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ORIGINAL ARTICLE

Tracing of water movement through the unsaturated zone of a coarse gravel aquifer by means of dye and deuterated water

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Abstract To better understand the movement and transport of water and pollution through the coarse gravel unsaturated zone, the presented research was conducted to estimate water flow and transport processes with a tracing experiment in a lysimeter in the Selniška Dobrava. A combined tracing experiment was performed with deuterated water and the fluorescent dye—uranine. The fastest and dominant flow velocities were calculated based on injection time, the first tracer appearance time and the time of highest concentration. Mean flow velocity and vertical dispersion were estimated by an analytical best-fit method using one-dimensional convection–dispersion model. Deuterium was confirmed as an ideal conservative tracer and a more suitable tracer than dye (uranine) for the study of water flow in the unsaturated zone of a coarse gravel aquifer. The retardation factor of the dye as compared with deuterium was 1.13–1.75, which is in agreement with previously published results. Artificial tracers, especially deuterated water, were also identified as a very useful tool to assess other properties and differences in water flow in the unsaturated zone of a coarse gravel aquifer such as velocity and dispersion.

Introduction

Contamination of aquifers is a growing and demanding problem. In situ characterization of the hydraulic properties of materials within the unsaturated zone has become increasingly important over the past years. One of the major problems is how to fully characterize the unsaturated zone. The implementation of measurements in a high-permeable gravel unsaturated zone is quite difficult. Sometimes it is almost impossible to measure in situ parameters which define unsaturated zone characteristics, and also pore water sampling is difficult.

The water flow and solute transport in the unsaturated zone has been the topic of many investigations. Articles and surveys have pointed out the importance of preferential flow in the unsaturated zone (Schoen et al. 1999; Van der Hoven et al. 2002). Dye as a tracer is a useful tool for revealing spatial flow patterns, and has been used by soil scientists for years (Kung et al. 2000; Yasuda et al. 2001; Öhrström et al. 2004). The adsorption of the dye differs between soil types; soils with a high clay content and low in content of organic carbon tend to adsorb more dye than others (Ketelen and Meyer-Windel 1999). Jabro et al. (1994) and also Fank and Berg (2001) have showed how bromide makes a useful tracer to investigate the flow, solute transport processes and determine preferential flow in various experiments. Measurements of salt tracer

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concentration have been widely used to determine transport parameters like velocity and dispersion (Wild and Babiker 1976; Jury 1982). Also natural isotopes like deuterium, tritium (T) and ^{18}O have been used to study water flow (Maciejewski et al. 2006; Maloszewski et al. 2006; Rank et al. 2001). Different tracers have also been combined in the same solution, for example, chloride and nitrate (Biggar and Nielsen 1976), different fluorescent tracers (Aeby et al. 2001), bromide and deuterium (Nützmann and Stichler 2001; Schoen et al. 1999), and chloride, bromide, dye and a colloidal tracer (Mortensen et al. 2004). Flury and Fluhler (1995) have reported on the simultaneous application of the dyes brilliant blue and bromide.

Several studies of solute transport in the unsaturated zone of fractured and karstified rocks have been performed in Slovenia. The uranine and some selected geochemical parameters (discharge, pH, conductivity, carbonates, calcium, magnesium, chloride, nitrate, sulphate and phosphate) were used to study the flux and non-reactive contamination transport through the unsaturated zone in Postojna cave system (Kogovšek and Šebela 2004). Veselič and Čenčur-Curk (2001) investigated the flow and solute transport in the fractured and karstified rocks, above all in the unsaturated zone and its epikarstic zone at the Sinji Vrh experimental field site. The long duration multitracer experiment was conducted with the use of several tracers (uranine, NaCl, KCl, $MnCl_2$, $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}6H_2O$) to define the impact of rock structure on transport processes in unsaturated zone.

The processes in the coarse gravel unsaturated zone develop quite differently from those in aquifers with finer unsaturated zone granulation. The aim of this study was to describe the transport processes in a high-permeable coarse gravel unsaturated zone by means of a tracing experiment using a lysimeter in the Selniška Dobrava aquifer. The lysimeter was designed on the basis of previous hydrogeological investigations of the area where fast vertical and horizontal flow of groundwater had been reported. The aquifer of Selniška Dobrava, 20 km away from Maribor, has been investigated since 1993. Investigation results have confirmed that this aquifer is a suitable alternative water resource for supplying Maribor and its surroundings (Mali and Janža 2005). Within a few years the Selniška Dobrava gravel aquifer will become an important water resource. Its effective protection requires an understanding of the properties of the unsaturated zone, in order to determine land-use restrictions. An evaluation of a coarse gravel aquifer's vulnerability with regard to the protective function of the unsaturated zone also requires a detailed knowledge of possible transport mechanisms through the aquifer.

A combined tracing experiment was performed using both deuterated water and uranine. Conservative tracers are necessary to obtain groundwater transport properties. Deuterated water is known as an effective tracer for this purpose (Becker and Coplen 2001) due to its chemical stability, non-reactivity, ease of handling and sampling and reasonable price. Deuterated water has been used as a reference tracer in karst and porous aquifers aquifer studies, but only few studies have focused on the unsaturated zone. Compared with other groundwater tracers, deuterium shows the highest degree of conservativeness (Leis and Benischke 2004). Fluorescent dyes react readily with subsurface materials, particularly in groundwaters of neutral and lower pH values, so their transport is often retarded with respect to water movement (Kasnavia et al. 1999). For this reason deuterium was chosen to study water movement, while uranine with its sorption capacity was used as an indicator of possible pollution.

Materials and methods

Area description

Selniška Dobrava is situated in the north-east of Slovenia near Maribor, the capital of the region. The area lies on the north bank of the Drava river (Fig. 1). The main aquifer runs along the Drava stream channel. The aquifer is recharged by the Drava, infiltration and seepage from the upper terrace aquifer. The thickest coarse gravel deposit is 50-m thick. Groundwater table is found at an average depth of 25–37 m, thus the thickness of the saturated layer along the aquifer axis is 7–14 m, possibly even more in the deepest sections. The hydraulic conductivity of the principal aquifer has been reported as $5{\times}10^{-3}$ m/s (Mali and Janža 2005). The research area belongs to the moderate continental climate of central Slovenia with a typical continental precipitation regime and an average yearly precipitation between 1,200 and 1,300 mm. The average yearly air temperature lies between 8 and 12°C.

The lysimeter is in the area of the principal aquifer Selniška Dobrava, downstream from the pumping station GV-1. The lysimeter location is presented on the map in Fig. 1. The lysimeter is at piezometer PS-5, which was constructed down to the basement and enables the measuring of groundwater tables and sampling of groundwater. The vegetation covering the larger area of the lower aquifer is a mixed forest and the soil type is a district cambisol. The gravel has a

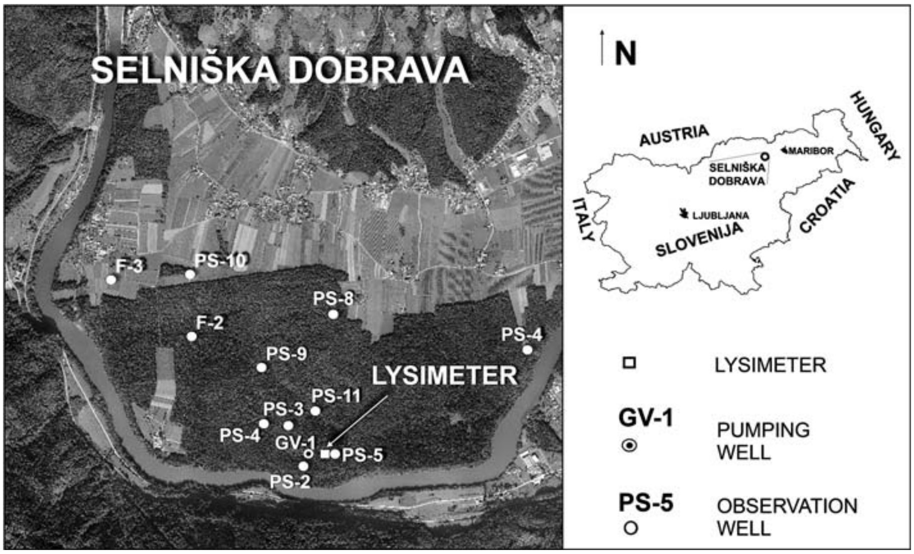


Fig. 1 Study area—location map of the lysimeter Selniška Dobrava

mixed lithological structure, composed of metamorphic rocks and carbonates, intermittently incrustated by calcite. Based on granulometric analyses, the hydraulic conductivity of the coarse gravel at the lysimeter location is estimated at 2.9×10^{-3}–6.8×10^{-2} m/s. The infiltration tests show that the hydraulic conductivity of the soil is 3.5×10^{-6}–7.7×10^{-7} m/s by Hvorslev slug test and 1.3×10^{-5}–3.8×10^{-5}m/s by the double ring method. In the conceptual model, the lysimeter area is defined as homogeneous coarse gravel aquifer.

Experimental set-up

The lysimeter was constructed as a 2 m×2 m, 5-m deep concrete box, with 0.2-m thick walls (Fig. 2). It has ten sampling and measuring points at different depths (JV-1 to JV-10). Sampling point positioning followed a randomized selection over lysimeter width but at approximately equal distances from its depth. The lysimeter was located next to a piezometer which enables sampling in both the unsaturated and saturated zones at the same time.

For groundwater sampling in the unsaturated zone, drainage samplers were installed. The stainless steel drains are 1.7-m long profiles (10 cm×10 cm), with inverse inner perforated profiles (5 cm×5 cm) and with a collection system at the end. The steel drains were inserted horizontally into undisturbed wall, with 1.5 m of drains installed in the unsaturated zone. Each sampling point was equipped with a water collection system, constructed from one 400-ml glass bottle and collecting containers. The drains, bottles and water

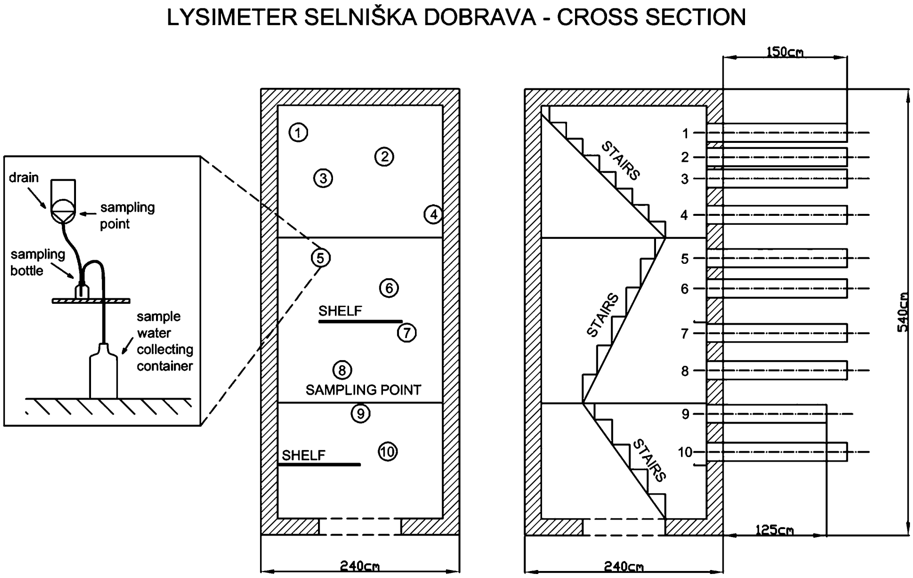


Fig. 2 Lysimeter cross-section and sampling point set-up

collectors were linked with silicon small tubes, shown in Fig. 2. To sample precipitation, a precipitation station was sited near the lysimeter, while the nearby Ruše station of the Environmental Agency of the Republic of Slovenia provided precipitation data.

Combined dye and deuterium tracing experiment

A tracing experiment was performed on April 21, 2004, using deuterated water and uranine as artificial tracers. The period prior to tracer injection was a period of intense snow melting and the saturation of the soil profile was near the field capacity. Before tracer injection, irrigation with groundwater was performed to reach good field capacity. Seventy-five grams of uranine and 1,100 ml of D_2O (55%) were dissolved in 50 l of groundwater and injected by sprinkler irrigation. After injection, the tracer was again splashed by irrigation groundwater. The area of irrigation was 9.5 m^2 and the injection took 5 h to complete. The distribution of the artificial rainfall was controlled by ten precipitation measuring points. The average amount of irrigated water, 107 mm, corresponds to a summer thunderstorm event.

After tracer injection, water in all the outflow sampling points was collected in 120-ml plastic bottles twice on the first day, then once daily for 1 week; afterwards sampling was performed weekly till October 2005. Both tracers were analysed in the same samples.

Analyses

Deuterium was measured in continuous flow mode by chromium reduction using a ceramic reactor slightly modified from Morrison et al. (2001). A high-temperature oven (HEKAtech, Germany) was fitted with a EuroAS 300 liquid auto sampler (EuroVector, Italy). The elemental analyser was configured with a Cr-packed reactor held isothermally at 1,050°C. Water samples contained in 2 ml capacity septa-sealed vials were placed on the carousel of the liquid auto sampler, which was fitted with a 10-µl injection syringe (SGE Europe). A sequence of one wash cycle of 3.5-µl volume was carried out for each sample prior to injection into the Cr reactor. Water samples were injected into septa-sealed injector port. The resulting water vapour was flushed into the reactor by the carrier helium gas via a 1-mm-i.d. stainless steel probe extending into the ceramic reactor tube (Al_2O_3). A sample size of 1.4 µl of water was used for the analysis. Water injected into the reactor was reduced by the Cr, resulting in the quantitative conversion to hydrogen gas according to Eq. 1.

$$2Cr_{(s)} + 3H_2O_{(l)} = Cr_2O_{3(s)} + 3H_{2(g)} \tag{1}$$

The H_2 generated in the Cr reactor was carried in the He stream through the GC column to an open split sampling capillary and into the source of a Finnigan DELTA$^{\text{plus}}$ continuous flow stable isotope ratio mass spectrometer.

Uranine measurements were made using a Shimadzu RF-5000 spectrofluorophotometer. The dye was quantitatively measured using a synchron-scanmethod (Behrens 1970) where the excitation and emission wavelengths are varied with a constant wavelength separation.

Evaluation and interpretation of tracing tests

Based on the injection time, the first tracer appearance time, time of highest concentration and the distance between the top of the lysimeter and observation point, the fastest flow velocity and dominant flow velocity were calculated.

A mathematical evaluation of breakthrough curves from a tracing test is possible using analytical and numerical procedures. It is possible to estimate the mean flow velocity and vertical dispersion from the results of the tracing experiment using a best-fit method of the computer program TRACI'95 (1998). The analytical solution with one-dimensional convection–dispersion model with standardizing values for single porosity was chosen.

$$C_{\mathrm{fN}}(x,t) = \frac{C_{\mathrm{f}}(x,t)}{C_{\mathrm{N}}(x,t)} = \sqrt{\left(\frac{t_{\mathrm{N}}}{t}\right)^{3}} \exp\left[\frac{1-\frac{t_{\mathrm{N}}}{t}}{4t_{\mathrm{N}}t_0}\left(P_{\mathrm{D}} - \frac{t_{\mathrm{N}}t}{P_{\mathrm{D}}}\right)\right] \tag{2}$$

with boundary conditions:

$$\begin{aligned} C_{\mathrm{f}}(0,t) &= \frac{M}{Q}\delta(t) \\ C_{\mathrm{f}}(\infty,t) &= 0 \\ C_{\mathrm{f}}(x,t) &= 0 \end{aligned}$$

where C_{f} is the tracer concentration in water, C_{N} is the normalized concentration, t_0 is the mean transit time, t is the time variable, t_{N} is the time after injection when normalized concentration was observed, x is the distance between the injection and the observation point and P_{D} is a dispersion parameter. Dispersion parameter P_{D} is related to the dispersion coefficient by:

$$P_{\mathrm{D}} = \frac{D}{v \times x} \tag{3}$$

where D is in this case the vertical dispersion coefficient and v is the mean flow velocity.

The analytical results are presented in ‰ δ^2H [difference between the measured ratios of the sample and reference VSMOW (Vienna Standard Mean Ocean Water)]. Because the basis of the analytical best-fit model is the concentration of the tracer (mg/m^3), the ‰ δ^2H values of results had to be converted. The mg/l concentrations of ^{2}H were calculated from the slightly modified equation published by Becker and Coplen (2001) taking into account the influence of the density of water.

$$\mathrm{Deuterium_{conc}} = 34.721\left[\frac{1,000 + \delta D_{\mathrm{VSMOW}}}{1,000}\right] \tag{4}$$

Results and discussion

Deuterium

The deuterium tracer was detected in all ten sampling points (Fig. 3). The maximal concentration of tracer at each single measuring point does not depend on depth or distance from the lysimeter surface. The highest values of δ^2H (3,100‰) occurred in the first sampling point JV-1 immediately after tracer injection. This is most likely a consequence of intensive irrigation at the time of tracing injection or its contamination. Beside at JV-1, the successive maximum values were detected at sampling points JV-5 (572.94‰) and JV-8 (315.7‰). At the other observation point maximum values were below 200‰. Based on the analytical results, it was possible to construct breakthrough curves for all observation points which together with precipitation amount at the time of the tracing experiment are presented in Fig. 3. The graphs show that a clear recognition of tracer effect started at the end of May 2005 at sampling points JV-2, JV-5 and JV-4. From May until the middle of July there was a period of high precipitation at which time the changes in the δ^2H values at all the other sampling points were recognized too. From the plot of precipitation and δ^2H values it is evident that the high intensity and amount of precipitation forced the appearance of the tracer at the different observation points at the same time. The last reacting sampling point was JV-7. Amplitude peaks and lengths of the breakthrough curves are different. In some higher located sampling points (JV-1, JV-2, JV-3, JV-4) in spring 2005 there was no tracing signal, and by August 2005 no tracer effect was recognized in any of sampling points.

Obtaining more information about the tracer movement in time is possibly recognized from the profiles in Fig. 4. In June 2004 with the exception of JV-3 the upper sampling points already reacted (Fig. 4a). At that time the values at JV-2 reached the peak. In July the increase in deuterium values was apparent at all the sampling points except in JV-7 (Fig. 4b), while the maximum values occurred at sampling points JV-1, JV-4 and JV-5. At the end of August (Fig. 4c), the peaks of tracer values reached deeper in lysimeter at JV-3, JV-6, JV-8, JV-9 and JV-10. At other upper points, the values had already decreased. The suffocation of tracer signal was recognized in October 2004 (Fig. 4d), but at that time also JV-7, which delayed, reached the maximum value. After that time all values of deuterium decreased. These profiles show that the water flow through sampling points JV-3 and JV-7 is slower than at other points.

On the basis of methods described in the previous section, the fastest flow velocity and dominant flow velocity were calculated (Table 1). Based on the results of tracing experiment, estimations of the mean flow velocity and vertical dispersion (Table 1) were made by analytical best-fit method. One-dimensional convection–dispersion model with standardizing values for single porosity was used. Figure 5 shows best-fit curves for all sampling points except JV-1.

The fastest flow velocity shows (Table 1) an extremely fast connection of sampling point JV-5 with the surface (0.102 m/day). Other values of fastest flow velocity rise with depth from 0.023 to 0.071 m/day, but this is only apparent. From the breakthrough curves, precipitation and the first detection time of the tracer it can be observed that the influence of a strong rain event on the tracer is reflected in the measuring points. In the rain period during June 2004, in the deepest sampling points from JV-6 to JV-10 (except JV-7) the recognition of tracer occurred simultaneously. Because of the different depth position of the sampling points and because of the recognition of tracer at the same sampling time it seems that velocity increases with depth. Irrespective of this, it is important for the estimation of the fastest flow velocity to assess the probability of fastest pollution effect on the aquifer through the unsaturated zone.

Dominant flow velocity is connected with the time of highest concentration. The graph of precipitation and δ^2H values shows that also the occurrence of highest δ^2H values coincide with the stronger precipitation event. The lowest values of dominant velocity occurred in JV-3 and JV-7 (0.014–0.015 m/d), JV-6 has dominant flow velocity 0.19 m/day, in other sampling

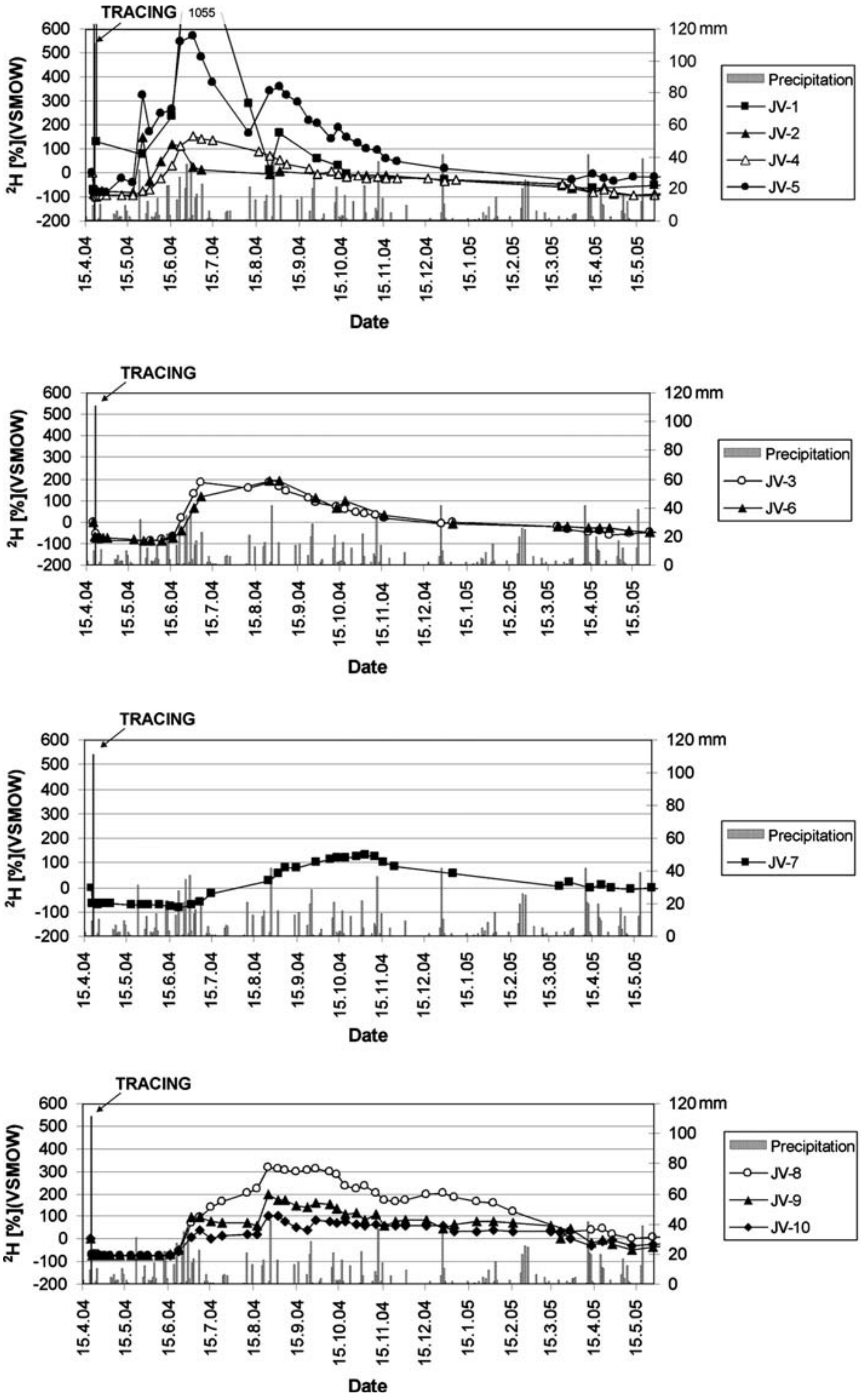


Fig. 3 Deuterium breakthrough curves and precipitations during the tracing experiment

points dominant flow velocity ranges from 0.21 to 0.33 m/day (Table 1).

The best evaluation of the matrix water flow is the mean flow velocity (Table 1). Through the entire lysimeter the estimation of mean flow velocity based on ^{2}H concentrations is 0.014–0.017 m/day, except in sampling points JV-3 and JV-7, where it is 0.008–0.011 m/day. Dispersion increased from the top of lysimeter to the bottom. If the first measuring point is omitted, the highest dispersion coefficient is reached in JV-10 0.015 m^{2}/day.

Discharge volume of water in the drain systems was measured as a water volume in the water collector. In the winter from January 2005 until snow melting in

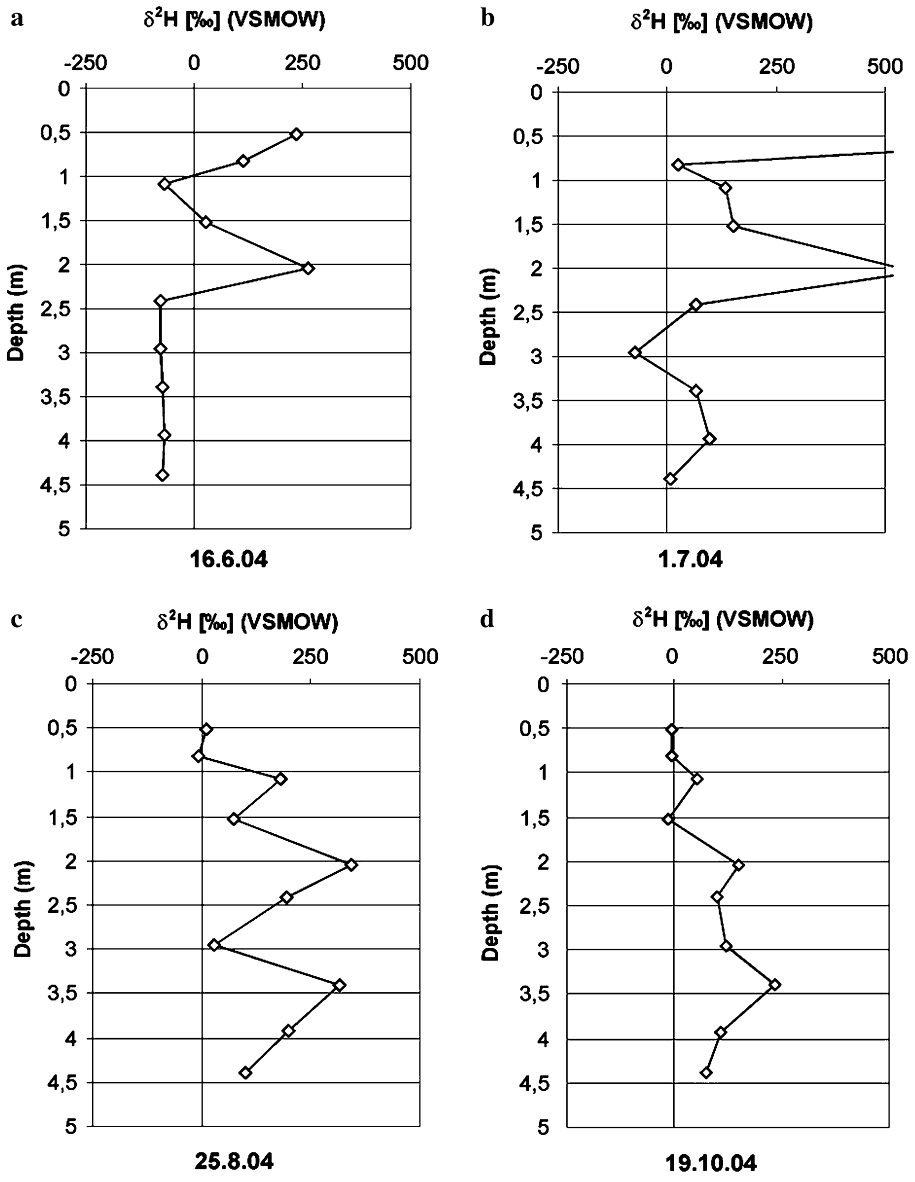


Fig. 4 Vertical reviews of δ^2H values of water in unsaturated zone. **a** Perception of the tracer signal in June 2004. **b** Strengthening of the tracing signal (July 2004). **c** Moving of the tracing signal downwards in lyimeter (August 2004). **d** Suffocation of the tracing signal (October 2004)

March 2005 there was no outflow water from JV-1 up to sampling point JV-7 included. Because of snow cover and frozen soil there were no conditions for water flow in the unsaturated zone. At different periods and at different sampling points there were also the same short stopping of the tubes and the measuring of outflow water volume is incorrect. However, from cumulative values of outflow water volume (Table 2) the discharge dynamics can be evaluated. From the initial injection to 21st July 2005 at the deepest sampling point the outflow volume of the water was about 400 l. The next most productive drain was JV-8 with 258 l. The deepest sampling point drains discharge more groundwater from unsaturated zone (JV-10, JV-

Table 1 Calculated fastest, dominant and mean flow velocities of deuterium tracer

	JV-1	JV-2	JV-3	JV-4	JV-5	JV-6	JV-7	JV-8	JV-9	JV-10
Distance (m)	0.52	0.82	1.08	1.52	2.04	2.41	2.95	3.4	3.93	4.39
Fastest f. (m/day)	0.520	0.023	0.023	0.043	0.102	0.043	0.042	0.055	0.070	0.071
Dom. f. (m/day)	0.520	0.023	0.014	0.021	0.029	0.019	0.015	0.027	0.031	0.033
Mean f. (m/day)	–	0.014	0.008	0.014	0.017	0.017	0.011	0.015	0.017	0.016
Dispersion (m^2/s)	0.488	0	0.001	0.002	0.005	0.003	0.004	0.007	0.011	0.015

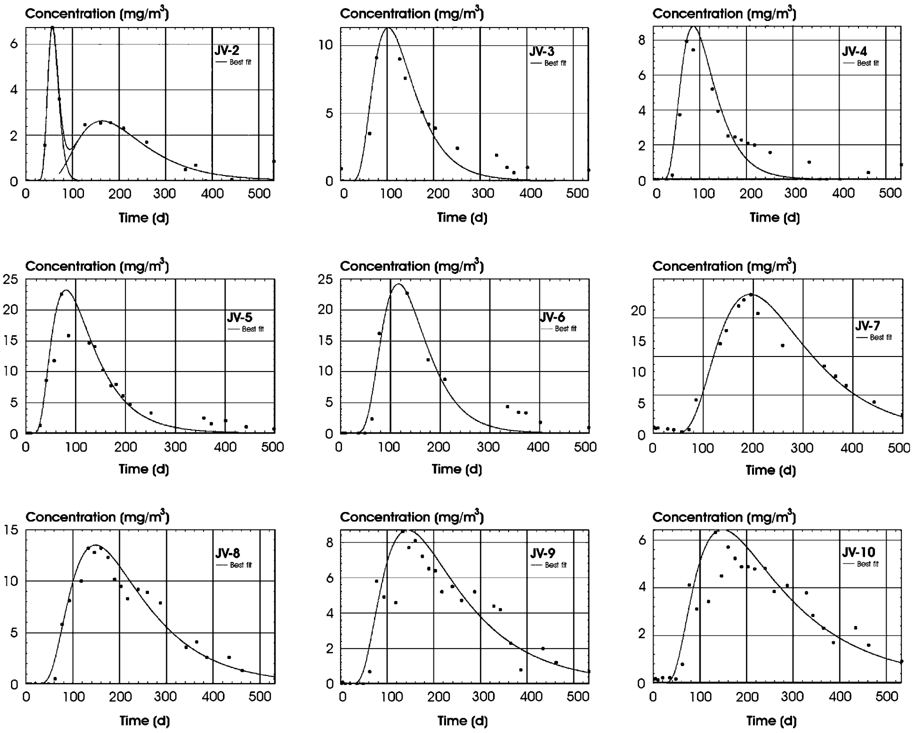


Fig. 5 Best-fit curves for deuterium concentrations by convection–dispersion model for all sampling points in lysimeter

9, JV-8) than the upper sampling points (JV-1, JV-2, JV-3). In the gravel deposit deeper than 3 m from the ground (JV-8, JV-9, JV-10), the field capacity was constantly high, so vertical water flow existed all the time. Other points were affected more by the dry conditions during the periods of low precipitation and ground frost.

Tracer recovery was estimated based on outflow water volume and ^{2}H concentrations. Table 2 shows the quantities, percentages of recovered and injected deuterium tracer by the sampling points. Until the end of July 2005, 4,573 mg of ^{2}H were calculated in collected outflow water which presents 3.78% of the total injected tracer. The largest quantities of deuterium tracer were coming out at sampling points JV-8 and JV-10, 1,297 and 947 mg, which account for 30 and 22% of the all recovered tracer and 0.8–1% of the total injected tracer each. In the remaining sampling points tracer recovery values were in the range between 32 and 678 mg representing 0.77–16% of all recovered tracer and 0.03–0.6% of the whole injected tracer. At JV-1 almost all recovered tracer came out in the first day after injection. If this amount of tracer is not considered, 30 mg of ^{2}H is recovered in this point.

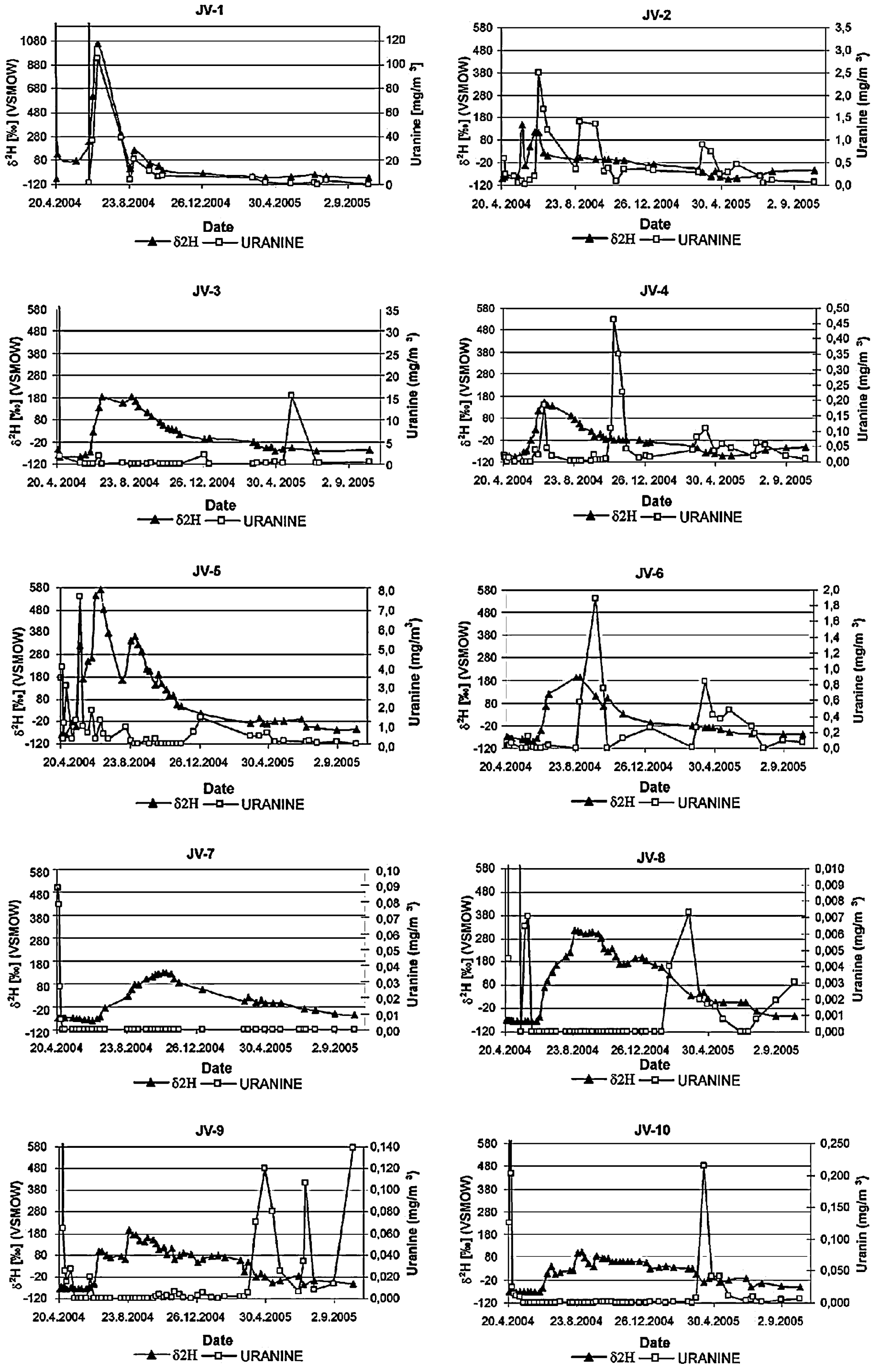
Uranine

Uranine was detected at all sampling points. In the first 2 days after injection of the tracers very high uranine concentrations occurred in several sampling points (JV-1, JV-3, JV-5, JV-7, JV-8, JV-9, JV-10), after which concentrations declined. At sampling point JV-7, there was no more uranine detected until the end of the tracing experiment. It cannot be excluded that contamination of some sampling point happened at the time of tracer injection. Breakthrough curves of uranine (Fig. 6) show that higher concentrations of uranine appear impulsively, depending on the quantity and intensity of precipitation. A comparison of the deuterium and uranine breakthrough curves shows that the results of deuterium tracing give more regular distribution of tracer than uranine which shows a strong impulsive

Table 2 Cumulative outflow water volume and recovery amount of deuterium tracer

	JV-1	JV-2	JV-3	JV-4	JV-5	JV-6	JV-7	JV-8	JV-9	JV-10	Cumulative
Outflow water volume (l)	4.93	18.35	23.92	96.47	105.39	35.93	82.75	258.13	161.22	398.62	
Amount of recovery tracer (mg)	221.49	32.44	58.77	153.47	678.11	49.24	136.79	1,297.89	618.24	947.75	4,194.20
% of recovery tracer amount (%)	5.28	0.77	1.40	3.66	16.17	1.17	3.26	30.94	14.74	22.60	100.00
% of whole amount of tracer (%)	0.18	0.03	0.05	0.13	0.56	0.04	0.11	1.07	0.51	0.78	3.47

Fig. 6 Comparison of deuterium and dye breakthrough curves



appearance of tracer (Fig. 6). If the increase of uranine concentration during the first 2 days is not considered, a delay in the appearance of the uranine tracer compared with deuterium is recognized. At sampling point JV-1 breakthrough curves of deuterium and uranine tracer have the same shape at the same time. A maximum concentration of dye at sampling point JV-5 coincides with the first higher increase in deuterium values during a period of high precipitation in May 2004. At the other sampling points the maximum concentrations of uranine lag behind that of deuterium. At deepest points (JV-8, JV-9, JV-10), plots indicate that the actual uranine occurrence should have happened after the end of the tracing experiment.

Table 3 gives the estimation of water flow velocity obtained from the uranine tracing results. Because the dye tracer appeared almost immediately after injection on a count of contamination, the maximum velocity has not been determined. Based on the knowledge of the aquifer and water flow properties in the lysimeter system, the concentrations of the first few days were omitted from the calculation of dominant velocity. The maximal concentrations of dye tracer after this period were taken into account. For sampling points JV-3 and JV-7 there were no typical breakthrough curves. Lower dominant velocity is established at sampling points JV-1 and JV-4 (0.007–0.008 m/day). The highest dominant flow velocity, 0.058 m/day, is found out at JV-5. Dominant velocity for other sampling points moves from 0.010 to 0.013 m/day. Analytical best-fit method with computer program TRACI'95 was used to estimate mean flow velocity with uranine concentration breakthrough curves for sampling points JV-2, JV-4, JV-6, JV-8, JV-9 and JV-10. Calculation was made for typical (significant) signals. Among these sampling points the lower mean flow velocity, 0.008 m/day, was established at sampling point JV-4. Mean flow velocity at other points is between 0.010 and 0.015 m/day. The uranine tracer recovery was poor reaching only 0.001% of the total injected tracer.

Comparison of deuterium and dye tracer

Breakthrough curves of both tracers show retardation in maximum values of dye compared with deuterium. It is presumed that the retardation and impulsive increase of dye tracer concentrations are the result of sorption–desorption processes. With sorption the immobilization of a substance dissolved in water onto the surface of grains in the aquifer occurs, and desorption releases the substance back into solution. A portion of the tracer is always unavailable for transport, as it is fixed to the rock. Only the part of the tracer dissolved in the water can be transported away. As soon the portion of the originally sorbed dye tracer dissolves, it can also be transported. These processes slow down the transport, as large parts of the tracer are immobilized on the solid phase for part of the time.

The calculation of the retardation factor for the uranine was made using results of a convection–dispersion model for the estimation of mean flow velocity. Only sampling points JV-2, JV-4, JV-6, JV-8, JV-9 and JV-10 were included because for these points analytical approaches to calculate mean flow velocity for uranine data could be performed. The retardation factor R was calculated by:

$$R = \frac{v_{\mathrm{aD}}}{v_{\mathrm{au}}} \tag{5}$$

where R is retardation factor, v_{aD} is mean flow velocity of the deuterium tracer and v_{au} is mean flow velocity of the uranine. The range of retardation factor (Table 3) is from 1.133 (JV-6) to 1.75 (JV-4). Usually retardation factors for different tracers are determined by laboratory tests. The results correspond to the published retardation factors for uranine in gravel media determined in the laboratory. Based on column tests, Klotz (1982) reported retardation factor for uranine 1.13 (0.99–1.22) in gravely sand. Values from modelling tests were slightly higher but less than 2.

Based on δ^2H value profiles, breakthrough curves of both tracers, calculations of different flow velocity parameters and recovery curves of deuterium as a tracer, a strong preferential flow is assumed at sampling point JV-5. Recovery amounts of the deuterium tracer show that at higher amounts, the tracer comes out through sampling points JV-8 (30% of recovered tracer). Besides JV-5 at JV-8, the highest values of δ^2H were signed and JV-8 sampling point location is below JV-5. For these reasons, conclusions about preferential flow appearance on the left (north) side of the lysimeter observation wall can be made.

Conclusions

A lysimeter tracing experiment showed that deuterated water is a more suitable tracer than uranine for the study of water flow properties in unsaturated zone. Both tracers appeared at the sampling points and their arrival to single sampling points was related in both cases to the intensity and amount of precipitation. Uranine that came in sight was very impulsive (Fig. 6) and its breakthrough curves showed several peaks, for

Table 3 Calculated dominant, mean flow velocity and retardation factor of uranine

	JV-1	JV-2	JV-3	JV-4	JV-5	JV-6	JV-7	JV-8	JV-9	JV-10
Distance (m)	0.52	0.82	1.08	1.52	2.04	2.41	2.95	3.4	3.93	4.39
Dom. f. (m/day)	–	0.013	–	0.008	0.058	0.015	–	0.010	0.011	0.012
Mean f. (m/day)	–	0.012	–	0.008	–	0.015	–	0.012	0.01	0.012
R_{d}-mean flow	–	1.167	–	1.750	–	1.133	–	1.250	1.700	1.333

which it is difficult to recognize any significant breakthrough curve. On the other hand, the results of deuterium tracer showed a typical breakthrough curve (Fig. 3). The retardation factor of the dye as compared with deuterium was 1.13–1.75, which is in agreement with previously published results. Deuterated water is thus a useful tracer to detect water movement, while the use of uranine may reflect organic compounds transport. In this study, deuterium was confirmed as an ideal conservative tracer for tracer studies in the unsaturated zone.

Based on results of tracing experiment some properties of coarse gravel unsaturated zone at the location of the lysimeter could be described. Results generally show that the water discharge in the drain system and dispersion coefficient for deuterium increase with the depth. The estimation of the mean flow velocity of the matrix flow is between 0.014 and 0.017 m/day (Table 1). If it is assumed that the ground water level is 27-m deep, it could be concluded that the mean residence time through unsaturated zone in Selniška Dobrava coarse gravel aquifer is 4.4–5.4 years. For groundwater protection and for measures performed because of this protection, the first arrival of the tracer through unsaturated zone is important. If it is accepted that the pollutant behaves like a conservative tracer, and with the estimation of the fastest flow velocity in lysimeter in the range 0.1–0.07 m/day (Table 1), a pollutant can reach groundwater in 9–12 months. Based on the dominant flow velocity 0.03 m/day the percolation time is 2.5 years.

Even if the aquifer of Selniška Dobrava is treated as homogeneous, there are some differences in the results between single observation points that show distinctions in local unsaturated zone structure. The heterogeneous matrix in micro-scale causes the differences in water flow. Results (profiles δ^2H values, breakthrough curves of both tracers, calculations of different flow velocity parameters and recovery curves of deuterium) show that on the north side of lysimeter observation wall more preferential flows occur. It can be concluded, that also in the unsaturated zone, especially in the high-permeable coarse gravel aquifer the local structure of the unsaturated zone has great influence on the water flow properties.

Tracing with artificial tracers, especially with deuterated water, was found as a very useful tool to assess the properties of water flow in the unsaturated zone also of a coarse gravel aquifer. On the basis of the determined range of the water flow properties the estimations of groundwater recharge, pollution influence on aquifer and groundwater protection measures can be provided.

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References

Aeby P, Schultze U, Braichotte D, Bundt M, Moser-Boroumand F, Wydler H, Fluhler H (2001) Fluorescence imaging of tracer distributions in soil profiles. Environ Sci Technol 35:753–760

Becker MW, Coplen TB (2001) Use of deuterated water as a conservative artificial groundwater tracer. Hydrogeol J 9:512–516

Behrens H (1970) Zur Messung von Fluoreszenzfarbstoffen (measuring of fluorescent dyes). Inst. f. Radiohydrometrie, Jahresbericht 1969, GSF-Bericht R 25, pp 92–96

Biggar JW, Nielsen DR (1976) Spatial variability of the leaching characteristics of a field soil. Water Resour Res 12:78–84

Fank J, Berg W (2001) Tracers in unsaturated zone—results from experimental sites—test site Leibnitz, Strya, Austria. In: ATH (ed) Tracer studies in the unsaturated zone and groundwater (investigations 1996–2001). Beiträge zur Hydrogeologie 52:25–38

Flury M, Fluhler H (1995) Tracer characteristics of brilliant blue FCF. Soil Sci Soc Am J 59:22–27

Jabro JD, Lotse EG, Fritton DD, Baker DE (1994) Estimation of preferential movement of bromide tracer under field conditions. J Hydrol 156:61–71

Jury WA (1982) Simulation of solute transport using a transfer function model. Water Resour Res 18:363–368

Kasnavia T, Vu D, Sabatini DA (1999) Fluorescent dye and media properties affecting sorption and tracer selection. Ground Water 37:376–381

Ketelen H, Meyer-Windel S (1999) Adsorption of brilliant blue FCF by soils. Geoderma 90:131–145

Klotz D (1982) Verhalten hydrologischer Tracer in ausgewählten Sanden und Kiesen (characteristics of hydrological tracers in sand and gravel deposits). GSF-Bericht 290:17–29

Kogovšek J, Šabela S (2004) Water tracing through the vadose zone above Postojnska Jama, Slovenia. Environ Geol 45:992–1001

Kung KJS, Steenhuis TS, Kladivko EJ, Gish TJ, Bubenzer G, Helling CS (2000) Impact of preferential flow on the transport of adsorbing and non-adsorbing tracers. Soil Sci Soc Am J 64:1290–1296

Leis A, Benischke R (2004) Comparison of different stable hydrogen isotope-ratio measurement techniques for tracer studies with deuterated water in the unsaturated zone in groundwater. In: Paper presented at the 7th workshop of European Society for Isotope Research (ESIR), Berichte des Institutes für Erdwissenschaften Karl-Franzes-Universität Graz, Seggauberg, 27 June–1 July 2004

Maciejewski S, Maloszewski P, Stumpp C, Klotz D (2006) Modelling of water flow through typical Bavarian soils (Germany) based on lysimeter experiments: 1. Estimation of hydraulic characteristics of the unsaturated zone. Hydrol Sci J 51(2):285–297

Mali N, Janža M (2005) Ocena možnosti zajema podzemne vode z uporabo MIKE SHE programskega orodja za hidrogeološko modeliranje (evaluation of water resource exploitation options using the MIKE-SHE integrated hydrogeological modelling package—case study Selniška Dobrava). Geologija 48/2:281–294

Maloszewski P, Maciejewski S, Stumpp C, Stichler W, Trimborn P, Klotz D (2006) Modelling of water flow through typical Bavarian soils (Germany) based on lysimeter experiments: 2. Environmental deuterium transport. Hydrol Sci J 51(2):298–313

Morrison J, Brockwell T, Merren T, Fourel F, Philips AM (2001) On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. Anal Chem 73:3570–3575

Mortensen AP, Jensen KH, Nilsson B, Juhler RK (2004) Multiple tracing experiments in unsaturated fractured clayey till. Vadose Zone J 3:634–644

Nützmann G, Stichler W (2001) Tracers in the unsaturated zone—results from experimental sites—Berlin test site. In: ATH (ed) Tracer studies in the unsaturated zone and groundwater (investigations 1996–2001). Beiträge zur Hydrogeologie 52:19–25

Öhrström P, Hamed Y, Persson M, Berndtsson R (2004) Characterizing unsaturated solute transport by simultaneous use of dye and bromide. J Hydrol 289:23–35

Rank D, Papesch W, Rajner V, Steiner KH, Vargay Z (2001) Tracers in unsaturated zone—results from experimental sites—lysimeter study on infiltration processes in the sandy soil of the Great Hungarian Plain. In: ATH (ed) Tracer studies in the unsaturated zone and groundwater (investigations 1996–2001). Beiträge zur Hydrogeologie 52:60–73

Schoen R, Gaudet JP, Bariac T (1999) Preferential flow and solute transport in a large lysimeter, under controlled boundary conditions. J Hydrol 215:70–81

TRACI'95 (1998) Computer program. In: Kass W (ed) Tracing techniques in geohydrology. A.A. Balkema, Rotterdam

Van der Hoven SJ, Solomon DK, Moline GR (2002) Numerical simulation of unsaturated flow along preferential pathways: implications for the use of mass balance calculations for isotope storm hydrograph separation. J Hydrol 268:214–233

Veselič M, Čenčur-Curk B (2001) Test studies of flow and solute transport in the unsaturated fractured and karstified rock on the experimental field site Sinji Vrh, Slovenia. In: Seiler KP, Wohnlich S (eds) New approaches characterizing groundwater flow. Proceedings of the XXXI IAH congress, Munich, 10–14 September 2001. A.A. Balkema, Rotterdam, pp. 211–214

Wild A, Babiker IA (1976) The asymmetric leaching pattern of nitrate and chloride in loamy sand under field conditions. J Soil Sci 27:460–466

Yasuda H, Berndtsson R, Persson H, Bahri A, Takuma K (2001) Characterizing preferential transport during flood irrigation of a heavy clay soil using the dye Vitasyn Blau. Geoderma 100:49–66