Gelhar, 1996), was observed, even though sorption equilibrium was achieved very fast within laboratory batch experiments, without any significant sorption kinetics at the time scale of the tracer experiments (7–14 days). Therefore a high Damkohler number, i.e. the ratio of hydrodynamic residence time and characteristic time of the sorption process, was obtained.

The observed sorption macrokinetics of the sorbing tracer Rhodamine WT can thus be explained as a consequence of physical and chemical aquifer heterogeneities. Within the tracer experiments at small-scale (8.9 and 12.8 m), in the heterogeneous aquifer most of the tracer mass was transported in highly conductive preferential pathways, since the horizontal correlation length of the hydraulic conductivity field at the test site is in the order of 10 m (Ptak and Teutsch, 1994b), which is about the transport distance of the two experiments. Therefore, the probability for connected preferential pathways between the pumping and injection wells is relatively high for the small transport distances. Within the intermediate transport distance tracer experiment (32.7 m), 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 has therefore to pass low conductivity aquifer zones, too. Such low conductivity zones are generally composed of finer grains compared to the high conductivity zones. From the batch experiments using the reactive tracer (Ptak and Strobel, 1998), it could be shown that the sorption capacity is inversely related to aquifer material grain size, and (at the test site investigated) independent of the lithological composition. Then, if surface sorption is controlling the reactive transport process, 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

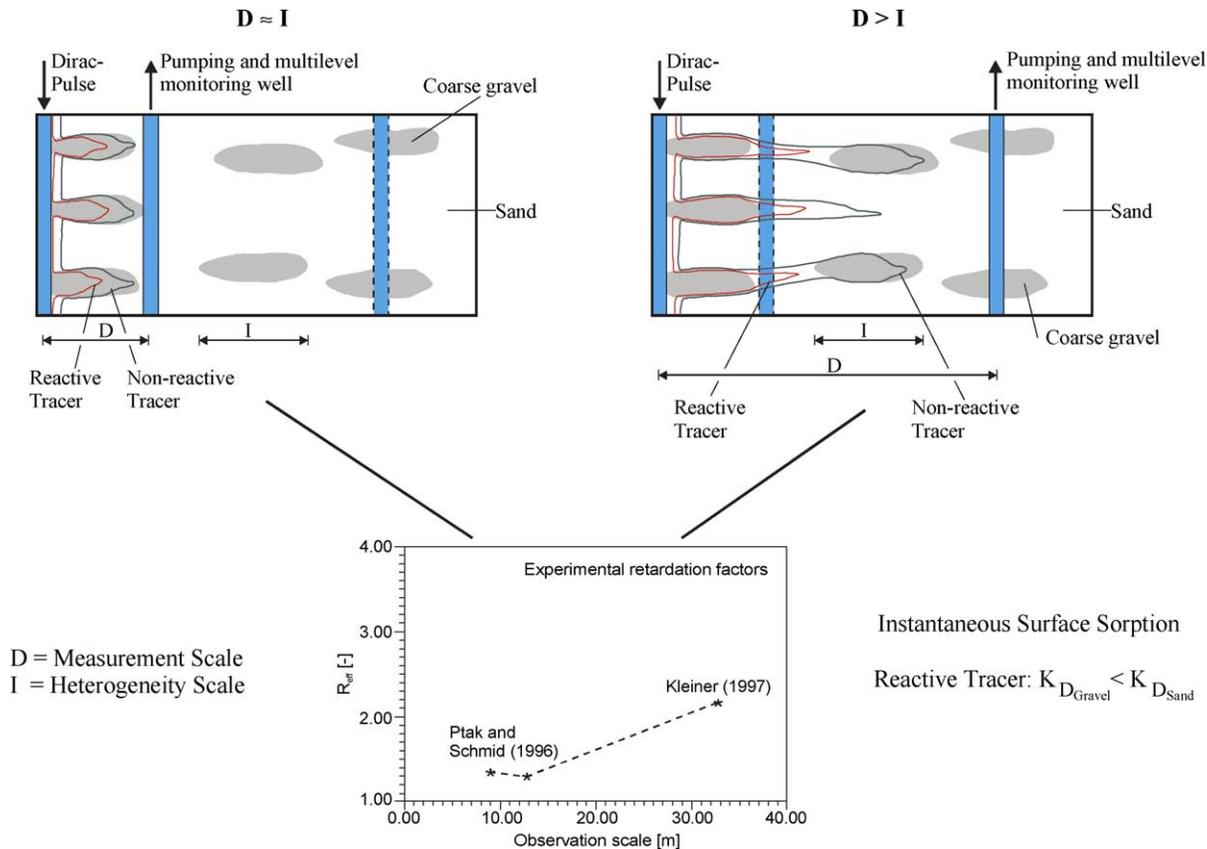


Fig. 10. Conceptual model explaining sorption macrokinetics of compounds sorbing on mineral surfaces (Ptak and Kleiner, 1998).

increases with travel distance. It could be shown, based on a comparison of characteristic time scales and on parameter studies, that during the experiments diffusion is insignificant both at grain scale as well as at the scale of low conductivity, clayey zones. Fig. 10 summarizes the conceptual model to explain the observed sorption macrokinetics.

3.5.1.2. Investigation of effective aquifer material grain diameters. From the batch experiments using Rhodamine WT, the following relationship between sorption capacity and grain size, based on a Freundlich isotherm model, could be established:

$$K_{Di} = \frac{1}{n_i} K_{Fr_i} c_{eq}^{\frac{1}{n_i} - 1} = 0.85 \times 0.132 d_i^{-1.0} c_{eq}^{0.85-1} \quad (3)$$

where K_{Di} (l/kg) is the distribution coefficient at sorption equilibrium (i.e. the derivative of the Freundlich isotherm with respect to the equilibrium

concentration), K_{Fr_i} ((l/kg)^{1/n_i}) is the Freundlich coefficient, c_{eq} (μg/l) is the equilibrium concentration, n_i^{-1} (–) is the Freundlich exponent of a grain size fraction i , and d_i is the representative diameter (mm) of i . It could 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. Using Eq. (3), the effective field-scale retardation factors R observed in the tracer experiments can be expressed as:

$$R = 1 + \frac{\rho_b}{\theta} K_{D_{eff}}$$

with:

$$K_{D_{eff}} = 0.85 \times 0.132 d_{eff}^{-1.0} c_{eq}^{0.85-1} \quad (4)$$

where ρ_b (kg/m) is the bulk density of the aquifer material and θ (–) is the porosity. Then, from Eq. (4),

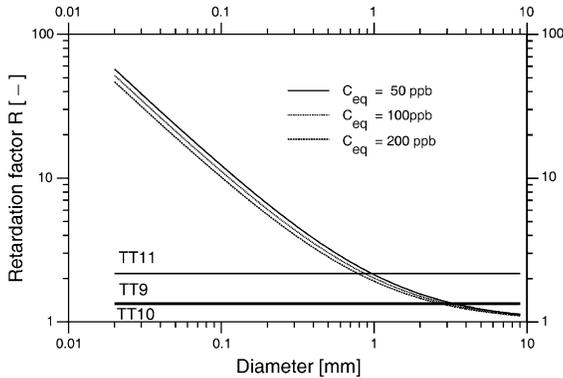


Fig. 11. Retardation factor as a function of the effective grain diameter and measured effective field-scale retardation factors (shown as horizontal straight lines) (Ptak and Kleiner, 1998).

the effective diameter d_{eff} (mm) of the aquifer material grains within the tracer transport paths can be estimated. The relationship between the measured field-scale retardation factor R and the effective grain diameter as described by Eq. (4) is graphically depicted in Fig. 11. It is seen from Fig. 11 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 effective grain diameter is indicated by the crossings of the measured retardation factors R (horizontal straight lines in Fig. 11) and the R values estimated using Eq. (4) (curves in Fig. 11). The decrease of the effective grain diameter with transport distance is in accordance with the discussion of the macrokinetic sorption behavior presented above, which states that for the longer transport distance the tracer has to pass also aquifer zones with a relatively low hydraulic conductivity, which are composed of finer grains.

This estimated 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, since due to law regulations it is in general impossible to use the contaminants directly for field experiments. Then, if

the relationship of the distribution coefficient and the grain size is known for a specific surface sorbing contaminant (for instance from laboratory measurements), the retardation factor can easily be predicted from the estimated grain diameter, and its scale dependence can be taken into account.

Of course, other tracer types can be applied in the multitracer technique as well, for example interfacial tracers to estimate the effective surface of residual NAPLs and/or partitioning tracers to estimate the residual NAPL saturation, or biodegradable tracers to investigate biological processes and/or biodegradation of contaminants.

3.5.2. Application of multitracer forced gradient transport experiments for the quantification of NAPL phases

Contaminant release from residual, non-aqueous phase liquids (NAPLs) into groundwater depends on the composition of the NAPL, the NAPL volume and the interfacial area between NAPL and groundwater. The determination of these essential source zone parameters with common sampling methods such as core sampling and well logging provides only point scale data at discrete locations, thereby suffering from the principal problem to yield values that are only averages over very small aquifer volumes. Spatially more extensive site characterization methods, such as geophysical techniques, are often difficult or even impossible to be used as means of determining the amount of NAPL present without knowing the initial geophysical properties of the site before it was contaminated.

This chapter describes controlled experiments of in situ multitracer partitioning and interfacial tracer tests (PITTs) at laboratory scale, which allow the integral determination of the NAPL (here a coal tar DNAPL) amount and distribution throughout the water saturated subsurface area that is flushed during the experiment.

Partitioning tracer tests (PTTs) as employed in these experiments were initially developed in oil reservoir engineering using both single well tests (Tomich et al., 1973; Sheely, 1978) and interwell tests (Tang, 1992). Here, a typical single well test is carried out by injecting a certain tracer slug of a dissolved primary partitioning tracer (ethyl acetate) into a formation that is at residual oil saturation. The initial

tracer slug is then followed by a slug of tracer free water. Afterwards the well is shut in. During the residence period in the formation (at elevated oil reservoir temperatures and negligible drift due to typically very small background flow velocities) a portion of the primary tracer (ethyl acetate) hydrolyzes to form the secondary non-partitioning tracer (ethyl alcohol). Finally, the well is pumped and the concentrations of both tracers are measured during the extraction phase. Residual crude oil saturation is determined by the delayed arrival of the partitioning tracer (ethyl acetate) breakthrough curve relative to the non-partitioning tracer (ethanol) breakthrough curve and their correlation to the independently obtained distribution coefficients. At potentially NAPL contaminated, typical shallow aquifers, the above described single-well set-up cannot be realized due to insufficient hydrolyzation rates which are a result of the lower formation temperatures, and due to an excessive drift of the injected tracer body which is a result of the typically higher background flow velocities. Additionally it should be mentioned that this method may suffer from the limitations (non-uniqueness of interpreted parameters) of single-well push–pull tests (Hall, 1993; Hall, 1996; Haggerty et al., 1998; Schroth et al., 2001; Novakowski et al., 1998; Kunstmann et al., 1997). The interwell PTTs conducted by Tang (1992) overcome these limitations by injecting tritiated water as non-partitioning tracer and tritiated *n*-butanol as well as ^{14}C labeled *i*-amyl alcohol as partitioning tracers in one well and extracting it at the other. The determination of residual crude oil saturation was again based on distribution coefficients and the relative separation of the two breakthrough curves. However, according to Chen and Knox (1997) the applicable residual crude oil saturation for both kinds of oil reservoir engineering tests ranged from 20 to 40%.

As mentioned above the injection of two solutes with different partitioning properties made the method much more robust but it also terminated the potential application as single well tests (at least for the classical arrival-time based evaluation concept). Two tracers with different distribution coefficients will start to separate as soon as they leave the well bore and are transported through a residual oil bearing aquifer. But if the flow direction is subsequently reversed by pumping from the same well, the separation may

disappear again as the tracers return to the well bore, i.e. the arrival times of the partitioning and of the non-partitioning tracer at the well may be identical. Therefore a reasonable way to conduct PTTs employing a single well bore (in combination with the classical arrival-time based evaluation) is using a vertical circulation well set-up, for example as presented by Chen and Knox (1997) and Brooks et al. (2002). In their most recent single well push–pull PTT study Istok et al. (2002) used a new approach given by Schroth et al. (2001) to estimate the residual saturation based on an increase in apparent dispersion observed in extraction-phase breakthrough curves. The presence of NAPL is indicated by an increase in apparent dispersion of the partitioning tracer relative to the non-partitioning tracer. However, they had to admit that additional research is needed to verify the ability of this method to quantify NAPL saturations.

The concept of interwell PTTs to detect residual crude oil saturation has been modified and applied for the detection and quantification of residual NAPL phase at contaminated field sites by several researchers (Jin et al., 1995; Wilson and Mackay, 1995; Nelson and Brusseau, 1996; Jin et al., 1997; Annable et al., 1998b; Gierke et al., 1999; Nelson et al., 1999a, b; Young et al., 1999; Brooks et al., 2002). Meanwhile PTTs are quite frequently used for the assessment of various in situ clean-up methods (e.g. surfactant and alcohol flushing) applied at field-scale (Cain et al., 2000; Young et al., 1999; Brooks et al., 2002; Meinardus et al., 2002; Rao et al., 2000; Rao et al., 1997; Sillan et al., 1998; Jawitz et al., 2000). The theoretical studies of James et al. (1997), James et al. (2000), and Zhang and Graham (2001a, b) focused on the performance optimization of PTTs under non-ideal conditions (e.g. non-uniform flow fields and hydrogeochemically heterogeneous aquifers). Wilson et al. (2000) present a mathematical model for the simulation of PTTs. In contrast to the quite often applied UTCHEM-code (Brown et al., 1994; Delshad et al., 1996) modelling under local equilibrium assumption (Jin et al., 1995; Jin et al., 1997; Young et al., 1999), which thereby omits the governing mass transfer limitations, their (Wilson et al., 2000) process based model includes the kinetically limited mass transport of the partitioning tracer from and to the NAPL, and is therefore potentially capable to fit

the highly asymmetrical breakthrough curves that were obtained in many PTT studies.

The determination of NAPL-water interfacial areas via interfacial tracer tests (ITTs) is a quite recent development (Saripalli et al., 1997; Saripalli et al., 1998; Annable et al., 1998a; Kim et al., 1999). Experiments with subsequent runs of both, PTTs and ITTs were conducted by Annable et al. (1998a) and Dai et al. (2001).

First laboratory experiments with PITTs (combining both partitioning and interfacial tracers in one run) and a complex multicomponent NAPL (tar oil) were conducted by Setarge et al. (1999).

Due to the convincing concept the PTT and ITT methodology originating in the saturated zone branched rapidly and is meanwhile also available for different applications in the vadose zone. Deeds et al. (1999, 2000) used perfluorocarbon gas tracers for the determination of NAPL saturation in an air/water/NAPL system situated in the unsaturated zone. Mariner et al. (1999) investigated a comparable system (air/water/NAPL), but used an additional tracer (difluoromethane) that was suitable for the determination of water saturation. Nelson et al. (1999a, b) conducted gas-phase partitioning tracer experiments for the measurement of soil water content in a well controlled lysimeter study (air/water). The air/water system at various degrees of saturation was also investigated employing a PTT by Vulava et al. (2002). The effective air–water interfacial area in partially saturated media was the target parameter in the studies of Kim et al. (1997) and Anwar et al. (2000). Both authors used a surfactant as interfacial tracer. While Kim et al. (1997) conducted classical column studies and recorded tracer breakthrough curves, Anwar et al. (2000) had to sacrifice and extract their columns (after the injection of the tracer) to obtain their results.

The same concept but a different tracer philosophy is the background of the PTT experiments performed by Hunkeler et al. (1997) and Semprini et al. (2000). While all aforementioned studies used artificial tracers these authors used a naturally occurring radioactive isotope, ^{222}Rn , that is found in groundwater as a dissolved gas, as partitioning tracer to detect and quantify residual NAPLs in contaminated aquifers. Due to its non-polarity ^{222}Rn has a high affinity to partition into NAPLs. The field applications

rely on observable decreases in ^{222}Rn concentrations in areas with residual NAPL present, compared to its background concentrations in the surrounding uncontaminated areas. Recently, Davis et al. (2002) presented a single well, push–pull tracer test methodology using ^{222}Rn to quantify TCE residual saturations. The computation of the NAPL saturation was based on an increased apparent dispersion of ^{222}Rn relative to the conservative tracer (Bromide) that was recorded during the extraction phase when residual NAPL was present.

3.5.2.1. Retardation factor. The PITT consists of an injection of a suite of partitioning, interfacial and conservative tracers into a well (column inlet) and the recovery of the tracer solution at an extraction well (column outlet). While the conservative tracers will stay unaffected by the presence of DNAPL, the reactive compounds (partitioning and interfacial tracers) undergo retardation due to their absorption and adsorption behavior. The result is a chromatographic separation of the tracers that can be recorded at the extraction well. The higher the affinity to the DNAPL phase the better is the separation of the individual breakthrough curves (BTCs). This effect is quantified by the retardation factor R (–) which is defined as:

$$R_{\text{reactive}} = \frac{\mu_{\text{reactive}}}{\mu_{\text{conservative}}} \quad (5)$$

where μ is the first normalized temporal moment of the respective tracers at a monitoring location. For a pulse-type experiment this is given by Eq. (6), (according to Valocchi, 1985; Jin et al., 1995):

$$\mu = \frac{\int_0^{\infty} t \frac{C(t)}{C_0} dt}{\int_0^{\infty} \frac{C(t)}{C_0} dt} - \frac{t_p}{2} \quad (6)$$

where $C(t)$ is the monitored tracer concentration (either reactive or conservative tracer) that is normalized by its input concentration C_0 , t is the experimental time and $t_p/2$ is the time correction-term for the duration of the tracer-pulse injection (t_p).

3.5.2.2. Retardation of partitioning tracers. The dimensionless equilibrium partitioning coefficient

K_{NW} (–) is defined as:

$$K_{NW} = \frac{C_N}{C_W} \quad (7)$$

where C_N (g/cm^3) is the concentration of the tracer in the DNAPL and C_W (g/cm^3) is the concentration of the tracer in the water phase. Conservative tracers have a partitioning coefficient of zero.

The general equation of partitioning tracer retardation (R_{PART}) can be written as (Nelson and Brusseau, 1996; Setarge et al., 1999):

$$R_{PART} = \frac{\mu_{PART}}{\mu_{conservative}} - 1 + \frac{K_{NW}S_n}{1 - S_n} + \frac{\rho_d K_d}{n} \quad (8)$$

where S_n , ρ_d , K_d , and n denote the DNAPL residual saturation (–), the bulk density of the aquifer material (g/cm^3), the solid–water distribution coefficient (cm^3/g) and the water filled porosity (–), respectively. If the tracers are not adsorbed by the aquifer material ($K_d = 0$) the last term equals zero, and thus the retardation factor depends solely on S_n and K_{NW} .

Because the retardation factor for each partitioning tracer is a function of both the partitioning coefficient of the tracer and the average DNAPL residual saturation of the contaminated aquifer, S_n can only be determined by measuring R_{PART} for tracers with known partitioning coefficient, K_{NW} .

If the average residual saturation is unknown, which is most likely for all field tests, a whole suite of partitioning tracers with varying partitioning coefficients should be used to ensure, that at least one breakthrough curve will have sufficient separation ($1.2 < R_{PART} < 4$; recommended by Jin et al., 1997) from the conservative tracer breakthrough curve, to calculate S_n . Additional breakthrough curves with sufficient separation increase the confidence level of the PITT results.

3.5.2.3. Retardation of interfacial tracers. As an interfacial tracer, for example a surfactant such as Sodium Laurylthethersulfate (SLES) can be used. The interfacial accumulation of SLES can be described by the Gibbs sorption isotherm (Adamson, 1982):

$$\Gamma = -\frac{1}{2RT} \left(\frac{d\gamma}{dC} \right) C \quad (9)$$

where Γ , γ , C , R , and T denote the interfacial adsorption (mmol/cm^2), the DNAPL–water interfacial

tension (dynes/cm), the concentration of surfactant (mmol/cm^3), the universal gas constant (dyne $\text{cm}/\text{mmol K}$) and the absolute temperature (K). The DNAPL–water interfacial tension (γ) can be measured as a function of concentration using the drop-weight method (Earnshaw et al., 1996).

The equilibrium interfacial adsorption coefficient, K_{IFT} (cm), can be determined by the following equation (Saripalli et al., 1998):

$$K_{IFT} = -\frac{1}{2RT} \left(\frac{d\gamma}{dC} \right) \Big|_{C_{IFT}} \quad (10)$$

K_{IFT} can be calculated for a given surfactant concentration (C_{IFT}) and varies with the slope of the γ versus C plot, which was obtained by the drop weight method (Fig. 13). When pulse input tracer tests are applied, a constant K_{IFT} value can be estimated in a first approximation by using the maximum interfacial tracer concentration of each breakthrough curve (Annable et al., 1998a).

The general equation of interfacial tracer retardation (R_{IFT}) can be written as (Saripalli et al., 1998):

$$R_{IFT} = \frac{\mu_{IFT}}{\mu_{conservative}} = 1 + \frac{A_{NW}K_{IFT}}{\theta} + \frac{\rho_d K_d}{\theta} \quad (11)$$

where A_{NW} , ρ_d , K_d , and θ denote the DNAPL–water interfacial area (cm^2/cm^3), the bulk density of the aquifer material (g/cm^3), the solid–water distribution coefficient (cm^3/g) and the volumetric water content (–), respectively. If the interfacial tracer adsorption by the aquifer material is negligibly small ($K_d \approx 0$), the last term equals zero and thus the retardation factor depends only on A_{NW} and K_{IFT} .

By measuring the retardation factor of the interfacial tracer, the DNAPL–water interfacial area can be estimated if the adsorption isotherm for the interfacial accumulation is known.

3.5.2.4. Materials and methods. In our laboratory column and tank PITT experiments, the alcohols 4-Methyl-2-Pentanol (4M2P), 1-Hexanol (1HEX) and 2,4-Dimethyl-3-Pentanol (2,4DM3P) were used as partitioning tracers. They are easily detected by GC-FID analysis, even in the presence of high contaminant concentrations in the water. The anionic surfactant Sodium Laurylthethersulfate (SLES, see also above) was used as interfacial tracer and was analyzed by IC conductivity measurements. Isopropanol (IPA)

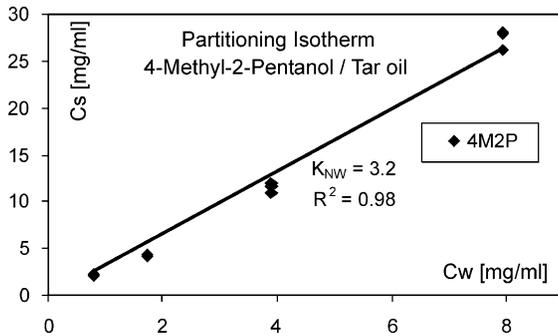


Fig. 12. Partitioning of 4-Methyl-2-Pentanol in aqueous and DNAPL phases.

and Sodium Chloride (NaCl) were used as conservative tracers. NaCl was quantified by conductivity measurements.

As DNAPL, an industrial coal tar (Rütgers, Germany) with a density of 1.2 g/cm^3 was employed

in all types of experiments. Well-graded sand from the River Rhine quaternary alluvium (1–2 mm diameter) was used to fill the laboratory tank and columns.

The specific objectives of the experiments were: (1) evaluation of the suitability of the combined PITT for complex multicomponent DNAPLs (here coal tar), (2) improvement and evaluation of the PITT-based determination of coal tar saturation in dependence of different flow velocities, and (3) improvement and evaluation of the PITT-based determination of the specific DNAPL/water interfacial areas of three different DNAPL distributions.

3.5.2.5. Batch experiments and drop-weight method.

Batch experiments were performed to determine the equilibrium partitioning coefficients of the alcohols and the tar oil which were used in the laboratory studies. The results are shown in Fig. 12 and Table 3.

Table 3
Summary of results from the batch, column and large-scale tank experiments

Experiment ↓ / Tracer →	NaCl	IPA	4M2P	1HEX	2,4DM3P	SLES
<i>Batch Experiments</i>						
K_{NW} (–)	0	0.8	3.2	9.6	16	–
K_{IFT} (cm)	–	–	–	–	–	$9.73 \times 10^{-5} - 9.24 \times 10^{-4}$
<i>Column Experiments</i>						
<i>Column # 8b, S_n: 20%, DNAPL blobs, v_a: 6.1 m/d</i>						
R_d (–) expected	1	1.2	1.8	3.4	5.0	n.d.
R_d (–) measured	1.11	1.00	1.30	1.79	1.94	1.09
S_n (%) calculated	0	0	8.6	7.6	5.5	–
A_{NW} (cm^2/cm^3) calc.	–	–	–	–	–	86
<i>Column # 8c, S_n: 20%, DNAPL blobs, v_a: 3.5 m/d</i>						
R_d (–) expected	1	1.2	1.8	3.4	5.0	n.d.
R_d (–) measured	1.16	1.00	1.45	2.03	2.59	1.09
S_n (%) calculated	0	0	12.3	9.7	9.0	–
A_{NW} (cm^2/cm^3) calc.	–	–	–	–	–	76
<i>Column # 9b, S_n: 20%, DNAPL coatings, v_a: 1.9 m/d</i>						
R_d (–) expected	1	1.2	1.8	3.4	5.0	n.d.
R_d (–) measured	1.08	1.00	1.52	2.69	3.85	2.69
S_n (%) calculated	0	0	14.2	15.0	14.9	–
A_{NW} (cm^2/cm^3) calc.	–	–	–	–	–	884
<i>Large-scale tank Experiments</i>						
<i>Well # C, S_n: 5%, DNAPL blobs, v_a: 5 m/d</i>						
R_d (–) expected	1	1.04	1.16	–	1.84	n.d.
R_d (–) measured	1	1.006	1.014	–	1.028	1.04
S_n (%) calculated	0	0.7	0.4	–	0.17	–
A_{NW} (cm^2/cm^3) calc.	–	–	–	–	–	24

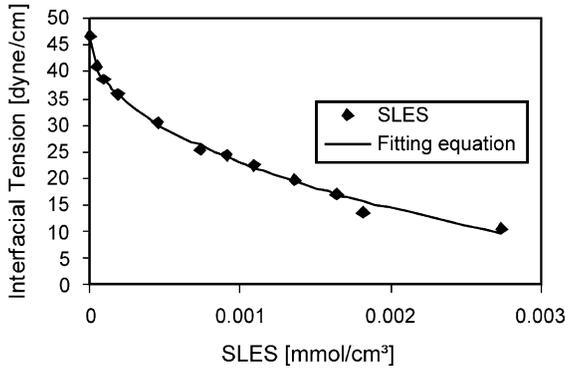


Fig. 13. Measurement of interfacial tension of Sodium Laurylesulfate (SLES) using the drop-weight method.

Fig. 13 shows the results from the drop-weight method, which was applied to measure the DNAPL-water interfacial tension versus interfacial tracer concentration for the Sodium Laurylesulfate (SLES) tracer. The obtained interfacial tension data were fitted by the following procedure (Annable et al., 1998a):

$$\gamma = \left[1 - \left(\frac{C}{\text{CMC}_{\text{FIT}}} \right)^\beta \right] (\gamma_{\text{max}} - \gamma_{\text{min}}) + \gamma_{\text{min}} \quad (12)$$

where CMC_{FIT} (mmol/cm^3) and β (–) are the fitting factors. γ_{min} and γ_{max} (dynes/cm) are the minimum and maximum interfacial tensions measured. This function was differentiated to estimate the local slope at the desired C_{IFT} concentration. The introduction of this derivative into Eq. (10) gives the respective interfacial adsorption coefficient:

$$K_{\text{IFT}} = \frac{\beta(\gamma_{\text{max}} - \gamma_{\text{min}})}{2RT(\text{CMC}_{\text{FIT}})^\beta} C^{\beta-1} \quad (13)$$

With $\gamma_{\text{min}} = 10.74$ dynes/cm, $\gamma_{\text{max}} = 46.74$ dynes/cm, $\text{CMC}_{\text{FIT}} = 0.0045$ mmol/cm^3 and $\beta = 0.45$ the corresponding K_{IFT} values for the varying C_{IFT} values were in the range of 4.7×10^{-4} – 7.6×10^{-4} cm (Fig. 13, Tab. 3).

3.5.2.6. Column experiments. All PITTs were conducted as pulse type experiments in glass columns (6 cm diameter, 15 cm length) filled with sand (River Rhine quaternary alluvium, 1–2 mm diameter) containing a tar oil residual saturation (S_n) of exactly 20%. The flow-velocity was varied between 1.9 and 6.1 m/d to evaluate the influence of non-equilibrium

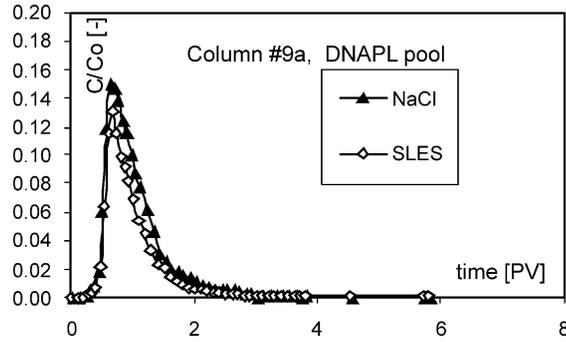


Fig. 14. Breakthrough curve of SLES passed through a DNAPL pool zone.

transport (Tab. 3). A further series of columns contained DNAPL as grain-coatings, as blobs, and as pools/ganglia at the same residual DNAPL saturation ($S_n = 20\%$), in order to study the influence of the different types of DNAPL distribution on the measured breakthrough curves. The varying DNAPL–water interfacial area of these experimental set-ups was used to get a first validation of interfacial tracer data (Figs. 14 and 15 and Table 3).

In column #9a containing the DNAPL pool zone the breakthrough curve of the interfacial tracer SLES is not retarded with respect to the conservative tracer NaCl (Fig. 14), while in column #9b containing the DNAPL coatings the SLES breakthrough curve is strongly retarded comparing to the conservative tracer NaCl (Fig. 15). This behavior was anticipated as the DNAPL–water interfacial area of the DNAPL pool is more or less negligible in comparison to the interfacial area of the DNAPL coatings. Furthermore, these results show that the employment of

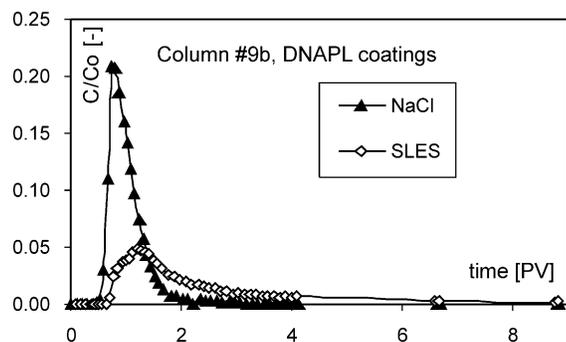


Fig. 15. Breakthrough curve of SLES passed through DNAPL coatings.

the interfacial tracer technique enables to distinguish between the two most extreme contaminant distribution scenarios which (even when the same amount of NAPL is present) will result in completely different time scales when it comes to DNAPL dissolution/site remediation.

3.5.2.7. Large-scale tank experiment. Additional pulse type PITTs were conducted in a large-scale tank (8 m × 3 m × 1 m), filled with sand (1–2 mm), by continuous injection/pumping to create a forced gradient flow field. The withdrawal rate was 1.6 times the injection rate. The injection and extraction wells were only partially penetrating, separated by 0.6 m and aligned in the direction of the flow field (5 m/d). The wells were located just at the edge of a tar oil blob zone (0.5 m × 1 m × 1 m, S_n : 5%). Results are summarized in Table 3.

The results of the PITTs were in general agreement with the current understanding of partitioning and interfacial tracer behavior. Suitability of the PITT was proven for the complex multicomponent mixtures (coal tar/tar oil) which can be found at former gasworks sites.

The combination of interfacial and partitioning tracers during the PITT studies not only determined the DNAPL saturation, it also clearly distinguished between major different DNAPL distribution geometries (tar oil coatings vs. blob zone), which are important parameters concerning (1) the prediction of the long-time behavior of the source zone and (2) the feasibility of in situ remediation techniques. However, the PITT-determined tar oil residual saturation of each experiment conducted during this study was smaller than the actual DNAPL volume. This is believed to be a coupled effect of non-equilibrium tracer transport (resulting in strongly asymmetric breakthrough curves) and the interpretation of pulse-type tests using the method of temporal moments. Despite the theoretical independence of the first moment of mass transfer limitations, spreading and asymmetry (the second and third moments) will increase with increasing mass transfer limitations (Valocchi, 1985; Brooks et al., 2002; Imhoff et al., 2003). Both is likely to increase truncation errors which consequently result in underestimation of the DNAPL saturation. It should be noted, that all column experiments conducted in this study showed clear mass transfer

limitations (highly asymmetric breakthrough curves) of partitioning tracers into the quite viscous coal tar, and, due to the unavoidable truncation of the breakthrough curve tailings by the detection limit of the individual tracer substances, a reduced tracer retardation was recorded. Consequently, a smaller DNAPL saturation compared to the actual one was calculated.

The observed slow mass transfer kinetics may cause limitations of the applicability of PITTs at coal tar contaminated field sites. Therefore, overall residual coal tar saturation should exceed 5% to obtain significant retardation of the tracers used in this study. The approximate location and extension of the zone of residual DNAPL saturation should be known in advance, and the flow velocity should be smaller than 5 m/d to approach conditions closer to equilibrium. Also, improved evaluation approaches, based for example on fitting of solutions from process-based formulations of the partitioning tracer transport (e.g. based on the model of Wilson et al., 2000), should be developed to account for the truncation of the breakthrough curves.

3.5.3. Application of multitracer forced gradient transport experiments for the investigation of microbial activities

Istok et al. (1997) proposed a single well push–pull method for the in situ determination of microbial respiration rates in groundwater. They injected test solutions containing a tracer (Bromide) and one or more reactive solutes (O_2 , NO_3^- , SO_4^{2-}), selected to investigate specific microbial activities. During the following residence time in the aquifer (which has to be varied depending on the kinetics of the microbial process) a portion of the injected reactant was consumed. The breakthrough curves and the mass recovery recorded during the subsequent extraction phase were used to calculate the quantities of consumed reactants and newly formed products, and finally to obtain the microbial respiration rates.

Based on the above approach, Schroth et al. (1998) successfully quantified the horizontal and spatial variability of aerobic respiration and denitrification rates in a petroleum hydrocarbon contaminated aquifer.

Haggerty et al. (1998) developed a simplified method of push–pull test data analysis providing first-order reaction rate coefficients from measured non-reactive and reactive breakthrough curves. They also presented an example of field-scale

application to estimate reaction rate coefficients for microbiological denitrification in a petroleum-contaminated aquifer.

However, following Istok et al. (1997), it has to be taken into account that also non-biological processes may contribute to the consumption of the reactive solutes, and, as electron acceptors are added during the tests, the actual reaction rates may be smaller compared to the estimated ones. Therefore a good understanding of the investigated hydrogeochemical/microbiological system is a prerequisite for the interpretation of the experimental data.

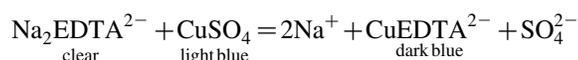
3.5.4. Application of multitracer forced gradient transport experiments for the investigation of longitudinal and transverse mixing

Natural attenuation (mainly biodegradation) of organic pollutants in groundwater is usually controlled and limited by transverse mixing of electron donors and acceptors at the contaminant plume fringe (Grathwohl et al., 2001; Thornton et al., 2001). The quantification of parameters characterizing subsurface mixing processes (i.e. dispersivities both in longitudinal and especially in the transverse directions) is a prerequisite for the prediction of natural attenuation. Therefore a number of forced gradient bench scale tank experiments with tracers/surrogate reactants were performed by different researchers in order to investigate fringe mixing processes. Obtaining the required high-resolution data at field-scale is very difficult due to the resulting monitoring efforts. Therefore well-controlled laboratory experiments are most suitable for the investigation of fundamental processes at plume fringes and for the validation of numerical models dealing with natural attenuation.

As the transverse mixing zone at the plume fringe is usually very thin (on the order of cm, i.e. the concentration gradients are very steep) it can easily be disturbed by conventional sampling methods. Therefore measurements based on non-invasive imaging techniques are especially advantageous. Some examples of such (two-dimensional) visualization experiments reported in literature are given in the following. As this is a quite new field of application of reactive tracers, the focus is on suitable tracer substances and reactions.

Gramlin et al. (2002) experimentally quantified the longitudinal mixing process of a transient plume front

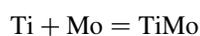
in a 30 cm long translucent 2D tank filled with a transparent aquifer matrix (cryolite) by imaging an instantaneous colorimetric Cu/EDTA complexation reaction:



Huang et al. (2003) used a novel combination of non-invasive imaging with an oxygen sensitive fluorescent indicator to investigate the biodegradation processes occurring at the fringe of a solute plume (acetate) within a 15.6 cm long, 3 mm thin transparent 2D tank filled with quartz sand and spiked with suitable bacteria. The fluorescence of the used fluorescent indicator (Ru(phen)₃Cl₂) is quenched in the presence of oxygen. The consumption of oxygen by the biodegradation of the contaminant (acetate) was monitored by exciting the fluorescence indicator with UV light and recording the emission with a CCD camera.

Theodoropoulou et al. (2003) performed visualization experiments in transparent glass-etched strictly 2D pore networks (14.5 cm length) to estimate the longitudinal and transversal dispersion coefficients as functions of the Peclet number. They monitored the pH-indicator based color changes during the mixing of two different HCl solutions. pH changes are induced by dispersive mixing of the more concentrated acid solution (0.43 M) with the more dilute one (0.03 M). At these concentrations the HCl solutions are completely dissociated (as H₃O⁺ and Cl⁻), and pH depends only on dilution by dispersion.

Oates (2003) used a complexation reaction between molybdate and a chelating agent with the commercial name Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid), which is colourless in aqueous solution, to investigate plume fringe mixing. At a certain pH range (6 < pH < 7) molybdate (Mo) exists as mono-anions, MoO₄²⁻, which are colourless in solution. Tiron (Ti) will chelate up to two molybdate anions in two consecutive steps:



In the experiments, Tiron (0.05 M) and molybdate (0.025 M) were mixed and buffered at pH 6.1 using succinate (0.13 M). pH was adjusted with NaOH to

a final pH of 6.1. The mixing of the two clear solutions produces a wine-red solution, which progressively appears orange and then yellow as the solution gets diluted by dispersion. The reaction products can be optically quantified using absorbance spectrometry.

This tracer technology is presently being tested, improved and implemented for different plume and subsurface scenarios. The resulting mixing parameters will be used for numerical reactive transport modelling, and the predicted plume development will be compared with field observations.

4. Example of tracer test data application in the context of stochastic simulations: modelling of non-reactive and reactive tracer transport in heterogeneous aquifers based on a geostatistical facies approach

An appropriate modelling approach, suitable for the simulation of solute transport within heterogeneous aquifers, has to render the observed scale dependence of (non-reactive and reactive) transport parameters, for instance macrodispersivities or field-scale retardation factors. It should be able to upscale measurements (for example effective parameters from tests at small-scale (order of cm to m) to a larger intermediate scale (order of 100 m)), and it should not require a priori equations for the scale dependence of the effective retardation factor, or of other parameters describing reactive transport. The reason is that the formulation of such equations is generally difficult in practice, requiring costly measurements, and the equation parameters are mostly only valid for the specific site and the transport scales investigated. The modelling approach should also account for concentration dependent distribution coefficients, i.e. non-linear sorption isotherms, or kinetic reactive processes, such as e.g. intraparticle diffusion and sorption within intraparticle pores.

Simulation results should also be possible for the near-source, non-ergodic stage of solute plume development, where single realizations of the transport process are likely to deviate from the ensemble mean behavior (which can for example be described using closed form solutions from stochastic theory). Near-source transport problems, where the solutes travelled only a few correlation lengths of

the subsurface structure, are especially relevant for the planning of aquifer remediation activities. The modelling approach should finally account for the remaining parameter uncertainty due to the fact, that a deterministic description of the aquifer parameter distribution is practically impossible in the case of heterogeneous aquifers.

In a three-dimensional numerical Monte Carlo type stochastic flow and transport modelling framework, the above restrictions do not apply. Complex boundary conditions and flow fields can be considered, and principally any type of reactive processes can be introduced, independent of the complexity of mathematical process descriptions. Due to its flexibility and advantages, a Monte Carlo type numerical-stochastic modelling approach, summarized in the following, was developed for modelling of flow and (non-reactive and reactive) transport in heterogeneous porous aquifers.

4.1. Separation of aquifer material into lithological components and grain size fractions for laboratory experiments to estimate hydrogeochemical aquifer parameters

In stochastic reactive transport modelling studies, chemical aquifer properties are often treated as constants, or introduced using (theoretical) relationships describing a correlation of hydraulic conductivity and chemical parameters (e.g. Cvetkovic and Shapiro, 1990; Bellin et al., 1993; Tompson, 1993; Burr et al., 1994; Bellin and Rinaldo, 1995; Bosma et al., 1996; Miralles-Wilhelm and Gelhar, 1996; Tompson et al., 1996). However, it is generally very difficult to establish such correlation relationships from measurements. Another serious drawback of using simple correlation relationships is that the chemical parameter field is forced to have the same structural properties like the hydraulic conductivity field. This outcome may be not justified, since it is well known that aquifer sediments are in general a heterogeneous mixture of different lithocomponents and different grain size fractions (e.g. Grathwohl and Kleineidam, 1995), and that both the lithological composition and the grain size may affect the interaction of reactive solutes with the aquifer material and therefore control reactive transport behavior.

An approach to correctly describe the interaction of reactive solutes with the aquifer material, may be based on decomposing of aquifer material into lithological components and grain size fractions and performing laboratory batch experiments. Using this approach, hydrogeochemical aquifer parameters are characterized as functions of grain size and lithological properties.

The batch experiments allow the investigation of sorption kinetics, measurement of sorption isotherms and derivation of point scale hydrogeochemical and transport parameters (for example apparent diffusion coefficients, retardation factors). Relationships of hydrogeochemical parameters and characteristic properties of the aquifer material can be established and introduced into (stochastic) flow and transport models (Ptak, 1997a).

The separation approach was applied for organic contaminants (Grathwohl and Kleineidam, 1995; Karapanagioti et al., 1999; Kleineidam et al., 1999; Rügner et al., 1999; Ptak and Liedl, 2002), where the dominant reactive process is intraparticle diffusion, as well as for fluorescent tracers (Ptak and Strobel, 1998), being sorbed on mineral surfaces. As an example, Fig. 16 shows the sorption isotherms

(Freundlich type) for the fluorescent tracer Rhodamine WT.

If the sorption parameters are known for each lithocomponent, and if the typical lithological composition is known for each grain size class, it is possible to describe the sorption behavior of solutes in the bulk sample (Grathwohl and Kleineidam, 1995). Using aquifer material from the Neckar River valley in Stuttgart, Germany, it could be shown, that the lithological composition of a grain size class is independent of the sedimentological facies (sand, gravel, etc.) where the sample was taken from. This strongly simplifies the characterization of hydrogeochemical aquifer properties. If the relation of grain size and lithological composition has been established for a specific type of aquifer, then the hydrogeochemical properties and their spatial distribution can be estimated from the relatively easily to be obtained grain size distribution curves (Ptak, 1997a; Herfort et al., 1998).

4.2. Numerical-stochastic simulations based on categorical (facies) variables

The Monte Carlo type transport modelling technique comprises three main steps. First, a geostatis-

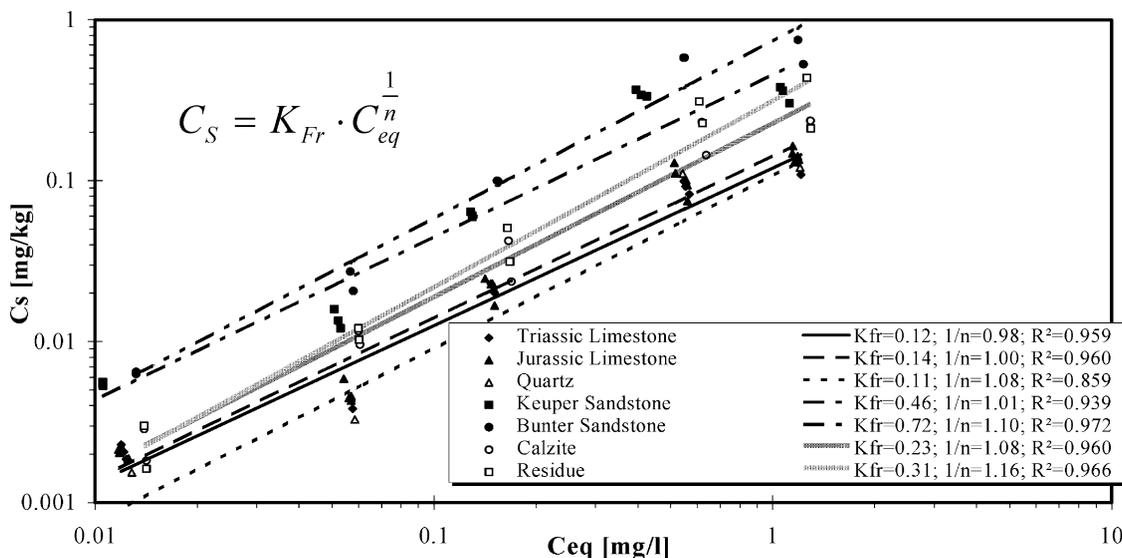


Fig. 16. Example of sorption isotherms of Rhodamine WT for different lithocomponents obtained from a 2–4 mm grain size fraction (Ptak and Strobel, 1998).

tical analysis of grain size distribution curves obtained from aquifer material core samples is performed. Second, equiprobable three-dimensional realizations of the spatial distribution of grain size distribution curves are generated using an indicator-based geostatistical simulation approach. From the simulated grain size distribution curves, obtained at each nodal position of the simulation domain, local hydraulic conductivity values and chemical aquifer parameters are estimated. Third, flow and transport simulations are performed within each generated aquifer realization, with initial and boundary conditions and geometry according to the field situation. This yields again an ensemble of realizations of both non-reactive and reactive transport process outcomes, which can be compared for instance with field measurements. The three steps are described more detailed in the following and summarized in Fig. 17 for the example of instantaneous surface sorption.

4.2.1. Geostatistical analysis of grain size distribution curves

In a heterogeneous aquifer, usually different sedimentary texture classes with different degrees of spatial continuity like for instance gravel, sand, clay etc. can be identified. Instead of analyzing hydraulic conductivities, data on the sedimentary texture can be used directly for an indicator-based structural analysis of the aquifer as well. Since sedimentary structural elements respective sedimentological facies are considered directly, it is believed that this approach is more related to geology compared to an analysis based on derived physical properties of the aquifer material.

To classify sedimentary texture, categorical variables may be defined based on measured grain size distribution curves. These categorical variables describe qualitative attributes of the individual aquifer material samples, respective the type of sedimentological facies, i.e. they indicate if a sample contains gravel, or sand etc. In the analysis, out of the ensemble of N measured grain size distribution curves (observations), curves with similar properties are clustered into M groups (M clusters) with the multivariate statistical method of K-means clustering (McQueen, 1967). Each grain size distribution curve is discretized into P classes, represented by class variables, which

describe the mass fractional contributions of individual grain size fractions to the total sample mass (Fig. 17).

After clustering, binary categorical variables ($\text{cluster}_1 - \text{cluster}_M$) are defined for each observation. Since categorical variables are exclusive, one of these M variables is assigned the value 1 and the remaining are assigned the value 0, thus yielding M binary data sets, one for each cluster. Then, the statistics (mean and variance) of the P class variables are computed for each of the M clusters.

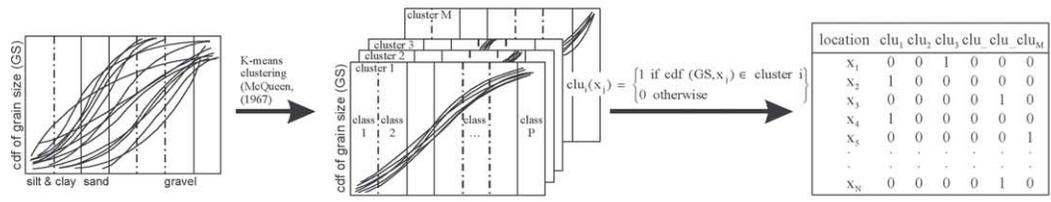
Subsequently, the spatial correlation of the M categorical variables is investigated by computing experimental indicator variograms and fitting variogram models in vertical and horizontal directions (Fig. 17).

4.2.2. Generation of three-dimensional hydraulic conductivity and chemical parameter fields

In the next step, the experimental histogram of the clusters ($\text{cluster}_1 - \text{cluster}_M$) and the cluster variogram models are used to generate Q equiprobable three-dimensional realizations of the categorical variable (facies) field. The conditional sequential indicator simulation method (SIS) for categorical variables (Deutsch and Journel, 1992) is applied. Compared to Gaussian approaches, the advantage of indicator-based approaches is that they offer the possibility to consider more than one covariance structure and therefore to better represent structural properties of extreme values within the pdf. It is no more required to assume, in contrary to sedimentological expert knowledge, that aquifer portions with different hydraulic properties, i.e. high conductivity gravel zones forming preferential flow paths and low conductivity silt/clay zones forming flow barriers, have the same spatial structure. With the indicator approach, analysis and simulation is no more restricted to a log-normal type of pdf.

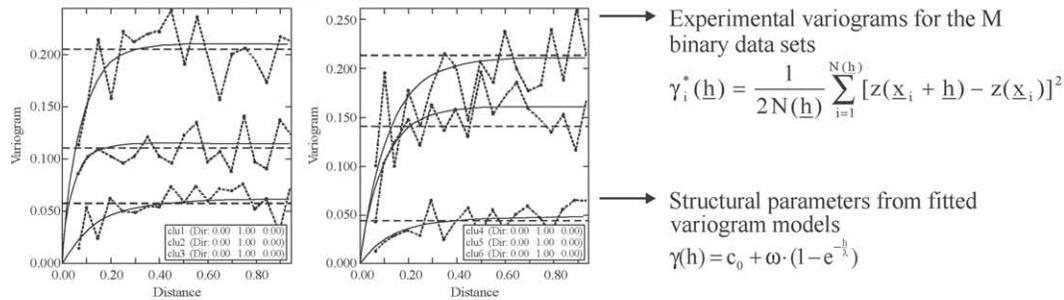
Each cluster from the simulated categorical variable field represents a mean grain size distribution curve (Fig. 17), consisting of the means of the P class variables. The means of these class variables are then perturbed with a normally distributed random component following the individual class variable statistics estimated from the measurements. The resulting simulated grain size distribution curves are then evaluated in terms of local hydraulic

Geostatistical Analysis of Grain Size Distribution Curves



- K-means clustering of N grain size distribution curves (McQueen, 1967) → M categorical (cluster) variables, each consisting of P grain size classes
- M binary data sets

- Global pdf of categorical variables
- Variography of categorical variables



Generation of 3D K and K_D Fields, Monte-Carlo-Simulation of Field Scale Transport

- Conditional sequential indicator simulation of M categorical variables, Q realizations → Q categorical variable (cluster) fields
- Assignment of mean grain size distribution curves to each categorical variable (cluster) and perturbation of the grain size class means → Grain size distribution curve at each node of the model grid
- Computation of K values at each node (Beyer, 1964)
 $K = c(u) \cdot d_{10}^2$ $c(u) = d_{60}/d_{10}$
- Computation of K_D values at each node
 $K_{Di} = \frac{1}{n_i} \cdot K_{Fni} \cdot c_{sqi}^{i-1}$ $K_D = \sum_{i=1}^P X_i \cdot K_{Di}$
- Flow and transport modelling (MODFLOW, modified MT3D), Q realizations → Local retardation factor, updated after each transport step
 $R = 1 + \frac{\rho_b}{\theta} \cdot K_D$

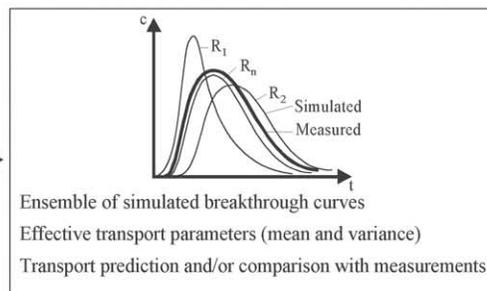
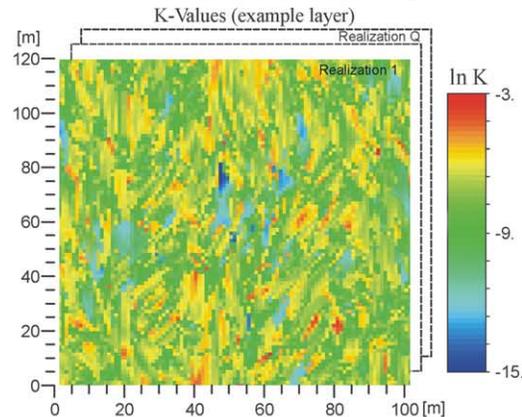


Fig. 17. Principle of numerical–stochastic reactive transport modelling based on categorical variables and lithological decomposition of aquifer material (reactive transport process shown here is instantaneous surface sorption).

conductivity values K and local chemical parameters.

In case of the example shown in Fig. 17, which deals with the stochastic simulation of the Fluoresceine and Rhodamine WT multitracer forced gradient transport experiment in a radially converging flow field and a transport distance of 8.9 m (see above), hydraulic conductivity K was obtained using Beyer's (1964) empirical relationship between hydraulic conductivity and grain size distribution.

The reactive process investigated was instantaneous surface sorption of a reactive tracer (Rhodamine WT) onto mineral surfaces (see also sections above). Using the approach of decomposing the aquifer material into different grain size fractions and lithocomponents, it could be shown for Rhodamine WT and the aquifer material investigated, that it was not necessary to regard the lithological composition as an aquifer property controlling the sorption process (see also above). A relationship describing the distribution coefficient K_{Di} of a grain size class i could be established based on a Freundlich isotherm model (Fig. 17). The local effective K_D value at each node of the model domain was then obtained using a weighting function for the individual contributions K_{Di} shown in Fig. 17 (x_i is the mass fractional contribution of each grain size fraction i to the total sample mass). To illustrate the simulation results, Fig. 17 also shows a section from a layer of the generated hydraulic conductivity field, where the heterogeneity and the structural anisotropy obtained from the SIS simulation can be recognized.

4.2.3. Flow and transport simulations

In this step of the Monte Carlo approach, flow and transport is computed for each aquifer realization, i.e. for each three-dimensional hydraulic conductivity/chemical parameter field, in order to obtain a stochastic ensemble of results for transport predictions and/or comparison with transport measurements.

In the multitracer forced gradient transport experiment discussed here, the two tracers, Fluoresceine (non-reactive) and Rhodamine WT (reactive), were injected simultaneously into the same monitoring well. According to the conditions within the field test, a steady state flow field was computed for each

stochastic aquifer realization first, using the program code MODFLOW (McDonald and Harbaugh, 1984). Subsequently, for each aquifer realization breakthrough curves were simulated at the pumping well for Fluoresceine without sorption and for Rhodamine WT with sorption, using an extended version of the program MT3D (Zheng, 1991). Simulation routines were added to the MT3D code to consider the grain size based description of the sorption process, which is finally introduced by a retardation factor R (Fig. 17; ρ_b is the bulk density and θ is the porosity). The retardation factor is updated after each transport step due to its concentration dependence. A variable effective porosity, following a correlation function of porosity (estimated from permeameter measurements) with hydraulic conductivity, was used for the transport calculations.

It should be mentioned here, that principally any reactive transport process such as intraparticle diffusion and sorption within intraparticle pore space (Ptak and Liedl, 2002), or (bio-)degradation etc. can be simulated using this new approach, depending on the transport model code used. And of course lithological properties can be introduced as well, if for instance the relation of grain size class and lithological composition has been established for a specific type of aquifer (Herfort et al., 1998).

To give an example of results from the forward simulation based on measured input parameters, Fig. 18 shows for both tracers Fluoresceine and Rhodamine WT the comparison of measured and simulated vertical profiles of peak concentration values at the pumping well.

A problem arises in the comparison of numerical stochastic transport simulation results with field tracer test measurements due the fact, that a single realization outcome, i.e. the measurements, have to be compared with a stochastically simulated ensemble. It has to be considered that within a highly heterogeneous aquifer at the small to intermediate, near-source transport scale investigated here, an ergodic stage of solute plume development cannot be expected. Therefore single realizations of the transport process are likely to deviate from the ensemble mean behavior. Another difficulty to be managed is that due to the usually limited number of concentration measurement locations, in highly heterogeneous aquifers a computation of concentration

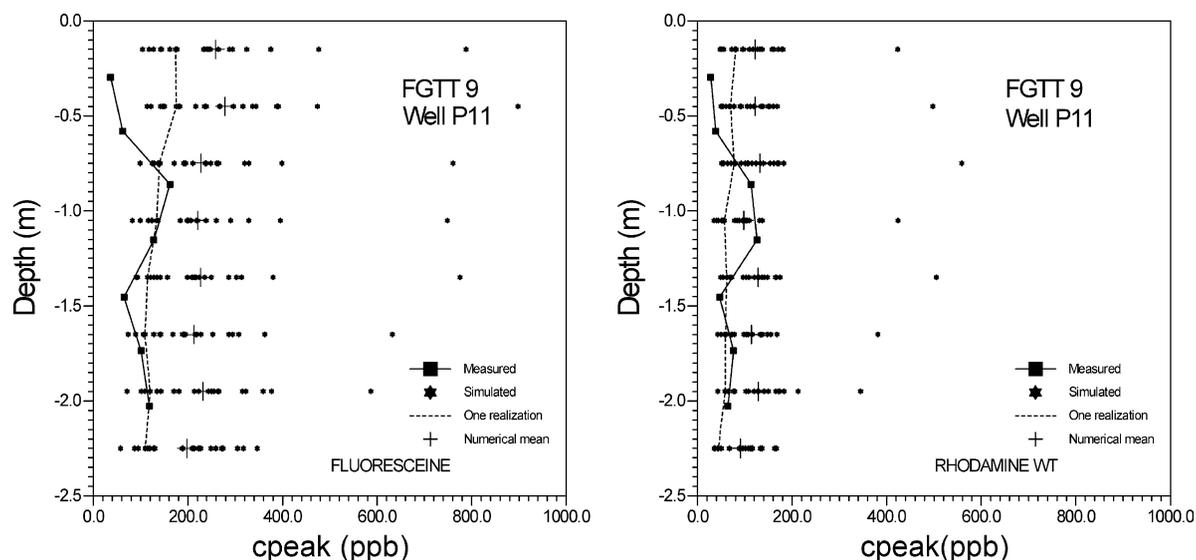


Fig. 18. Example of comparison of measured and simulated breakthrough curve peak concentrations (Ptak, 1997a).

isolines or spatial moments cannot be performed reliably enough. Therefore, the comparison of simulated and measured tracer transport was performed using breakthrough curves. This model testing approach is based on effective transport parameters obtained from breakthrough curves either directly (peak concentration, peak concentration arrival time etc.), or from the calculation of temporal moments, or from fitting analytical solutions to the breakthrough curves (mean transport velocity, longitudinal dispersivity, etc.). Each measured and numerically simulated breakthrough curve is evaluated individually. Then, effective transport parameters derived from one measured breakthrough curve are compared with a stochastic ensemble of breakthrough curve parameters, which were numerically simulated at locations within the model domain corresponding to the measurement positions within the field tracer test. The variance of a parameter within the simulated ensemble is a measure of model input uncertainty. Aquifer heterogeneity is evident from a spatial variability of the transport parameters.

A numerical stochastic model outcome in a non-ergodic transport situation can be regarded as satisfying and reliable, if the measured parameter values are within the stochastically simulated ensemble, and if the outcome is unbiased, i.e. if there is no

systematic deviation of simulated and measured parameter values. Deviation measures can be defined to test this condition (e.g. Ptak, 1997b). With respect to prediction capability, one would like the most frequently simulated parameter value (which is the ensemble mean in case of a symmetric distribution) to come close to the actually measured value. However, as explained before a stochastic simulation under non-ergodic conditions cannot be rejected as wrong if this condition is not fulfilled.

In Fig. 18 the measured peak concentration values are mostly close to the arithmetic ensemble means and mostly within the range of the numerically simulated concentration values. A deviation of measured transport parameters from their corresponding stochastic arithmetic ensemble means can be expected, because the measurements were performed in a near source, non-ergodic stage of tracer plume development. The measured concentrations tend to be smaller compared to the simulated ensemble means. The deviations are larger for Fluoresceine. This might be caused by biodegradation of Fluoresceine, which was already observed in former tracer experiments (e.g. Käss, 1998). The prediction uncertainty is smaller for Rhodamine WT compared to Fluoresceine. A possible reason for this is the enhanced spread of the Rhodamine WT plume due to sorption, which is recognized from

the normalized second central temporal moments of the Rhodamine WT breakthrough curves, being about a factor 12 higher compared to Fluoresceine. Due to the enhanced spread of the Rhodamine WT plume, its irregularities, caused by aquifer heterogeneity, are already more averaged out compared with the Fluoresceine plume. Similar results can be obtained also for another effective transport parameters.

Following the simulation results, it is believed that the flexible numerical stochastic transport simulation technique based on facies characterization and categorical variables can be successfully applied in highly heterogeneous porous aquifers. The geostatistical approach using sequential indicator simulation of categorical variables allows the generation of spatially variable hydraulic conductivity and chemical parameter fields, without the need for a priori correlation functions of hydraulic conductivity and chemical parameters, or for assumptions about the spatial structure of chemical parameters. The stochastic simulation technique presented therefore offers a broad field of applications.

5. Conclusions

The described tracer test methods offer a lot of application possibilities. The recorded multilevel–multitracer breakthrough curves can for example serve to estimate aquifer transport parameters, to characterize subsurface heterogeneity and subsurface structure at different scales, to identify potential contamination pathways, to delineate wellhead protection zones and, to perform upscaling studies, to test and condition transport predictions obtained from deterministic or stochastic model approaches, to provide a database for development and testing of new modelling approaches etc. Using the proposed multilevel–multitracer set-up, information with a high temporal and spatial resolution can be obtained at acceptable expenses.

New reactive tracers, applied in a multitracer set-up together with non-reactive tracers, allow the characterization of reactive transport processes in the subsurface and of residual NAPL phases. Due to the possibility of using practically an unlimited number of different tracers with a very low detection limit within one multitracer experiment, quantitative

DNA tracing may become a powerful tool for (three-dimensional) subsurface investigation at a variety of transport scales. More detailed laboratory and field experiments are needed to achieve a comprehensive understanding and quantification of the (reactive) tracer–aquifer material interaction processes and to establish evaluation procedures and modelling tools for the interpretation of the measurements.

Following the experiences, it is believed that the flexible numerical Monte Carlo type stochastic transport simulation technique based on categorical variables can be successfully applied in hydraulically and hydrogeochemically highly heterogeneous porous aquifers. The geostatistical approach using sequential indicator simulation of categorical variables (facies) allows the generation of spatially variable hydraulic conductivity, porosity and hydrogeochemical parameter fields, without the need for an a priori correlation function of hydraulic conductivities and parameters characterizing reactive transport such as e.g. distribution coefficients. The stochastic simulation technique can consider multiple reactive transport processes, e.g. surface sorption, diffusion, (bio-)degradation, dissolution etc. It therefore offers many possibilities of further development and applications, for example for the testing of upscaling of laboratory measurements to the field-scale, for the investigation of scale dependence of effective parameters describing reactive transport, or for the planning of remediation activities.

The research and development activities may yield a set of subsurface investigation and modelling tools, which can be finally applied by industry and consultants as standard methods in hydrogeological practice.

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