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Comparative Tracer Studies in Groundwater

Vergleichende Studien über Markierungsversuche im Grundwasser

(R. BÄUMLE, H. BEHRENS, F. EINSIEDL, N. GOLDSCHEIDER, K. GRUST, H. HÖTZL, W. KÄSS, K. KENNEDY, W. KINZELBACH, R. KOZEL, I. MÜLLER, J. MÜLLER, S. NIEHREN, P. ROSSI, P.-A. SCHNEGG, K.-P. SEILER, K. WITTHÜSER, S. WOHNLICH, H. ZOJER)

Content

1. Application of Artificial Tracers in Comparative Tracer Experiments (H. BEHRENS, H. HÖTZL, W. KÄSS)

1.1. Objectives

The term "comparative tracer experiment" is used quite differently in connection with groundwater studies. In senso stricto it refers to more or less parallel injection of two or more tracers at one site under the same hydrologic and hydraulic conditions. In this case, there are the tracers which are compared with regard to their properties and transport behaviour during the underground passage. Sometimes the term is used for "combined" or "multitracer" experiments (V. MAURIN & J. ZÖTL, 1959, H. BATSCHE et al., 1970, H. HÖTZL & A. WERNER, 1992, A. DASSARGUES, 2000), where tracers are injected into different locations at the same time or it is applied to repeated experiments at the same location but at different time and probably different hydrologic conditions. In these two last options there are not the tracers but the discharge conditions of the underground flow from different sites or respectively the hydrologic conditions at different time which are to be compared.

The objectives of this study are of course the direct comparison of the tracers themselves. There are the specific physico-chemical properties of the tracers and their resulting interaction with soil and rock particles as well as their transport behaviour which are to be compared directly. The question is how far the possible deviating results of different experiments with different tracers are due to intrinsic properties of the aquifer systems or they are due to the behaviour of the tracers. Though multitracer experiments are not regarded here as comparative tracer experiments, the increasing application of multitracer experiments in the past thirty years raised up the demand for comparative tracer studies, to see if the tracers are directly comparable under the conditions of groundwater flow. Another question is how far the tracers influence each other if they are mixed within one aquifer system (H. BEHRENS et al., 1992, W. KÄSS, 1998).

Nowadays, the aims of purposefully injected artificial tracers are mainly:

- Proof of existence or non-existence of hydraulic connection between points of tracer injection and observation.
- Determination of hydraulic parameters such as flow (residence) time, flow rate, dispersivity, water yield.
- Assessment of contaminant transport and retardation.
- Application of the tracer information in the fields of water exploration, protection of drinking water resources, investigation of contaminant immissions and other water management tasks.

Generally in connection with a single question the application of just one suitable tracer appears as sufficient. In this case it needs to be guaranteed that the tracer properties meet the requirements of the experiment. In most cases the needed property is an identical propagation behaviour compared with the movement of water itself ("ideal tracer" or "conservative tracer"). There are many reasons to propose the simultaneous injection of several tracers in an aquifer system:

- From the hydrological aspect of getting information on the whole catchment at equal hydraulic conditions as well as of the economical point of view it is of advantage to inject comparable tracers at different places simultaneously.
- The different behaviour of tracers can give information on the retardation capacity of a certain aquifer.
  The behaviour of new or relatively unknown tracers can only be assessed under complex natural conditions by comparison with that of a well known reference tracer. A special case of such an application is the investigation of the transport behaviour of contaminants.
- The use of different tracers which per se display different transport behaviour due to special properties of the aquifer may help to obtain additional information on hydraulic or other parameters of the investigated system.

Furthermore, comparison of independently obtained insights into properties of different tracers can be regarded as comparative tracer studies if the tests have been performed under closely related conditions. This especially is the case if multitracer experiments have been performed with the individual tracers on different flowpaths but in the same study area simultaneously under identical hydrological conditions.

1.2. Performance of Comparative Tracer Experiments

1.2.1. Recommendation for Test Areas

For groundwater studies, the main objectives of comparative tracer experiments are the direct comparison of tracers or the comparison of a new tracer with a well known reference tracer. For this purpose it is important to find out the differences of tracer properties under equal test conditions. A requirement for the interpretation and assessment of tracer differences is that the experimental conditions are well known. For special investigations sometimes the comparison is done under clearly defined laboratory assembly, e.g. diffusion cells or test columns are used for the determination of diffusion or sorption coefficients of tracers for special rock materials. The disadvantage of laboratory tests is that they can't reproduce generally the natural variability of an aquifer environment. Therefore additional in situ tests under aquifer conditions are requested.

Natural test sites should be selected and prestudied carefully according the aim. One of the precondition is the detailed knowledge of the hydrogeologic frame (V. MAURIN, 1967, H. BATSCHE et al., 1970, H. HÖTZL & B. REICHERT, 1996). Normally a tracing distance is chosen for such experiments, where travel times of few hours up to several days are expected. The distance should be representative for the flow condition of the selected aquifer. For tests along single fissures (Fig. 1.1) or karst conduit flow distances of few hours might be the right time (T. HIMMELSBACH et al., 1992). But the flow behaviour would be mainly that of a channel flow with minor contacts of the tracers to the matrix. In order to get a more representative result of the tracer interaction with the porous, fissured or karstic aquifer, a travel time along the test distance of several and more days might be more appropriate (H. BEHRENS et al., 1992, H. HÖTZL & B. REICHERT, 1996).

For the injection of the tracers existing natural accesses to the groundwater, like swallow holes or open fissures, or artificial openings, like hand dug wells or drilled wells, are preferably chosen (V. MAURIN, 1967, W. KÄSS, 1998). In the case of just testing the behaviour of the tracers in the underground it is not so important if an additional short distance through the unsaturated zone is included before the tracer reaches the groundwater table. In case of a diffuse distribution of the tracers on the surface and natural infiltration (partly also due to artificial irrigation) the percolation or migration through

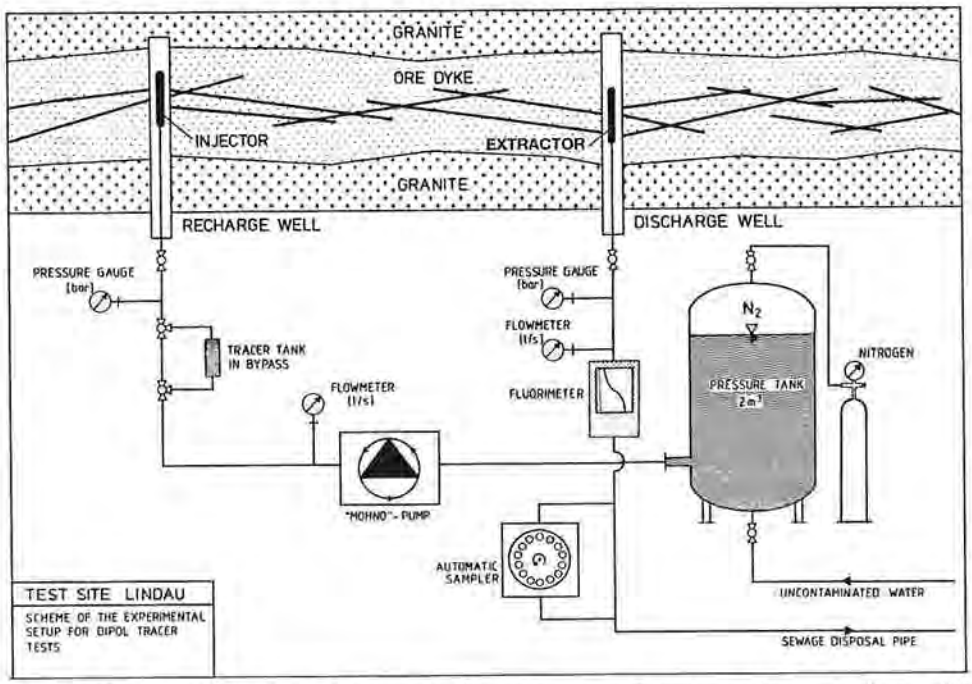


Fig. 1.1: Test site "Lindau", Black Forest, Southwest Germany: Experimental set up in the parallel tunnel used for comparative tracer experiments and the investigation of contaminant transport along a defined fracture system. The graph shows the schematic experimental set-up for tracer experiments (T. HIMMELSBACH et al., 1992).
Testfeld „Lindau", Schwarzwald, Südwestdeutschland: Versuchsanordnung im Parallelstollen für vergleichende Markierungsversuche und für die Schadstofftransportuntersuchung entlang eines definierten Kluftsystems. Die Abbildung zeigt den schematischen Aufbau der Markierungsversuche (T. HIMMELSBACH et al., 1992).

the unsaturated zone down to the groundwater table might last weeks or months. Such tests should be carried out where the unsaturated zone itself or special questions of unsaturated transport is the goal of the investigation (compare chapter "Tracers in the Unsaturated Zone"). If the results of the tracer comparison pertain to the behaviour in groundwater flow or even to a special type, like porous or fissured flow, then the injection should be done directly into the groundwater, for instance by means of a natural shaft or by a well. Wells in hard rocks frequently don't have direct contact with the main flow. Sometimes the hydraulic connection occurs only along intersections of joints reacting like communicating pipes. In such cases the flush out of the tracers from the wells into the aquifer has to be ensured by a sufficient rinse of clear water.

The flow direction from the injection place should be known in advance of the comparative tracer experiment. The observation and sampling point, a well or a spring, should be selected directly downstream within the main flow. A marginal discharge with low recovery rate may lead to a wrong interpretation of the compared tracers especially if one of them has a low detection limit, so that it can't be detected in the chosen sample site. On the other hand, if significant hydraulic dispersion from the injection place occurs, it can be very helpful to control the whole dispersion fan by several sampling stations. Special test fields with dense pattern of observation and sampling wells (Fig. 1.2) were established in many countries for tracer experiments and the investigation of contaminant transport (D. M. MACKAY et al., 1986, H. HÖTZL & B. REICHERT, 1996).

Sometimes comparative tracing experiments are carried out in a yet hydraulically unknown area. This happens when a regular tracer experiment is planned for the solution of a regional question and a new tracer is injected in parallel for comparison. In this case the known tracer, which serves as the reference standard, should be a conservative tracer with low detection limits.

Another problem may arise in test areas with fast and slow flow components in the relevant aquifer system (H. MOSER & W. RAUERT, 1980, Y. YURTSEVER & L. ARAGUAS, 1993). The reasons are different hydraulic conditions, depending either on deep aquifers or aquifers with high heterogeneity of the permeability distribution or aquifers with double porosity effects. The retardation which is caused by the slow flow component can amount up to several years and more, whereby the shares of the fast and slow flow components can vary with the hydrologic conditions. In general the observation of breakthrough curves of tracers record only the fast flow. For the slow flow the observation time is normally too short and on the other hand the tracer concentrations are then too strongly attenuated to be detectable. The recovery rate gives a chance to calculate the share of the fast flow component. But to come to a right interpretation of the observed recovery rate for a new tracer, it is important that the reference tracer is an absolute conservative tracer. Otherwise sorptivity or possible degradation of the new tracer might be over- or underestimated.

For the assessment of sorption and degradation processes additional informations are necessary on the lithology of the aquifer, the mineralogy of the rocks as well as the chemical and biological milieu conditions.

Summarizing the arguments for the selection of certain test areas in connection with a planned comparative tracer experiment, it can be recommended to select rather a simple aquifer system. Its structures and flow conditions need to be very well known. For the comparative experiment not only the hydrogeologic characterization but also the time-depending hydraulic conditions have to be considered. Otherwise the interpretation of the comparative tracer experiment might lead to wrong conclusions regarding the properties and suitability of the new tracers.

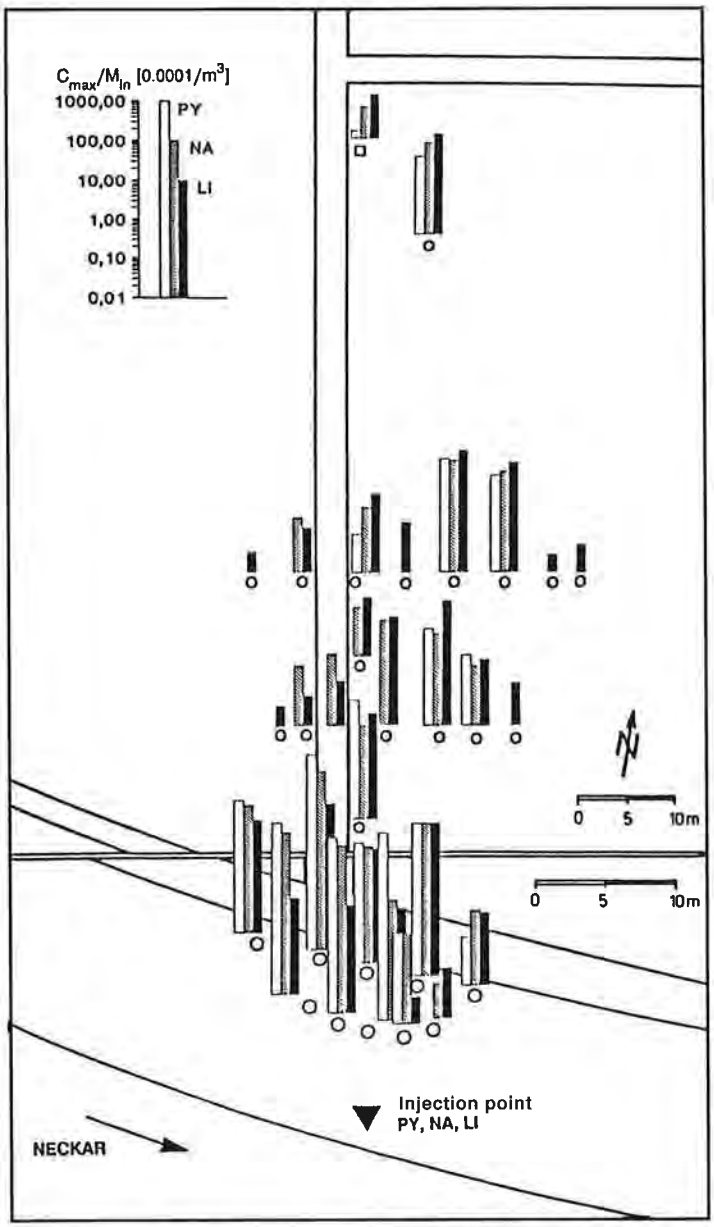


Fig. 1.2: Test site "Böckinger Wiesen", Heilbronn, Southwest Germany. Experimental well field in a 4 m thick confined gravel aquifer along an infiltration profile from the bank of river Neckar to a 100 m distant pumped well. The graph shows the result of a comparative tracer experiment with pyranine (PY), napthionate (NA) and lithium (LI) (B. REICHERT, 1991).
Testfeld „Böckinger Wiesen", Heilbronn, Südwestdeutschland. Versuchsfeld in einem 4 m mächtigen, gespannten Kiesgrundwasserleiter entlang eines Infiltrationsprofils zwischen dem Neckar-Ufer und einem 100 m entfernt gelegenen Entnahmebrunnen. Die Abbildung zeigt das Ergebnis eines vergleichenden Markierungsversuchs mit Pyranin (PY), Naphtionat (NA) und Lithium (LI) (B. REICHERT, 1991).

1.2.2. Preferential Reference Tracers

Principles of Tracers

Water tracers are used to study processes which are connected with the movement of water. In the first place this concerns the movement of water itself. In the second place it concerns the movement of substances which are transported by the moving water. Water tracers are substances or signals which are contained in or added to the water and are suited to observe the movement of a discrete body of water within a hydrologic system. As far it concerns the water movement itself, the tracer should exhibit an identical motion with the water. Of course, this requirement seems best be realizable if the tracer would be incorporated in the water molecules, e.g. in form of deuterium or tritium atoms. However, for several reasons this is not a generally applicable option because:

- The radioactive tritium can only be used under strict regulation and permission, and it requires qualified personal and special equipment. Its extensive use could disturb the possibilities of hydrological investigation of the low-level environmental tritium. Further, because of the general lack of public acceptance it is nowadays almost impossible to obtain permission to release radioactive materials into the environment even if the application would be safe.
- For the stable deuterium the danger to jeopardize the possibilities of the environmental isotope hydrology is almost the same. Furthermore, given the fluctuating natural background of deuterium, already for relatively small water systems, large amounts of deuterated water had to be used.

So far these isotope tracers can only be used in small systems, mainly on the laboratory level. It will also be shown that these seemingly perfect tracers are not always like that. Consequently, other materials which are added to the water have to be used as tracers. This had in fact already begun before the modern isotopic tools were available. To be useful, the tracer must have a number of properties:

- The first and indispensable is a physical and chemical structure which let the tracer travel in such a manner that it represents the hydraulic parameter to be measured perfectly. Therefore it should not be sorbed to aquifer materials or lost by filtration. It must be chemically stable and not be lost by any process of degradation (including for instance microbial attacks).
- The tracer must have properties that make it detectable also in very high dilution. The detection should not be disturbed by any other substance. That includes that the tracer should not or only on a tolerable level be abundant in the aquatic environment.
- The tracer must be non-toxic and in no way harmful to life or any other environmental belonging and its use should also be economic.

The development of modern water tracing has brought out a number of different tracers, also with the desire for more than one tracer for so-called multitracer experiments, that means simultaneous application of several tracers in a study area, either to have more complex information under the same hydrological condition or also just to make investigations more economic. There is evidence that most of the tracers used so far have some disadvantages and the search for "new", that means better or just more tracers, is still going on. One has always been thinking of an "ideal" tracer, which would meet all the above requirements in a perfect way. However, the following example

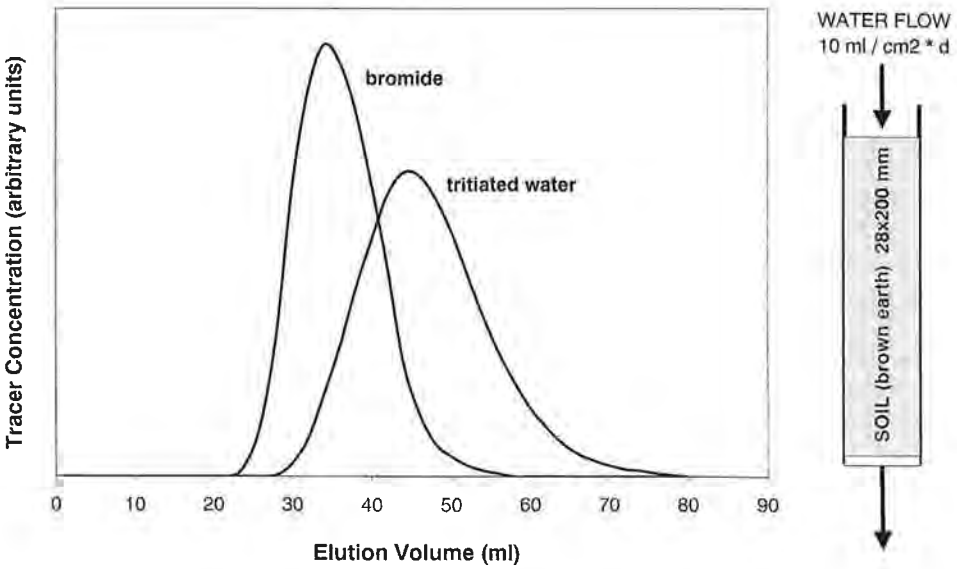


Fig. 1.3: Tracer breakthrough in a comparing tracing test with bromide and tritiated water in a laboratory column (after H. BEHRENS, 1986).
Tracerdurchgang in einem vergleichenden Markierungsversuch mit Bromid und tritiiertem Wasser in einer Versuchssäule (nach H. BEHRENS, 1986).

may show that ideal tracers basically do not exist (Fig. 1.3). Here two tracers (the bromide anion and tritiated water) possessing more or less no negative properties, have been injected simultaneously into the flow through a soil column. Remarkably, they display very different breakthrough and thus different residence times or flow velocities in the column. The reason for that difference is that the neutral tritiated water exchanges with immobile water in the column, which the negatively charged bromide cannot enter (partly due to ion exclusion). Thus, the tritiated water represents the movement of more or less the total water in the column while the bromide represents the freely-moving water, the so-called flux. In that sense, both tracers reflect different flow parameters, in a more or less perfect way each. Therefore, a tracer will always be representative for a certain parameter to be determined. Such and other phenomena (e.g. sorption, diffusion) should be taken into consideration whenever a tracer is selected as a "reference tracer" for testing other tracers.

Classification of Tracers and Some Important Properties

According to their very different nature, the common tracers are divided into different groups. These reflect on the one hand their physical and chemical nature, on the other, however, their detection method. These groups are:

- **Dyes, especially fluorescent dyes:** The most important group of all tracers at present is that of the fluorescent dyes which are mainly of the xanthene type. The main reasons for their popularity are: extreme detection sensitivity, low or almost no background abundance in the environment, relatively easy and quick detection which is also very well quantitatively achievable, and good environmental tolerance. Their sorptive behaviour which is different, varies from low, for uranine, over moderate, for eosin, to stronger in the sequence sulforhodamines and rhodamine B; it is influenced

by the nature of the sorbing material (minerals) and by the pH of the traced water. A slight disadvantage of the fluorescent dyes can be seen in their relatively wide-shaped spectral peaks which are all in the visible range and by overlapping cause some difficulties in the resolution of tracer mixtures.

- **Other fluorescent materials:** The idea of using also spectral regions other than the visible led to the use of UV-fluorescing chemical naphthionate (H. R. WERNLI, 1986), which also shows good transport behaviour, and to the use of optical brighteners, which until now have not proven very effective due to problems of poor solubility; both tracers suffer from interference by the fluorescence of organic substances.
- **Radioactive tracers:** In the 1950's they brought about a jump in the development of hydrologic tracer techniques thanks to their sensitive, selective and precise detectability. Also a wide variety with different chemical properties became available. A special type of these tracers are the chemically very stable chelate complexes of various radioactive isotopes (e.g. of chromium, indium, dysprosium, cobalt, gold, and more). However, nowadays radioactive tracers have lost their importance because of environmental objections and due to progresses in the detectability of other tracers, especially of the fluorimetric ones. Tracers which are detected by neutron activation analysis are often counted among the radioactive tracers. However, as they are used in inactive form, they actually represent chemical tracers which just use radioactivity for the detection – thus not posing related environmental problems. An advantage of radioactive tracers is that sufficient radioactivity is bound on very small amounts of matter. Thus radioactive tracers normally do not present a chemical poisonous stress to the environment. Due to the radioactive decay, they disappear "automatically".
- **Particulate tracers:** Several types of natural matter existing in small units have been proposed and used as water tracers. Lycopodium spores were used systematically since the 1950's, besides others also by the karst research group in Graz (see V. MAURIN & J. ZÖTL, 1959) where great improvements were achieved in respect to techniques for the spores preparation; a speciality was the colouring of the spores with three different dyes, so that four discernible tracers resulted. The scale was further expanded by W. KÄSS (1998) who developed the dyeing of spores with three fluorescent materials. The size of spores is about 30 µm and their form allows their identification under the microscope.

  Bacteria have already been used as tracers since the end of the 19th century, at that time mainly to investigate the propagation of bacteria in water supply installations. To be suited as water tracers in hydrologic systems, the bacteria should have some properties like: they should survive for sufficiently long times in the hydrologic systems, however not reproduce. They should be absolutely non-pathogenic. For the detection they should form colonies, easy to identify. To be not disturbed by backgrounds they should not be resident in the system under investigation. These requirements are very well fulfilled by *Serratia marcescence*, which produces bright red colonies on agar plates. Also *Escherichia coli* has successfully been used as water tracer. The size of bacteria is mainly in the 1 µm range.

  Another type of microbial tracers are **viruses and phages:** While viruses are pathogenic to animals (including man) and plants, phages are so only to bacteria. Therefore phages are strongly preferable to viruses for use as water tracers. Like for bacteria, the field of application of viruses and phages is mainly for reconnaissance of spreading of pathogens in hygiene issues. However, phages have also been used as

water tracers, especially in karst systems, on long flow conduits. The size of viruses and phages ranges below that of bacteria down to about 0.2 µm.
In contrast to the described particulate tracers of natural origin, a further type of water tracer are **artificial microspheres** which are endowed with fluorescent dyes for their detection, and have been developed among other purposes for testing blood circulation. Like the spores, they are identified and counted, after filtration, under the microscope, whereby their adhering fluorescence greatly helps to find them. Of all the different types, only the neutral forms with a polystyrene matrix were found to be useful as tracers, the others were always lost completely in groundwater systems, presumably by sorption. Microspheres are available in a wide range of sizes; if they are applied in a size of about 1 µm, then they can serve to simulate the transport and spreading of a bacterial contamination.

All particulate tracers have common propagation properties: they can be lost by filtration or sedimentation, and have been found to reappear mostly only in small yields. It appears that they need fast and best close to turbulent water flow to be transported. Therefore, they frequently show up at the beginning of the breakthrough, some time prior to dissolved water tracers and decline faster than these; the loss rate of the particles is obviously the higher, the longer they have resided. This behaviour results in an apparently enhanced transport velocity of the particles.

- **Salts and other chemical tracers:** Since the beginning of modern water tracing, sodium chloride and some time later potassium chloride have been used as tracers, which can be detected by chemical analysis or flame emission spectroscopy. Later, lithium and also strontium were introduced; while lithium is relatively well suited thanks to moderate sorption and low background, strontium is impaired by much stronger sorption due to its nature as a divalent cation. The sorption is a negative effect on all cations, mainly by ion exchange at minerals which much less acts on anions. Salts consist of the two components, anion and cation which dissociate after dissolution. Therefore, in principle, with the use of a salt, two substances have been introduced which both can act as a tracer and according to their different physico-chemical properties, display different transport properties. The effect of reversible ion exchange of cations, which results in their retardation compared to the flow of water, is moderate in karst systems with their mostly moderate ratio of sorbing surfaces and water volume; however, it can seriously increase in fine-grained unconsolidated aquifers (sands and silt). Mostly one of the salt's components is analysed as a tracer. However, if both have tracer character (that means low background and high detection sensitivity, e.g. lithium bromide), then they can be used, together, for comparative tracer tests. Salt tracer breakthroughs are easily detected just by the increase of electrical conductivity of the water, however non-specifically and with low detection sensitivity. Better suited are specific chemical reactions like titrations, and nowadays ever more instrumental analytical techniques, like ion chromatography and various kinds of spectroscopy. Of other chemicals, different types of complexes, especially the chelate complexes, shall be mentioned which until now have proven good tracer properties, and possess further potential for deriving new tracers. Of all salt tracers, the bromide anion owing to its low sorption, its stability, and relatively low background values has gained particular importance as a reference tracer.

Tracer Selection for Comparative Tests

The selection of tracers for multitracer tests depends on the aim and strategy of the respective experiment, with the two extremes (see also chap. 1.1.), either

- simultaneous injection of the tracers individually into different sites within one research area, mainly with the aim of evaluating different flow paths simultaneously;
- injection of all tracers under investigation together into the same injection site (real condition for tracer comparison).

It is evident that also a mixture of these two cases can be arranged in combined experiments: injection of two or more tracers into one or several of the injection sites for either comparison of the tracers or confirmation of the result by the comparison.

In the first case the distribution of the tracers onto the single sites can be determined by different aspects: tracers with high detection sensitivity are preferably to be used on longer flow paths or where high dilution is expected.

Tracers whose detection bases on the same principle, and could disturb each other (e.g. fluorescent dyes) should be positioned in such a distribution that their breakthroughs overlap as little as possible; on the other hand tracers with quite different detection modes can be preferably combined without such problems. Tracers which could be lost by filtration through fine pores should be kept off from flow paths where such effects are suspected.

In the second case such considerations are inapplicable. For a correct comparison, the tracers should be injected from one mixture (solution). Especially when the tracers are injected into wells, they could take different ways when injected separately and/or at different times, for example caused by different densities (salt solutions).

Selection of Reference Tracers

The two main parameters in the assessment of a tracer's behaviour are transport velocity and recovery. It seems easy to find out how well a certain tracer to be tested is able to be representative for these flow parameters, if it is compared to a reference tracer which is sufficiently perfect in this respect. The problem is the availability of such a reference tracer and how its own properties can be validated.

One approach could be to make tests in systems which are hydraulically very well explored and thus can serve as calibration courses (somewhat similar to the calibration of hydraulic measuring devices in a hydraulic laboratory). This can be done for example in a porous aquifer which is pumped in such a manner that all the water from a distant injection site reappears in the production well. If at least for one tracer a 100 % recovery has been found, then the test field may be suited for the determination of the wanted sorption parameter. However, it seems almost impossible to obtain precise data on flow velocities in natural flow fields other than by tracers.

For that the other approach, the involvement of laboratory test could be helpful. Tests with columns which must be sufficiently large and especially long, can give exact data on the relation between water and tracer flow velocity. For support, processes which are responsible for retardation, like sorption or matrix diffusion, can be investigated in adequate tests like batch sorption/desorption experiments. Finally, critical evaluation of experiences gained in field tests could also contribute to some clarity about tracer transport velocity.

After experiences made hitherto, the bromide anion seems to be the best candidate for a reference tracer among the established water tracers, and for research on tracer properties it should be included in comparative experiments whenever possible. Tracing with spiked water (deuterated or tritiated) could serve as a reference tracer which includes the exchangeable water in the system. If there are differences in the breakthrough between bromide and spiked water, then this difference can give information about the ratio of the exchangeable immobile water to the moving water.

Uranine and other dyes which were long time regarded as the most conservative tracers, cannot hold this position. In contrast to experiences which have been made in karst systems with their relatively low sorption capacity, in porous media aquifers retention factors of uranine between 1.3 and 2 have been reported (D. KLOTZ, 1982, A. DE CARVALHO DILL et al., 1992).

1.3. Evaluation of Comparative Tracer Experiments

The time and space depending spreading of tracers in the underground is controlled by the temporal changes in the concentration at certain observation points. The observed breakthrough curves are the expression of the hydrodynamic and – in case of reactive tracers – the physico-chemical and biological processes to which the tracers are subjected along their underground transport path (J. BEAR, 1972, A. LENDA & A. ZUBER, 1970, D. M. MACKAY et al., 1986, H. D. SCHULZ, 1998). To compare the properties and the behaviour of tracers in groundwater, a very detailed breakthrough curve is requested. As it was mentioned in the previous subchapter either a continuous measurement of the tracer concentration over the breakthrough time or a very dense sampling programme is necessary to reproduce the concentration changes with all requested details.

The breakthrough curve forms the base for the analysis of the tracer behaviour as well as of their comparison. The results of measured concentration are drawn in form of the time depending tracer concentration curve and so far discharge rates are available also in form of the time depending cumulative tracer recovery curve (Fig. 1.4). For the comparison of tracers it is important to normalize the concentration as fraction of the injected amount of tracers. Different normalization procedures are in use. Some refer to the fraction of initial concentration which is applied preferentially in connection with step input injections:

$$c_{tnorm} = c_t \cdot c_{in}^{-1} [-]. \tag{1.1}$$

In the case of instantaneous (DIRAC) injection the normalization refers generally to the injected amount of tracers (M_{in} = mass, numbers etc.):

$$c_{tnorm} = c_t \cdot M_{in}^{-1} [m^{-3}]. \tag{1.2}$$

In order not to obtain too small numbers for the normalized concentrations, it has become practical to refer the normalization to certain fractions of the injected amounts of tracers. E.g., in the Lurbach experiments (H. BEHRENS et al., 1992) a factor of $f = 10^5$ was chosen, whereby such factors do not result from a conversion of physical units, but express the overall degree of dilution attained in the respective traced system, taking, within one experiment, the same value for all used tracers, independent of their amounts:

$$c_{tnorm} = c_t \cdot M_{in}^{-1} \cdot f [m^{-3}]. \tag{1.3}$$

For comparing the recovery of different tracers, it is recommended to give the recovery rate either in shares of the unit = 1 or as percentage of the injected tracer amount.

The comparison of the tracer behaviour with one another or with that of a reference tracer focuses primarily on the travel time and the shape of the breakthrough curve. For this purpose four characteristic flow velocities can be defined:

v_{max} = maximal effective flow velocity determined by the time of first detection of the tracer (begin of breakthrough, t_{beg}),

v_{dom} = dominant effective flow velocity determined by the time of the maximal tracer concentration (t_{dom}),

v_{mean} = mean effective flow velocity determined by the time of the center of gravity of the area below the breakthrough curve (t_{mean}),

$$t_{mean} = \int_0^\infty c_t \cdot t \, dt / \int_0^\infty c \, dt, \tag{1.4}$$

v_{min} = minimal effective flow velocity determined by the end of measurable tracer breakthrough (t_{end}).

Breakthrough curves with the same velocity values but different normalized concentrations indicate losses of tracer by irreversible sorption or/and chemical/biological degradation of at least the tracer with the lower concentration.

Retardation with respect to the reference tracer, shown in delayed and decreased peaks as well as in elongated tailings, can be caused by different factors, amongst which

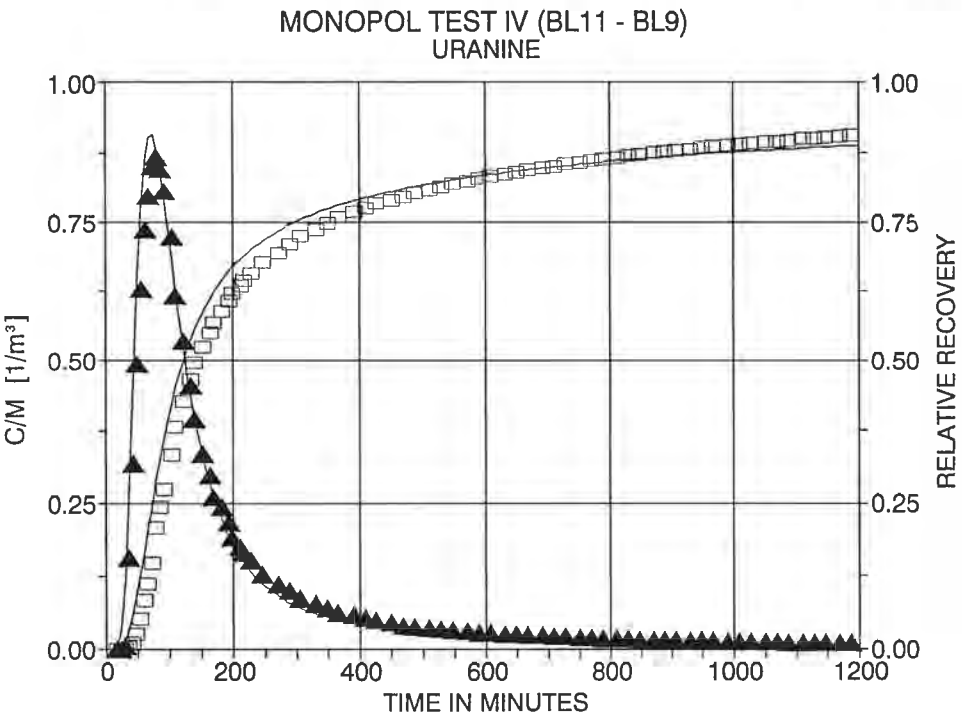


Fig. 1.4: Breakthrough curve of uranine and cumulative recovery curve from a short distance tracer experiment along a fracture system at the test site "Lindau" (comp. fig. 1.1). Triangle and squares represent the measured values, the through-going line gives the best fit calculated with the single fissured dispersion model (SFDM) (T. HIMMELSBACH et al., 1992).
Durchgangskurve von Uranin und Wiedererhaltskurve eines kleinräumigen Markierungsversuches entlang eines Kluftsystems im Testfeld „Lindau" (vgl. Fig. 1.1). Dreiecke und Quadrate stellen die gemessenen Werte dar. Die durchgezogenen Linien zeigen die jeweils beste Anpassung berechnet mit dem Einzelkluftdispersionsmodell (SFDM) (T. HIMMELSBACH et al., 1992).

(reversible) sorption processes, matrix diffusion or special injection conditions (restricting an immediate inclusion of the whole tracer mass in the groundwater flow). In any case, the interpretation of retardation effects needs a comprehensive evaluation of all hydrogeologic, hydraulic, hydrochemical, and biochemical factors of influence.

Beside the breakthrough curves, the (cumulative) recovery curves also give information for comparing the behaviour of tracers along the transport path; especially, by comparing the yield over different flow distances, information on the applicability of a tracer for long-distance experiments can be obtained.

For an improved evaluation and better quantification of tracing results, appropriate models (usually providing "analytical", that means closed-form solutions) are used (Fig. 1.4). The measured tracer concentrations may show more or less strong deviations from theoretical curves. The parameters occurring in the analytical solutions may be determined by best-fit methods. As a theoretical background to analytical solutions, different model assumptions exist. Advection-dispersion models describe only the physical transport conditions; for reactive processes, pertinent model assumptions have to be included in the theoretical approaches. For more details the reader is referred to the comprehensive literature on this topic, e.g. J. BEAR (1972), G. E. GRISACK & J. F. PICKENS (1980), T. LEGE et al. (1996), P. MALOSZEWSKI & A. ZUBER (1993) and P. MALOSZEWSKI (2000).

2. Review of Earlier Comparative Experiments of the ATH Group

(H. BEHRENS)

2.1. Lurbach and Buchkogel Systems, 1966

In 1966 several institutes from Austria, Germany and Slovenia which were active in the field of water tracing joined together in Graz (Austria) to present and exchange experiences on a Symposium (V. MAURIN & J. ZÖTL, 1967) and in order to perform joint tracing experiments in the study areas Lurbach system and Buchkogel, both karst systems, which are located close to Graz.

Radioactive tracers (tritiated water, chromium-51-EDTA-complex, iodine-131), activable tracers (manganese-EDTA-salt, bromide), fluorescent dyes (uranine = disodiumfluorescein), sulforhodamine G, rhodamine B), sodium and potassium salts, lycopodium spores, and a foaming agent (alkylbenzenesulfonate) were injected for comparison of their suitability and testing the detection techniques.

While most of the tracers worked in these systems in a satisfactory manner, also negative properties of some of them were revealed: diminished reappearance and tailing of the iodide tracer by probable biochemical sorption, retardation of cationic tracers by ion exchange and complete loss of the manganese tracer by probable insufficient stability of the complex (H. BATSCHE et al., 1967).

The different behaviour of the particulate tracer (earlier appearance than the dissolved tracers, reduced tailing in the straightthrough conduit of the Buchkogel, enhanced tailing in the Lurbach system with its many dead waters) suggested that "substantial differences in the response of different tracers could reflect essential hydrogeologic characteristics of the investigated systems".

This event at Graz inspired future common work on water tracing with periodical arrangement of symposia, and can be regarded as the foundation of the later ATH.

2.2. Danube Infiltration and Riegelenge Tracing Experiments 1967–1969

The next joint tracing event was performed in SW Germany in 1967–1969, the experiments from now on preceding the final symposium, 1970 in Freiburg (W. KÄSS, 1972). One of the selected study areas was the region of the upper Danube which looses near Immendingen a considerable fraction and at low flow all of its water to the karst underground. In contrast to the Graz experiments, this time it was tried to trace beside the river infiltration itself as many as possible injection points in the surrounding area to obtain a full overview of the hydrogeologic system (the reappearance of the infiltrated Danube water in a large 14 km distant karst spring, the Aach-Quelle, had already been proved in several preceding tests, among these the historically first application of the dye fluorescein by A. KNOP, 1878, cited in W. KÄSS, 1998). Thirteen different tracers (the fluorescent dyes uranine and sulforhodamine G, the salts sodium and potassium chloride, brown and green coloured lycopodium spores, lanthane-EDTA-complex and bromide for activation analysis, the radioactive chromium-51-EDTA-complex, two surfactants, the bacterium *Serratia marcescens* as a microbial tracer, and the more "exotic" fragrances limonene and isobornylacetate) were applied at 10 injection points. This distribution of the tracers allowed less direct comparison, however, it was again found that the chromium complex worked very well, while the lanthanum appeared mainly to be transported adsorbed on suspended matter after disintegration of the less stable complex. On the other hand, the combination of simultaneously injected tracers gave deepened insights into the hydrogeologic system (H. BATSCHE et al., 1970).

The Riegelenge experiment was an early example of combined tracing in a pleistocene unconsolidated rock aquifer. The test field was developed by numerous 2-inch wells in three horizons in a depth between 5 and 45 m and over horizontal flow distances up to 30 m. Uranine and the bacterium *Serratia marcescence* were injected in the upper aquifer, tritiated water, iodate as an activable tracer, and a detergent (at the high amount of 30 kg) into the medium layer, and eosin together with potassium chloride into the lower horizon. Uranine worked well, while the bacteria were completely lost by what was to be assumed filtration. Tritium and iodine could not be detected, probably due to high dilution and falling below the detection limits, while the detergent was found in a 10 m distant well with a maximal concentration of 1,200 ppb 60 days after injection (tritium was not measured with the high sensitive technique as used for the environmental isotope but rather with normal liquid scintillation counting). Potassium could not be found in any observation well, but the belonging chloride showed clear breakthrough curves. The obvious loss of the potassium by ion exchange was confirmed by corresponding increase of calcium and magnesium concentrations. Eosin showed regular breakthrough curves, however, in comparison to the conservative chloride breakthrough some delay by reversible sorption was indicated. In this experiment additionally single-well tracer techniques and investigations of the environmental isotopes tritium and carbon-14 were successfully included, demonstrating the gain in information by combination of various methodologies (H. BATSCHE et al., 1970).

2.3. Underground Water Tracing in Slovenia 1975

The next common experiments of the ATH took place in the Karst area between Ljubljana and Postojna, the catchment basin of the Ljubljanica. This field work developed as one of the largest combined tracing events made until, comprising an area of more than 500 km^2. Again the sequence, first doing the field work and then presenting the results

within the frame of a general water tracing symposium (1976 in Bled) was followed. This study was not the first in this hydrogeologically complex system, since the scientific research, including tracings, was already begun in the 19th century. However, it was now expected that the effort of a combined investigation with simultaneous tracings could clear up still hidden secrets of this important hydrological system. Likewise, the experiments were regarded as a training field for the further development of the tracing techniques and an opportunity for scientific exchange between experts. After extensive meteorological, hydrological, speleological, hydrochemical, environmental-isotopic and microbiologic prestudies, begun in 1972, the actual tracing experiments were performed during spring and summer 1975. Besides this karst investigation, tracing experiments were made in Quaternary sediments in the Savinja valley during 1973. All this work and the results are described in a special report (R. GOSPODRIČ & P. HABIČ,1976).

Fourteen different tracers were injected almost simultaneously on the same day (May 27, 1975) except the lithium salt which was applied five days later. The tracing was made into 12 different ponors. The distribution of the different tracers on the individual ponors was made according to their detection sensitivity (high sensitive tracer at expected high dilution); for similar tracers (e.g. dyes) which could interfere in the detection, the injection points were selected in such a way that a least overlap in the observation stations was anticipated.

Four fluorescent dyes (uranine, eosin, sulforhodamine G, rhodamine B), one optical brightener (Tinopal CBS-X), four different coloured spores, lithium and potassium salts, one detergent (Marlon 375), indium-EDTA-complex as activable and chromium-51-EDTA-complex as a radioactive tracer were chosen for the experiment.

The selection of the injection points and of the numerous observation points was made on the basis of detailed preinvestigations. Only two ponors were endowed with two tracers, one with the indium and the lithium salt, and the other with two spore types, which were treated and prepared in a different way.

The observation of the tracers reappearance was mainly made by taking water samples according to a detailed schedule. In addition, for the spores plankton nets and for the dyes charcoal bags were installed. Alltogether 35 sampling stations were operated with a sampling frequence of up to four hours. Sampling was extended until 47 days after tracer injection.

Analyses of the samples were made as soon as possible. Especially in the case of the fluorescent tracers, detergent, potassium salt and spores a field laboratory was installed. In the case of special analytical procedures, e.g. the activable and radioactive tracers, the samples were analysed at the respective laboratories in Munich and Ljubljana; charcoal bags were analysed in Vienna and the detergent in Freiburg. In respect to comparison of the analytical reliability of tracer techniques it was agreed, that the samples for the fluorescent tracers were taken in duplicate; one set was analysed by the Slovenian group and the other by GSF/Munich. This comparison resulted in a remarkable observation, which without this comparison certainly would have remained undisclosed and eventually would have misled the interpretation of the tracer breakthrough: while for most of the registered dye tracer breakthrough curves satisfactory agreement between the two laboratories was seen, especially for the uranine in a few springs dramatic differences appeared, which could not be explained by analytical uncertainties (Fig. 2.1). Repeated measurements of these samples showed generally a continuing decrease of uranine concentrations, which finally stopped after some months. At that time just the decay of the uranine was stated and a contamination by sewage in the respective springs was considered as involved in the phenomenon, but no specific process was found.

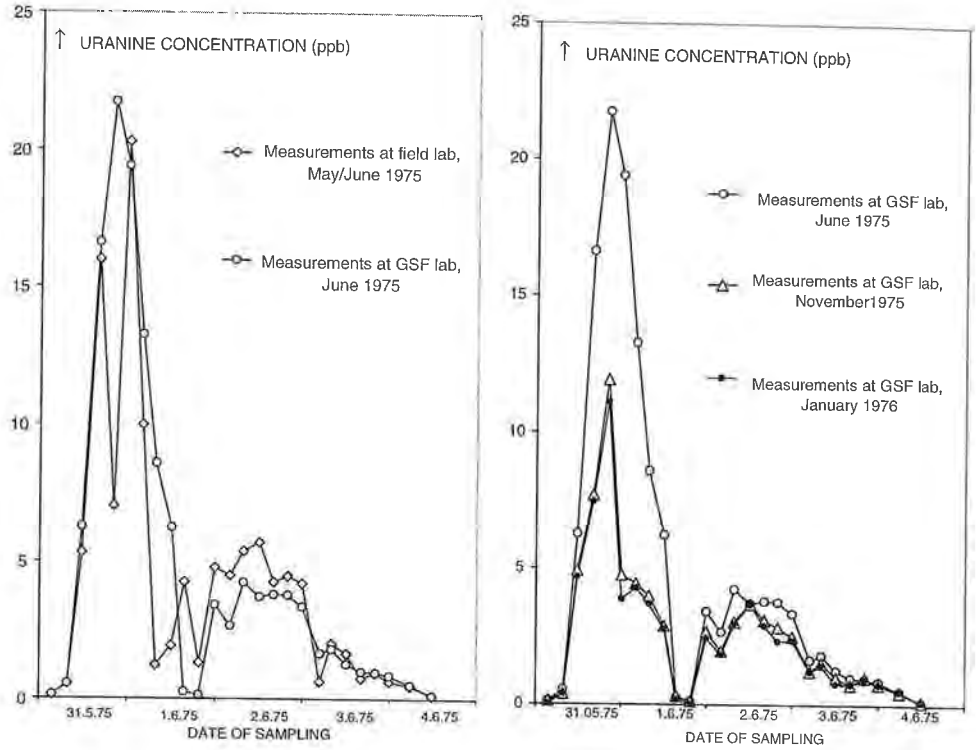


Fig. 2.1: Comparison of the measured uranine concentrations by two laboratories on samples from spring 1.13 (Underground Water Tracing in Slovenia 1975) which had been taken identically in duplicate (left picture) and repetition of the measurements by the GSF-laboratory (right picture) after some intervals (after H. BEHRENS et al., 1976).
Vergleich der im Markierungsversuch 1975 in Slowenien in Proben der Messstelle 1.13 von zwei Laboratorien ermittelten Uraninkonzentrationen (linkes Bild) und spätere Nachmessungen des GSF-Labors (rechtes Bild); die Proben wurden in zwei Serien für die beiden Laboratorien identisch entnommen (nach H. BEHRENS et al., 1976).

According to later experiences microbial decay can be assumed as a cause for this effect by which occasionally uranine, and even more so pyranine, is affected.

All applied fluorescent tracers (dyes and optical brightener) delivered clear and easy to interpret breakthrough curves in the different spring groups of the Ljubljanica (Fig. 2.2). Sulforhodamine G which was injected most to the N (Hotenka polje) was also detected in almost opposite direction in springs at the Idrija river. The tracer concentrations reached in the main passages values of about 10 ppb, which is very proper for the tracer detection; this fact confirmed that choice of the amounts of injected tracer material was optimal. The optical brightener Tinopal CBS-X did not fully meet the high expectations behause of low solubility in the natural water and high background fluorescence values, however, in the observed concentration range also useful information was obtained. The lycopodium spores yielded very detailed informations about flow paths in the whole study area which can not be listed individually here. However, the green and the brown spores which had been injected at the same point, showed distinct recoveries. This was attributed to differences in the preparation of the two spore types

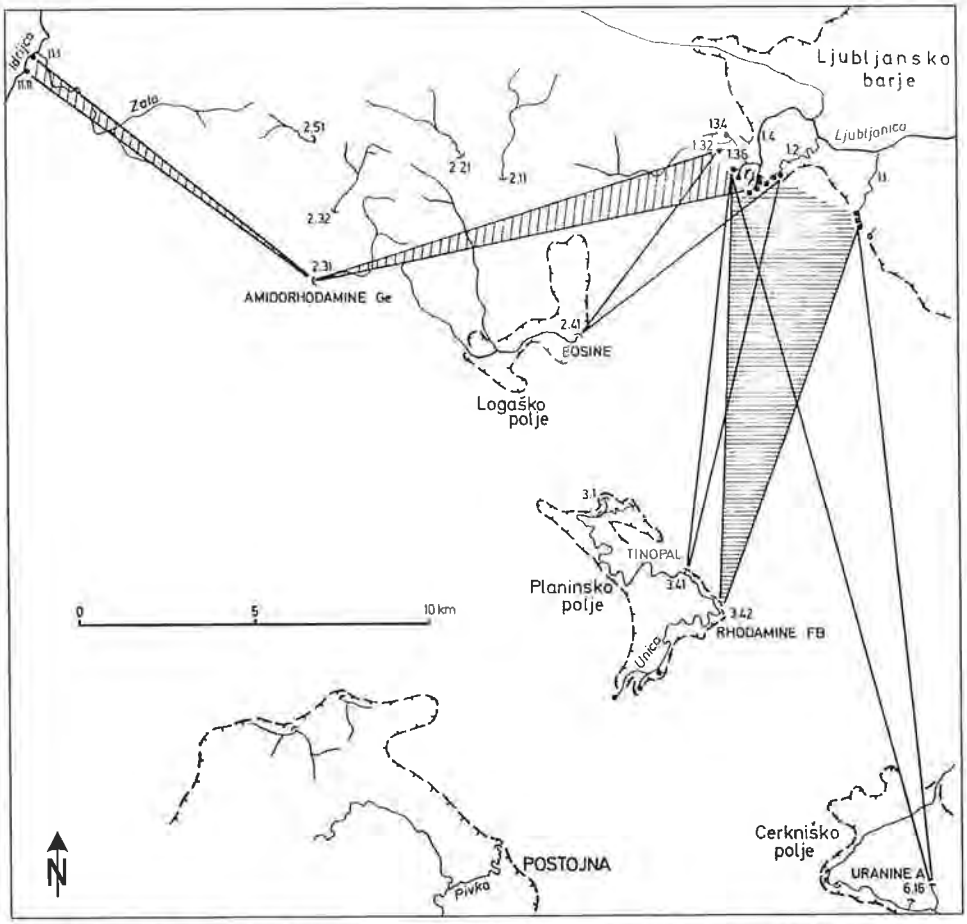


Fig. 2.2: Distribution of the fluorescent tracers in the Ljubljanica catchment area in the comparative tracer experiment 1975 (from R. GOSPODARIČ & P. HABIČ, 1976).
Überblick über die im Einzugsgebiet der Ljubjanica im vergleichenden Markierungsversuch 1975 nachgewiesene Ausbreitung der Fluoreszenztracer (aus R. GOSPODARIČ & P. HABIČ, 1976).

which may have effected different swelling and other physical properties and thus be a hint on possible sensitivity of tracer transport behaviour against small variations of their physical or chemical structure. Nevertheless, the value of this old method for karst investigations was thus again confirmed. The potassium salt delivered also information on some connections, however, because of relatively low detection sensitivity and high background values the suitability of this tracer is limited. The lithium tracer suffered also from the problem, but to a lower extent. Its breakthrough curves gave good information on flow connections and residence times, however, the recovery was difficult to calculate on account of some incertainty of the background values. The radioactive chromium gave a good breakthrough information with more than 60 % recovery in just one spring and a much smaller one in a neighbouring spring. The activable indium indicated the same flow connections as the lithium, however, with some dif-

ferences in residence times and relative tracer concentration on account of some differences in the injection mode and change of the hydrometeorological situation between the two days of tracer injection.

2.4. Muota Valley (Alpine Karst, 1979–1980), Neuenburg Jurassic (Folded Karst, 1979) and Langeten Valley (Unconsolidated Rock, 1979–1980)

After the experiments in Slovenia, study areas in Switzerland were included in the research work of the ATH. These were an alpine karst in the Muota valley (around the famous Hölloch cavern) and a Quaternary unconsolidated aquifer in the Langeten valley, which was subject of hydrological research of the University of Bern. In addition by the University of Neuchâtel another karst area, the Neuenburg Jurassic, was proposed.

In the Muota valley karst system the investigations were done unter two aspects:

- test and comparison of the available tracers under the condition of this system, especially in respect to the strongly differentiated rock structure with clay interlayers,
- further hydrological reconnaissance of the local and regional karst system and its draining processes, especially with the advantage of investigating the different components of the system simultaneously under the same hydrological condition with the multitracer technique.

Four well known fluorescent dyes were used as tracers. Furthermore another optical brightener was included in the tests: after unfavourable experiences in previous experiments with the tinopal CBS-X, a powdery substance which was found to be scarcely soluble in calcarous water, now another optical brightener, the tinopal ABP was tested, which is traded as a 50 % solution. The salts lithium chloride and sodium chloride were involved, and four types of coloured spores, amoung these for the first time a fluorescing spore (dyed with acridine orange). Finally an alkylbenzene sulfonate detergent was applied.

In respect to tracer analytics, emphasis was laid on the resolution of dye tracer mixtures. The direct determination of the tracers in water samples was tried to improve by using different pH-adjustments. Improved solvents for extracting charcoal bags were applied. Thinlayer chromatographic separation was especially tested for the resolution of dye mixtures in charcoal extracts. However, while there was satisfactory discrimination with the direct spectroscopy of water samples, the investigation of charcoal extracts suffered mainly from interference by unknown water ingredients, among these probably humic substances.

From the new tested tracer materials, the tinopal ABP was not satisfactory, mainly due to poor detectability. In contrast, the fluorescently dyed spores were found to be very effective in respect to their more easy detectability with help of fluorescence microscopy. The lithium proved again as a good tracer, while the sodium salt and also the detergent gave relatively poor results mainly due to their limited sensitivity of detection. The information on the influence of sorption on the migration of the dissolved tracers was limited because, due to the distribution on different injection points, no direct comparison could be made. Interesting was that the particulate spores travelled also on flow connections which beforehand were expected to have low permeability. The experiments are detailed by A. BÖGLI & T. HARUM (1981).

In the experiments in the Neuenburg Jurassic the scale of the applied tracers was almost the same as in the Muota valley, with the difference that not lithium but po-

tassium chloride was used. Also the experiences on tracer efficiency and analytical problems were comparable. The sodium and potassium salts however gave better results, mainly due to the fact that they could be applied on the basis of earlier tracing experiences in this system in injection points which matched their suitability (I. MÜLLER & J. G. ZÖTL, 1980).

Most of the comparative studies of underground water tracing had been made in karst and to a lesser extent also in fissured rock aquifers where the influence of the solid phase surface on the tracer transport (e.g. by sorption, filtration etc.) is relatively limited. However, much more serious problems in this respect arise in unconfined porous aquifers with a much larger ratio between of solid phase surface and water volume. Because the application of water tracing has increasingly turned to investigations in such media (e.g. for demarcation of water protection zones or dispersion of contaminants), there is strong demand for knowledge on suitability of the established tracers and possibly new more perfect materials for this purpose. The experiments in the Langeten valley were an attempt in this direction. The respective aquifer consists of alpine Quaternary gravels which is developed over an extension of more than 3,000 m by a good number of observation wells and has a downstream outlet in springs.

In the experiment six tracers were applied in three pairs: 20 kg of eosin and 100 kg of tinopal ABP, 10 kg of uranine and 100 kg of borax, and 205 g of indium-EDTA together with 15 m^3 of a sodium chloride brine were injected on April 28, 1979 into three selected wells, with flow distances up to about 3,000 m to the downstream spring area. Sampling from wells and springs was done for about one year. While uranine could be followed over the whole extension of the aquifer, the borax was only found in the most close observation well with a roughly comparable breakthrough curve but however half the relative maximum concentration. The yield of uranine in the downstream springs was about 5 %. The eosin could be followed half the way at much lower concentrations as the uranine. There is some conjecture that not all wells were in positions to be reached by the main body of the tracer clouds, a problem that generally occures in porous media tracings as a result of mainly small transversal dispersion. The tinopal could not be detected at all. The low concentrations of eosin indicated a possible maximum concentration of tinopal below its detection limit; furthermore the tinopal detection was impaired by variable background fluorescence. Finally, the indium was detected also only in two wells in the upper region of the aquifer at low concentrations, while the sodium chloride also was not detected (F. BAUER et al., 1981).

The results of the investigations are also reported in the symposium proceedings (HYDROL. KOM. SCHWEIZ. NATURF. GES., 1982).

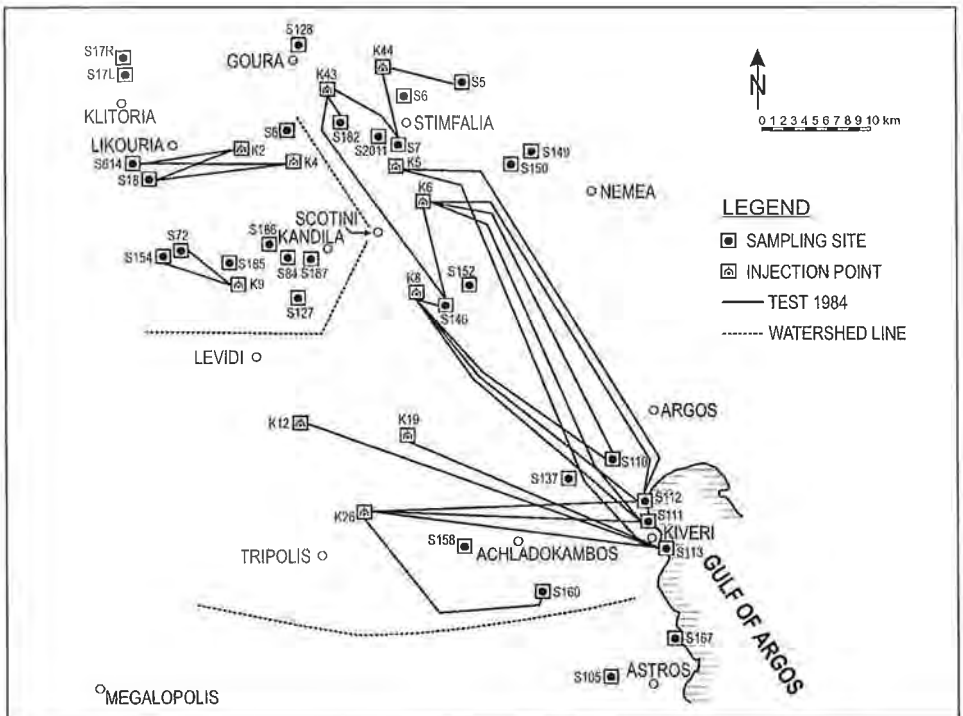
2.5. Combined Tracing Experiments in the Peloponnesus (1984–1985)

The next joint tracing action of ATH was organized by the IGH (Institut für Geothermie und Hydrogeologie, Graz) and IGME (Institute of Geology and Mineral Exploration, Athens, Greece). The experiments were performed in the eastern part of the Peloponnesus. There were mainly two aims in the experiments:

- to determine residence times and flow velocities of the karst water and the distribution of the water from individual sinkholes over the different springs as well as study of the recharge and storage processes in this complex system,
- to do comparative studies of suitability and behaviour of the established and the "new" tracers on the different flow paths, especially over the long flow distances given here.

The experiment started with the injections on March 30, 1984 at the end of the snow melt, which is an important contribution to the karst water recharge; the Ziria was still snow covered down to about 1,600 m a.s.l.

Seventeen different tracers were applied in the combined experiment (the numbers (K*) indicate the injection points in fig. 2.3):



TRACER INJECTION

K2	Pyranine Sodium chloride	K12	Phagus H5
K4	Uranine	K19	Coliphage "f_2"
K5	Rhodamine	K26	Chromium-51
K6	Red spores		Coliphage "G" and "f_2"
K8	Naphtionate	K43	Tinopal
	Fluorescent spores		Fluorescent spores (Tinopal)
	(Acridinorange)		Lithium chloride
K9	Eosin	K44	Blue spores
	Potassium chloride		

Fig. 2.3: Underground water connections between karst poljes (katavothre) and springs in the investigation area of the Peloponnesus, found by tracing tests with artificial tracers (from A. MORFIS & H. ZOJER, 1986).
Im Markierungsversuch 1984 im Peloponnes zwischen Poljen und Quellen mit künstlichen Markierungen nachgewiesene Fließwege (aus A. MORFIS & H. ZOJER, 1986).

- the six fluorescent tracers uranine (K 4), eosin (K 9), rhodamine B (K 5), tinopal CBS-X (K 43), pyranine (K 2) and naphthionate (K 8), the last two for the first time in this joint tracing campaign,
- the salt tracers sodium chloride (K 2), potassium chloride (K 9) and lithium chloride (K 43),
- the radioactive tracer chromium-51-EDTA-complex (K 26),
- two coloured spores, blue (K 44) and red (K 6),
- two fluorescent spores, dyed with tinopal (K 43) and with acridin orange (K 8),
- the three bacteriophages H5 (K 12), coliphagus G (K 26) and coliphagus f2 (K 19).

In five cases more than one tracer was applied in an injection site:

- tinopal, the tinopal-dyed spores and the lithium chloride (into the katavothre of Skafidia, K 43),
- the acridin-dyed spores and the naphthionate in the Stymfalia polje (K 8),
- the chromium- 51 and phages G at the Kanata sinkhole (K 26),
- the eosin together with potassium chloride at Hotoussa (K 9),
- the pyranine together with sodium chloride at Feneos W (K 2).

The reappearance of tracers was checked in 37 springs; some of them, S 113 and S 106 (Anavalos) were submarine karst springs in the Gulf of Argos, where special installations for sampling had to be made. Furthermore seven small submarine springs at the Argos coastline were included. The investigations were mainly made by taking water samples which were brought to the respective laboratories. In Kiveri, at the Gulf of Argos coastlinie, a field laboratory was installed, where mainly the tests on the phages were performed, and simultaneously this lab served also as a logistic center for collecting and registration of the water samples. The observation by water samples lasted mainly until the end of April 1984 except monitoring for salt concentrations and exposition of charcoal bags which was continued over several months.

The samples for the dye tracer investigation were brought as fast possible to Athens for spectrofluorimetric measurement in the newly installed IGME laboratory. In addition, the tracer breakthroughs were also monitored at two springs, Ladona (S 18) and Panagitsa (S 72) in situ with field filter fluorimeters; in addition, in numerous springs charcoal bags for collection of dye tracers were exposed, mainly over intervals of one day in the begin and several days with proceding of the experiment; charcoal sampling was extended over several months. Examples of comparison of results from in situ measurement versus those of samples as well as from charcoals are given in fig. 2.4. It was found that pyranine which came out in Ladona spring (S 18) decayed strongly within several days in the samples; the uranine which appeared almost simultaneously in the same spring was also degraded but at a lower rate. Eosin proved to be fully stable in the samples and rhodamine B also did so. A more or less funny but not unimportant experience was made during the later analysis of the many samples in the IGME laboratory: here a fluorescence was detected which could be attributed to rhodamine B on behalf of the spectra, was found sporadically in samples from the whole study area. This was in a manner which could not be explained with hydraulic flow paths. Finally a connection with the pretty red nail paint of a lab woman operating the spectrofluorimeter was supposed. After removing the paint and thoroughly cleaning the hands the ghostly tracer evidence had vanished. However, this may lighten the fact how easy, considering the enormous sensitivity of fluorimetry, measuring results may be impaired.

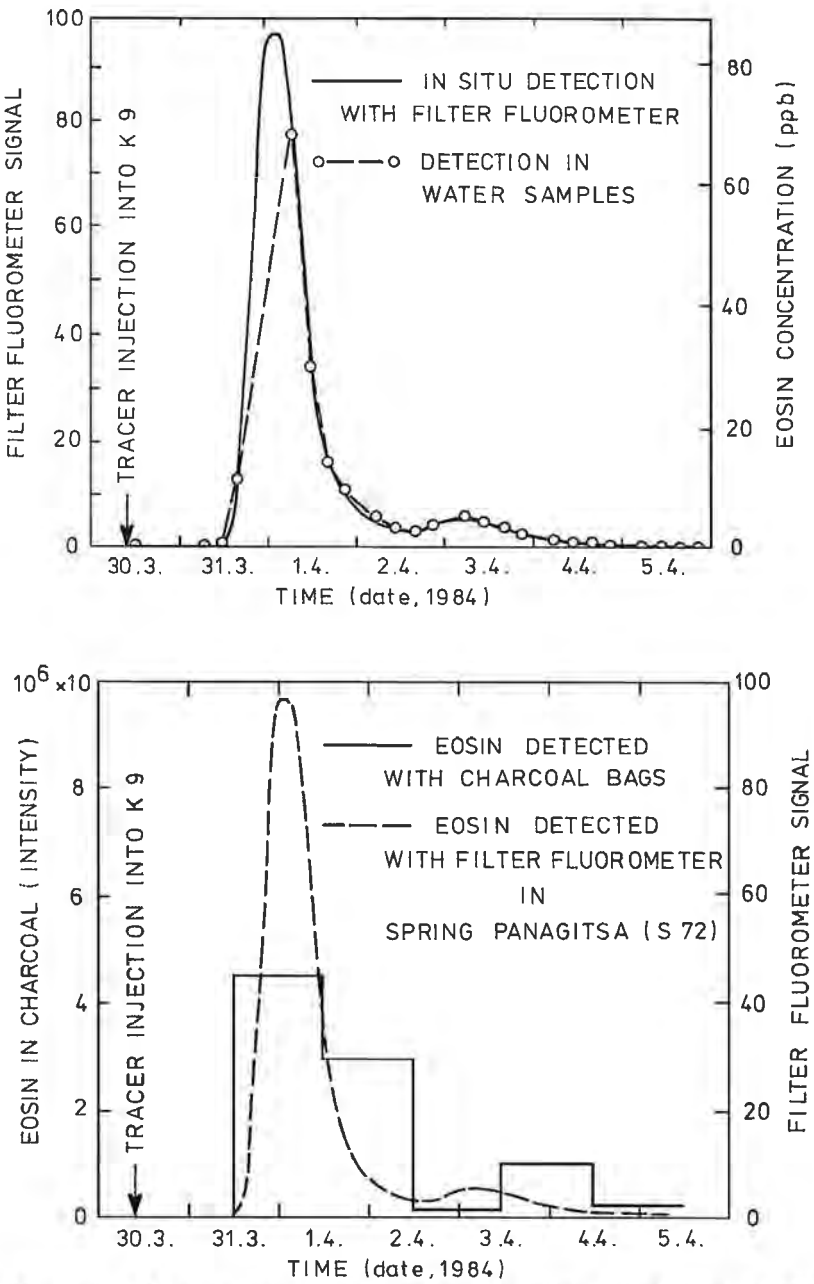


Fig. 2.4: Comparison of tracer measurements: eosin breakthrough in spring Panagitsa (S 72) in the 1984 Peloponnesus test (from A. MORFIS & H. ZOJER, 1986). Up: sample measurements vs. in situ-fluorimetric detection; down: charcoal sampling vs. in situ-fluorimetric detection. Vergleich von Tracermessmethoden: Der Eosindurchgang in der Quelle Panagitsa (S 72) im Markierungsversuch 1984 im Peloponnes (aus A. MORFIS & H. ZOJER, 1986). Oben: Probenmessung im Vergleich zur in situ-Fluorimetrie, unten: Aktivkohlemessung im Vergleich zur in situ-Fluorimetrie.

The radioactive chromium was monitored in situ in some stations with immersed probes. In other springs sampling by flow of water through charcoal columns was applied; by this enrichment the detection limit was specified as one nCi/m³. The injected amount of chromium–51 was 11 Ci. Compared with uranine, this would be equivalent with about 20 kg of the dye, but certainly at needed measuring times of almost a quarter of an hour per sample. The chromium-51, injected into the sinkhole of Kanata, appeared with a yield of 95 % in the spring of Kiveri (S 113) and a very small rate at Xovrios (S 160).

Complex results were obtained with the spores. Only the blue dyed spores appeared in larger numbers in the spring Stymfalia (S 7). All other spores and also the blue spores in other springs appeared only sporadically in very small numbers, so that no sound values for the reappearance and only the flow velocity to S 7 can be given. At least some flow connections were proved, albeit with low percentages of the infiltrated water or poor conditions for the transport of the particulate tracers.

The comparison of tracers which had been injected into the same sinkhole gave only limited information. The acridine orange dyed spores were only found sporadically at low counts in springs S 110, S 111 and S 112 (Argos group) while naphthionate was only detected at spring S 110 at low concentration of 0,3 ppb with unclear differences of the registrated breakthrough time between different involved laboratories. The combined tracing with lithium chloride, tinopal and tinopal-dyed spores in K 43 gave only sporadic indications close to the detection limit, in the spring Kastania (S 182) where alltogether five spores were found and also some indications of lithium; the existence of a flow connection was hardened by two samples with tinopal just above the detection limit but not sufficient for construction of breakthrough curves for detailed comparison on this obviously meagre flow connection. Better information was obtained from the injection of chromium-51 and phages G, both injected in Kanata. Both were detected in the Kiveri spring (S 113) and at smaller rate at Xovrios (S 160) in the same time period. However, in contrast to the homogeneous breakthrough curves of the chromium tracer with calculated outcome of more than 95 %, the phage yielded only about 20 % with more rugged breakthrough curves; another breakthrough of the phages in Lerni S 111) was not found with the chromium tracer. Good agreement was obtained between the pyranine and the sodium chloride at spring Ladon (S 18), as well as in the flow time as in the reappearance of > 67 % and 80 % respectively (the pyranine was already partially degraded when quantitatively analysed). The situation with the uranine and potassium chloride injected in K 4 was similar with corresponding flow velocities to spring S 18 (uranine: 2,616 m/d and potassium chloride: 2,717 m/d) and reappearances (uranine: 86 %, salt: 80 %).

2.6. Combined Tracer Experiment in the Lurbach System 1988

After the past multitracer experiments with many injection points in a large study field, it was now decided to perform a tracing action with limitation to one flow system for comparison of all actual tracers under identical flow conditions. The hydrogeologically and hydraulically very well explored Lurbach system near Graz was chosen for this purpose. This karst system had already served as a test field for the first comparative test field in the first common experiments 1966. Seven institutes participated in the tests. The test flume was the creek which flows underground, partly with open access and partly hidden, through the Lurgrotte cave system.

The tracers were injected within the cave into the creek which shortly downstream of the injection site disappears in the underground. The distance to the monitored karst

springs was about 3,000 m. The tracing was made on June 28, 1984. The tracers were injected with short intervalls in the sequence as shown in tab. 2.1.

The karst springs Hammerbach, six small adjacent springs to the Hammerbach and the Schmelzbach were monitored for the tracer reappearance. Mainly the samples of the Hammerbach were distributed between the involved eight institutes. But all other sampling points were checked at least for the dye tracers by the "Institut für Geothermie und Hydrogeologie" (IGH) in Graz. The fluorescent tracers were measured by all institutes as far as they were equipped for this tracer type, except the naphthionate which was only measured by the "Institut für Hydrologie in Freiburg" and by GSF. In the analysis of the dyes difficulties arose by the spectral overlap of them in the mixture which had to be overcome by special sample treatment and correcting calculations. So far, this experiment was also a comparison of the analytical performance of the involved laboratories. Microspheres were only measured by W. KÄSS, bromide and indium-114m only by the GSF, phages only by the Institute of Biology in Ljubljana, chloride only by the IGH, and lithium only by W. KÄSS and GSF.

For the comparison of the different tracers the breakthrough curves from the Hammerbach were normalized to the injected amounts. It was decided to regard the bromide which appeared to be the most conservative tracer, as a reference. All the tracers showed breakthrough curves of the same shape as it could be expected in this system with low influences e.g. from sorbing surfaces. However, there were differences in the yield (reappearance) and in the stability of the different tracers which has to be seen under the fact that the karst inflow is somewhat contaminated by municipal wastes. In detail the following characteristics were found:

- **Uranine** showed the same relative reappearance as the bromide (RRB = 100 %) except the samples which were measured by GSF with delay and showed some decay of uranine in some of them (Fig. 2.5).
- **Eosin** showed a little diminished concentrations in the peak maximum and stronger tailing which could be caused by some reversible sorption. RRB was 81 % by one institute and 103.5 by two others which could reflect difficulties in the resolution from the other dyes.

Tab. 2.1: Tracer test at the Hammerbach, June 28, 1988: tested tracers, their injected amounts and time of injection (after H. BEHRENS et al., 1992).
Vergleichender Tracertest am Hammerbach, 28. Juni 1988: die getesteten Tracer, ihre Eingabemengen und die Eingabezeiten (nach H. BEHRENS et al., 1992).

Tracer	Amount	Injection time
Pyranine	5 kg	09.00–09.02
Microspheres, YO, 0,89 µ	$6{,}5 \times 10^{10}$	09.15
Microspheres, YG, 0,95 µ	$5{,}3 \times 10^{10}$	09.15
Microspheres, BB, 1,00 µ	$4{,}5 \times 10^{10}$	09.15
Phages P22H5	8×10^{14}	09.28
Rhodamine B	4 kg	09.34–09.36
Sodium bromide	50 kg	09.55–09.57
Lithium chloride	100 kg	10.10–10.12
Indium-114m-EDTA	60 mCi	10.22
Sulforhodamine G	3 kg	10.25–10.29
Eosin	5 kg	10.35–10.38
Naphthionate	25 kg	10.45–10.48
Uranine	2 kg	10.50–10.54

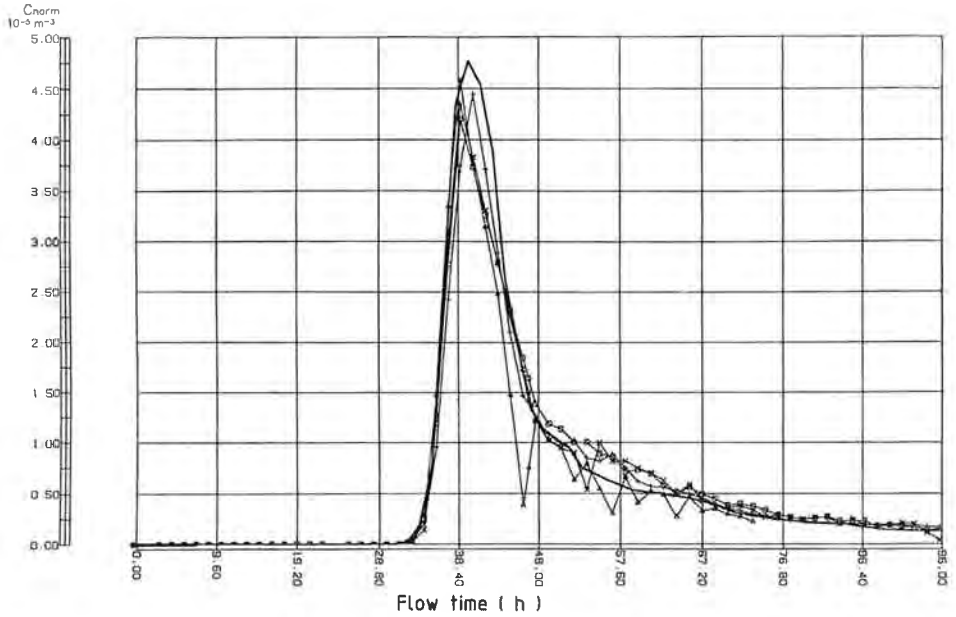


Fig. 2.5: Tracing experiment 1988: breakthrough curves at Hammerbach spring of the tracer uranine measured by different laboratories, compared with bromide as a reference (boldfaced line), after H. BEHRENS et al. (1992).
Markierungsversuch 1988: Durchgang des Tracers Uranin in der Hammerbachquelle nach Messungen verschiedener Laboratorien im Vergleich zum Bromiddurchgang (fette Kurve), nach H. BEHRENS et al. (1992).

- **Naphthionate** had a RRB of 81.5 % in soon measured samples, while the samples measured at GSF with large delay showed stronger decay (RRB of 23.5 %).
- **Pyranine** suffered strongly from its instability with RRB's of 21.5 and 13 % and only 3 % in the samples measured with delay at GSF.
- **Sulforhodamine G** had clearly losses by sorption; however, the RRB's varied strongly with 106, 74, 73 and 42 %, probably because of difficulties in the analytical separation.
- **Rhodamine B** showed even stronger losses by sorption with RRB's of 64, 58 and 46 %.
- **Lithium** had a RRB of 122 % probably due to difficulties in a precise subtraction of the natural background. The breakthrough curve showed some reduction in the peak and enhanced tailing indicating an influence of reversible sorption.
- **Indium-114m** had a RRB of 100 %. However, the breakthrough curve indicated a small delay in the peak and enhanced tailing. This could perhaps be attributed to incomplete complexation – the radiochemical preparation was made under rough field conditions just on the site.
- **Microspheres** of the three types YO, BB and YG, only the uncharged YG type with a polystyrene matrix reappeared with a RRB of 14 %, while the YO and BB microspheres with a positively charged carboxylate surface completely disappeared. However, the concentrations of the microspheres fluctuated extremely from sample to sample, indicating a not yet understood factor in the transport of the particles (Fig. 2.6).

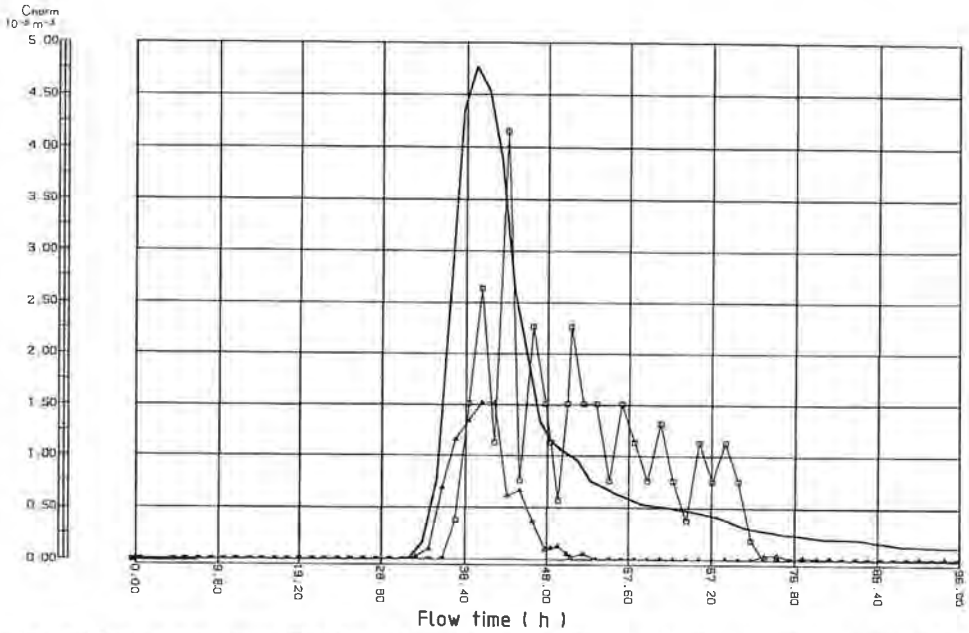


Fig. 2.6: Tracing experiment 1988: breakthrough curves at Hammerbach spring of the tracers polystyrene microspheres (squares) and phage P22H5 (triangles) compared with bromide as a reference (boldfaced line), after H. BEHRENS et al. (1992).
Markierungsversuch 1988: Durchgang der Tracer Polystyrol-Mikrokugeln (Quadrate) und Phagen P22H5 (Dreiecke) im Vergleich zum Bromiddurchgang (fette Kurve), nach H. BEHRENS et al. (1992).

The microspheres were together with the phages the only tracers which reappeared at very low counts also in the Schmelzbach and thus indicated a very weak flow connection to this outlet (RRB = 0.1 %).

- **Phages** reappeared with a breakthrough curve similar to that of the dissolved tracers in the Hammerbach spring, however, with lower recovery (RRB = 4.6 %) and with less tailing (Fig. 2.6), a behaviour which is frequently observed in the breakthrough of particulate matter due to transport prevailing in the main flow.
- **Chloride**, this tracer was that chloride which with the lithium salt necessarily was injected (chloride content in the lithium chloride: 83.3 %). The breakthrough curve of this very conservative tracer was of good shape, however, due to uncertainties in the natural background values, the recovery was obtained with RRB = 132 %.

Maps of the study area with its hydrogeologic and hydrographic evaluation and detailed description of the experiments are given by H. BEHRENS et al. (1992).

2.7. Further Comparative Experiments

More tracing tests have been made in which the ATH group was involved. One series was made in a fissured rock system at Lindau (SW Germany) which is developed by a tunnel system (T. HIMMELSBACH et al., 1992). Numerous tests with different tracers have been performed in the porous aquifer testfield at Merdingen in the upper

Rhine valley (A. DE CARVALHO DILL et al., 1992). Details on the work in these two study fields can be found in special chapters in this issue. Finally, tests were also going on in the Slovenian karst in the period from 1993–1995 (A. KRANJC, 1997).

2.8. Résumé

Water tracing is an important tool in hydrology and hydrogeology to obtain information e.g. on flow connections, on the flow velocities or residence times on these flow connections, yields of water reservoirs, vulnerability of water supplies, the fate of disposed waste, and more. It is important to know how well this tool works, where and in which manner it can be applied and where not or only with reservation, where deficits are and how these can be overcome. The past work of the ATH was mainly dedicated to this task. The experiences in the tracing of groundwater have shown that incompetent application of the tracing techniques, so easy they appear (just throw any tracer substance into a sinkhole and look for its reappearance), can lead to wrong results. It has been found that in groundwater tracing the structure of the investigated systems has a strong influence on the tracers performance and that vice versa the tracer properties play a role in this interaction. The main problems are sorption of tracers, filtration or sedimentation (particulate tracers), instability, perturbation of the tracer detectability by background signals etc. So far, the "ideal tracer" which is not impaired at all and yields the desired information correctly in all respects, has not yet been found and is not likely to come in the future. However, competent application of the knowledge available until now is a sound basis for succesful work with the tool of water tracing.

During the work of the ATH good methodological progresses have been made e.g. in the detection techniques of the most important tracers, the fluorescent dyes. The range of these and other tracers has been extended by several new tracers. Important progress was brought by applying the procedures on the field of contaminant transport. Sufficient experience has been gained by the practical comparative application of the tracing techniques, such that its systematic evaluation is a good starting point for continuing work on water tracing development.

3. Test Sites

3.1. Glaciers (K. GRUST, W. KÄSS)

It has been argued that meltwater movement through temperate glaciers is analogous to groundwater flow in karst aquifers (R. L. SHREVE, 1972, D. E. SUGDEN & B. S. JOHN, 1976). In both systems, flow occurs through a porous aquifer as well as through a fissured system of comprising caverns and cavities. However, the chemical and physical qualities of water in the two systems are quite different (Tab. 3.1).

Salt tracers have previously been used in groundwater investigations including lithium chloride (LiCl) and strontium chloride ($SrCl_2 \cdot 6H_2O$) (W. KÄSS, 1998).

Due to the very low levels of mineralization in glacial meltwaters, the use of salts seemed to be opportune in tracer experiments on glaciers. The natural concentrations of lithium and strontium in the meltwaters of Vernagtferner (Province Tyrol, Austria) are approximately 1 µg/l for lithium and 5 µg/l for strontium. A pre-test at Unteraar

Tab. 3.1: Chemical and physical qualities of water in karstic and glacial drainage systems. Chemische und physikalische Eigenschaften von Karst- und Gletscherwässern.

Parameter	Karst water	Glacier water
Temperature	Medium seasonal surrounding temperature plus 2–4° C	0–1° C
Conductivity	400–650 µS/cm	4–12 µS/cm
Turbidity	0.1–30 TU/F	5–500 TU/F

glacier (Kanton Valais, Switzerland) proved that useful breakthrough curves could be obtained with lithium chloride.

3.1.1. Comparative Tracer Tests at Vernagtferner

A series of experiments to investigate the behaviour of salt tracers in comparison with well known fluorescent dye tracers were undertaken at Vernagtferner, a 9 km² temperate glacier in the Oetzvalley, Austria, in August 1998 (Fig. 3.1). The tracers ura-

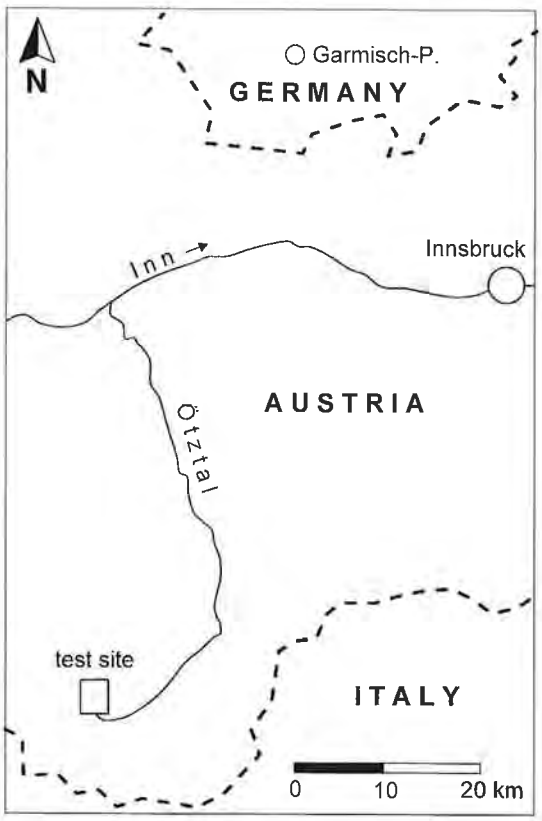


Fig: 3.1: Location map of the geographic situation at Vernagtferner. □ – test area, fig. 3.2. Übersichtskarte zur geographischen Lage des Untersuchungsgebietes. □ – Untersuchungsgebiet, Fig. 3.2.

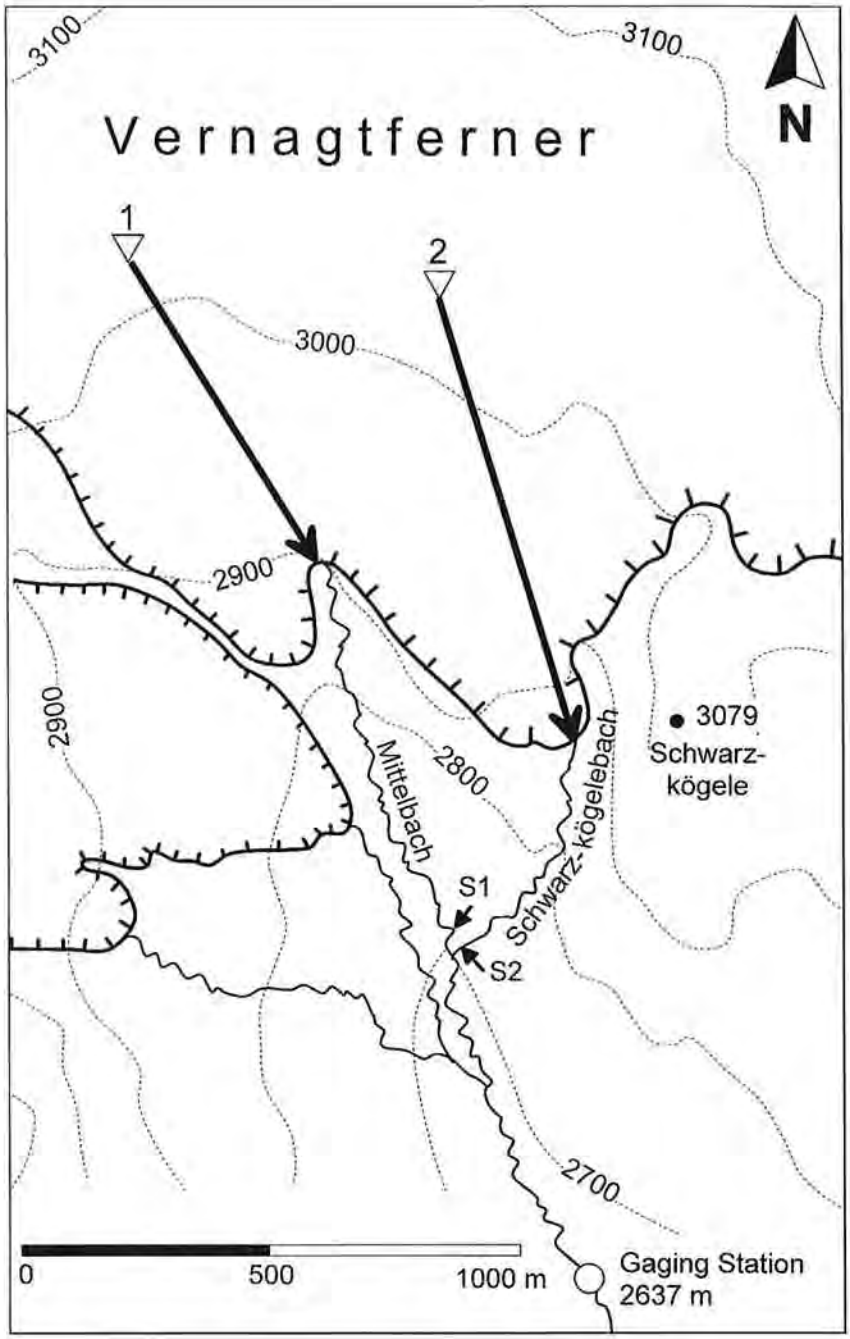


Fig. 3.2: Test area at Vernagt glacier. ▽ – injection points 1 and 2, ↙,↖ – sampling points S_1, S_2, thick arrows – hypothetical subglacial water flows. Isohypses in metres above see level. Kartenskizze des Untersuchungsgebietes auf dem Vernagtferner. ▽ – Einspeisestellen 1 und 2, ↙,↖ – Beobachtungsstellen, dicke Pfeile – angenommene direkte Abflussbahnen der Markierstoffe.

nine, sulforhodamine B which are dyes, lithium as lithium chloride and strontium as strontium chloride which are salts, were injected simultaneously into a number of moulins in the ablation area. Two experiments (Fig. 3.2) are presented here, details of which are shown in tab. 3.2.

Tab. 3.2: Details of multiple tracer experiments at Vernagtferner, August 1998.
Daten zu den Mehrfach-Markierversuchen am Vernagtferner, August 1998.

	Experiment 1	Experiment 2
Injection point	Moulin, 3,022 m a.s.l.	Moulin, 3,015 m a.s.l.
Injection date/time	9. August, 1998/14.35	11. August, 1998/11.25
Tracer	weight [kg]	weight [kg]
Uranine	0.04	0.10
Sulforhodamine B	0.10	0.20
LiCl/Li	0.89/0.146	1.12/0.18
$SrCl_2 \cdot 6H_2O$/Sr	3.089/1.015	4.0/1.314
Sampling point	Mittelbach	Schwarzkögelebach
Distance from injection point [m]	1,592	1,474
Distance from glacier snout [m]	525	570
Discharge [m^3/s]	3.52	3.70

3.1.2. Results

The similar behaviour of the simultaneously injected tracers in the glacial drainage system are clearly evident (Fig. 3.3). All four tracers show very similar return curves, transit times, flow velocities, and dispersivities. However, recovery rates differ significantly, ranging between 24 and 92 %. The recovery rates of each of the tracers in both experiments are shown in tab. 3.3.

Tab. 3.3: Recovery rates for the tracers used in experiments 1 and 2.
Wiedererhalt der in den Versuchen 1 und 2 verwendeten Markierstoffe.

Tracer	Experiment 1	Experiment 2
Sulforhodamine B	80 %	88 %
Lithium	76 %	73 %
Uranine	54 %	61 %
Strontium	25 %	23 %

High recovery rates for **sulforhodamine B** are a consequence of both little adsorption to suspended sediments in glacial runoffs and its light-resistance. The **lithium ion**, even though light-resistant, shows a light tendency towards either sorption or ion-exchange on bedrock and turbid matters. **Uranine** has been proven to be light-sensitive (P. L. SMART & I. M. S. LAIDLAW, 1977, H. BEHRENS & G. TEICHMANN, 1982), and intensive radiation with a high UV-content at midday and at high altitude (nearly 3,000 m) may have caused photochemical decay of uranine in the proglacial stream before the observation point. The **strontium ion** seems to be strongly sorptive and tends to ion-exchange.

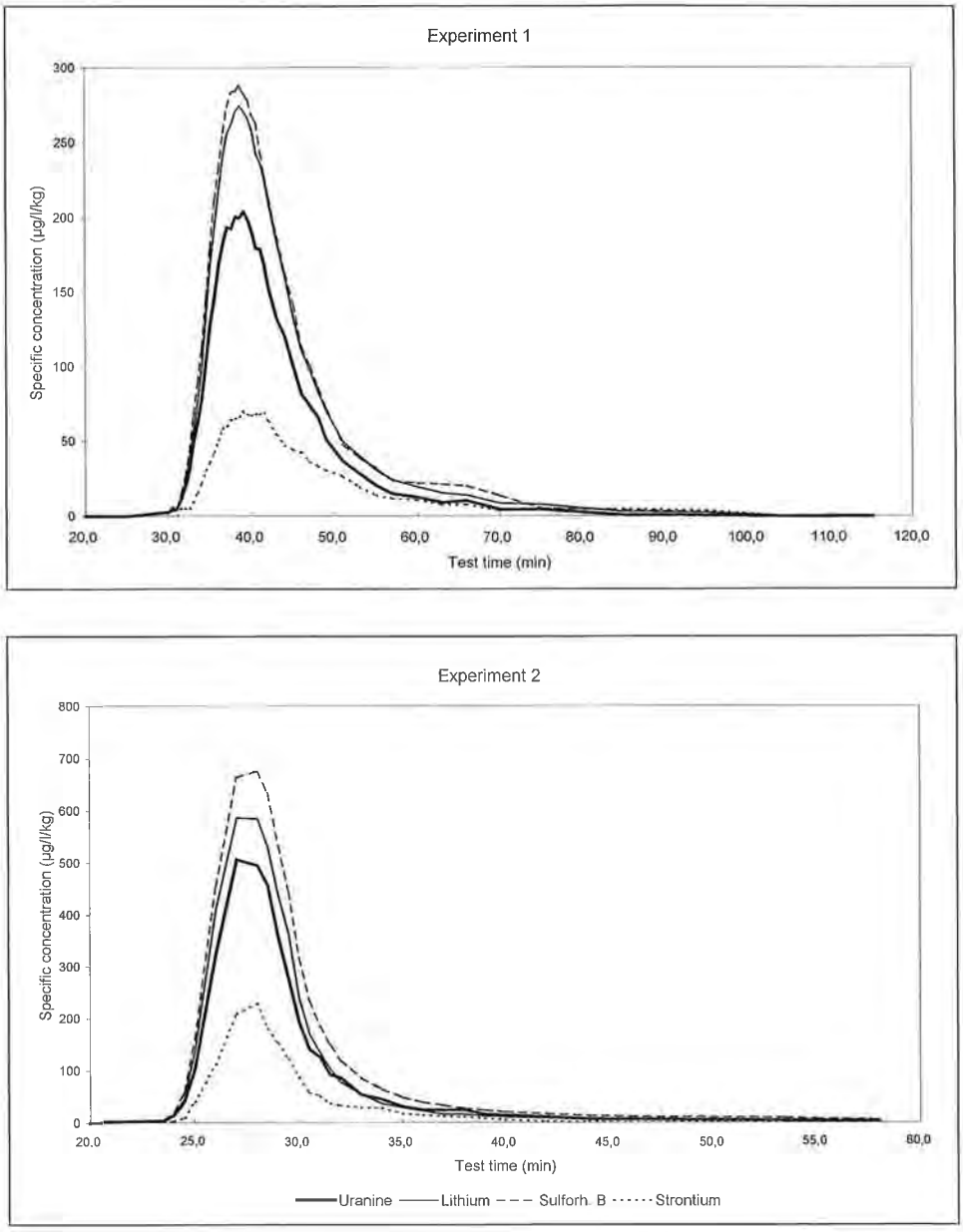


Fig. 3.3: Specific breakthrough curves of the four different tracers of the experiments 1 and 2. Normierte Durchgangskurven von den vier Markiermitteln der Versuche 1 und 2.

3.1.3. Conclusions

Of the four tested tracers, sulforhodamine B and lithium chloride appear to be the most useful tracers in glacial meltwaters. Uranine is a useful tracer, if it is not exposed to intensive sun light during the experiment. Strontium chloride shows significant

recovery losses in glacial waters. Thus, to obtain adequate return curves relatively high amounts are necessary, which leaves the tracer far more extensive and less practical compared to the other tracers tested.

Acknowledgements

We thank the Commission for Glaciology, Bavarian Academy of Sciences, Munich, for their great co-operation, logistic support and for provision of facilities at their field station. Many thanks to M. SIEBERS and Th. SCHULER for their help and comradeship in the field.

3.2. Comparative Tracer Studies in a Highly Permeable Fault Zone at the Lindau Fractured Rock Test Site, SW Germany

(R. BÄUMLE, F. EINSIEDL, H. HÖTZL, W. KÄSS, K. WITTHÜSER, S. WOHNLICH)

3.2.1. Introduction

During the last decade, tracer techniques have been established as a method to characterize flow and transport processes in fractured rock. Among the most commonly used tracers are fluorescent dyes, salts or microparticles (W. KÄSS, 1998). For most purposes conservative tracers with non-reactive behaviour are requested. Comparative tracer studies in fractured rock environments are nevertheless quite sparse.

S. S. D. FOSTER (1975) and I. NERETNIEKS (1980) pointed out that the advective-dispersive transport of solutes in the fractures may be significantly influenced by a diffusive transport into the adjacent rock matrix. Hence, the varying diffusion coefficients of the tracers must be considered within comparative tracer studies.

Former investigations at the Lindau rock test site focused on the site characterization and on the methodology of solute transport modelling in fractured rock (T. HIMMELSBACH et al., 1992, 1998, R. BÄUMLE et al., 2000). Although many different tracers were utilized by these investigators, no methodical study was performed until now in order to achieve a comparative tracer characterization at the Lindau test site.

The objective of this paper hence is to describe and to compare the advective-dispersive and the diffusive transport behaviour of the most common and of some recently developed artificial tracers for small-scale experiments in fractured rocks. Besides the comparative tracer study, methodological problems will be discussed which could be revealed by the validation of the applied transport models.

3.2.2. Hydrogeology

The Lindau test site (Fig. 3.4) is located within the Albtal granite Pluton (Southern Black Forest, SW Germany).

The sparsely fractured granitic rock is almost vertically intersected by a N–S striking ore dyke. The thickness of the dyke varies between a few decimetres and 3 m. The permeability of the dyke and its contact zone is some magnitudes higher than the permeability of the adjacent granitic rock as a result of intense fracturing by tectonic shear processes, hydrothermal alteration, increased weathering by descendant aqueous solutions and of cavities created by the dissolution of the more soluble ore minerals such as fluorite and baryte. The hydraulic conductivity of the granitic rock varies between 5×10^{-10} and 1×10^{-8} m/s whereas the K-values for the dyke range from 5×10^{-6} to 1×10^{-4} m/s (T. HIMMELSBACH et al., 1998) and may reach even higher values according to more recent investigations. Due to this permeability contrast, the dyke drains the

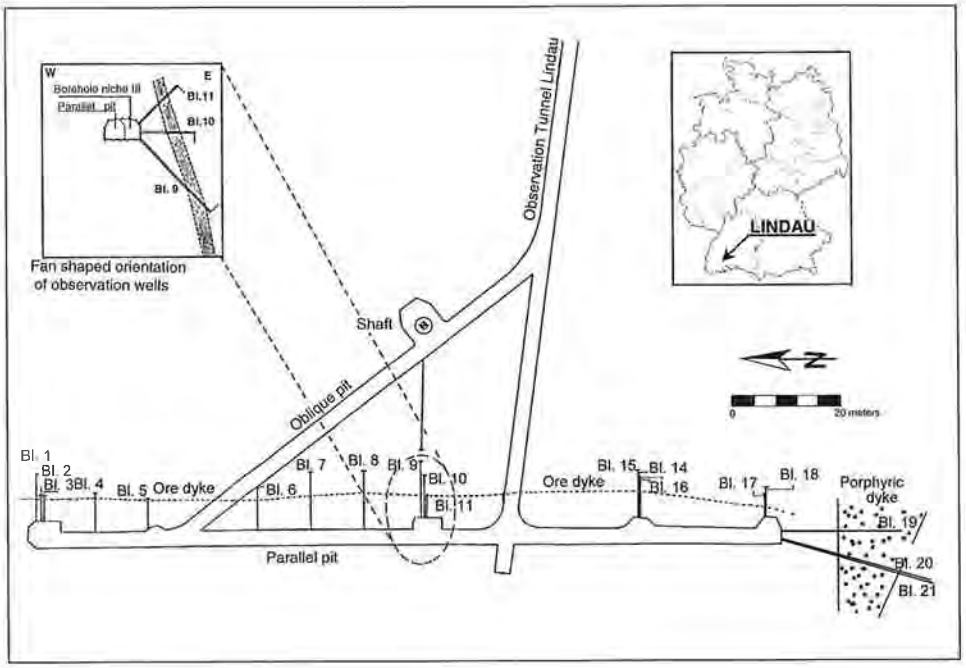


Fig. 3.4: Plan of the Lindau fractured rock test site showing the injection borehole Bl. 8 and the observation borehole Bl. 10.
Lageplan des Versuchsstollens Lindau mit dem Eingabebohrloch Bl. 8 und dem Beobachtungsbohrloch Bl. 10.

catchment and creates a trough of hydraulic head depression with steep hydraulic gradients on both of its sides. The dyke can be examined 80 m below the ground by the investigation tunnel sketched in fig. 3.4. Along the parallel pit altogether 19 boreholes were drilled into the ore body which served as injection and observation boreholes for the tracer tests.

3.2.3. Methodology

3.2.3.1. Test Configuration

Two forced gradient tracer experiments were carried out in the parallel pit. The tracers were injected into the fractured zone once a steady-state radial-convergent flow field was established around the observation well. The dissolved or suspended tracers were carefully poured into a tube and pushed into the borehole as a short pulse by a pressurized chase fluid. Both tracer experiments were performed in a discrete set of fractures connecting the borehole Bl. 8 with Bl. 10. An overview of the experimental design is provided in tab. 3.4.

Experiment no. 1 was carried out in March 1999. The recently developed fluorescent dye tracer T4 (F. EINSIEDL et al., 1999a, 1999b) and uranine were injected simultaneously into well Bl. 8. The tracer volume was 1 l and the injection time was comparable with experiment no. 2.

Experiment no. 2 was carried out in September 2000. The injected tracers included the fluorescent dyes uranine (C.I. Acid Yellow 73), pyranine (C.I. Solvent Green 7),

Tab 3.4: Summary of the experimental design for the two comparative tracer experiments. Zusammenstellung der Daten zum Versuchsaufbau der beiden Tracerexperimente.

Experiment no. 1										
Date: March 1999 Injection borehole: Bl. 8 Observation borehole: Bl. 10 Distance: 11.6 m				Production rate: 0.8 m³/h Injected tracer volume: 1 l Volume of chase fluid: 20 l						
Tracer:	Uranine	T4								
Injected mass [g]	0.5	0.25								
Experiment no. 2										
Date: Sept 2000 Injection borehole: Bl. 8 Observation borehole: Bl. 10 Distance: 11.6 m				Production rate: 0.6 m³/h Injected tracer volume: 2 l Volume of chase fluid: 5 l						
Tracer:	Uranine	Sulpho-rhod. B	Pyranine	Naph-thionate	Br^-	Cl^-	Li^+	Sr^{2+}	Fluores-brite YG	Fluores-brite Red
Injected mass [g]	1.0	5.0	5.0	20.0	362.0	436.5	85.5	198.5	–	–
Injected no. of particles	–	–	–	–	–	–	–	–	2.3×10^{10}	2.3×10^{10}

sulphorhodamine B (C.I. Acid Red 52) and sodium naphthionate, the salt tracers strontium bromide and lithium chloride and the fluorescent polystrene latex microspheres *Fluoresbrite™ YG* (yellow green) and *Fluoresbrite™ Red*. Fluoresbrite Red was used the first time as an artificial tracer. The microspheres with a diameter of 1 µ are electrostatically neutral. Further information on the chemical and physical properties of these tracers are covered in detail by W. KÄSS (1998). The average production rate during the experiment at the borehole Bl. 10 amounted to approximately 0.6 m³/h. The distance from the injection to the observation borehole is 11.6 m. Recent research at the Lindau rock test site highlighted the influence of the injection type on the measured breakthrough curves (BTC) for small-scale tracer experiments (K. WITTHÜSER, 2001). According to these results, the use of packer systems is recommended. A double packe was therefore inserted into the injection borehole Bl. 8. The packer test interval of 1 m corresponds to a volume of 3.4 l. The tracer volume (2 l) and the volume of the chase fluid (5 l) were reduced to the smallest possible amount in order to minimize the initial spreading of the tracer plume around the injection borehole. The injection could be accomplished within 20 s.

The fluorescent dyes were analysed using spectrofluorimetry (laboratories of the Institute of General and Applied Geology, University of Munich and of the Institute of Applied Geology, University of Karlsruhe). The lithium and strontium concentrations were measured by Atomic Emission Spectroscopy (laboratory of W. KÄSS). Ionic chromatography was used to determine the chloride and bromide content of the samples (laboratory of the Environmental Research Centre, University of Karlsruhe). The microspheres of the 250 ml samples were counted using a fluorescence microscope (laboratory of W. KÄSS).

3.2.3.2. Modelling Concepts

One-dimensional analytical solutions to the transport equation were applied for the modelling of the convergent flow tracer tests. The applied models postulate that the tracer behaviour is ideal, i.e. that neither sorption nor degradation or chemical reactions will considerably affect the tracer transport. Additionally, density effects are assumed to be negligible despite the high tracer input concentrations. It was furthermore assumed that the condition of an instantaneous injection which can be mathematically expressed by the DIRAC-delta function, is fulfilled.

The well-known ordinary Advection-Dispersion Model (ADM) by A. LENDA & A. ZUBER (1970) was considered an appropriate approach if the diffusive transport from the fractures into the adjacent rock matrix water is either negligible or, as for the microspheres, does not occur. The Single Fissure Dispersion Model (SFDM), developed by P. MALOSZEWSKI & A. ZUBER (1985), assumes that the fracture system can be substituted by a single fracture. This model accounts for diffusion processes into an adjacent infinitely extended matrix. The concentration C at the production well can be expressed in terms of the mean residence time (t_0), the Peclet number (Pe) and a third fitting parameter (a):

$$C(t,t_0,Pe) = \frac{aM}{2\pi Q}\sqrt{Pet_0}\int_0^t \exp\left[-\frac{Pe(t_0-\tau)^2}{4t_0\tau}-\frac{(\tau a)^2}{(t-\tau)}\right]\frac{d\tau}{\sqrt{\tau(t-\tau)^3}}, \qquad (3.1)$$

where τ is an integration variable. Q represents the average production rate and M the injected tracer mass. The model parameter (a) is defined in terms of the matrix porosity (n_p), the fracture half width (b), the molecular diffusion coefficient in free water (D_m), the tortousity factor for micropores (τ_p) and the constrictivity factor (ε) by:

$$a = \frac{n_p}{2b}\sqrt{\frac{\varepsilon D_m}{\tau_p}}. \qquad (3.2)$$

The SFDM has been applied successfully in earlier studies at the Lindau rock test site (e.g. T. HIMMELSBACH et al., 1992, 1994).

3.2.4. Results

3.2.4.1. Tracer Performance

Figure 3.5 shows the tracer BTC and the relative recovery RR for experiment no. 1. In comparison to the conservative tracer uranine, the new tracer shows the same transport characteristics during the flow through the fracture system. Thus, it can be used as a reference (ideal) tracer. The peak of the C/M-data and the tailing of the fluorescent dye T4 demonstrates a minor difference which can be interpreted as a result of matrix diffusion.

The BTC of the fluorescent dyes, the salt tracers and the microspheres obtained from the experiment no. 2 are presented in the fig. 3.6, 3.7 and 3.8. Each figure contains the uranine BTC as a reference. We prefer double logarithmic plots in this study because, in a log-log scale, small concentrations are better displayed and the tailings of the BTCs can be more easily distinguished from each other. The diffusive transport of the tracer into the adjacent matrix can be identified by a tailing with a slope of –1.5 (Y. W. TSANG, 1995). Overall, the presented BTCs obtained from this experiment are rather similar.

According to tab. 3.5, the **time of first appearance** varies between 1.17 h and 1.50 h. However, these differences do not solely represent the tracer behaviour, but can par-

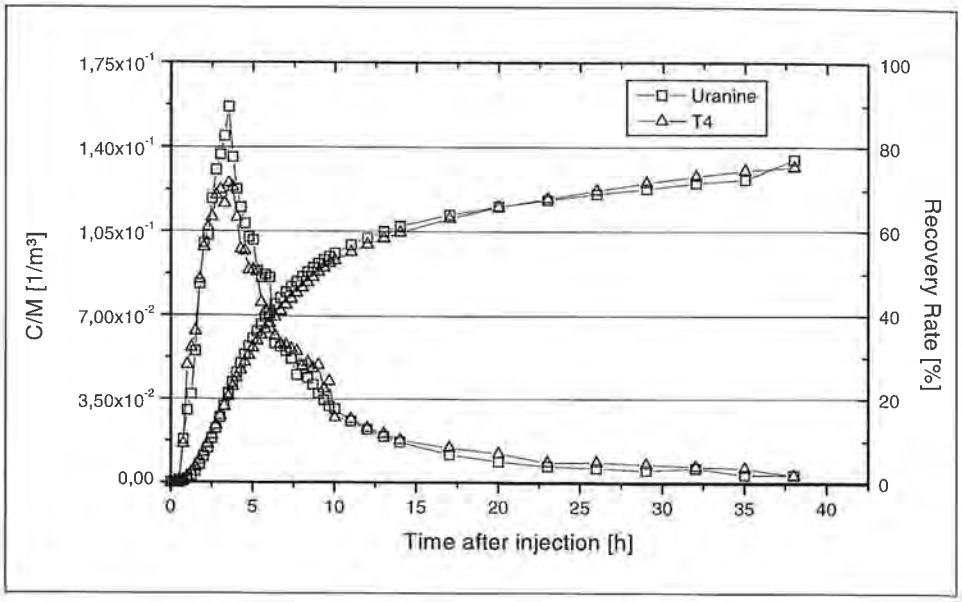


Fig. 3.5: Tracer BTC and relative recovery of the tracer T4 compared with uranine (experiment no. 1). Tracerdurchgangskurve und -rückerhalt des Tracers T4 im Vergleich zu Uranin.

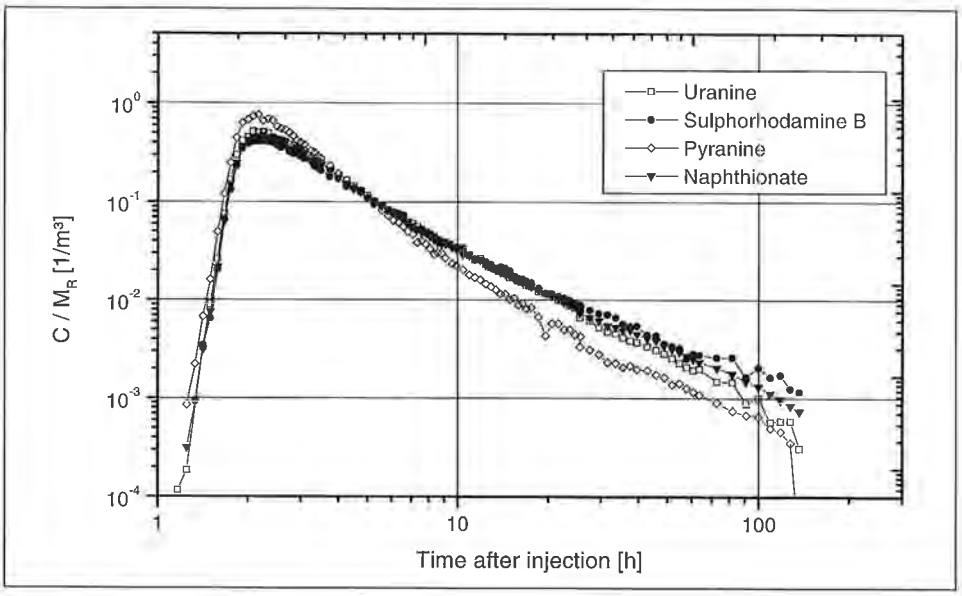


Fig. 3.6: Tracer concentration C divided by the recovered tracer mass M_R vs. time after injection for the applied fluorescent dyes (experiment no. 2). Tracerkonzentration C der Fluoreszenztracer geteilt durch die rückgewonnene Tracermasse M_R gegen die Zeit nach Einspeisungsbeginn.

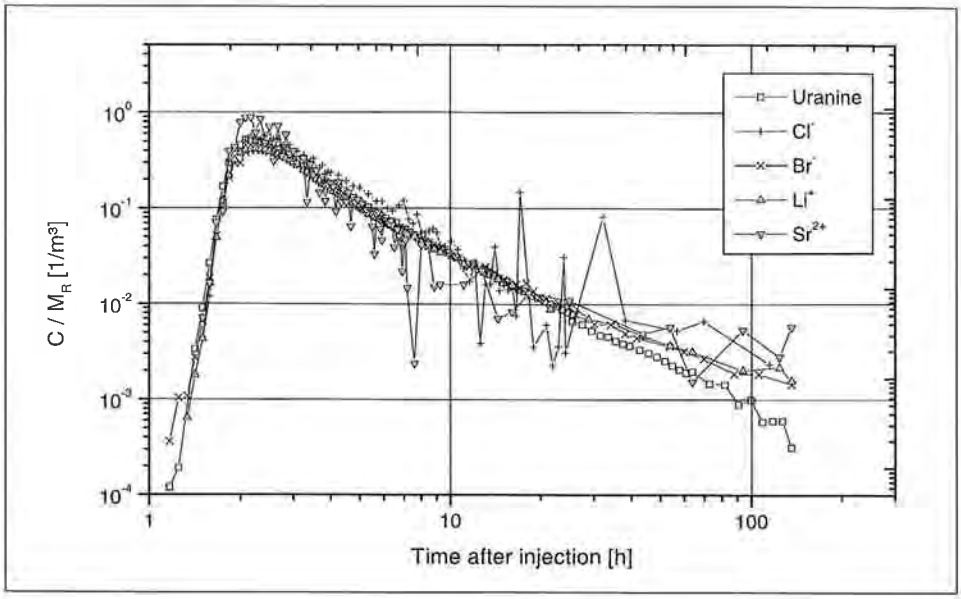


Fig. 3.7: Tracer concentration C divided by the recovered tracer mass M_R vs. time after injection for uranine and the salt tracers (experiment no. 2).
Tracerkonzentration C für Uranin und die Salztracer geteilt durch die rückgewonnene Tracermasse M_R gegen die Zeit nach Einspeisungsbeginn.

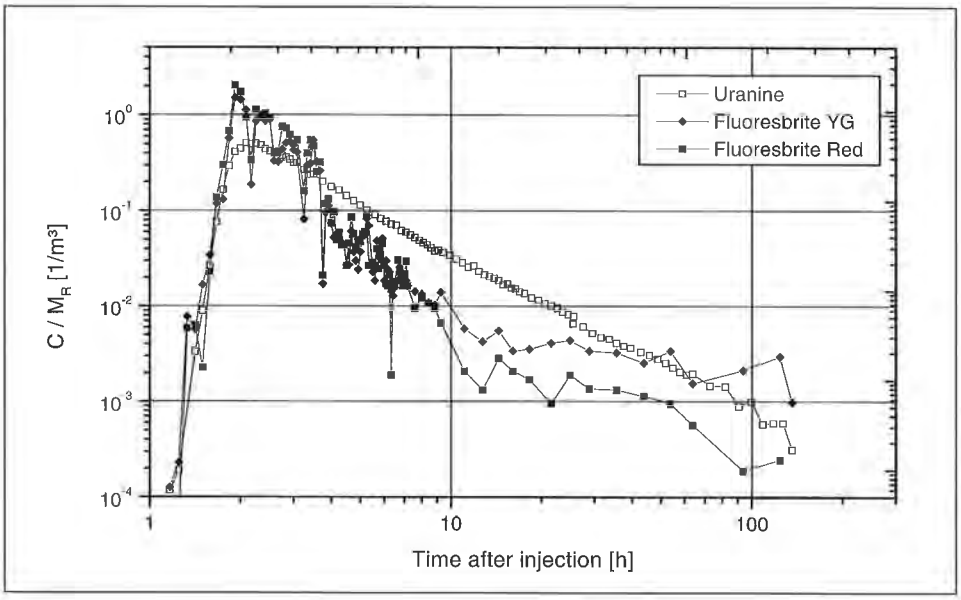


Fig. 3.8: Tracer concentration C divided by the recovered tracer mass/no. of particles M_R vs. time after injection for uranine and the microspheres (experiment no. 2).
Tracerkonzentration C für Uranin und die Mikropartikel geteilt durch die rückgewonnene Tracermasse M_R gegen die Zeit nach Einspeisungsbeginn.

Tab. 3.5: Time of first appearance (t_1), maximum actual flow velocity (v_{max}), concentration peak arrival time (t_{dom}), dominant actual flow velocity (v_{dom}), and relative recovery of the tracers applied in the comparative tracer experiments.
Erstankunftszeit (t_1), maximale Abstandsgeschwindigkeit (v_{max}), Zeitpunkt des Auftretens der Maximalkonzentration (t_{dom}), dominierende Abstandsgeschwindigkeit (v_{dom}) und relativer Tracerrückerhalt.

Experiment no. 1										
Tracer:	Uranine	T4								
t_1 [h]	0.75	0.75								
v_{max} [m/h]	15.5	15.5								
t_{dom} [h]	3.25	3.5								
v_{dom} [m/h]	3.56	3.31								
Recovery [%]	74	76								
Experiment no. 2										
Tracer:	Uranine	Sulpho-rhod. B	Pyranine	Naph-thionate	Br^-	Cl^-	Li^+	Sr^{2+}	Fluores-brite YG	Fluores-brite Red
t_1 [h]	1.42	1.33	1.25	1.25	1.17	1.50	1.33	1.50	1.17	1.25
v_{max} [m/h]	7.90	8.40	8.96	8.96	9.60	7.47	8.40	7.47	9.60	8.96
t_{dom} [h]	2.08	2.25	2.17	2.25	2.25	2.17	2.25	2.17	1.92	1.92
v_{dom} [m/h]	5.38	4.98	5.17	4.98	4.98	5.17	4.98	5.17	5.84	5.84
Recovery [%]	5.2	5.5	1.0	4.0	5.3	4.2	3.0	1.2	1.2	0.9

tially be explained by the different detection limits (highest for the microspheres) and background concentrations (highest for uranine and chloride in this experiment). In general, the microspheres will yield the highest actual velocities because their detection limit under the fluorescence microscope is extremely low and because they will preferentially flow in the mid-current of the stream where the highest flow velocities are encountered.

A less ambiguous tracer characterization can be achieved by the comparison of the **peak arrival time**. The peak concentrations occur between 1.92 h and 2.25 h after the injection. The maximum error in determining the peak arrival time is given by the sampling interval and amounts to –0.08 h (approximately –4 %) for each tracer. Hence, the observed range of the peak arrival times which yields 0.33 h (± 16 %) is significantly higher than the error created by the sampling interval. Although these differences are of minor importance in this study, they should be taken into consideration for large-scale experiments. The dominant flow velocity follows the sequence:

(Fluoresbrite YG, Fluoresbrite Red) > uranine > (pyranine, Cl^-, Sr^{2+}) >
> (sulphorhodamine B, naphthionate, Br^-, Li^+).

An explanation for the higher velocities of the microspheres was already given above. The lower velocities of strontium, lithium and sulphorhodamine B may be due to a slight sorption at the observed fracture coatings consisting of clay minerals.

The **tracer recovery** for experiment no. 1 is about 13 times higher compared with the experiment no. 2. The reason could be the injection of 20 l of chase fluid after the short tracer pulse injection of experiment no. 1. For experiment no. 2, the relative recoveries did not exceed 6 % (tab. 3.5). The circumstances that led to such low recoveries are not yet fully understood. Roughly 10–15 % of the tracer mass was lost during the injection by leakage around the packer system. Additionally, a large amount of the

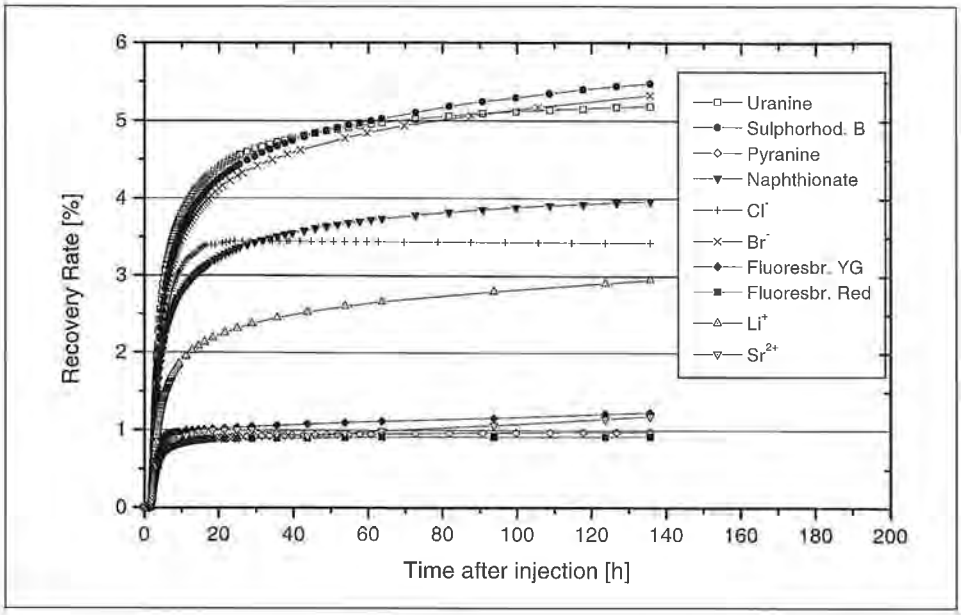


Fig. 3.9: Relative tracer recovery vs. time after injection at the borehole Bl. 10 (experiment no. 2). Relativer Tracerrückerhalt gegen die Zeit nach Einspeisungsbeginn am Bohrloch Bl. 10.

tracer mass was presumably injected into fracture systems which do not connect the injection with the observation borehole. Among the applied tracers, sulphorhodamine B, uranine and bromide reached the highest relative recoveries (Fig. 3.9). The lowest recovery was obtained for the microspheres, strontium and pyranine. The lower recovery of the microspheres could be explained by filtration during the passage through micro fissures. Strontium is the only divalent ion among the injected tracers and may have undergone sorption at the clay minerals. Pyranine was repeatedly reported to yield poor recoveries (e.g. N. GOLDSCHEIDER et al., 2001). Microbiological degradation may cause the loss of pyranine, but research will have to come up with further insight into this topic.

3.2.4.2. Model Validation

Experiment no. 1 was described by the SFDM. Calibration of the SFDM for a radial-convergent flow yields a mean transit time t_0 of 2.4 h and a Peclet number Pe of 20. Compared with the experiment no. 2, a significantly higher longitudinal dispersivity (α_L = 0.56 m) was determined. The reason for this could be the lack of a double packer in the injection borehole causing a slow release of the tracer during experiment no. 1.

The uranine BTC obtained from the experiment no. 2 could be excellently fitted to the SFDM (Fig. 3.10). However, the best fit yielded non-plausible values for the Peclet number (Pe = 300) and the longitudinal dispersivity (α_L = 0.04 m). Furthermore, the Peclet number proved to be a rather insensitive fitting parameter. Similar fitting results could be obtained from the other BTCs. In order to examine the somewhat dubious results, the following model validation was carried out.

Assuming that the assumptions made within the SFDM are fulfilled and, hence, that the fitted values obtained for uranine are accurate, a forward modelling of the bro-

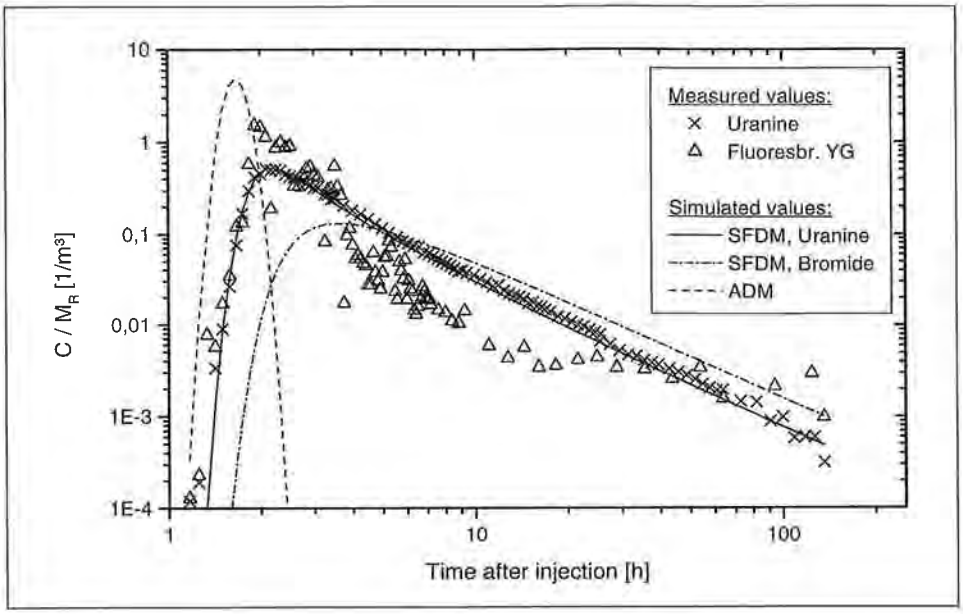


Fig. 3.10: Measured tracer concentration C divided by the recovered tracer mass M_R vs. time after injection for uranine and Fluoresbrite YG. Best fit of the uranine data using the SFDM yields $t_0 = 1.7$ h, Pe = 300 and $a = 0.48\ h^{-1/2}$. Theoretically, the simulated ADM-curve (t_0 and Pe identical) and the simulated SFDM curve for bromide ($a = 1.01\ h^{-1/2}$) should fit the BTC for microspheres and bromide, respectively (experiment no. 2).
Gemessene Tracerkonzentration C von Uranin und Fluoresbrite YG geteilt durch die rückgewonnene Tracermasse M_R gegen die Zeit nach Einspeisungsbeginn. Beste Anpassung an das SFDM ergibt: $t_0 = 1.7$ h, Pe = 300, $a = 0.48\ h^{-1/2}$. Die simulierte ADM-Kurve mit identischer mittlerer Verweilzeit t_0 und Peclet-Zahl Pe sollte theoretisch der gemessenen Kurve der Partikel folgen; entsprechend sollte die simulierte SFDM-Kurve mit $a = 1.01\ h^{-1/2}$ die Bromiddurchgangskurve wiedergeben.

mide (or any other) BTC is straightforward. According to equation (3.2), the fit parameter a of bromide for a combined tracer experiment can be calculated:

$$a_{uranine} = \sqrt{\frac{D_m^{uranine}}{D_m^{bromide}}} \cdot a_{bromide} \approx 0.47 \cdot a_{bromide}. \qquad (3.3)$$

The simulated bromide BTC is presented in fig. 3.10. The matrix diffusion will produce a slight increase of the tailing and a strong reduction of the peak concentration. However, these effects could not be observed in experiment no. 2 for the fluorescent dyes and the salt tracers (Fig. 3.7). Only the microspheres (Fig. 3.8) show a reduced peak concentration and a lower tailing, yet not to the extent predicted by the transport models. As a consequence, the tailing of the BTCs can only partly be attributed to the effect of matrix diffusion. The tailings are most likely produced during the injection by an initial spreading of the tracer plume around the injection borehole. Depending on the volume of the chase fluid, a portion of the tracer is pushed upstream and has to migrate a longer distance. This effect is crucial for the interpretation of small-scale experiments. Besides, we assume that a part of the tracer mass was injected into dead-

end fractures and was only slowly released into the fractures connecting the borehole Bl. 8 with Bl. 10.

Non-diffusive tailings of the BTCs have already been observed in earlier tracer studies at the Lindau rock test. A. KASELOW (1999) performed tracer tests using an injection pipe and observed a huge volume of stagnant and spiked water in the injection hole. He proved by numerical modelling that the observed tailing could not be entirely produced by matrix diffusion. F. EINSIEDL et al. (2000) obtained identical tailings of the BTCs for tracer experiments between borehole Bl 10 and Bl. 11 despite the strongly differing diffusion coefficients of the injected fluorescent dyes and particle tracers. K. WITTHÜSER (2001) concluded from comparative tracer studies that the spreading as well as the tailing of the resulting BTCs, commonly interpreted as dispersion and diffusion, will be remarkably reduced if a double packer injection system is applied.

3.2.5. Conclusions

The fluorescent dyes uranine, sulphorhodamine B, pyranine and naphthionate, the salt tracers lithium chloride and strontium bromide, the particle tracers Fluoresbrite YG and Red as well as the newly developed tracer T4 could all be successfully applied in fractured granitic rock for small-scale experiments. The BTCs showed good resemblance, although the actual flow velocities varied up to 16 %. Pyranine, strontium and the Fluoresbrite microspheres yielded the lowest relative recoveries among the tracers applied in the comparative studies. For the design of large-scale experiments, both the differing flow velocities and the recoveries should be taken into consideration.

The BTCs of both the soluble and the particle tracers are characterized by strong tailings. Since the BTCs of the particle tracers show higher peak concentrations and lower tailings compared to the dyes and the salt tracers, it is likely that diffusion of the soluble tracers into the adjacent rock or stagnant zones occurred. However, the tailings can only to a minor extent be interpreted as matrix diffusion. In fact, the BTCs proved to be very sensitive to the injection system and the volume of the chase fluid. Fitting the empirical BTCs to analytical solutions of the transport equations like the SFDM or the ADM will lead to inaccurate transport parameters if the model assumptions are violated. The combined injection of tracers proved to be very useful for the model validation. It is recommended to simultaneously inject tracers with strongly differing diffusion coefficients, e.g. soluble and particle tracers, in order to distinguish the effect of matrix diffusion from the influence of the injection mode.

For small-scale tracer tests, injection systems like a triple packer system (e.g. M. W. BECKER & A. M. SHAPIRO, 2000) are required by which an instantaneous injection of the tracer can be assured. Without such an accurate injection system, the interpretation of the BTCs with regard to matrix diffusion in low porosity granites can be misleading.

3.3. Comparative Tracer Test in the Alpine Karst System Hochifen-Gottesacker, German-Austrian Alps (N. GOLDSCHEIDER, H. HÖTZL, W. KÄSS)

3.3.1. Overview

The Hochifen-Gottesacker area is situated in the northern Alps at the German-Austrian border. With an altitude of 2,230 m, Mount Hochifen (also called Hoher Ifen) is the highest summit. The northward bordering Gottesacker covers an area of about

10 km² and is considered to be one of the most spectacular alpine karst landscapes ("Gottesacker" means "field of god" or "graveyard").

It is built up by only about 100 m thick limestone, the so-called Schrattenkalk, which covers the surface of the Gottesacker like a karstified skin ("Schrattenkalk" means "karren limestone") (Fig. 3.11). The site does not belong to the type of plateau-like karst massifs but is a typical representative of folded alpine karst systems (N. GOLDSCHEIDER & H. HÖTZL, 1999). However, it is often called a "plateau". The fold axes culminate in the central part of the area and plunge under the bordering Schwarzwasser valley in southeastern direction.

Hydrogeological research, especially tracer tests, made it possible to understand the underground drainage pattern: The elevated areas discharge via the plunging synclines into the bordering valleys. In the Schwarzwasser valley, a hydraulically connected karst aquifer collects all the waters and is discharged by a few karst springs in the lower section of the valley. The entire Gottesacker and the upper Schwarzwasser valley belong to the zone of shallow and open karst, in the lowest section of the valley we find deep, confined and, locally, artesian conditions (N. GOLDSCHEIDER & H. HÖTZL, 2000).

In order to compare the behaviour of different tracers in a well known alpine karst system, the Hochifen-Gottesacker area was selected as a test site.

According to the suggestions given by W. KÄSS to the Association of Tracerhydrology (ATH), ten substances were used as tracers: the fluorescent dyes naphthionate, pyranine, uranine and sulforhodamine, three different salts with lithium, strontium and bromide as ionic tracers and fluorescent microspheres in red and green as particle tracers. Additionally, J. BOHNERT invented and produced so-called bioparticles, which were used as a tracer for the first time.

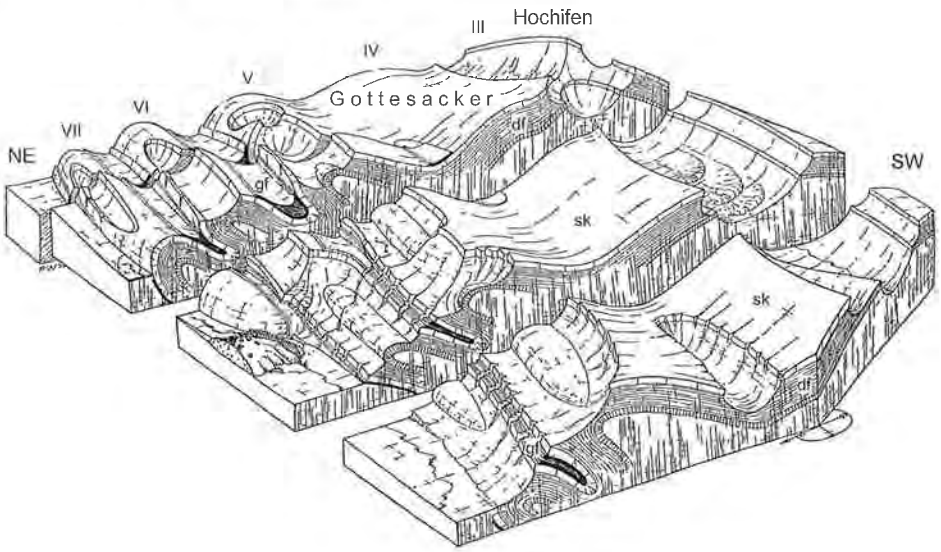


Fig. 3.11: Block diagram of the Hochifen-Gottesacker area (G. WAGNER, 1950). df – Drusberg formation or older, sk – Schrattenkalk limestone, gf – Garschella formation or younger, III–VII – anticlines.
Blockbild des Hochifen-Gottesacker-Gebietes (G. WAGNER, 1950). df – Drusberg Formation oder älter, sk – Schrattenkalk, gf – Garschella Formation oder jünger, III–VII – Antiklinalen.

All tracers were injected simultaneously in a cave entrance in the middle section of the Schwarzwasser valley which acted as a swallow hole during the tracer test. The samples were taken at two karst springs in the lower section of the valley. The connection between the cave and the springs, as well as the hydraulic characteristics of the aquifer, had already been studied before by means of a tracer test (N. GOLDSCHEIDER, 1998).

3.3.2. Geology and Hydrogeology

3.3.2.1. Geology

The Hochifen-Gottesacker area belongs to the Säntis nappe, the largest thrust sheet within the Helvetic nappe system (named after the 2,502 m high Mt. Säntis in the Swiss Alps). In western Austria, the Säntis nappe is surrounded by the so-called Ultrahelvetic and Rhenodanubic Flysch nappes in the N, E and S, forming a large tectonic half window. The area of study is situated on its eastern margin (D. RICHTER, 1984, G. WYSSLING, 1986).

The area is built up by Cretaceous sedimentary rocks: The oldest relevant formation is the Drusberg marl with a maximum thickness of 250 m. The Schrattenkalk is an extremely pure limestone with a total thickness between 75 and 125 m. The Garschella formation is often represented by glauconitic sandstones which are only a few meters thick. The youngest relevant formation is the Amdener marl with a thickness of up to 250 m (W. ZACHER, 1973, H. SCHOLZ, 1995).

To the W of the area, the folds trend W–E. They form an axial depression in the Subersach valley and rise to an axial culmination on the top of the Hochifen-Gottesacker area. Here, the fold axes turn in SE-direction and plunge under the Flysch nappes along the Schwarzwasser valley (Fig. 3.12).

As anticlines often form ridges while synclines often form valleys, the folds can easily be recognized in the field (Fig. 3.11). The Hochifen-Gottesacker area is both a culmination of fold axes and an anticlinorium. Therefore, G. WAGNER (1950) calls it an "Cretaceous Shield". In the following, the anticlines are numbered from S to N in roman numbers; the synclines are numbered by combining the numbers of the bordering anticlines (according to G. WAGNER, 1950).

The Schrattenkalk limestone is intensively cut by faults which belong to two main systems: SW–NE trending left-lateral strike-slip faults with a significant extensional component and SE–NW trending normal faults with right-lateral strike-slip displacement. A major SW–NE fault zone runs parallel to the Schwarzwasser valley. The fold pattern is different on both sides of this zone, indicating that the faulting started before the end of the folding (N. GOLDSCHEIDER,1997).

3.3.2.2. Karstification, Springs and Surface Waters

The Schrattenkalk limestone is extremely karstified and forms almost the entire surface of the Gottesacker. Its highest parts are nearly bare of soil and vegetation and form large karrenfields. Deep potholes are frequent at the intersection of faults, some of them are the entrance of a cave. The lower parts of the Gottesacker are covered with shallow soil and coniferous forest. Above the level of the surrounding valleys, no surface waters exist on the areas with outcropping Schrattenkalk limestone (compare fig. 3.12 and fig. 3.13).

Most other relevant sedimentary rocks in the area are characterized by low permeability and, consequently, by surface runoff. The underlying marls and slates of the

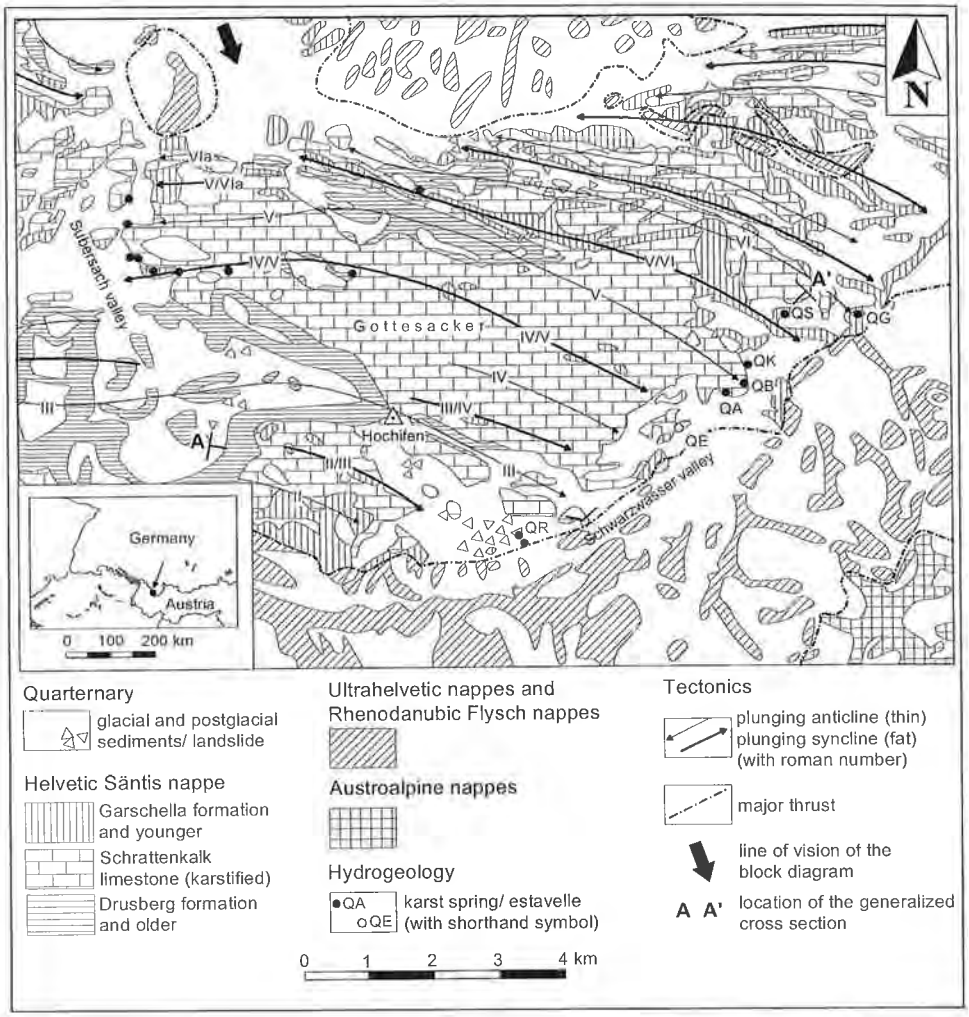


Fig. 3.12: Location and hydrogeological map of the test site (N. GOLDSCHEIDER & H. HÖTZL, 2000). Lage und hydrogeologische Karte des Testgebietes (N. GOLDSCHEIDER & H. HÖTZL, 2000).

Drusberg formation form the base of karstification. They often outcrop in the cores of anticlines where the Schrattenkalk is eroded. The overlying glauconitic sandstones and the extremely low permeable Amdener marls are only preserved in the cores of synclines (Fig. 3.11). Also the rocks of the Ultrahelvetic and Rhenodanubic Flysch nappes are of low permeability.

In the Schwarzwasser valley, the karstified limestone plunges under the Flysch nappes in southern and eastern direction. This geological asymmetry leads to a hydrological asymmetry: The Flysch mountains at the SE (right) side of the valley are drained by surface runoff, while the karst area at the NW (left) side is drained underground. Therefore the Schwarzwasser river is supplemented by many tributaries from the right side of the valley but no tributaries from the left side.

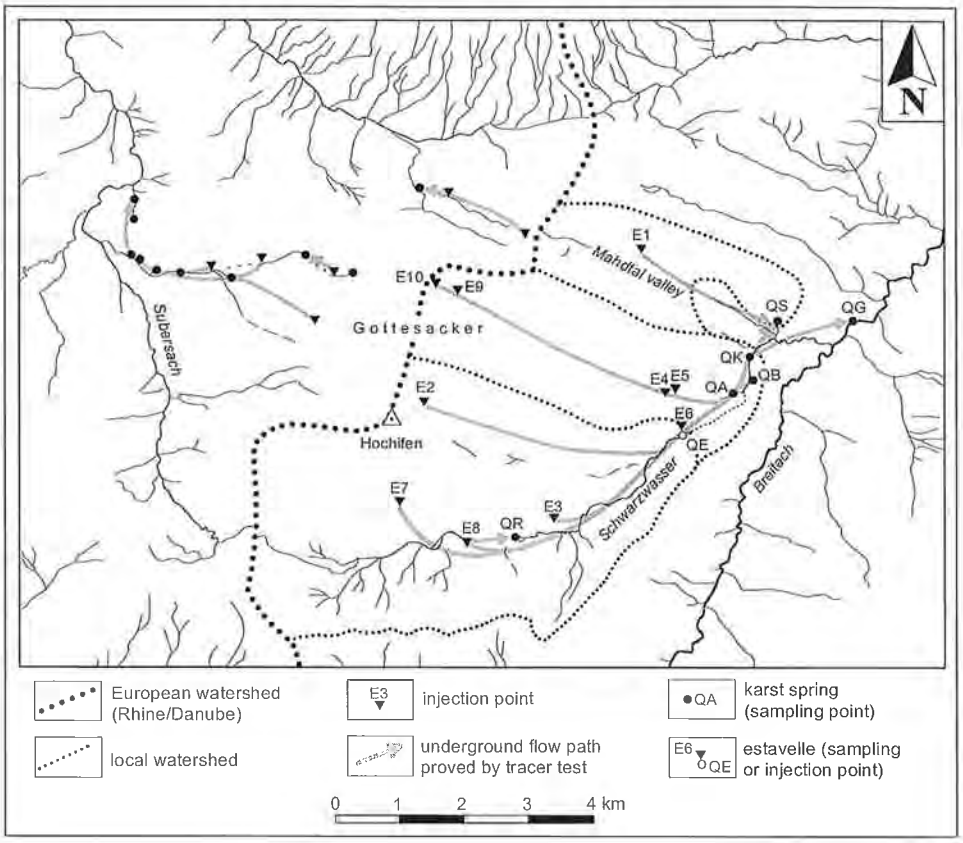


Fig. 3.13: Surface waters, karst springs with their catchments and underground flow paths proved by tracer tests (N. GOLDSCHEIDER & H. HÖTZL, 2000). The shorthand symbols of the springs are explained in the text.
Gewässernetz, Karstquellen mit ihren Einzugsgebieten und durch Markierungsversuche belegte unterirdische Fließpfade (N. GOLDSCHEIDER & H. HÖTZL, 2000). Die Kürzel der Quellen sind im Text erklärt.

Consequently, there are **two flow systems** in the valley (see N. GOLDSCHEIDER & H. HÖTZL, 2000): the surface river that drains the right side of the valley and the underground karst water flow.

The Schwarzwasser river has its source at the so-called European watershed between Rhine and Danube and is tributary to the Danube. In an altitude of 1,340 m it sinks in swallow holes in a huge landslide which came down from Mt. Hochifen after deglaciation and caused obstruction in the valley (G. WAGNER, 1950, M. SINREICH, 1998). A portion of the stream reappears 1 km below in a resurgence (QR in fig. 3.13).

In the middle part of the valley, the anticline IV plunges under the valley, so that the karstified limestone outcrops and is cut by the river, forming a gorge (Fig. 3.14). Under low water conditions, the river sinks in the entrance of the so-called "Schwarzwasser" cave which is situated in this gorge at 1,120 m. Under high water conditions the cave entrance becomes a spring. Thus, the cave is an estavelle – probably the lar-

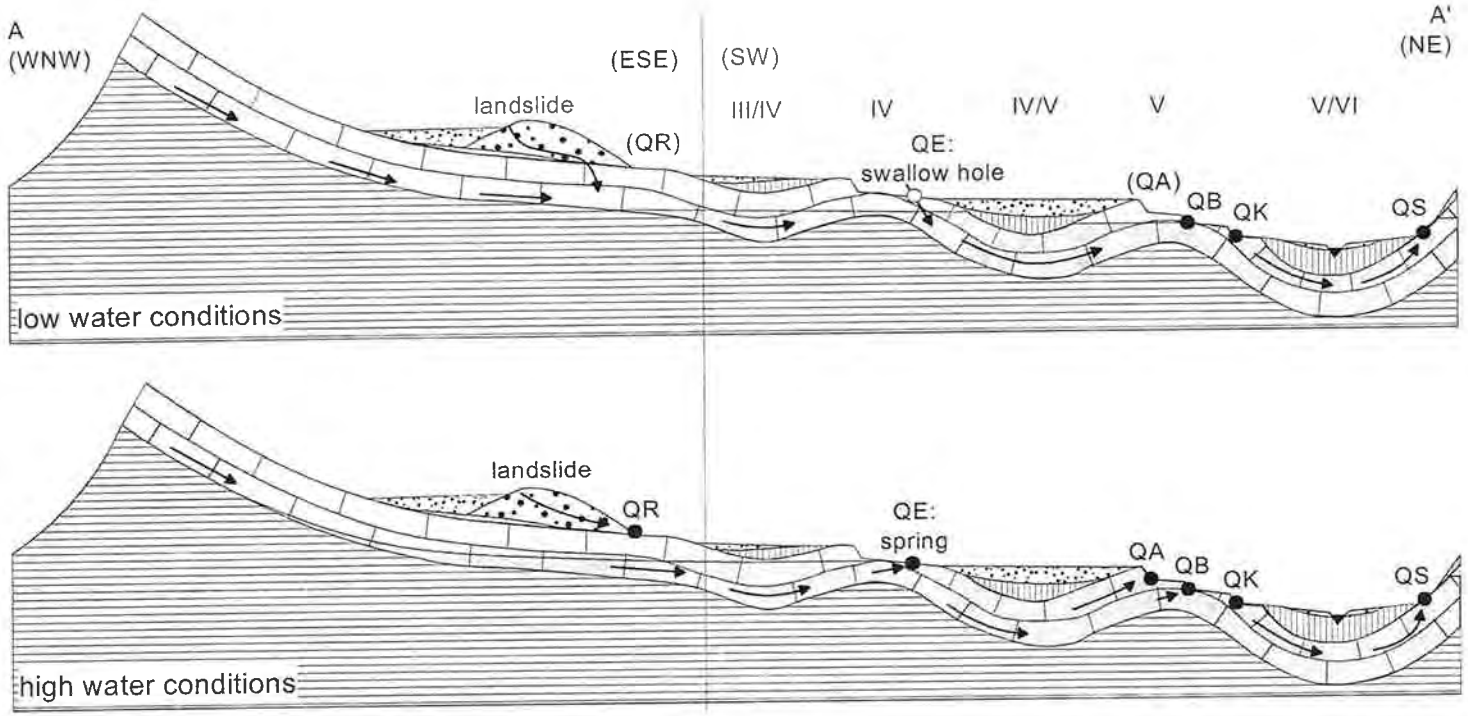


Fig. 3.14: Generalized hydrogeological cross section of the Schwarzwasser valley under extremely low and high water conditions (N. GOLDSCHEIDER & H. HÖTZL, 2000). Location of the section and geological legend see fig. 3.12. For the comparative tracer test, the estavelle QE served as the injection point; QA and QS were sampled.
Generalisierter hydrogeologischer Profilschnitt des Schwarzwassertals bei extrem niedrigen und hohen Abflüssen (N. GOLDSCHEIDER & H. HÖTZL, 2000). Lage des Profilschnitts und geologische Signaturen siehe Fig. 3.12. Für den vergleichenden Markierungsversuch diente die Estavelle QE als Eingabestelle, QA und QS wurden beprobt.

gest in the Alps. It connects the surface river with the underground karst water flow (N. GOLDSCHEIDER et al., 1999).

In the lower part of the valley, the anticline V plunges under the valley, so that the limestone outcrops and is cut by the river once again. This is the location of three karst springs: The Aubach spring (QA) at 1,080 m discharges up to 6 m^3/s but dries up in long dry periods. The springs QB at 1,050 m and QK at 1,040 m discharge nearly constantly about 40 and 15 l/s respectively. Below these springs, the limestone is covered by the low permeable younger strata in the core of the syncline V/VI. At 1,035 m, these strata are eroded locally along a normal fault, so that the karst aquifer outcrops in a low topographic position. This is the location of the Sägebach spring (QS) that discharges between 150 and about 2,000 l/s.

Below the confluence of the Schwarzwasser river and the Breitach river, the limestone outcrops again in the anticline VI. Here, it was possible to detect an anomaly in temperature indicating the upwelling of cold karst groundwater. By measuring the discharge of the river above and below this anomaly using the salt-dilution method, the discharge of this – invisible – bottom spring (QG) was determined: about 200 l/s (N. GOLDSCHEIDER & H. HÖTZL, 2000).

3.3.2.3. Results of Earlier Tracer Tests

Three large tracing experiments with 15 injections points were carried out in the Hochifen-Gottesacker area by the scientists N. GOLDSCHEIDER (1997, 1998), Ch. TOMSU (1998) and M. SINREICH (1998). Figure 3.13 shows the hydraulic connections which were proved by these tracer tests. The tracers which were injected in the upper section of the Schwarzwasser valley (E3, E7 in fig. 3.13) and in the southern part of the Gottesacker (E2) first reached the estavelle (QE) and later on all the karst springs in the lower section of the valley (QA, QB, QK, QS). The tracers which were injected in the central (E9-10) and eastern (E1) part of the area and in the lower section of the valley (E4-5) reached the karst springs, but not the estavelle. The connection between the Hölloch cave (E1) and the Sägebach spring (QS) had already been proved by tracer tests in 1949 and 1955 (R. G. SPÖCKER, 1961).

These observations prove the hydrogeological function of the karst aquifer in the Schwarzwasser valley as a drainage system for the karst waters coming down from the elevated areas along the plunging synclines. No trace of the fluorescent dyes was detected in the river upstream of the estavelle. This is the evidence that it receives no water from the karst area at the NW (left) side of the valley but is exclusively supplemented by tributaries from the Flysch mountains at the SE (right) side and from the landslide in the upper section of the valley.

The connection between the sink of the Schwarzwasser river into the landslide and its resurgence (QR) was proved by the injection E8. It was possible to demonstrate that a portion of the sinking stream water does not reach the resurgence, but seeps into the karst aquifer and reappears in the estavelle and the springs in the lower valley. The results from the western part of the area are not relevant here. A comprehensive and detailed discussion of all the tracer tests is given by N. GOLDSCHEIDER & H. HÖTZL (2000).

In order to prove the connection between the Schwarzwasser cave (the estavelle) and the karst springs in the lower section of the valley, 200 g of uranine were injected in the entrance of the cave (E6) which acted as a swallow hole during the experiment (N. GOLDSCHEIDER, 1998). The results of this experiment (Tab. 3.6) were the basis for the comparative tracer test described in this publication.

Tab. 3.6: The results of the earlier tracer test in the Schwarzwasser valley (N. GOLDSCHEIDER, 1998) served as the basis for the comparative tracer test described in this paper.
Die Ergebnisse des früheren Tracertests im Schwarzwassertal (N. GOLDSCHEIDER, 1998) dienten als Grundlage für den hier beschriebenen vergleichenden Markierungsversuch.

Injection point:	Schwarzwasser cave (estavelle)	Short symbol: QE, E6
Tracer:	200 g of uranine	
Hydrologic conditions:	medium discharge; estavelle acts as a swallow hole (6.6 l/s)	
Date:	97/08/14	

Spring (short-hand symbol)	Discharge [l/s]	Distance [m]	Time of first appearance [h]	Time of max. [h]	Time of last detection [h]	Max. conc. [µg/l]	Flow velocity max. [m/h]	Flow velocity dom. [m/h]	Recovery [%]	Dispersivity [m]
QA	210	1,000	6.8	11.8	67.0	14.0	147.1	84.6	45.2	20.9
QB	38	1,325	7.8	12.8	67.1	13.6	169.9	103.4	8.3	24.5
QK	15	1,550	8.8	14.8	66.8	12.2	176.1	104.6	3.0	23.0
QS	199	2,225	22.2	31.4	118.7	6.1	100.2	70.9	34.4	15.7
Total average	**462**						**148.3**	**90.9**	**90.9**	**21.0**

3.3.2.4. Underground Drainage Pattern of the Karst System

The tracer tests proved that the Hochifen-Gottesacker area is representative for the hydrogeological type of folded alpine karst systems with a relatively thin karstified carbonate sequence (N. GOLDSCHEIDER & H. HÖTZL, 1999). As the limestone is underlain or interstratified by low permeability layers, the underground flow occurs at its base and follows the stratification – at least in the elevated areas above the level of the surrounding valleys.

The underground drainage pattern is influenced by the fold tectonics: The synclines form the main flow paths, the anticlines form local watersheds and the culmination line is a part of the European watershed between Rhine and Danube river (see fig. 3.13).

The entire karst area east of the culmination line is discharged underground in SE-direction into the bordering Schwarzwasser valley. Along the whole valley, the gently folded limestone forms a hydraulically connected karst aquifer which collects the underground water from the left side of the valley (the Hochifen-Gottesacker area). Under low water conditions, the estavelle acts as a swallow hole and the surface water from the right side of the valley (the Flysch mountains) are also collected in this aquifer. In the Schwarzwasser valley, the underground flow follows the axis of the valley crossing several synclines and anticlines (Fig. 3.14).

The aquifer is discharged by the springs in the lower section of the valley. Their hydrological behaviour depends on their topographic position: The permanent bottom spring is the deepest outlet of the system; the springs QB, QK and QS are also permanent.

The intermittent Aubach spring is in a higher position and is only active if the water level is medium to high. The estavelle is in the highest position and becomes a spring only under high water conditions (N. GOLDSCHEIDER & H. HÖTZL, 2000).

3.3.3. Comparative Tracer Test

3.3.3.1. Selection of Tracers, Injection, Sampling and Analyses

The comparative tracer test in the Hochifen-Gottesacker area was carried out by N. GOLDSCHEIDER, N. GÖPPERT and W. KÄSS October 19, 2000 under low water conditions. The Schwarzwasser cave (the estavelle) was the injection point (QE/E6 in fig. 3.12–3.14); automatic samplers were installed at the Aubach (QA) and the Sägebach spring (QS) until October 23, 2000.

Ten different substances, belonging to three classes of tracers, were used: fluorescent dyes, salts (ions) and particle tracers (Tab. 3.7). Bioparticles are killed *Escherichia coli* bacteria, fluorescent dyed with acridin orange. They were invented and produced by J. BOHNERT (University of Tübingen) and used as a tracer for the first time. The optimum injection mass for each tracer was calculated on the basis of the results of the earlier tracer test in the Schwarzwasser valley (Tab. 3.6).

All the tracers were injected simultaneously in the cave entrance which acted as a swallow hole during the experiment. Consequently, no flushing water was required. Only about 25 ml/s were sinking in the cave and the water had to pass through sediments and autumn leaves which covered the bottom of the cave entrance.

The discharge of the springs was measured using the salt-dilution method. During the experiment, the discharge of the Aubach spring (QA) decreased from 101 to 18.2 l/s and the discharge of the Sägebach spring (QS) decreased from 265 to 199 l/s. The other springs were not sampled because it was not the purpose of this experiment to prove again well-known hydraulic connections, but to compare different tracers. Consequently, it is evident that the recovery rate of the tracers is less than 100 %.

The fluorescent dyes were analysed at the laboratory of the AGK (Applied Geology Karlsruhe) using the Synchron-Scan-Method. Bromide and chloride were analysed at the AGK laboratory with an ionic chromatograph. However, the variations of the natural background of chloride in the spring water were too high and the amount of injected chloride was too low to use this anion as a tracer. The cations lithium and strontium were analysed by W. KÄSS with the AES-method. W. KÄSS analysed the particle tracers by filtering 250 ml samples and counting the particles under a fluorescence microscope. It is possible to identify and distinguish the three different particles

Tab. 3.7: Class, type and amount of injected tracer. The names which are used in the text are in bold. Klasse, Typ und Menge der eingegebenen Markierungsstoffe. Die im Text verwendeten Bezeichnungen sind fett hervorgehoben.

Class	Type of tracer	Injected amount
Fluorescent dyes	Sodium **naphthionate** **Pyranine** 120 % **Uranine** **Sulforhodamine** B	M = 1,000 g M = 100 g M = 20 g M = 100 g
Salts	**Strontium** (as $SrCl_2 \cdot 6H_2O$) **Lithium** (as LiCl) **Bromide** (as NH_4Br)	M = 7.26 kg M = 2.62 kg M = 5.71 kg
Particles	Fluoresbrite Yellow **Green** (YG) **Microspheres**, 1.00 µm Fluoresbrite Polychromatic **Red Microspheres**, 1.00 µm **Bioparticles** (killed, fluorescent dyed *Escherichia coli*)	$n = 2.05 \times 10^{11}$ $n = 4.32 \times 10^{11}$ $n = 10^{12}$

by means of five criteria: size, shape, intensity of fluorescence, fluorescence coulour using blue light and fluorescence coulour using UV-light.

3.3.3.2. Results

For a better comparison of the obtained breakthrough and recovery curves, all concentrations were divided by the injected tracer mass (c/M) and the recovery rate is calculated in percent.

The breakthrough curves of the recent tracer test are completely different than those of the earlier experiment which was carried out in the same system in 1997 (Fig. 3.15). In the recent experiment, the transit time is longer, the concentrations are significantly lower and the recovery rate is also lower than in the earlier experiment. Both experiments were carried out under low water conditions. However, the discharge of QA was lower in the recent experiment. The main reason for the observed differences is probably the amount of water sinking into the cave entrance during the injection: In the earlier experiment, it was 6.6 l/s, in the recent one, it was only about 25 ml/s. Probably the tracers were delayed significantly on their way down to the groundwater which is about 20 m below the ground surface under low water conditions (N. GOLDSCHEIDER et al., 1999).

Four of the 10 tracers disappeared (almost) completely (Tab. 3.8): No trace of pyranine was detected in the springs even though the expected concentration should have been significantly higher than the limit of detection. This result can only be explained by fast microbiological or chemical decay or irreversible adsorption. Also all the particle tracers disappeared (except from three green microsphere in QA). As the microspheres have almost the same density as water, the sedimentation is too slow to explain this result. Probably, the particles were taken away by filtration through the

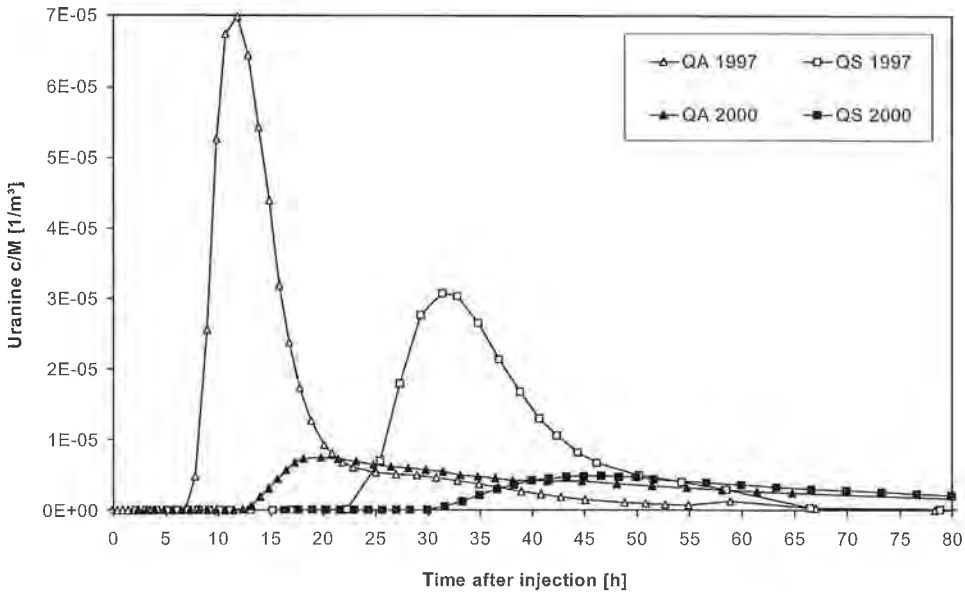


Fig. 3.15: Comparison of the breakthrough curves of the tracer tests in 1997 (N. GOLDSCHEIDER, 1998) and 2000.
Vergleich der Durchgangskurven der Versuche von 1997 (N. GOLDSCHEIDER, 1998) und 2000.

*Tab. 3.8: Results of the comparative tracer test in the Hochifen-Gottesacker area. *1 – preconditions of the analytical model are not fullfilled; only relative values; *2 – high variations of natural Sr-background; no precise values, irregular breakthrough curve; *3 – concentrations are close to the detection limit; no precise values, irregular breakthrough curve.*
*Ergebnisse des vergleichenden Markierungsversuchs im Gebiet Hochifen-Gottesacker im Überblick. *1 – Voraussetzungen für die analytische Modellierung nicht erfüllt; daher nur relative Werte; *2 – hohe Schwankungen des natürlichen Sr-Untergrundes; daher ungenaue Werte; unregelmäßige Durchgangskurve; *3 – Konzentrationen nahe der analytischen Nachweisgrenze; daher ungenaue Werte; unregelmäßige Durchgangskurve.*

Injection point:	Schwarzwasser cave (estavelle)	Short symbol: QE, E6
Sampling point:	Sägebach spring	Short symbol: QS
Distance QE–QS:	2,225 m	
Discharge of QS:	decreasing from 265 to 199 l/s	
Hydrologic conditions:	low water; estavelle acts as a swallow hole (–25 ml/s)	
Date of injection:	00/10/19	

Tracer	Time of first appearance [h]	Time of max. [h]	Max. conc. [µg/l]	Max. c/M [l/m³]	Flow velocity max. [m/h]	Flow velocity dom. [m/h]	Recovery [%]	Dispersivity (*1) [m]
Naphthionate	29.9	43.3	7.4	7.4E–06	74.4	51.4	19.7	44.6
Pyranine	–	–	–	–	–	–	–	–
Uranine	31.6	46.6	0.10	4.8E–06	70.5	47.8	14.9	49.2
Sulforhodamine	29.9	46.6	0.16	1.6E–06	74.4	47.8	5.0	43.1
Strontium (*2)	–	44.9	41	5.6E–06	–	49.5	16.3	–
Lithium	31.6	44.9	14	5.4E–06	70.5	49.5	15.7	43.2
Bromide (*3)	33.3	48.3	71	1.3E–05	66.9	46.1	32.8	–
Green microspheres	–	–	–	–	–	–	–	–
Red microspheres	–	–	–	–	–	–	–	–
Bioparticles	–	–	–	–	–	–	–	–
Average	31	46	–	6.2E–06	71	49	17	45

sand, gravel and leaves on the bottom of the cave entrance or somewhere else in the system.

The six other tracers were detected in both springs (Fig. 3.16). As the results for the two springs show no relevant differences, only the results of the Sägebach spring (QS) are discussed in the following. Please note: The maximum concentration of bromide (71 µg/l) is close to the limit of detection (25 µg/l) and the maximum concentration of strontium (287 µg/l) is close to the natural background in the water (238 µg/l) which was increasing during the experiment.

Consequently, the measured values are not very precise and the breakthrough curves are too irregular to be modelled. In the following, question marks (?) are used to remind the reader of this fact.

The differences in travel time and flow velocity between the tracers are detectable but not significant: All tracers appeared at QS between 30 and 33 h after the injection and reached the maximum concentration after 43–48 h. Taking into account the dominant flow velocity (time of maximum concentration), naphthionate was the fastest, strontium (?), lithium, uranine and sulforhodamine were slower and bromide (?) was the slowest tracer.

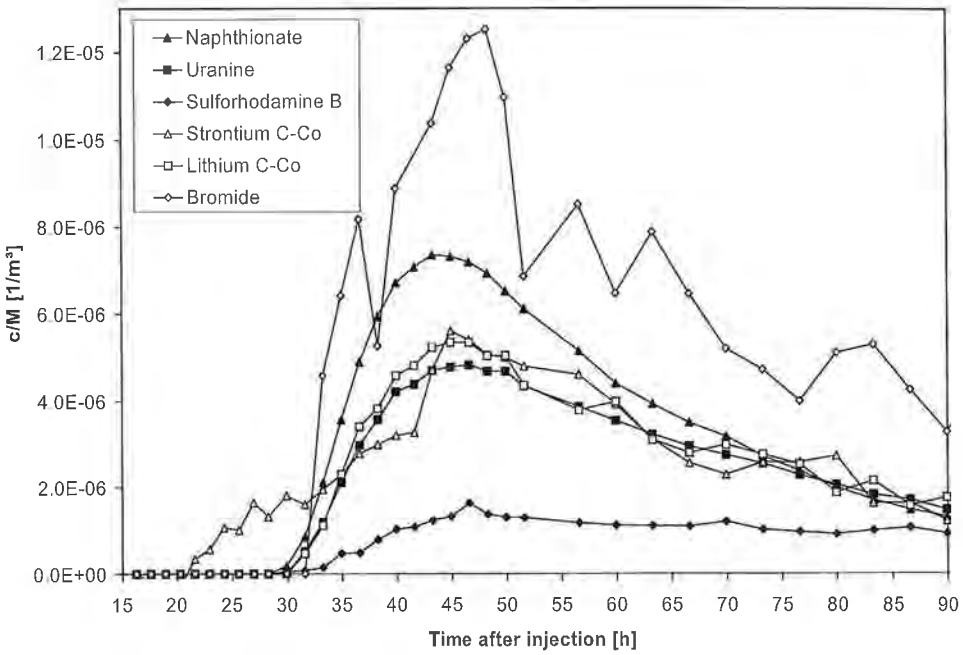


Fig. 3.16: Comparison of the breakthrough curves in the Sägebach spring (QS).
Vergleich der Durchgangskurven der verschiedenen Tracer an der Sägebachquelle (QS).

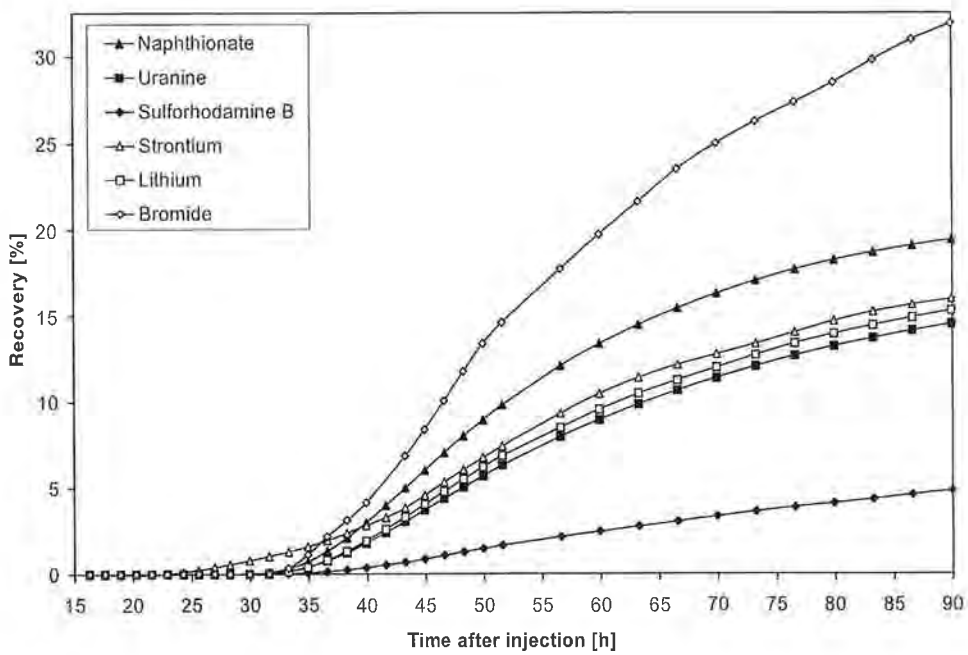


Fig. 3.17: Comparison of the recovery curves in the Sägebach spring (QS).
Vergleich des Wiedererhalts der verschiedenen Tracer an der Sägebachquelle (QS).

Due to the low amount of sinking water and the sediments in the cave entrance, the injection of the tracers was not an ideal momentous input. Consequently, the preconditions for analytical models are not fulfilled. However, the longitudinal dispersivities were calculated using a multi dispersion model (A. WERNER, 1998). The values of the first peak are presented in tab. 3.8. They cannot be taken as absolute values but only as relative values.

The most relevant differences between the tracers are the recovery rates (Fig. 3.17): 32.8 % for bromide (?), 19.7 % for naphthionate, 16.3 % for strontium (?), 15.7 % for lithium, 14.9 % for uranine but only 5.0 % for sulforhodamine. The maximum concentrations (c/M) show the same order.

3.3.4. Conclusions

The most important result of the comparative tracer test in the Hochifen-Gottesacker area is that four of the 10 injected tracer did not reappear in the springs – pyranine and the three particle tracers.

Pyranine was obviously decayed. Another example of the disappearence of pyranine is a tracer test in the catchment of the mineral springs of Stuttgart: 140 kg of pyranine were injected in a karst aquifer and no trace of it was detected in the wells and springs (N. GOLDSCHEIDER et al., 2001). For as long as there is no detailed knowledge on the decay of this tracer, it should not be used.

The failure of all particle tracers may be due to the filtration effect of the sediments and autumn leaves at the injection point. W. KÄSS (1992) describes several examples of the successful application of microspheres and comes to the conclusion that they are a good tracer.

The bioparticles which were invented by J. BOHNERT (University of Tübingen) are a promising new tracer: They are cheap, can easily be detected under the fluorescence microscope, allow the simulation of bacteria transport and are not harmfull. They should be tested in further comparative tracer tests.

Bromide and strontium are only suitable for short distance tracing, otherwise the required tracer mass is too large due to the relatively high limit of detection and natural background respectively. Amongst the salts (ions), lithium is probably the best tracer because of its low natural background and limit of detection and because of its conservative behaviour.

Amongst the fluorescent dyes, naphthionate turned out to be the most conservative tracer in this experiment. Both the recovery rate and the flow velocitiy is significantly higher than for the other dyes. Furthermore, this tracer is not visible and can consequently be used in the catchments of drinking water sources without any problems.

The disadvantages are: relatively high limit of detection, interference with the fluorescence of organic substances and microbiological decay which, however, does not take place in the aquifer but in the sampling bottles (K. KOTTKE, 2000).

Of course, uranine is also an excellent tracer because of its extremely low limit of detection and its relatively conservative behaviour. However, in this experiment, the recovery rate and the dominant flow velocities for uranine are significantly lower than those for naphthionate.

The behaviour of sulforhodamine was strongly reactive: The recovery rate is four times lower than for naphthionate and the breakthrough curve shows a characteristic tailing effect.

Acknowledgements

The authors want to thank Dipl.-Geol. J. BOHNERT (University of Tübingen) for the production of the bioparticels and for the cooperation. Many thanks to Dr. D. DREW (Trinity College, Dublin) for valuable suggestions and corrections. Many thanks to N. GÖPPERT (Student of Geology, Karlsruhe) for the great help in the field.

4. Unconsolidated Rocks

4.1. Characterization of the Kappelen Groundwater Research Site (BE), Switzerland, and Preliminary Bacteriophage and Solute Tracer Component Responses

(K. KENNEDY, I. MÜLLER, P.-A. SCHNEGG, P. ROSSI, R. KOZEL)

4.1.1. Introduction

Groundwater research activities at the Kappelen test site (Fig. 4.1) were initiated in 1996 following its sponsorship by the Swiss National Science Foundation (FNS) as part of contract FNS 20-46726.96. The purpose of this paper is to outline the work that has been undertaken at the site and present results to date in terms of site and tracer component (bacteriophages and uranine) transport characterization in this setting. The principal work activities were undertaken at the site over a period of two years ending in October 1998. Further work is ongoing at the site under continued sponsorship of the FNS related to aquifer heterogeneity.

Objectives

The objectives of the field research work at Kappelen were part of a continuing scientific program to characterize bacteriophage (phage) migration and to develop and carry out comparative particle and solute transport investigations in porous media aquifers. The three principal goals of the field research program were to:

1) define the patterns of phage behaviour as they interact with porous media environments in terms of physical, chemical and biological processes in the subsurface,
2) evaluate phages as tracers by conducting repetitive multi phage tracer experiments in field environments and
3) compare phage responses to classical artificial fluorescent tracers.

Meeting these goals would ultimately develop a better understanding of how to document and define particle transport conditions and assess their related migration processes. This could provide critical input needed to improve groundwater protection strategies for aquifers particularly with respect to viral and other biological particles.

Scope of Work

The activities undertaken at the site have followed four programs. The first program consisted of surface geophysical investigations, first at a regional and subsequently at a site scale. Follow-up detailed work addressed technique improvement. The second program addressed hydrogeological characterization. Regional wells within 2 km were measured and gradients were confirmed. Installing two shallow piezometers filled a water level data gap in the immediate site vicinity allowing confirmation that it aligned with regional hydrodynamic gradients. Sixteen, 102-mm diameter wells were installed to depths of about 15 m, developed and hydraulically tested over a 90 by 40 m area.

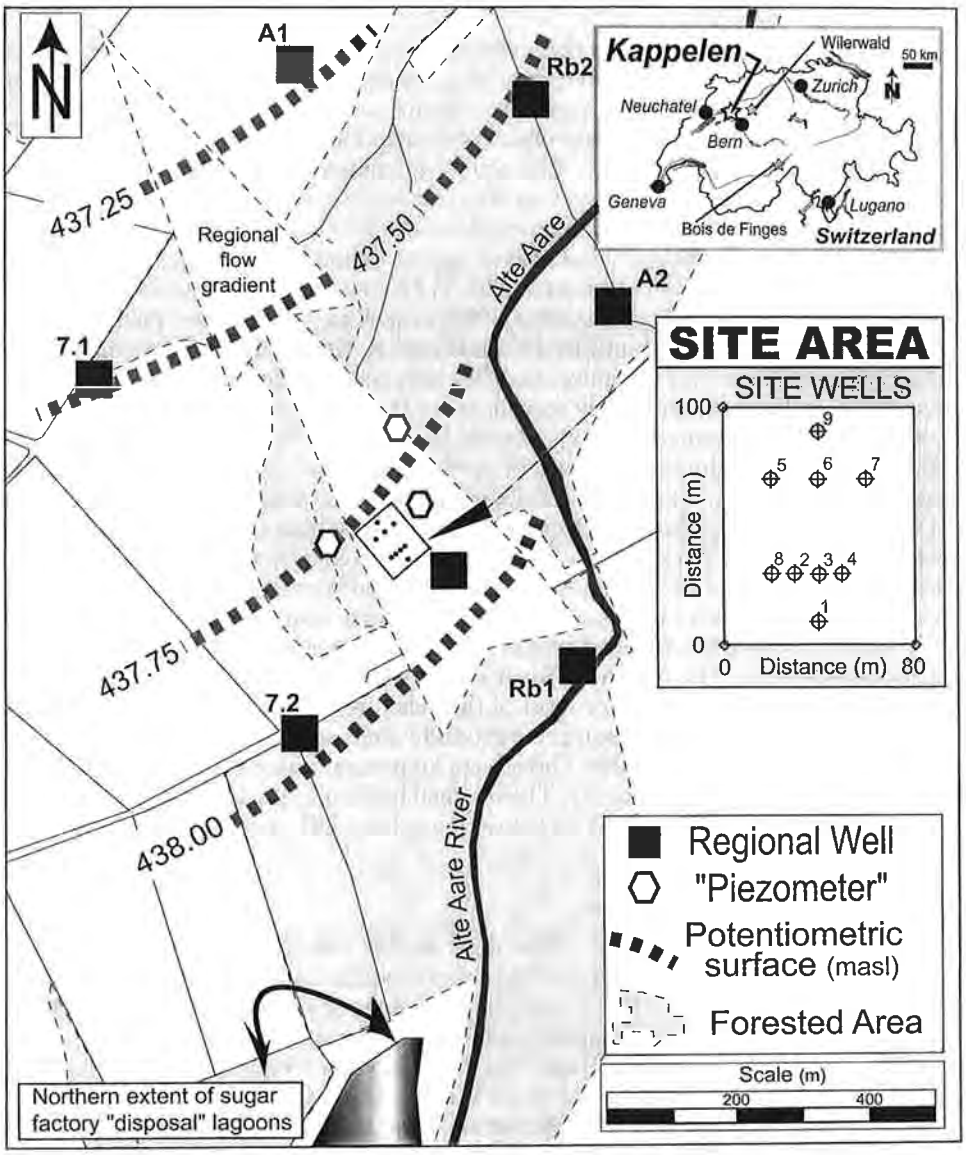


Fig. 4.1: Site location map with regional wells and Seeland aquifer potentiometric surface (October, 1996).
Übersichtskarte mit Bohrungen und Seeland-Aquifer Pegeloberfläche (Oktober 1996).

The third program was a reconnaissance biogeochemical characterization that was intensified due to the impact of redox conditions in the lower part of the site aquifer. Finally, a tracer testing program was initiated. Seven tests were undertaken, with two in the upper and five in the lower part of the aquifer. The results presented herein are for the most part based on work conducted during the contract period between September 1996 and September 1998.

Site Setting

The site is located in an area of the Seeland aquifer, which consists principally of post-glacially deposited sand and gravel overlying Tertiary marl and sandstone. This important aquifer has been the subject of studies for several decades. P. KELLERHALS & B.TRÖHLER (1976) provide a comprehensive description of the regional geological setting and groundwater conditions. The aquifer is an important public water as well as agricultural supply. It extends over an area of about 70 km^2, has a depth up to 25 m, and a water table about 2–5 m below ground surface. Work to date has included: regional aquifer modelling (D. BIAGGI et al., 1994), impact definition from sugar refining and other waste site releases (C. HALMES, 1993, P. HOFFMEYER, 1995), artificial recharge studies (P. KELLERHALS & C. HAEFELI, 1988) as well as groundwater protection and monitoring of the quality of subsurface conditions (R. KOZEL, 1992). While many wells and piezometers exist over the entire area, they have been installed in a variety of manners over the past 25 years, are widely spaced, are of uncertain construction and many do not have well-documented lithology. Rarely have samples been retained. The past use of an area north of the nearby town of Aarberg included discharge of liquid wastes from a sugar refining operation to leaking lagoons. This practice extended over tens of decades and has resulted in a plume of organic and sulfate contaminants extending several kilometers down gradient. This was investigated over widely spread areas but no detailed sampling of the aquifer near the lagoons had been undertaken. The Kappelen site is less than 1 km from the northern extent of these historical lagoons.

The site is located in a forested area of relatively flat terrain situated at an elevation of about 440–445 m. The Alte Aare River lies about 250–300 m to the E. Incised paleo-channels of the Aare account for most of this relief. Agricultural areas that surround the forest have associated consumptive groundwater use in the summer months that directly influence the water table. This effect plus natural seasonal variation may result in fluctuations of up to 2 m locally. The regional hydraulic gradient is to the NW and is relatively low at about 0.001 (0.1 %) with localized influences along the course of the Alte Aare River.

4.1.2. Geophysical Exploration

Surface geophysical exploration was done to find and develop an appropriate site and took place at both a regional and then more localized scale. Additional geophysical investigations were later done to compare the results of variable spacing and alternate methods of evaluating the subsurface conditions at the site.

RMT (Radio magneto telluric) and VLF-EM (very low frequency electro magnetic) surveys similar to those conducted at the Wilerwald (A. CARVALHO DILL, 1993) and other porous media sites (P. TURBERG et al., 1994) were conducted during July and August, 1996.

Six sites over an area of about 6 km^2 were evaluated near Lyss and Aarberg (BE). Two of the six sites had relatively homogeneous stratigraphic materials and consistent contact depths with the underlying silts. Follow-up detailed geophysics was done at both sites. One site had 14 landowners and the depth to the underlying aquitard was measured at about 25 m. The other site belonged to the village of Kappelen landowners and the depth to the underlying aquitard was estimated at from 13–18 m. The latter site was selected and is now referred to as the Kappelen Research Site (KAP).

Detailed geophysics using both RMT and VLF-EM was done at the site on 10 m by 20 m spacing in 1996 as described in E. OYONO (1996) and on 5 m by 10 m spacing by some of the current authors in 1997. Figures 4.2a and 4.2c illustrate VLF-EM data

from the site. Figure 4.2a is a 3-D depiction of the interpreted VLF-EM surface based on interpolation of 10 adjacent lateral transects. The results illustrate the relatively consistent depth and type of materials found in the upper materials overlying a lower conductivity material. Figure 4.2c shows the results of one of the VLF-EM transects over a distance of about 80 m across the site showing the lateral continuity to the E. The higher percent outphase values seen to the W on this and also reflected to the NW in the 3-D image are believed to be an artifact from a buried line or metal tubing along the access road through the forested area. Interpreted depth to the underlying aquitard and resistivity of the materials in the aquifer itself are shown on fig. 4.2b and 4.2d. The 3-D visualization of the interpreted thickness of the sand and gravel aquifer overlying the silt aquitard (Fig. 4.2b) shows a variable but relatively smooth contact. The depth varied in total from about 13–19 m but over much of the mapped area appears to have a 3 m depth range from about 15 and 18 m. Figure 4.2d illustrates a profile along one of the RMT transects illustrating the relatively high true resistivity values (300–500 Ωm) in these layered and heterogeneous gravel aquifer materials. The depth interpreted along the profile is from 13–18 m without the presence of sharp and incised channel features that were observed at the other locations investigated regionally.

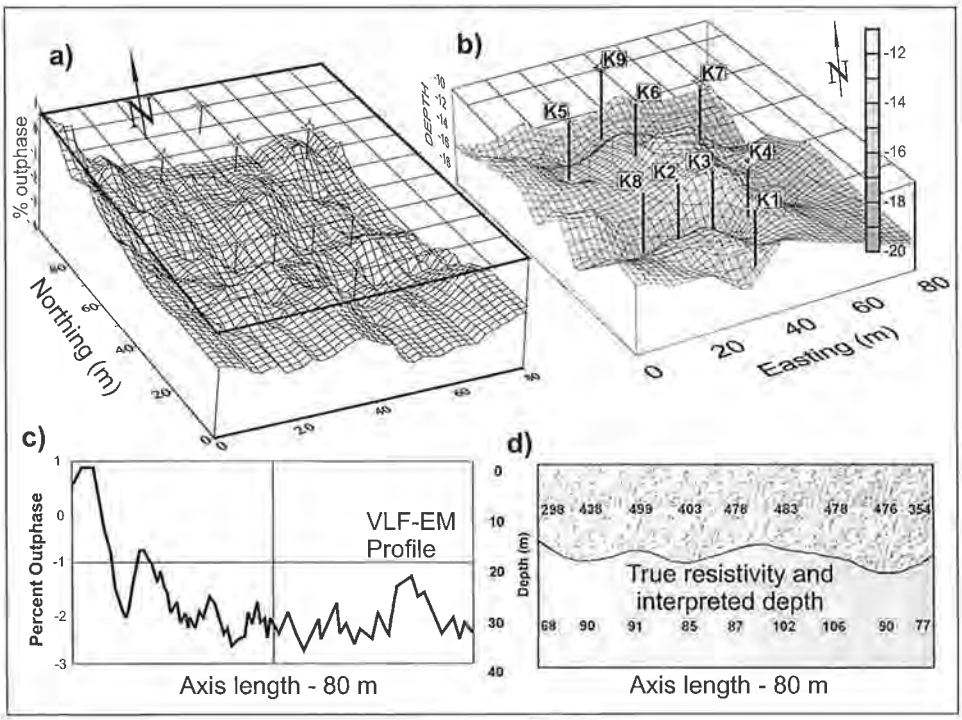
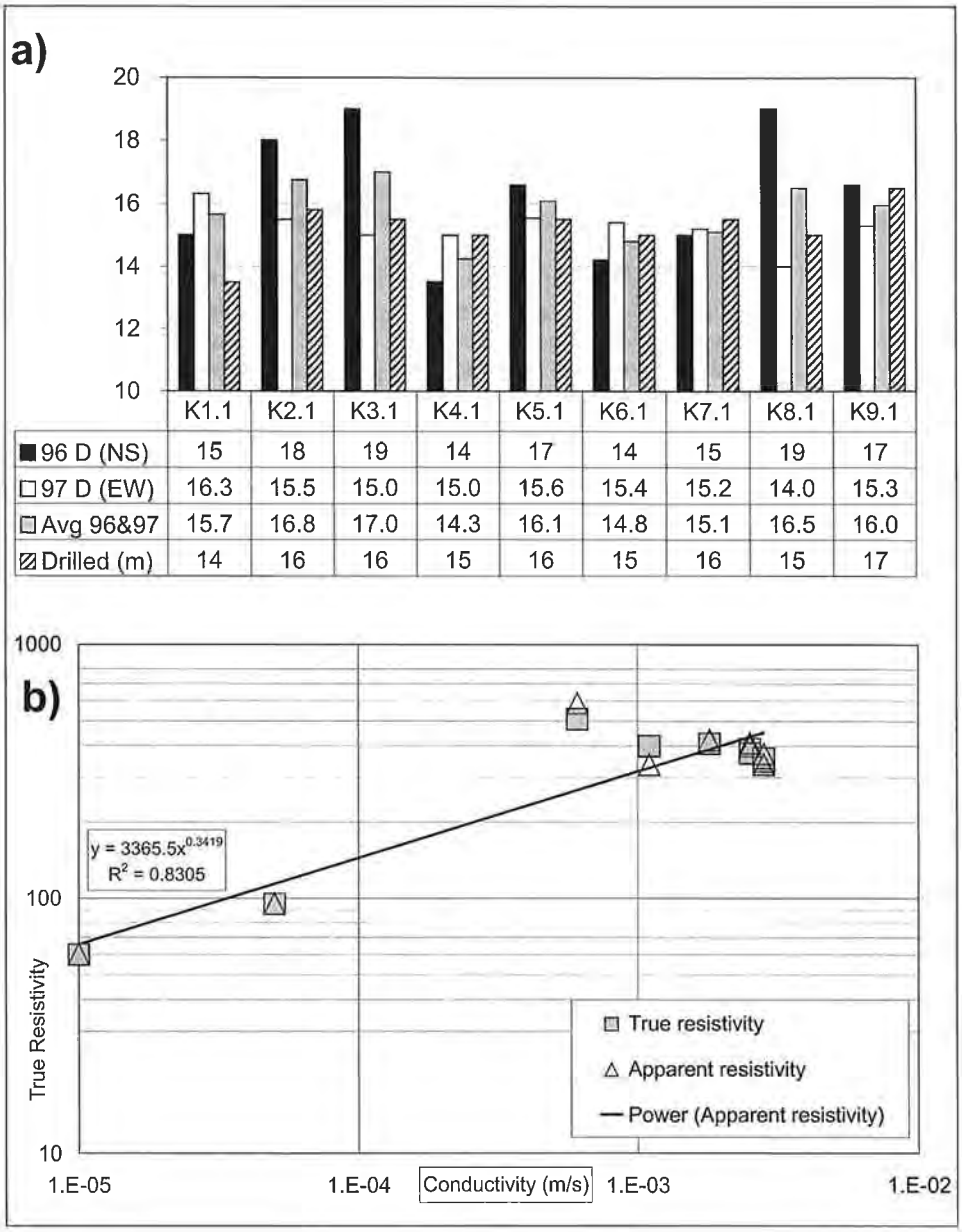


Fig. 4.2: Geophysical results from the site investigations. a) VLF-EM 3-D contour map, b) interpreted resistivity data providing 3-D depth projection to aquitard, c) VLF-EM profile along an E–W transect, d) true resistivity values and the interpreted depth to aquitard profile along an E–W transect.
Ergebnisse der geophysikalischen Untersuchungen. a) VLF-EM 3-D-Konturkarte, b) interpretierte Widerstandsdaten mit 3-D-Projektion zum Stauer, c) VLF-EM Profil in E-W-Richtung, d) berechnete echte Widerstände und Tiefen zum Stauer entlang eines E-W-Profils.

The reliability of the estimated aquitard depth measurements was evaluated after the monitoring wells had been drilled at the site in 1996 and again in 1997. These esti-



	K1.1	K2.1	K3.1	K4.1	K5.1	K6.1	K7.1	K8.1	K9.1
■ 96 D (NS)	15	18	19	14	17	14	15	19	17
□ 97 D (EW)	16.3	15.5	15.0	15.0	15.6	15.4	15.2	14.0	15.3
▨ Avg 96&97	15.7	16.8	17.0	14.3	16.1	14.8	15.1	16.5	16.0
▨ Drilled (m)	14	16	16	15	16	15	16	15	17

Fig. 4.3: Geophysical correlation. a) measured vs. geophysics-based predictions of aquitard depth, b) true, apparent resistivity and hydraulic conductivity.
Vergleich von a) Schichtmächtigkeiten nach geophysikalischer Interpretation mit erbohrten Mächtigkeiten, b) Korrelation wahrer und scheinbarer elektrischer Widerstand mit hydraulischer Leitfähigkeit.

mated depths are shown on fig. 4.3a for the RMT transects done with a N–S orientation in 1996 and an E–W orientation in 1997. Compared to the drilled well depths (Fig. 4.3a), the geophysically interpreted average depth results for both surveys had differences at two locations of 1.5 and 1.7 m and the remaining seven locations of less than 1 m.

The correlation between true resistivity defined from the RMT geophysical work in 1996 and the hydraulic conductivity (K) estimates for the underlying aquitard and overlying gravel aquifer material was evaluated (Fig. 4.3b). Results showed a grouping of the underlying silt materials with true resistivity results from 70–100 Ωm and 350–500 Ωm corresponding to K-range estimates of about $1e^{-05}$ m/s and $7e^{-04}$ to $3e^{-03}$ m/s, respectively. K-values were taken from grain size analyses as well as preliminary site hydrogeologic characterization activities at individual wells. There is a reasonable agreement in the relationship and consistency of the two values given the range in properties of the two types of materials.

4.1.3. Hydrogeological Characterization

Background water level information was obtained from the well-established regional groundwater monitoring network. About 12 existing wells, six of which are shown on fig. 4.1, were used to update the regional picture of the groundwater flow system and quantify the potentiometric surface. Water level measurements were made over a period of about two months and the groundwater flow direction pattern from September and October 1996 was compared to the historical data going back over 10 years. The 1996 data fit well with previous records indicating a general northwesterly flow direction at the site. A visual reconnaissance revealed the existence of three nearby and previously undocumented extraction points that could be utilized for groundwater monitoring locations. Two of these could be readily accessed and water levels measurements and surveying were done to combine these site-specific data with the regional information. Data gaps, however, existed in the coverage at the site and the influence of the Alte Aare River to the E of the site was not well understood. Accordingly, a shallow (Rammsondierung) probe and piezometer installation program was carried out prior to proceeding with actual site drilling. Five locations were evaluated by driving a metal rod to refusal, recording the blow count and checking for the presence of water. Detection of water at three could not be confirmed. At the other two locations, slotted pipes were installed and allow continued water level measurements.

The ground water flow direction estimated from the nearby regional well measurements and the results of the surface RMT geophysics were used to lay out the proposed initial well locations. The proposed field was designed to have an injection and pumping location separated by a distance of about 90 m. In between, additional wells at six locations were proposed at distances of about 20 m (row 1) and 40 m (row 2) from the injection well.

Well locations 1 through 7 (14 wells) were completed in October and November 1996 (Fig. 4.4). Wells 8 and 9 were installed in July 1997. Except for wells 8 and 9, each location has both a shallow well screened from about 4 or 5 m to 8–9 m and a deeper well screened over 4 or 5 m from about 10–15 m (Tab. 4.1). Typical geology from the wells is illustrated in fig. 4.5a. Typical well construction is shown in fig. 4.5b. All wells were completed with 102 mm ID poly-type casing, screens with a slot size of 1.5 mm and a gravel pack of 2.0–3.2 mm or 4–6 mm. Wells were surveyed and a permanent benchmark was established at the site.

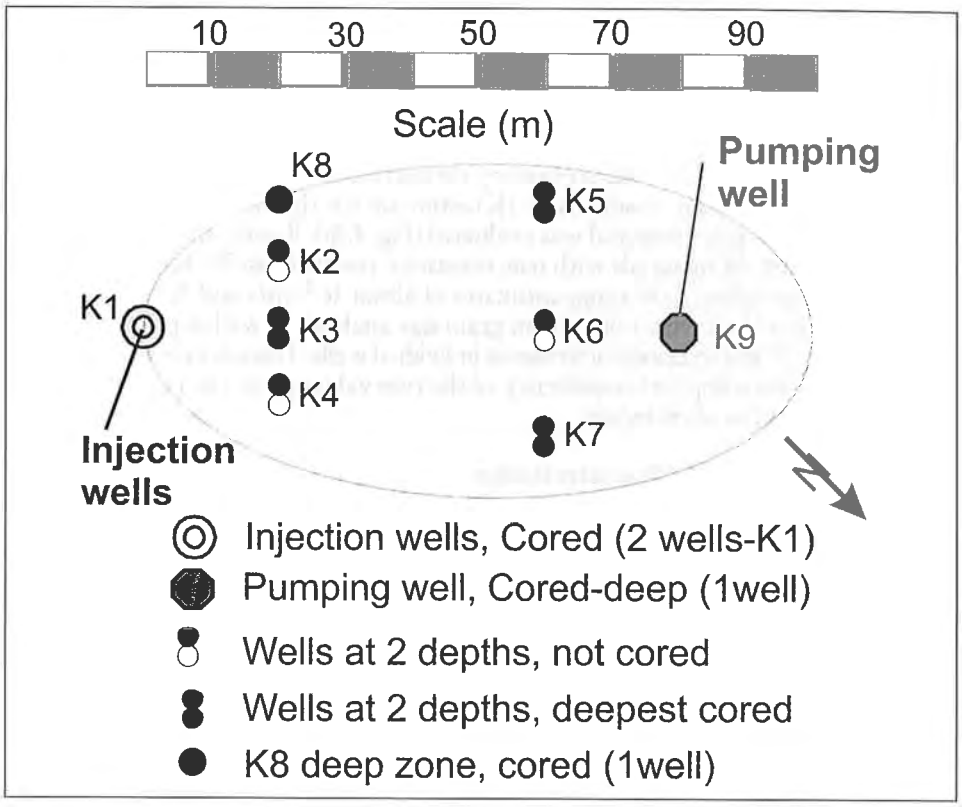


Fig. 4.4: Kappelen well field layout.
Lage der Kappelen-Bohrlöcher.

After drilling, wells were initially developed by pumping continuously with an submersible pump for 30 min opposite the well screens at rates of about 180–200 l/min. Later, the wells were pumped at similar rates over several hours per well with a suction pump. Specific capacity of the wells was determined during development and in separate site testing activities. Short-term pump testing was done in the deeper well locations in November 1996 and in the shallow wells in 1997. In 1996, pumping was done at both wells K1.1 and K3.1 using a large capacity 600 l/min pump. Measurements were made at other wells over a period of about 2 h. Water levels at the surrounding well locations dropped initially within about 2 min and appeared to stabilize in less than 30 min. No measurements were possible in the pumping well due to the size of the suction pump intake. In May 1997, additional short-term tests were done with pumping at about 300 l/min from wells K3.1 and K7.1. Similar rapid drawdown and stability patterns were observed with the monitoring wells as had been seen earlier. In this case, water levels in the pumping wells were observed. In the two wells pumped, the water levels stabilized within a few minutes during the two tests. All indications during well testing showed that the recovery from pumping occurred within a matter of seconds to minutes and accordingly, there was little opportunity to manually document this return to stabilization. Similar effects were also observed in the observation wells. The prolific aspect of the aquifer combined with the low volume capacity of the available pumping equipment

Tab. 4.1: Kappelen well completion data based on E. OYONO (1996) with wells K8 and K9 added. n/a – not applicable; all wells have surface seal at ~ 1 m with 0.5 m compactonite. Kappelen Bohrlochbeschreibung nach E. OYONO (1996), K8 und K9 hinzugefügt. n/a – nicht verfügbar; alle Bohrungen sind oberflächenversiegelt bei ~ 1 m mit 0.5 m Kompaktonit.

Well	Borehole			Well		Screen			Gravel pack		Well seal	
	Ground elev.	Drill & Install	Depth	Depth	Stick-up	Base	Length	Top	Base	Top	Plug base	Plug top
	[m a.s.l.]	Date	[m]	[m]	[m]	[m]	[m]	[m]	[m]	[m]	[m]	[m]
K1.1	442.54	10/14-10-96	15.5	13.2	–0.10	13.0	3	10.0	13.0	9.2	9.2	8.0
K1.2	442.46	23/24-10-96	9.3	7.8	0.25	7.8	3	4.8	8.9	3.8	n/a	n/a
K2.1	442.24	28-10-96	16.0	15.0	0.00	15.0	5	10.0	14.4	9.2	9.2	7.8
K2.2	442.23	29-10-96	8.9	8.0	–0.05	8.0	3	5.0	8.5	4.0	n/a	n/a
K3.1	442.45	14/16-10-96	15.0	14.9	0.15	14.9	5	9.9	15.0	9.0	9.0	7.1
K3.2	442.53	24/25-10-96	8.6	8.2	–0.20	8.2	3	5.2	8.5	3.9	n/a	n/a
K4.1	442.62	29/30-10-96	15.7	15.2	–0.15	15.2	5	10.2	15.7	9.1	9.1	7.6
K4.2	442.56	30/31-10-96	8.9	7.9	0.05	7.9	4	3.9	8.9	4.2	n/a	n/a
K5.1	441.78	21/23-10-96	16.2	15.0	0.00	15.0	5	10.0	15.0	8.9	8.1	6.7
K5.2	442.09	23/25-10-96	8.9	8.1	–0.10	8.0	3	5.0	8.1	4.6	n/a	n/a
K6.1	442.35	25/29-10-96	16.5	15.1	–0.10	15.1	5	10.1	15	9.8	9.8	8.5
K6.2	442.33	29/30-10-96	8.5	7.9	0.15	7.9	3	4.9	8.0	3.4	n/a	n/a
K7.1	442.37	16/21-10-96	15.0	15.0	0.00	15.0	5	10.0	15.0	9.1	9.1	7.6
K7.2	442.35	30-10-96	8.5	8.1	0.10	8.1	3.2	4.9	8.5	3.5	n/a	n/a
K8.1	~442.44	21/22-07-97	15.7	15.5	~0.50	14.5	4	10.5	15.7	9.7	9.7	8.6
K9.1	~442.42	22/25-07-97	16.3	16.0	~0.70	15.0	4	11.0	16.3	10.5	10.5	8.8

precluded inducing a significant and widespread aerial drawdown thus limiting our characterization to date as those that could be determined from individual wells.

Analysis of the hydrogeological characterization data indicated that the tested lower zone had a K-range from about $5e^{-04}$ to $1e^{-02}$ m/s with implied semi- to confined conditions in lower zone and water table conditions in the upper zone. Similar results were obtained from short-term pumping tests in the upper zone except at K5.2 where the drawdown was rapid and reflected a lower hydraulic conductivity of about $1e^{-04}$ m/s. Most calculations of hydraulic conductivity carried out at the site assumed the thickness of the contributing zone was equivalent to the screen for the lower zone and to the saturated thickness in the well for the upper zone.

Water level measurements repeated over about one year at the site indicated a stable hydraulic gradient in both zones that was similar and ranged from 0.0005–0.001. Seasonally, depth to water table changed, but the gradient remained essentially constant at the site.

Based on the determination of the hydraulic conditions, we also made scoping calculations to estimate the average transport velocity of planned tracer tests. Input was the hydraulic gradient and K-value characterizations and an estimated range in effective (transport) porosity. Preliminary average aquifer flow velocities for the site area had been estimated by Cantonal staff to be about 1 m/d in our site vicinity. We undertook scoping based on this simplistic set of assumptions using a range of hydraulic conductivity from $5e^{-03}$ to $1e^{-02}$ m/s, a hydraulic gradient of 0.001 and an effective (transport) porosity (n) range of 7.5–20 %. Well logging by P. HOFFMEYER (1995) had shown that in a well about 500 m south of the site, preferential pathways in lenses in the gravel aquifer were present in the gravel sequence. Accordingly, we used a reduced value for

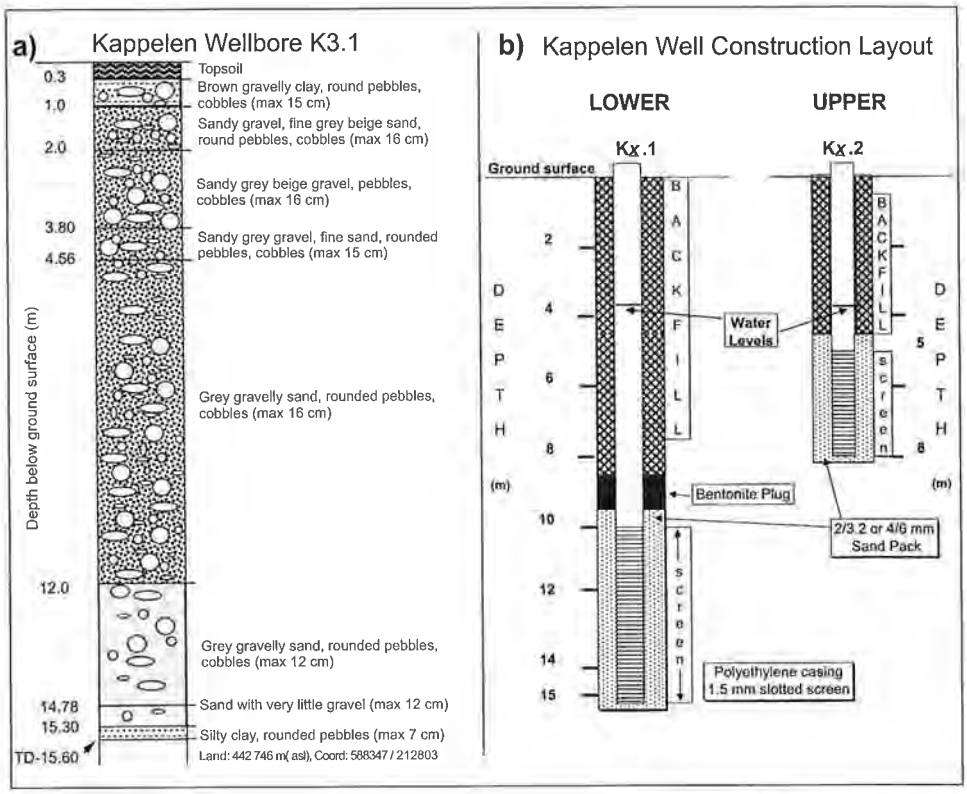


Fig. 4.5: Geological interpretation. a) well log for K3.1, b) schematic of typical well completions. Geologische Beschreibung. a) Bohrlochprofil für K3.1, b) schematische Darstellung der Doppelbohrungen.

the lower range of the transport porosity value. Results suggested that for a conservative (non-sorptive) solute tracer, the peak concentration time to a distance of 20 m, where the first row of wells was located, would be from about 2–10 d.

4.1.4. Biogeochemical Characterization

Diverse and widespread reduced oxygen conditions exist in the Seeland aquifer. To the SE these are mainly due to the seepage, rich in degradable organics, from unlined discharge at the sugar refinery lagoons. Studies in the 1950s and 1970s showed an extended plume of reduced groundwater deteriorating water supplies. This heterogeneity makes it difficult to determine exact horizontal/vertical plume extent, its redox conditions and the transport of contaminants DOC, Fe^{2+}, Mn^{2+} and K^{+}. Recent regional surveys showed limited rehabilitation from the infiltrating Alte Aare River. Redox environments in groundwater situations are common. However, the rate of reactive changes are typically site specific. Documenting the chemical, sedimentary and microbiologic parameters was critical to carry out further groundwater research and assess the migration potential of tracers at the site.

In 1997, a program to characterize the bacteria and hydrochemistry in the wells impacted by redox conditions was developed. The participants included University

Tab. 4.2: Groundwater chemistry in the vicinity of the Kappelen site. D_{tot} – total hardness; < – indicates below detection limit; no result – not measured. Sample results from Canton Bern Analytical Laboratories, 1997, 1998.
Grundwasserchemie in der Nähe des Kappelen Testgebiets. D_{tot} – Wasserhärte; < – unter der Nachweisgrenze; „kein Wert" – nicht gemessen. Resultate des kantonalen Labors Kanton Bern, 1997, 1998.

Parameter	Cond. [µS/cm]	pH	O_2 [mg/l]	DOC [mg/l]	D_{tot} [mmol/l]	Na^+ [mg/l]	K^+ [mg/l]	Fe^{2+} [mg/l]	Mn^{2+} [mg/l]	NH_4^+ [mg/l]	Cl^- [mg/l]	SO_4^{2-} [mg/l]	NO_3^- [mg/l]	Eh [mV]
Regional wells and river														
Alte Aare		8.1	9.2	1.7	1.32	2.0	1.0	0.06	0.01	0.2	2.6	24.6	4.8	
7.2	705	7.0	1.3	1.3	3.91	4.97	11.5	0.08	0.02	<	7.9	41.1	4.2	
RB1	314	7.5	<	0.6	1.64	2.23	1.7	0.05	<	<	2.4	27.6	0.51	
RB1 (lower)	337	7.5	<	0.6	1.75	2.83	2.0	0.47	0.23	0.07	2.5	31.5	0.14	
A2	406	7.3	<	0.5	2.13	3.75	3.9	0.92	0.47	0.06	5.6	34.4	0.03	
A1	610	6.9	7.0	1.4	3.37	6.32	5.6	0.38	0.06	0.02	7.8	36.7	1.17	
RB2	448	7.2	1.2	0.9	2.4	3.29	1.8	0.05	0.02	<	3.6	27.7	0.84	
RB2 (lower)	389	7.2	1.1	0.7	2.07	3.06	1.8	0.05	0.02	<	3.1	27.4	0.44	
Site wells/Upper zone														
K1.2	465	7.7	0.5	0.8	2.25	3.9	3.3	0.21	0.79	0.14	4.0	36	<	– 51
K3.2	483	7.7	1.0	0.7	2.4	4.5	3.8	0.17	0.31	0.1	4.4	37	<	– 91
K4.2	545	7.6	2.7	0.6	2.5	4.6	3.8	0.037	0.2	0.045	5.1	36	0.26	45
K5.2	545	7.6	0.5	0.7	2.65	4.0	5.3	0.76	0.63	0.029	5.4	38	<	– 86
K7.2	534	7.6	1.1	0.6	2.65	5.0	3.9	<	0.01	<	6.0	36	<	61
Site wells/Lower zone														
K1.1	465	7.7	0.5	0.8	2.15	5.2	4.6	0.98	0.56	0.51	5.5	37	<	– 85
K3.1	467	7.7	0.5	1.5	2.25	5.8	4.5	1.1	0.58	0.52	6.9	37	<	–105
K4.1	488	7.5	0.6	0.8	2.55	6.6	4.4	1.3	0.71	0.31	7.3	35	<	– 90
K5.1	504	7.8	0.6	0.8	2.4	4.7	6.0	1.4	0.66	0.31	5.9	39	<	–128
K7.1	513	7.7	0.5	0.8	2.4	6.2	4.7	0.92	0.65	0.39	7.4	37	<	– 38

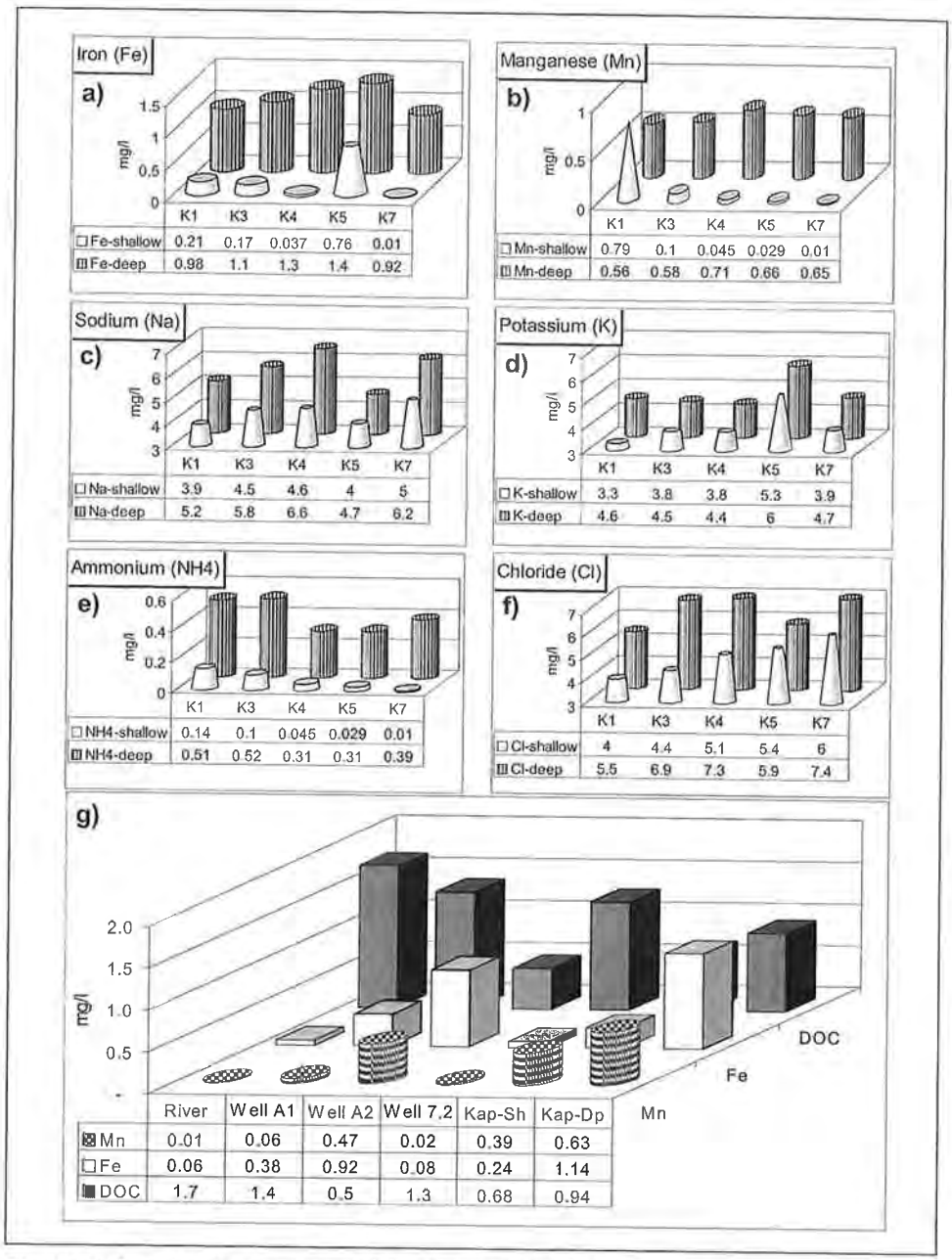


Fig. 4.6: Redox-related parameter variability in the vicinity of the Kappelen site. a) iron, b) manganese, c) sodium, d) potassium, e) ammonium, f) chloride, g) aerial variations in Fe^{2+}, Mn^{2+} and DOC in the Kappelen vicinity. Data in plots a) through f) are wells at Kappelen site.
Verteilung der redoxabhängigen Parameter in der Nähe des Testgebietes. a) Eisen, b) Mangan, c) Natrium, d) Kalium, e) Ammonium, f) Chlorid, g) regionale Variationen von Fe^{2+}, Mn^{2+} und DOC in der Umgebung vom Kappelen. Daten in den Grafiken a) bis f) stammen von den Bohrungen innerhalb des Testgebietes.

Neuchâtel (CHYN) hydrogeologists and (LAMUN) microbiologists and the Canton of Bern's Analytical Laboratory and Environmental and Groundwater Protection Department staff. Redox chemistry and microbial activity were evaluated in 10 wells at Kappelen. These wells are about 750 m from the northern extent of the sugar factory settling ponds (Fig. 4.1). Redox conditions varied strongly even over the limited distance of 70 m and between the shallow and deeper aquifer layers. Characterization with results of sampling is listed in tab. 4.2. Eh varied from –130 mV to +61 mV. Dissolved oxygen ranged from near zero to 25 % of saturation.

Results of geochemical sampling at the site (Fig. 4.6a through 4.6f) indicate that, between the upper and lower zone, there is a high degree of variability in redox-related indicators. Consistently, the Fe^{2+}, Mn^{2+}, Na^{+}, K^{+}, NH_4^{+} were significantly lower in the upper 8–9 m of the aquifer than in the lower 10–15 m zone. Some components of the regional redox studies have been erratic and hard to define with continuity throughout the area down gradient from the disposal lagoons. It was not always able to determine which depth samples actually represented. Mixing source vertical depths when depicting aerial concentrations in a heterogeneous gravel aquifer may not allow adequate characterization of a plume's nature and extent particularly when the setting is heterogeneous fluvio-glacial gravel and sand deposits. Figure 4.6g illustrates the degree of variability in Mn^{2+}, Fe^{2+} and DOC in regional wells, the Alte Aare River and the upper and lower zones at the site. We were interested in observing the extent to which parameters at the site varied over several tens of meters. These data were compared to changes documented over wider areas of the Seeland aquifer. Results suggest that for parameters Mn^{2+} and Fe^{2+} (Fig. 4.6a, 4.6b), the shallow and deep zones at Kappelen show considerable variability illustrating that at one site there is as much variability as is documented regionally at wells A1, A2 and 7.2.

There was under saturation with respect to oxygen in the lower part of the aquifer at the site. Installing the wells at the site created an artificial access source for oxygen. The well provided a vertical migration path for air to diffuse downward in its standing column of water. Oxygen reaching this under saturated environment caused changes in the bacterial activity in the near vicinity of the well, particularly in the lower zones. The oxygen appears to have caused relatively rapid indigenous iron and manganese oxidizing bacterial growth. Microbiological characterization of the strains that could have created the biofouling included *Siderocapsa sp.*, *Gallionella sp.* and *Leptothrix sp.* The extent of the biofouling has not yet been well characterized. However, it has been sufficient, as described below, to effectively seal the well preventing mixing of this water with the naturally occurring recharge in the local groundwater flow.

4.1.5. Tracer Testing

The site was prepared so as to begin tracer testing in the deeper part of the aquifer in December 1997. All seven deep locations were equipped with dedicated tubing sampling equipment. In addition, low volume peristaltic pumps were set up to extract from wells K2.1 and K3.1 closest to the injection well K1.1. Freezing weather precluded initiating the testing until the end of February 1997. In the following 18-month period, seven tracer tests were done with five in the deep/lower and two in the shallow/upper zone. Testing focussed on the deeper zone in the first year and the shallow zone in year two. In the lower zone, the first three tests were successful in terms of defining response timing and magnitude. Tests 4 and 5 were not successful due to significant biofouling in the well screens in wells K3 and K2. Both tests 6 and 7 in the upper

zone were successful although there were only limited responses in row 2. Tables 4.3 and 4.4 summarize the tracer components, the input conditions, analytical methods used and the characterization results for the bacteriophage and uranine responses in tests 3 and 7. These two tests represent the best tracer observations we have to date for the site. The test descriptions in the following section summarize the rationale and results arising from each of the seven tests undertaken.

Tracer Test KAP 1

KAP 1 began in late February 1997 with the injection of about 80 g of uranine and lasted about 10 d. Being the first test, its purpose was feasibility and reconnaissance, namely to document the groundwater travel time to plan future tests. The injection was done by pumping about 20 l of tracer cocktail containing about 80 g of uranine

Tab. 4.3: Tracer component characteristics, analysis methods and injection conditions. Tracer tests KAP 3 (lower zone) and KAP 7 (upper zone). [1] *– colloid details are size (head, tail), morphotype (family), genetic material (gm) – single (ss) or double (ds) stranded, isoelectric point (pH at which the particles possess zero net charge) and zeta potential (mV – the charge balance, expressed in millivolts measured at a pH of 7.4 at a given ionic strength) for the bacteriophages;* [2] *– described in P.-A. Schnegg & N. Doerfliger (1997) and similar to new equipment with the same resolution as in P.-A. Schnegg & K. Kennedy (1998);* [3] *– bacteriophage H40 developed for tracer studies by LAMUN, Microbiology Department, University of Neuchâtel (P. Rossi, 1994);* [4] *– H.-W. Ackermann & M. S. DuBow (1987a, b); nm – not measured.*
Tracercharakteristika, Analysemethoden und Einspeisebedingungen. Tracer Tests KAP 3 (untere Zone) und KAP 7 (obere Zone). [1] *– die Kolloideigenschaften sind: Größe (Kopf, Schwanz), Morphotyp (Familie), genetisches Material (gm; RNA, DNA), isoelektrischer Punkt (pH-Wert bei dem die Partikel Null-Ladung besitzen) und Zeta-Potential in mV (Ladungsgleichgewicht gemessen in mV bei einem pH-Wert von 7.4) für die Phagen-Tracer;* [2] *– beschrieben in P.-A. Schnegg & N. Doerfliger (1997) und vergleichbar mit neuer Ausrüstung mit gleicher Auflösung wie in P.-A. Schnegg & K. Kennedy (1998);* [3] *– Bakteriophage H40 entwickelt für Traceruntersuchungen durch LAMUN, Microbiology Department, Universität Neuchâtel (P. Rossi, 1994);* [4] *– H.-W. Ackermann & M. S. DuBow (1987a, b); nm – nicht gemessen.*

Tracer component	Type	Component details [1]	Test – injected component mass		Analysis method (Resolution)
			KAP 3	KAP 7	
Uranine	Solute	Sodium fluorescene MW 376.28 $C_{20}H_{10}O_5Na_2$	25 g	53 g	On-line spectrofluorometry CHYN/UNINE Field fluorometer [2] (~ 0.1–0.5 ppb resolution)
Bacteriophage H40	Biocolloid	44,130 nm [3], *Siphoviridae* gm (dsDNA), IP (nm), zp (–42.0)	1.5e^{14} pfu	1.6e^{15} pfu	Bacterial host cultivation/ growth association, plate counting – petri dish (UNINE-Microbiol. Lab.) (1 phage per 2 ml resolution)
Bacteriophage H4	Biocolloid	24 nm [4], *Leviviridae*, gm (ssRNA), IP (3.5, 3.9), zp (nm)		5.7e^{14} pfu (Well K3.2)	

into well K1.1. This was done at a rate of about 20 l/min and was followed by pumping about 40 l of clear water. Sampling concentrated on the three wells in row 1. Clear PVC tubing was used to take a vertical profile sample opposite the screen in well 4.1. We were interested in seeing if any tracer segregation would be manifest with a layer opposite discrete screened sections. Wells K2.1 and K3.1 were equipped with peristaltic pumps at the surface connected to intakes at their screen midpoint depths of about

Tab. 4.4: Tracer component response characteristics for bacteriophages and uranine (tracer tests KAP 3 (lower zone) and KAP 7 (upper zone)). [1]) – uranine is a solute that is commonly referred to as a conservative tracer – and we designate Tr as the solute component concentration label. Accordingly, we refer to $t_{tr\text{-}arr}$ and $t_{tr\text{-}max}$ as the times associated with arrival and maximum solute concentrations, respectively. This differentiates it from the tc time terms associated with the colloids; uranine Tr_0 units are ppb; [2]) – $t_{c\text{-}max}$: time of maximum colloidal particle concentration; we refer to this as a pseudo-peak (ps-peak) since it does not have the same implied or associated characteristics as conservative solute tracer peaks do for mass transport behaviour; [3]) – retardation factor RF is the ratio of the time of maximum particle or colloid (in this case phage) concentration compared to that of the solute; [4]) – relative breakthrough RB as defined in R. HARVEY et al. (1989); [5]) – attenuation % = 100 % – RB %. Durchgangcharakteristika für Uranin und Bedingungen (Tracertest KAP 3 (untere Zone) und KAP 7 (obere Zone)). [1]) – Uranin ist eine Lösung, die allgemein als konservativer Tracer betrachtet wird; wir betiteln Tr als die gelöste Komponente; entsprechend bezeichnen wir mit $t_{tr\text{-}arr}$ und $t_{tr\text{-}max}$ die Zeiten für den Konzentrationsersteinsatz und –maximum; dies dient zur Unterscheidung von den für die Kolloide verwendeten tc-Zeitbezeichnungen; die Uranin-Tr_0-Einheiten lauten ppb; [2]) – $t_{c\text{-}max}$: Zeit für maximale Kolloidkonzentration; wir bezeichnen diese als „Pseudo-Peak" (ps-peak) weil sie nicht die selben Eigenschaften besitzen wie konservative, gelöste Tracer-Massentransport-Peaks; [3]) – der Retardationsfaktor RF ist das Verhältnis von Partikel- oder Kolloid- (in diesem Fall Phage) maximumzeit zur Uraninmaximumzeit; [4]) – „relativer Breakthrough" RB wie definiert in R. HARVEY et al. (1989); [5]) – Dämpfung % = 100 % – RB %.

Down gradient well	Distance from injection [m]	Uranine response[1])			Bacteriophage H40 response					
		$t_{tr\text{-}arr}$ [h]	$t_{tr\text{-}max}$ [h]	$(Tr/Tr_0)_{max}$	$t_{c\text{-}arr}$ [h]	$t_{c\text{-}max}$[2]) (ps-peak) [h]	RF[3])	$(C/C_0)_{max}$	RB[4]) [%]	Att'n[5]) [%]
Test 3										
K2.1	21	15	42	$2e^{-03}$	13	38	0.9	$9e^{-07}$	0.02	99.98
K3.1	20	11	29	$2e^{-03}$	11	16	0.6	$1e^{-06}$	0.02	99.98
K4.1	21	22	36	$2e^{-05}$	not adequately sampled					
K5.1	63	present, not quantified			none detected					
K6.1	60	< 44	129	$2e^{-04}$	< 44	62	0.5	$3e^{-08}$	0.005	99.995
K7.1	63	present, not quantified			present, not quantified					
Test 7										
K2.2	21	none detected			18	30	n. a. s.	$3e^{-10}$	n. adeq. samp.	
K3.2	20	13	83	$1e^{-03}$	12	27	0.3	$2e^{-06}$	0.01	99.99
K4.2	21	14	89	$1e^{-05}$	11	17	0.2	$6e^{-08}$	0.01	99.99
K7.2	63	~ 144	~ 600	$5e^{-06}$	none detected					

12.5 m. The sampling flow was 0.2 up to 0.5 l/min. Uranine was measured every four minutes for these two wells with field fluorometers set up so that the pumped flow passed directly through the detector channel (modified from the equipment described in P.-A. SCHNEGG & N. DOERFLIGER, 1997).

Uranine was detected in row 1 at wells K2.1 and K3.1 (Fig. 4.7a) but not at well K4.1 or any of the row 2 wells. First detection and maximum concentrations occurred at the two wells at about 14 and 40 h and 13 and 34 h, respectively. This corresponded to an arrival and transport velocity of 37 and 14 m/d, respectively. The arrival of the tracer in less than 24 h was considered a satisfactory and encouraging response particularly considering the relatively flat hydraulic gradient (0.001).

Tracer Test KAP 2

KAP 2 followed back-to-back KAP 1 and was carried out over about 14 d in March 1997. It was done to observe the phage efficacy and travel time to row 1 and to evaluate if the redox environment at the site would still allow favorable phage response. It had similar hydraulic conditions to KAP 1 but uranine levels were well above background noise. KAP 2 involved the injection of about 10 l of water containing 25 g of uranine and two different marine phages (H4 – $1.4e^{13}$ pfu, H40 – $1.3e^{13}$ pfu). Injection was done by adding this solution to a volume circulating from the bottom of the well screen into a surface vessel and returning to below the water table at a rate of about 20 l/min. Sampling was done as for KAP 1 except that well K6.1 in row 2 was also equipped with a peristaltic pump and wells K5.1 and K7.1 were also sampled. Samples were taken periodically on site and transported within 12–24 h to the University Neuchâtel (LAMUN) for immediate bacteriophage analysis.

Phage H4 was not detected during the test. Phage H40 was first detected in wells K2.1 and K3.1 after about 14 h (Fig. 4.7b) and continued to be present over the entire 14 d of sampling. The Maximum phage concentrations reached at the two wells were

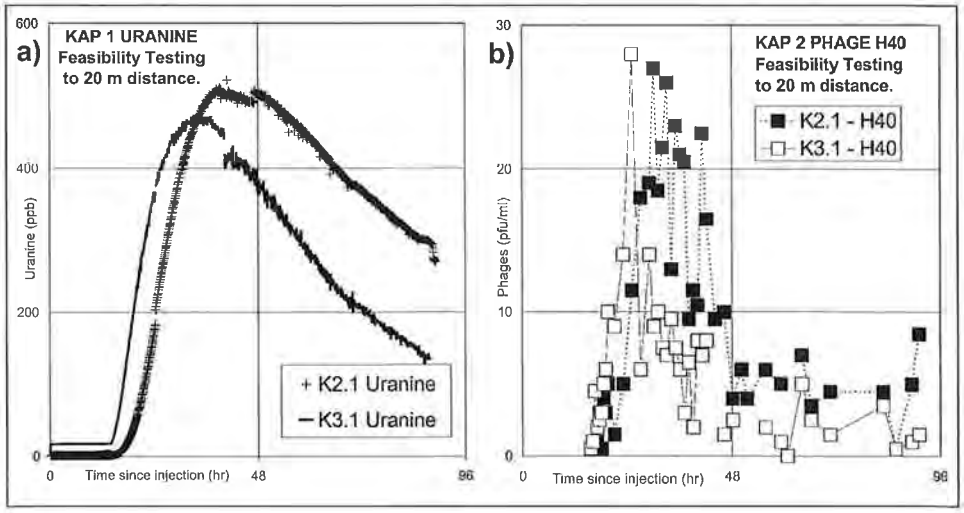


Fig. 4.7: Tracer tests KAP 1 and KAP 2 concentration history at wells K2.1 and 3.1. a) KAP 1 (uranine), b) KAP 2 (phage H40).
Tracertests KAP 1 und KAP 2, Durchgangskurven bei den Bohrungen K2.1 und 3.1. a) KAP 1 (Uranin), b) KAP 2 (Phage H40).

about 30 pfu/ml. After 48 h, most values were at levels of less than 6 pfu/ml. Phage H40 was not detected at the other row 1 well (K4.1) nor was it detected at wells K5.1 or K7.1 in row 2. It was, however, observed to levels of about 4 pfu/ml in well K6.1 beginning about 64 h after injection and was no longer detected after about 110 h. Uranine was detected again in wells K2.1 and 3.1. The concentrations stopped decreasing in well K2.1 at about 17 h after injection reflecting the arrival of the KAP 2 injected solute at levels above the reducing background from KAP 1. The lack of testing for uranine at well K6.1 during KAP 1 precluded any comperative assessment about its behaviour during KAP 2.

Results of KAP 2 were consistent with the KAP 1 results for the uranine in terms of first detection times being similar in row 1. That both phages and uranine were found at K2.1 and K3.1 and not at well K4.1 was also consistent. The first conclusion from this test was that uranine and phage H40 transport was consistent in terms of their arrival times. We did not expect similar times for the phage and solute maximum concentrations. Phage levels at both wells began to decrease after about 24–30 h whereas the uranine maximum values occurred at about from 36–52 h as during KAP 1. The second conclusion was that higher initial mass and concentrations of phages were needed to yield acceptable results. The H4 phage was not detected and the H40 phage levels did not provide sufficient resolution to well characterize their response. Finally, it was apparent that the level of attenuation of the phages to 20 and 60 m was over 99 %, as had been observed for bacteria and microspheres albeit over shorter distances in finer grained porous media at the Cape Cod site (R. W. HARVEY et al., 1989).

Tracer Test KAP 3

KAP 3 began May 1, 1997 and lasted 10 d. The tracer cocktail was prepared by adding 25 g uranine and 2 l of phage H40 solution ($1.5e^{14}$ pfu) to 8 l of water pumped from the deep zone just prior to beginning the test. Injection was done by adding this solution to a volume circulating from the bottom of the well screen into a surface vessel and returning to below the water table at a rate of about 60 l/min. The injection circulation was continued over about 30 min to ensure it was well mixed. An additional 60 l of tracer-free site groundwater were pumped at a reduced rate into the well to displace the original tracer after which time it diluted under naturally conditions with flow through the well. Sampling was done with low volume peristaltic pumps at the screen mid-point at all but the injection well.

KAP 3 results are characterized by the results shown in fig. 4.8 and are quantified in tab. 4.4. The early time analysis plot (Fig. 4.8a) shows the row 1 well (K3.1) at which there was an apparent gradual rise in uranine levels preceding the phages first detection at about 11 h. About 1 h later, the uranine slope increased significantly and it is this slope that likely represents the uranine levels finally reaching above background variability. Figure 4.8b illustrates the breakthrough curve to 100 h showing the maximum concentration of phages occurring at about 15–17 h and the uranine maximum (peak) at 28–30 h. In well K2.1, there was more irregularity in the phage data as had occurred during KAP 2. The phage and uranine arrival and maximum concentration times were 13 and 38 and 15 and 42 h, respectively. Maximum dimensionless concentrations (MDC) for uranine were about 2,000-fold higher than for phages. Both uranine and phages were detected in well K4.1 but at concentrations 50- to 100-fold lower than in the other two row 1 wells. In row 2, uranine was detected in all three wells but only at well K6.1 were concentrations adequate for its response to be characterized. Phages were detected at K6.1 and K7.1 but were of sufficient magnitude only at K6.1 to cha-

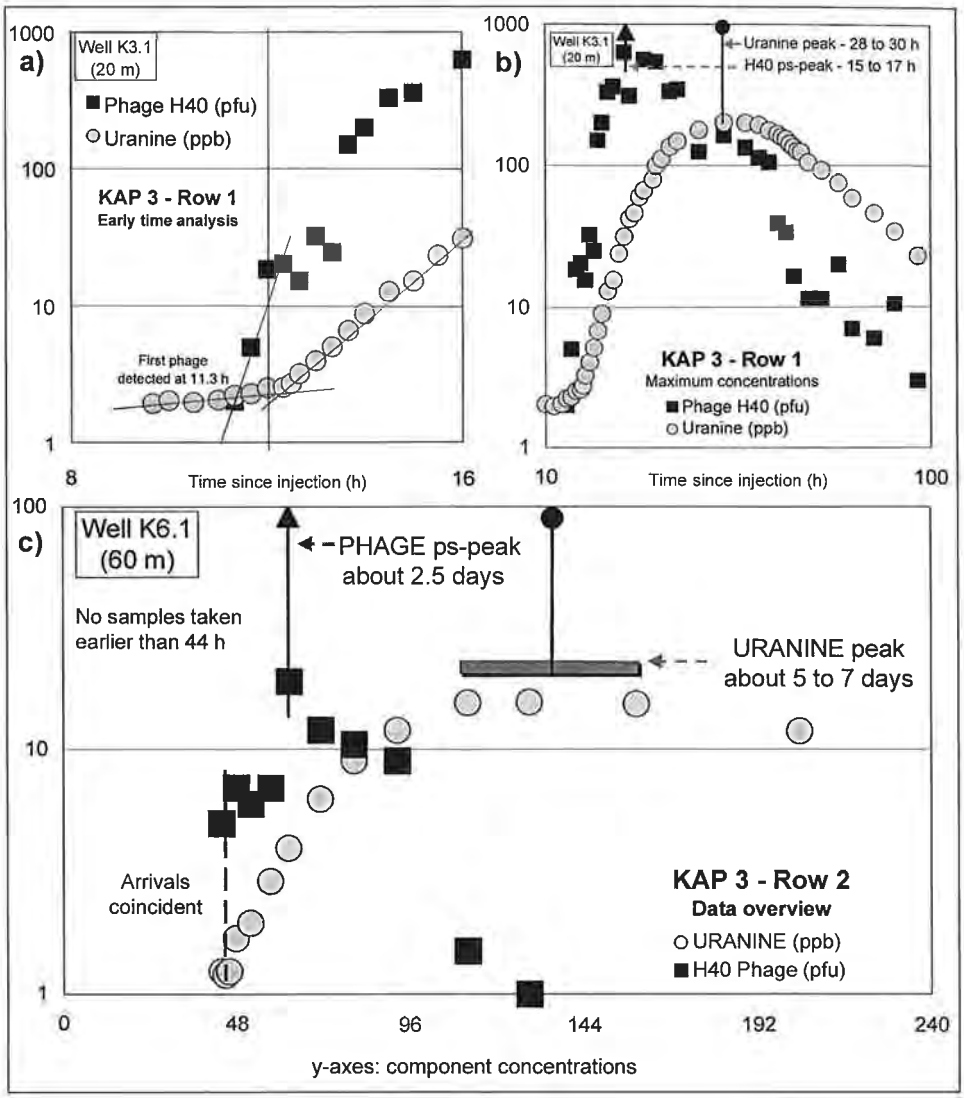


Fig. 4.8: Tracer test KAP 3 concentration history. a) well K3.1 early time analysis, b) well K3.1 maximum concentrations, c) well K6.1 data overview.
Tracertest KAP 3, Durchgangskurven. a) Bohrung K3.1 Ersteinsatz-Analyse, b) Bohrung K3.1 maximale Konzentrationen, c) Bohrung K6.1 Datenübersicht.

racterize the response. The H40 and uranine response at K6.1 (Fig. 4.8c), while not as well defined as in row 1, showed both components with similar early time or near-arrival patterns after about 44 h. Phage and uranine maximums were at about 2.5 d and over a broader range of 5–7 d, respectively. The MDC-difference increased compared to row 1 with uranine about 7,000-fold greater than H40. The uranine breakthrough data correspond to arrival and transport velocities of about 29–53 and 14–21 m/d in both rows, respectively.

Recovery calculations for phages based on relative breakthrough compared to uranine (Tab. 4.4) were 0.02 % for both wells in row 1 and about four times lower at 0.005 % for well K6.1. Relative breakthrough integrates the particle component responses over time and compares this total relative recovery to the integrated solute response assumed to represent 100 % recovery.

In KAP 3, the MDC- and RB-factors decreased consistently by a factor of 3.5–4 over the 40 m from row 1 to row 2 wells. Retardation factor compares the time at which the particles reach their maximum with the time of maximum solute concentration. The phage maximum concentrations occurred consistently earlier than the solute maximums in this test and the RF-values were 0.9, 0.6 and 0.5 at wells K2.1, K3.1 and K6.1, respectively.

Tracer Tests KAP 4 and KAP 5

Test 4 and 5 were done in August 1997 about three months after completion of KAP 3. The specific objective of the testing was to compare the response of 1-micron diameter fluorescent microsphere colloids with phages and uranine. Neither test was successful in that the injected component responses were either non-detectable or too low to characterize the breakthrough. The test using the microspheres was rescheduled and performed at another nearby test site, Wilerwald in August, and September 1997.

In KAP 4, no uranine and no microspheres were detected over about one week. Phage detections were intermittent in the first 2 d of samples at row 1 wells. This was in clear contrast to the patterns well established with the KAP 3 results. No response was observed in row 2 despite more frequent sampling and increased injection concentrations. The test was terminated after about ten days and K. KENNEDY, I. MÜLLER, P.-A. SCHNEGG, P. ROSSI, R. KOZEL restarted as KAP 5 about a week later. In KAP 5, similar negligible responses from phages were observed and no uranine and microspheres were detected over 5 d. At this time we acknowledged that there was clearly a problem and something was taking place we did not understand. We terminated the test realizing that the lack of detected colloids was potentially reasonable, but the failure to detect uranine was not. The water levels were lower than during KAP 3, but the gradient had not changed. Our first action was to pump at about 100 l/min from the K2.1 and K3.1 wells in Row 1 and the K6.1 well in row 2. K3.1 yielded water that was clear for the initial 2 min, became dark brownish-red with a defined residue for the next 2 min and was followed by water with a fluorescent green color indicating uranine in substantive concentrations. Well K2.1 yielded a similar red color and residue but no uranine was observed. Red coloration from well K6.1 lasted only a few seconds and no uranine was observed. We concluded that the KAP 4 and KAP 5 limited response had likely been caused by biofouling of the well screens. The extent of the biofouling was surprising in that it had been complete enough that the injected tracer components were prevented from entering the well. They were discovered in close proximity when active pumping took place, but had been blocked from entry by the bacterial growth.

Tracer Test KAP 6

KAP 6 and KAP 7 undertaken at Kappelen assessed the response characteristics of phages and uranine in the upper zone to depths from about 4–8 m. Pumping in the seven shallower wells had not historically shown any noticeable red discoloration. We undertook the upper zone tests hoping that to an 8 m depth, there would be a less reactive response to the introduction of oxygen than what we had occurred in the 10–15 m lower zone.

Tracer Test KAP 6 was similar to KAP 1 and KAP 2 in that it was a preliminary feasibility test to scope the response patterns of the upper zone. Phage H40 ($1.7e^{14}$ pfu) and uranine (26 g) were injected in well K1.2 on November 4, 1997 and sampling carried on through November 13, 1997. Sampling was done using a closed circuit circulation system. In this situation, rather than pumping from a particular depth at a low rate, the well water was circulated opposite the entire length of the screened zone thereby creating a fully mixed column of water. Flow was about 4 l/min suggesting a cycle of return for the well screen volume was from 10–12 min. Sampling was done for the bacteriophages by removing the required 80 ml volume from an in-line 3-way valve. The circulation flow was also able to be connected to the field fluorometer as in previous testing to obtain a real-time readout of the uranine concentrations. Injection was done using a similar basic system. The tracer cocktail volume flowed under VENTURI conditions into the circulating line equipped with a 3-way valve. Injection circulation continued over about 4 d at which time the phage and uranine concentrations were approaching 10 pfu/ml and 1 ppb, respectively.

Both phages and uranine were detected in row 1 at the three wells but neither component was detected in row 2. The components were transported in a more northeasterly direction than had occurred in the lower zone. Phage and uranine initial detection was at about 12 and 15, 15 and 20 and 20 and 25 h at wells K4.2, K3.2 and K2.2, respectively. The concentration of phages reached a maximum at about 17, 21 and 26 h. Uranine peaks at these wells were less regular at 90, 65 and 45 h. The uranine response at well K2.2 was not well characterized. Phage concentrations were about 10- to 50-fold too low for optimal counting in row 1 and neither component was detected at row 2.

Conclusions from KAP 6 were that: no biofouling had impacted the testing, phage and uranine responses were able to be characterized at K4.2 and 3.2, phage response but not uranine could be characterized at K2.2, the direction of flow was different than in the lower zone and the phage injection concentrations should be increased with the mass injected over longer periods of time to establish a better breakthrough response pattern to characterize.

Tracer Test KAP 7

KAP 7 began on July 12, 1998 and lasted over three months. The tracer cocktail was prepared by mixing uranine (53 g) and phage H40 ($1.6e^{15}$ pfu) in about 20 l of solution which was injected under VENTURI effect with circulation conditions over a period of 1.5 h at well K1.2. Circulation continued in the injection well over a period of about 2 d at which time uranine concentrations approached 1 ppb. H40 phage levels had decreased to about 1,200 pfu/ml and remained in the range from about 350–2,350 pfu/ml over the duration of testing. After 24 h , 38.5 l of solution with phage H4 ($5.7e^{14}$ pfu) was injected in the first row well K3.1 using a similar method. The objective of adding the second phage was to enhance the possibility of its detection in the second row at a reduced distance of 40 rather than 60 m. Continuous monitoring of the uranine response was done at different periods at the three upper zone row 1 wells and at two row 2 wells. Sampling was done as described for the KAP 6 test. Phage sampling was done over about 10 d at all six wells. Uranine was measured over the full 10 d at all wells and then continued for about one and two months in wells K7.2 and K3.2, respectively.

Figure 4.9 shows five plots with different aspects of the KAP 7 test component response characterization. Table 4.4 summarizes the quantified aspects of these responses. Figure 4.9a shows the test record for all components detected in wells K3.2 and K4.2 in row 1. Phages were also detected in well K2.2 but only with a minor response

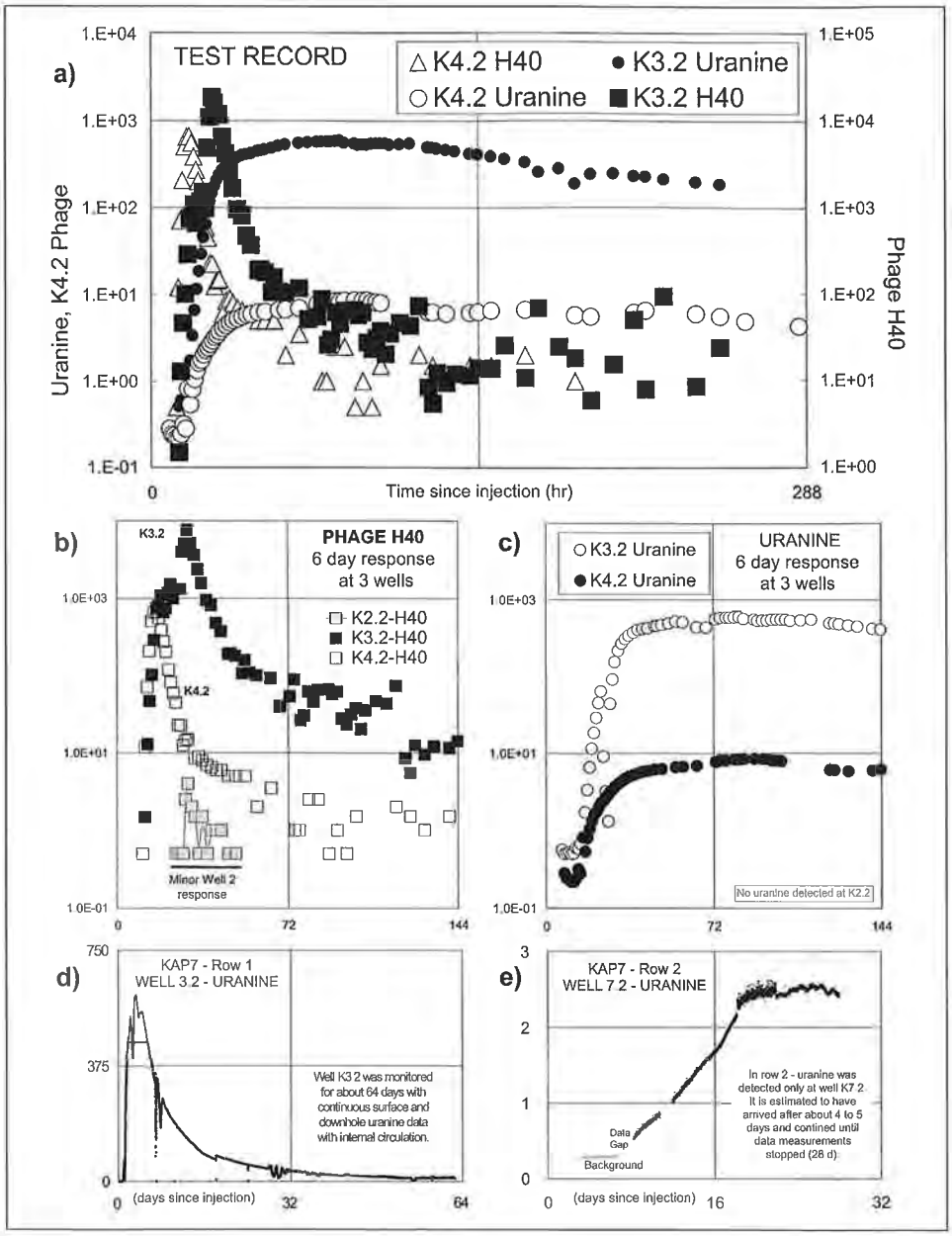


Fig. 4.9: Test KAP 7 concentration history. a) test record for K3.2 and K4.2 – uranine and H40, b) phage H40 – 6 d response at K2.2, K3.2 and K4.2, c) uranine – 6 d response at K2.2 (none), K3.2 and K4.2, d) uranine – K3.2 (row 1) 2 month continuous record, e) uranine – K7.2 (row 2) 1 month continuous record.
Test KAP 7 Durchgangskurven. a) Testaufnahme für K3.2 und K4.2 – Uranin und H40, b) Phage H40 – 6-Tages-Antwort bei K2.2, K3.2 und K4.2, c) Uranin – 6-Tages-Antwort bei K2.2 (kein Signal), K3.2 und K4.2, d) Uranin – K3.2 (Reihe 1) 2-Monate-Aufnahme, e) Uranin – K7.2 (Reihe 2) 1-Monat-Aufnahme.

several orders of magnitude less than in well K3.2 (Fig. 4.9b). The first 6 d of the test response in row 1 illustrate that the breakthrough responses for both phages and uranine were distinct at wells K3.2 and K4.2 (Fig. 4.9b, 4.9c). Phages and uranine were first detected in these two wells after 12 and 13 and 11 and 14 h , respectively. The maximum phage and uranine concentrations occurred at about 27 and 83 h and 17 and 89 h, respectively. The uranine response at well K3.2 (Fig. 4.9d) illustrates that the technique of long-term response characterization was effective using the closed circuit circulation combined with continuous on-line recording of uranine with either a surface or downhole (P.-A. SCHNEGG & K. KENNEDY, 1998) field fluorometer unit. Only short-term pump-related interruptions in the data occurred. MDCs for uranine were in the range of $1e^{-03}$ and $1e^{-05}$ at K3.2 and K4.2, about 640- and 260-fold higher than for phages. We observed that uranine detection was better using the newly designed downhole fluorometer located in the well directly and that it attained a resolution of about 0.1 ppb within the continuous circulation closed-circuit system.

At well K2.2, the phage maximum occurred at 18 h although its record is not considered sufficient for component response characterization at this location (Fig. 4.9b). The H40 MDC at K2.2 was about 5,000-fold lower than at K3.2. In row 2, neither the H40 phages injected at well K1.2 nor the H4 phage injected in well K3.2 were detected. Uranine was detected only at well K7.2 (Fig. 4.9e) after about 5 d. It continued a slow and consistent increase to levels of about 2.6 ppb and stayed in this relative range over about 6 d at which time it began to decrease. MDC for the uranine at well K7.2 was about $5e^{-06}$, about three-fold lower than at K4.2 and 200-fold lower than at K3.2. Monitoring ended earlier than desired at K7.2 due to other equipment commitments. The K3.2 and K4.2 uranine breakthrough data correspond to arrival and transport velocities of about 46 and 7 m/d in both rows, respectively. They would be a factor of 2–4 lower in row 2 based on the K7.2 response characterization.

Phage recovery at wells K3.2 and K4.2 in row 1, based on relative breakthrough compared to uranine (Tab. 4.4), was about 0.01 %. The site monitoring ended before there was a complete uranine recovery at either well. Therefore, these recovery numbers represent upper limits and could likely decrease by as much as a factor of 2. There was no phage recovery in row 2. Phage maximum concentrations consistently occurred earlier than the solute maximums in this test. RF-values were 0.3 and 0.2 at wells K3.2 and 1 and K6.1, respectively.

Conclusions from both the KAP 6 and KAP 7 tests were that phage and uranine responses were well characterized at the row 1 distance of about 20 m but that neither phage nor uranine response was adequate at 60 m, even with a dual and prolonged injection of phages. Compared to the lower zone, the transport direction was more easterly and the solute mean transport velocity was two- to four-fold lower. First detection time of both tracers was similar and that the phages being detected earlier may be more dependent on the detection limit differences than on preferential colloid transport occurring in this setting.

4.1.6. Summary and Conclusions

Characterization of the groundwater environment at the Kappelen site began by using surface geophysical exploration methods. Results from VLF-EM and RMT techniques allowed development of a conceptualized geologic model depicting the nature and extent of the relatively prolific gravel-dominated aquifer found beneath the site. This model suggested a highly permeable aquifer extended over the investigated 100

by 100 m area, that it had a high degree of continuity and that its thickness varied principally from about 15–18 m. Underlying this was a lower permeability zone – an aquitard, that at this site did not have the dramatic changes in relief that had been observed at other fluvial-glacial settings nearby in the region. Drilling for well installation confirmed that the actual depths to the aquitard were generally within one meter of the geophysical interpretation. The good correlation between the geophysics and the geologic data illustrates that these methods can be relied upon in this setting to distinguish between the two contrasting lithologic types and arrive at a reasonable estimate of the aquifer thickness.

Hydrogeologic characterization started with updating the regional and local water levels to document the aquifer's potentiometric surface. A relatively stable and flat gradient of about 0.0005–0.001 has existed during the site research. Confirming the ground water flow direction and magnitude was followed by the installation of two piezometers and 16 wells in the upper and lower parts of the aquifer. The wells were aligned along the expected northwesterly gradient over a length of 90 m and a width of 40 m. Localized pumping in each well was principally relied upon to arrive at estimates of hydraulic conductivity ranging from $1e^{-04}$ to $1e^{-02}$ m/s. Travel times observed in the tracer testing imply that there may be preferential pathway lenses in the gravel structure that are more transmissive than the higher value in this range.

Biogeochemical characterization of the groundwater began by defining the redox conditions as they existed particularly in the lower part of the aquifer at the site. Site wells may have inadvertently provided a path for oxygen to migrate by diffusion to the base of the aquifer. This oxygen could have lead to the bacterial biofouling that has been documented. These conditions may continue to have an impact and it so could affect the ability to successfully undertake tracer tests in the lower zone. High rate pumping and possible treatment or specialized well and cleaning of the well screen and surrounding gravel pack will likely be required for future testing in this lower zone at the site to be successful.

Bacteriophage H4 response has not been able to be well defined and it may not be suitable for use at this site. However, bacteriophage H40 could be defined and its response, along with uranine have been well characterized to distances of about 20 m (row 1). Both the particle and solute tracer component responses in the two zones exhibited different transport direction and velocity characteristics. To 60 m, there was less detection of either phages or uranine and precise arrival times have not been well documented. Only one well in each zone to date has had a response adequate to characterize tracer component behaviour. The lack of a greater detection of at least the solute uranine in row 2 is surprising unless there are preferential pathways between the wells and the dispersion expected is not occurring effectively outside these channels to create a wider plume at that distance. Regardless, longer injection times on the order of days should be anticipated along with increased phage mass in order to be able to observe and better characterize the phage responses to distances greater than 20 m.

Phage and solute initial detection times were not sufficiently different to conclude whether or not there was clear evidence of phages undergoing preferential advection compared to the solute. Solute velocities based on the time of maximum concentration ranged from about 14–21 m/d and 3–7 m/d in the lower and upper zones, respectively. Transport velocities based on arrival times were two- to four-fold higher. MDCs for the phages were from 2- to 4-orders of magnitude lower than for the solute. Phage maximum concentrations consistently occurred substantially earlier than those of uranine consistent with diminishing mass source along the transport pathway due to particle

adsorption/attenuation. Retardation Factor values were from 0.2–0.9. Phage H40 recovery, based on relative breakthrough normalized to uranine recovery, was about 0.02 % and 0.005 % in the lower zone at 20 and 60 m distances, respectively. In the upper zone, it was 0.01 % at two locations at about 20 m. Accordingly, the phages have been attenuated to in excess of 99.9 %.

Despite the large attenuation, the H40 phage responses in KAP 3 and 7 have illustrated that bacteriophages do have consistent and continuous breakthrough patterns and that with adequate planning and resources even in difficult field settings, these can be well defined.

This suggests that the Kappelen site's use, given that the redox conditions remain understood and controlled, could likely be expanded to conduct further more detailed biocolloid/particulate migration and the adsorption process research in its special environment.

Acknowledgements

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4.2. Results of Bacteriophage, Microsphere and Solute Tracer Migration Comparison at Wilerwald Test Field, Switzerland

(K. KENNEDY, S. NIEHREN, P. ROSSI, P-A. SCHNEGG, I. MÜLLER, W. KINZELBACH)

4.2.1. Introduction

Comparing the behaviour of colloids and solutes as tracers in heterogeneous porous media aquifer environments is complicated by a variety of factors related to the aquifer materials, water chemistry, and tracer interactions with both the solid and liquid phases with which they come into contact. Laboratory experiments tend to show idealized responses from isolated variables being evaluated rather than the composite effects that are inherent in any real world set of conditions. Field tests are the basis for documenting actual transport conditions and providing a base to better simulate and calibrate predictive transport models. The site layout and geophysically interpreted hydrogeological heterogeneity of the Wilerwald site where this work was carried out in the fall of 1997 is in fig. 4.10.

Objectives and Rationale

The primary purpose of our work at this site was to document and evaluate the nature and extent of transport and attenuation of different types of phages and compare their behaviour with a conventional solute tracer. We coordinated with P-A. SCHNEGG

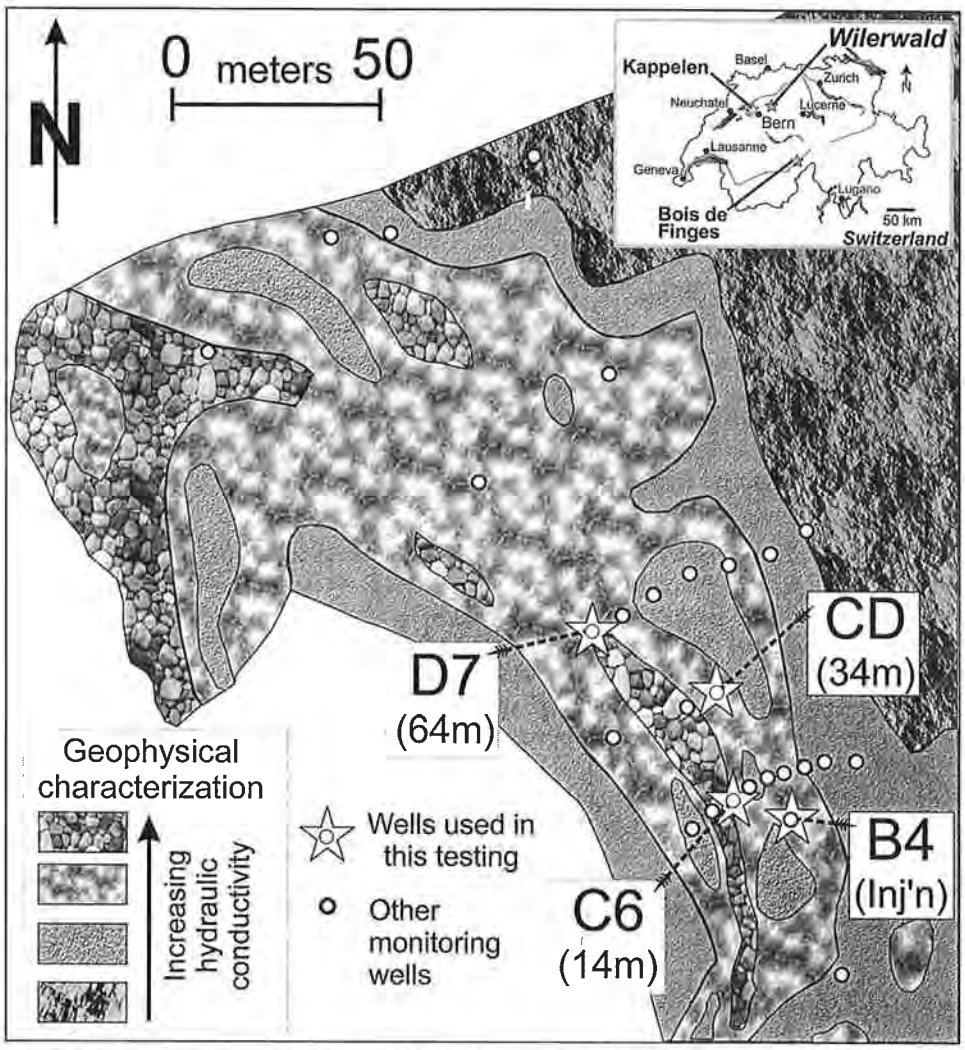


Fig. 4.10: Site location map including geophysical interpretation (after A. DE CARVALHO DILL, 1993). Lageplan mit geophysikalischer Auswertung (nach A. DE CARVALHO DILL, 1993).

from the Hydrogeology Center at the University of Neuchâtel and S. NIEHREN and W. KINZELBACH from ETH's Water Resources Management Department to evaluate field instrumentation measuring uranine and synthetic colloidal particles, respectively, during actual testing

The rationale associated with this work was three-fold. First, by using both particles and a solute tracer at the same time, we would better understand and characterize the transport-related phenomena of the subsurface media. Second, bacteriophages can mimic the manner and extent to which viral particles are removed from the environment during transport. One of the phages used was MS2 that has seen relatively widespread use internationally as a viral surrogate but has been restricted in its use here in Switzer-

land due to its genetically altered source. We wanted to compare that phage's performance with a marine bacteriophage, H40 that had been developed and for the most part used for particle migration studies in karst and river settings in Switzerland. Third, the sampling strategy in such testing activities is commonly difficult to determine beforehand. The use of on-line instrumentation to measure in real time both the particle and solute tracer concentrations at the wells allowed a focussed and more efficient approach in addition to dramatically reducing the time required to complete the work.

The four specific objectives of the tracer testing work done during this specific activity at Wilerwald were:

1) to document and compare the behaviour of three different bacteriophages,
2) to evaluate the use of continuous flow through a field fluorometer and a prototype fluorescent microsphere counter under field and environmental conditions,
3) to document and compare the response of the four different particle types with a conservative solute tracer, uranine, and
4) to evaluate real-time on-line measurements as a technique for optimizing field tracer test procedures and sampling strategies.

Project Scope

The scope of work involved three basic steps – preparation, testing and data analysis. First, the site was prepared for use. Well conditions were documented. Wells from the injection site to a distance of about 75 m were pumped to determine which were suitable for use and to clean out any residuals that had accumulated since the last testing by P. ROSSI, 1995 (P. ROSSI et al., 1998) and S. HADI in 1995, 1996 (S. HADI, 1997). Samples of water were submitted for bacteriophage analysis to determine if there was any background level in the water remaining since the last testing by P. ROSSI in 1995. After evaluation of the pre-testing results, three wells were selected for the field trial and the site was equipped with power and a temporary shelter. Instrumentation in the wells was emplaced and tested. Second, the field testing activity was undertaken over a period of about two weeks during which time samples for uranine and microspheres were analyzed in the field and phages in an off-site laboratory. Third, the data were analyzed using both quantitative comparisons and a numerical modelling approach (see S. NIEHREN, 1998).

4.2.2. Wilerwald Site (Canton Bern, Switzerland)

4.2.2.1. Hydrogeologic Setting

The purpose of this section is to describe the site and its characterized subsurface as it relates to a setting for migration of particles and solute tracers during the test. The site, located in the Emme valley in Canton Berne about 6 km south of Solothurn, is in a flat-lying forested area (wald) just outside the village of Wiler at an elevation of about 465 m. It was instrumented originally in 1986 by driving slotted metal pipes into the ground to depths of between about 8 m and 12 m. Subsequently additional metal slotted pipes were installed and a single well, CD was cored and instrumented with 2-inch OD PVC-tubing (Tab. 4.5).

The site has been used for various groundwater research activities over the past 14 years (M. SANSONI et al., 1987, 1988, Ch. LEIBUNDGUT et al., 1992, A. CARVALHO DILL, 1993 and S. HADI, 1997). A. CARVALHO DILL (1993) describes well the setting and the rationale for the development of the site with its current groundwater instrumentation. Regionally, the aquifer consists of Quaternary gravel present to variable depths

Tab. 4.5: Site well characteristics and water level measurements. [1]) – wells in bold text font are those that were used during the tracer testing described in this publication; [2]) – construction was either a driven metal slotted pipe or in the case of CD – slotted PVC-casing installed in the borehole; nd – not determined.
Beobachtungsrohrcharakteristika und Grundwasserpegelmessungen. [1]) – Text in Fettdruck kennzeichnet die für die in diesem Artikel beschriebenen Tracertests genutzten Bohrlöcher; [2]) – die Filterrohre bestanden in den geschlagenen Beobachtungsrohren aus Metall, in Bohrung CD wurde PVC verwendet; nd – nicht bestimmt.

Well[1]) [m]	Depth [mm]	Internal Diameter	Construction[2])	Coordinates		Measured water depth		
				East	North	26-Aug.	30-Aug.	6-Sep.
B4	**11.3**	**32**	**Driven – metal**	**609.766**	**222.05**	**3.56**	**3.57**	**3.57**
C0	4.5	32	Driven – metal	609.783	222.066	3.41	3.41	3.41
C1	4.4	32	Driven – metal	609.776	222.066	3.50	3.50	3.51
C2	1.8	32	Driven – metal	609.77	222.065	3.58	3.58	3.58
C3	10.4	32	Driven – metal	609.766	222.064	3.58	3.58	3.58
C4	12.2	32	Driven – metal	609.761	222.062	3.49	3.49	3.49
C5	12.5	32	Driven – metal	609.757	222.06	3.39	3.40	3.40
C6	**11.8**	**32**	**Driven – metal**	**609.753**	**222.057**	**3.38**	**3.39**	**3.38**
C7	12.1	32	Driven – metal	609.749	222.053	3.53	3.53	3.53
C8	12.2	32	Driven – metal	609.744	222.05	3.40	3.40	3.41
CD	**12.3**	**51**	**Borehole – PVC**	**609.749**	**222.083**	**3.40**	**3.39**	**3.39**
D1	nd	32	Driven – metal	609.771	222.12	3.28	3.28	3.28
D2	nd	32	Driven – metal	609.762	222.113	3.26	3.26	3.26
D3	nd	32	Driven – metal	609.753	222.111	3.25	3.25	3.26
D4	nd	32	Driven – metal	609.743	222.109	3.26	3.26	3.26
D5	nd	32	Driven – metal	609.734	222.104	3.35	3.35	3.34
D6	nd	32	Driven – metal	609.727	222.099	3.34	3.34	3.35
D7	**12.3**	**32**	**Driven – metal**	**609.72**	**222.095**	**3.27**	**3.26**	**3.27**

from 10 to about 50 m and comprised of gravel with sand and more coarse-grained fractions (pebbles, cobbles and boulders) and rarely with silt. Its composition and high degree of lithologic variability reflects its glacial provenance derived from sedimentation and erosion cycles in an alpine foreland of the Swiss Central Plateau. At a site scale, despite considerable interest and tracer-related work, there has been little lithologic documentation. The original assumption was that groundwater flow and transport in the aquifer at a 100 to 200 m site scale would be relatively homogeneous and isotropic. Lithology was originally expected to be sandy gravel lying between lower permeability alluvial sediments and underlying lacustrine sediments. Accordingly, the only site borehole was at CD (on fig. 4.10) and the lithology at this location was determined only in 1992 – in part to try to understand why earlier tracer test results could not be well matched with model results.

Lacking sufficient lithologic details, variability in the aquifer subsurface materials was subsequently approached using surface and downhole geophysical investigations. The variability in hydraulic conductivity, both vertically and laterally at the site, is extensive. Significant changes in transport pathways based on interpreted lithologic variability are now believed to be on the one to 10 m scale. This was determined based principally on interpretations of the limited geologic record, piezometer penetration records and the geophysics done by A. DE CARVALHO DILL (1993).

A. CARVALHO DILL's extensive characterization works at the site showed compelling geophysical interpretations over the instrumented and surrounding area. She interpreted aerial patterns observed from extensive and closely spaced Radio-Magnetotelluric Resistivity (RMT-R) surveys. Interpreted results indicate preferential pathways present in the form of glacial-era deposited paleo channels as well as lower permeability islands of silts and clays along and within these more highly transmissivity zones. Vertically, due to the lack of borehole data for model calibration, more detailed interpretations were not possible. Despite this work, however, the resolution of the geophysics, particularly vertically, likely does not allow a reasonable approximation of the details in transport pathways that occur in short distance at the site.

Water levels have historically been measured at from about 1.5–4 m below ground surface and varies seasonally. Hydraulic gradient conditions at the site are generally regarded as high and have been documented at about 0.004 m/m. Similar gradient conditions were apparent during our work.

The hydraulic conductivity at the site was determined at 21 monitoring well locations during the original work at the site as reported by M. SANSONI et al. (1987) in A. DE CARVALHO DILL (1993). Values of transmissivity (T) were calculated for each of these wells using the methods described in SNF (1984) for single well pump tests. Each well was pumped at two rates over a relatively short duration and measurements were made of the stabilized drawdown. Transmissivity values were calculated assuming the mean aquifer thickness and calculated values ranged over about two orders of magnitude from about $4\,e^{-03}$ to $4\,e^{-01}$ m^2/s. Associated hydraulic conductivity (K) values were of from $6e^{-04}$ to $5e^{-02}$ m/s. These K-values, however, based on using thinner effective contributing layer thickness contributions could be much as 20 times higher.

4.2.2.2. Previous Site Tracer Testing and Related Activities

S. HADI (1997) summarizes the work that was done previously at the site with works reported by M. SANSONI et al. (1988), J. MÄGDEFESSEL (1990) and A. DE CARVALHO DILL (1993). In 1995 and 1996, the Universities of Neuchâtel and Freiburg both continued use of the site for focussed feasibility studies of a) biocolloid particle migration in porous media (P. ROSSI et al., 1998) and b) newly developed fluorescent tracers (S. HADI, 1997), respectively.

Consistent observations and conclusions coming from the prior tracer work were that the research field was highly heterogeneous. There was no apparent or readily defined geometry for the porous media aquifer that had been well enough documented to explain the irregularity and variability in transport phenomena manifest at the site with these tests.

A. DE CARVALHO DILL summarizes the early idealized and analytically derived solution attempts at modelling the site transport by M. SANSONI et al. (1988) and J. SCHNEIDER (1991), respectively, and their approach to match the earlier tracer test results. She concluded that attempts based on continuous layer or the necessarily idealized conditions associated with analytical solutions were problematic.

4.2.2.3. Current Research Perspective

Our research furthered earlier work at Wilerwald by A. CARVALHO DILL and P. ROSSI (P. ROSSI, 1994, P. ROSSI et al., 1994) that established bacteriophages as feasible to use to document transport behaviour of viral sized particles in porous media. We selected the Wilerwald site specifically to undertake a detailed sampling program at three wells, two believed to be located in the high permeability paleo channel (C6, D7)

and one situated just off the defined channel but still in gravel with sand (CD). Our testing was clearly targeted at documenting behaviour and evaluating the efficacy of real-time on-line solute and particle detection analysis methods. It was not a further attempt to assess the existing and remaining high degree of uncertainty associated with transport conditions in the aquifer heterogeneity at the site. The earlier bacteriophage feasibility testing had been limited in that it did not have resources to establish the adequate sampling density required to fully evaluate the detailed patterns of breakthrough at all the wells that were sampled. Faced with similar resource constraints, we decided to reduce the number of wells sampled and increase our sampling density at three wells. This fit more within our objectives of multi-particle/solute comparison and determining the efficacy of continuous on-line uranine and microsphere detection field equipment.

4.2.3. Methods

The purpose of this section is to describe in detail:

1) well equipment, injection and sampling equipment,
2) test injection conditions,
3) tracer components, and
4) the manner in which the analyses were done for uranine and microspheres in the field and for bacteriophages in the laboratory.

Site pH and electrical conductivity measurements were made prior to and during testing (Tab. 4.6). A single tracer cocktail mixture consisting of the solute uranine, three bacteriophages (H40, MS2 and Psf2) and a latex microsphere were injected into well B4. Water was circulated in the wells. Real-time continuous on-line measurements for uranine and the microspheres were done at two of the three monitoring wells. Samples were taken periodically from the circulating flow for both uranine and bacteriophage analyses. Uranine concentration was determined on site soon after sampling using a second field fluorometer. Bacteriophage enumeration was determined with analyses done at the Microbiology Laboratory of the University of Neuchâtel commonly within 48–72 h of sampling.

Tab. 4.6: Site pH and electrical conductivity (EC) measurements. [1]) – pH measured in samples during tracer testing (August/September 1997); [2]) – EC measured in samples during site preparation 28 d prior to testing.
pH- und elektrische Leitfähigkeitsmessung. [1]) – gemessene pH-Werte der Proben der Tracertests (August/September 1997); [2]) – gemessene elektrische Leitfähigkeit der Proben während der 28-tägigen Vorbereitungszeit vor den Tests.

Well	pH[1])	Temp. [Deg. C]	EC[2]) [µs/cm]
B4		**10.3**	**539**
C3		10.5	559
C4		11.3	549
C5		11.6	544
C6	**7.01**	**11.6**	**542**
C7		10.4	552
CD	**6.74**	**11.0**	**559**
D4		10.3	547
D5		10.4	545
D6		10.4	543
D7	**7.08**	**10.6**	**560**

4.2.3.1. Well Instrumentation, Injection and Sampling Methods

The equipment layout for the injection and sampling well components is schematically shown in fig. 4.11. Each of the wells were equipped with a battery-driven downhole pump (Comet/Reich, 12–18 l/min, 0.8–1.5 bar, 12V DC), a delivery line from the pump to the surface, and a return line to just below the water table (PVC tubing, 14 mm OD, 10 mm ID). This established internal circulation opposite to that believed to be the actively transmissive layers. Circulation rates were from about 1.5–2 l/min – a rate which was considered adequate to create a homogeneous column of water moving downward between just below the water table depth and the pump return delivery point. The original design for the pump and return line depths was to have them each set at about 10 and 4 m, respectively. The pump depth was chosen based on the history of tracer test results reported by various authors for the site. The return line depth was set at from about 10–20 cm below the water table. Flow meters were put in line periodically to measure the circulation rate. The tubing at the surface could be passed through a field fluorometer to obtain real-time on-line uranine measurements. At wells C6 and D7, a T-joint was installed directly in line allowing withdrawal of a representative aliquot of 1 ml/min to determine real-time on-line microsphere particle detection.

Discrete samples were taken from the injection well and three down gradient monitoring wells during testing. To facilitate this, a three-way valve was installed in the circulating water line to allow flow deviation to the sample bottle without affecting the continuity of the return line volume. Samples were placed in new, 100 ml PVC dark brown bottles, were capped and temporarily stored in a refrigerated container at the site, prior to shipment to the off-site microbiological laboratory for analysis.

A generator provided continuous power to battery chargers for downhole pumps, computer equipment, refrigerated sample storage container, microsphere counting equipment and the site shelter.

4.2.3.2. Injection Conditions

The methodology of creating the tracer test "input signal" is important to understand and for our work this was certainly no exception. After a few minutes of injection, we received our first surprising results related to the flow conditions at the injection well. The tracer cocktail total mixed volume was injected into well B4 by connecting the container with the tracer to the flow return line and allowing the volume to flow, under VENTURI effect, to be pumped at the circulation rate into the well. This process lasted 11 min. We realized, however, that there was no colour in the return water coming from the pump depth set at 10 m. After 5 min of no return, the pump was raised to 8 and then to 6 m, but still without any visible fluorescene in the return part of the designed circulation. This condition continued with the pump set at 6 m until that remaining volume of tracer was gone. The pump was raised slowly thereafter during the rinse period up to about 5.5 m, about 1.5 m below the return line, and there was still no evidence of tracer. It was also not detected subsequently in the injection well circulation samples that had been taken during the injection period. We concluded on site that the entire flow rate of 1.5 l/min had left the well and migrated in a high permeability layer at a depth between about 4 and 5 m. Realizing this, and wishing to have a consistent set of measurements at the down gradient wells, the down gradient well pump settings were raised from 10 m to 6 m at C6 and to 7 m at CD and D7 where they remained over the duration of testing.

To a degree, the input signal condition was not critical to our objectives – since we are focussed on comparing tracer components' response and field instrumentation

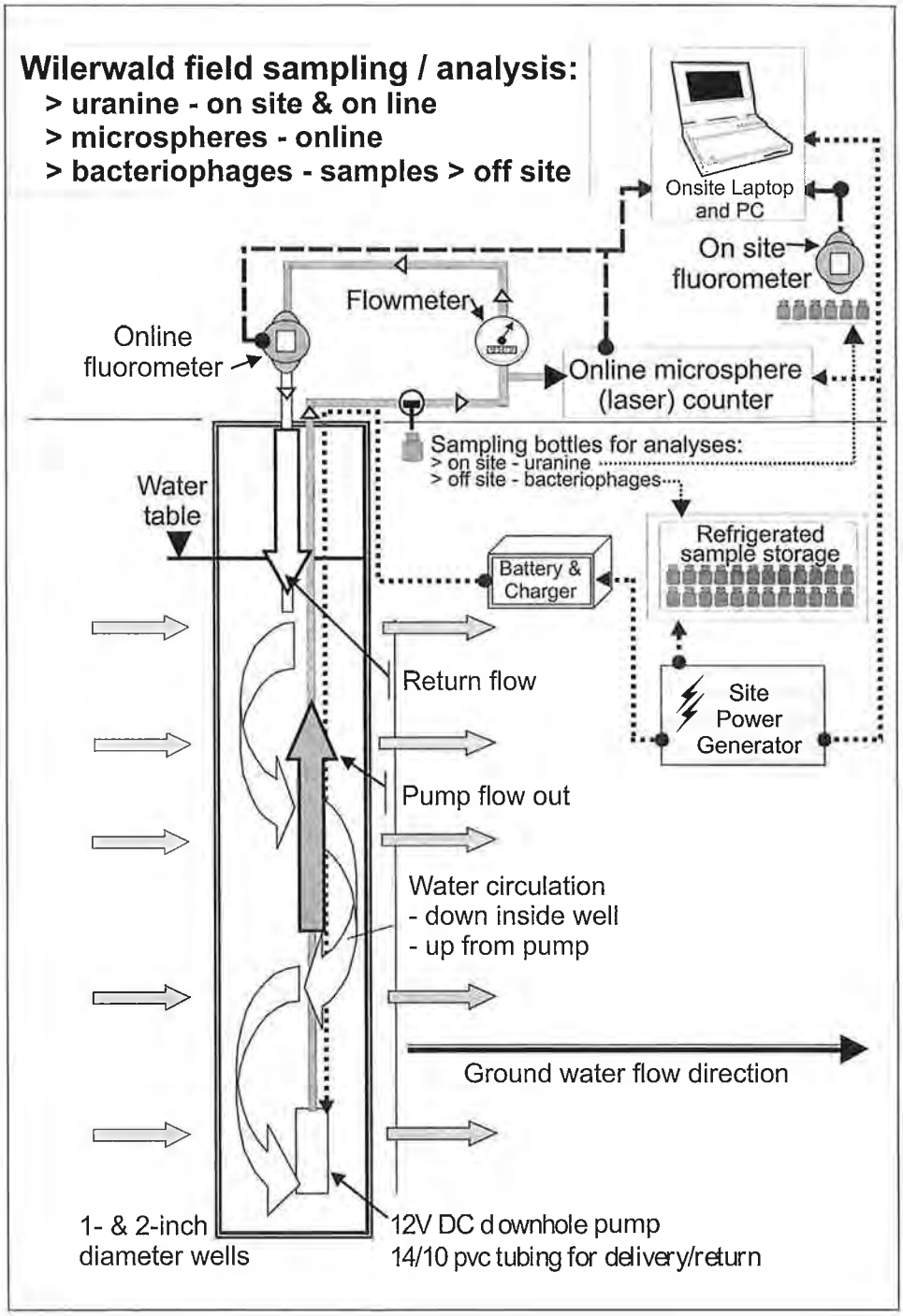


Fig. 4.11: Well equipment, sampling and on-site analysis instrumentation schematic diagram. Schematisches Diagramm: Bohrlochausrüstung, Probenentnahme- und in situ-Analysegeräte.

efficacy. All tracer components compared were injected and sampled together. Therefore, our evaluations, given that all input and output conditions were equal and consistent were pertinent and valid regardless of the surprising situation that developed with lack of circulation return during the injection period.

4.2.3.3. Tracer Components

The tracers used consisted of uranine, fluorescent microspheres and bacteriophages H40, MS2 and Psf2 biocolloids. Details related to the five tracer components are in tab. 4.7. Uranine was selected as the conservative solute tracer because of its ease of use, low detection limits and the relatively low weight of material needed to undertake the test. About 154 g of the powdered material were dissolved in 5 l of water. This amount selected was about 50 % of the weight used previously by P. ROSSI in 1995 as we were interested in lower concentrations in the observation wells than had been reported for that work (P. ROSSI et al., 1998).

The 1-micron diameter, carboxylate-modified, fluorescent microspheres (Molecular probes BV, Catalog No. F-8816) are artificial, commercially produced, latex beads (Fig. 4.12). They have a density of 1.06 g/cm^3, a highly negative surface charge and are relatively hydrophilic. They are labeled with an incorporated crimson-coloured fluorescent dye with excitation and emission spectrum wavelengths of 623 nm and 640 nm, respectively, allowing them to be detected using a low power laser source.

Three biocolloid components – bacteriophages H40, MS2 and Psf2 were selected for this work based on prior experience at this and other karst settings and in associated migration feasibility demonstration tests in a 6 m long sand tank model (MARCEAUs) at the ULP-Strasbourg Fluid Mechanics Department (K. KENNEDY, 2000). The three phages are about eight to 40 times smaller than the microspheres ranging in size from about 25–130 nm. Images of MS2 and H40 phages are in fig. 4.13. Like the microspheres, they have negative surface charges.

Surface charges are commonly referred to in terms of isoelectric point (IP) or zeta potential (ZP). IP is the value of the pH of the solution containing the particles in suspension at which the particle exhibits a neutral surface charge and thus does move in an electric field. Otherwise, it is simply stated as the pH at which the particles possess zero net charge. ZP is the charge balance, expressed in millivolts measured at a pH of 7.4. The higher the ZP, the more stable the colloidal suspension and the less chance of aggregation of colloidal particles.

MS2 is a member of the family *Leviviridae*, which have isometric head shapes and no tail. MS2 is a single stranded RNA phage with a size of from 24–26 nm and IP of from 3.5–3.9. Both H40 and Psf2 are members of the family *Siphoviridae* which are phages with long, non-contractile tails. Their known characteristics are limited to those defined by P. ROSSI (1994). Psf2 family characteristics suggest that it will have a head of about 70 nm and a tail from 65–570 nm long and from 8–10 nm wide. Its ZP was measured at –36.0 mV. H40 has been characterized by P. ROSSI (1994) indicating that its genetic material is double stranded DNA, has an icosahedral head of about 44 nm, a tail of about 85 nm, and a ZP of –42.0 mV.

4.2.3.4. Field Analyses

On-line real-time measurements were made in the field for uranine, the dissolved solute and microspheres, the colloidal particle. On-site measurements were also made for uranine analyses for the sampled water subsequently to be analyzed for bacteriophages. The data available to be observed during testing is shown on fig. 4.14.

The uranine was measured using two field fluorometers. An in-line unit was placed in the immediate vicinity of the C6 wellhead through which the circulation water could flow without constriction. Readings were made every 4 min. The second field fluorometer measured the discrete sample values commonly within a few minutes of

Tab. 4.7: Tracer test component characteristics and analysis methods. [1] *– colloid details are size (head, tail), morphotype (family), genetic material (gm) – single (ss) or double (ds) stranded, isoelectric point (pH at which the particles possess zero net charge) and zeta potential (zp) mV (the charge balance, expressed in millivolts (mV) measured at a pH of 7.4) for the bacteriophages and the manufacturers cited characteristics for microspheres;* [2] *– the tracer cocktail contained all components and was injected in well B4 in 11 min at a circulation rate of 1.5 ml/min; an estimated 95 % of the components' mass was assumed as injected (the balance input under more dilute "rinsing" conditions);* [3] *– P.-A. SCHNEGG & N. DOERFLIGER (1997), P.-A. SCHNEGG & K. KENNEDY (1998);* [4] *– bacteriophage H40, P. ROSSI (1994);* [5] *– H.-W. ACKERMANN & M. S. DUBOW (1987a, b);* [6] *– Molecular Probes Europe BV, Holland, Catalog No. F-8816, no IP or zeta potential values available;* [7] *– S. NIEHREN & W. KINZELBACH (1998); nm – not measured.*

Tracercharakteristika, *Analysemethoden und Einspeisebedingungen.* [1] *– die Kolloideigenschaften sind: Grösse (Kopf, Schwanz), Morphotyp (Familie), genetisches Material (RNA, DNA), isoelektrischer Punkt (pH-Wert bei dem die Partikel Null-Ladung besitzen) und Zeta-Potential (zp) in mV (Ladungsgleichgewicht gemessen in mV bei einem pH-Wert von 7.4) für die Phagen; für die Mikrosphären gelten die vom Hersteller angegebenen Eigenschaften;* [2] *– der Tracercocktail enthielt alle Komponenten und wurde innerhalb von 11 min mit einer Zirkulationsrate von 1.5 ml/min in Bohrung B4 eingespeist. 95 % der Einspeisemasse wurde als injiziert angenommen;* [3] *– P.-A SCHNEGG & N. DOERFLIGER (1997), P.-A. SCHNEGG & K. KENNEDY (1998);* [4] *– Bakteriophage H40, P. ROSSI (1994);* [5] *– H. W. ACKERMANN & M. S. DUBOW (1987a, b);* [6] *– Molecular Probes Europe BV, Holland, Katalog Nr. F-8816, keine IP- oder Zeta-Potentialwerte vorhanden;* [7] *– S. NIEHREN & W. KINZELBACH (1998); nm – nicht gemessen.*

Tracer component	Type	Component details[1]	Initial mass (M0) (Volume in ml)[2]	Analysis method (Resolution)
Uranine	Solute	Sodium fluoresceine MW 376.28 $C_{20}H_{10}O_5Na_2$	154 g (5,000)	On-line spectrofluorometry CHYN/UNINE Field Fluorometer[3] (~ 0.1 to 0.5 ppb resolution)
Bacteriophage H40	Bio-colloid	[4] 44,130 nm, *Siphoviridae* gm (dsDNA), IP (nm), zp (–42.0)	1.10 e^{13} pfu (200)	Bacterial host cultivation / growth association, plate counting in petri dishes (UNINE-Microbiol. Lab.) (1 phage per 2 ml resolution)
Bacteriophage MS2	Bio-colloid	[5] 24 nm, *Leviviridae*, gm (ssRNA), IP (3.5, 3.9), zp (nm)	1.15 e^{13} pfu (40)	
Bacteriophage Psf2	Bio-colloid	~70, 65 to 570, *Siphoviridae* gm (nm), IP (nm), zp (–36.0)	5.25 e^{12} pfu (750)	
Microspheres[6]	Colloid	1.0 µm, Fluospheres: carboxylate modified, crimson fluorescent (625/645 spectra), neg. surface charge	3.6 e^{10} spheres (250)	On-line laser detection[7] with flow cytometry (1 sphere per 10 ml resolution)

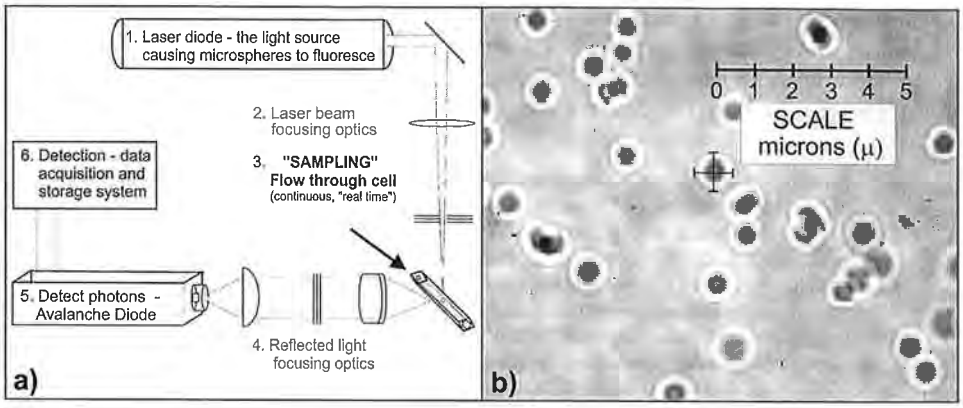


Fig. 4.12: Microspheres. a) instrumentation basis components, b) latex microspheres photomicrograph (after S. NIEHREN, 1998).
Mikrosphären. a) Grundkomponenten der Mikrosphären-Detektionsausrüstung, b) Latex-Mikrosphären-Photomikrograph (nach S. NIEHREN, 1998).

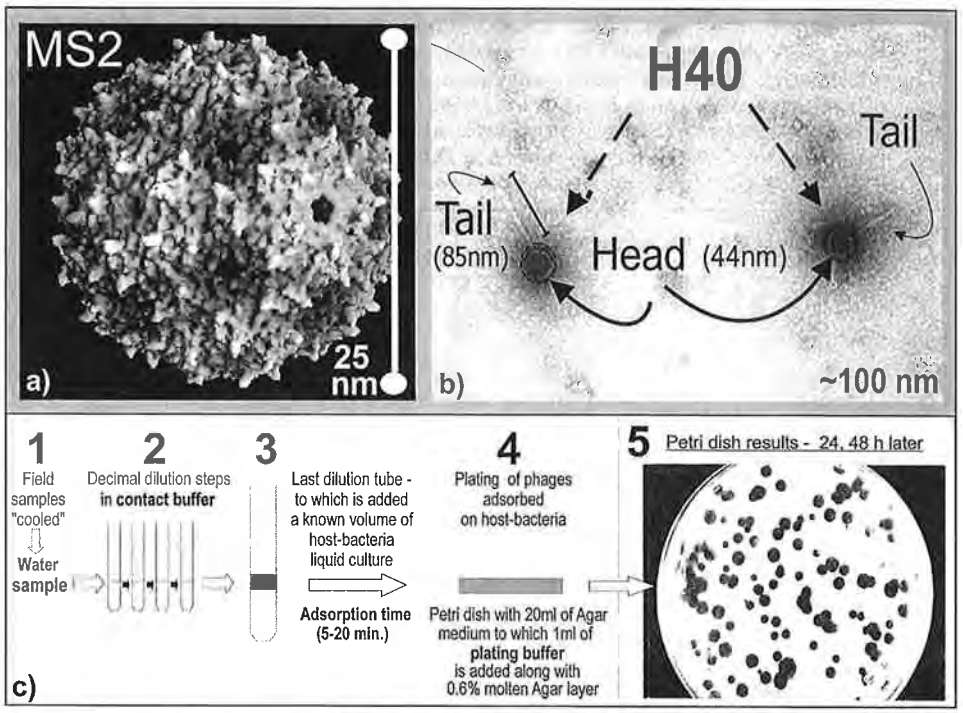


Fig. 4.13: Bacteriophage images and enumeration. a) phage MS2 (after J.-Y. SGRO, 1994), b) phage H40 (after P. ROSSI, 1994), c) principal bacteriophage analysis steps with example petri dish results for final counting (after P. ROSSI & K. KENNEDY, 1999).
Abbildungen von Bacteriophage und Grundsätze der Phagenanalyse. a) Phage MS2 (nach J.-Y. SGRO, 1994), b) Phage H40 (nach P. ROSSI, 1994), c) Grundsätze der Phagenanalyse mit Beispiel für Petrischalen-Ergebnisse nach Auszählung (nach P. ROSSI & K. KENNEDY, 1999).

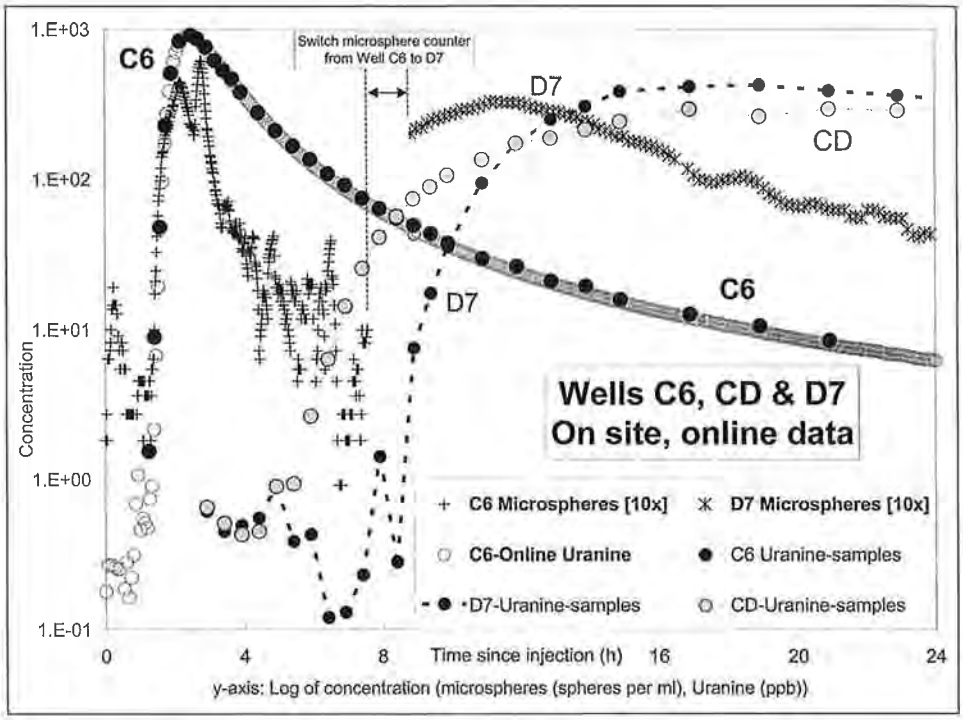


Fig. 4.14: On-line and on-site tracer component data available during testing (semi-log plot). On-line-Tracerfelddaten (semi-log Plot).

sampling using the faster measurement rate of six readings per minute. Each unit was connected over distances up to 15 m to their respective data loggers set in waterproof housings. All data collected was stored on the data logger's PCMCIA memory card as well as displayed, stored and manipulated on a site computer. The instruments' sensitivity was about 0.5 ppb with background measurements in the well waters ranging from about 0.4–1.0 ppb. There was good agreement between the in-line and sample bottle uranine values as illustrated on fig. 4.14.

Microspheres were measured using the laser-based fluorescent particle detector, the basics of which are shown schematically on fig. 4.12a along with a photomicrograph of the microspheres used in this work. This equipment was developed specifically for the purpose of measuring these particular latex beads and it's use has been described related to laboratory column studies (S. NIEHREN & W. KINZELBACH, 1998). An aliquot of the circulating water is passed through a 250-micron diameter flow-through cell. This cell is illuminated with a precisely focussed laser beam. Fluorescent light is emitted when a microsphere passes through the beam. This microsphere-based fluorescent signal is detected in real time by a single-photon-counting avalanche diode (SPCAD). The data from the SPCAD are transmitted to a data acquisition system that stores and displays the measurements. Measurement frequency is on the order of microseconds and data are adjusted to provide a result integrated initially over 0.25 sec and subsequently as a function of the dynamic response of the system being tested. The results of the counting are displayed in fig. 4.14. There was an interruption of about 90 min in data when

switching from well C6 to D7. It was unfortunate that the timing associated with end of measurements in C6 preceded the apparent arrival of the colloids at well D7. The particular and typical field-generated influences of weather and humidity, vibrations and changing operational conditions, generator power supply, line filtering of suspended sediment in the groundwater were manageable. The detection of these injected colloidal particles was clearly evident and consistent at both wells that were sequentially monitored continuously.

4.2.3.5. Phage Laboratory Analyses

The analysis of the bacteriophages is a modified version of the method developed by M. H. ADAMS (1959). Optimization techniques were developed, used and presented by P. ROSSI (1994) and P. ROSSI & W. KÄSS (1998).

Two stages of enumeration are commonly done both of which result in plaque forming units being counted in a petri dish.

The first is a presence/absence test that also serves to indicate the order of magnitude for dilution of the sample so that the next step result yields a manageable number of counts on the petri dish. The basic steps associated with the analysis are summarized schematically in fig. 4.13b along with the typical enumeration method illustrated. The microbiology laboratory's optimal processing capacity of about 25 samples per day was critical input to the sampling strategy. Each sample was analyzed for the concentration of each of the three phages simultaneously and in duplicate. A total of about 195 samples was taken during the testing that was concentrated heavily in the initial five days. The inactivation of the phages during the test was not considered to be a significant problem over the 12 day time period samples were taken. To evaluate this the three phages were mixed with the site water and kept in a constant temperature bath. Every one or two days, the concentrations of the phages present in the spiked site water were measured.

The results confirmed our expectation that there was no significant reduction over the time period. The reduction that did occur may have been caused by the air-water interface in the laboratory vessels or other laboratory situations not occurring naturally in the field's subsurface environment.

4.2.3.6. Response Assessment and Quantitative Analysis

Bacteriophage behaviour was compared to solute tracer responses in a manner similar to methods described originally by R. W. HARVEY et al. (1989). This included comparing concentration history and relative abundance (C/C_{max}), maximum dimensionless concentrations $(C/C_0)_{max}$ or $(Tr/Tr_0)_{max}$, retardation factor (RF) – the ratio of particle (pseudo-peak) vs. solute peak maximum times, relative breakthrough (RB) – particle mass recovered compared to solute recovery (normalized to 100 % using non-reactive solute assumptions) and attenuation (1 minus RB). In addition, same scale plots of the early breakthrough time of colloid and uranine concentrations normalized to their original concentrations were reviewed to evaluate if there was evidence of preferential colloid transport taking place.

Transport "arrival" velocities are calculated based on the time that a colloid is first detected at each well. Analytical detection limits affect the time at which any component is observable. Solutes commonly have practical DLs, equipment and background related, that may be orders of magnitude higher than for colloids. Colloids may have analytical-based background levels but in general have DLs several orders of magnitude lower than solutes. Differences in detection times are therefore difficult to com-

pare. Results suggesting earlier colloid than solute detection can be in error. Recognizing this as a practical analytical limitation, and, at times, confusing practice, has developed in several disciplines wherein the time to maximum concentration (t_{max}) or 50 % of the total recovered mass (t_{50}), of any materials, is referred to as "arrival time". These arrival times were then compared and materials were referred to as arriving earlier when this mean or median mass values were different. However, this comparison is inappropriate and confusing for colloids when they are being compared to non-reactive non-sorbing solutes. Colloids undergo a high degree of attachment and interface interaction in the subsurface environment during transport. Their mass being transported, unlike that of a conservative solute, changes, commonly decreasing, as it moves progressively down gradient during transport. When this occurs, the shape of the breakthrough curve at any further distance, including the time at which the maximum concentration occurs will be strongly influenced. Colloid attachment and removal that has taken place along the pathway to a sampling point can both lower and decrease the time at which the maximum concentration is reached. Therefore, we suggest calling a colloid's maximum concentration a "pseudo-peak" (ps-peak). It is not a parameter justified for neither calculating average velocity nor comparing as an arrival time relative to a conservative solute. It is a parameter that is highly variable – dependent on the media in which it is being transported as its interactions are both media and particle dependent. On the other hand, average velocities for solute migration are characteristically calculated based on t_{max}, the time of the solute peak and reflect the effective flow velocity in the media.

4.2.3.7. Numerical Modelling

A one-dimensional model was applied to the results of the solute and colloidal particle migration at well D7. The purpose of this modelling was to determine if the model parameters arrived at in matching the data were reasonable assuming a direct pathway existed over the 64 m between the injection and D7 wells. Data from the well at D7 was matched for uranine using a spherical two-region conceptualization and adsorption-desorption colloidal mechanisms. Details of adapting the combined solute advective-diffusive and colloidal attachment-detatchment processes in this model (CoTrans) are in S. NIEHREN & W. KINZELBACH (1998) and S. NIEHREN (1998).

4.2.4. Results and Discussion

The purpose of this section is to describe what happened experimentally at each location with respect to the different components used as tracers and discuss their implications as it relates to the components' transport characteristics under natural gradient conditions. The presentation is made by well and then by comparing the overall component behaviours and finally with the results of a 1-D numerical simulation used to compare the well D7 responses.

Figure 4.15 (semi-log) illustrates the five tracer components' concentration history as progressively observed down gradient at the three sampling wells. Figure 4.16a shows the concentration history by well for all sampled components at each well. Figure 4.16b shows the tracer component relative abundance with concentrations normalized to their maximum values detected at each well. Figures 4.17, 4.18, and 4.19 are log-log concentration history plots accentuating comparison of each component's time of first detection (arrival) and time to maximum concentrations by well. Figure 4.20a presents the component concentrations normalized to the original component concentrations for both solute and colloids on the same (semi-log) scale to evaluate the potential for differen-

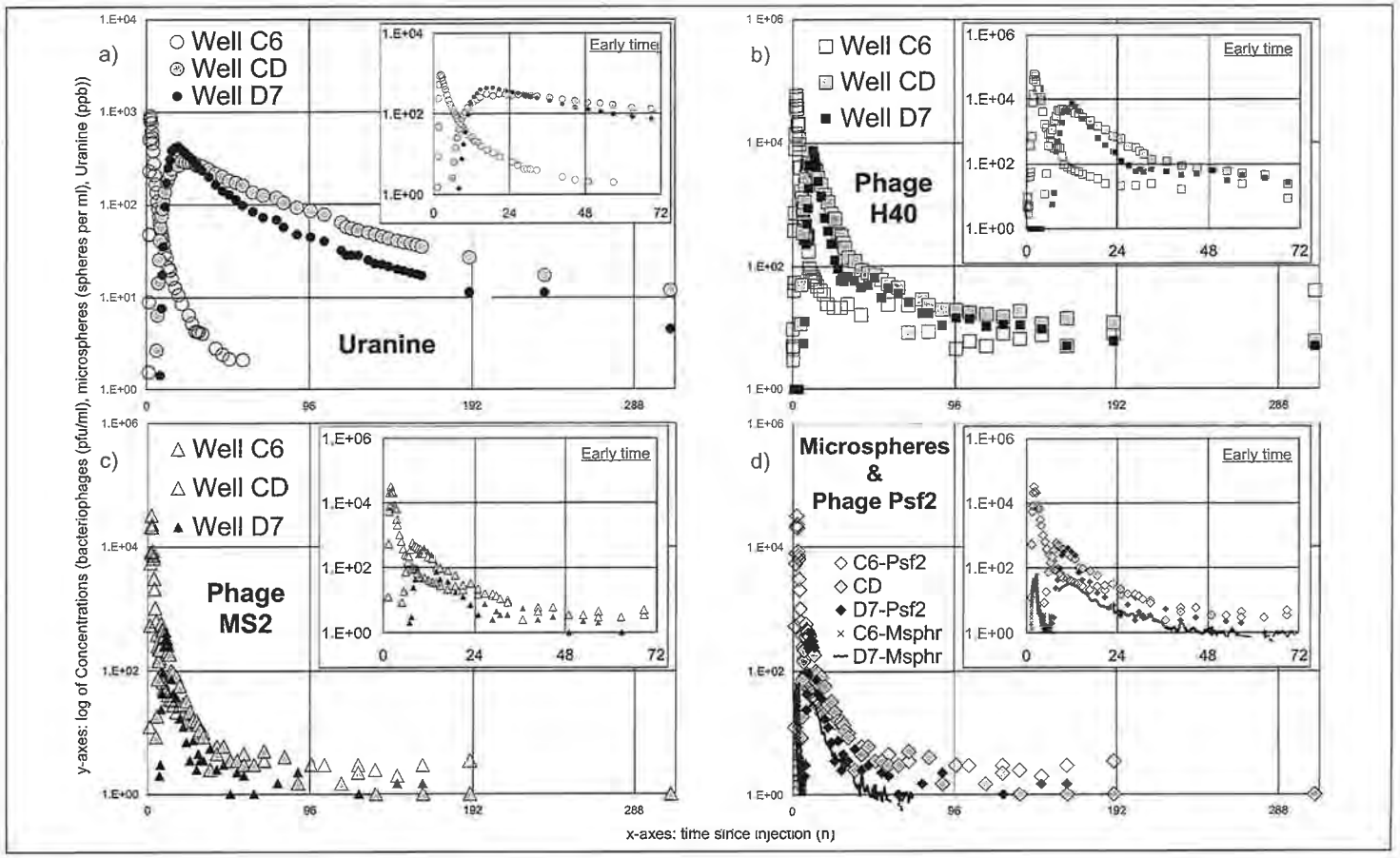


Fig. 4.15: Concentration history by component at each well (semi-log plot). a) uranine, b) phage H40, c) phage MS2, d) microspheres and phage Psf2.
Konzentrationsabfolge: Tracer pro Bohrloch (semi-log Plot). a) Uranin, b) Phage H40, c) Phage MS2, d) Mikrosphären und Phage Psf2.

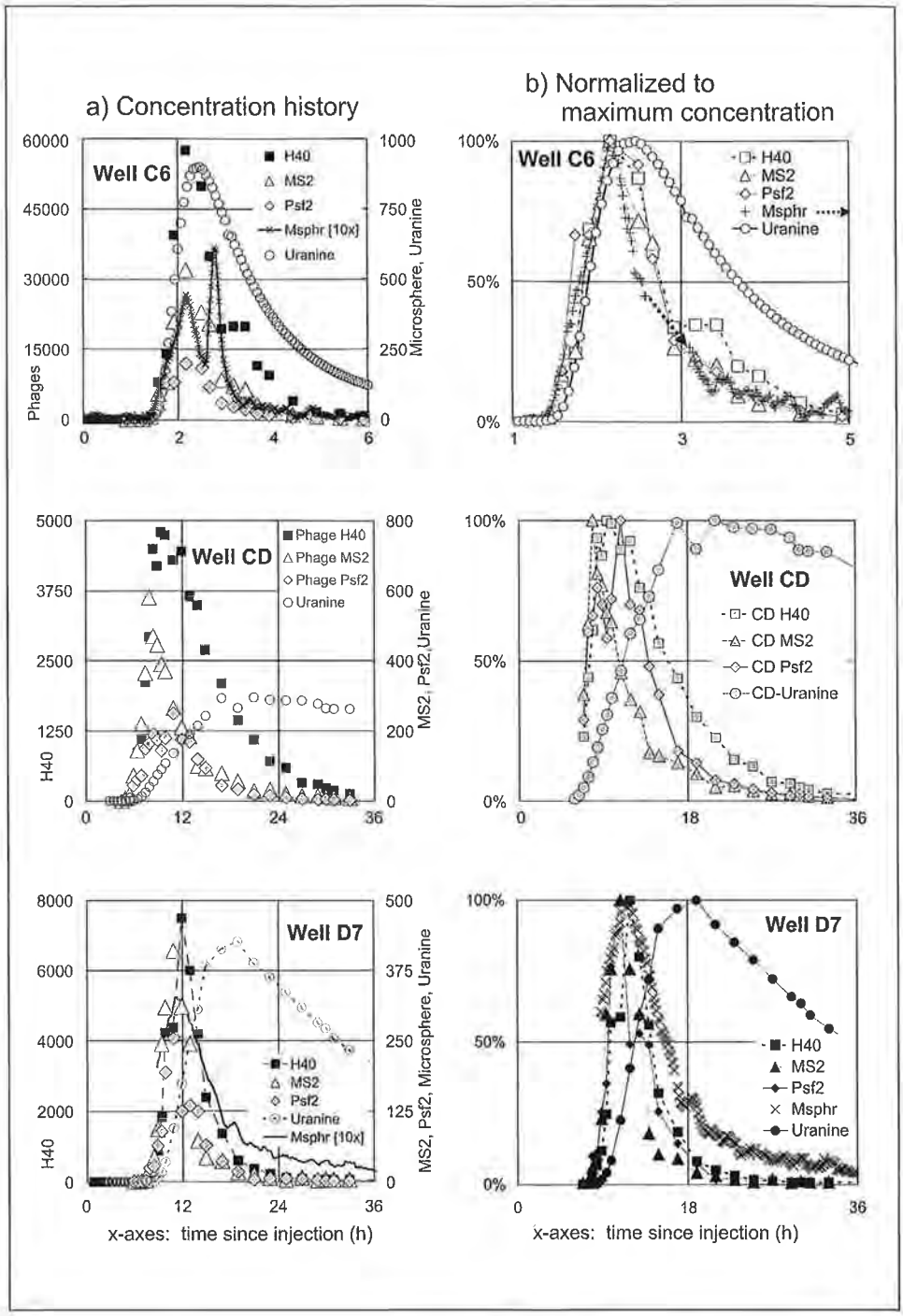


Fig. 4.16: Concentration history by well for all components. a) arithmetic plot, b) relative abundance. Konzentrationsabfolge: Je Bohrloch für alle Tracer. a) arithmetischer Plot, b) relative Menge.

ces between colloid and solute component advection (after P. ZHANG et al., 2000). Figure 4.20b shows the entire data set by well (log-log) for evaluating changes in slope on the falling limb of the breakthrough curve indicating differences in later time behaviour. Figure 4.21 summarizes the five tracer components' relative breakthrough both as it evolved and as absolute comparative totals at the three wells. Table 4.8 summarizes the characteristics of the breakthrough responses at the wells by tracer component. Figure 4.22 is the result of the preliminary 1-D modelling work done to compare the microsphere, bacteriophage and uranine response at well D7.

4.2.4.1. Well B4 Response and Injection Conditions

This natural gradient test began with results at the injection well B4 that documented that the tracer cocktail had left the well in a thin lens likely on the order of 1 m at a depth of from 4–5.5 m below ground surface. The original design had expected circulation to occur over 6 m. No samples taken in the water pumped from the lower part of the well, either visibly or analytically, indicated that the tracer components had reached the pump depth and circulated between the pump and the surface, and therefore, the return line placed just below the water table depth. This observed result is consistent, however, with A. DE CARVALHO DILL's electrical soundings at B4 (1993, fig. 34) with a specific layer of high resistivity values (>500 Ωm) between 4 and 6 m. The 1.5 l/min circulation rate of the pump was clearly not high enough to overcome the lateral flow from the well that contained the tracer components.

The aquifer's vertical heterogeneity confirmed immediately in the field at B4 influenced the refined sampling design that we implemented soon thereafter at the three down gradient wells. The circulation pump depths were changed at C6, CD and D7 so that the circulating interval was reduced from 6 m to between about 3 and 4 m. Using a more narrow width impacted the maximum tracer values observed in the wells as a result of less dilution that would have occurred in the sampling wells. For example, at B4 in 1995, P. ROSSI had injected about 300 g of uranine and would likely have followed the same narrow lateral path to leave the well. The resulting maximum uranine concentrations he obtained at C6 and D7 were about 1,300 and 90 ppb, respectively. These sample results were based on removing and subsequently mixing the volume taken from the well in a translucent tubing filled with a continuous column of water to a depth of about 10 m. P. ROSSI anecdotally has described that in certain situations bands of fluorescent tracer could be observed in thin layers in the sample tubing. Using different sampling equipment and 2.6 and 3.7 m circulation intervals at the down gradient wells, the maximum uranine values during this testing were about 910 and 425 ppb. The surprising result was that the effective order of magnitude higher results at D7 since we had injected only half the mass (154 g) used by P. ROSSI. Therefore, the injection conditions and sampling protocols, possibly also along with changes in the transport pathways at the different test times clearly have significant affects on the migration response at individual wells. S. HADI's 1995 and 1996 tracer work using the B4 injection well had involved injection but below the depth of a packer set at 10 m, so the results are not comparable in terms of down gradient results.

4.2.4.2. Well C6

The concentration history to 6 h (Fig. 4.16a) shows that the breakthrough curve rising and falling limbs of uranine and the phages were continuous and consistent. Uranine had a Tr_{max}-value of 912 ppb corresponding to a $(Tr/Tr_0)_{max}$ of $1e^{-04}$. H40, MS2 and Psf2 had C_{max}-values of 57,500, 12,000 and 32,000 pfu/ml corresponding to decreasing ori-

ginal-concentration-normalized $(C/C_0)_{max}$-values of $9e^{-05}$, $5e^{-05}$ and $4e^{-05}$, respectively. The microsphere response also shows consistent data but deviates from the other colloids' response in that it depicts two separate peaks with C_{max}-values of 45 and 62 microspheres/ml (ms/ml) corresponding to $(C/C_0)_{max}$-values of 2–3 e^{-05}, similar to, but lower than the phages.

C6 Background levels

The C6 plot showing the time at which different tracer components were initially detected (Fig. 4.17) illustrates that there was a background level associated with uranine, phage H40 and the microspheres. A background for uranine was expected based on the considerable previous use of this tracer plus the instrumentation's natural lower limit related to the instrument itself and the level of natural fluorescence in any water. We expected that these two site factors would mean that only measurements above 1 ppb would be considered as positive presence of the tracer in this test. The microsphere background level was also expected due to light scattering from particles other than the fluorescent beads injected. The counter background ranged from 0.2–0.6 ms/ml. The unexpected background levels were those for H40 ranging from about 4–10 pfu/ml. H40 was detected to concentrations of one to two hundred pfu/ml in samples taken from well B4 during the site preparation. It was also detected at levels to 10 pfu/ml in wells C6 and D7 prior to testing. The site had last been tested using the H40 phage

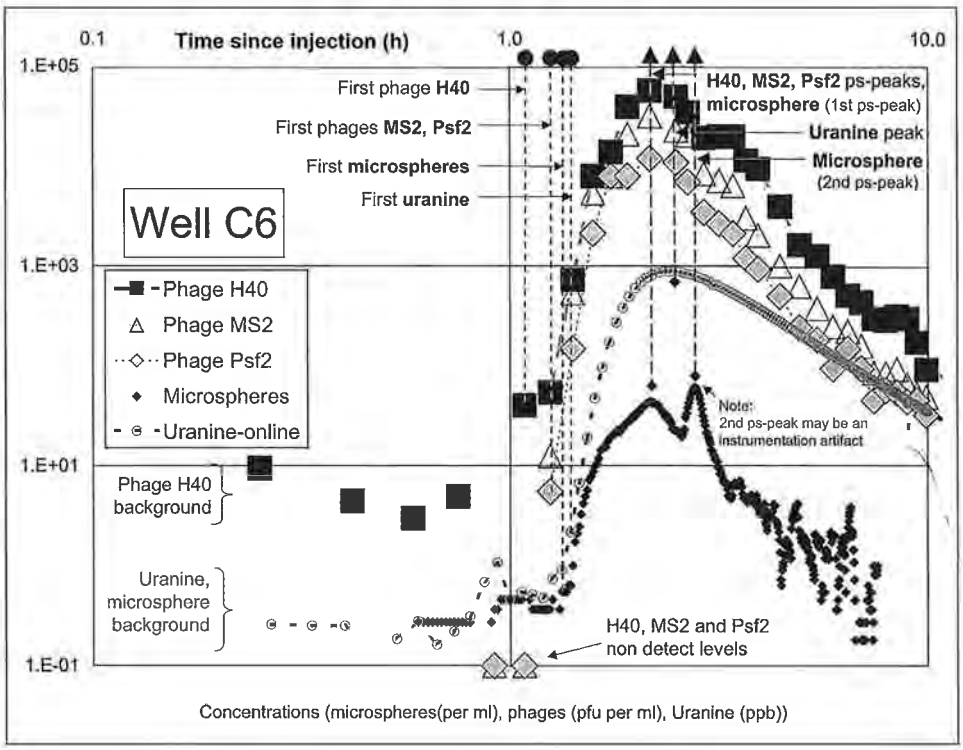


Fig. 4.17: Well C6 arrival and uranine peak and colloid pseudo-peak properties (log-log plot). Beobachtungsrohr C6, Ankunft und Uraninpeak und Kolloid-Pseudopeak-Eigenschaften (log-log Plot).

over two years earlier. According to their typical cycle, they would not be detectable after a few months. The most likely explanation is that the phages we detected had previously become attached to adjacent matrix material but they had not lost their virulence during this attachment period. Similar results have been noted in batch tests (P. Rossi, 1994). Our pre-test pumping could have mobilized sediment particles from the aquifer to which these phages were attached and left these present in the water column prior to start of testing. The test circulation activity would have resulted in mixing of these phages within the water column and establishing a residual level at the beginning of the test. Fortunately, the background levels of H40 were not high enough to detract from the quality of the results.

C6 Arrival/Detection

First detection of the MS2 and Psf2 phages, for which there had been no previous site use, were both in the sample taken 75 min after injection (Fig. 4.17). H40 was also present in this and the sample taken 10 min earlier. Microspheres, while being measured on line, were detected above background at about 80 min and their pattern of increase could be documented thereafter. The first in-line uranine measurement occurred above 1 ppb at about 85 min after injection, demonstrating that the flow through cell measurements were systematically well documented. Phage and microsphere detection limits are about equal (0.5 particles/ml) and lower than that of the uranine so that the small differences in time of detection between the colloids and uranine are not conclusive as to preferential advection of the colloids. It was clear from the fast migration seen for both the colloids and the uranine that the advective-dispersive transport in the flow system was relatively rapid. Migration of both the colloids and the solute over the 14 m distance in from 65–85 min indicates an "arrival velocity" of about 240–310 m/d. Figure 4.20a shows little difference in the uranine and colloids C/C_0-values to about $1e^{-05}$ at which point the colloids begin to fall below the uranine normalized concentrations. Thus there is no clear evidence of preferential colloidal advection even with the 12- to 40-fold size difference between the bacteriophage and microsphere colloids. In this situation, then the more representative travel-time velocities are the higher ones related to the colloids with their lower detection limits.

C6 Maximum Concentration Times and Peaks

The relative abundance plot of the five components (Fig. 4.16) illustrates that the four colloids all had similar pseudo-peak times at about 2.2 h occurring about 0.3 h before the uranine peak. There was little evident error in the timing of these maximum values as the sampling density was every 10–15 min for the phages, every 4 min for the uranine and presented as averaged over every 10 min for the microspheres. The calculated mean solute velocity was about 130 m/d determined using the time to the uranine maximum concentration. The colloidal $(C/C_0)_{max}$-values, while predictably lower, were closer to the uranine value than expected with H40 only 13 % less and MS2, Psf2 and microspheres about two-, three- and five-fold less. C6 data on fig. 4.20b show the difference in the breakthrough normalized to the total injected mass. The colloid data all appear similar with a smooth breakthrough in the rising and falling limb (slope 1) until about 6 h. At that time, the slope flattens and extends out to about 20 h for H40 and 70 h for MS2 and Psf2 (slope 2). Thereafter, there are low but relatively constant concentrations possibly associated with continuing levels of reversible detachment in the final tailing part of the curve (slope 3). The uranine data exhibits no significant changes in its pattern over the first 56 h at which time its concentration was within two-fold of background levels and detailed monitoring ended.

C6 Recovery

The calculated relative breakthroughs as they evolved with time for the colloids and uranine at C6 are in fig. 4.21a. Compared to uranine assumed to reach 100 %, the colloid total relative breakthrough recovery was 40 %, 16 % and 18 % for H40, MS2 and Psf2, respectively, and about 9 % for the microspheres (Fig. 4.21b). The calculated microsphere recovery was calculated to about 7 h rather than the 72 h measured for the phages. However, based on the similarity in the microsphere response to the other colloids to that point, it is unlikely that the final number rise by more than a few percent over the remaining time.

4.2.4.3. Well CD

The concentration history to 36 h (Fig. 4.16a) shows that the breakthrough curve rising and falling limbs of uranine and the H40 and MS2 phages were continuous and consistent. Uranine had a Tr_{max}-value of 296 ppb corresponding to a $(Tr/Tr_0)_{max}$ of $3e^{-05}$. H40 and MS2 had C_{max}-values of 4,800 and 580 pfu/ml corresponding to $(C/C_0)_{max}$-values of $8e^{-06}$ and $9e^{-07}$, respectively. Psf2 had double ps-peaks of 190 and 250 pfu/ml separated by about 2.5 h ($(C/C_0)_{max}$ of $6e^{-07}$, $8e^{-07}$). The initial ps-peak for Psf2 was similar to the other two phages. The uranine C_{max} decreased three-fold compared to D6 whereas H40 decreased 12-fold and MS2 and Psf2 decreased about 50-fold. The H40, MS2 and Psf2 intra-phage $(C/C_0)_{max}$-difference was about two at C6. This increased to nine at CD. An increased relative attenuation of the MS2 and Psf2 phage compared to H40 had occurred in transport to CD compared to C6.

CD Background Levels

At CD, there was a background level associated only with uranine (Fig. 4.18). The uranine background was expected as discussed above and was about 0.7 ppb at this location. The CD results were from discrete samples measured on site shortly after sampling rather than at C6 where they were in line. No background levels of any of the phages were detected in the samples prior to their testing-related arrival.

CD Arrival/Detection

First detection of the MS2 and Psf2 phages, for which there had been no previous site use, were both in the sample taken about 4.5 h after injection (Fig. 4.18). H40 was first present in the sample taken 30 min later. The first uranine detected above the documented background was also at the same time as the H40 occurrence. CD is located off the main channel and exhibits a more dispersive shape for all tracer components than at C6 and D7 (Fig. 4.15). Regardless, both uranine and phages exhibited relatively fast transport. Migration of both the colloids and the solute over the 34 m distance in about 4.5–5 h indicates an "arrival velocity" of about 170–185 m/d. The 30 min difference in detection between the colloids and uranine are not conclusive as to preferential advection of the colloids. The C/C_0-diagnostic plot (Fig. 4.20a) does not show phage values with timing significantly in advance of the uranine suggesting there is no evidence of preferential colloidal advection. H40 values were ahead (above those) of uranine in two samples at about 6 and 6.5 h but the other phage and the remaining H40 samples show the colloids under the uranine curve.

CD Maximum Concentration Times and Peaks

The relative abundance plot of the five components (Fig. 4.16b) illustrates that the three phages had ps-peak times of between 8.0 and 9.4 h that occurred about 11–12 h before the uranine peak. There was a double Psf2 ps-peak and the second, higher one,

occurred at about 11 h compared to the first one at 8.4 h. Timing of these maximum values was based on 30 min sampling. The calculated mean solute velocity was about 40 m/d determined using the $t_{tr\text{-}max}$-value. The colloidal $(C/C_0)_{max}$-values, were lower as expected from the off-channel setting in which this well is located according to the site geophysical studies. H40 and MS2 and Psf2 were about four- and 40-fold less than uranine, respectively. CD data on fig. 4.20b show the differences in the breakthrough normalized to the total injected mass. The phage responses were similar with a smooth breakthrough in the rising and falling limb (slope 1) until about 35–40 h. At that time, the slope flattens and extends out as the tailing features of the colloid response begin to influence the later time period of the plot (slope 2). There was no late-time constant-concentration period as had been observed in well C6. The uranine data exhibited a more dispersed form than the phages with no significant changes in its pattern over the approximate 300 h it was measured at which time its concentration was still 12-fold higher than the background levels.

CD Recovery

The calculated relative breakthroughs as they evolved with time for the colloids and uranine at CD are in fig. 4.21a. Compared to uranine assumed to reach 100 %, the colloid total relative breakthrough recovery was 3.4 %, 0.3 % and 0.2 % for H40, MS2 and Psf2, respectively (Fig. 4.21b). Compared to the recovery at C6, there was a 12-, 64- and 85-fold decrease in H40, MS2 and Psf2.

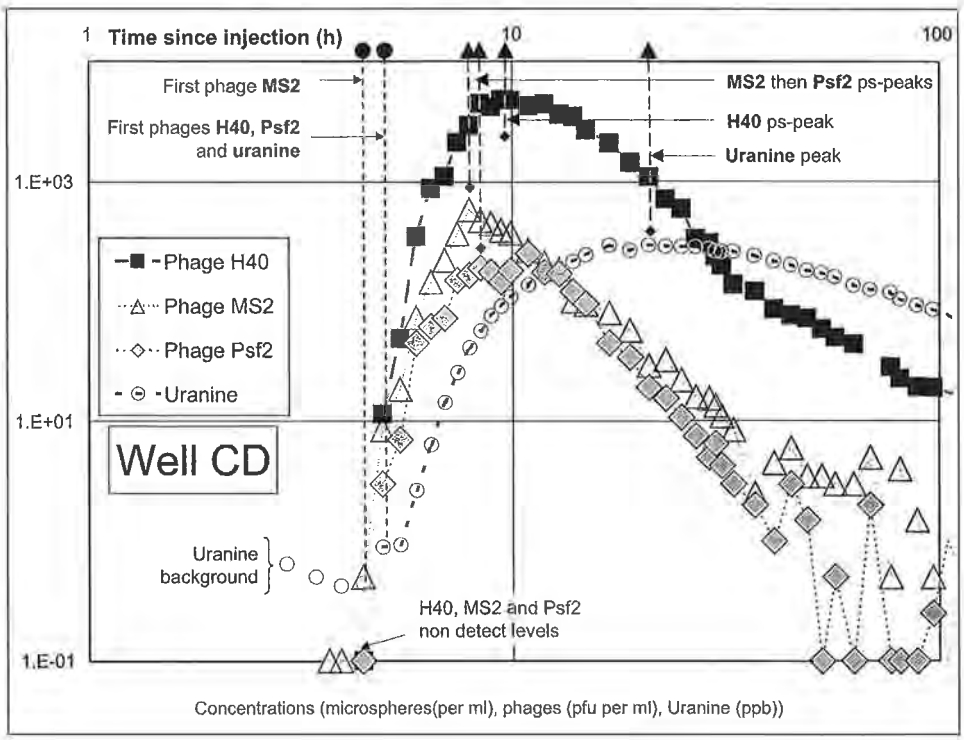


Fig. 4.18: Well CD arrival and uranine peak and colloid pseudo-peak properties (log-log plot). Bohrloch CD, Ankunft und Uraninpeak und Kolloid-Pseudopeak-Eigenschaften (log-log Plot).

4.2.4.4. Well D7

The concentration history to 36 h (Fig. 4.16a) shows that the breakthrough curve rising and falling limbs of uranine, phages and microspheres (once monitoring began) were continuous and consistent. Uranine had a Tr_{max}-value of 426 ppb corresponding to a $(Tr/Tr_0)_{max}$ of $5e^{-05}$. H40, MS2 and Psf2 had C_{max}-values of 7,500, 410 and 255 pfu/ml corresponding to $(C/C_0)_{max}$-values of $1e^{-05}$, $8e^{-07}$ and $9e^{-07}$, respectively. Microspheres had a C_{max} of 33 with a $(C/C_0)_{max}$-value of $2e^{-05}$, the highest of all the colloids. The uranine C_{max} decreased three-fold compared to the C6 value whereas H40, MS2, Psf2 and microspheres decreased eight-, 78-, 47- and 1.4-fold, respectively. The H40, MS2 and Psf2 intraphage $(C/C_0)_{max}$ difference of about two at C6 had increased to 19 and 14 for MS2 and Psf2, respectively at D7 indicating that as between C6 and CD, there had been an increase in the relative attenuation of the MS2 and Psf2 phage compared to H40.

D7 Background Levels

At D7, there were documented background levels associated with uranine and H40 (Fig. 4.19). The uranine and phage backgrounds of 0.9 pb and 1 pfu/ml, respectively, were anticipated as discussed above. No background levels of the other the phages were detected in the samples prior to their testing-related arrival. Background levels were not measured for the microspheres as the equipment was set up in line at C6 and moved to D7 only after the colloidal particles were already present.

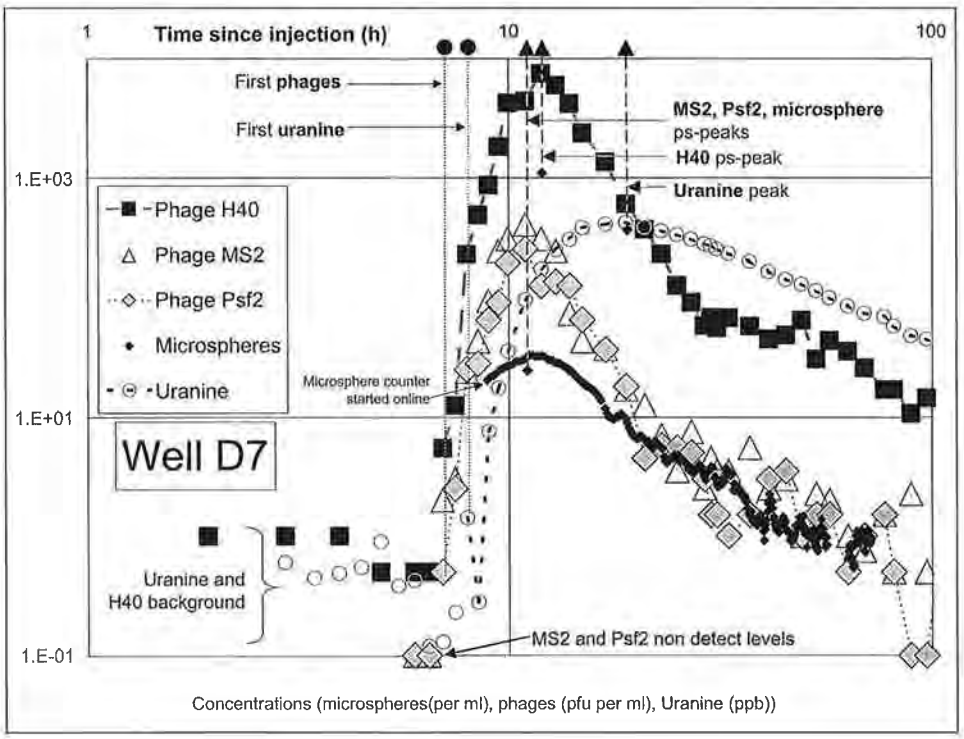


Fig. 4.19: Well D7 arrival and uranine peak and colloid pseudo-peak properties (log-log plot). Beobachtungsrohr D7, Ankunft und Uraninpeak und Kolloid-Pseudopeak-Eigenschaften (log-log Plot).

D7 Arrival/Detection

First detection of the MS2 and Psf2 phages, for which there had been no previous site use, were both in the sample taken about 6.9 h after injection (Fig. 4.19). H40 was also first present above background in this sample. The first uranine detected above the documented background of 0.9 was at about 7.9 h. The subsequent sample 30 min later dropped below background but thereafter was again above background and continued to rise. D7 is located directly along the line of the geophysically interpreted high permeability channel and components exhibited a less dispersed shape than at CD although more dispersed than at C6 (Fig. 4.15). Both uranine and phages exhibited relatively fast transport. Migration of both the colloids and the solute over the 64 m distance in about 7–8 h indicates an "arrival velocity" of about 190–220 m/d, higher than the velocity calculated for transport to CD. This supports the preferential channel concept for the site with longitudinal migration along this pathway being dominant between B4, C6 and D7 and with lateral transport towards CD. Relative to the transport rate, the solute and colloid arrival velocities to D7 were about 72–82 % as fast to C6. The 1 h difference in detection time between the colloids and uranine suggests the potential for preferential colloidal advection. Indeed, the same-scale C/C_0-diagnostic plot (Fig. 4.20a) shows first, five H40 and second, the start of the microsphere record, with values from about 8–10 h above the uranine suggesting the possibility of colloids had higher advective rates than the solutes. The other phage and the remaining H40 samples show the colloids under the uranine curve.

D7 Maximum Concentration Times and Peaks

The relative abundance plot of the five components (Fig. 4.16b) illustrates that the three phages and microspheres had ps-peak times of between 11 and 12 h that occurred about 7–8 h before the uranine peak. Timing of the phage maximum values was based on 30 min samples and the uranine on 2 h samples. The calculated mean solute velocity was about 80 m/d determined using the $t_{tr\text{-}max}$-value. Colloidal $(C/C_0)_{max}$-values were lower than at C6 as expected and higher than at CD, the off-channel setting. H40, MS2, Psf2 and microspheres were about four-, 78-, 57- and three-fold less than uranine. D7 data on fig. 4.20b shows the differences in the breakthrough normalized to the total injected mass. The colloid data for the three phages are similar with a smooth breakthrough in the rising and falling limb until about 30 h (slope 1). At that time, the slope flattened and extended to late time as it did at CD (slope 2). For the microspheres, the pattern is similar but the break in slope occurs earlier than 20 h. There was no evident late-time tailing for the colloids as had been observed at C6. The microsphere data was dissimilar to the phages at the initial part of the documentation. The overall pattern however, matched well with the other colloids. The uranine data exhibited a more dispersed form than the phages with no significant changes in its pattern over the approximate 300 h it was measured at which time its concentration was about five-fold higher than the background levels.

D7 Recovery

The calculated relative breakthroughs as they evolved with time for the colloids and uranine at D7 are in fig. 4.21a. Compared to uranine, the colloid total relative breakthrough recovery was 3.3 %, 0.2 %, 0.2 % and 8.2 % for H40, MS2, Psf2 and microspheres, respectively (Fig. 4.21b). Compared to the recovery at C6, there was a 12- and 64-fold decrease in H40 and MS2 and Psf2 values. The microspheres, however, only showed a decrease of about 10 % in their recovery. The microsphere recovery would actually be higher as the equipment was not on line to monitor the entire breakthrough.

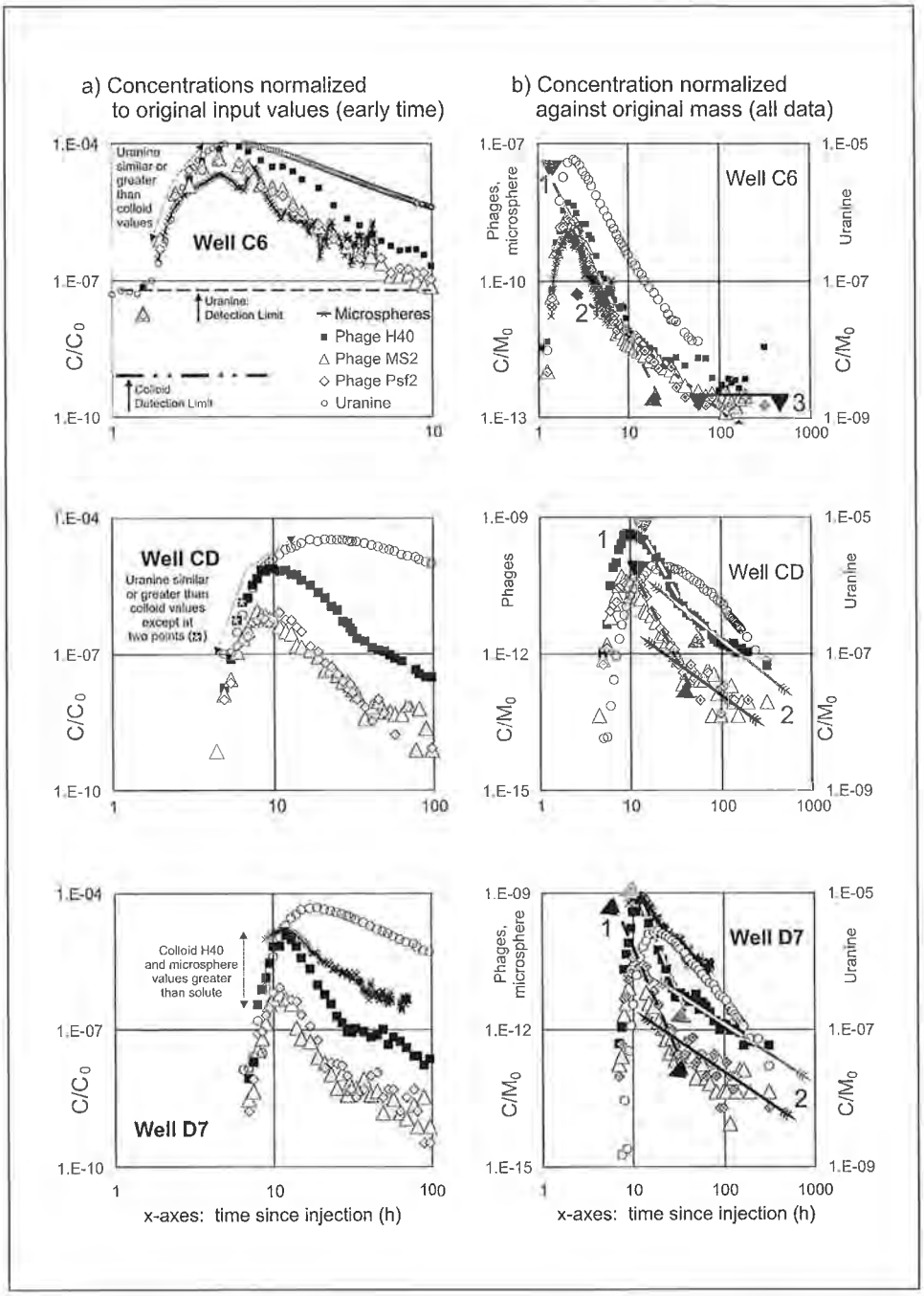
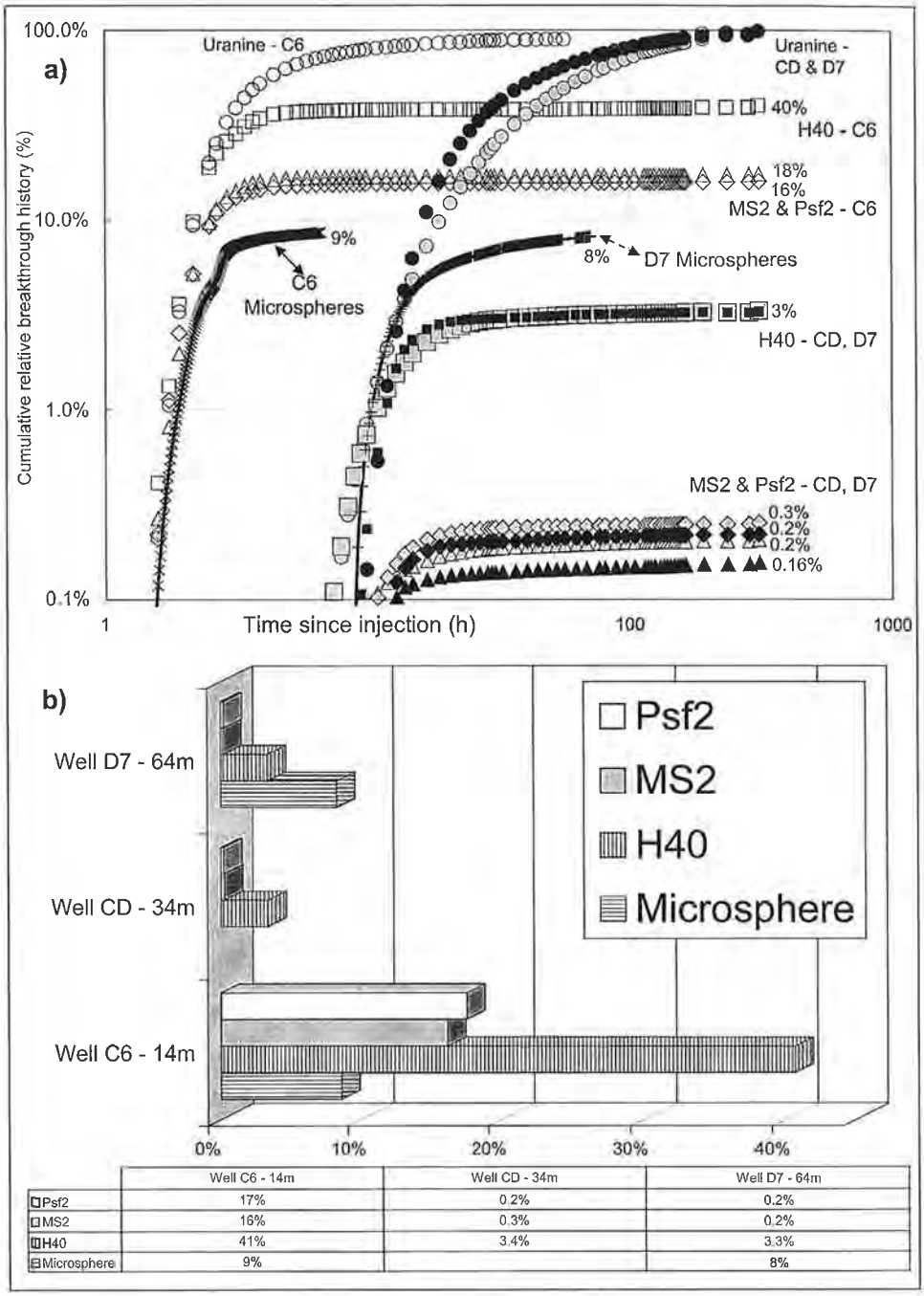


Fig. 4.20: Component concentration by well normalized to a) injectate concentration (C/C_0) and b) injectate mass (C/M_0) (log-log plot).
Tracerkonzentration je Bohrung normalisiert auf a) Injektatkonzentration (C/C_0) und b) Injektatmasse (C/M_0) (log-log Plot).



	Well C6 - 14m	Well CD - 34m	Well D7 - 64m
Psf2	17%	0.2%	0.2%
MS2	16%	0.3%	0.2%
H40	41%	3.4%	3.3%
Microsphere	9%		8%

Fig. 4.21: Cumulative relative breakthrough (a) (log-log plot) and total relative breakthrough comparison by component (b).
Kumulativer „relativer Breakthrough" (a) (log-log Plot) und totaler „relativer Breakthrough" im Vergleich pro Tracer (b).

This additional amount, based on the comparable phage RB evolution to those C/C_0-values where monitoring began, would add about 10 % to the total observed, raising it to ~ 9–10 %.

4.2.4.5. Component Response Comparison

The magnitude of the uranine and phage H40 response was greater than expected at all wells given the injection concentrations and past test experiences at the site. This was likely caused by the flow occurring in a relatively narrow layer of less than 1 m, at least in the vicinity of well B4, and this preferential lens or channel and continuing without much vertical dispersion down gradient to C6. The high relative breakthrough of from 16–41 % for the phages at C6 supports this direct channel connection hypothesis. Both uranine and colloids thereafter had expected increases down gradient in both dispersion and attenuation, but not directly as a function of distance. There was clear influence of transverse dispersion in the component responses at CD.

The colloids were differentially attenuated as follows:

- phage H40 < Psf2 ≅ MS2 < microspheres (C6),
- microspheres < phage H40 << Psf2 ≅ MS2 (CD (phages) and D7).

Attenuation ranges (Tab. 4.8) at 14 m at C6 ranged from 59–84 % for the phages. The degree of attenuation dropped dramatically between C6 and was essentially the same for the phages at both 34 and 64 m. At CD and D7, the attenuation ranges were over 99.7 % for MS2 and Psf2. However, the attenuation values of H40 and microspheres were significantly lower in the range of 96–92 %. The clean, clay-free and large pore spaces in the gravel lenses of this aquifer are likely the reasons there is such a relatively low degree of attenuation.

The four colloids arrived at each well at relatively similar times so there was no apparent transport of one phage preferentially over another. Uranine generally was detected after the colloids. Only at D7 was there enough difference to suggest that it could be related to other than detection limit variability. The colloid pseudo-peaks were equal or similar at the wells in the channel, C6 and D7 with retardation factors (RF) of 0.9 and 0.6, respectively. At CD, the RF-values were 0.4 for MS2 and 0.5 for H40 and Psf2. The RF-value needs to be put in context based on the earlier discussion of what affects the time at which the ps-peak occurs. RF-values may be useful to consider, just as plots of relative abundance to show or portray where the ps-peak and solute peaks occur in time. This is useful in a single setting assuming that the processes affecting the colloidal responses are similar throughout that setting. It is unlikely, however, that comparing the RF-values among different environmental settings is appropriate.

Two dual peaks occurred that could not be readily explained based on the hydrogeological setting. The microsphere data at C6 was both continuous and consistent. Yet, it did not match any trend in the phages over this period. Despite the higher considerably higher sampling frequency, it is difficult to imagine a transport mechanism in this channeled rapid migration setting that would not affect all colloids in a similar manner. So the microsphere dual peak at C6 remains unexplained based on the subsurface conditions. The Psf2 dual peak was not as dramatic as the C6 microsphere pattern and could be more related to analytical variability than site conditions. Both instances had the original ps-peak patterns similar to the other colloid response at these locations. We suggest that no special significance be given to these two occurrences without further confirmation testing.

Tab. 4.8: Tracer breakthrough characteristics for uranine, bacteriophages and microspheres. [1]) – uranine is a solute that is commonly referred to as a conservative tracer – and we designate Tr as the solute component concentration label. Accordingly, we refer to $t_{tr\text{-}arr}$ and $t_{tr\text{-}max}$ as the times associated with arrival and maximum solute concentrations, respectively. This differentiates it from the t_c time terms associated with the colloids; [2]) – uranine Tr_0 units are ppb; [3]) – $t_{c\text{-}max}$: time of maximum colloidal particle concentration. We refer to this as a pseudo-peak (ps-peak) since it does not have the same implied or associated characteristics as conservative solute tracer peaks do for mass transport behaviour; [4]) – bacteriophage units are pfu/ml, microsphere units are microspheres/ml (ms/ml). Microsphere values have not been corrected (increased) for the counter efficiency may be as low as 50 % depending on environmental and water conditions during testing; [5]) –microspheres showed two pseudo-peaks at C6 at 2.2 and 2.8 h. The earlier pseudo-peak at 2.2 h more closely matches phage results; [6]) – phage Psf2 showed two pseudo-peaks at CD at both 8.4 and 10.9 h. The pseudo-peak at 8.4 h more closely matches other phage results; RF – retardation factor is the ratio of the time of maximum particle or colloid concentration compared to that of the solute; RB – relative breakthrough; Att'n – attenuation % is 100 % – RB %; nd – not determined. (Continuation p. 207.)

Durchgangscharakteristika für Uranin, Bacteriophagen und Mikrosphären. [1]) – Uranin ist eine Lösung, die allgemein als konservativer Tracer betrachtet wird; wir betiteln Tr als die gelöste Komponente. Entsprechend bezeichnen wir mit $t_{tr\text{-}arr}$ und $t_{tr\text{-}max}$ die Zeiten für den Konzentrationsersteinsatz und –maximum; dies dient zur Unterscheidung von den für die Kolloide verwendeten t_c-Zeitbezeichnungen; [2]) – Uranin-Tr_0-Einheiten in ppb; [3]) – $t_{c\text{-}max}$: Zeit für maximale Kolloidkonzentration; wir bezeichnen diese als „Pseudo-Peak" (ps-peak) weil sie nicht die selben Eigenschaften besitzen wie konservative, gelöste Tracer-Massentransport-Peaks; [4]) – Bakteriophageneinheiten sind pfu/ml, Mikrosphäreneinheiten sind Mikrosphären/ml (ms/ml); die Mikrosphärenwerte wurden nicht korrigiert (angehoben), da die Zählergenauigkeit, abhängig von den Umwelt- und Wasserbedingungen während des Versuchs, bis zu unter 50 % sein könnte; [5]) – die Mikrosphären zeigten zwei Pseudo-Peaks bei C6 nach 2.2 und 2.8 h; der frühere Pseudo-Peak bei 2.2 h ähnelt mehr Phagenresultaten; [6]) – die Phage Psf2 zeigt zwei Pseudo-Peaks bei CD: 8.4 und 10.9 h; der Pseudo-Peak bei 8.4 h ähnelt mehr anderen Phagenresultaten; RF – Retardationsfaktor ist das Verhältnis von Partikel- oder Kolloidmaximumzeit zur Uraninmaximumzeit; RB – „relativer Breakthrough"; Att'n – Dämpfung % ist 100 % – RB %; nd – nicht bestimmt. (Fortsetzung S. 207.)

Microsphere recovery was high at both C6 and D7. Its RB at 64 m was at least two-fold that of H40. All the colloids are negatively charged with H40 being more negative than Psf2. Unfortunately, the isoelectric point values of the microspheres and MS2 are not well documented so we cannot compare this parameter directly. The size difference is large between the microspheres and the phages. With similar negative charges, size could account for the higher microsphere recovery at the further distance. However, size differences are generally not considered as important to differentiate among colloid recovery, as are variations in colloidal surface properties. And surface properties affect the response also in accordance with the chemistry of the water in which the transport is taking place. Regardless, with H40 recovery higher than the microspheres at 14 m (C6), this suggests that colloidal differentiation may have occurred along the transport paths between the injection well and D7. There is a high degree of heterogeneity in the aquifer and there were higher C/C_0-microspheres vs. uranine Tr/Tr_0-values at the beginning of the D7 data record. Given these conditions, co-mingled and varying pathways for the different colloids to travel through is a possible hydrodynamic explanation for an increase in microsphere presence further down gradient.

4.2.4.6. CoTrans Model Preliminary Interpretation Results

CoTrans calculates transport of a conservative tracer and colloids in suspension in a flow model. Details are in S. NIEHREN (1998). A double porosity (two regions, mo-

Down gradient well	Uranine response[1]				Bacteriophage and microsphere responses						
	Distance from injection [m]	$t_{tr\text{-}arr}$ [h]	$t_{tr\text{-}max}$ [h]	Tr_{max}[2] / $(Tr/Tr_0)_{max}$	Particle	$t_{c\text{-}arr}$ [h]	$t_{c\text{-}max}$[3] [h] (ps-peak)	RF	C_{max}[4] / $(C/C_0)_{max}$	RB [%]	Att'n [%]
C6	14	1.5	2.5	912 / $1e^{-04}$	H40	1.1	2.2	0.9	57,000 / $9e^{-05}$	41	59
					MS2	1.3	2.2	0.9	32,000 / $5e^{-05}$	17	83
					Psf2	1.3	2.2	0.9	12,000 / $4e^{-05}$	16	84
					Micro-sphere	1.4	2.2, 2.8[5]	0.9	45,62 / $2e^{-05}$, $3e^{-05}$	9	91
CD	34	5	21	296 / $3e^{-05}$	H40	4.9	9.4	0.5	4,800 / $8e^{-06}$	3.4	96.6
					MS2	4.4	7.9	0.4	580 / $9e^{-07}$	0.2	99.8
					Psf2	4.9	8.4, 10.9[6]	0.5	190, 250 / $6e^{-07}$, $8e^{-07}$	0.3	99.7
D7	64	8	19	426 / $5e^{-05}$	H40	6.9	11.9	0.6	7,500 / $1e^{-05}$	3.3	96.7
					MS2	6.9	10.9	0.6	410 / $6e^{-07}$	0.2	99.8
					Psf2	6.9	10.9	0.6	255 / $8e^{-07}$	0.2	99.8
					Micro-sphere	nd	11.3	0.6	33 / $2e^{-05}$	8.2	91.8

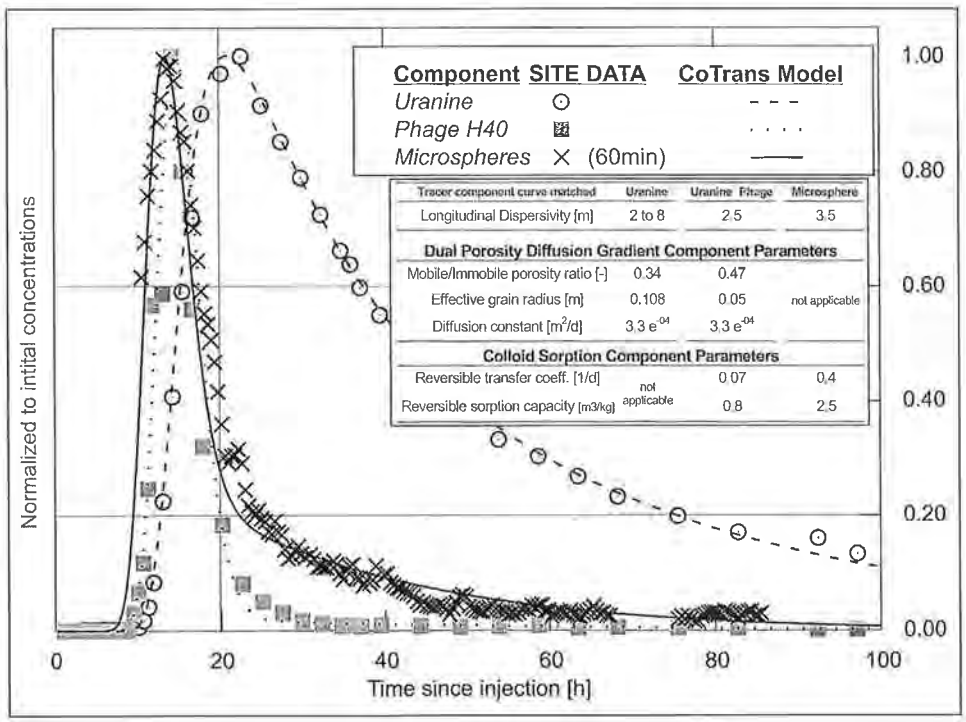
bile/immobile zone) model is used for the ideal conservative solute tracer – in our case, uranine. The solute can occur in both the mobile and the immobile zone. CoTrans assumes that the particles follow active porosity zone "flow paths" in which there is a physical migration (advective-dispersive conditions). The solute moves in these pores and as well, diffuses into the "dead end" pores into which there is essentially no advective-dispersive effect, but there is diffusion. Further, this dual continuum model has the added condition that there is a diffusion "gradient" both into and out of the adjacent immobile porosity zone as the tracer migrates along the mobile pathway pores. In this manner there is a better consistency associated with the approach to modelling not just the rising limb of the breakthrough curve but also the tailing over the long term of solute data. Colloid migration occurs only in the mobile zone and is also excluded from the low-velocity regime near matrix surfaces. This requires a colloid porosity para-

meter that is lower than the mobile zone porosity. Colloid adsorption mechanisms associated with the matrix are:

a) reversible adsorption of the colloid on the matrix (without maximum capacity),
b) irreversible adsorption of the colloid on the matrix with a maximum capacity, and,
c) irreversible adsorption on the already irreversibly adsorbed colloids (colony building) without a maximum capacity.

Each sorption mechanism is represented in the model as a transfer coefficient and there is also a term for reversible sorption capacity.

The modelling was done to better understand and portray the behavioural characteristics of the two types of tracers in the heterogeneous porous media at Wilerwald. In choosing the 1-D version of CoTrans as a preliminary model to apply at Wilerwald, we assumed that the channel well (D7) behaves as a function of distance from the injection point that is also in the active channel. CoTrans was used with uranine data that could be matched along both the rising and falling limb including tailing with dispersivity ranging from about 2–8 m. Figure 4.22 illustrates and lists the parameter values used to fit the data. By using a dispersivity of about 2.5–3.5 m, we were able to match the uranine, H40 and microsphere data, respectively. By including the colloid in the matching, we narrowed the range of the possible dispersivity values selected for the system. The figure also lists the parameter values used to fit the test data. The data fit



Tracer component curve matched	Uranine	Uranine Phage	Microsphere
Longitudinal Dispersivity [m]	2 to 8	2.5	3.5
Dual Porosity Diffusion Gradient Component Parameters			
Mobile/Immobile porosity ratio [-]	0.34	0.47	
Effective grain radius [m]	0.108	0.05	not applicable
Diffusion constant [m^2/d]	$3.3\ e^{-04}$	$3.3\ e^{-04}$	
Colloid Sorption Component Parameters			
Reversible transfer coeff. [1/d]	not applicable	0.07	0.4
Reversible sorption capacity [m3/kg]		0.8	2.5

Fig. 4.22: CoTrans modelling results for well D7 (after S. NIEHREN, 1998, S. NIEHREN & K. KENNEDY, 1999).
Ergebnisse der CoTrans-Modellierung für Bohrung D7 (nach S. NIEHREN, 1998, S. NIEHREN & K. KENNEDY, 1999).

well to the model parameters selected. Despite the model simplicity and inherent assumptions, it shows that reasonable values of longitudinal dispersivity can be combined with colloid sorption and two-region solute model parameters to achieve a simulation of the observed field behaviour.

4.2.5. Conclusions

We have approached this work principally from an experimentalist viewpoint with objectives targeted principally at two areas – field equipment verification and particle and solute efficacy evaluation. Injection conditions influence the test results and should not be minimized either in their importance or in their detailed presentation for any tracer work done. The higher the degree of subsurface heterogeneity, the more critical are the precise definitions of the actions taken during this phase and in the down gradient sampling locations. Comparison of test data from one series of investigators to another is typically complicated and without clear presentation of the field approach and results, it at best provides a potentially erroneous database. This is particularly true in Wilerwald with its high degree of heterogeneity. The following are our principal conclusions:

1) During injection at B4, we discovered flow from the well was into a discrete and relatively thin lens/layer between the depths of 4 and 6 m. A similar condition was subsequently documented at another glacio-fluvial site in the Rhone River valley. This finding suggests that hydraulic conductivity used in transport scenarios may be significantly understated. The effective zone contributing to lateral migration in this aquifer may be preferentially occurring in a limited zone on the order of 0.5–1 m thick rather than the fully-screened 10 m interval. This preferential flow layer was also apparent down gradient at C6 and D7 where concentrations were higher than historical tests using the same wells and tracer components.
2) "Arrival" times based on first detection at each well were similar for all phages and at C6 also for the microspheres. Solute detection, principally due to lower detection limits and background levels at the site, occurred consistently later at C6 and D7 and at the same time at CD. Wells C6 and D7, based on both the tracer response and geophysical interpretation, are located along the longitudinal flow direction of the channel down gradient from the B4 injection point. Well CD is off the main channel and its results indicate more transverse dispersion than seen at C6 or D7. There was no indication of preferential colloidal advection at C6. At CD and D7, H40 exhibited a partial earlier response than uranine for periods of 30 min and 2 h, respectively, during the rising limb, but this is not considered conclusive of earlier colloid arrival.
3) Transport velocity values pertinent to viral surrogates, such as the colloids we used, may be more relevant when based on the first detection time rather than the time of maximum concentration. At C6 and D7, phages had migration rates of 285 (colloid average) and 223 m/d, respectively. The phage-based arrival velocity to CD off the main channel was 167 m/d. These values are from two- to four-fold higher than the average velocities of 135, 80 and 40 m/d calculated from the observed peak uranine concentration times at the same wells. Using colloid pseudo-peak and solute peak time to determine, which "arrived" earlier, may not be appropriate given the high colloid adsorption along the pathway.
4) Both H40 and microspheres were significantly less attenuated compared to MS2 and Psf2. The relative breakthrough (recovery) of each colloid at a distance of 14 m (C6) ranged from 9–41 %. This is a significantly higher recovery than has been reported for other similar-sized tracer components in sand and gravel porous aquifers. The

high values suggest little filtration is occurring over this 14 m distance. Differences in H40 and MS2 and Psf2 recovery were only about 2.5-fold at C6, but their differences increased to about 10- to 17-fold at CD and D7. Similar results occur when comparing the C/C_0-values of their pseudo-peaks. Having similar recovery results at both 34 and 64 m but in two different subsurface settings illustrates the non-uniqueness of solutions suggested for the variations in the colloid behaviour. There was, however, little visual difference in the slopes and patterns of their individual responses in the falling limb and tailing section at each well suggesting the processes acting on the individual phages, prior to their arrival may be scalable and proportional, at least among these three phages. Only at CD were the shapes of the phage responses after about 50 h less alike and this may have been related to the MS2 and Psf2 concentrations approaching their detection limits. The dispersion characteristic of each phage appears similar based on the consistent breakthrough shapes at each well.

5) Matching the response of H40, microspheres and uranine at well D7 was done using CoTrans, a 1-D numerical code. The initial approach with attempts to match the uranine data had indicated matching the solute response was possible with a longitudinal dispersivity range of from 2–8 m. By matching the particle data at well D7, a longitudinal dispersivity of about 3 m was determined. Using this input from the colloid data matching, the dispersivity values of all three components were able to be limited to a smaller range while matching all component data. The presence of both colloid and solute tracer helped reach consistent model results using a double porosity (two-region) model for solute migration and a variable sorption conditions for the colloids.

6) The prototype instrumentation was able to be successfully deployed under typical field conditions. Microspheres and uranine were well documented continuously in the field and rapid analyses were possible of the discrete samples for uranine analysis as well. The in-line equipment provided real-time assessment of both colloid and uranine tracers allowed site sampling to be effectively modified and optimized. This was particularly important when considering the sampling for phages given that the solute arrival and maximum concentrations observed commonly followed the first colloid detection and pseudo-peaks. Relying on solute responses to sample for colloids was shown not to be appropriate. Phage laboratory results were also consistent and reliable. The high density sampling during this test allowed definition of precise breakthrough curve shapes and characteristics. Despite large losses in the colloid quantities, they had a regular breakthrough pattern illustrating that their persistence can be effective to evaluate and document viral migration patterns. Additional characterization of the individual colloids used for field tests, however, is needed in order to improve our detailed understanding of what particle parameters and in situ processes can cause the observed differences in their adsorption behaviour.

Acknowledgements

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4.3. Merdingen (W. KÄSS)

4.3.1. Tracer Tests

The testfield Merdingen as well as a combined test in the unconsolidated rocks there with the tracers uranine, bromide, and strontium was thoroughly described by A. DE CARVALHO-DILL et al. (1992) in this journal.

The results of a not yet published comparative tracer test from 1988 are presented here (see tab. 4.9, fig. 4.23 and 4.24).

Four tracers were applied:

- uranine (0.02 kg),
- tinopal CBS-X (0.05 kg),
- cadmiumsulfate-solution (3.5 l = 1000 g Cd^{2+}),
- and microspheres YG ($n = 46 \times 10^9$).

Tab. 4.9: Results of a fourfold tracer test in the test field of Merdingen (unconsolidated rocks). Ergebnisse des 4-fach-Markierversuchs im Versuchsfeld Merdingen (Lockergestein).

Test time [d]	Distance [m]	Uranine [µg/l]	Microspheres [n/100ml]	Tinopal [µg/l]	Cadmium [µg/l]
10	0	–	–	–	–
	3	9.5	380	127	52
	6.25	10.9	610	183	95
	12.5	26	3,450	159	98
	25	33	4	4	0
	50	16.5	0	0	0
	100	0.12	1	0	0
30	0	–	–	–	–
	3	1.07	1,240	115	41
	6.25	0.57	1,380	20	30
	25	1.28	2,560	39	36
	50	60	3	0	0.5
	5	5	0	0	0
	100	0.025	0	0	0
100	0	0.19	–	5000	160
	3	0.19	2,000	42	25
	6.25	0.092	1,300	21	20
	12.5	0.14	2,800	27	19
	25	1	8	0	0.5
	50	0.08	0	0	0
	100	0.17	0	0	0
	200	0.032	–	–	–
300	0	0.07	–	580	70
	3	0.026	1,500	1.5	12
	6.25	0.017	1,270	7.6	12
	12.5	0.018	1,300	6	11
	25	0.1	2	1.5	0
	50	0.4	0	0	0
	100	0.018	0	0	0
	200	0.01	–	–	–

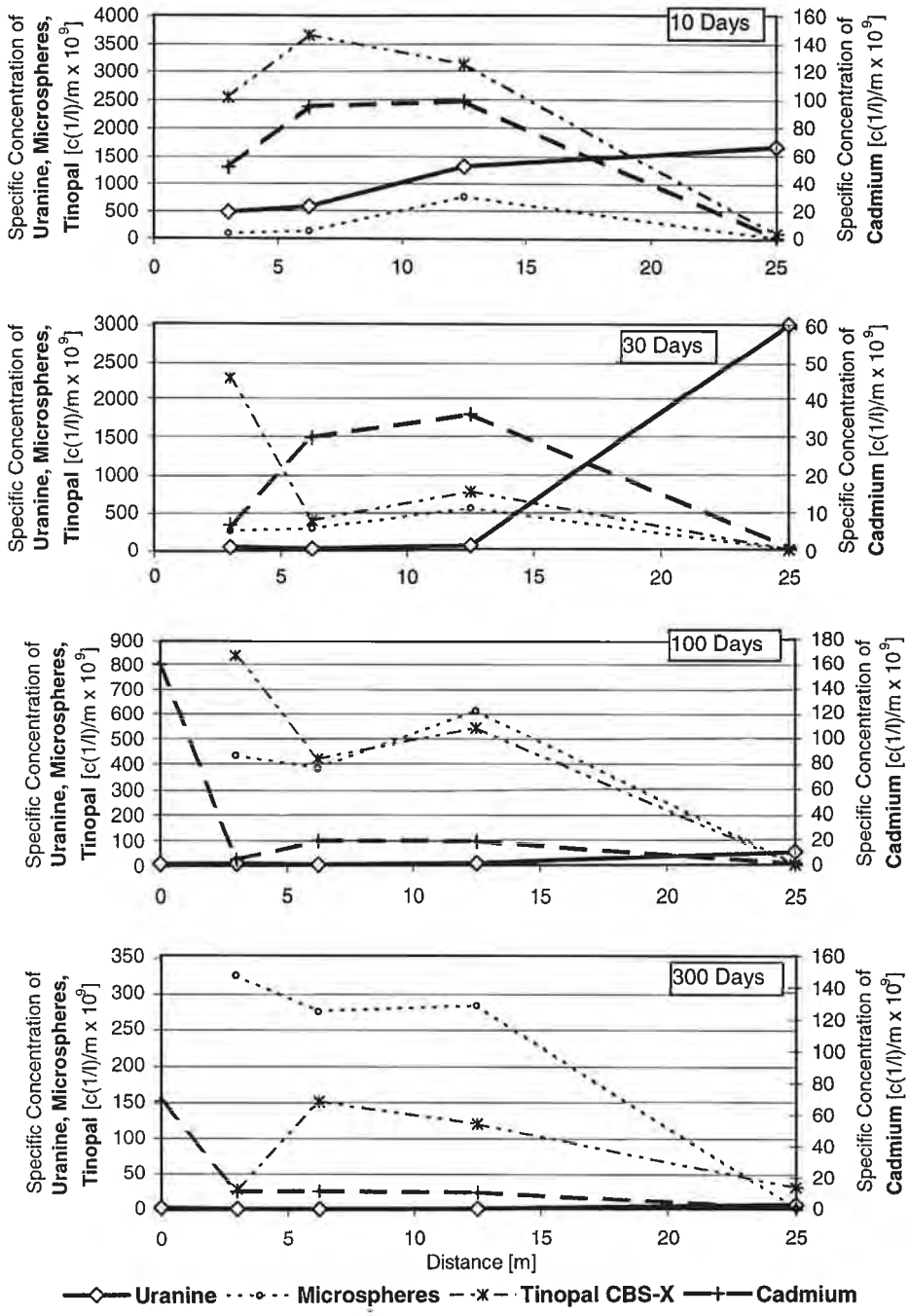

Fig. 4.23: Longitudinal profiles (0–25 m) for the observation times of 10, 30, 100, and 300 d with the four test substances. c(1/l) – concentration per litre, m – amount of injection.
Längsprofile (0–25 m) für die Versuchszeiten 10, 30, 100 und 300 Tage mit den vier Testsubstanzen. c(1/l) – Literkonzentration, m – Einsatzmengen.

Only the comparison uranine/microspheres was published in the textbook (W. KÄSS, 1998) and only in the profiles 50 m and 100 m.

On April 5, 1988, the four tracers were injected into the natural groundwater flow at a two-hours-interval.

The measured maximum concentrations in the transections between the injection point (0 m) and a distance up to 200 m are listed in tab. 4.9.

The comparative results in the transections 3 m, 6.25 m, 12.5 m, and 25 m after a test time of 10, 30, 100, and 300 d are shown in fig. 4.23. Specific concentrations were used to a better comparison in this figure. The remarkable behaviour of the cadmium ion is separately presented in fig. 4.24.

4.3.2. Results

Uranine can be described as a more or less ideal tracer. How quickly uranine is transported, is clearly recognizable in fig. 4.23. There is practically no uranine left in the test route 0–25 m after a test time of 300 d.

All the other injected tracers reach the 25-m-transverse profile only in small concentrations. The sporadic appearance of microspheres in the 100- and 200-m-transverse profile is worth mentioning.

Although a comparably large amount of **cadmium** was injected, a strong sorption of this heavy metal to the surface of soil particles and clay took place on the flow path up to 25 m. Figure 4.24 shows, that a real transport of cadmium could only be observed shortly after the injection.

Furthermore fig. 4.24 shows that a further sorption of cadmium obviously took place by diffusion from the liquid phase.

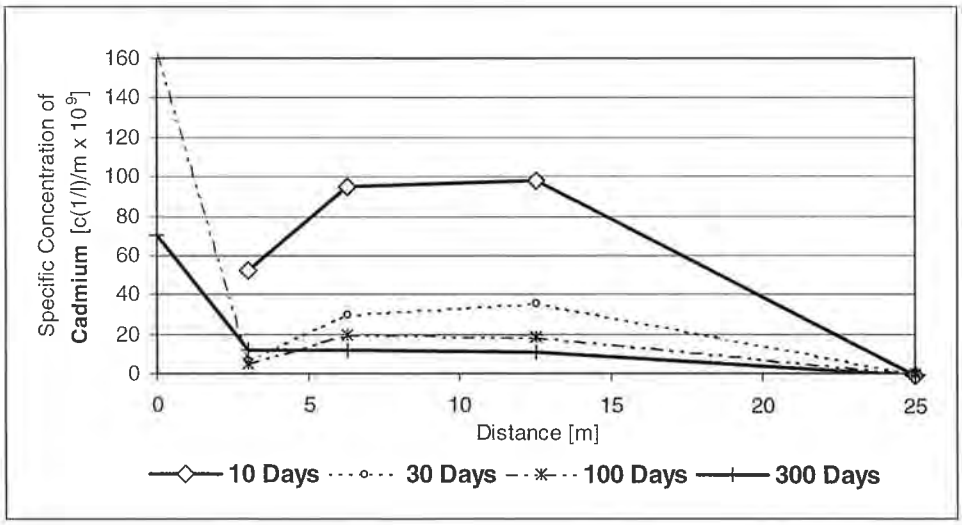

Fig. 4.24: Longitudinal profile (0–25 m) for cadmium. Observation times and specific concentration in Y-axis (left) as shown in fig. 4.23.
Längsprofil (0–25 m) für Kadmium. Versuchszeiten und Normkonzentration (Y-Achse links) wie in Fig 4.23.

4.4. Comparative Studies on Tracer Propagation in Quaternary Gravels and Tertiary Sands of South Germany (K.-P. SEILER, J. MÜLLER)

4.4.1. Introduction

In South Germany glacio-fluviatile and fluviatile Quaternary gravels as well as fluviatile Tertiary sands represent the best yielding unconsolidated aquifers. With 700 mm/y of precipitation and 500 mm/y of actual evapotranspiration, these aquifers are recharged with more than 150 mm/y; less than 50 mm/y produce overland – and interflow (direct discharge) (K.-P. SEILER et al., 2000). This significant groundwater recharge produces high distance- (0.5–50 m/d) and filter velocities (0.2–5 m/d) in sands respectively gravels. As a rule, these flow velocities can be measured with tracers using monopole (W. DROST, 1997) or dipole (K.-P. SEILER, 1977) designs or are approximated on the basis of hydraulic conductivities and the slope of the groundwater surface. All these methods refer to different basic assumptions, and to different scales. Monopole measurements deliver mostly short and variable results, whereas dipole measurements and pumping tests end in large scale and less differing results.

Since susceptibility of these aquifers for contamination is significant, good estimates of flow velocities are requested to better contribute to groundwater protection. Since different tracers are applied in hydrogeology, often without individually checking the non-reactive tracer behaviour in the saturated zone, a comparative dipole tracer study in representative sand and gravel areas was initiated to check the applicability of some of the commonly used hydrological tracers for determining hydraulic parameters.

The groundwater experimental site Dornach with Quaternary gravels seems to be the first and oldest in Germany. It has been demonstrated repeatedly (K.-P. SEILER, 1977, K.-P. SEILER, 1985, M. T. ZAHN & K.-P. SEILER, 1992) that the results of this field on the propagation of non-reactive tracers and many reactive pollutants are representative and applies for all glacio-fluviatile gravels in South Germany; recent unpublished experiments of both authors confirm it. For the groundwater experimental site Neuherberg with Tertiary sands this has not yet sufficiently proved.

4.4.2. Geological and Experimental Set Up

In Dornach gravels of the last two glacial cycles (Riss and Würm) have been explored above Tertiary clays in a thickness of 13.8 m by fully penetrating wells. In most, but not all the wells of the test site, in 9.5 m depth a 15 m thick red soil from the Riss-/Würm-Interglacial occurs separating young gravels above from old gravels beneath. This soil horizon is not wide spread; therefore groundwater in both gravels is unconfined and has the same piezometric height. Also the grain size distribution of both gravels (Fig. 4.25) does not differ and follows (Σ 127 samples) a marrow band as it typically is met in all glacio-fluviatile gravels of South Germany (K.-P. SEILER, 1977) and which significantly differ from moraine gravels. The hydraulic conductivity of all these gravels is 4×10^{-3} m/s and the percentage of clay and silts is lower than 10 weight-%.

In the groundwater experimental site of Neuherberg Tertiary sediments are covered by 9 m thick Quaternary gravels free of groundwater which end to the former erosion surface with 15 m of clays. In the Tertiary sediments a sequence of sands and clays has been explored and within 50 m depth different sandy grain size distributions typically occurring in Bavaria (K.-P. Seiler, 1983) have been screened and separated from one another by full tubes and a tixotrophic clay. The lump grain size distribution of one of the screened window is shown in fig. 4.26. Groundwater in each screened win-

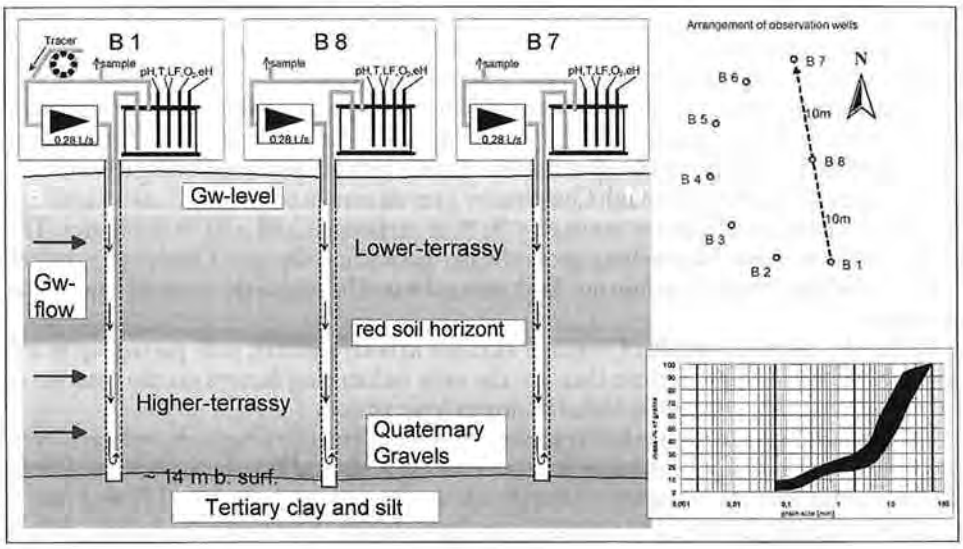

Fig. 4.25: Lumped grain size distribution and the arrangement of wells with respect to groundwater flow at the Dornach test side (Quaternary gravels).
Summenkurve der Korngrößenverteilung und Lage der Bohrungen in Bezug auf die Grundwasserströmung im Testgebiet Dornach (quartäre Kiese).

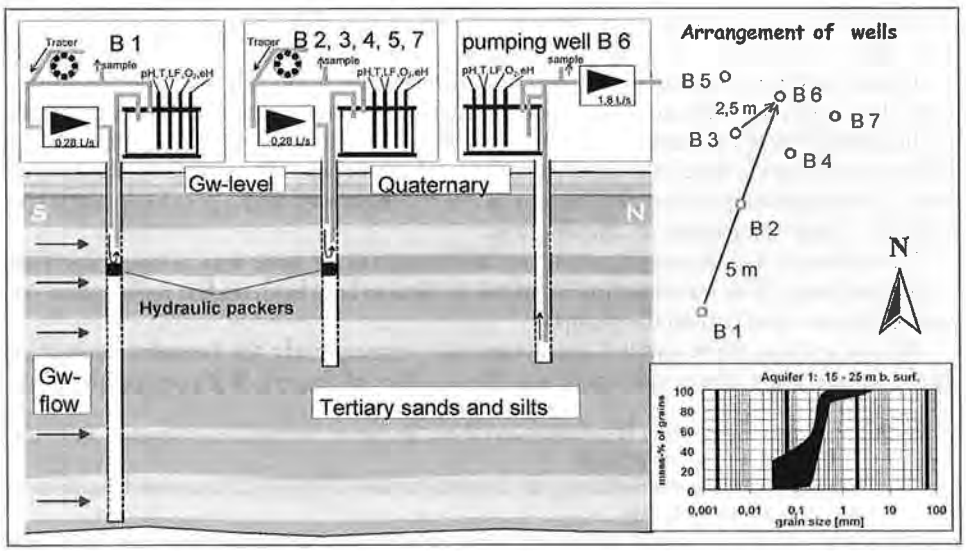

Fig. 4.26: Lumped grain size distribution for the upper screened horizon on the groundwater experimental side of Neuherberg and the arrangement of wells with respect to groundwater flow (Tertiary sands).
Summenkurve der Korngrößenverteilung des oberen Horizonts im Grundwassertestgebiet Neuherberg und Lage der Bohrungen in Bezug auf die Grundwasserströmung (tertiäre Sande).

dow is confined and the hydraulic potentials differ in between the three layers; they are always somewhat higher in the upper than in the next lower layer and without packers cause vertical downward flow along the well axis.

Experiments in the Neuherberg test side have been performed in the upper screened sand with a hydraulic conductivity of 7×10^{-4} m/s and the clay and silt content is about 20 weight-%. Hydrochemically, groundwater from Dornach and Neuherberg has the same composition (Tab. 4.10) although Quaternary gravels consist to > 95 % of carbonates and < 5 % of silicates and Tertiary sands of < 20 % of carbonates and > 80 % of silicates. This is due to the fact that Neuherberg groundwater passes first through Quaternary gravels before reaching Tertiary sediments. Both groundwater have also the same pH and redox potential.

Since the chemical matrix of water is identical in both aquifers, only petrography and grain sizes differ and therefore they are the only influencing factors on the reactive or non-reactive behaviour of the tested hydrogeologic tracers.

The experimental design in both experimental sites differs. In Dornach, wells are screened all over the depth, representing fully penetrating wells and have been positioned along a half around with the diameter in flow direction (Fig. 4.25) and a radius of 10 m. Longest test distance is two times 10 m and stretches downstream from wells 1 to 8 and 7. All the other test distances are shorter. Experiments on the Dornach site have all been performed under natural gradient conditions.

In the Neuherberg test site three screens, isolated by full tubes and tixotrophic clay, open windows to Tertiary sands each on the same level of depth (Fig. 4.26). The observation wells are 10 m, 5 m and 2.5 m distant to the extraction well and follow more or less a stream channel. Sideward of the abstraction well (B6) are the wells 5 and 7 to study not only the longitudinal but also the transverse dispersion. The three screens have been isolated by packers to study the tracer propagation individually. All tracer experiments in Neuherberg are performed with groundwater abstraction of 1.5 l/s out of well 6. Extracted water is rejected and does not recycle to the Tertiary aquifer.

Tracer injection has been performed on both test sites identically by either instantaneous (Dornach) or continuous injection (Neuherberg); to do so the tracer was circulated in the injection well by pumping according to the direction of vertical flow in the well; in both cases tracers entered the circulating water by a bypass. This mode of injection allows a homogeneous tracer distribution in the injection well and a good approach to a DIRAC signal as initial tracer distribution.

Tracer detection and sampling was done in Dornach in the same way as tracer injection; so, groundwater flow remained undisturbed. In Neuherberg both on-line registration and sampling was done behind the pump.

All tracers have been injected simultaneously; consequently the boundary condition during each comparative experiment was the same for all tracers. With respect to hydro-

Tab. 4.10: Chemical composition of groundwater from the experimental site of Dornach and Neuherberg. n.d. – not detectable.
Die chemische Zusammensetzung des Grundwassers im Testgebiet Dornach und Neuherberg. n.d. – nicht nachweisbar.

Test site	°C	pH	Ca^{2+} [mg/l]	Mg^{2+} [mg/l]	Na^{+} [mg/l]	K^{+} [mg/l]	NH_4^{+} [mg/l]	HCO_3^{-} [mg/l]	SO_4^{2-} [mg/l]	Cl^{-} [mg/l]	NO_3^{-} [mg/l]	NO_2^{-} [mg/l]
Dornach	9.4	7.5	90.0	24.0	21.0	2.8	n.d.	350	20.0	27.0	20.0	n.d.
Neuherberg	9.4	7.5	80.0	27.0	8.0	1.0	n.d.	340	20.0	9.3	15.0	n.d.

dynamic dispersion and tracer balances, however, results of Dornach experiments, performed under natural gradients, are especially representative for dispersivities and of Neuherberg especially representative for tracer balances under forced gradients.

4.4.3. Applied Tracers and Tracer Analytic

In this study the tracers

- bromide,
- lithium,
- fluoreszeine (uranine),
- sulphorhodamine,
- naphthionate,
- strontium

have been applied.

These tracers are often successfully applied in fissured and karst rocks; experiences in unconsolidated rocks, however, are mostly missing.

During each comparative tracer experiment pH, temperature and O_2 have been measured on line and proved to be constant during all experiments.

Tracer detection was performed on line with a field fluorimeter calibrated for fluoresceine and a conductivity meter, and with automatic sampling at a frequency related to the conductivity measurement. Water samples have all been analyzed in the laboratory

- by spectral fluorimetry at individual pH levels to increase the sensitivity of analysis (H. BEHRENS, 1971),
- by ion-chromatography and ICP-AES without any sample preparation.

As a rule analytic results were available two to three days after sampling and meanwhile water samples have been stored at 12° C (groundwater temperature 9.5° C).

Since flow velocities in sands are lower than in gravels it was supposed that interactions of soluted tracers with solid surfaces may be more pronounced in Tertiary than in Quaternary sediments and therefore continuous injection was applied to the Neuherberg aquifer to guarantee a significant breakthrough and a measurable recovery; this continuous injection lasted two days.

In both experimental fields the injected tracer quantity was chosen according to a breakthrough of minimum one to two orders of magnitude above the detection limit of the respective tracer. Detection limits (Tab. 4.11) and initial tracer quantities (Tab. 4.12) are listed.

Tab. 4.11: Detection limits of the tracers applied in both groundwater experimental sites. SF – spectral fluorimetry, IC – ion chromatography, ICP-AES – inductively coupled plasma atomic emissions spectroscopy.
Nachweizgrenzen der in den beiden Testgebieten angewandten Markierungsstoffe. SF – Spektralfluorimetrie, IC – Ionenchromatographie, ICP-AES – Plasma-Emissionsspektroskopie.

Fluoresceine	Sulphorhodamine	Naphthionate	Br^-	Li^+	Sr^{2+}
2×10^{-12} [kg/l] SF	7×10^{-12} [kg/l] SF	7×10^{-11} [kg/l] SF	0.01 [mg/l] IC	0.1 [mg/l] IC	0.01 [mg/l] ICP-AES

Tab. 4.12: Quantity of tracers applied in both groundwater experimental sites.
Einspeisungsmenge der Markierungsstoffe in den beiden Grundwassertestgebieten.

Test site	Fluoresceine [mg/l]	Sulforhodamine [mg/l]	Naphthionate [mg/l]	Br^- [mg/l]	Li^+ [mg/l]	Sr^{2+} [mg/l]
Dornach	10	60	350	230	20	20
Neuherberg	10	60	350	230	20	20

4.4.4. Evaluation Methods

The result of tracer experiments and the tracer analytic contribute to breakthrough curves that have been fitted applying the equation of hydrodynamic dispersion. Additionally tracer balances have been performed which are incomplete for natural and complete for forced gradient experiments on short distances.

Longitudinal dispersion (D_L), residence times (t) and the interaction of tracers with the solid matrix (sorption) are the parameters to fit the breakthrough curves at a fixed location x. Since longitudinal dispersion is approximately known from former experiments (K.-P. SEILER, 1985) and from literature (A. LALLEMAND-BARRES & P. PEAUDECERF, 1978) residence time and sorption are the most important fit parameters in the equation (P. MALOSZEWSKI, 1997)

$$D_L \frac{\delta^2 C}{\delta x^2} - v \frac{\delta C}{\delta x} = \frac{\delta C}{\delta t} + \frac{1-n}{n} S(t) \tag{4.1}$$

with:

$$S_1(t) = \frac{\delta C_{s1}}{\delta t} = k_1 C - k_2 C_{s1}, \tag{4.2}$$

$$S_2(t) = \frac{\delta C_{s2}}{\delta t} = k_3 \frac{\delta C}{\delta t}, \tag{4.3}$$

$$S(t) = S_1(t) + S_2(t), \tag{4.4}$$

where

C = concentration,
v = distance velocity,
S = mass transfer function between water and solid surface,
k_1 and k_2 = reaction rate constants,
k_3 = distribution coefficient.

Tracer balance was calculated following the classical equation

$$R(t) = \frac{\int_{t=t_0}^{t=t_e} qC(t)dt}{M} \times 100\ [\%], \tag{4.5}$$

where

R = recovery,
q = water flux [m^3/m^2t],
M = injected quantity [mg/m^2],
C = concentration [mg/m^3].

Strictly spoken, in our experiments this balance is only valid for the captured sector of the propagation plume, which corresponds in Dornach about twice the borehole diameter and represents in Neuherberg approximately the whole propagation plume as far as tracing distance is short. It further supposes that molecular diffusion of the applied tracers does not differ significantly. From many studies it is known that transverse propagation amounts to 1/10 to 1/100 of longitudinal dispersion. In Quaternary gravels this may be well approximated by the width of the tracer plume with respect to the detection limited of fluoresceine (2 ng/l, tab. 4.11). This corresponds to a width of about 1/10 to 1/5 of the flow distance and can be applied to distances of less than 1,500 m (K.-P. SEILER, 1985).

4.4.5. Results and Discussion

Distance velocities have been calculated from breakthrough curves for Dornach at 30 m/d and for Neuherberg at 1.5 m/d. With respect to the tracing distance residence time of tracers was half a day and three days underground in Dornach and Neuherberg, respectively.

Figure 4.27 stands for the tracing results obtained in Dornach. It expresses clearly that fluoresceine can still be assessed as an ideal tracer as compared to bromide (K.-P. SEILER, 1977). All other tracers, however, experience

- instantaneous sorption without short-term de-sorption (naphthionate),
- instantaneous sorption with some de-sorption (lithium),
- strong instantaneous sorption (sulphorhodamine B) or

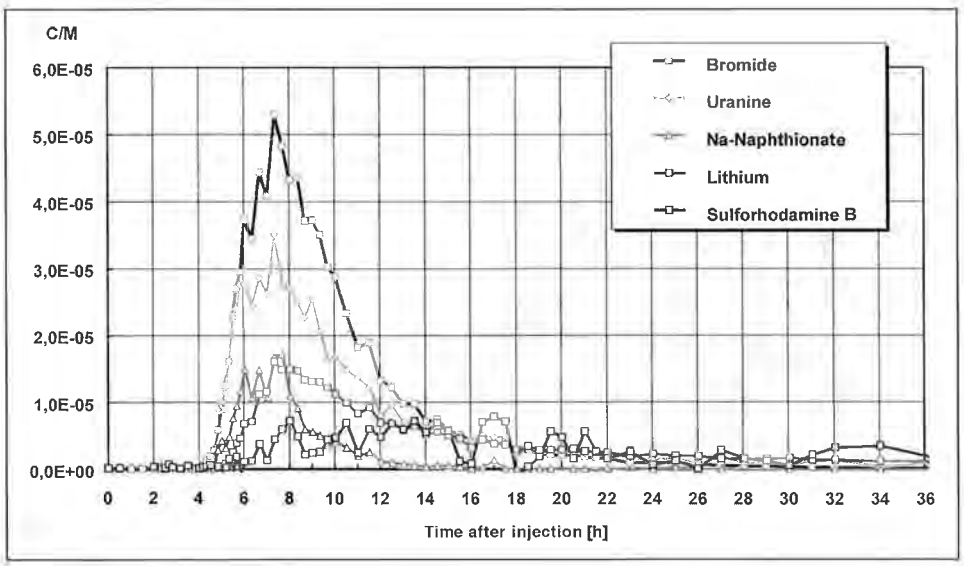

Fig. 4.27: Breakthrough curves from the Dornach experiment (Quaternary gravels). The measured concentrations are related to the injected quantity of tracers and thus allow a direct comparison.
Durchgangskurven im Testgebiet Dornach (quartäre Kiese). Die gemessenen Konzentrationen stehen in Bezug zur eingespeisten Menge des Markierungsstoffes und ermöglichen so einen direkten Vergleich.

– very strong instantaneous sorption like strontium that doesn't appear any more and therefore is missing on fig. 4.27.

Figure 4.28 shows the continuous tracing result from Neuherberg in the upper-screened window. It clearly shows that

– bromide and lithium behave conservatively,
– naphthionate experiences some instantaneous sorption, without knowing if this is related to slow or quick kinetics,
– fluoresceine is retarded,
– sulforhodamine is close to its detection limit and
– strontium – as expected – disappears.

Comparing the lithium results from the glacier (see chap. 3.1. in this volume) with Neuherberg and Dornach, it gets obvious that silicate rock-materials (glacier and Neuherberg) sorbe lithium not as much as carbonates. Contrary strontium, which is also cationic as lithium, it is totally sorbing in both carbonate (Dornach) and silicate rocks (Neuherberg) and even in the glacier environment with few sediments it is still sorbing. Obviously the strontium cation has very strong polarization properties.

Since eosin was already known as a retarded tracer in the Quaternary gravels (K.-P. SEILER, 1977), in coarse-grained sediments only halogenides and fluoresceine can be applied to determine distance velocities. Also lithium was applicable if the sediment composition is of silicate type. In fine-grained sediments again halogenides are applicable but none of the tested fluorescent tracers. Also here lithium was an appropriate tracer as far as silicates are dominating.

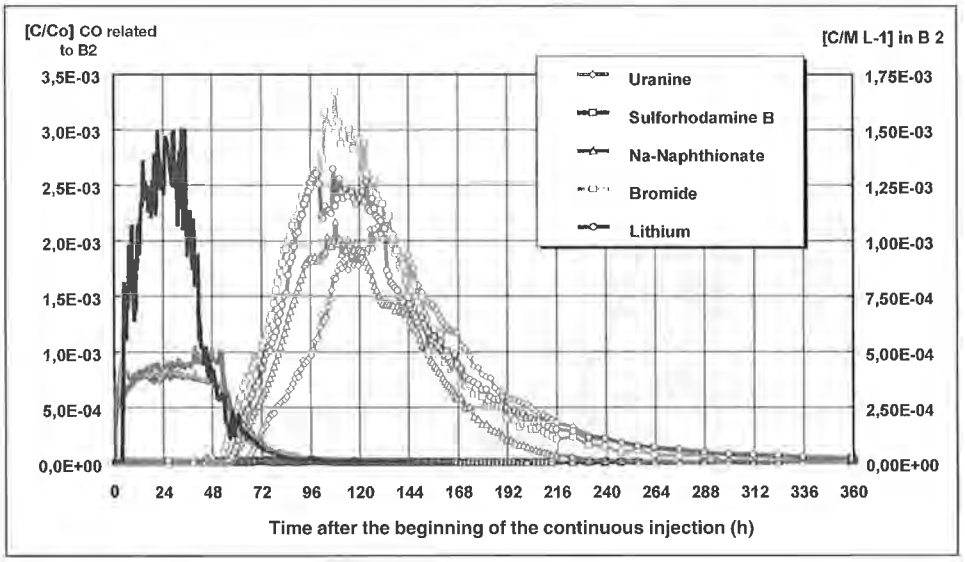

Fig. 4.28: Breakthrough curves (right part) from the Neuherberg experiment (Tertiary sands, upper window). The measured concentrations are related to the injected quantity of tracers and thus allow a direct comparison. The left part represents the continuous injection. Durchgangskurven (rechter Teil) im Testgebiet Neuherberg (tertiäre Sande, oberes Fenster). Die gemessenen Konzentrationen stehen in Bezug zur eingespeisten Menge des Markierungsstoffes und ermöglichen so einen direkten Vergleich. Der linke Teil widerspiegelt die kontinuierliche Injektion.

Summary and Conclusions (K.-P. SEILER)

In groundwater hydrology flow of water is calculated either by hydraulic or tracer techniques. In modern hydrogeology, however, a significant interest consists in modelling and assessing transport processes. The necessary and representative parameters to follow this line are dispersion and sorption, which can only be determined through tracer experiments on different scales. Here, monopol tracer experiments refer as a rule to scales below the REV (reference elementary volume) and provide good information about the variability of flow parameters; contrary, dipole tracing with and without forced gradients refers to both small and large scales, thus bridges scales and links to hydraulic results.

Many published tracer experiments in the subsurface have been executed according to recommendations about the non-reactive or reactive behaviour of the respective tracer. It is however known that the tracer behaviour is different according to mineralogy, grain sizes of aquifers and the chemical matrix of waters and may significantly get influenced by the mode of tracing and sampling.

Therefore, ATH focussed its interest in the past 36 years in comparing the behaviour of different tracers injected either in one place under typical hydraulic boundary conditions or to defining hydraulic boundary conditions in a catchment through simultaneous tracing in different places. These activities led to the use of 16 different tracers, the combination of environmental tracer with artificial tracing information and the development of low paraterized mathematical evaluation tools, all of which are now well known in practice.

Most of the past ATH tracing activities refer to karst areas, only few experiments have been executed in fissured or unconsolidated rocks. Therefore the actual ATH activities focussed to artificial, comparative tracing in

- unconsolidated sands (Neuherberg, Germany) with less than 20 weight-% of carbonates,
- unconsolidated gravels (Kappelen and Wilerwald, Switzerland; Dornach and Freiburg, Germany) with more than 50 weight-% of carbonates and
- a glacier with few crytalline sediment load.

Experiments have been executed with the tracers

- fluoresceine (uranine),
- lithium chloride,
- the fluorescent dye T4,
- pyranine,
- sulphorhodamine,
- sodium naphthionate,
- strontium bromide,
- latex microspheres (1 µm),
- bacteriophages H40, H4, HS2 and Psf2 (2–130nm) and
- bioparticles (coloured dead *Escherichia coli*)

on tracing distances ranging from 2.5, 5, 10, 11, 20, 60 to 75 m.

In all investigations cocktail tracing was applied with simultaneous pumping of the water in the injection and detection well in a circuit or in the karst area by injecting the tracer cocktail into a sinkhole receiving surface water.

Tracer injection technique has a pronounced impact on the geometry of the breakthrough curve; this is specially true for short distances in both consolidated and unconsolidated rocks.

The analysis of organic tracers should be executed immediately or short after sampling to avoid tracer decay by abiotic or biotic mechanisms.

In between all the applied tracers

- all of the particle tracers suffered in both unconsolidated and consolidated rocks from partial or total mechanical filtering; often the non-filtered portion analysed in the detection well was somewhat quicker than the non-reactive tracer. Only in gravels with hydraulically active interface layers (K.-P. SEILER, 1974) filtering of particles is significantly reduced and may get negligible;
- pyranine, sulphorhodamine B, strontium and particle tracers proved to behave reactively independently from the grain size, mineralogy and diagenesis of the investigated media;
- lithium behaves significantly reactive in carbonate gravels and proved to be a reliable non-reactive tracer in the glacier with crytalline particles and in quartz sands with few carbonates;
- fluoresceine (uranine) suffers negligible sorption in most gravels but gets significantly retarded in sands.
- sodium naphthionate is in both gravels and sands reactive and undergoes instantaneous sorption;
- the new fluorescent dye T4 was only checked in crystalline hard rocks and proved non-reactive.

In both consolidated and unconsolidated rocks matrix porosity or stagnant waters, respectively may significantly influence tracer propagation according to differences in molecular diffusion as compared to flow velocities.

As a general result it was stated that we do not dispose of sufficient reliable non-reactive tracers to be applied in unconsolidated rocks; this number is somewhat higher in consolidated rocks but not at all high enough to initiate tracer experiments at different places within a catchment to determine the ruling boundary conditions for groundwater flow.

Since groundwater flow in unconsolidated rocks usually does not converge to one outflow but directs mostly to line exfiltrations, since transverse dispersion is weak in it and double porosity systems are scarce, only few non-reactive tracers are needed to investigate such media. Contrary, in consolidated rocks with both line and punctual exfiltrations a wide array of non-reactive tracers was desirable. Therefore it is recommended that

- new non-reactive tracers should be developed and
- tracer application should always first assure the non-reactive behaviour of selected tracers.

The scale for such a check is bromide, but could also be tritium, oxygen-18 or deuterium. These tracers of the water molecule, however, are seldom used in groundwater studies in order to not destroying the environmental information of the isotopes of the water molecule.

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Zusammenfassung (H. ZOJER)

In der modernen Grundwasserhydrologie hat die Modellierung schon vor einiger Zeit Eingang gefunden. Die hydraulische Modellentwicklung folgt, sofern es die Homogenität des Aquifers zulässt, den Grundlagen von DARCY, stoffbezogene Transportprozesse können über Tracer simuliert werden, für den molekularen Wassertransport bieten sich multi-cell Modelle auf der Basis von Isotopendaten an.

Bei vielen Tracerversuchen wurde auf die Stoffeigenschaften Rücksicht genommen. Jeder Tracer reagiert unterschiedlich, abhängig vom mineralogischen Aufbau des Aquifers und vom chemisch-physikalischen Habitus des Grundwassers. Die ATH hat sich seit langem mit diesen Fragen auseinandergesetzt und Tracerversuche unter bestimmten hydraulischen Randbedingungen durchgeführt, auch um Tracereigenschaften zu vergleichen. Darüberhinaus wurde versucht, Untersuchungen künstlicher Tracer mit Umweltisotopen und hydrochemischen Ansätzen zu verknüpfen, um die Aussagekraft zu erhöhen.

Die Tracerarbeitsgruppe hat viele Versuche in Karstgebieten ausgeführt, hinsichtlich der Lockersedimente liegen Ergebnisse von kleinräumigen Versuchen in einem Sand- und in einem Kieshorizont vor. Zur Eingabe gelangten Fluoreszenztracer als organische Salze, anorganische Salze, Mikropartikel und Bakteriophagen. Leider reagieren die meisten Tracer auf Umwelteinflüsse und ändern ihre Fließeigenschaften. In diesem Zusammenhang haben sich Bromidverbindungen als äußerst konservativ erwiesen. Versuche mit Wasser aus anderen Einzugsgebieten und mit einem anderen Deuterium- oder Sauerstoff-18-Signal stellen zweifellos eine Bereicherung in der Traceranwendung dar, zumal sie als Bestandteil des Wassermoleküls keinen chemischen oder biologischen Reaktionen ausgesetzt sind.

Die Strategien zur Durchführung von Tracerversuchen in Festgesteinen, hauptsächlich in Karstgebieten, haben sich in den letzten Dezennien deutlich geändert. Während man in früheren Zeiten mit der Durchführung von Großversuchen optimale Informationen zu erlangen glaubte, spielt heute die Berücksichtigung von hydrologischen Rahmenbedingungen eine große Rolle, auch unter der Vorgabe, durch Tracerversuche nicht das gesamte hydrogeologische System eines Gebirgsstockes zu erfassen. Es werden Tracerversuche unter verschiedenen hydrologischen Verhältnissen wiederholt, um die Variabilität der Fließbewegung im Aquifer und damit auch des Einzugsgebietes von Quellen abzuklären. Erst dadurch ist es möglich, Inhomogenitäten im System zu lokalisieren und die entsprechenden hydrogeologischen Schlüsse zu ziehen.

Hingegen bieten Daten der Umweltisotope die Möglichkeit das gesamte Einzugsgebiet von Quellen oder Brunnen zu bewerten und auch Einzelereignisse des Abflusses auszuwerten. Entsprechende Modellansätze sind zu hinterfragen, um Vergleiche der Speicheranalyse mit anderen Methoden anzustellen.