Tracer test and behavior of selected pharmaceuticals

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ABSTRACT

Study of the behavior and transport of pharmaceuticals in groundwater is significant for understanding the processes of natural attenuation and potential use of filtration through the aquifer to evaluate the most effective way to remove pharmaceuticals that occur under anthropogenic influence. This paper presents the results of a field experiment at the location of the drainage system of Kovin-Dubovac in Serbia, during which a tracer test was conducted and the behavior of selected pharmaceuticals (trimethoprim, carbamazepine, diclofenac and metamizole metabolite N-acetyl-4-aminoantipyrine (4–AAA)) was monitored. The objective of the paper is to show and analyze the results of the tracer test, during which the tracer NaCl was injected, and to correlate the obtained characteristics of the subsurface and the breakthrough curves of the selected pharmaceuticals, so that the effects of sorption can be quantified. During the tracer test, the hydraulic head, flow, electric conductivity and concentrations of the pharmaceuticals were monitored continuously to collect sufficient data. The results show that sorption coefficients can be determined from experimental data and the NaCl breakthrough curve.

Key words | behavior, pharmaceuticals, sorption, tracer

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INTRODUCTION

The pharmaceuticals which were investigated in this study are frequently detected in surface water and corresponding alluvial groundwater, according to several short-term studies conducted in Serbia (Radović *et al.* 2012, 2015; Petrović *et al.* 2014). These pharmaceuticals can be removed by riverbank filtration (RBF) to improve groundwater quality for potable water use (Hiscock & Grischek 2002). The removal of pharmaceuticals during RBF is mainly caused by microbiological degradation, while sorption slows down transport (Dimkić *et al.* 2012; Henzler *et al.* 2014).

The quantification of the effects of sorption during a field tracer test has not been sufficiently studied in Serbia. Tracer tests are very useful for collecting better and more precise data. Previously in Serbia, Dimkić conducted tracer tests and monitored the behavior of heavy metals and phenols near Žičko Polje, as reported in Dimkić (2008). The need for a tracer test arose from a lack of experimental data on the behavior of pharmaceuticals in groundwater. In the case of intergranular aquifers, the simulation and prediction of groundwater flow and transport of substances, in this case pharmaceuticals, require detailed knowledge of the nature and spatial distribution of the aquifer (Dimkić *et al.* 2011). In most cases, such data are not easy to collect and detailed research and experiments are therefore necessary. A tracer test is a very powerful tool for characterizing the subsurface. There is a large variety of application possibilities: tracer testing can be used for conventional subsurface investigations that yield effective transport parameters (transport velocity, porosity, and dispersivity), which can describe non-reactive as well as reactive (contaminant) transport processes within an aquifer (Ptak *et al.* 2004), as in the present study. Information on the subsurface structure (preferential flow paths and structural anisotropy) can be obtained as well (Käss & Behrens

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1998). Tracer tests also help generate a database (tracer breakthrough curves and their respective derived statistical transport parameters), which can be used to test forward transport predictions obtained from deterministic or stochastic model approaches and reduce prediction uncertainty within stochastic modeling frameworks, or to develop and apply inverse stochastic flow and transport modeling methods (Ptak *et al.* 2004).

The main objective of this research was to collect sufficient data about hydrogeological parameters *in situ* and quantify sorption based on the results of the field experiment. The tracer test reported in this paper was conducted under forced gradient conditions, induced by groundwater pumping because of the duration of the test and other limiting factors (Sutton *et al.* 2000). In this test the convergent flow field approach was used: groundwater was pumped out of an extraction well, the tracer was injected continuously into an injection piezometer over a limited period of time, and breakthrough curves were plotted at the extraction site based on the example from Ptak & Schmid (1996). NaCl was used as the tracer for many practical reasons: nontoxic, readily available, affordable, good solubility for injection, low detection limits, low natural background concentrations, negligible effect on transport properties (density, viscosity, pH, etc.), stable or well-characterized low and very slow degradation, thermal or radioactive decay acceptable, and no sorption processes on the tracer substance. During this test, the concentrations of the selected pharmaceuticals (trimethoprim, carbamazepine, diclofenac and the metamizole metabolite *N*-acetyl-4-aminoantipyrine (4-AAA)) were monitored at the extraction well and then a sampling and analysis program was established to define breakthrough curves. Data were collected to determine linear sorption coefficients, based on the results of monitoring of the hydraulic head, well flow, electric conductivity, pH, oxic state of groundwater, and concentrations of the selected pharmaceuticals.

MATERIALS AND METHODS

Location and hydrogeological conditions

The test site was the Kovin-Dubovac drainage system (Figure 1).

The sediments of the uppermost porous aquifer from which bank filtrate is abstracted are older Quaternary. The upper part of the deposits are at the end of the late Pleistocene and Holocene deposit – gravel–sand, and the lower alevrite clay sediments in the upper part of the alluvial plain. The thickness of the Upper Quaternary gravel–sand deposits in this region is ≈ 20 m. The Quaternary sediments lie discordantly over Upper Pontic layers. The shelves in the area of the gravel–sand deposits are alevrite sands,

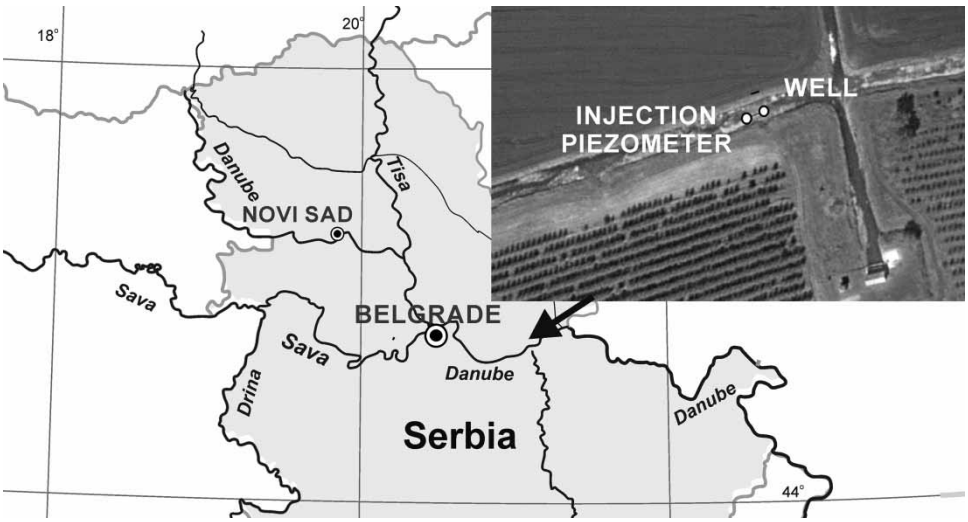

Figure 1 | Map of Serbia and location of field tracer experiment at Kovin-Dubovac drainage system.

puddle clay and peat. The average thickness of the shelf layer is about 7.5 m.

The hydraulic conductivity of the water-bearing layer in the Kovin-Dubovac drainage system area of the alluvial plain of the Danube was found to be $K = 0.5–7 \times 10^{-3}$ m/s. Based on the filtration characteristics of the aquifer and overlying strata, in hydrodynamic terms this part of the alluvial plain of the Danube is a typical three-layer setting (roof–aquifer–bottom), where hydraulic conductivity is relatively homogeneous. The wells and piezometers are located at about 300 metres from the Danube River. The aquifer is relatively homogenous, with possible preferential flow layers, and the water largely travels from the river to the wells with no dilution from the hinterland.

New borehole

A new piezometer borehole was drilled by the conventional method with the use of flasks. During drilling, water was sampled at every 3 metres and then a composite sample was collected from pelite fractions for further examination. Each core was crated and transferred to the Jaroslav Černi Institute for the Development of Water Resources for further investigation, mapping and sampling for detailed analysis. The purpose of drilling was to form an injection piezometer near a drainage well of the Kovin-Dubovac drainage system, where testing took place. The particle size distribution was determined by sieving the materials using sets of sieves according to JUS L.J9.010, with the following mesh sizes in mm: 0.063; 0.090; 0.125; 0.250; 0.500; 0.710; 1.0; 2.0; 4.0; 8.0; 11.2; 16.0; 22.4; 31.5; 63.0; and 125.0. Based on previously collected data, the theoretical hydraulic conductivity was calculated using the USBR empirical equation (Vukovic & Soro 1992), where $d_{ef} = d_{20}$ and the results were compared with obtained hydraulic conductivity results.

Sampling and analysis

All groundwater samples were collected using 1-litre amber glass bottles. The samples were stored unpreserved in a freezer and were frozen immediately after sampling. Prior to analysis (2–3 days after sampling), the samples were passed through 1 μm glass-fiber filters (Whitman GmbH, Dassel, Germany). *In situ* monitoring was carried out with a probe immersed at the point of outflow from the well and in the injection piezometer, which was about 20 metres deep. Electrical conductivity, pH, dissolved oxygen and Eh – oxidation/reduction potential – were observed continuously during the field tracer test with an HQ40d multi-parameter probe. Organic carbon was analyzed in the laboratory using a Shimadzu Total Organic Carbon Analyzer (TOC-5050a). *In situ* titration was conducted with an Eppendorf top buret M device.

Chemicals

High purity (>95%) analytical standards were procured from Sigma Aldrich. All solvents used were HPLC grade from Fluka (Buchs, Switzerland) or Sigma-Aldrich (St Louis, MO, USA), and all other reagents were of analytical grade. Concentrated acetic acid and ammonia were used for pH-value adjustment of the water samples. Deionized water was produced by passing tap water through a GenPure ultrapure water system (TKA, Niederelbert, Germany). Stock solutions of individual standards were prepared in methanol, in a concentration of 100 mg/L, every few months, and stored in the freezer. The working standard solutions were prepared weekly in different concentrations, by mixing appropriate amounts of single standard stock solutions and further dilution with methanol. All working solutions were stored at $-4\ ^{\circ}C$.

Analytical method

The water samples for pharmaceutical analysis were prepared applying the solid phase extraction (SPE) method and extracts were analyzed by the liquid chromatography tandem mass spectrometry (LC-MS/MS) method. Detailed information about the analytical procedure, instrumental parameters, SPE recoveries, calibration curves, accuracy, precision, detection limits, and quantification limits is available in a previously published study (Radović *et al.* 2015).

SPE was used as a proven, effective method for the isolation, pre-concentration, and clean-up of trace amounts of pharmaceuticals from a variety of water matrices, and the Oasis hydrophilic–lipophilic balance (HLB, 200 mg/6 mL) cartridge from Waters (Milford, MA, USA) was chosen.

Briefly, it was determined that the optimal SPE of the analytes was achieved using 250 mL of the water sample with two pH values: pH ~7.5 (without pH adjustment) and pH 3, depending on the analyte and the methanol–dichloromethane mixture as the eluent. A strongly acidic environment is required for the extraction of azithromycin, doxycycline and acetylsalicylic acid. High recoveries were obtained for all PACs (>70%), in both surface water and groundwater, with the exception of atorvastatin (26.1%). Low limits of detection – LODs (1–2 ng/L), and limits of quantification – LOQs (3–7 ng/L), were achieved for all the investigated compounds. The calibration curves exhibited good linearity. Matrix-matched standards were used to eliminate the matrix effect, with signal enhancement or suppression up to 35%. The relative standard deviations of the developed methods were generally lower than 20%. Positive results were confirmed by repeated injection of positive sample extracts using a confirmatory method with additional transitions.

A Surveyor LC system (Thermo Fisher Scientific, Waltham, MA, USA) was used for the separation of analytes on a reverse-phase Zorbax Eclipse® XDB–C18 column, 75 mm × 4.6 mm ID and 3.5 μm particle size (Agilent Technologies, Santa Clara, CA, USA). A precolumn, 12.5 mm × 4.6 mm ID and 5 μm particle size (Agilent Technologies), was also used. For the LC–MSn analysis of the pharmaceuticals in the positive ionization mode, the mobile phase was composed of methanol (A), deionized water (B), and 10% acetic acid (C). The mobile-phase gradient varied as follows: 0 min, B 33%, C 2%; 12 min, B 98%, C 2%; and 15 min, B 98%, C 2%. The initial conditions were then re-established and held for 15 min. The flow rate of the mobile phase was 0.6 mL/min. The injection volume was 10 μL. Mass spectra were obtained using an LTQ Fleet linear ion trap mass spectrometer (Thermo Fisher Scientific). Electrospray ionization was applied to perform the mass spectrometric analyses. The spray voltage was set to 4.5 kV and the sheath gas flow was optimized at 25 au (i.e., 25 arbitrary units, from the scale of arbitrary units in the 0–100 range defined by the LTQ Fleet system). The capillary temperature was set to 290 °C. For each analyte, the precursor ion, optimal collision energy, and most abundant fragment ion were chosen in the selected reaction monitoring mode, for quantification purposes. Additional fragmentation reaction was chosen for confirmation purposes.

Experimental setup

The field experiment lasted for 16 days and the experimental parameters were monitored continuously. Before the experiment started, baseline quality was monitored to determine the initial conditions. One sample was collected from the observation well before the field experiment. Initial conditions were monitored continuously (every hour) and included hydraulic head, flow and electrical conductivity. Additionally, pH, O_2 (dissolved oxygen in groundwater) and oxidation/reduction potential – Eh, were monitored periodically during the experiment. The physico-chemical characteristics of the investigated compounds, LODs and LOQs are presented in Table 1.

During the tracer test, the nonreactive tracer NaCl and reactive pharmaceuticals were injected into the injection piezometer (Figure 2), approximately 8.5 metres from the observation well. The depth of injection was about 15–20 metres. A continuous-flow peristaltic pump was set up in the observation well at 6 L/s. Also, groundwater levels were monitored with data loggers (divers).

The flow was monitored by a Thompson overflow, the volumetric method and ultrasonic flow meter 'Nivus PCM Pro'. The NaCl tracer was mixed and dissolved in 1,000 litres of water extracted from the observation well. The pharmaceuticals, obtained from Sigma Aldrich, were dissolved in 1 litre of methanol, then mixed with 100 litres of extracted groundwater and injected into the same piezometer as the NaCl tracer. During the experiment, specific conductivity was monitored as the parameter for calculating the concentration of the NaCl tracer. Samples of the reactive compounds were collected periodically and frozen

Table 1 | Physico-chemical characteristics, LOD and LOQ of the investigated compounds (pK_a – acid dissociation constant, K_{OC} – soil organic carbon–water partitioning coefficient)

Compounds	LOD (ng/L)	LOQ (ng/L)	Water solubility (mg/L) (25 °C)	pK_a[a]	K_{oc}[b] (mL/g)
Trimethoprim	1	3	2334	7.1	905
4-AAA	1	3	1590	11.9	240.7
Carbamazepine	1	3	17.7	2.4	3871
Diclofenac	2	7	4.5	4.1	833.3

[a]The e–Chemical Compound Database, http://www.chemspider.com.
[b]The e–Hazardous Substances Data Bank, http://www.toxnet.nlm.nih.gov.

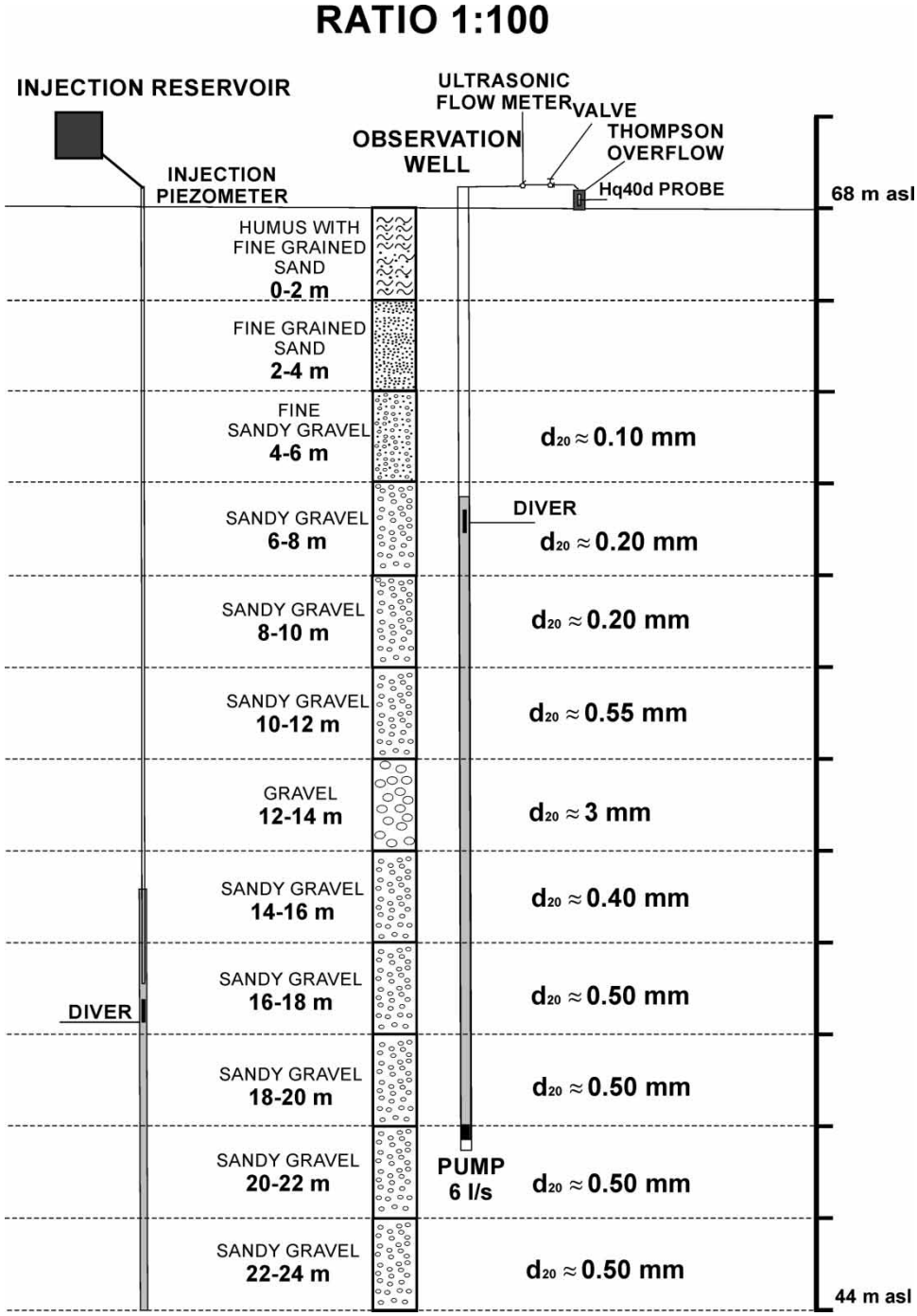

Figure 2 | Schematic illustration of the experimental setup and geological cross-section (asl – above sea level, d_{20} – 20% graduation curve particle size diameter (mm)).

immediately. The tracer test was conducted in 2014 at one specific observation well and one piezometer (Figure 2).

At the beginning of the test, NaCl was dissolved in an injection tank. The amount of pure NaCl that was poured into the tank was 35.7 kg, calculated on the basis of plots of electrical conductivity as a function of NaCl concentration (Figure 3). After dissolution of NaCl in the 1,000-litre injection tank, the NaCl was injected for approximately 52 minutes.

The injection piezometer was then flushed with 500 litres of groundwater. The average specific conductivity in

the injection tank was 73,250 μS/cm. For higher reliability and checking of the result, electric conductivity was measured *in situ* with titration and an electrical conductivity probe. Figure 3 shows the correlation between the electric conductivity measured by the probe and the NaCl concentration measured with titration in the laboratory.

The pharmaceuticals were injected after the NaCl tracer. Their initial concentrations in a 100-litre injection tank were: trimethoprim 2.5 mg/L, carbamazepine 1 mg/L, diclofenac 1 mg/L, and 4–AAA 1 mg/L. Injection was continuous and lasted for approximately 36 minutes. Following injection, the piezometer was flushed with 200 litres of groundwater previously extracted from the observation well and then sampling was initiated based on an established program.

RESULTS AND DISCUSSION

Before the experiment started, initial conditions were monitored every hour for 1 day. The results showed that the average values of the monitored parameters were: electrical conductivity ≈649 μS/cm, pH ≈6.9, O_2 (dissolved oxygen in the groundwater) ≈0.05 mg/L, oxidation/reduction potential ≈91 mV, observation well flow ≈6 L/s, injection piezometer hydraulic head ≈65.77 m (above sea level), and hydraulic head in the observation well ≈65.61 m (above sea level). The initial concentrations of the selected pharmaceuticals in the observation well, before the experiment, were: carbamazepine ≈6 ng/L and 4-AAA ≈2 ng/L. The other analyzed pharmaceuticals (trimethoprim and diclofenac) were not detected before the experiment started.

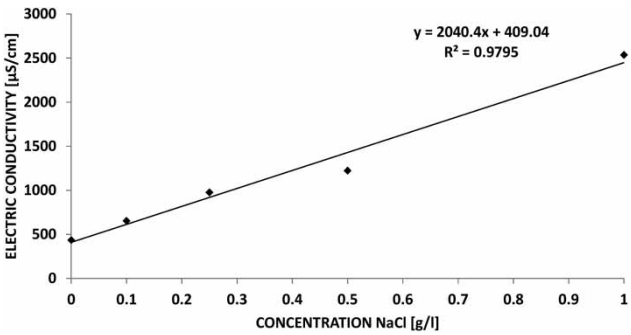

Figure 3 | Electrical conductivity as a function of NaCl concentration (25 °C).

The results of initial monitoring of the groundwater showed that it was anoxic and that the hydraulic and flow conditions were quasi-stationary. The results also showed that carbamazepine and diclofenac had background concentrations from the Danube River.

The sediment sample from the new borehole was analyzed and the organic carbon content was found to be approximately 0.229%. The organic carbon content was relatively low, so it was not the predominant driver of the sorption process. The dominant fraction of the sample was 2–16 mm and consisted of: clay (0%), silt (0.42%), sand (38.83%), and gravel (60.52%). The particle size distribution curve for different sample depths was determined and the results are presented (Figure 4).

The highest concentration of the NaCl tracer was established 200 minutes after the beginning of the test (Figure 5). Average calculated hydraulic conductivity based on the water-bearing geometry and tracer (NaCl) velocity was 4×10^{-2} m/s. Theoretical hydraulic conductivity calculated based on the empirical formula (USBR) was found to be between 4×10^{-2} m/s and 8×10^{-4} m/s for different sample depths, which indicate that preferential flow paths have the highest impact on the velocity of groundwater. Hydraulic conductivity could vary locally but obtained results are consistent with previous research work.

Organic matter is highly variable among different sediment samples, and K_d can alternatively be expressed as a function of the fraction of organic carbon in the sediment, f_{OC} [%], and the organic carbon partitioning coefficient, K_{OC} [mL/g], of the compounds according to Equation (1):

$$K_d = f_{OC} \cdot K_{OC} \quad (1)$$

where K_d is the linear sorption coefficient [mL/g]; f_{OC} is the fraction of organic carbon in the sediment [%]; and K_{OC} is the carbon normalized sorption coefficient [mL/g].

During the experiment, the average values of the monitored non-variable parameters were: pH ≈ 7, O_2 (dissolved oxygen in the groundwater) ≈0.06 mg/L, oxidation/reduction potential ≈90 mV, injection piezometer hydraulic head ≈65.73 m (asl), and hydraulic head in the observation well ≈65.54 m (asl). The results of the monitoring of the non-variable parameters during the experiment showed that the conditions were similar to the initial conditions,

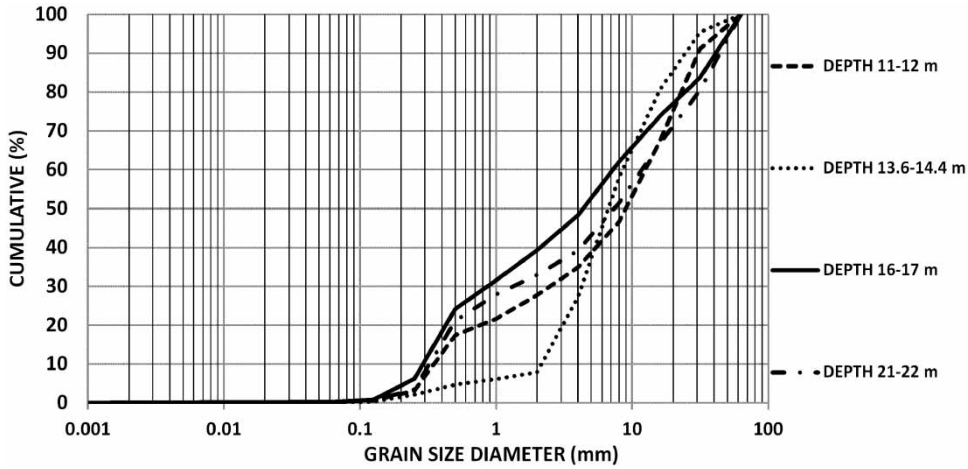

Figure 4 | Particle grain size distribution curve diagram for different samples and different sample depths.

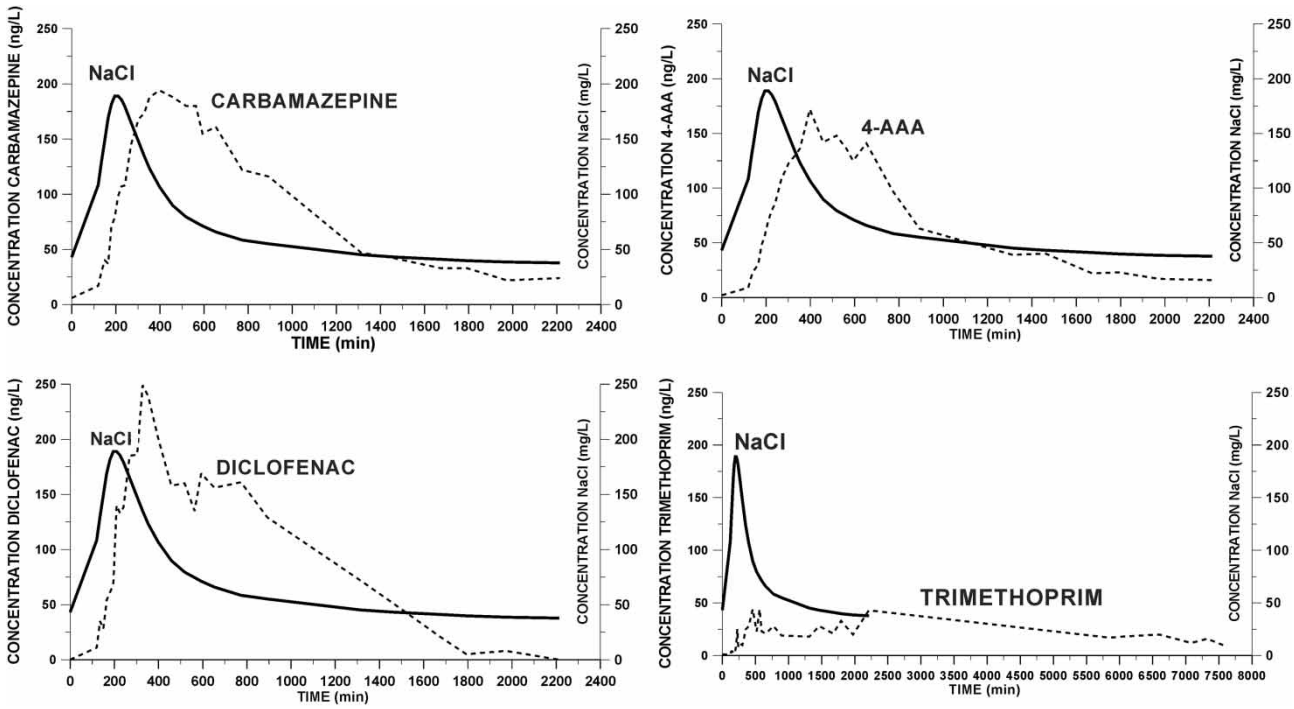

Figure 5 | Breakthrough curve of NaCl vs breakthrough curve of investigated pharmaceuticals.

the groundwater was anoxic, the hydraulic and flow conditions were quasi-stationary, and a quasi-steady-state radial divergent flow field was established.

After sampling and analysis, the results of the field experiment revealed retardation of all pharmaceuticals relative to the non-reactive tracer NaCl. A breakthrough curve of NaCl vs. that of the investigated pharmaceuticals was obtained (Figure 5) based on the results of the tracer test and monitoring of the behavior of the selected pharmaceuticals.

The following equation was used to calculate K_d (linear sorption coefficient) for all analyzed pharmaceuticals:

$$R_d = \frac{v_{NaCl}}{v_{pharmaceutical}} = 1 + \frac{\rho_b}{n} K_d \quad (2)$$

where R_d is the retardation coefficient [–]; V_{NaCl} is the velocity of the NaCl tracer [m/s]; $V_{pharmaceutical}$ is the velocity of the pharmaceutical [m/s]; ρ_b is the bulk density of the aquifer material [g/mL]; n is the effective porosity [–]; and K_d is the linear sorption coefficient [mL/g].

Effective porosity was calculated based on the grain size distribution curve; in this study the effective porosity was 0.15 and the theoretical soil bulk density of 1.65 g/cm^3 was used for the aquifer gravel and sand. The velocities of the NaCl tracer and the pharmaceuticals were calculated from the results of the tracer test and monitoring of the behavior of the selected pharmaceuticals. The linear sorption coefficient K_d, retardation coefficient R_d and carbon normalized sorption coefficient K_{OC} for all the pharmaceuticals was calculated on the basis of the experimental data (Table 2).

According to the results of the field experiment and available data ($f_{OC} = 0.29\%$) and calculated carbon normalized sorption coefficient ($K_{OC} = 2.79$ mL/g), trimethoprim had the highest R_d (7.7) value and the highest K_d (0.64 mL/g) value. In a study with 13 different soil types (Kodešová *et al.* 2015), which was conducted under different experimental conditions (batch experiment), the results showed a higher K_d (3.5 mL/g) value for sediment with a higher carbon normalized sorption coefficient ($K_{OC} = 9.72$ mL/g).

In this study the carbamazepine K_d (0.18 mL/g) value was relatively low with a low carbon normalized sorption coefficient ($K_{OC} = 0.65$ mL/g). In a batch experiment study (Scheytt *et al.* 2005), the carbon normalized sorption coefficient for carbamazepine was significantly higher ($K_{OC} = 100.76$ mL/g) and the K_d (0.13 mL/g) value was lower than in this study. In another batch experiment study (Yu *et al.* 2013), the carbon normalized sorption coefficient for carbamazepine was slightly higher ($K_{OC} = 3.62$ mL/g), and the K_d (1.45 mL/g) value was also higher than in the present study. In a column experiment study (Scheytt *et al.* 2006), with a significantly higher carbon normalized sorption coefficient ($K_{OC} = 715$ mL/g), the K_d (1.43 mL/g) value was higher than in the present study.

Diclofenac and 4-AAA had the same R_d (1.88) and K_d (0.15 mL/g) values in the present study. In a batch experiment study (Scheytt *et al.* 2005), with a higher carbon normalized sorption coefficient ($K_{OC} = 438$ mL/g) than in the present study ($K_{OC} = 0.78$ mL/g), the K_d (1.87 mL/g) value for diclofenac was much higher than in the present study ($K_d = 0.15$ mL/g). In another batch experiment study (Xu *et al.* 2009), with a slightly higher value of carbon normalized sorption coefficient for diclofenac ($K_{OC} = 1.1$ mL/g), the K_d (0.55 mL/g) value was higher than in the present study. In a column experiment study (Scheytt *et al.* 2006), with a significantly higher carbon normalized sorption coefficient ($K_{OC} = 935$ mL/g), the K_d (0.57 mL/g) value for diclofenac was also higher than in the present study.

The metamizole metabolite 4-AAA had a low K_d value (0.15 mL/g). So far, little information on R_d and K_d values of 4–AAA can be found in literature sources. Only one study (Burke *et al.* 2013) has reported that 4-AAA was not sorbed on the sediment with similar $f_{OC} = 0.20\%$.

CONCLUSIONS

Based on the results of the tracer test and other experimental data, the linear sorption coefficients K_d of the selected

Table 2 | Linear sorption coefficients *Kd* [mL/g], carbon normalized sorption coefficients K_{OC} [mL/g] retardation coefficients Rd[–] and fraction of organic carbon f_{OC} [%] (present study and literature data, f_{OC} =0.29% for present study)

Pharmaceutical	R_d present study	K_d (mL/g) present study	K_{OC}(mL/g) present study	K_d (mL/g) literature	K_{OC} (mL/g) literature	f_{OC} (%) literature	Literature
Trimethoprim	7.7	0.64	2.79	[1]3.5	[1]9.72	0.36	[1]Kodešová *et al.* (2015), [2]Scheytt *et al.* (2005), [3]Scheytt *et al.* (2006), [4]Yu *et al.* (2013), [5]Xu *et al.* (2009), [6]Burke *et al.* (2013)
Carbamazepine	2.2	0.18	0.65	[2]0.13 [3]1.43 [4]1.45	[2]100.76 [3]715 [4]3.62	[2]0.002 [3]0.0013 [4]0.41	
Diclofenac	1.88	0.15	0.78	[5]0.55 [3]0.57 [2]1.87	[5]1.1 [2]438 [3]935	[5]0.5 [2]0.002 [3]0.0013	
4–AAA	1.88	0.15	0.65	–	–	[6]0.2	

pharmaceuticals and carbon normalized sorption coefficients K_{OC} under field experimental conditions could readily be calculated. It is very important to note that sorption of the selected pharmaceuticals, with a relatively low linear sorption coefficient compared to the data reported in the literature, represents a significant factor that influences the behavior of pharmaceuticals in groundwater.

Calculated carbon normalized sorption coefficients K_{OC} are lower than those reported in the literature data (Scheytt *et al.* 2005, 2006; Xu *et al.* 2009; Yu *et al.* 2013; Kodešová *et al.* 2015). Obtained R_d values have importance because they show that there is a significant retardation of selected pharmaceuticals, although calculated K_{OC} values in the present study are significantly lower than those reported in the literature. The results of the present study clearly indicate that besides the total organic carbon content, another sorption mechanism plays an important role in the total sorption potential of the investigated pharmaceuticals in field experiments.

However, much of the literature contains results obtained under laboratory conditions (batch or column experiments) for different sediment types, so that such results need to be used carefully in practice.

Field conditions differ from laboratory conditions and the effect of scale is very important, with a significant impact on the final results. Apart from the experimental scale, the effects of preferential flow paths during groundwater flow influence the velocity of groundwater in natural conditions and therefore affect the final results of field experiments.

The field experiment result a for K_d values in the present paper represent some relatively unique data, because the obtained results are closest to real values for site-specific conditions. In practice when pharmaceutical transport model calculations are conducted, literature K_d values should be used carefully, because the calculation results of transport parameters may significantly deviate from real data.

In this study, trimethoprim had the highest R_d and K_d values and carbamazepine exhibited higher R_d and K_d than diclofenac and 4-AAA, which is consistent with literature data. According to the results, the fastest-moving pharmaceuticals on this experimental site were diclofenac and 4-AAA, and trimethoprim was the slowest. Calculated R_d, K_{OC} and K_d values were lower than in other studies or laboratory experiments, except for 4-AAA where R_d was calculated for the first time in a field experiment.

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