Environmental Geology (1994) 23: 23–29

W. A. Käss

Hydrological tracing practice on underground contaminations

Received: 6 April 1993 / Accepted: 11 May 1993

Abstract The hydrological tracing technique is an important tool for the risk assessment of problem sites, the so-called "Altlasten" (old underground contaminations). The penetration of leachate through the unsaturated zone, the transport velocity, the migration pathways, as well as the dispersion in the aquifer can be determined by tracing experiments. A wide range of tracers offer sufficient possibilities to get the necessary hydrogeologic parameters for any kind of Altlasten. This is shown by some examples.

Key words Groundwater — Remediation — Tracing

Introduction

The tracing of water has become a scientific branch in which, besides hydrogeology, the disciplines of hydrology, chemistry, physics, biology, engineering, and hygienics are included. The tracing technique requires precision for the analytical procedures used in water analysis, as the tracing substances to be determined are mostly present in trace amounts.

At the beginning, wooden balls, sawdust, and chaff were used as tracers without success. The first scientifically evaluated test was performed in 1872 with rock salt in north Switzerland. When, in 1871, the chemist Baeyer for the first time synthesized fluorescein, he could have hardly anticipated having established the basis of the modern tracing technique. Sodium fluorescein is today known as uranin. It was first applied in 1877 in the sinkholes of the Upper Danube (Knop 1878). This first tracing experiment with uranin proved the excellent and to this day unsurpassed properties of this dye tracer. The increasing demands on appropriate tracing techniques required the development of new tracers as well as the improvement of the analytical methods. Both have been proved a success, so that tracing technical solutions now exist for all situations.

Tracers

A number of requirements must be accomplished by a tracer that is to be used for water tracing (Table 1). An ideal tracer, that meets all requirements, is not available, but some are close to the ideal. Each tracer in practice has advantages and disadvantages, which have to be considered. Uranin almost has ideal properties; only in pH ranges under 6 its sorptivity increases in such a degree as its fluorescence intensity diminishes. In surface water uranin is not or only restrictedly applicable. The isotopes tritium (^3H) and deuterium (^2H, D) are also almost ideal tracers. As a part of the water molecule, they almost move like the water stream. Permission to use tritiated water for a tracing test is difficult to obtain from authorities because of its

Table 1. Requirements for hydrological tracers

Criteria	Explanations
Water solubility	Good solubility in water at low temperature; drifting particles should be easily dispersible and should not deposit
Stability	No interaction with the water molecule, no biological decomposition, insensitive to light, resistant against pH and redox variations
Neutrality	No interaction with aquifer material by sorption and ionic exchange (not reactive)
Detection	Low detection limits, moderate costs for quantitative detection
Physiology	Harmless to man, animals, and plants
Economy	Amounts of injection and analytical costs should be adequate to the tracing project

---

W. A. Käss
Universität Freiburg, Geologisches Institut Freiburg/Br., Germany

An English version of "Hydrologische Markierungstechnik bei der Altlastensanierung" in: Die Geowissenschaften, Weinheim 10(2):199–205

Table 2. Groups of hydrological tracers

Water-soluble substances	Fluorescent and nonfluorescent dyes, salts, chemicals
Isotopes	Environmental isotopes, active isotopes, activated isotopes
Drifting particles	Spores, bacteria, microspheres, bacteriophages

radioactivity. A tracing test using heavy water (HDO) would require excessive cost in amount of tracer required and in analysis.

The different groups of substance suitable for water tracing are summarized in Table 2.

Dyes

This is the most important group of hydrological tracers, and here dyes with fluorescent properties allow an extremely low concentration for analysis. Nonfluorescent dyes such as fuchsin and methyl violet have negligible significance and are only used as substitutes on short flow ways or to trace sewage channels. Among the fluorescent dyes uranin has become the indispensable tool in tracer techniques. Its extremely green fluorescence intensity is the highest known. There is no sorption in neutral to alkaline milieus; uranin can be applied even in a cohesive underground. As mentioned above, it will only fail in an acid reaction, such as humic sands, since a sorptive cation is developed. The most important hydrological properties of the fluorescent dyes for water tracing are compiled in Table 3.

Eosin is often used together with uranin. Due to the fact that eosin decomposes in daylight, it is not suitable as a tracer in surface water. It shows a certain tendency to sorption onto grain surface but is well soluble in water.

Table 3. Properties of the most important fluorescent dyes

Common name	Properties
Uranin = (sodium fluorescein)	High fluorescent intensity, nonsorptive (pH > 6), sorptive (pH < 6), light sensitive, decomposable by strong oxidants (Cl_2, Cl_2O, O_3), well soluble in water, low costs
Eosin	Medium fluorescent intensity, little sorption, high light sensitivity, moderately pH dependent
Rhodamine B	Medium fluorescent intensity, no pH and redox dependence, no light sensitivity strongly sorptive
Amidorhodamine G, rhodamine WT, sulforhodamine B	Medium fluorescent intensity, little sorption, no pH and redox dependence, no light sensitivity
Pyranine	Low fluorescent intensity; fluorescence spectrum overlaps with uranin, not sorptive
Sodium-naphthionate	Low blue-violet fluorescent, not sorptive
Optical brighteners	Low fluorescent intensity, water solubility and sorptivity depend on chemical structure

Rhodamine B has been added to Table 3 as it is frequently listed as a tracer in literature. Rhodamine B is sorptive and capable of ionic exchange because of its cationic character. Therefore its application is restricted to short flow ways in surface water. This dye is suspected to have carcinogenic properties, which has led to further restrictions in some countries.

The rhodamine dyes amidorhodamine G, rhodamine WT, and sulforhodamine B fluoresce in the orange–red spectral range and are largely independent of influences of light and pH, but they are slightly sorptive. Sulforhodamine B lies spectrally very far from uranin so that differences of concentration at the rate of 1 : 10,000 can be determined without any separation (Fig. 1). Both uranin and sulforhodamine B are preferably used in combined tests.

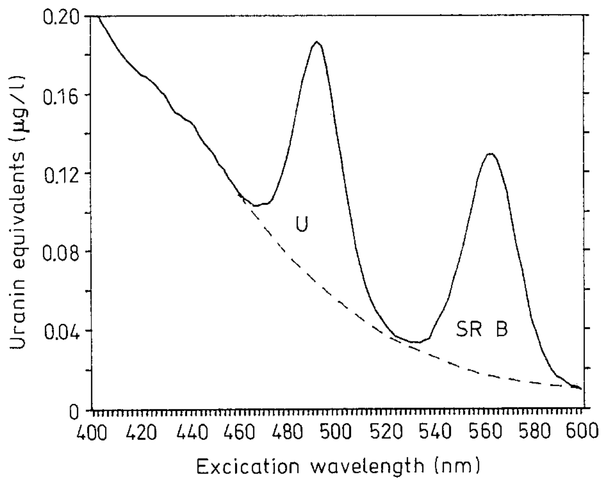

Fig. 1. Synchronscan fluorescence spectrum of turbid water with uranin (U) and sulforhodamine B (SR B). Both fluorescent dyes are detectable side by side up to a mixing ratio of 1:10,000

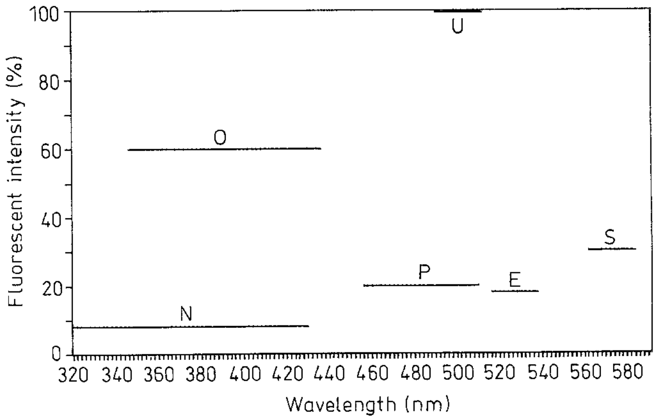

Fig. 2. Optical properties of some fluorescent dyes. Left end of the beam: excitation wavelength, right end of the beam: fluorescent wavelength. The ordinate indicates the intensity of equal concentrations in relation to uranin (=100%). U = uranin, E = eosin, S = sulforhodamine B, P = pyranine, N = sodium naphthionate, O = optical brightener Tinopal CBS-X

Pyranine is suited for tracing in acid pH ranges but can otherwise not be applied with uranin as the wave lengths of the fluorescence of the two dyes coincide (Fig. 2).

Combined tracing tests in clear groundwater can be successfully performed with uranin and sodium naphthionate or with uranin and optical brighteners. For both substances relatively large amounts have to be applied because of the high background.

Salts

Besides fluorescence dyes, salts can be used without any cross-interference (Table 4). Salts are applicable as second- or third-ranging tracers if the background of the salt applied is comparably low. Contaminated areas generally show a higher background of sodium and chloride, so that sodium chloride is usually not suitable.

The most important properties of sodium chloride, lithium chloride, strontium salts, bromide, and borax are listed in Table 4. Although all salts can be analyzed together without any interference, their application has disadvantages such as ionic exchange, water solubility, or high analytical costs. Only lithium chloride shows a distinct suitability as a hydrological salt tracer because of its low sorptivity, high water solubility, and its generally low background.

Chemicals elsewhere recommended as hydrological tracers, e.g., polyfluorated hydrocarbons, detergents, foams, and odoriferous chemicals, are not used for water tracing in an area contaminated with harmful substances.

Isotopes

The environmental isotopes tritium, oxygen-18, and deuterium (^{2}H) are of little help at Altlasten (old problem sites). The results of their use as tracers provide information on the recharge area and on the resident time of the groundwater rather than on the behavior of the discharge. The differentiation of geological horizons can best be performed with isotopes.

Table 4. Hydrological tracers: salts

Salt	Properties
Sodium chloride (NaCl)	Na$^+$ and Cl$^-$ ion, separately detectable, large amounts are needed because of high background
Potassium chloride (KCl)	In comparison to NaCl only 10% over background necessary for injection amount, K$^+$ ion exchange in porous aquifers
Lithium chloride (LiCl)	Low background, little sorption, good water solubility (hygroscopic)
Strontium salt (Sr^{2+})	Suitable for short distances, medium sorption, medium background
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	Low background, hardly sorptive, low solubility in water (16.2 g/l, 10°C)

Tracing with active isotopes can be perforned together with other tracers because the determination of their presence is independent of the determination required for other tracers. The application of isotopes as tracers is becoming increasingly limited because of concern over environmental protection.

Rare chemical elements that do not usually occur in groundwater (e.g., lanthanum, indium, and others) are used for postsampling activation analyses. Their application requires that the samples that may contain these elements be activated in a nuclear reactor. The occasional decrease in activity requires measurement immediately after the activation.

Drifting particles

In the scope of the investigation and remediation of old problem sites (Altlasten), only bacteria or microspheres are efficiently applicable as drifting particles; both can show pathways that may be used by germs if Altlasten are considered to leach pathogenic germs.

Test aims

The hydrological tracing technique can aid in the initial investigation and remediation of Altlasten. Hydrologic connections can either be confirmed or negated during the investigation on the point source of the contamination. The often-cited argument that a negative result of a tracing test is not a negative proof cannot be maintained. Nowadays there are numerous tracers that can prove a hydrological connection between two points if there is a sufficient amount for the application and a sufficiently long time of observation. The applied analytic method must, of course, show an adequate sensitivity. Only analytic methods which are able to determine the natural variations of the background are appropriate.

Tracing tests provide information that can be used to determine the direction and velocity of groundwater movement. Data can also be evaluated on the dispersibility, i.e., the dilution by dispersion effects. These are basic requirements for the assessment of a potential risk of a problem site for, e.g., a water supply.

A number of tracers are more or less sorptive and/or underlie the ionic exchange. These tracers allow evidence about the sorptivity and the ability of ionic exchanges of a traced flow when nonreactive tracers are simultaneously applied.

In the course of restoration measures, groundwater is either taken out for remediation and reinjected or the remediated water is drained off. There is also the "vacuum vaporizer well" method (German: Unterdruck-Verdampfer-Brunnen, UVB) where the groundwater is forced into direct circulation in the underground. All these restoration methods change the natural groundwater flow. The changes in groundwater movement can certainly be determined by mathematical modeling but such models often fail to meet reality. It is generally surprising how much the results of groundwater tracing tests in remediation sites differ from the model calculation.

Hydrological tracing at Altlasten

A number of points have to be considered concerning the tracing of groundwater in Altlasten that depart from tests in noncontaminated groundwater.

First of all, the water to be traced has to be tested for its compatibility with the planned tracers. In most cases there is already a background of uranin, partly due to former tests. A pH range strongly deviating from the neutral point determines which fluorescent tracer will be used. At Altlasten, the groundwater is in a reduced state. That means when a water sample containing an increased content of bivalent iron comes in contact with air, oxygen precipitates occur as colloid iron(III) hydrated oxide. Such colloids—as well as humin acids—partly disturb the fluorimetric analyses. Contaminated groundwater generally has a higher content of salt. In addition to an increased content of sodium chloride, lithium and strontium also show high values.

Sometimes pretests can replace tracing experiments or reduce their range. Parameters relevant to Altlasten, which are neither very much confined by sorption nor by ionic exchange, have shown excellent promise for areas of a risk assessment (Käss 1992).

It is not possible to give recipes for the selection of tracers and for the amounts applied. There are, of course, numerous formulas for the calculation of amounts of application in literature but some instructions are contradictory. The disposition of the amounts of application as well as the selection of the tracers should be left to experts. The plan for collecting samples should be made by an expert, too. As with all tracing tests, people responsible for sample collection have to be timely and locally organized so that waterways can be detected that are surprisingly rapid and far-reaching. There is no guarantee against surprises in the course of performing a tracing test; therefore, observation points with an improbable appearance of tracers should not be disregarded.

Not all tracers are equally applicable in the different groundwater aquifers. Table 5 summarizes this applicability and the restrictions for the three types of groundwater aquifers.

The analyst has to be provided with small amounts of all applied tracers to calibrate the analytical apparatus and check impurities.

Permission for performing the planned tracing test should be obtained from the appropriate authorities.

Table 5. Criteria for groundwater tracing tests

Type of aquifer	Criteria
Karst	All tracers are applicable without restriction
Fissure	Water-soluble tracers mostly, drifting particles restrictively applicable
Porous	Nonreactive water-soluble tracers applicable, drifting particles, except spores, for short distances

Examples of tracing tests at Altlasten

Three examples of tracing tests at Altlasten are described.

Gasoline spill in Öhringen

In a small town in southwest Germany the water supply had to be changed because of the infiltration of benzine hydrocarbon into the supply well. The ground surrounding the abandoned supply well consists (from top to bottom) of loess loam and loess, Lettenkeuper with dolomite layers, and Muschelkalk (Fig. 3).

After the spill had become known, all gasoline storage in the vicinity of the supply well were tested for leaks and contamination underground. It was surprising that all of the storage had losses of gasoline (Fig. 4). Test drilling located gasoline polluted ground at storage "53 m^3" 250 m SE of the well. All tests indicated that over several years about 50 m^3 gasoline had got into the ground from the storage via a fault in the Muschelkalk into the well. More than 10 m^3 gasoline and water-soluble hydrocarbons have been discharged from the well over 14 years. During remediation, a tracing test was performed in which tracer was detected in the well after the second day of the test (Fig. 5). The proof of the connection between the storage and the well was evidenced by the quick reappearence of the tracer.

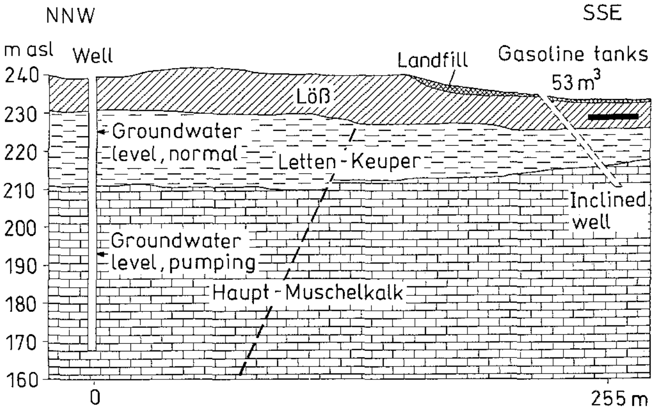

Fig. 3. Geological profile for the water supply well in the town of Öhringen (see Fig. 4)

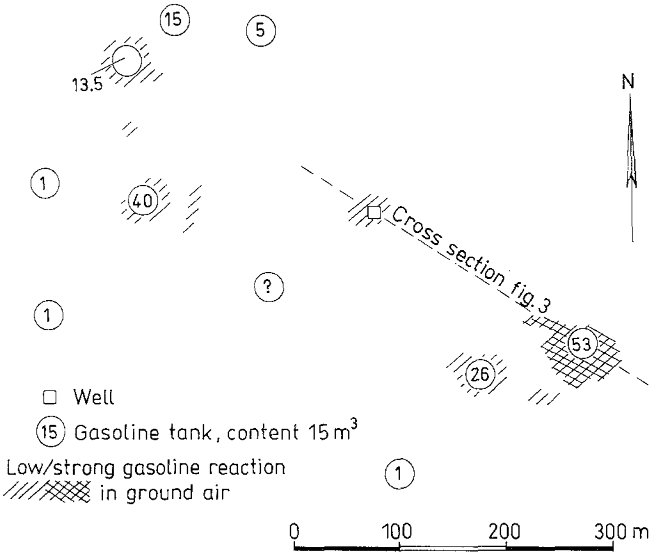

Fig. 4. Gasoline storage in the surroundings of the water supply well of the town Öhringen. The numbers indicate the storage volume in cubic meters

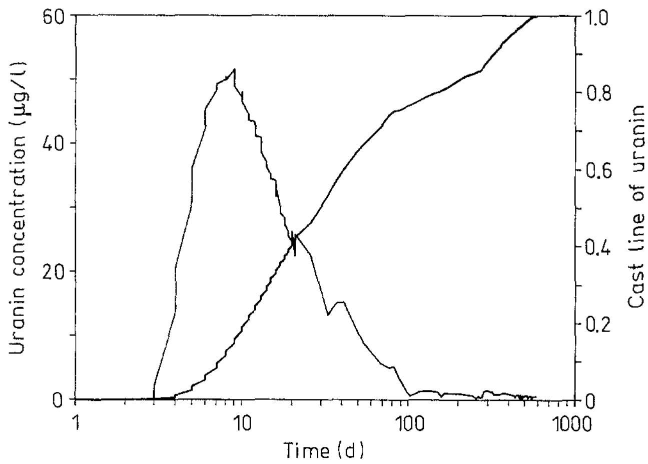

Fig. 5. Breakthrough curve and cast line of the tracing test between tank "53 m³" and the water well Öhringen. (Fig. 4). The x axis is logarithmic

Spill with chlorinated hydrocarbons—restoration with vacuum vaporizor well (UVB)

A strong contamination containing chlorinated hydrocarbons was discovered in groundwater down-gradient of a factory in a pre-Alpine river valley (Fig. 6). Several vacuum vaporizor wells (UVB) were installed for the restoration. Ten paired piezometers were installed next to one of these wells to show the result of the circulation of the UVB by means of tracing tests. The subsurface consists of gravel and sand, 4.6 m thick, covered by layers of loamy–peaty overburden 1 m thick. The aquitard is formed by molasse marls (Fig. 7). The first tracing test was performed with imperfect separation of the two UVB filter lines. After hydraulically separating the two filter lines by a separation plate, the second tracing test was started. The results of the

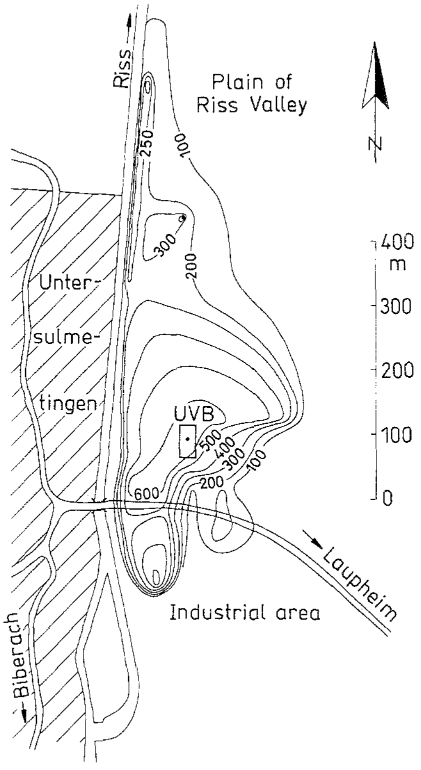

Fig. 6. Underground contamination in a pre-Alpine valley. Extension of the chlorinated hydrocarbons during the time of the test. UVB: location of the remediation well with the described groundwater tracing

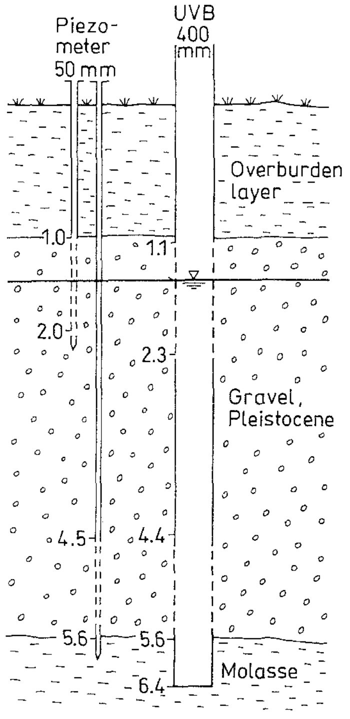

Fig. 7. Geological cross-section for the UVB site (see Fig. 6). Technical situation of the well and the piezometers nearby

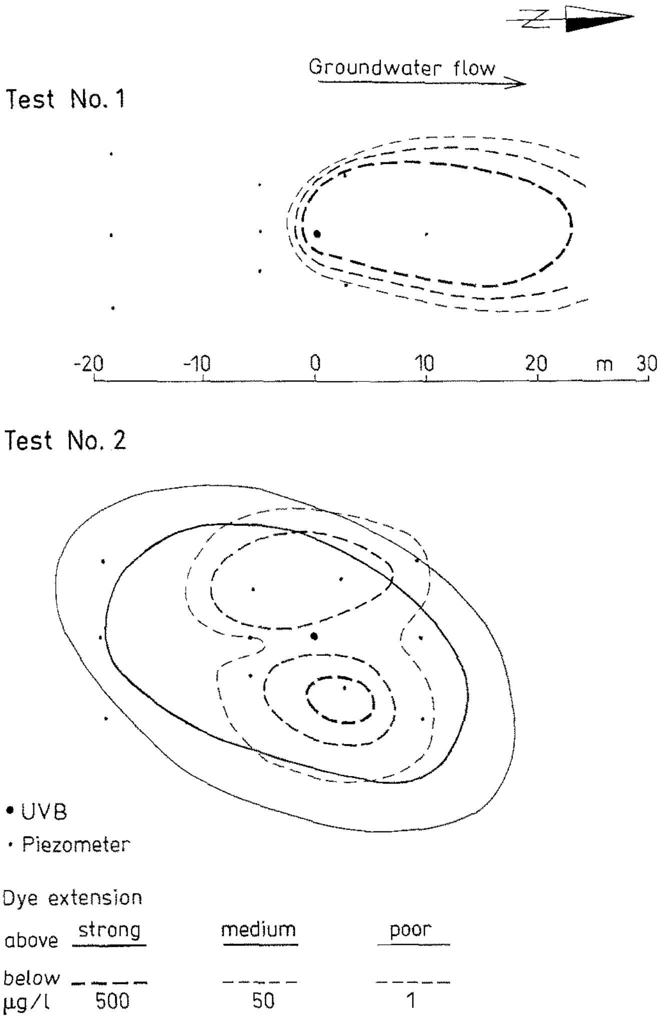

Fig. 8. Extension of the dye after 32 h for both experiments in the UVB. Above: The two filter lines in the well are not completely separated, therefore the dye only drained into the deeper horizon. Below: With the complete separation of the filter lines, the water tracing proves a far-reaching circulation. Irregular isolines indicate inhomogenities in the lower horizon

tracing tests definitely show that with the exact separation of the filter line an effective circulation can be reached in the surroundings of the UVB (Käss and Strayle 1990). The migration of the dye during both tests after 32 h is shown in Fig. 8.

Fourfold tracing test in pore groundwater in a site contaminated with hydrocarbons

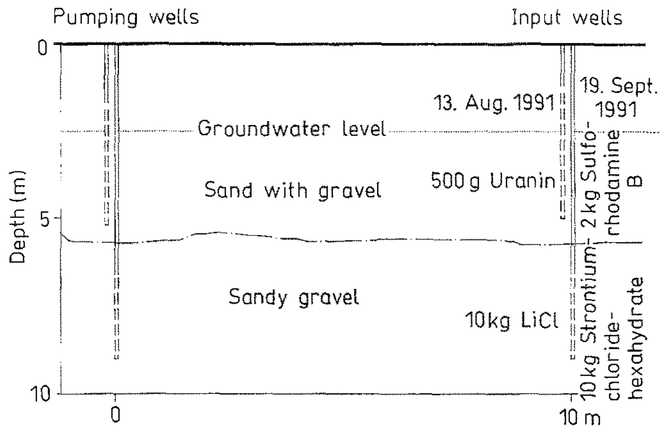

Fig. 9. Longitudinal section through the test site of an underground contaminated with mineral oil and oil products where a combined experiment with four tracers was carried out. On the first test day there were injected above: 500 g uranin, below: 10 kg LiCl; on the 38th testing day above: 2 kg sulforhodamine B, below: 10 kg strontium chloride hexahydrate. The breakthrough curves in the pumping well are shown in Fig. 10

The subsurface under a refinery in the Upper Rhine Valley was strongly polluted with mineral oil and products of mineral oil. The local aquifer consists of fine sands at the top increasing to coarse-grained materials with depth. The restoration plan provided for a groundwater remediation at two different depths. In the restoration well and in the measuring wells two filter lines, which are separated from each other, were set as manifold piezometers (Fig. 9). The two injection points at the paired measuring wells, 15 m from the test well, were treated with four different tracers; on the first day during the experiment the upper filter line was pumped and 38 days later the lower filter line was pumped:

	above	below
Test day 1	0.5 kg uranin	10 kg lithium chloride
Test day 38	2 kg sulforhodamine B	10 kg strontium chloride hexahydrate

The injections were done within a few minutes in each case with about half-concentrated solutions. Due to the fineness of the gravel in the level of the upper filter lines, the outflow rate was only a few liters per minute. The water samples to be tested for the tracers were partly polluted with dark mineral oil. At the end of the first test series uranin appeared in visible concentration; a lithium in-

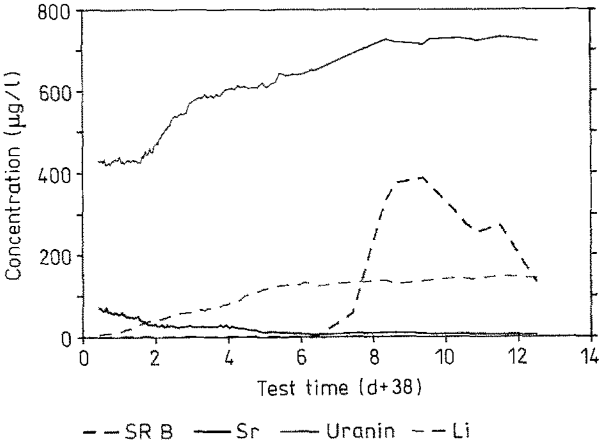

Fig. 10. Breakthrough curves of uranin, lithium, sulforhodamine B, and strontium analyzed in only one water sample

crease above background was not registered. From the 38th test day the lower filter line of the test well was pumped with about 1 m^3/h. At the same time the tracers sulforhodamine B and strontium chloride were injected into the same injection points as in the first test phase. In the second test phase, all four injected tracers appeared in the pumping well (Fig. 10). The presence of uranin that had been injected 38 days prior into the upper horizon is remarkable. Moreover, sulforhodamine B from the upper horizon of the second test phase appeared in the lower horizon of the pumping well one week after injection. The cations lithium and strontium showed a significant increase above background of about 3 μg/l Li and 430 μg/l Sr, respectively. The first increase of strontium occurred 1.5 days after the injection.

It could be shown by this test that despite pollution of the samples, four tracers can be analyzed in one water sample quantitively and totally independently of each other.

References

Knop A (1878) Über die hydrographischen Beziehungen zwischen der Donau und der Aachquelle im badischen Oberlande: N. Jb. Mineral (1878), pp 350–363

Käss W (1992) Geohydrologische Markierungstechnik, Band 9 des Lehrbuchs der Hydrogeologie, 529 p., Berlin: Gebr. Borntraeger Verlag

Käss W and Strayle G (1990) UVB-Verfahren aus der Sicht des Anwenders – Ergebnisse von Markierversuchen, In: Bock P, Hötzl H, Nahold M (Eds), Untergrundsanierung mittels Bodenluftabsaugung und In-Situ-Strippen, Karlsruhe: Schr. Angew. Geol. vol. 9, pp 291–304