Published in Environmental Geology, 43, issue 8, 922-929, 2003
which should be used for any reference to this work

Combined tracer tests in the karst aquifer of the artesian mineral springs of Stuttgart, Germany

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Abstract Chlorinated solvents have been detected at low concentrations in some of the mineral and medicinal springs (spas) of Stuttgart since 1984. These springs discharge from a confined karst aquifer. In order to investigate both the properties of the aquifer and the mechanisms of contaminant transport, two multi-tracer tests were carried out in 1998 and 1999. Both fluorescent tracers (naphthionate, eosin, pyranine) and particle tracers (clubmoss spores, microspheres) were used. All available wells and springs were sampled for at least 12 months. In these experiments naphthionate produced the best results. Maximum flow velocities were established to be within the range of 53 and 230 m/day. The breakthrough curves demonstrated a heterogeneous aquifer. The results identified flow to the springs from the west and south-west. It was possible to prove an assumed boundary between the northern zone of low mineralised water and the southern zone of highly mineralised water.

Keywords Artesian mineral springs · Combined tracer tests · Karst aquifer · Spas · Stuttgart (Baden-Württemberg, Germany)

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Introduction

The spas in the city of Stuttgart, in south-west Germany, represent the second largest mineral water system in Europe after Budapest (Fig. 1). The spas are located in the valley floor of the River Neckar and discharge from karstified Upper Muschelkalk limestone. The spas in the southern part of the area are more highly mineralised than those in the north. Construction works into the confining layers of the aquifer and the presence of historic contamination by hazardous substances represent a risk to the integrity of the water quality. Within the central part of the system – the Stuttgart basin and the city centre – there are numerous contaminated sites, located on the overlying fractured Keuper rocks, which are thought to be the source of groundwater contamination with chlorinated solvents. Vertical interaction with the underlying Muschelkalk karst aquifer, which discharges at the mineral water springs at Stuttgart, was established. However, it has not yet been possible to identify and delineate particular areas of contaminant inflow. Water quality data demonstrate that the low mineralised springs have been contaminated since 1984, whilst only minor traces of chlorinated solvents have been identified since 1991 in the highly mineralised springs.

In order to obtain a better understanding of the mineral water system of Stuttgart, a comprehensive hydrogeological research programme was set up in 1989 (Ufrecht 1998a). Within this framework, tracer tests have been planned and were carried out in 1998 and 1999 (Goldscheider and others 2001c; Kottke 2000). These experiments were aimed at assessing the risk of additional highly mineralised springs showing some degree of contamination, and on verifying the modelled properties of groundwater flow and contaminant transport within the aquifer.

The complex hydrogeological setting of the test area (confined aquifer with artesian outflow, highly mineralised water rich in carbonic acid, as well as vertical interaction with under- and overlying groundwater bodies) demanded detailed design and planning of sophisticated tracer tests. Data on tracer tests undertaken in comparable conditions were not available. The highly mineralised water is used for medicinal purposes and is also the source of water for three spas, while the low mineralised water is used to supply water for stock watering at the zoo. As a result, the selection of appropriate tracers and the determination of the optimum injection masses was crucial. Strict toxicological and ecotoxicological criteria were applied (Behrens

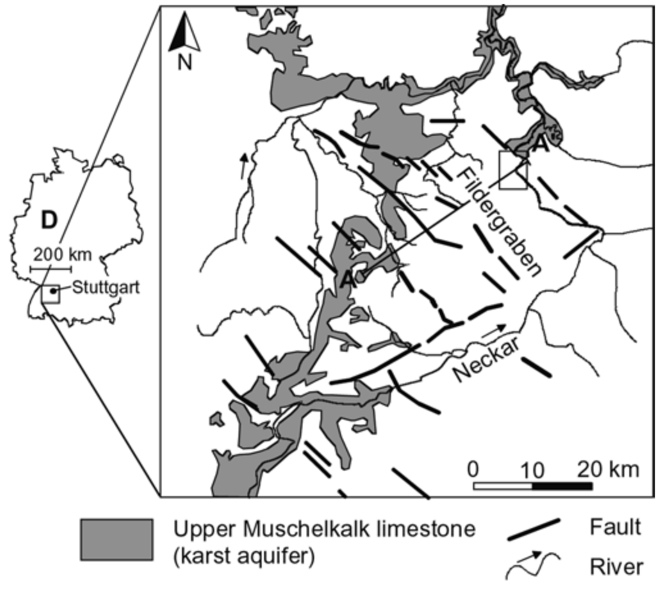


Fig. 1
Location and geology of the study area with location of the profile *A–A′* in Fig. 2 and the map in Fig. 3

and others 2001) and any risk of colouring had to be avoided. Due to the high flow rates in the karst aquifer and the large distances between the injection points and the springs, a significant dilution was expected and up to 155 kg of fluorescent tracer was used for each injection.

Geological and hydrogeological framework

The city of Stuttgart is located on the downthrown block of a NW–SE-striking graben, the Fildergraben, where the karst and mineral water aquifer of the Upper Muschelkalk limestone is completely confined by claystones, dolomites, evaporites and sandstones of the Keuper and, further to the south, by claystones and sandstones of the Lower Jurassic (Figs. 1 and 2). Only in the Neckar valley near Bad Canstatt (basin of Bad Canstatt) and in the side valleys (Nesenbachtal, basin of Stuttgart), is a large part of the Keuper rocks eroded, so that a residual thickness of locally less than 60 m remain. The formation of the valleys and basins is influenced by a zone of faults and fractures, which run oblique or perpendicular to the eastern main boundary fault of the graben. Dating of sinter proved that the fractures have allowed the artesian mineral water to rise up into the alluvial gravel of the Neckar valley floor or into the river itself since the Pleistocene.

Specific attempts to develop the mineral water resource started in the beginning of the 19th century. For many years, the mineral water has been used for medicinal purposes as well as supplying water to three spas. The total discharge rate of the system is around 500 l/s (Armbruster and others 1998). There are 20 abstraction points in the Upper Muschelkalk and Lower Keuper formations (Fig. 3); 12 in the southern and eastern part of the Neckar valley are ‘state-certified medicinal springs’ with a total discharge of

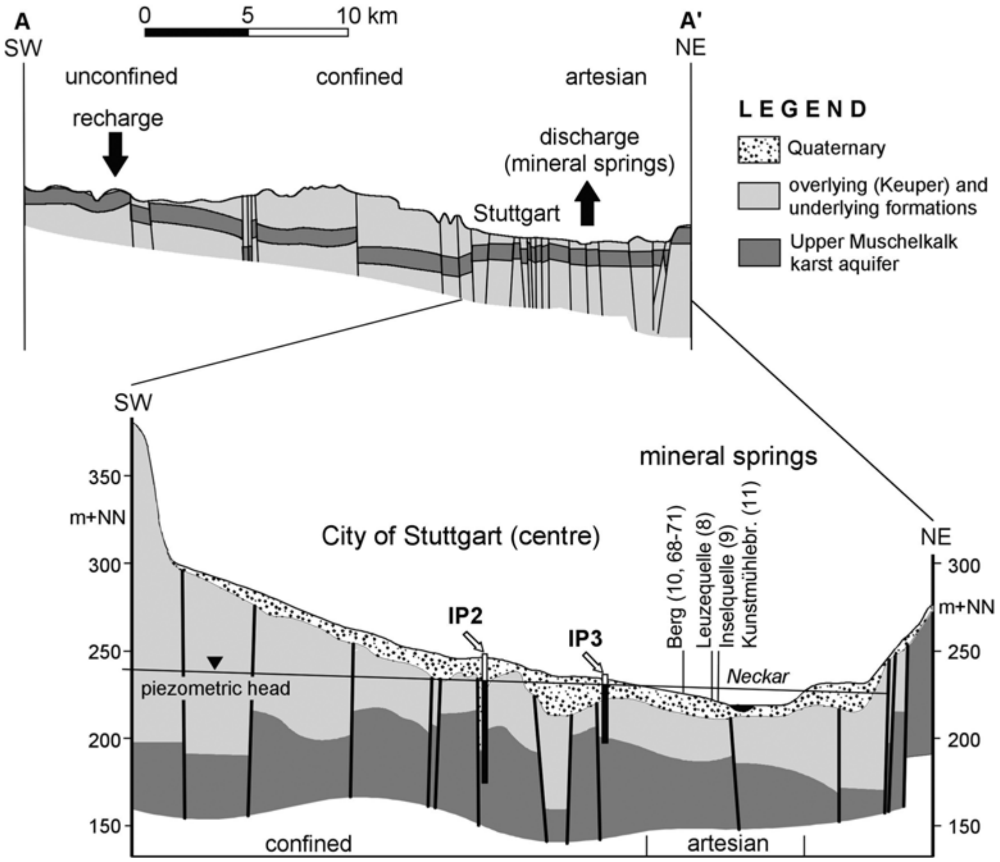


Fig. 2
Hydrogeological section of the mineral water resource of Stuttgart from the recharge area to the springs (location see Fig. 1) and detailed section of the area of study with location of the injection points IP2 and IP3

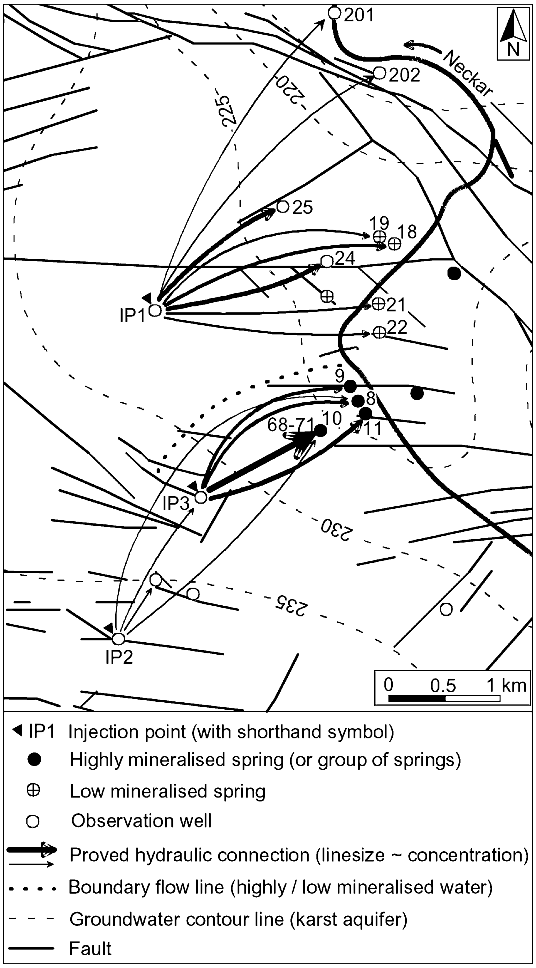


Fig. 3
Arrangement and results of the tracer tests of 1998 and 1999

165 l/s. The 'highly mineralised' water of these spas is rich in sodium, calcium, chloride, sulphate, bicarbonate, and carbonic acid (3,000–7,000 mg/l of dissolved solids, 1,300–2,400 mg/l CO_2). The 'low mineralised' water in the northern and north-western part of the area is a calcium-(magnesium)-sulphate–bicarbonate mineral water (500–1,600 mg/l of dissolved solids) with less than 250 mg/l of CO_2. The greater proportion of the mineral water originates from the Upper Muschelkalk karst aquifer, while the geochemical quality originates from mixing with saline waters from underlying formations. These processes start down hydraulic gradient from the centre of the Stuttgart basin. The origin and genesis of the mineral water is discussed in detail by Graf and others (1994), Plümacher (1999) and Plümacher and Ufrecht (2000).

The combined tracer test of 1998

Aim and arrangement

Two observation wells in the karst aquifer were selected as injection points (Fig. 3): IP1 is situated in the conceptual catchment of the low mineralised springs in the northern part of the city; IP2 is located further towards the south, next to the old castle in the city centre, in the conceptual catchment of the highly mineralised springs. One soluble and one particle tracer were injected in each of the two injection points in order to compare the behaviour of soluble and particle tracers and to reduce the risk of a negative result if one tracer failed.

The fluorescent dyes sodium-naphthionate (short: naphthionate) and eosin were selected as soluble tracers. Naphthionate is an UV-fluorescent dye and thus invisible in water in concentrations less than 1,000 mg/l – a major consideration for use in the catchment of these spas. However, the detection limit of about 0.1 μg/l is significantly higher than for most other fluorescent dyes (e.g. uranine: 0.005 μg/l), and so the required injection mass is correspondingly higher. Eosin was selected because it is less prone to sorption in slightly acidic CO_2-rich mineral water than uranine. The detection limit is 0.06 μg/l. As eosin causes reddish colouring in concentrations higher than 60 μg/l, only a very small (too small) injection mass was allowed for this experiment. Fluorescent microspheres (1 μm diameter) and clubmoss spores of *Lycopodium clavatum* (30 μm), dyed with fluorescent acridine orange, were selected as particle tracers. Clubmoss spores are not visible in the water and have often been successfully used in karst groundwater (e.g. Bauer 1967; Käss and Reichert 1988), but not in a mineral water source from a confined aquifer.

The tracers were introduced into the aquifer on the 23 July 1998. Masses of 150 kg of naphthionate and 5 kg of clubmoss spores – approximately 0.6×10^{12} particles – were injected in IP1. The tracer substances were prepared in a water tank of 2 m^3 and injected into the well via a flexible tube, 5 m^3 of water was used for flushing before and after the injection. Eosin (2 kg), dissolved in 10 l of water, and 30 ml of microspheres – about 1.7×10^{12} particles – were injected via a flexible tube into the observation well IP2, and 2 m^3 of water was used for flushing. In order to detect a possible tracer breakthrough, water samples, stored in brown glass bottles of 50 and 1,000 ml, were taken and/or spore nets were installed at a total of 23 observation wells and mineral springs. The 50-ml water samples were analysed for the fluorescent dyes in the laboratory of the Department of Applied Geology in Karlsruhe (AGK). W. Käss performed the analyses for particle tracers in his private laboratory. The 1,000-ml water samples were filtered in order to obtain the microspheres, while the spore nets were checked for accumulated clubmoss spores. Both particle tracers were then determined by counting them under a fluorescence microscope.

Results

Fifteen days after the injection, naphthionate was detected in two observation wells, nos. 24 and 25, which are located 1.6 and 1.7 km downstream from the injection point IP1. After 32–39 days, the breakthrough started in four of the low mineralised springs (nos. 18, 19, 21, 22) at a distance of 2.1–2.3 km east of IP1 (Fig. 4). The maximum concentration occurred 32–67 days after the injection. Thus, the maximum flow velocities (calculated from the time of first appearance) are 53–104 m/day, whereas the dominant

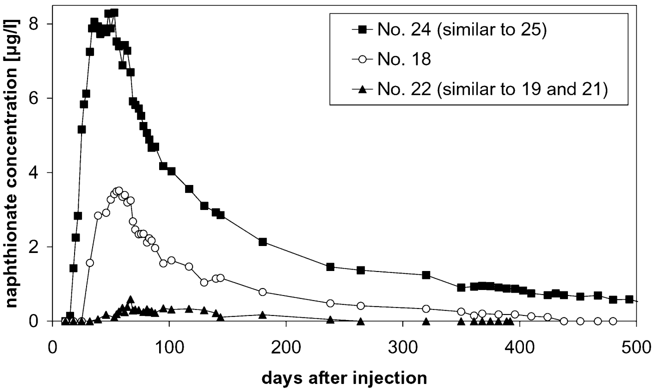


Fig. 4
Selected breakthrough curves of the tracer test in the zone of low mineralised water

velocities (calculated from the time of maximum concentration) are 31–49 m/day. The surprisingly low recovered mass of tracer from the above mentioned sampling points, of only 0.81 %, may be as a result of the following:

- Some of the breakthrough curves were not complete at the end of the observation period and high concentrations of naphthionate were still being detected in the injection well. Thus, it would appear that a significant portion of this tracer remained close to the injection point, indicating that it was only poorly connected with active flow paths within the aquifer.
- A portion of the tracer failed to reach the low mineralised springs that were being monitored (total discharge rate: 81 l/s), but was discharged by bottom springs (total discharge rate: 200 l/s) directly into the River Neckar and sediments on the valley floor, which were not being monitored.
- A proportion of the tracer travelled in a north-east direction towards wells 201 and 202, where traces of naphthionate have been detected, which merely allowed a half-quantitative evaluation.

The sampling points 201 and 202 are located on the eastern upthrown block of the Fildergraben. The fluorescence analysis of naphthionate in these samples was disturbed by abnormally high background fluorescence due to colloidal iron hydroxides and/or organic water constituents. However, at between 20 and 100 days post-injection, an increase in the UV-fluorescence of the membrane filtrates was observed, indicating the presence of traces of naphthionate in these two wells, which is consistent with the underground drainage pattern in terms of direction, flow velocity and concentration.

Only a single clubmoss spore, of the 600 billions that had been injected in the same well as the naphthionate, was recovered in observation well no. 25.

The eosin injected into IP2, in the city centre, was detected in only one sample from the western spring of the mineral bath Berg (no. 71) at very low concentrations. The failure of eosin detection is probably a consequence of the very low tracer mass that was allowed in order to avoid any risk of colouring of the mineral and medicinal springs.

Only 14 of the 1.7×10^{12} of microspheres were recovered in four observation wells and two mineral springs in the area of highly mineralised water. These were obtained along a conceptual flow line from the injection point via the Berg springs towards the Leuze spring near the River Neckar. Flow velocities calculated from first arrival range between 7 and 61 m/h. The low number of recovered particles makes further evaluations impossible.

The combined tracer test of 1999

Aim and arrangement

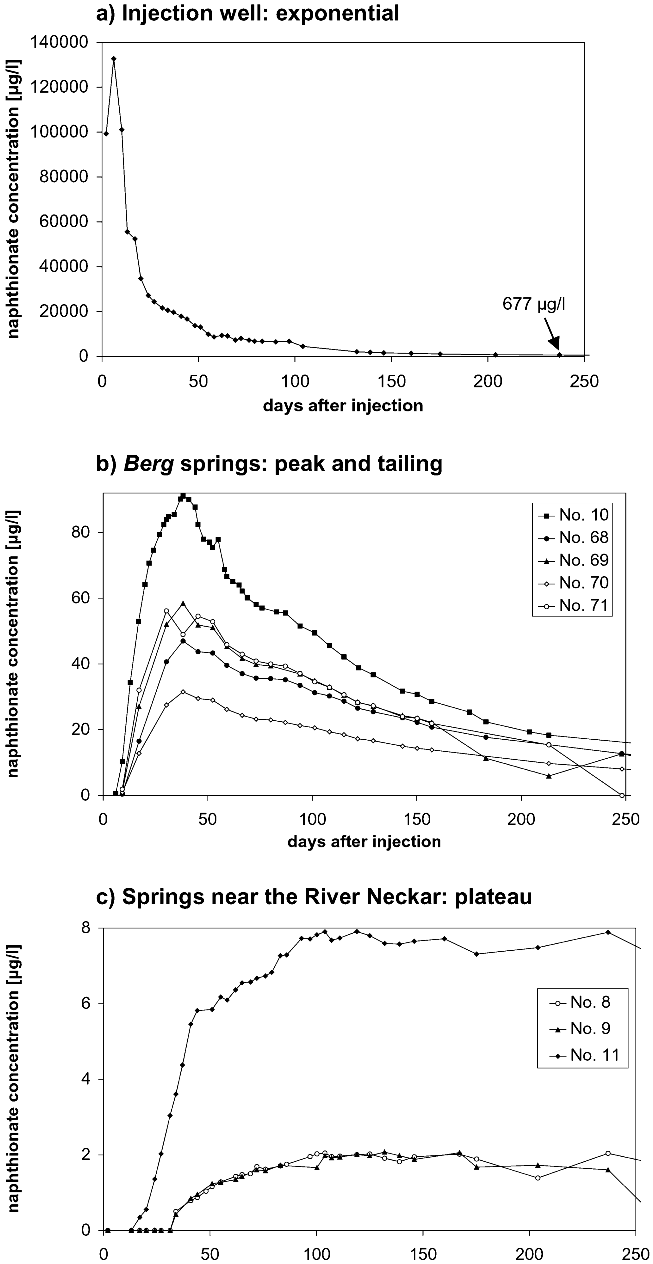
In order to obtain better information about the zone of highly mineralised water, a second combined tracer test was performed in 1999. The injection point, IP2 used in the 1998 tests, was again used to introduce tracer. Additionally, an observation well closer to the River Neckar and the mineral springs was selected as an injection point and was named IP3 (Fig. 3). Both points are located along a conjectural flow line that discharges at the highly mineralised springs.

As a result of the poor performance of the particle tracers in the 1998 tests only soluble fluorescent dyes were used. Naphthionate was once again selected because of its invisibility and the good performance in 1998. Due to the large spatial and temporal distance between the naphthionate injections in 1998 and 1999, the risk of interference and disturbance was considered to be negligible. The green fluorescent dye pyranine was selected as a second tracer because it was considered to behave conservatively and to be less prone to sorption in these slightly acid waters (Käss 1998). Assuming that the dilutions in the zones of highly and low mineralised springs were in the same order of magnitude, the results obtained with naphthionate in 1998 were used to estimate the appropriate injection mass for pyranine so that the expected maximum concentrations at the springs would range between the limits of detection (0.06 µg/l) and visibility (about 60 µg/l).

The injections were performed at the 6 July 1999, 140 kg of pyranine was injected in IP2 and 155 kg of naphthionate in IP3. The tracers were dissolved in tanks of each 2 m^3 and injected via flexible tubes directly into the screened section of the observation wells. After the injections, 40 m^3 of flushing water were pumped in IP2 and 22 m^3 in IP3 in order to make sure that the tracer was displaced out of the wells towards the active conduits in the karst aquifer. Water samples for fluorescence analyses were taken at 23 wells and springs. Later on, charcoal bags were also used within the long-term monitoring programme in order to detect small traces of pyranine in concentrations below the detection limit in the water samples.

Results

Naphthionate was detected in eight of the highly mineralised springs west of the River Neckar, but in none of the low mineralised springs or other sampling points east of the river (Figs. 3 and 5). The tracer was first detected after 6–9 days in the five springs that make up the source for the Berg mineral bath (nos. 10, 68–71). Breakthrough of



a) Injection well: exponential

b) *Berg* springs: peak and tailing

c) Springs near the River Neckar: plateau

Fig. 5
Synopsis of the results obtained with naphthionate in the zone of highly mineralised water

tracer also occurred in springs near the River Neckar – after 17 days (no. 11), and after 34 days in the two springs that make up the source for the Leuze mineral bath (nos. 8 and 9).

The breakthrough curves of the Berg spas show a clear peak whereas the curves of the springs close to the river reach a plateau after about 100 days (see Conclusions). There are notable differences in concentration between neighbouring springs, although their breakthrough curves show an almost identical shape.

The maximum flow velocities calculated from the breakthrough curves of the Berg spas range between 153 and 230 m/day, while the dominant flow velocity is 36 m/day for all five curves (identical time to maximum concentration). As the curves of the springs near the River Neckar show no clear concentration-peak, it is not possible to calculate the dominant flow velocity. The maximum flow velocity, calculated from the time of first detection, is 54–55 m/day for the springs of the Leuze mineral bath and 105 m/day for spring no. 11.

The total recovery rate of naphthionate for this experiment is 29 % (44.9 kg), and is significantly higher than for the tracer test in the zone of low mineralised water in 1998. At the end of the 1-year observation period, none of the breakthrough curves were completely finished – this may take several more months. As a result, the recovery rate will continue to increase without being monitored. Another significant portion of the tracer is thought to have been discharged into the River Neckar through its bed in discrete locations without being sampled and analysed for the tracer. The total discharge rate through the riverbed in the zone of highly mineralised water is around 80 l/s (Armbruster and others 1998).

None of the 140 kg of pyranine injected into IP2 was ever detected, even though all springs and wells were observed for 307 days with both water samples and charcoal bags. This represents a very large loss of fluorescent tracer. A poor connection of the injection well with the aquifer can be excluded as a reason for failure because a large amount of flushing water (22 m^3) was used in order to make sure that the tracer was displaced out of the well and reached active flowpaths within the aquifer. Further indicators for good hydraulic connection of the well with the aquifer are pumping tests, tracing with microspheres in 1998 and the identical isotopic pattern of the water from the injection well and groundwater from the aquifer. As flow velocity in the aquifer is known from the other tracer tests, an inappropriate monitoring period and sampling interval can also be discounted as reasons for failure. Pyranine is a nonsorptive tracer and the injected tracer mass was sufficiently high, so that sorption and high dilution can also be excluded. The arrangement of sampling points within the flow field was designed to minimise the risk of tracer passing the sampling points. However, there are no appropriate observation wells east and north of IP2 and so it may be possible that a part of the tracer cloud flew in a northern or eastern direction without being monitored. The most likely explanation for the loss of pyranine is fast and complete microbial degradation in the aquifer – a phenomenon that is occasionally observed in karst groundwater (for a discussion and examples see the Conclusions).

Conclusions

Suitability and properties of the tracers

The success of the two combined tracer tests in the catchment of the mineral and medicinal springs of Stuttgart is mainly based on the results obtained with naphthionate. In order to maintain the integrity of the spas, this UV-fluorescent dye was selected as a tracer because it is invisible in the water and is not harmful. However, as these were the first tracer tests in the area, it was difficult to determine the optimum injection masses. Due to potentially high dilution in the aquifer and to minimise the risk of failure, large quantities were used, up to 155 kg. However, the analyses and storage of naphthionate samples is more problematic than for most other fluorescent dyes. In two sampling points (201, 202), high levels of colloidal iron hydroxide and/or organic water constituents disturbed the fluorescence analyses. Furthermore, degradation of naphthionate was observed in water samples from some of the spas. However, detailed laboratory experiments and the evaluation of breakthrough curves proved that degradation did not occur in the aquifer, but starts in the brown glass bottles after sampling. Microbes may degrade naphthionate in water samples within approximately 2 weeks. Thus, all further samples were cooled to 5 °C and analysed within 1–4 days of sampling (Kottke 2000; Goldscheider and others 2001a).

The disappearance of pyranine, which is notable in view of the large injection mass and the long observation period, may be a consequence of fast and complete microbial degradation in the aquifer. Microbiological degradation was proven for several fluorescent dyes, e.g. for naphthionate (see above), uranine and pyranine (Sayer 1991; Nahold 1996; Käss 1998). Within a recent comparative tracer test in an Alpine karst system, pyranine also failed, while six other tracers reached the monitoring points (Goldscheider and others 2001b). The failure of eosin in the 1998 experiment is probably a consequence of the too low injected tracer mass rather than its chemical properties. Clubmoss spores have often successfully been applied in Alpine karst systems, but failed in the 1998 tracer test in Stuttgart. Under the non-turbulent flow regime of this confined aquifer, particles are obviously retained effectively by sedimentation, filtration and possibly adsorption at biofilms. Additionally, the sampling was often hampered by precipitation of iron hydroxides, which blocked the spore nets and rendered them ineffective.

Of the three different tracers that were injected in IP2, the best results were obtained with microspheres. However, only 14 of the 1.7×10^{12} particles were recovered, supporting the observation of ineffective particle transport in the aquifer.

Groundwater flow and contaminant transport in the aquifer

The combined tracer tests of 1998 and 1999 increase the understanding of groundwater flow and contaminant transport in the vicinity of the mineral and medicinal springs. As the number of observation wells in the study area were limited, the groundwater contour lines are uncertain and the definition between the zone of low and high mineralised water has been historically problematic. The tracer tests help to close these gaps of knowledge and refine our conceptual hydrogeological model of the springs. While earlier conceptual hydrogeological models suggested that the catchment of the low mineralised springs to be located NW of the springs, the tracer tests (injection point IP1) have proven inflow from W to SW direction. These results are consistent with the conclusions drawn from hydrochemical and isotope studies (Ufrecht 1998b; Plümacher 1999; Plümacher and Ufrecht 2000).

The naphthionate that was injected in IP3 in the central to south-eastern part of the basin was only detected in the highly mineralised springs; this was supported by data using the microspheres tracer, as these were also only detected in the zone of highly mineralised water. Putting together the results of the tracer tests in 1998 and 1999, it is possible to define a conjectural boundary between the zone of the low and the highly mineralised springs (Fig. 3). The two catchments are clearly separated from each other and do not overlap. In the catchment of the highly mineralised springs west of the River Neckar (nos. 8–11, 68–71), the dominant groundwater flow direction is towards the E to ENE. However, it is impossible to delimit the catchments of single springs, as the naphthionate reached all the springs. Significantly different maximum concentrations were detected in directly neighbouring springs. The highest values were measured in the spring nos. 11 (Kunstmühlebrunnen) and 10 (Berger Urquell).

The tracer tests with naphthionate allowed the quantification of apparent groundwater flow velocities (Table 1). In the northern zone of low mineralised water (tracer test 1998), maximum flow velocities of 53–112 m/day and dominant flow velocities of 31–48 m/day were observed. In the southern zone of highly mineralised water (tracer test 1999), the maximum velocities range between 54 and 230 m/day, while the dominant flow velocity is 36 m/day. For spring nos. 8, 9 and 11 it is not possible to determine dominant velocities, as the breakthrough curves show no clear maximum, but reach a plateau concentration. The flow velocities assessed on the basis of the first detection of microspheres range between only 7 and 61 m/day.

Numerous tracer tests have been undertaken over many years on outcrops of the Upper Muschelkalk limestone, 20 km west of Stuttgart. Flow velocities of up to 210 m/h (5,040 m/day) have been determined – significantly higher than in the area of the mineral springs. However, the degree of karstification is comparably high in both areas. The reason for the different velocities is the hydraulic gradient and the difference between an open, shallow karst aquifer and a confined, deep aquifer.

Only 0.81 % of the naphthionate used in the catchment of low mineralised springs in 1998 was recovered. A large portion of the karst groundwater in this area is obviously not drained by those mineral springs sampled as part of this tracer test. Groundwater contour lines indicate that one portion of the groundwater probably flows to the north-east and passes by well no. 25, which showed the highest concentrations during the whole monitoring period. Another portion probably reached springs that were not sampled as they discharge into the bed of the River Neckar. During the tracer test in 1999, 29% of the naphthionate was recovered in the highly mineralised springs. For the tracer tests with naphthionate, two types of breakthrough curves were distinguished (Figs. 4 and 5): curves with a clear concentration peak and a long tailing

Table 1
Overview of the results obtained with naphthionate in the zones of high and low mineralised water. The apparent opening angle was determined on the basis of the existing observation points; the true angle cannot be determined

	Tracer test 1998	Tracer test 1999
Injection point	IP1	IP3
Injected naphthionate mass	150 kg	155 kg
Sampling points with breakthrough curve	18, 19, 21, 22, 24, 25 (201, 202)	8, 9, 10, 11, 68, 69, 70, 71
Geochemical character of the test area	Low mineralised water	Highly mineralised water
Longest proved flowpath	3,340 m	1,860 m
Maximum effective velocity	53–112 m/day	54–230 m/day
Dominant effective velocity	31–49 m/day	36 m/day
Shape of the breakthrough curves	Peak with tailing (or irregular)	Peak with tailing or concentration plateau
Apparent opening angle of the tracer cloud	65°	6°
Range of maximum concentrations	0.25–10 μg/l	2–91 μg/l
Total discharge rate of sampled springs	81 l/s	129 l/s
Total discharge rate of bottom springs	300 l/s	80 l/s
Recovery rate	1,213 g (0.81%)	44,917 g (28.98%)

(nos. 10, 18, 24, 25, 68–71), and curves that reach a plateau concentration (nos. 8, 9, 11).

Even though a large amount of flushing water was used after the injections, a delayed displacement of the tracers from the injection wells was proved. Nevertheless, the shape of the breakthrough curves cannot only be explained by a delayed injection. Bäumle (2001) evaluated the breakthrough curves using newly developed analytical solutions of the 1-D transport equation. The DIRAC function for instantaneous tracer injection was replaced by exponential equations, which describe the slow decreasing of concentrations in the injection well. However, during the tracer test in 1999, the two different types of breakthrough curves were observed at the same time in adjacent springs. The curves for the Berg springs (nos. 10, 68–71), closer to the injection point, show peaks, whilst the curves of the springs near the Neckar (nos. 8, 9, 11) show plateau concentrations. Although the curves of the first type can be modelled taking into account the exponentially delayed injection mode, it was impossible to model the second type: a plateau-like breakthrough can only be modelled for a continuous injection, whereas in the present case the injection was carried out instantaneously however. A possible explanation for the observed plateau concentrations is significant storage of tracer in large cavities within the karst aquifer up hydraulic gradient from the springs near the Neckar and the subsequent slow release of the stored tracer into the aquifer.

Risk and protection of the mineral water resources of Stuttgart

As the spas are located in a city they are threatened by a wide range of human activities, which may affect both the quality and quantity (discharge rate) of the water. Chlorinated solvents, which were detected in the overlying Keuper aquifer, pose a significant risk to the resource. Both the confining layers and the artesian pressure close to the springs provide some natural protection. A high vulnerability has to be expected in zones where hydraulic connection and contaminant transfer is possible, i.e. in highly fractured zones, in areas where the hydraulic potential in the overlying Keuper aquifer is greater than within the karst aquifer and in zones where the confining layers are eroded or removed due to construction work. The tracer test proved that contaminants are transported rapidly (up to 230 m/day) over large distances (several km). One single contamination can reach several mineral springs. The breakthrough of the tracers – which were injected instantaneously – lasted more than 1 year. Consequently, a short-term pollution event in the city might cause a long-term impact on the quality of the spas. The low recovery of spores and microspheres proves that particle contaminants can be retained in the aquifer. The most probable explanation for the loss of pyranine is microbial degradation, which indicates an effective natural attenuation of at least some specific organic substances.

Acknowledgements The authors want to thank the city of Stuttgart for funding and technical support, Mr Roland Bäumle and Mrs Kerstin Kottke (Department of Applied Geology Karlsruhe) for the good co-operation and Mr Simon Neale, (Environmental Agency Wales) for valuable corrections and suggestions.

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