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Comparative tracing experiments to investigate epikarst structural and compositional heterogeneity

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Abstract: *Comparative tracer testing may be used to evaluate the vulnerability of groundwater to specific contaminants by comparing reactive tracer response to that of a simultaneously injected non-reactive "conservative" substance. Conversely, knowledge of tracer reaction with specific materials permits information about subsurface heterogeneity to be inferred. A series of tests completed in the vadose zone overlying a limestone aquifer employed a cocktail of particles along with reactive and non-reactive solute tracers to investigate transport rates between the ground surface and monitoring points approximately 10 m below ground. Short pulse tests revealed both solutes and particulate contaminants could travel at rates of over 10 m/h. Comparison of particle (microorganisms) and non-reactive solute tracer breakthrough revealed that particle tracers experience pore exclusion resulting in higher peak relative concentrations which arrive earlier than those of the solute. Prolonged tracer injection during subsequent experiments confirmed the response observed and illustrated that over 40 % of flow paths between injection and monitoring points were inaccessible to particles, but could allow solutes to pass through them. Similarly, the difference in response between various reactive tracers demonstrated tracers reached monitoring points via multiple flow paths and suggests geochemical heterogeneity plays an important role in influencing tracer behaviour. The results of this investigation highlight the complexity of water flow through the epikarst and the vulnerability of groundwater in karst aquifers to contamination when soil cover is thin to absent.*
Keywords: *tracer; solute and particle transport; microorganisms; vadose zone; epikarst*

1. Introduction

Tracing techniques are widely used for proving hydraulic connections, assessing groundwater flow parameters and quantifying mixing in the subsurface. These tests require conservative tracers be employed in order to obtain breakthrough curves that fully mimic the behaviour of the traced water. In contrast, comparative tracer tests compare a conservative tracer's response, which reflects water flow, to that of other tracer types with specific characteristics. This has been done in order to define the properties of the tracers and to evaluate their suitability for use in the field (Behrens et al., 1992; Bäumle et al., 2001).

This information, in turn, can be used to simulate the behaviour of specific reactive contaminants. Real contamination events in karst settings can rarely be investigated using appropriate sampling and monitoring strategies, particularly in fast flowing systems. In contrast, injection and sampling of tracers that act as contaminant surrogates under well-controlled conditions can provide important information on the transport of relevant contaminants.

An alternative application of comparative tracer testing involves using tracers, whose interaction with particular materials is well characterised, to obtain an insight into conditions in inaccessible regions of the subsurface. This includes conditions in limestone bedrock. Consequently, comparative tracing may be used to characterise the structure and composition of the uppermost part of a limestone formation, i.e. the epikarst.

This paper presents selected results and conclusions from a 3-year project investigating solute and particle transport in heterogeneous unsaturated limestone bedrock. The collective responses of various tracers injected into the epikarst below a test site under variable injection conditions provide information on mass transport processes in the vadose zone of limestone

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aquifers as well as an indication of the role of heterogeneity along the flow paths connecting injection and sampling intervals.

2. Field site and experimental setup

Experiments were completed at the Gännsbrunnen test site in the Swiss Jura Mountains, Canton of Solothurn, Switzerland. An artificial gallery located about 10 m below ground surface provided access to the vadose zone of a fissured moderately karstified Jurassic limestone formation (Fig. 1). During heavy rainfall prior to the test programme, percolating water was observed entering through several discrete outlets in the ceiling of the gallery at rates of up to several L/min. These percolation points were related to fractures and bedding plains arising from structural heterogeneities in the limestone, some of which were subsequently widened by karstification.

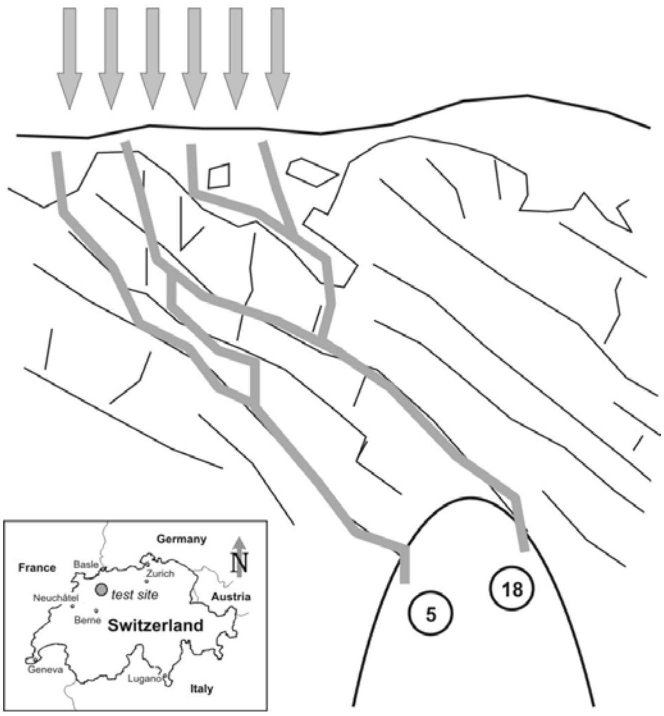

Fig. 1. Schematic illustration of the test site. Irrigation and tracer application occurred at ground surface above an artificial gallery site. Samples were collected at discrete percolation point (outlets 5 and 18).

A series of tracer experiments completed at the site under controlled flow conditions involved injecting a cocktail of reactive and non-reactive solute tracers and particle tracers in a diffuse manner over a 12 m² plot at the ground surface above the gallery. Conservative solute tracers included Br^-, I^- and Cl^-, while reactive solutes consisted of a range of dye tracers, anions and cations. Particle tracers consisted of inorganic fluorescent microspheres and microorganisms (bacteria: *R. eutropha*, bacteriophages: H40/1 and T7).

Irrigation rate and tracer injection mode differed between experiments (Table 1). Irrigation rate varied from one experiment to the other but remained constant during each experiment. Experiments lasted for at least 6 hours. Tracers were applied either as a pulse injection or as a prolonged injection step.

Table 1.

Irrigation and injection key characteristics.

	Injection type	Irrigation pattern	Flow conditions
Experiment type I	pulse	after injection	transient
Experiment type II	pulse	before + after injection	steady-state
Experiment type III	step	before + during injection	steady-state

Water samples were regularly collected from different percolation points in the gallery's ceiling during irrigation and stored in cool dark sample boxes prior to analyses. All analyses were completed at the Neuchâtel University, except microsphere analyses, which were determined by W. Käss, Umkirch/Germany. Tracer relative concentration (C/C_0) variation with time permitted breakthrough curves to be generated for each sampling point; the use of relative concentrations facilitated comparison of responses for different tracers as well as quantitative interpretation.

3. Results and interpretation

3.1. Solute transport and attenuation

Figure 2 represents conservative solute breakthrough (iodine) at two percolation points (outlets 5 and 18) in the gallery under steady-state flow conditions, as reflected by stable discharge rates. These conditions, coupled with an instantaneous pulse injection provide a promising means of determining flow and transport parameters.

First detection of iodide tracer occurred within less than 10 minutes after injection. Peak arrival times indicate dominant flow velocities in the range of 10 m/h. Flow rate weighted mass recovery within the sampling period was 59 % for point 5 and 34 % for point 18; this was partially due to incomplete breakthrough at the end of the experimental period. Differences in tracer breakthrough at percolation points, which are placed at a distance of a few meters only, highlight the large-scale spatial heterogeneity of the epikarst zone. No water flow occurred in the gallery between these discrete percolation points. In the following, all figures refer to monitoring point 5.

Conservative solute response illustrates the rapid arrival of diffusely-infiltrated water despite the moderate levels of karstification visible in the gallery and the lack of visible preferential infiltration points at the ground surface. These results suggest that contaminants can be flushed into the system in the course of heavy rainfall events and thus rapidly penetrate into the vadose zone. On the other hand, long tailing indicates that a significant proportion of active flow paths have considerably longer residence times. This duality between flow components is crucial for assessing potential contaminant attenuation and groundwater vulnerability.

Low flow rates, and mobilisation of stored water, become particularly important when dealing with some reactive contaminants, for which a prolonged residence time favours additional attenuation. Comparative tracer testing employing reactive tracers shed considerable light on these processes. These tracers were regarded as surrogates for real organic and inorganic contaminants that may potentially impact karst groundwater quality thus allowing attenuation processes in the epikarst zone to be better evaluated. Table 2 summarises the responses of selected solute tracers relative to the conservative solutes. Significant additional peak attenuation and mass loss are considered to be the result of sorption and/or degradation processes, according to the tracer-specific properties.

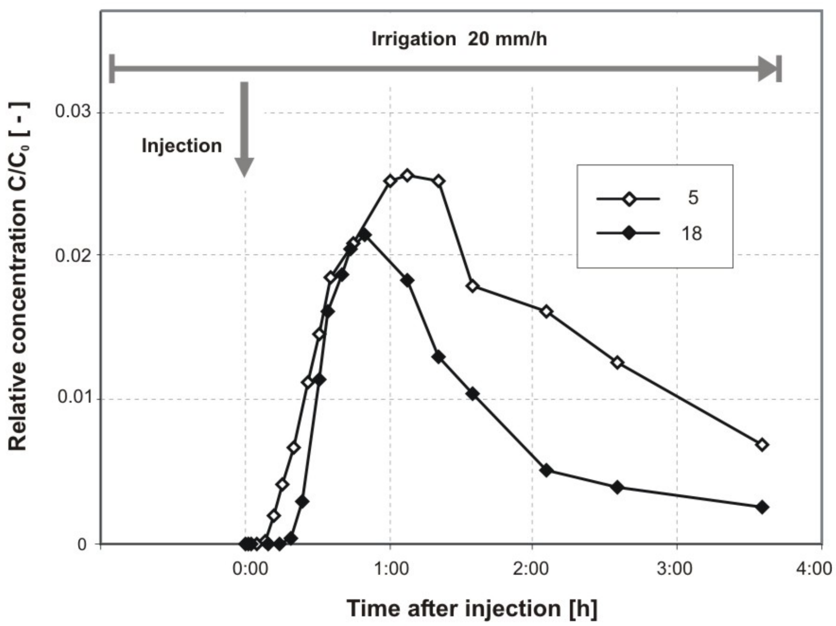

Fig. 2. Iodide (I^-) solute tracer breakthrough curve for monitoring points 5 and 18 (experiment type II).

Table 2.

Summary of key parameters for selected reactive tracer breakthrough curves (all values relative to conservative solute) at sampling point 5.

	Nature of tracer	Rel. max. conc. C/C_0	Relative recovery
Sulforh. G	organic	0.23	0.19
Pyranine	organic	0.26	0.32
PO_4^{2-}	inorganic	0.17	0.23
NH_4^+	inorganic	0.012	0.014
K^+	inorganic	0.008	0.010
Sr^{2+}	inorganic	< 0.004	< 0.0001

3.2. Particle transport and attenuation

Knowledge of mass transport rates through the vadose zone overlying aquifers also provides important information that is critical in determining whether prolonged residence times will afford a degree of protection from microbiological contamination to underlying water resources. Understanding particle response is helpful for interpreting the structure and relative importance of different flow paths through the system. Conservative and reactive solutes may use the same flow paths depending on reaction rates; these rates ultimately control responses observed at monitoring points. Particle flow is fundamentally different because of the potential limitation of pore volume access. The comparative application of both solute and particle tracer types may thus discriminate between those fractions of the effective porosity that exclude particulate contaminants and those which allow them to pass through.

Figure 3 displays breakthrough curves of some of the particle tracers employed for experiment type II. Solute and particle breakthrough curves have distinctly different shapes. H40/1 and *R. eutropia* breakthrough curves are less disperse and have peak concentrations that occur significantly earlier than those of the conservative solute, indicating exclusion processes. Similar responses are observed of T7 and the various sizes of fluorescent microspheres although they are considerably more attenuated. The lower concentrations of the latter can be explained by first-order kinetic sorption of these more reactive particles along the same flow paths (Sinreich et al., 2009).

Despite the earlier arrival of particle tracers compared to conservative solutes, this alone does not necessarily prove that exclusion processes are operating. Zhang et al. (2000) effectively demonstrated that peak concentrations shift towards earlier times when first-order kinetic adsorption operates. Under these circumstances, comparative plotting of solute and particle tracers with absolute concentrations is of little value in terms of visualizing exclusion processes. Comparison of relative concentrations eliminates this problem.

The bacterial tracer *R. eutropha* and the bacteriophage H40/1 reach maximum relative concentrations that are twice as large as those of conservative solutes, but display comparable dispersion one to each other. These data provide convincing evidence of the operation of exclusion processes during the tracer test. Moreover, the breakthrough curve for the 40 nm diameter H40/1 phage tracer being similar to that of *R. eutropha*, which is approximately 80 times larger, suggests pore exclusion is responsible for this behaviour (Sinreich and Flynn, 2008). Such a result could not be obtained if size exclusion were the driving process for the particle response observed (Fig. 4).

Based on the above results it is apparent that, despite attenuation, microorganisms may be transported through the vadose zone more rapidly than non-reactive solute tracers.

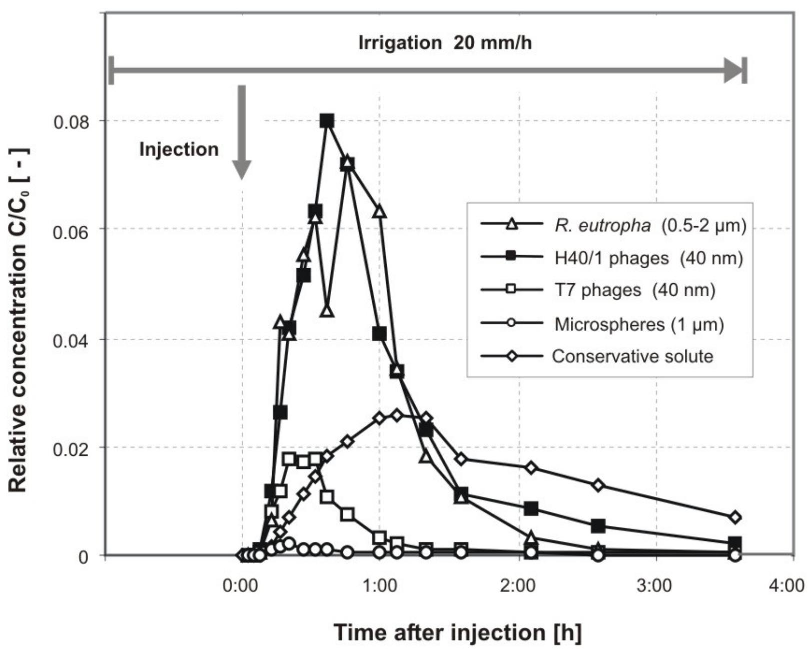

Fig. 3. Breakthrough plot of various particle tracers in comparison to the conservative solute.

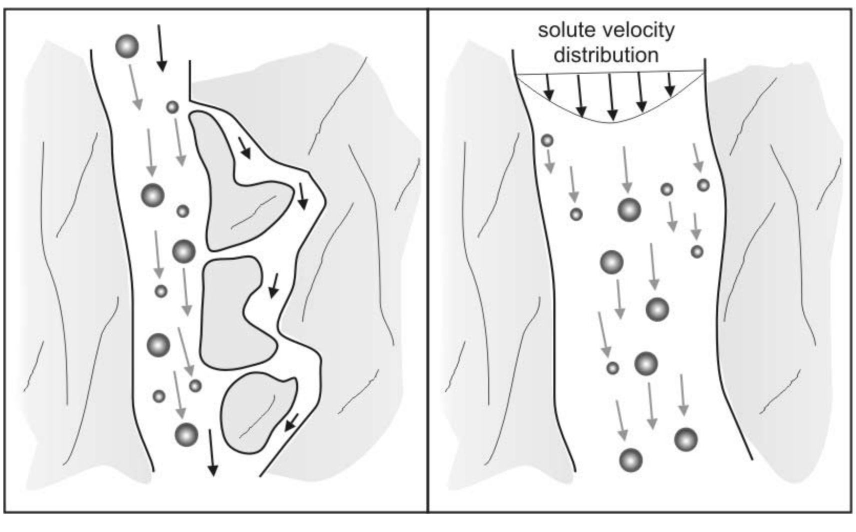

Fig. 4. Schematic description of pore (left) and size exclusion (right) processes in fractured karstified rock.

3.3. Multi-component flow and storage

In order to better characterise the different flow components below the test site, an alternative injection signal was applied, again under steady-state flow conditions. This involved applying the tracer cocktail to the irrigation plot at a constant rate for nearly 6 hours (experiment type III). This approach allowed for a better quantitative estimate of the portion of the total pore volume that was accessible to certain tracer types.

Conservative solute and H40/1 phage breakthrough curves observed using this setup are plotted in Figure 5. A very fast flow component is indicated by the steep rise of phage concentrations. 90 minutes after tracer injection started, H40/1 concentration plateaus out with about 0.6 times the input concentration and stops increasing despite sustained tracer injection. This suggests that all pore volumes accessible for particles are filled with tracer and that 40 % of the phage tracer is permanently retained by the system under these conditions. Indeed, the portion of faster flowing water is certainly lower than 60 % of the total flux, since these channels also contain particles excluded from other flow paths accessible to water.

Conservative solute concentrations rise more smoothly than particles and approach a plateau of constant relative concentration of 0.8 approximately 5 hours after the start of injection. This portion corresponds to the sum flow components travelling along paths that can reach sampling points over the duration of the injection. A proportion of these pathways are accessible to solute and particulate tracers, whereas others are accessible to solute tracers alone.

At the end of the continuous tracer injection period, there was still a near-constant contribution of about 20 % of the total flux that was tracer-free, which represented the proportion of total flow travelling along pathways that are insufficiently fast to permit tracer to reach sampling points within the experimental timeframe. The contrast in solute and bacteriophage responses suggests that particulate tracers are unable to reach the sampling points via these routes.

It is hypothesised that the conservative solute concentration would continue to rise asymptotically towards unity, were tracer application to continue. Part of the reason for this response is suspected to be a consequence of older water, present in the

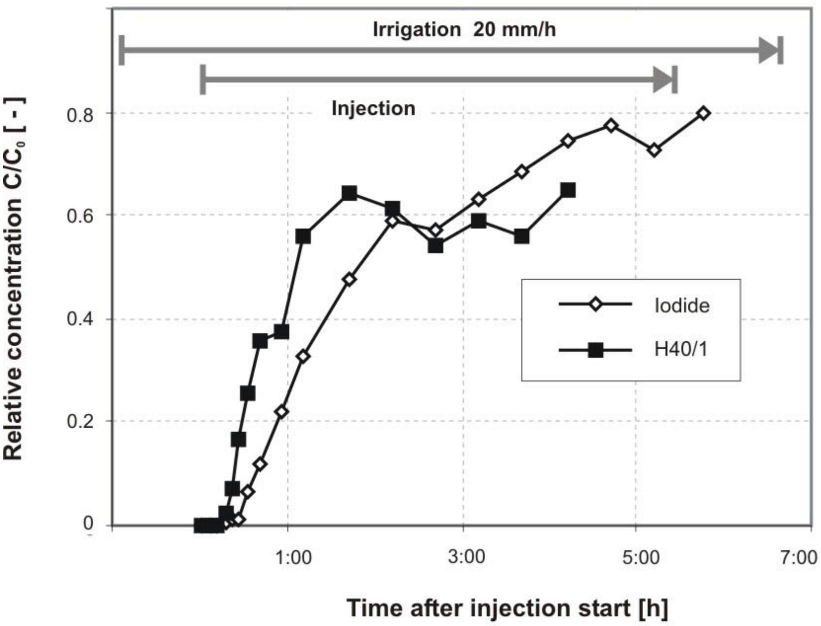

Fig. 5. Iodide and H40/1 concentration evolution during prolonged tracer injection experiment.

system prior to irrigation, being forced out of storage by the hydraulic action of the water being added at the ground surface (piston flow). In fact, the detection of non-reactive tracers in the sample discharge water prior to tracer addition during this experiment indicates that some of the tracer applied during the previous experiment remained stored in the system during the intervening six month period.

This is consistent with data presented in Figure 6. Irrigation at a rate of 55 mm/h resulted in a steady-state inflow of 1.8 L/min at the percolation point 2.5 hours after irrigation started. Following this interval, flow into the gallery remained constant until irrigation ceased. After this point inflow rates into the gallery declined rapidly. Indeed the volume of water draining following the end of irrigation was considerably less than the volume flowing into the gallery prior to onset of steady-state flow. These results suggest that additional water may have been taken into storage in the interval between the start and end of the experimental period.

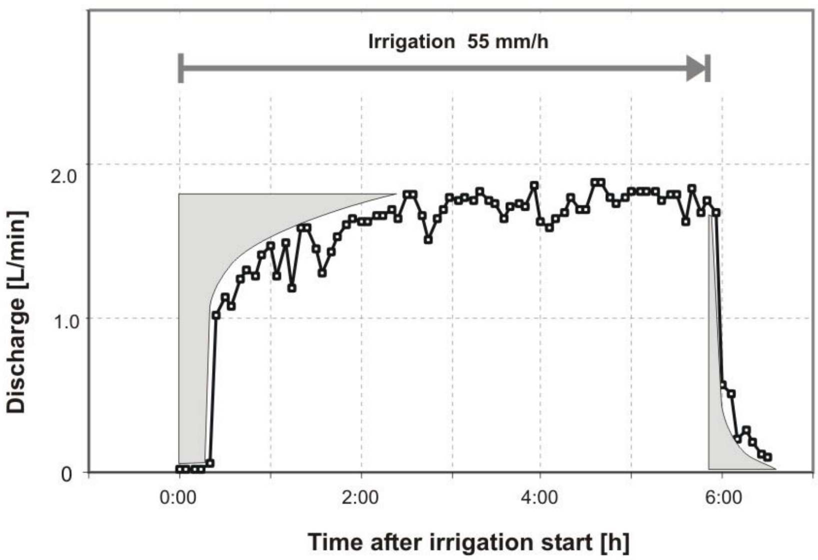

Fig. 6. Percolation discharge and related estimations for storage volume.

3.4. Rock-tracer interaction

Figure 3 presents evidence of the strong attenuation of some of the particle tracers employed during pulse injection experiment, such as T7 and the microspheres. Even for the less reactive H40/1 phage type, the step injection experiment shows a permanent attenuation rate of 0.4 (Fig. 5).

These results are suspected to be a consequence of particle filtration along flow paths between injection and sampling points. Filtration depends on both the sticking efficiency of the particles and their collision frequency with reactive surfaces (Elimelech et al., 1995). Sticking efficiency is mainly a function of the physical-chemical surface properties of both the particles and the rock, such as charge and hydrophobicity. This in turn is a function of the chemistry of the water in the system. Collision frequency, i.e. the frequency of contact between particles and rock surfaces, is mainly controlled by physical aspects of the system such as particle size and the aperture of pores and fractures, as well as the flow characteristics.

The upper part of Figure 7 represents the same experiment as Figure 5, but plotted over a longer period and with an additional breakthrough curve for the T7 phage and electric conductivity data; the latter acts as a surrogate for the ionic strength of the water being sampled. The high ionic strength in the irrigation water during the experiment was due to the high load of ionic tracers. The gradual increase in ionic strength provided much important additional information about particle filtration in the rocks underlying the site (Flynn and Sinreich, 2010).

A strong decrease of phage concentration occurred at 40 minutes after injection start for T7 and 4 hours later for H40/1 (Fig. 7). T7 concentrations declined more gradually with increasing electric conductivity until no phage were detected in samples despite constant tracer application. This behaviour contrasted with that of H40/1, which maintained a constant concentration until a critical deposition point was reached when concentrations declined dramatically. Associated laboratory-based batch experiments demonstrated that phage inactivation/adsorption at the air-water interface were negligible processes suggesting that both viruses were predominantly adsorbed to rock surfaces under the prevailing chemical conditions. This is corroborated by a dramatic release (desorption) of both phage types following the application of low ionic strength water to the system at the end of tracer injection. The lower part of Figure 7 schematically displays the effect of changing sticking efficiencies during the different phases of the experiment.

These results illustrate, on the one hand, how changing hydrochemical conditions influence attenuation of the various particle tracers employed, with T7 being much more sensitive to ionic strength increase than H40/1. On the other hand, the experiment strongly indicates that all of the particle tracers employed have very high collision frequencies, i.e virtually all particles can collide with fixed surfaces.

Solute tracer responses are also believed to reflect geochemical variability in the epikarst along flow paths connecting the irrigation zone with sampling points (Fig. 8). The organic dye tracer Sulforhodamine G has a well-characterised sorption affinity to other hydrophobic materials such as organic matter (Käss, 1998). Breakthrough curves for this tracer demonstrated a reduced tendency to react along flow paths with short travel times compared to tracers arriving later. This in turn indicates that the surfaces along these later paths contained more hydrophobic materials, possibly due to fissures filled with soil matter comparable to those observed in outcrop close to the test site. Following the same line of reasoning, phosphate tracer appears more attenuated along flow paths with low residence times.

Preliminary hydrochemical modelling for experiment type III results indicate ionic exchange as the predominate process responsible for the gradual change in phosphate and other ions in tracer samples (Laurent André, pers. comm.).

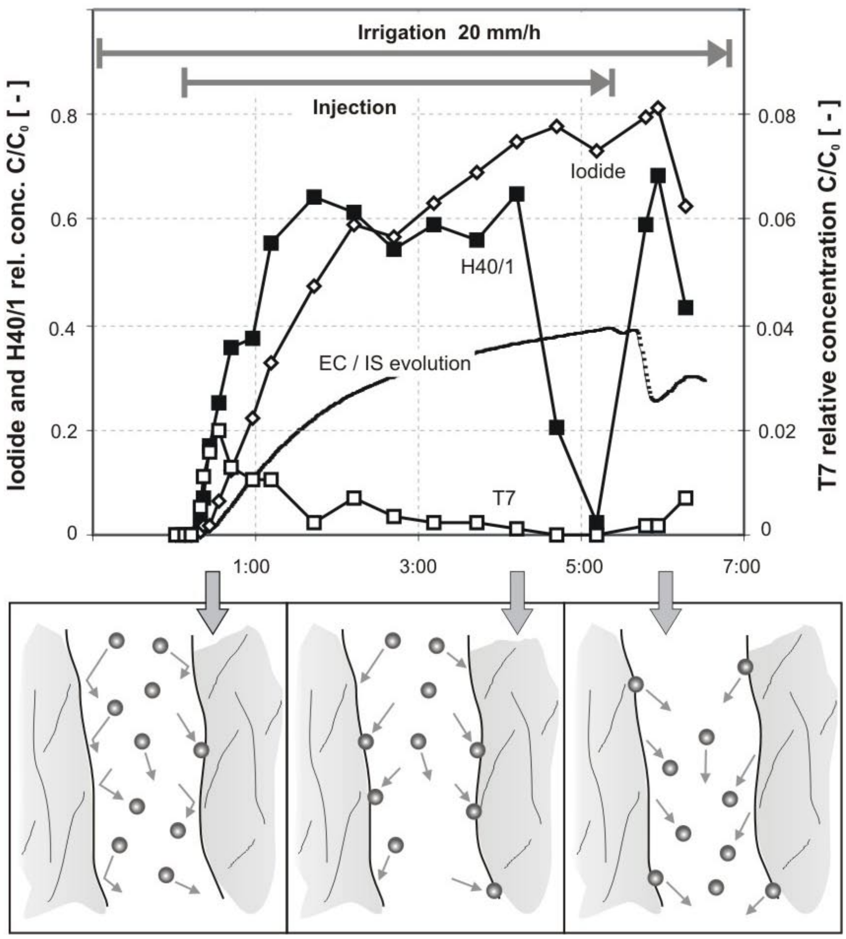

Fig. 7. Breakthrough curves for selected tracers in experiment type III. Full sorption of T7 and H40/1 phages occurs when reaching critical ionic strength (IS) resp. electric conductivity (EC) values (above). According conceptual scheme for three experiment phases (below).

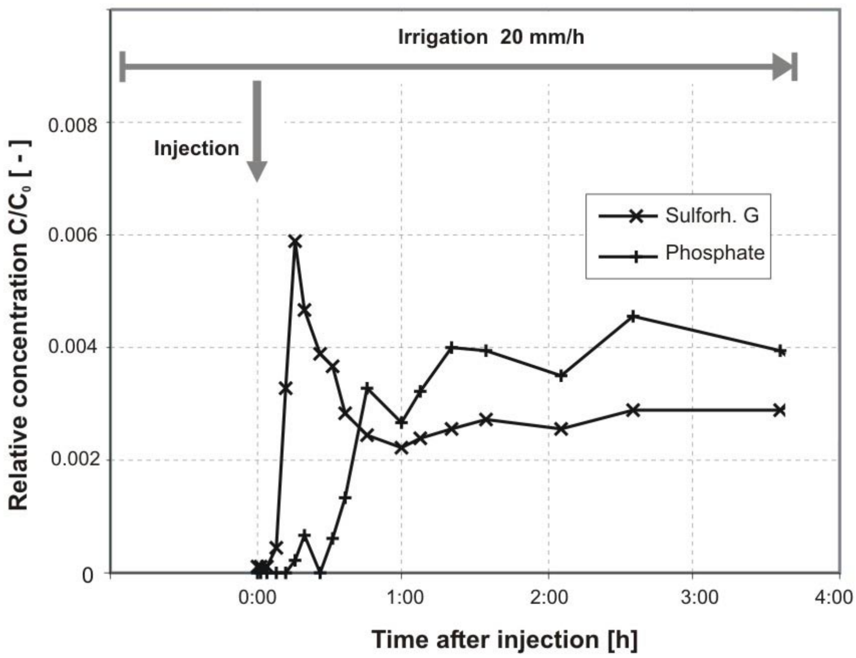

Fig. 8. Sulforhodamine G and phosphate breakthrough curves for experiment type II with prevailing attenuation for differing flow components.

4. Conclusions and conceptual model

The facilities available at the field site, together with specific experimental setup, permit specific flow and storage characteristics of the karst vadose zone to be investigated in detail. Since the soil cover above the limestone is very thin, the main effects on water drainage and tracer transport can be attributed to the epikarst layer. Its dual function for both focusing recharge into preferential vertical flow paths and for storing infiltrating water makes it an important karst sub-system.

Experiments at the site provide an insight into phenomena that can be encountered in the karst vadose zone including the following:

- Flow heterogeneity within epikarst,
- rapid transport of potential contaminants despite diffuse infiltration and moderate karstification,
- attenuation potential for reactive solutes and some particle contaminants,
- exclusion processes leading to earlier arrival of particles (including microorganisms) relative to solutes,
- multi-component flow with fast preferential and slower pathways,
- long-term storage providing prolonged time periods for solute and microorganism attenuation,
- very high collision frequency of particles in conduit along fracture flow paths,
- the role of geochemical heterogeneities in generating irregular breakthrough curves.

These phenomena could be highlighted by means of evaluating different injection scenarios with various tracer types. Regarding the epikarst as a multi-component system and using well-defined tracer experiment input and output functions allows for quantification of the components reaching the sampling point via different flow paths. For a multi-component flow, solute breakthrough can be split into several partial breakthrough curves representing separate populations of flow paths, as shown by Behrens et al. (1992).

Breakthrough curves presented in Figure 9 reflect analytical solutions for non-reactive solute transport, simulating overall breakthrough using three flow components based on concepts developed in the above experiments. Reactive solute tracer response can be deduced by adding a kinetic and/or equilibrium sorption term to the various components of flow.

A comparable hydrogeological conceptual model for transport through epikarst has also been established in terms of a multi-reservoir model using discharge data (Perrin and Kopp, 2005). Figure 10 schematically summarises the epikarst at the experimental site as a three-reservoir system transporting irrigation/rainfall water from the surface and discharge it to the gallery at 10 m below ground surface.

The model tentatively proposes that the fast flow component results from preferential fracture/conduit flow. Slower flow components result from flow through finer fissures and/or fissures filled with soil material. A very slow component arises due to water flowing through very fine fissure network or limestone porous matrix. The conceptual model is considered preliminary without integrating all data obtained from the experimental series. It neglects potential lateral boundary effects, which were suspected to be of minor influence.

Some specific conclusions became apparent in the scope of this research with respect to groundwater protection, which may also be valid for the saturated zone of a karst aquifer:

Specific transport and attenuation for individual contaminant types, as well as the contamination scenario, should be taken into account when dealing with groundwater vulnerability assessment.

Exclusion processes should be accounted for to explain early particle arrival. Solute response may not always be an appropriate indicator for microbiological transport and attenuation.

Size alone has proved inadequate for understanding particle fate and transport at the site, as illustrated by the comparative behaviour of fluorescent microsphere tracers and similarly sized *R. eutropha* bacteria, with attenuation rate of the spheres 30 times that of the bacteria.

The chemical composition of water may play an important role in particle attenuation. Rapid changes in hydrochemistry are frequent in the course of recharge events in karst aquifers. The increase of microbiological contamination during recharge events may thus partly be explained by desorption of previously adsorbed particles due to the presence of lower ionic strength

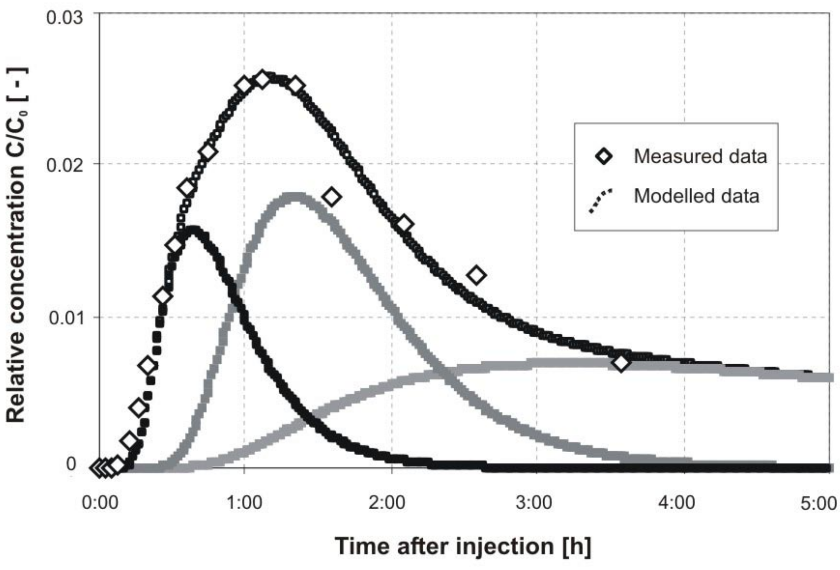

Fig. 9. Preliminary multi-flowpath model for solute tracer breakthrough.

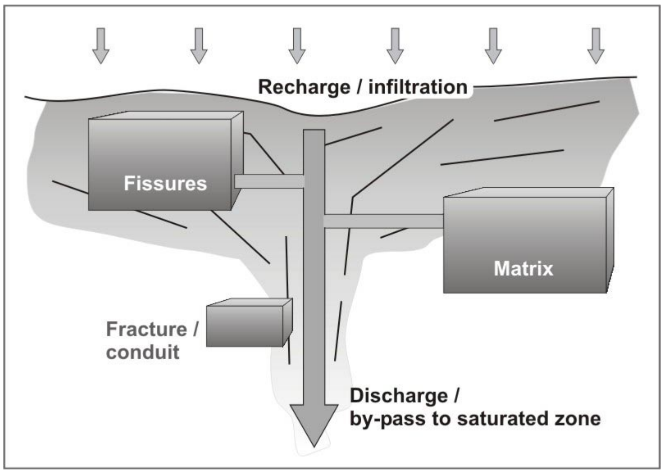

Fig. 10. Simplified three-reservoir conceptual model at the epikarst test site.

water rather than the transport of fresh infiltration containing microorganisms. This phenomenon will depend strongly on the rate of die-off of adsorbed microorganisms.

Understanding attenuation processes in the vadose zone overlying karstified aquifers is essential if water quality is to be adequately protected. The results presented from this site are believed to provide information that may also valid for the epikarst zone of other moderately karstified and diffusely recharged limestone terrains.

Acknowledgements

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