A new quantitative interpretation of the long-tail and plateau-like breakthrough curves from tracer tests in the artesian karst aquifer of Stuttgart, Germany

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Abstract In 1998 and 1999, two multi-tracer experiments were conducted in the artesian karst aquifer of the mineral springs of Stuttgart, Germany. The breakthrough curves (BTCs) monitored at the springs showed very long tails or developed plateau-like concentration levels for more than 200 days. Initially, this observation was qualitatively explained by exchange between cavities with stagnant water and the active conduits. Since then, a new analytical solution for tracer transport in karst aquifers has become available, the "two-region non-equilibrium model" (2RNE), which assumes the presence of mobile and immobile fluid regions, and mass transfer between these two regions. The experiments were thus revisited, and it was possible to provide a more quantitative explanation of the observed behaviour. The new model simulated all BTCs very well, thus confirming the earlier qualitative explanation. The prolonged BTCs can be attributed to intermediate storage in cavities containing quasi-immobile groundwater, and slow release into active fractures and conduits. The results also demonstrate that karst aquifers are not always fast-flushing systems, but contaminants can sometimes remain in immobile fluid regions for long periods.

Résumé En 1998 et 1999, deux tests avec des traçeurs multiples ont été effectués dans l'aquifère karstique des sources minérales de Stuttgart, Allemagne. Les courbes de restitution (BTCs) observées aux sources ont montré des niveaux de concentration à queue très étirée et à profil en plateau développées pendant plus de 200 jours. Initialement, cette observation a été expliquée qualitativement par un échange entre des cavités avec de l'eau stagnante et des conduits actifs. Depuis lors, une nouvelle solution analytique pour le transfert de traçeur dans un aquifère karstique est devenue disponible, le modèle hors équilibre à deux régions (2RNE), qui suppose la présence de régions à fluides mobiles et immobiles, et un transfert de masse entre ces deux régions. Les tests ont été réexaminés, et il a été possible de fournir une explication plus quantitative du comportement observé. Le nouveau modèle a très bien simulé tous les BTCs, confirmant ainsi l'explication qualitative antérieure. Les BTCs prolongées peuvent être attribuées à un stockage intermédiaire dans des cavités contenant de l'eau souterraine quasi immobile, et une restitution lente dans des fractures et des conduits actifs. Les résultats démontrent aussi que les aquifères karstiques ne sont pas toujours des systèmes à chasse rapide, mais les polluants peuvent parfois demeurer dans des zones de fluide immobile pendant de longues périodes.

Resumen En 1998 y 1999 se llevaron a cabo dos ensayos de trazadores múltiples en el acuífero cárstico artesiano que alimenta manantiales minerales de Stuttgart, Alemania. Las curvas de salida (CS) registradas en los manantiales mostraron colas muy largas o concentraciones en forma de meseta durante más de 200 días. Originalmente, esta observación fue cualitativamente interpretada por el intercambio entre cavidades con agua estancada y los conductos activos. Desde entonces, una nueva solución analítica para el transporte de trazadores en acuíferos cársticos ha sido desarrollada, el "modelo de no equilibrio de dos regiones" (MNE2R) que asume la presencia de dominios de flujo móviles e inmóviles, y transferencia de masas entre ambos. Los experimentos fueron reinterpretados y fue así posible arribar a explicaciones cuantitativas del comportamiento observado. El nuevo modelo simula adecuadamente todas las CS, y confirma la explicación cualitativa original. Las prolongadas colas de las CS pueden atribuirse a un almacenamiento temporario en cavidades que contienen agua casi inmóvil, y un lento desplazamiento hacia zonas de fracturas y conductos activos. Los resultados además muestran que los acuíferos cársticos no son siempre sistemas con flujos rápidos, sino que los contaminantes pueden a veces permanecer por largos períodos en regiones de aguas inmóviles.

Keywords Karst · Mineral water · Tracer tests · Analytical modelling · Germany

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Introduction

The baths of Stuttgart are supplied by Europe's second largest mineral water resource, after that of Budapest in Hungary. In both cases, the water springs from a karst aquifer located below a big city, which poses a potential threat to water quality. The Stuttgart mineral springs with a total discharge of 500 L/s are located in the Neckar River valley and emanate from a Middle Triassic limestone karst aquifer (Upper Muschelkalk). In the city area, the aquifer is confined by low permeability formations of the Upper Triassic (Keuper). The overlying layers and the artesian pressure in the aquifer provide some degree of protection against contamination. A peculiarity of the water lies in the high concentrations of CO_2 rising up from the Earth's mantle along deep faults (Ufrecht 2006). The springs can be subdivided into two groups (Fig. 1):

1. Low mineralised springs in the northern part of the area, 0.5–1.6 g/L of total dissolved solids (TDS), CO_2<250 mg/L, water temperature T=12–17°C
2. Highly mineralised, state-certified medicinal springs in the southern part of the area, used for cures and leisure baths, 3–7 g/L TDS, 1.3–2.4 g/L CO_2, T=17–21°C.

In order to obtain information about groundwater flow and potential contaminant transport in the aquifer, two large-scale multi-tracer tests were carried out in 1998 and 1999 (Goldscheider et al. 2003). Only the results of one tracer injection, which delivered the highest number of complete and relevant breakthrough curves (BTCs), are presented and reassessed here.

On 6 July 1999, 155 kg of sodium-naphthionate (CAS RN 130–13–2) were injected into an observation well in the zone of highly mineralised water. Naphthionate was selected as a tracer due to its favourable properties and invisibility at concentrations <1 g/L (Käss 1998). The tracer was injected quasi-instantaneously (within 3 h) into the screened part of the well. A large volume of flushing water (22 m^3) was subsequently introduced at a low pumping rate (0.3 L/s) in order to flush the tracer out of the well into the aquifer. The effectiveness of this

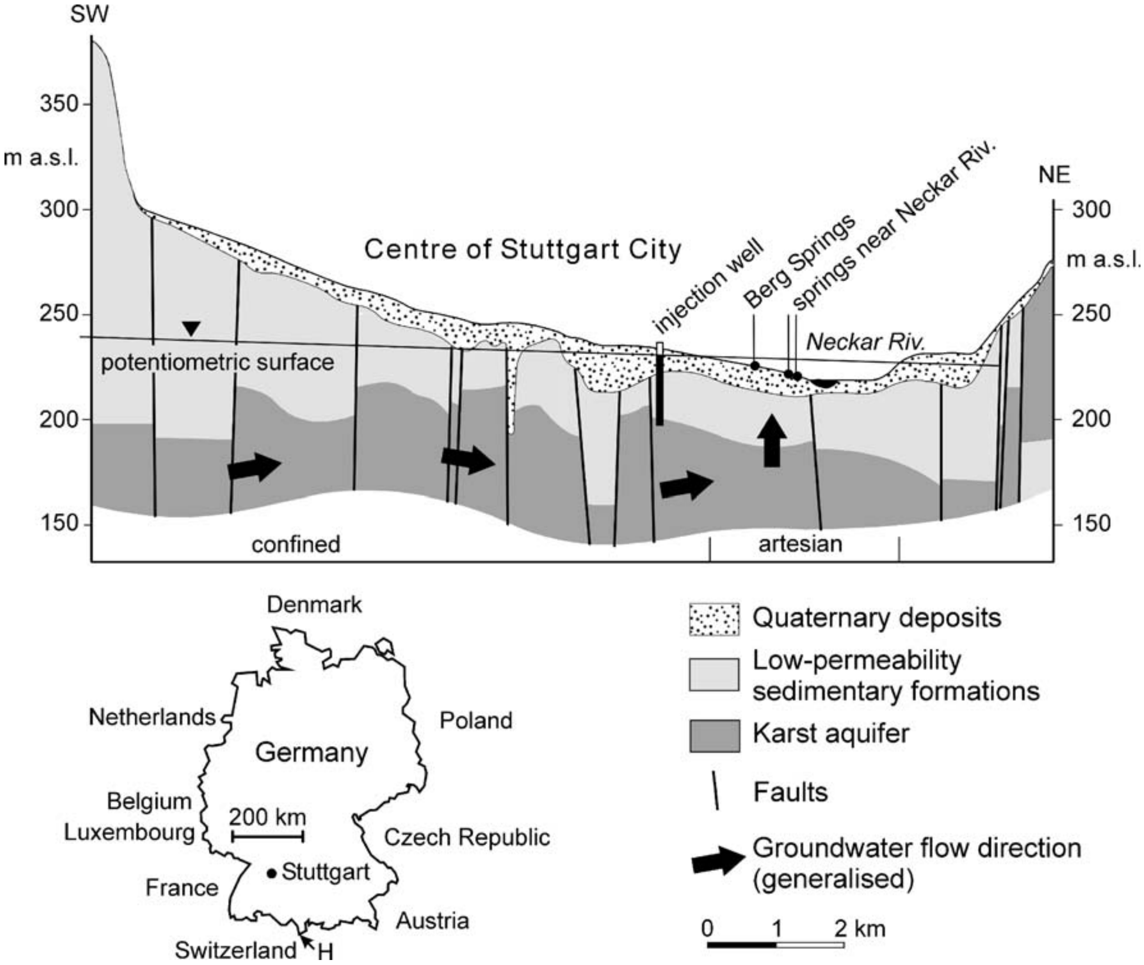

Fig. 1 Hydrogeological section of the artesian karst aquifer below the city of Stuttgart. The section cuts though the injection well and the two groups of mineral springs where the tracer breakthrough curves discussed in this article were observed. *Z-axis* strongly exaggerated (modified after Goldscheider et al. 2003). The location of the Hölloch cave (*H*) is also shown because data from there are presented for comparison

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technique was controlled by monitoring the concentration decline in the injection well.

Water samples for naphthionate were taken at 17 springs and wells and analysed in the laboratory of the Department of Applied Geology at Karlsruhe University, Germany, using a Perkin-Elmer LS 50 B spectrofluorometer. Samples were first taken twice per week and the intervals then increased to weekly and monthly. Sampling lasted 307 days; a total of 493 samples were taken (K. Kottke, University of Karlsruhe, unpublished data, 2000; Goldscheider et al. 2003).

The tracer reappeared at eight highly mineralised springs but none of the low mineralised springs. It was possible to determine the dominant flow velocities (36 m/day) and to better delimitate the zones of low and highly mineralised water. The results also showed that a single contamination release into the aquifer in the southern part of the area, the very city centre, could impact all medicinal springs west of the River Neckar.

The BTCs recorded at the five "Berg Springs" (Fig. 1), 1,380 m downgradient from the injection well, display a single peak after 38 days and long tails. The BTCs observed at three springs further downstream, near the Neckar River and 1,780–1,820 m away from the injection well, show a plateau-like shape as would be expected from a continuous tracer injection, i.e. the concentrations rise rapidly and then remain at a high and nearly constant level until about 300 days after the injection (200 days after the high concentration level was reached), when the sampling campaign was stopped.

Initially, the long tails and the plateau-like breakthrough curves were explained by "storage of tracer in large cavities within the karst aquifer up hydraulic gradient from the springs and the subsequent slow release of the stored tracer into the aquifer" (Goldscheider et al. 2003). However, it was not possible to provide a more quantitative interpretation, because available analytical solutions such as the conventional advection dispersion model (ADM, Kreft and Zuber 1978), failed to reproduce the BTCs. Imperfect injection conditions can also cause long tails (Brouyere et al. 2005), but in the present case, the slightly delayed tracer release from the injection well did not suffice to explain the observed behaviour (Bäumle 2001).

Recently, a new analytical model for solute transport in solution conduits in karst aquifers became available (Field and Pinsky 2000), which assumes partitioning of solute tracer into mobile and immobile fluid regions. Several groups have tested this model in several types of karst aquifers and found that it is capable of better simulating breakthrough curves than a conventional ADM, which often fails to reproduce the tails (Birk et al. 2005; Massei et al. 2006; Geyer et al. 2007; Göppert and Goldscheider 2008).

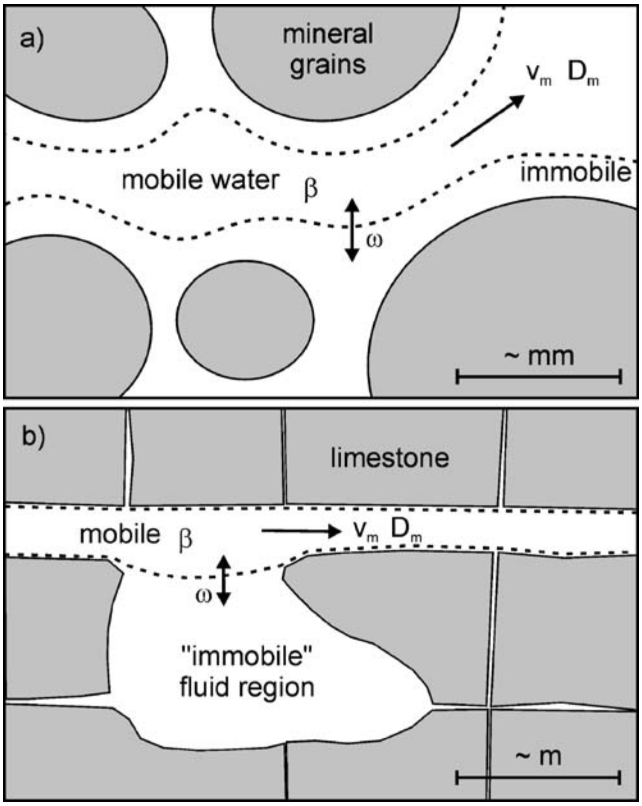

Fig. 2 **a** Illustration of the two-region non-equilibrium model on a pore scale, and **b** transfer of this model to the karst aquifer of Stuttgart, where intermediate tracer storage in more or less "immobile" water volumes is hypothesised. In the mobile fluid regions, the tracer is transported by advection (mobile fluid velocity, v_m) and dispersion (D_m). The partition coefficient β describes the proportion of mobile water; the mass transfer coefficient ω describes exchange between the two fluid regions

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However, plateau-like BTCs resulting from an instantaneous injection have never been observed or simulated.

The goals of this short report are (1) to provide a more quantitative analysis of the breakthrough curves with long tails and plateau-like shape obtained during the Stuttgart tracer tests in 1999; and (2) to gain further insight into the role of immobile fluid regions in karst aquifers and their possible role for contaminant transport.

Modelling approach

The two-region non-equilibrium model (2RNE; Toride et al. 1993) was initially developed for porous media, where partitioning of solutes between mobile water in the centres of the large pores and immobile water in fine pores or adsorbed to mineral surfaces can be observed. Field and Pinsky (2000) demonstrated that this model could also be applied to karst aquifers, where rapid flow velocities occur in the centres of active conduits (mobile fluid region), while flow velocities are much slower at the conduit margins, in adjacent fractured rock volumes, but also in eddies and pools, and in the pores of cave sediments (immobile fluid region).

A detailed mathematical description of the two-region non-equilibrium model and its application to karst can be found in the two papers cited above. For conservative solutes, the model assumes transport in the mobile fluid region by advection and dispersion, but additionally considers physical non-equilibrium exchange between the mobile fluid region and an immobile fluid region. The partition coefficient β describes the proportion of mobile water ($0<\beta<1$), where high values indicate a high proportion of mobile water affecting solute transport. The mass transfer coefficient ω describes exchange between the two fluid regions ($\omega>0$), where high values mean intense mass transfer between the two fluid regions (Fig. 2). Reactive processes such as retardation and degradation, can also be included (Toride et al. 1993) and were already implemented for karst aquifers (Geyer et al. 2007), but are not relevant in this case. In karst conduits, dispersion is often most relevant in the flow direction so that one-dimensional models represent a legitimate simplification.

The naphthionate BTCs of the tracer test from 1999 were thus reassessed and modelled analytically using the 2RNE. As naphthionate behaves conservatively in groundwater (although microbial decay can occur in water samples), four fit parameters were required: mean transit time t_0, longitudinal dispersion coefficient D, partition coefficient β, and mass transfer coefficient ω. The mean flow velocity was obtained as $v=L/t_0$, where L is the linear distance between the injection and sampling sites. These values made it possible to calculate the longitudinal dispersion coefficient for the mobile-fluid phase $D_m=D/\beta$, the mean transit time of the mobile fluid phase $t_m=\beta t_0$ and the average mobile fluid velocity $v_m=v/\beta=L/t_m$. The program CXTFIT (Toride et al. 1999) was used to fit the analytical model to the observed data.

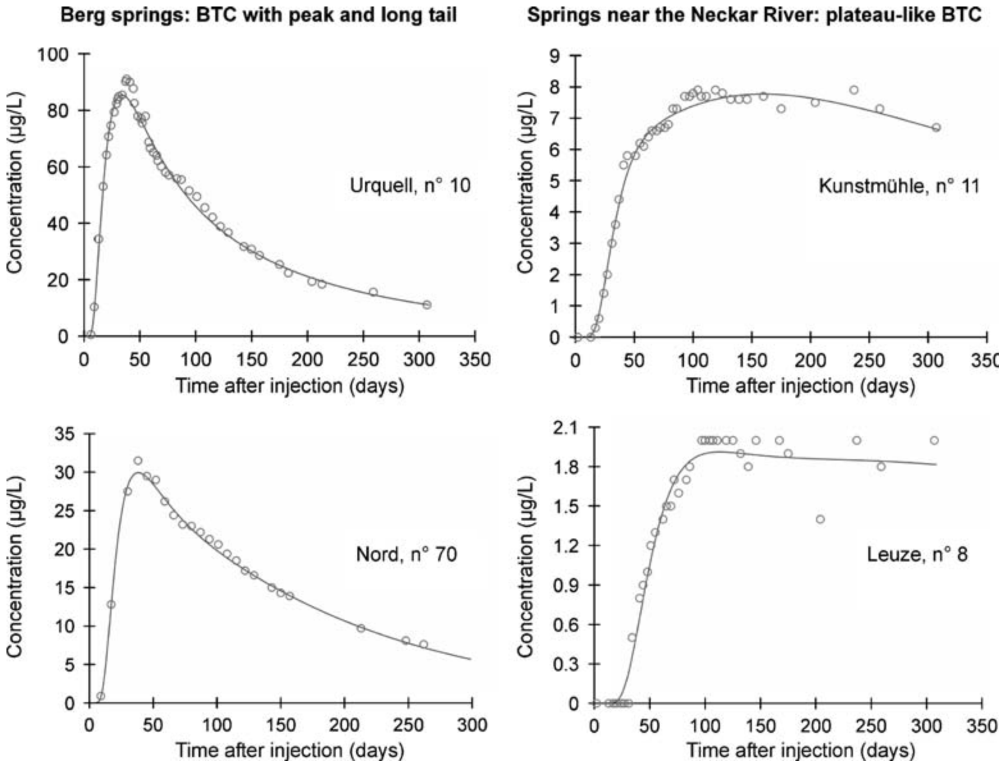

Fig. 3 Selected breakthrough curves for naphthionate from the Berg spring (*left panel*) and the springs near the Neckar River (*right panel*). The two-region non-equilibrium model (*line*) reproduces very well the measured concentrations (*circles*)

Results and discussion

Overview

The two-region non-equilibrium model was capable of reproducing the BTCs of the five Berg springs with a single peak and a long tail, and the plateau-like BTCs of the three springs near the River Neckar. Figure 3 presents the observed concentrations and the simulated curves of two springs from each group; Table 1 summarises all results. The coefficients of determination (R^2) ranged between 0.972 and 0.995 suggesting a very good model fit, which was also visibly evident. The slightly lower R^2 of some BTCs can rather be attributed to a scattering of the data points, while the general shape of the curve is very well reproduced (e.g. Leuze spring, Fig. 3). Table 1 also presents results from a recent tracer test in a typical karst conduit system (Hölloch cave, Austro-German Alps) for comparison (Göppert and Goldscheider 2008).

Breakthrough curves with a peak and long tail

The five nearby springs of the leisure bath Berg are located at a distance of 1,380 m down gradient from the injection well. Berger Urquell (No. 10) is the main spring, discharging 31 L/s, while the four other springs (No. 68–71) discharge 4.5 to 11 L/s. The tracer was first detected 6–9 days after injection and peaked after 38 days. The corresponding maximum velocities are 153–230 m/day; peak velocities are 36 m/day. The highest maximum concentration (91.0 μg/L) and tracer recovery (18.2%) were observed at the main spring, while the maximum concentrations at the other springs were 31.5–58.5 μg/L (Fig. 3, Table 1).

Due to the extreme asymmetry of the BTCs, the transit times determined by the 2RNE are substantially longer and less uniform than those directly obtained from the BTCs, ranging between 65 and 191 days. These transit times correspond to average mobile fluid velocities of 7.2–21.1 m/day. Dispersivities are within a range of 285–1,203 m^2/day.

Concerning the partition coefficient β and the mass transfer coefficient ω, there are noteworthy differences between the main spring and the four other springs. The BTC of the main spring delivers a partition coefficient of 0.84 and a mass transfer coefficient of 0.91, while the BTCs of the smaller springs yield lower partition coefficients (0.52–0.60) but higher mass transfer coefficients (1.9–2.1). These findings suggest that the tracer transport towards the smaller springs is characterised by a higher contribution of immobile fluid regions, and by more intense exchange between mobile and immobile water.

Compared to the data from the Hölloch cave, the BTCs of the Berg springs are characterised by much lower flow velocities, similar dispersions but much higher dispersivities α, lower partition coefficients β, and higher mass transfer coefficients ω. These findings indicate that the tracer transport in the artesian karst aquifer of Stuttgart is much slower, more heterogeneous and more influenced by immobile water than in a shallow conduit system.

Table 1 Summary of the tracer test results

				Berg Springs					Springs near Neckar River			Hölloch cave
	Property	Symbol	Unit	Urquell No. 10	Ost No. 68	Mittel No. 69	Nord No. 70	West No. 71	Kunst No. 11	Leuze No. 8	Insel No. 9	a
Basic data	Spring discharge	Q	L/s	31	4.9	11	6.6	4.5	ND	34	37	172
	Distance from injection well	L	m	1,380	1,380	1,380	1,380	1,380	1,780	1,820	1,860	2,500
	Time of first detection	t_1	days	6	9	9	9	9	17	34	34	2.8
	Peak time	t_p	days	38	38	38	38	38	NA	NA	NA	4.1
	Peak concentration	C_p	μg/L	91.0	47.0	58.5	31.5	56.1	7.9	2.0	2.1	9.3
	Maximum velocity	v_{max}	m/day	230	153	153	153	153	105	54	55	904
	Peak velocity	v_p	m/h	36	36	36	36	36	NA	NA	NA	610
	Tracer recovery	R	%	18.2	1.74	4.14	1.51	1.68	ND	0.84	0.83	98.5
2RNE	Average mobile-fluid velocity	v_m	m/day	7.2	14.6	21.1	13.2	15.1	2.9	0.8	0.4	613.0
	Corresponding transit time	t_m	days	191	95	65	105	91	606	2,228	4,227	4.1
	Longitudinal dispersion, mobile-fluid region	D_m	m^2/day	8,716	5,851	6,008	6,341	7,439	6,112	4,184	5,008	9,496
	Longitudinal dispersivity	α	m	1,203	402	285	480	491	2,081	5,123	11,381	15.5
	Partition coefficient	β	-	0.84	0.54	0.52	0.57	0.60	0.47	0.41	0.73	0.92
	Mass transfer coefficient	ω	-	0.91	2.02	1.93	1.96	2.09	15.5	30.3	33.2	0.39
	Coeff. of determination	R^2	-	0.989	0.993	0.975	0.995	0.983	0.990	0.972	0.979	0.999

[a] The data from the Hölloch cave are taken from Göppert and Goldscheider (2008) and are for comparison only

NA not applicable; *ND* not determined

Plateau-like breakthrough curves

The three springs near the Neckar River are 1,780–1,860 m away from the injection well. Spring No. 11 is small and it is technically difficult to determine the discharge. The Leuze (No. 8) and Insel spring (No. 9) make up the leisure pool Leuze and discharge 54 and 55 L/s, respectively. The tracer was first detected after 17 days (No. 11) and 34 days (Nos. 8 and 9), respectively, and then rose to concentrations of 7.9 μg/L (No. 11), 2.0 μg/L (No. 8) and 2.1 μg/L (No. 9), about 100 days after the injection. The BTCs do not display a clear maximum but the concentrations remain nearly constant for about 200 days, when the sampling had to be stopped for technical reasons. Based on the times of first arrival, it is possible to determine the maximum flow velocities (54–105 m/day), while the peak velocities are not defined in this case.

The 2RNE was capable of reproducing these plateau-like BTCs surprisingly well, with coefficients of determination ranging between 0.97 and 0.99. Compared to the BTCs with a peak and long tail, the mean transit times are much longer and the average mobile fluid velocities are correspondingly very low, 0.4–2.9 m/day. The dispersivities are also extremely high. The partition coefficients are very low, 0.47 (No. 11), 0.41 (No. 8) and 0.73 (No. 9), indicating a high proportion of immobile water. The mass transfer coefficients are very high, suggesting very intense exchange between mobile and immobile fluid regions. The modelling results thus confirm the hypothesis that the tracer was stored in large cavities of immobile water and then slowly released back into mobile fluid regions.

Conclusions

The tracer tests that were done in 1999 in the artesian aquifer of the mineral springs of Stuttgart delivered two types of breakthrough curves: BTCs with a clear peak and an exceptionally long tail, and plateau-like BTCs. Initially, this observation was qualitatively explained by intermediate storage in large cavities and subsequent slow release into the active conduit and fracture network (Goldscheider et al. 2003).

The application of the two-region non-equilibrium model (2RNE) has now made it possible to confirm and better quantify this earlier explanation. The model assumes exchange between mobile and immobile fluid regions in karst aquifers (Field and Pinsky 2000). The partition coefficient β describes the proportion of mobile water involved in tracer transport, while the mass transfer coefficient characterises the intensity of exchange between the two fluid regions. Compared to tracer test data from more ‘conventional’ karst aquifer systems, the BTCs with a peak and long tail are characterised by significantly lower partition coefficients and higher mass transfer coefficients, indicating that immobile fluid regions substantially influence tracer transport. The plateau-like BTCs show even lower partitioning coefficients and extremely high mass-transfer coefficients, which suggests that an important portion of the tracer actually entered the immobile fluid regions and was stored there for hundreds of days, before it was slowly released back into the active conduits.

A hydrogeological explanation for this behaviour can be found in the unique setting of the aquifer, which is confined and partly artesian, and thus fully saturated. Most other tracer tests described in the literature (cited in the introduction) have been done in shallow, unconfined and only partly saturated aquifers. A deep and artesian karst system is supposed to include larger volumes of immobile fluid regions. Furthermore, CO_2 from the mantle, which rises up into the aquifer and mixes with the shallower groundwater near the mineral springs, may have created a system of interconnected cavities, which stores substantial amounts of quasi-immobile groundwater. The tracer has sampled these immobile fluid regions, which caused the long tails or plateau-like shapes of the breakthrough curves.

The results also illustrate that karst aquifers are not necessarily “fast-flushing” systems. Tracers or contaminants can sometimes be stored in immobile fluid regions of the aquifer or epikarst and be slowly released into the active conduits, causing prolonged tracer breakthrough or contamination. A similar behaviour has been observed in a shallow, unconfined alpine karst aquifer, i.e. in a completely contrasting hydrogeological setting, where a flood pulse after the tracer injection caused infiltration of water and tracer into previously unsaturated aquifer volumes and/or into the fissured limestone matrix, from which it was slowly released during a recession period (Goldscheider 2005).

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