



Assessment of nitrate transport in the unsaturated (coarse gravel) zone by means of tracing experiment (Selniška dobrava, Slovenia)

Ocena transporta nitrata v nezasičeni coni prodnega vodonosnika s sledilnim poskusom (Selniška dobrava, Slovenija)

Nina MALI & Anja KOROŠA

Geological Survey of Slovenia, Dimičeva ul. 14, SI-1000 Ljubljana, Slovenia;
e-mail: anja.korosa@geo-zs.si

Prejeto / Received 9. 11. 2015; Sprejeto / Accepted 17. 12. 2015; Objavljeno na spletu / Published online 30. 12. 2015

Key words: nitrate transport, unsaturated zone, lysimeter, coarse gravel aquifer, tracing experiment

Ključne besede: transport nitrata, nezasičena cona, lizimeter, prodnati vodonosnik, sledilni poskus

Abstract

Nitrate pollution in groundwater, originating mainly from agricultural activities, remains a worldwide issue. This is also pertinent to Slovenia, where nitrate leaching from agricultural areas is one of the major groundwater resource management problems. The contamination spread in the aquifer is directly related to the hydraulic properties of the upper, unsaturated and the lower, saturated zone. The article presents study of water and nitrate pollution transport in the unsaturated zone in a field laboratory – lysimeter in Selniška dobrava. Water and nitrate transport parameters were estimated by a combined tracing experiment with deuterated water and $\text{Ca}(\text{NO}_3)_2$. Deuterium was used as a conservative tracer of water movement, and $\text{Ca}(\text{NO}_3)_2$ was used as a nitrate tracer in the unsaturated zone. The $\delta^2\text{H}$ and nitrate concentrations in the unsaturated zone water were measured monthly during the period from April 2006 to July 2007. All together 36 samplings were performed. 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 the one-dimensional convection–dispersion model. The results were used to estimate the nitrate transport parameters in the coarse gravel aquifer Selniška dobrava. They can be used also for nitrate transport estimations in other aquifers with similar hydrogeological characteristics and can serve as a base for determining the measures for nitrate reduction in groundwater.

Izvleček

Onesnaženje podzemne vode z nitratom, ki izvira predvsem iz kmetijske dejavnosti, še vedno ostaja v svetu velik problem. To velja tudi za Slovenijo, kjer je spiranje nitrata iz kmetijskih površin eden glavnih problemov pri upravljanju z viri podzemne vode. Širjenje onesnaženja v vodonosniku je neposredno povezano s hidravličnimi lastnostmi zgornje nezasičene in spodnje nasičene cone. Članek predstavlja študijo prenosa vode in onesnaženja z nitratom v nezasičeni coni v terenskem laboratoriju – lizimetru v Selniški dobri. Prenos vode in nitrata smo ocenili s kombiniranim sledilnim poskusom z uporabo devterijeve vode in $\text{Ca}(\text{NO}_3)_2$. Devterijevo vodo smo uporabili kot konzervativno sledilo, $\text{Ca}(\text{NO}_3)_2$ pa smo uporabili kot sledilo nitrata. V vodi nezasičene cone smo mesečno merili $\delta^2\text{H}$ in koncentracije nitrata v obdobju od aprila 2006 do julija 2007. Opravili smo 36 vzorčenj. Najhitrejša in dominantna hitrost toka smo izračunali na podlagi časa injiciranja, prvega pojava sledila in časa pojava najvišjih koncentracij. Povprečno hitrost toka in vertikalno disperzijo smo ocenili z analitično metodo, z uporabo enodimenzionalnega konvekcijsko-disperznega modela. Rezultate smo uporabili za oceno parametrov transporta nitrata v vodonosniku s podobnimi lastnostmi, visoko prepustnem vodonosniku Selniška dobrava. Rezultati raziskave se lahko uporabijo za oceno transporta nitrata tudi na drugih vodonosnikih s podobnimi hidrogeološkimi pogoji in lahko služijo kot osnova za določitev ukrepov za zmanjšanje pojavov nitratov v podzemni vodi.

Introduction

It is well known that groundwater contamination from agricultural nonpoint sources is one of the major pollution problems (LOCKHART et al., 2013; WANG et al., 2013; LOPEZ et al., 2015), often occurring as the result of anthropogenic activities, lack of management, and over-exploitation of groundwater

resources (PISCIOTTA et al., 2015). Excess nitrogen from agricultural fertilizers and manure poses a significant environmental issue (KRONVANG et al., 2009; REFSGAARD et al., 2015), pertaining also to Slovenia, where nitrate leaching from agricultural areas is one of the major groundwater resource management problems. In the last few decades in Slovenia, nitrate concentrations in granular

aquifers on same places have increased, mainly as a consequence of the agricultural application of manure and fertilizers (EARS, 2014). The excessive use of chemicals and fertilizers increases the risk of groundwater pollution. Thus, the prevention of contamination is the primary strategy of water quality management (ČEPLIČA et al., 2004).

The prevention, control and combat of groundwater pollution are addressed in various European Union (EU) and national legislative acts (PISCIOTTA et al., 2015). The EU Water Framework Directive (EC, 2000), WFD, and its daughter Directive on the Protection of groundwater against Pollution (EC, 2006), GWD, establish criteria for the characterization of groundwater status (quality and quantity). Regarding nitrates, GWD sets the quality standard for assessing groundwater chemical status at 50 mg/l. Moreover, the Nitrates Directive (EEC, 1991) is an integral part of the WFD and it was drawn up with the specific purpose to reduce water pollution caused by nitrates from agricultural sources, and to prevent further pollution from nitrates. EU members are required to identify waters affected by nitrate pollution and designate nitrate vulnerable zones. Slovenia acknowledged this directive with a national regulation The Water Act (OFFICIAL GAZETTE, 67/2002, 110/2002, 2/2004, 41/2004, 57/2008, 57/2012), and the Regulation on the protection of waters against pollution caused by nitrates from agricultural sources (OFFICIAL GAZETTE, 113/09, 5/13, 22/15).

Nitrogen is a widely used plant nutrient, which is essential for the growth and development of a healthy crop. Excessive application of nitrogen fertilizers can lead to significant nitrate leaching out of the root zone, because plant uptake and microbial immobilization cannot remove the entire nitrate from the solution (PRATT & ADRIANO, 1973). Nitrate is not actively absorbed by roots and has a high potential to move downwards. So the amount of nitrate lost is dependent on the quantity of nitrate available to be leached. Other factors affecting nitrate leaching are the precipitation-intense rainfall events or surplus of water provided by irrigation, evapotranspiration, drainage, soil texture, soil porosity, occurrence of preferential flow paths, etc. (WU et al., 1997; CAMERIA et al., 2003).

Since nitrate is soluble, it has high mobility and is thus easily leached from the unsaturated zone (VINOD et al., 2015). So, the spread of contamination in the aquifer is directly related to the hydraulic properties of the upper unsaturated and lower saturated zone (SEILER & ZOJER, 2001). In order to solve this problem it is very important to determine the hydraulic properties of materials in the unsaturated zone and pollutant transport through the unsaturated zone. The unsaturated zone largely controls groundwater recharge by retaining precipitation, while at the same time providing preferential flow paths for infiltration (KERZIMINSKA et al., 2014). The determination of unsaturated zone properties is an important point

to be tackled for an advanced understanding of hydrological systems. The residence time of water and its distribution within the aquifer may help to define the vulnerability of the groundwater system (SCHWIENIEK et al., 2009). Furthermore, it presents the time span provided for attenuation processes (dispersion, diffusion, and sorption). Therefore, it is crucial for scientific studies and for water resources management to know the transport characteristics and velocities within the investigated system (SCHWIENIEK et al., 2009).

Nitrate transport was studied with tracer experiments using a lysimeter facility in the Selniška dobrava aquifer, which lies in the north-east of Slovenia. The aim of this study was to describe the nitrate transport processes in a high-permeable coarse gravel unsaturated zone by means of a tracing experiment. The lysimeter was designed on the basis of previous hydrogeological investigations in the area (MALI et al., 2007). A combined tracing experiment was performed using both deuterated water and calcium nitrate as fertilizer. Conservative tracers are necessary to obtain groundwater transport properties. Deuterated water is known as a very useful tracer for this purpose (BECKER & COPLEN, 2001; MALI et al., 2007) due to its conservative behavior. Moreover, deuterated water is easy to handle, simple to analyse, non-toxic, and has a reasonable price. Compared to other groundwater tracers, deuterium shows the highest degree of conservativeness (LEIS & BENISCHKE, 2004), therefore it was chosen to study water movement.

The EU WFD (EC, 2000) requires an additional reduction of nitrate load, which will be very costly for the agricultural sector. To improve the groundwater quality status of groundwater bodies at risk, measures must be taken. For this purpose, it is necessary to determine the mass balance of nitrogen from the application to their occurrence in groundwater. The objective of this study was to determine the nitrate transport properties and velocity through the unsaturated zone of a gravel aquifer Selniška dobrava with a tracing experiment. One of the aims is to specify parameters of nitrate transport in coarse gravel unsaturated zone which will be used to model nitrate transport in other aquifers with similar hydrogeological characteristics such as for example Dravsko polje, which was declared as a water body at risk due to the presence of nitrate.

Material and methods

Lysimeter area description

The lysimeter is located in the area of the principal aquifer of Selniška dobrava, in the north-east of Slovenia (Fig. 1) (X = 5154641, Y = 5536401 according to Gauss-Krüger). The main aquifer Selniška dobrava can be classified as an intergranular aquifer of high permeability (MALI

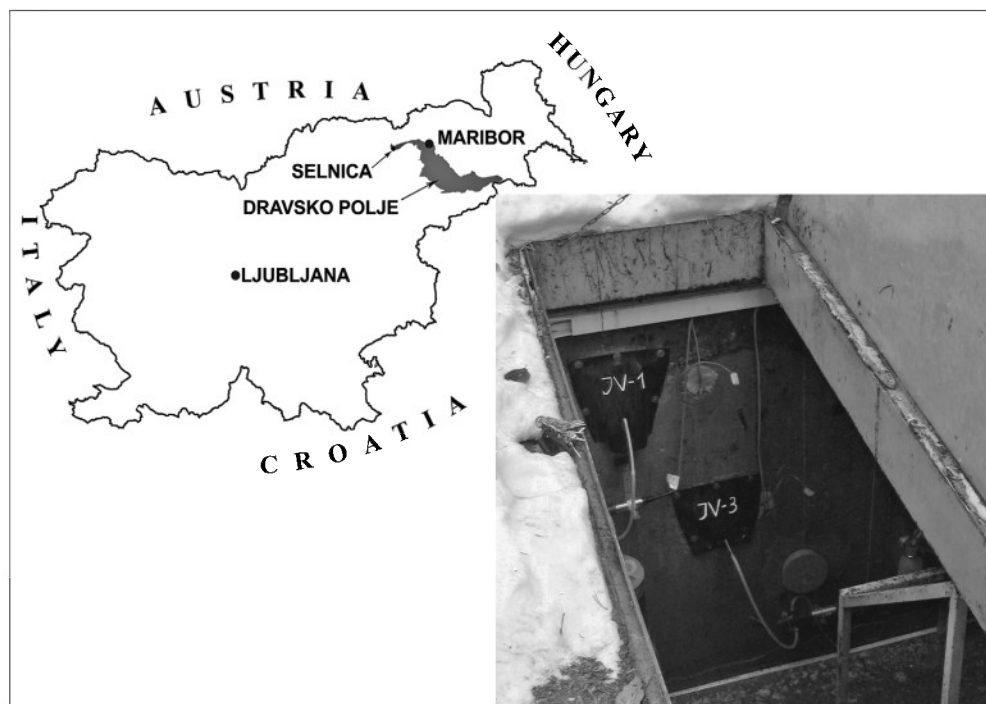


Fig. 1. Study area location
Sl. 1. Območje raziskav

et al., 2005; MALI, 2006). The thickest coarse gravel deposit is estimated at about 50 m. Thickness of unsaturated zone is specified from 25 to 37 m on the average. Thickness of the saturated layer along the aquifer is estimated at 7-14 m, and even more in the deepest sections (MALI et al., 2005; MALI, 2006). The hydraulic conductivity of the coarse gravel aquifer is estimated to be 5×10^{-3} m/s (MALI & JANŽA, 2005). The area has a moderate continental climate of central Slovenia with a typical continental precipitation regime and an average annual rainfall between 1200 and 1300 mm. The average annual air temperature lies between 8 and 12 °C (MALI & JANŽA, 2005).

The larger area of the lysimeter location is covered by mixed forest. The soil at this location was defined as distric cambisol (GOSAR, 2000). The hydraulic conductivity of the soil was estimated at $1.5-4.5 \times 10^{-5}$ m/s by double ring infiltrometer method (MALI, 2006). The gravel at lysimeter location consists of metamorphic rock and carbonates (limestone, marble-sandstone, marble and agglutinated carbonate gravel). In places, the gravel is incrustated by calcite. Based on granulometric analyses the hydraulic conductivity of the coarse gravel was estimated at $2.9 \times 10^{-3}-6.9 \times 10^{-2}$ m/s (MALI, 2006).

Experimental set-up

The lysimeter site is designed as a field laboratory (Fig. 2). Dimensions are 2 m × 2 m, 5 m deep, with walls 0.2 m thick. There are 10 sampling and measuring points at different depths (from JV-1 to JV-10) with approximately equal distances by depth. For groundwater sampling in the unsaturated zone drainage samplers connected to a water sampling system were installed (MALI, 2006). A detailed description of the lysimeter is in previously published papers (MALI et al. 2007; MALI & URBANC, 2009).

Deuterium and nitrate tracing experiment

The tracing experiment was performed in 20th of April 2006 after a period of intensive snow melting. Water and nitrate transport processes were assessed by a combined tracing experiment with deuterated water and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$). Deuterium was used as a conservative tracer of water movement, and $\text{Ca}(\text{NO}_3)_2$ was used as a tracer of nitrate in an unsaturated zone. Before tracer injection, irrigation with groundwater was performed to reach good field capacity. 1.2 kg of $\text{Ca}(\text{NO}_3)_2$ and 1000 ml of D_2O (70%) were dissolved in 50 l of pumped groundwater in barrel and injected by sprinkler irrigation. After injection the tracer was again splashed by irrigated groundwater. The area of irrigation was 9.5 m². The distribution of the artificial rainfall was controlled by 10 precipitation measuring points. The average amount of irrigated water was 50 mm.

Sampling and analytical methods

The $\delta^2\text{H}$ values and nitrate concentrations in the unsaturated zone water were measured monthly during the period from April 2006 to July 2007. During the first period, samples were collected at 14-day intervals, and then the sampling period was extended to one month. All together 36 samplings were performed.

Measurements for $\delta^2\text{H}$ were carried out in the laboratory of Joanneum Research Forschungsgesellschaft mbH, Institute of Water Resources Management, Hydrogeology and Geophysics, and chemical analyses of samples for nitrate were carried out in laboratory of Water Supply Company Vodovod-Kanalizacija from Ljubljana.

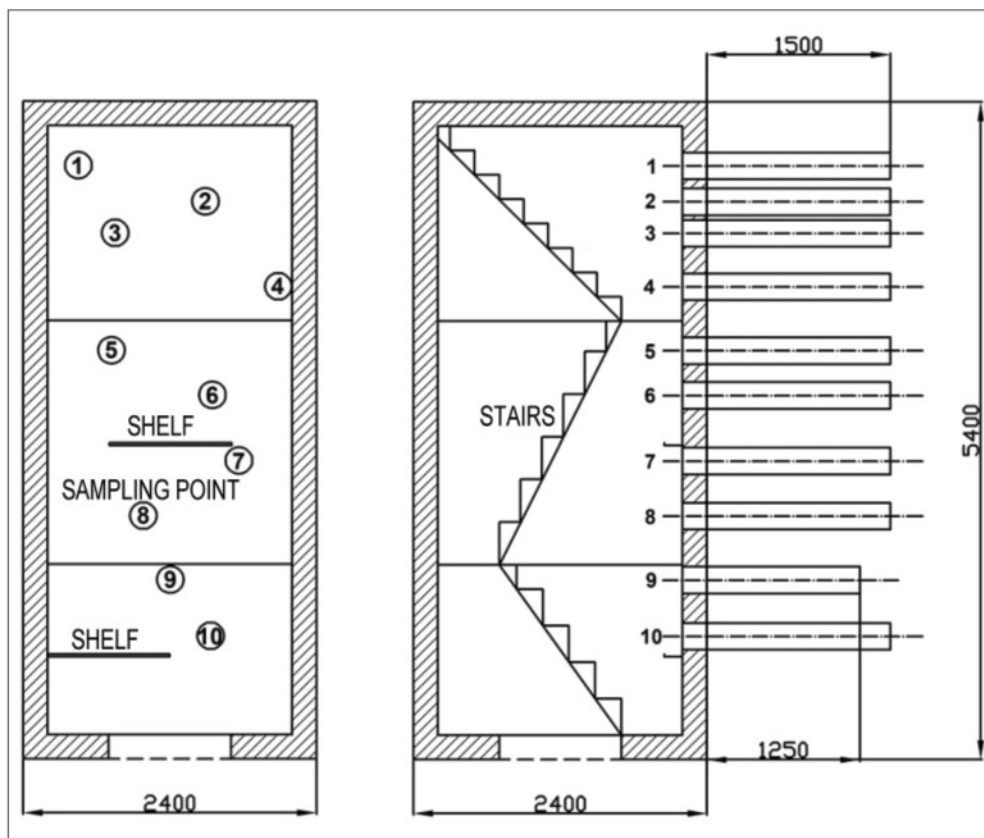
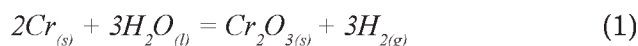


Fig. 2. Lysimeter cross-section
Sl. 2. Prerez lizimetra

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 (HEKAtch, Germany) was fitted with a EuroAS 300 liquid auto sampler (EuroVector, Italy). The elemental analyzer (EA) was configured with a Cr packed reactor held isothermally at 1050 °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 a 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 Cr, resulting in the quantitative conversion to hydrogen gas according to Eq 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^{plus} continuous flow stable isotope ratio mass spectrometer.

Nitrate analyses were performed in an ISO 17025 accredited laboratory by ion chromatography according to ISO 14911:1998

standard. The apparatus was ion chromatograph Metrohm MIC-3, Switzerland, controlled by IC Net 2.3 SR4 software. Calibrations were made by Merck CertiPUR reference materials, Germany. QC control samples were purchased from Fluka, Switzerland. All necessary dilutions were made with ultra-pure water from the system Easypure LF, Barnstead/Thermolyne International, USA. The working range was from 2.2 mg/L to 110 mg/L (as NO_3^-). Nitrate in the analysis is expressed as $\text{NO}_3\text{-N}$ concentrations. For evaluation of breakthrough curves $\text{NO}_3\text{-N}$ concentrations were used.

Evaluation and interpretation of tracing tests

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

For the evaluation of breakthrough curves from a tracing test we used a best-fit method of the computer program TRACI'95 (1998). TRACI'95 was used to estimate the mean flow velocity and vertical dispersion. For analytical solution, the one-dimensional convection-dispersion model with standardizing values for single porosity was chosen.

$$C_N(x, t) = \frac{C_f(x, t)}{C_N(x, t)} = \sqrt{\left(\frac{t_N}{t}\right)^3} \exp\left[\frac{1 - \frac{t_N}{t}}{4t_N t_0} \left(P_D - \frac{t_N t}{P_D}\right)\right] \quad (2)$$

with boundary conditions:

$$C_f(0,t) = \frac{M}{Q} \delta(t)$$

$$C_f(\infty,t) = 0$$

$$C_f(x,t) = 0$$

Where C_f is the tracer concentration in water, C_N normalized concentration, t_0 mean transit time, t time variable, t_N time after injection when normalized concentration was observed, x is the distance between the injection and the observation point, P_D is a dispersion parameter, M is the mass of injected tracer and Q is the volumetric flow rate.

In the case of the multiple peak phenomena in breakthrough curves the Multi-Peak-Modus model was used.

Dispersion parameter P_D is related to the dispersion coefficient by:

$$P_D = \frac{D}{v \cdot x} \quad (3)$$

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

Because the basis of the analytical best-fit model is the concentration of tracer (mg/m^3), the ‰ $\delta^2\text{H}$ values of results had to be converted. The mg/l concentrations of ^2H were calculated from the slightly modified equation published by BECKER AND COPLEN (2001), taking into account the influence of water density (MALI et al., 2007).

$$\text{Deuterium}_{\text{conc}} = 34.721 \left[\frac{1000 + \delta D_{\text{VSMOW}}}{1000} \right] \quad (4)$$

Results and discussion

Fig. 3 present breakthrough curves of both tracers with the precipitation amount for the entire sampling period. Both tracers were detected at all ten sampling points. The tracers occurred shortly after injection, within one day at almost all points. At some points the highest values were detected immediately after tracer injection (JV-1, JV-3, JV-4), and they are most likely a consequence of intensive irrigation at the time of injection or contamination. These values are not taken into account in further processing. At the first sampling point JV-1 that was the only peak of breakthrough curve, since which the values only decreased (Fig. 3). Therefore, this point is not included in further processing for determining transport parameters.

The precipitation data shows that several periods with heavy precipitation occurred during the tracing experiment (end of May 2006,

in the middle of August and September 2006, and in February 2007). All these events were well identified in breakthrough curves of both tracers. Diagrams show that the high amount and intensity of precipitation (heavy rain events) are reflected in some measuring points (JV-5, JV-6, JV-7, JV-9) and have effect on $\delta^2\text{H}$ values and nitrate concentrations (Fig. 3), but not equally in all sampling points.

On the basis of tracing experiment results for both tracers the fastest and dominant flow velocities were calculated (Table 1, Table 3). Based on tracing experiment results, estimations of the mean flow velocity and vertical dispersion (Table 1, Table 3) were made by analytical best-fit method, using a one-dimensional convection-dispersion model with standardising values for single porosity. At some sampling points more breakthrough curve peaks were detected. In these cases, for the evaluation of tracing experiment results the Multi-Peak-Modus model was used (JV-3, JV-5, JV-6, JV-9, and JV-10) (Fig. 4, Fig. 5).

Deuterium

The highest values of deuterium among all sampling points occurred in JV-1 (4670‰) immediately after injection. If we do not take into account the value of the first day, the maximum value detected in JV-1 was 1305‰ and in JV-3 1139‰. As in JV-3, the highest values in JV-2 (212‰), JV-4 (659‰) and JV-5 (509‰) were observed at the end of May, but in a different order of magnitude. In this period the highest concentrations were also observed in sampling points JV-9 (284‰) and JV-10 (175‰) at the bottom of the lysimeter. In both sampling points more peaks in the deuterium breakthrough curves were recorded in August 2006 and February 2007. The maximum value in JV-6 (159‰) was detected in September 2007, while in JV-8 at the end of November 2007. Finally, there was a maximum value at sample site JV-7 in February 2007, when the peaks in JV-9 and JV-10 were last registered. Different hydrogeological conditions at specific points result in a various occurrence and height of peaks at a certain time.

The fastest flow velocity (Table 1) increases with depth from 0.19 to 0.493 m/day. Due to the breakthrough of tracer at the time of irrigation, the fastest flow velocity was not calculated for JV-1, JV-2 and JV-3. Because of the different depth position of the sampling points and because of the detection 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.

The dominant flow velocity is related to the time of the highest concentration (KÄSS, 1998). The graph of precipitation and $\delta^2\text{H}$ values shows

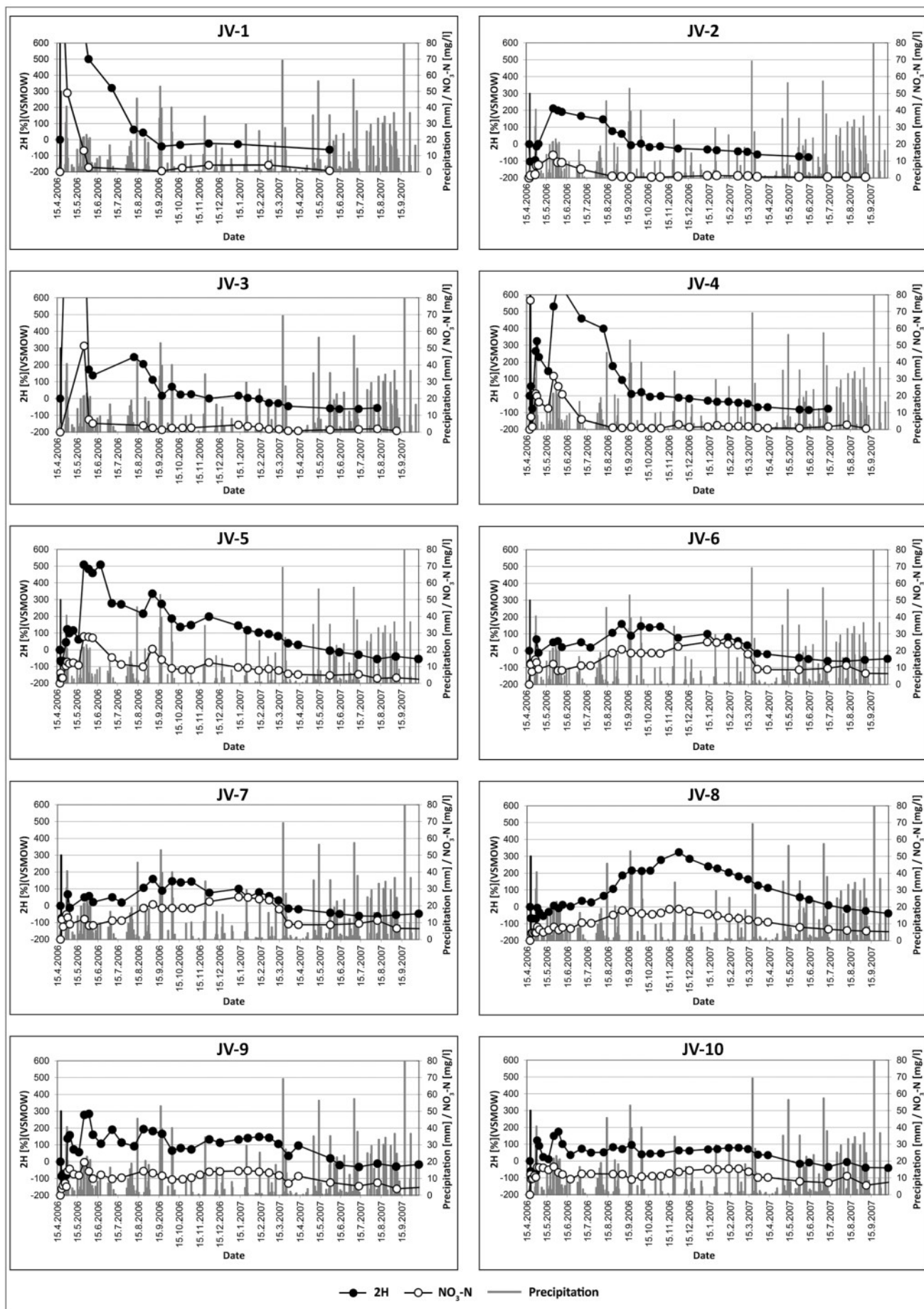


Fig. 3. Deuterium (‰) and nitrate (mg/l) breakthrough curves and precipitations (mm) during the tracing experiment.
 Sl. 3. Devterijeve (‰) in nitratne (mg/l) krivulje pojavljanja sledila ter količina padavin (mm) v času sledilnega poskusa.

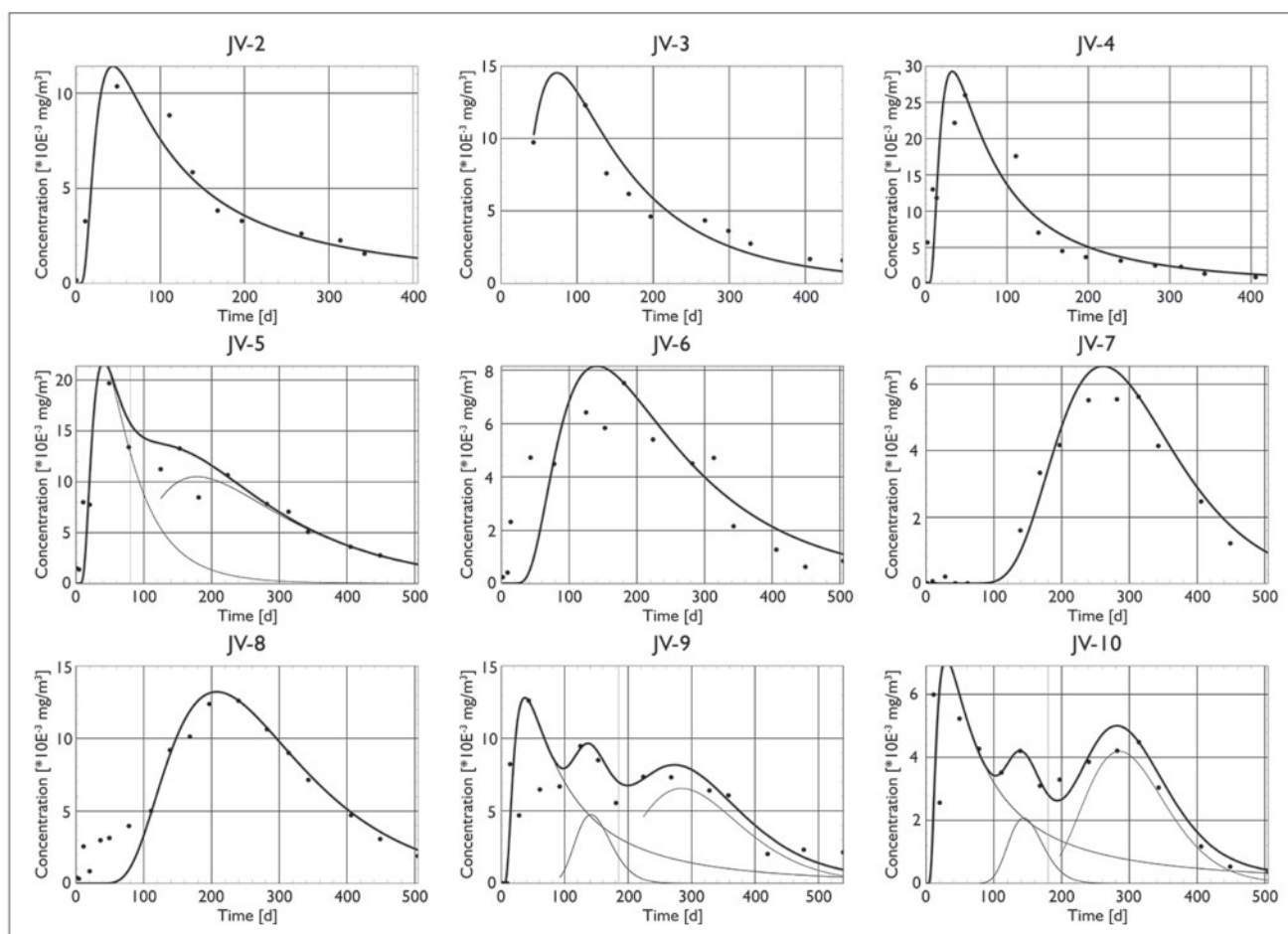


Fig. 4. Best fit curves for deuterium concentrations (10^{-3} mg/m^3).
 Sl. 4. Modelirane krivulje koncentracij devterija (10^{-3} mg/m^3).

that also the occurrence of the highest $\delta^2\text{H}$ values coincides with the stronger precipitation event. The lowest values of dominant velocity occurred in JV-3 and JV-7 (0.010 m/d). JV-8 has a dominant flow velocity of 0.015 m/day, and JV-6 of 0.017 m/day, whereas at other sampling points dominant flow velocities range from 0.023 to 0.036 m/day (Table 1).

The best evaluation of the matrix water flow is the mean flow velocity (Table 1). In Fig. 4 the modeled best fit curves for estimation of deuterium during the entire lysimeter, mean flow velocities based on $\delta^2\text{H}$ values were estimated between 0.002 and 0.029 m/day. In the upper part of the lysimeter the estimated mean flow velocities were lower compared to the lower part. To a depth of 1.08 m they were in the range from 0.002 m/d (JV-2) to 0.006 m/d (JV-3). From the depth of 1.5 m (JV-4) to the bottom of the lysimeter, the calculated mean flow velocities were higher, between 0.007–0.029 m/d. The average value of the mean flow velocity is estimated at 0.012 m/d and corresponds to the previously published results (MALI, 2006).

The volume of discharge water in the drain systems was measured as the water volume in the water collector. During the winter, because of snow cover and frozen soil, there were no conditions

for water flow in the unsaturated zone. So there was no outflow water from JV-1 up to including sampling point JV-7. However, from cumulative values of outflow water volume (Table 2) we can evaluate the discharge dynamics. From the initial injection to 12.7.2007 the outflow volume of the water at the deepest sampling point was 395 l. The next most productive drain was JV-8 (167 l). The deepest sampling drains discharge more groundwater from the unsaturated zone (JV-10, JV-9, and JV-8) than the upper sampling points (JV-1, JV-2, and JV-3) because of wider recharge area. In the gravel deposits deeper than 3 m (JV-8, JV-9 and JV-10) vertical water flow exists all the time so we assume the field capacity was constantly high. Other points are affected more by dry conditions during periods of low precipitation and ground frost.

Tracer recovery was estimated based on outflow water volume and ^2H concentrations. Table 2 shows the quantities, percentages of recovered and injected deuterium tracer by the sampling points. Until the end of July 2007, 5101 mg of ^2H in the outflow water represents 3.64 % of the total injected tracer. The highest amounts of deuterium occurred at JV-10, JV-9, and JV-8 (1612 mg, 986 mg, and 874 mg), which accounts for 32 %, 19 %, and 17 % of the entire recovered tracer and 0.6–1.1 % of the total injected tracer. In the

Table 1. Fastest, dominant (dom.) and mean flow velocities (m/s) of deuterium tracer.

Tabela 1. Najhitrejša, dominantna (dom.) in srednja hitrost toka (m/s) devterijevega sledila.

		JV-2	JV-3	JV-4	JV-5	JV-6	JV-7	JV-8	JV-9	JV-10
Distance	m	0.820	1.080	1.580	2.040	2.41	2.95	3.4	3.93	4.390
Fastest f.	m/d	-	-	0.190	0.255	0.241	0.295	0.34	0.393	0.439
Dom. f.	m/d	0.023	0.010	0.036	0.034	0.017	0.01	0.015	0.032	0.029
Mean f.-1	m/d	0.002	0.006	0.010	0.025	0.009	0.01	0.012	0.021	0.015
Mean f.-2	m/d	-	-	-	0.007	-	-	-	0.026	0.029
Mean f.-3	m/d	-	-	-	-	-	-	-	0.012	0.014
Dispersion-1	m ² /s	0.003	0.002	0.011	0.013	0.005	0.002	0.005	0.066	0.108
Dispersion-2	m ² /s	-	-	-	0.002	-	-	-	0.002	0.097
Dispersion-3	m ² /s	-	-	-	-	-	-	-	0.002	0.001

Table 2. Cumulative outflow water volume (l) and recovery amount (%) of deuterium tracer.

Tabela 2. Skupni iztok vode (l) in delež (%) povrnjenega devterijevega sledila.

		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	7.61	26.39	28.91	95.22	53.36	82.79	80.76	167.10	153.93	395.09	
amount of recovery tracer	mg	64.83	91.58	105.56	371.62	509.09	306.65	178.34	874.28	986.78	1612.64	5101.37
% of recovery tracer amount	%	1.27	1.80	2.07	7.29	9.98	6.01	3.50	17.14	19.34	31.60	100.00
% of whole amount of tracer	%	0.05	0.07	0.08	0.27	0.36	0.22	0.13	0.62	0.70	1.15	3.64

remaining sampling points tracer recovery values were between 64 mg and 509 mg accounting for 1.2–10 % of the total recovered tracer and 0.04–0.4 % of the initial amount of tracer injected.

Nitrate

Like deuterium, also nitrate was detected at all sampling points. From the breakthrough curves it appears that the nitrate behaves slightly differently from deuterium. Fig. 3 indicates that the nitrate breakthrough curves have several peaks. This is explained by the dependence on rainfall and vegetation activity which affects the nitrate content in the unsaturated zone. Even in zero sampling, different background concentrations of nitrate were detected. At lower sampling points, background concentrations reach also 12–19 mg/l ($\text{NO}_3\text{-N}$). Thus, in the diagrams the natural fluctuation of nitrate can be followed as a tracer. Like for deuterium, the highest concentration of nitrate was detected at JV-1 (134.4 mg/l $\text{NO}_3\text{-N}$) on the first day, and after that the concentrations fall. The next high concentration was recorded at JV-3 (51.4 mg/l $\text{NO}_3\text{-N}$) at the end of May. At that time the highest nitrate concentrations were reached also at sampling points JV-2 (13.3 mg/l $\text{NO}_3\text{-N}$), JV-4 (31.7 mg/l $\text{NO}_3\text{-N}$), and JV-5 (27.9 mg/l $\text{NO}_3\text{-N}$). At sample sites JV-9 (19.7 mg/l $\text{NO}_3\text{-N}$) and JV-10 (16.6 mg/l $\text{NO}_3\text{-N}$) the first peak appears at that time. The next two peaks followed at these sites in August 2006 and in February 2007. Nitrate concentrations at that time were 14.4–14.7 mg/l $\text{NO}_3\text{-N}$ at JV-9, and 12.4–15.5 mg/l $\text{NO}_3\text{-N}$ at JV-10. At sampling point JV-6 nitrate concentrations reach the first peak (20.8 mg/l $\text{NO}_3\text{-N}$) at the same time as deuterium reaches its maximum in September 2006. The next peak was documented in the end of January 2007 (25.2 mg/l $\text{NO}_3\text{-N}$). At sampling site JV-7 a completely different behavior of breakthrough curve was detected. In the first

period we perceive a lower curve due to the higher background concentrations of nitrate. Elevated levels as a result of the tracer injection occurred until the end of 2006 and increase to the maximal recorded concentration of nitrate at JV-7 (28.1 mg/l $\text{NO}_3\text{-N}$) in April 2007.

Table 3 gives the estimates of water flow velocity obtained from the nitrate tracing data. Because the nitrate tracer appears immediately after injection because of contamination, we do not give the maximum velocity for JV-2 and JV-3. The evaluation for the fastest flow velocity of nitrate is the same as in deuterium at sampling points JV-4 (0.190 m/d) and JV-5 (0.255 m/d) (Table 3). At points JV-6 to JV-10 the estimation of nitrate flow velocity is slightly higher than in case of deuterium (0.301–0.549 m/d).

The lowest dominant velocity of nitrate is determined at sampling points JV-6 and JV-7 (0.009 m/day) (Table 3). The highest dominant flow velocity, 0.036 m/day, is found at JV-4. Dominant velocities for other sampling points vary from 0.015 to 0.032 m/day (Table 2).

In Table 3 mean flow velocities for all recognized peaks of nitrate breakthrough curves are given. The mean flow velocities based on nitrate concentration breakthrough curves were estimated by analytical best-fit method (Fig. 5). For JV-2, JV-3, JV-5, JV-6, JV-9, and JV-10 the Multi-Peak-Modus model was used. Up to the depth of 1.08 m (JV-2, JV-3) the mean flow velocities are estimated at 0.003–0.019 m/d, on average 0.011 m/d. In JV-4 the mean flow velocity is 0.016 m/s. From sampling point JV-5 to JV-8 the mean flow velocities range between 0.008–0.12 m/d, on average 0.010 m/d. The highest mean flow velocities were calculated in the lower part of the lysimeter at JV-9 and JV-10. Tracer is moving between 0.014–0.197 m/d. Not considering

Table 3. Fastest, dominant (dom.) and mean flow velocities (m/s) of nitrate.

Tabela 3. Najhitrejša, dominantna (dom.) in srednja hitrost (m/s) toka nitrata.

		JV-2	JV-3	JV-4	JV-5	JV-6	JV-7	JV-8	JV-9	JV-10
Distance	m	0.82	1.08	1.58	2.04	2.41	2.95	3.4	3.93	4.39
Fastest f.	m/d	-	-	0.19	0.255	0.301	0.369	0.425	0.491	0.549
Dom. f.	m/d	0.02	0.026	0.036	0.032	0.009	0.009	0.015	0.028	0.023
Mean f.-1	m/d	0.019	0.019	0.016	0.01	0.011	0.008	0.012	0.117	0.197
Mean f.-2	m/d	0.003	0.004	-	0.01	0.009	-	-	0.03	0.015
Mean f.-3	m/d	-	-	-	-	-	-	-	0.014	-
Dispersion-1	m ² /s	0.003	0.003	0.024	0.016	0.003	0.000	0.006	0.019	0.051
Dispersion-2	m ² /s	0	0	-	0.016	0	-	-	0.005	0.001
Dispersion-3	m ² /s	-	-	-	-	-	-	-	0.001	-

Table 4. Cumulative outflow water volume (l) and recovery amount (%) of nitrate tracer.

Tabela 4. Skupni iztok vode (l) in delež (%) povrnjenega nitratnega sledila.

		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	7.61	26.39	28.91	95.22	53.36	82.79	80.76	167.10	153.93	395.09	
amount of recovery tracer	mg	46.87	59.61	102.19	503.40	607.87	360.45	289.05	965.45	725.18	1144.20	4804.27
% of recovery tracer amount	%	0.98	1.25	2.13	10.48	12.65	7.50	6.02	20.10	15.09	23.82	100.00
% of whole amount of tracer	%	0.02	0.03	0.05	0.25	0.30	0.18	0.14	0.47	0.35	0.56	2.35

the highest estimated mean flow velocities at JV-9 and JV-10, the average mean flow velocity is estimated at 0.013 m/d. We anticipate that these unrealistically high concentrations of first peak occurred due to high background concentrations.

Tracer recovery was estimated based on the outflow water volume and nitrate concentrations. Table 4 shows the quantities, percentages of recovered and injected tracer by the sampling points. Until the end of the tracing experiment (July 2007) 4804 mg of NO₃-N drained through the sampling system in the lysimeter, which is 2.35 % of the total injected tracer. The highest amounts of recovered nitrate were recorded at JV-8 and JV-10, 1144 mg and 965 mg NO₃-N, which accounts for 24 % and 20 % of the entire recovered tracer and 0.47-0.56 % of the total injected tracer. In the remaining sampling points tracer recovery concentrations were between 47 mg and 725 mg NO₃-N accounting for 0.98-15.09 % of the total recovered tracer and 0.02-0.35 % of the initial amount of tracer injected.

Discussion

A comparison of the deuterium and nitrate breakthrough curves shows that the results of deuterium and nitrate tracers give a similar distribution (Fig. 3). At sampling points JV-1, JV-5, JV-8, JV-9 and JV-10 breakthrough curves of deuterium and nitrate tracer have the same shape at the same time. A maximum concentration of nitrate at sampling points JV-4 and JV-5 coincides with the first higher increase in deuterium values during a period of high precipitation.

From the calculations of the fastest and dominant velocities for both tracers (Table 1 and Table 3), we can see that the results are comparable. The fastest average flow of nitrate in

the unsaturated zone is estimated at 0.369 (0.019-0.549) m/day, and of deuterium 0.308 (0.019-0.439) m/day. An estimate of the strongest impact of pollution can be made on the basis of the dominant flow, which is calculated on the basis of the occurrence of the highest tracer concentrations. The dominant flow in the unsaturated zone for nitrate is estimated at 0.022 (0.009-0.036) m/day, and for deuterium at 0.023 (0.01-0.036) m/day. The highest values of the dominant flow were assessed in the middle of the lysimeter at sampling sites JV-4 and JV-5, where the highest concentrations were achieved between 40 and 50 days from the beginning of the experiment. At the bottom of the lysimeter the highest concentrations occurred between 230 and 313 days.

The long-term impact of pollution is estimated on the basis of the mean flow velocity (Kass, 1998). This is the velocity which determines the transfer of most of the tracer. The mean flow velocity calculations of both tracers show some differences (Table 1, Table 3). In breakthrough curves of nitrate several peaks could be recognized (Fig. 5), while the deuterium breakthrough curves are more homogeneous, with one peak (Fig. 4). The phenomenon is the consequence of the presence of nitrate in the natural environment of the lysimeter. The content of nitrate in the soil and in the unsaturated zone is linked to the vegetation activity in relation to the use of nitrogen in various stages of plant growth. Background levels of nitrate have an impact on an indicated nitrate concentration during the tracer experiment. As a result, the calculated mean flow velocities of nitrate are slightly higher than of deuterium. Given the fact that deuterium is the ideal tracer, according to the results of individual peaks analysis and taking into account background nitrate concentrations, it can be concluded that the retention times of both tracers are comparable. The estimation of

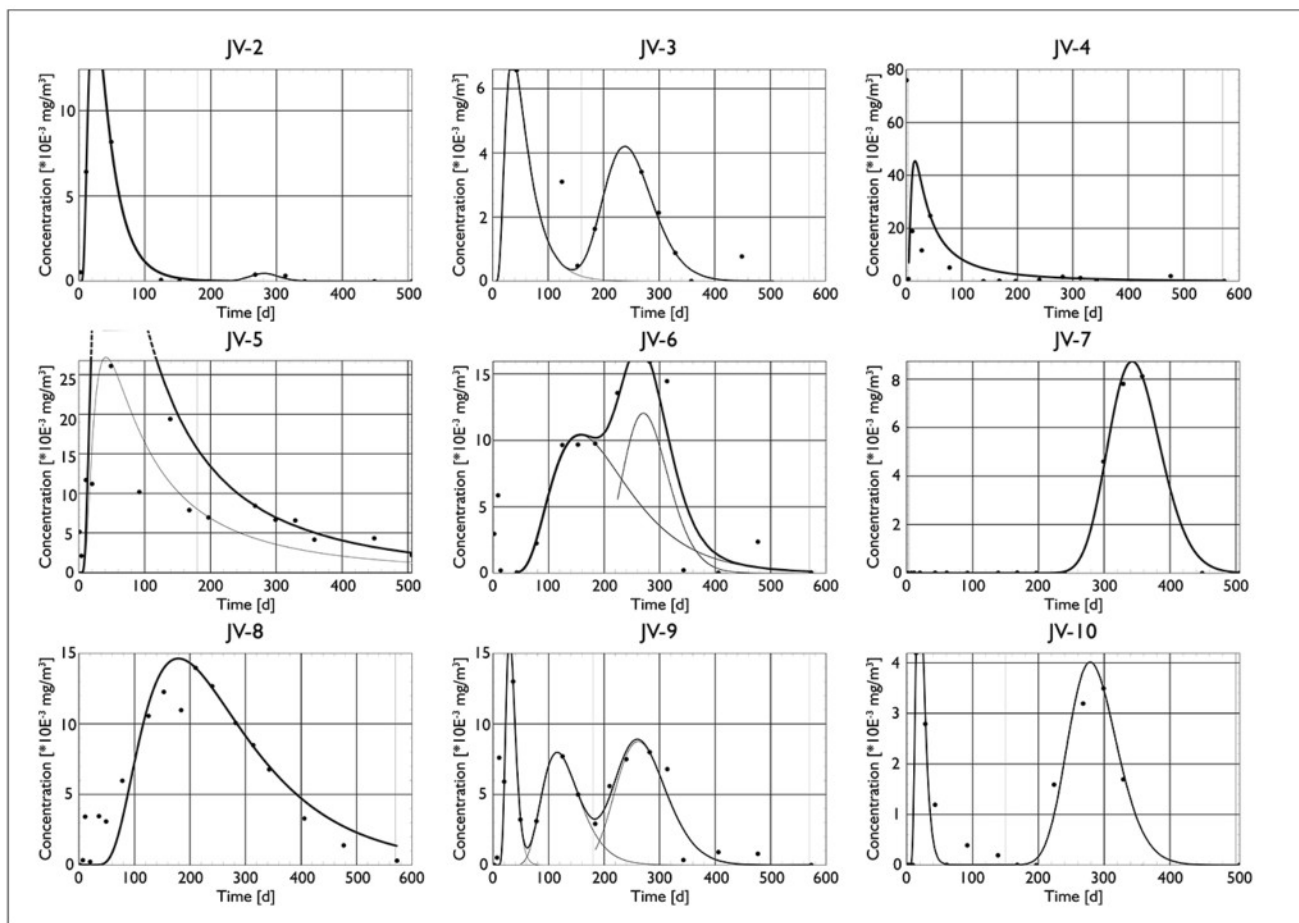


Fig. 5. Best fit curves for nitrate concentrations (10^{-3} mg/m^3)

Sl. 5. Modelirane krivulje koncentracij nitrata (10^{-3} mg/m^3)

the mean flow velocity for nitrate in coarse gravel unsaturated zone (the hydraulic conductivity 2.9×10^{-3} – $6.9 \times 10^{-2} \text{ m/s}$) is 0.0013 m/d .

The nitrate flow velocity in the unsaturated zone is important for assessing the impact of nitrogen excess from agriculture on groundwater. The problem is exceeded threshold nitrate concentrations at some places. The results of tracing experiment will be used in further modeling of nitrate transport in order to identify measures to improve groundwater quality status. Based on our results, some conclusions about transport of nitrate in Selniška dobrava can be made. The thickness of the unsaturated zone on lysimeter location reaches 27.5 m . If it is assumed that the ground water level is 27.5 , average first speed of nitrate is 0.369 m/d the first contamination can reach the water in 74 days. Based on the average dominant flow velocity (0.022 m/d) the percolation time is 3.42 years. When the estimated mean flow velocity is 0.013 m/d , the time of pollution arrival is estimated at 5.80 years.

Conclusions

The aim of the tracing experiment in a lysimeter was to determine the characteristics of nitrate transport in the unsaturated zone. The results revealed that nitrate travels with almost

the same dynamics as deuterium, which is used as a conservative tracer. The differences in results between individual points show local differences in the structure of the unsaturated zone, which affects different flow properties. Some differences between the two tracers' breakthrough curves were recognized. At the same sampling sites the nitrate breakthrough curves have more peaks. The phenomenon is the consequence of the presence of nitrate in the natural environment of the lysimeter. The content of nitrate in the soil and in the unsaturated zone is linked to the vegetation activity in relation to the use of nitrogen in various stages of plant growth. Background levels of nitrate have an impact on an indicated nitrate concentration during the tracer experiment.

Based on the results of the tracer experiment, the characteristics of nitrate flow dynamics through the coarse gravel unsaturated zone with a hydraulic conductivity in the range of 2.9×10^{-3} – $6.9 \times 10^{-2} \text{ m/s}$ were estimated. The evaluation for the fastest flow velocity of nitrate is 0.190 – 0.549 m/d , on average 0.369 m/d . The dominant flow of nitrate in the unsaturated zone is estimated at 0.022 (0.009 – 0.036) m/day . Calculations of the fastest and dominant velocities for both tracers are comparable, while the calculated mean flow velocities of nitrate are slightly higher than those of deuterium. Given the fact that

deuterium is the ideal tracer, according to the results of individual peaks analysis and taking into account background nitrate concentrations, it can be concluded that the retention times of both tracers are comparable. The estimation of the mean flow velocity for nitrate in our case is 0.013 m/d.

The purpose of determining the movement of nitrate through the unsaturated zone is also to assess the impact of nitrate pollution from agriculture on groundwater. If we assume an average thickness of the coarse gravel unsaturated zone at 27.5 m with a conductivity of about 5×10^{-3} m/s, as is the case in Selniški dobjava, we come to the following assessment of nitrate pollution movement:

- At an average fastest flow of 0.369 m/d, pollution reaches the groundwater level in 74 days.
- With the thickness of the unsaturated zone and the dominant velocity of 0.022 m/d, the percolation time is estimated at 3.42 years.
- The mean flow velocity in the matrix flow was estimated at 0.013 m/d. The mean residence time is estimated at 5.80 years.

The tracing experiment has again proved to be a very useful tool to assess the behavior of nitrate as the selected pollutant in the unsaturated zone. On the basis of the determined range of nitrate flow properties, the estimation of pollution influence on aquifer and groundwater measures can be provided. The results of tracing experiment will be used in further modelling of nitrate transport in order to identify measures for groundwater quality status improvement.

Acknowledgements

The study presented in the paper was carried out within the Research Programme Groundwater and geochemistry (P1-0020) and PhD work of A. Koroša financed by the Slovenian Research Agency (ARRS). Special thanks go to Primož Auersperger from Water Supply Company Vodovod-Kanalizacija for great help and suggestions and Albrecht Leis from JOANNEUM RESEARCH Forschungsgesellschaft mbH, Resources - Institute for Water, Energy and Sustainability.

Literature

- BECKER, M. W. & COPLEN, T. B. 2001: Use of deuterated water as a conservative artificial groundwater tracer. *Hydrogeological Journal*, 9/5: 512–516, doi:10.1007/s100400100157.
- CAMERIA, M.R., FERNANDO, R.M. & PEREIRA, L.S. 2003: Monitoring water and NO₃-N in irrigated maize fields in the Sorraia watershed. *Agricultural Water Management*, 60: 199–216.
- CEPLECHA, Z.L., WASKOM, R.M., BAUDER, T.A., SHARKOFF, J.L. & KHOSLA, R. 2004: Vulnerability assessments of Colorado ground water to nitrate contamination. *Water Air Soil Pollut*, 159: 373–394, doi:10.1023/B:WATE.0000049188.73506.c9.
- EARS (ENVIRONMENTAL AGENCY OF THE REPUBLIC OF SLOVENIA) 2014: Poročilo o kakovosti podzemne vode v Sloveniji v letu 20013. Ljubljana: 14–20 p.
- EC 2000: Water Framework Directive 2000/60/EC. European Commission.
- EC 2006: Groundwater Daughter Directive 2006/118/EC. European Commission.
- EEC1991: Council Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources 91/676/EEC. European Commission.
- GOSAR, M. 2000: Poročilo o preiskavi talnega profila PS-5 pri Selnici ob Dravi. Ljubljana, Geološki zavod Slovenije Report: 6 p.
- KÄSS, W. 1998: Tracing techniques in Geohydrology. Rotterdam, A.A. Balkema: 581 p.
- KRONVANG, B., BORGVANG, S.A. & BARKVED, L. J. 2009: Towards European harmonised procedures for quantification of nutrient losses from diffuse sources – the EUROHARP project. *Journal of Environmental Monitoring*, 11: 503–5, doi:10.1039/b902869m.
- KRZEMINSKA, D. M., BOGAARD, T. A., DEBIECHE, T.-H., CERVI, F., MARC, V. & MALET, J.-P. 2014: Field investigation of preferential fissure flow paths with hydrochemical analysis of small-scale sprinkling experiments. *Earth Surf. Dynam.* 2: 181–195, doi:10.5194/esurf-2-181-2014.
- 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. Paper presented at the 7th Workshop of European Society for Isotope Research (ESIR), Berichte des Institutes für Erdwissenschaften Karl-Franzes-Universität Graz, Seggau, 27 June – 1 July 2004.
- LOCKHART, K.M., KING, A.M. & HARTER, T. 2013: Identifying sources of groundwater nitrate contamination in a 2 large alluvial groundwater basin with highly diversified intensive agricultural production. *Journal of Contaminant Hydrology*, 151: 140–154, doi:10.1016/j.jconhyd.2013.05.008.
- LOPEZ, B., BARAN, N. & BOURGINE, B. 2015: An innovative procedure to assess multi-scale temporal trends in groundwater quality: Example of the nitrate in the Seine-Normandy basin, France. *Journal of Hydrology*, 522: 1–10, doi:10.1016/j.jhydrol.2014.12.002.
- MALI, N., JANŽA, M., RIKANOVIC, R., MARINKO, M., HERIC, J., LEVICNIK, L. & MOZETIC, S. 2005: Raziskave Selniške Dobrave - Raziskovalna dela z določitvijo lokacij vodnjakov in ogroženosti vodnega vira na Selniški Dobravi. *GeoZS*, Ljubljana: 16 p.
- MALI, N. & JANŽA, M. 2005: Ocena ranljivosti vodonosnika s SINTACS modelom v GIS okolju. *Geologija*, 48/1: 127–140, doi:10.5474/geologija.2005.012.
- MALI, N. 2006: Characterization of transport processes in the unsaturated zone of a gravel aquifer by natural and artificial tracers. Ph.D. thesis. University of Nova Gorica, Nova Gorica: 96 p.

- MALI, N., URBANC, J. & LEIS, A. 2007: Tracing of water movement through the unsaturated zone of a coarse gravel aquifer by means of dye and deuterated water. *Environmental Geology*, 51/8: 1401–1412, doi: 10.1007/s00254-006-0437-4.
- MALI, N. & URBANC, J. 2009: Isotope oxygen-18 as natural tracer of water movement in a coarse gravel unsaturated zone. *Water, air and soil pollution*, 203/1: 291–303, doi:10.1007/s11270-009-0012-1.
- MORRISON, J., BROCKWELL, T., MERREN, T., FOUREL, F. & PHILIPS, A.M. 2001: On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. *Analytical Chemistry*, 73, 3570–3575.
- PISCIOTTA, A., CUSIMANO, G. & FAVARA, R. 2015. Groundwater nitrate risk assessment using intrinsic vulnerability methods: A comparative study of environmental impact by intensive farming in the Mediterranean region of Sicily, Italy. *Journal of Geochemical Exploration*, 156: 89–100, doi:10.1016/j.gexplo.2015.05.002.
- PRATT P.F. & ADRIANO D.C. 1973: Nitrate concentrations in the unsaturated zone beneath irrigated fields in southern California. *Soil Science Society of America Journal*, 37: 321–322.
- REFSGAARD, J. C., AUKEN, E., BAMBERG, C. A., CHRISTENSEN, B. S. B., CLAUSEN, T., DALGAARD, E., EFFERSØ, F., ERNSTSEN, V., GERTZ, F., HANSEN, A. L., HE, X., JACOBSEN, B. H., HØGH JENSEN, K., JØRGENSEN, F., FLINDT JØRGENSEN, L., KOCH, J., NILSSON, B., PETERSEN, C., DE SCHEPPER, G., SCHAMPER, C., SØRENSEN, K. I., THERRIEN, R., THIRUP, C., VIEZZOLI, A. 2014: Nitrate reduction in geologically heterogeneous catchments - A framework for assessing the scale of predictive capability of hydrological models. *Science of the Total Environment*, 468–469: 1278–1288, doi:10.1016/j.scitotenv.2013.07.042.
- SCHWIENKE, M., MALOSZEWSKI, P., EINSIEDL, F. 2009: Effect of the unsaturated zone thickness on the distribution of water mean transit times in a porous aquifer. *Journal of Hydrology*, 373: 516–526, doi:10.1016/j.jhydrol.2009.05.015.
- SEILER, K.P. & ZOEJER, H. 2001: Role of tracers in the unsaturated zone. In: *Tracers in the Unsaturated Zone (Investigations 1996–2001)*. ATH (ed.): *Beiträge zur Hydrogeologie*, 52: 11–15.
- TRACI'95: 1998. Computer program. In: KASS, W (ed.): *Tracing techniques in Geohydrology*. A.A. Balkema, Rotterdam.
- OFFICIAL GAZETTE: Waters Act (ZV-1). No. 67/2002, 110/2002, 2/2004, 41/2004, 57/2008, 57/2012.
- OFFICIAL GAZETTE: Regulation on the protection of waters against pollution caused by nitrates from agricultural sources. No. 113/09, 5/13, 22/15, Ljubljana.
- URBANC, J., KRIVIC, J., MALI, N., FERJAN STANIČ, T., KOROŠA, A., ŠRAM, D., MEZGA, K., BIZJAK, M., MEDIC, M., BOLE, Z., LOJEN, S., PINTAR, M., UDOVČ, A., GLAVAN, M., KACJAN-MARŠIČ, N., JAMŠEK, A., VALENTAR, V., ZADRAVEC, D., PUŠENJAK, M. & KLEMENČIČ KOSI, S. 2014: Možnosti kmetovanja na vodovarstvenih območjih: zaključno poročilo projekta. Geološki zavod Slovenije; Univerza v Ljubljani, Biotehniška fakulteta; Institut Jožef Stefan; Kmetijsko gozdarski zavod; Ljubljana: 65.
- VINOD, P. N, CHANDRAMOULI, P. N. & KOCH, M. 2015: Estimation of Nitrate Leaching in Groundwater in an Agriculturally Used Area in the State Karnataka, India, Using Existing Model and GIS. *Aquatic Procedia*, 4: 1047 – 1053, doi:10.1016/j.aqpro.2015.02.132
- WANG, L., BUTCHER, A. S., STUART, M. E., GODDY, D.C. & BLOOMFIELD, J.P. 2013: The nitrate time bomb: a numerical way to investigate nitrate storage and lag time in the unsaturated zone. *Environmental Geochemistry and Health*, 35: 667–681.
- WU, J.J., BERNARDO, D.J., MAPP, H.P., GELETA, S., TEAGUE, M.L., WATKINS, K.B., SABBAGH, R.L., ELLIOTT, R.L. & STONE, J.F. 1997: An evolution of nitrogen runoff and leaching potential in the high plains. *Journal of Soil and Water Conservation*, 52: 73–80.
- ŽLEBNIK, L. 1982: Hydrogeology of the Drava field. *Geologija*, 25/1: 151–164.