**Sorption properties and behaviour at laboratory scale of selected pharmaceuticals using batch experiments**

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**Abstract**

Despite the increasing public concern about the frequent occurrence of pharmaceuticals in the water bodies, their transport and fate are not yet well known; in particular in groundwater. In this laboratory study, batch experiments were conducted to investigate the sorption behaviour of selected pharmaceuticals. The choice of compounds was motivated by their chemical properties as well as by their occurrence at the relevant field sites. It included: antipyrine, atenolol, caffeine, carbamazepine, ciprofloxacin, diclofenac, ketoprofen, ofloxacin, and sulfamethoxazole. Sorption behaviour has already been investigated for some of these compounds (e.g. carbamazepine), but for the others (e.g. antipyrine, ketoprofen), extensive studies are missing so far. For the experiments, artificial and actual aquifer materials from complementary field sites were selected: technical coarse quartz sand and sediments from alluvial Vistrenque Aquifer, France (sandy loam), and fluvio-deltaic Baix Fluvià Aquifer, Spain (sandy clay loam, clay, and medium sand). In these field sites occurrence of pharmaceuticals in groundwater was previously stated, and the presented laboratory experiments were complementary to the field investigations. Five concentration steps for determining the sorption isotherms were investigated. Correlation analysis showed dependencies of K-coefficients of individual compounds and sediment properties; however, no clear, universal patterns for all compounds were found. Batch experiments suggest that sorption behaviour was governed by compound-specific properties rather than by sediment properties. These results contribute to the understanding sorption behaviour of pharmaceuticals in heterogeneous sediments, although some inconsistencies were revealed between laboratory scale results and field scale observations.

Keywords: Batch experiment, sorption isotherm, emerging organic contaminants, pharmaceuticals

1. **Introduction**

The occurrence of pharmaceuticals in the environment, and particularly in water resources, is presently an issue of public concern (D’Alessio et al., 2015; Loos et al., 2013). Their effect in nature as a threat to aquatic ecosystems is highly recognized (e.g., Petrovic et al., 2016, 2013) as well as their relationship with the presence of antibiotic resistance genes in groundwater (Berendonk et al., 2015). Their effects on human health are found “rare but statistically meaningful” (Lei et al., 2015; Saikat et al., 2013). Despite this lack of certainty, the Precautionary Principle, stated in the 1992 Rio Declaration on Environment and Development, compels a scientific and management effort to unveil the processes by which pharmaceuticals, as a contaminant of emerging concern, migrates in the subsurface, and define their impact to groundwater resources quality.

The transport and fate of pharmaceuticals in groundwater is still not completely understood due to their complex behaviour, which is extremely variable depending on the molecule structure and the local subsurface environmental conditions (i.e., soil/sediment/rock type, pH, redox state, organic matter content, microbiological communities, …; e.g., Lapworth et al., 2012; Schaffer and Licha, 2015). In addition to the inherent spatial heterogeneity of the groundwater hydraulic transport components (advection and dispersion), reactive geochemical processes as sorption and degradation play a relevant influence on the migration of pharmaceutical compounds and, therefore, on their occurrence in vulnerable areas of the system, either ecosystems and abstraction wells for human supply. A widely applied approach to determine the magnitude and typology of both reactive processes is the use of laboratory analyses, either batch or column experiments, that provide the reaction coefficients under determined experimental conditions (e.g., Banzhaf and Hebig, 2016). Resulting values can then be applied to model and predict the migration of these reactive pollutants at field-scale as a managing tool to prevent or manage groundwater pollution. Nevertheless, the extrapolation of laboratory results to field data modelling is usually challenging as the high variability of actual environmental circumstances and the complicated geochemical behaviour of these pollutants hardly coincides with the experimental conditions (Boxall et al., 2012). Moreover, literature references for selected compounds offer a wide range of sorption coefficients for a single compound, which increases the uncertainty on the application of laboratory results to regional scale pollution cases.

Sorption processes are often represented by a linear isotherm and a distribution coefficient, Kd, between the solute concentration in the aqueous phase and the adsorbed mass in sediment. Kd finally determines the retardation factor for that specific solute (Appelo and Postma, 2005; Fetter, 1999). Furthermore, for the sorption of organic contaminants, and among them pharmaceutical compounds, other types of isotherms must be considered in soils and sediments that take into account a limited adsorption capacity (Langmuir) or a progressive saturation of the solid surface (Freundlich). In addition, while Kd values for non-ionisable compounds can be based on an empirical correlation of the octanol-water partition coefficient KOW, and the soil-water coefficient normalized to organic carbon KOC, those for ionisable compounds, as pharmaceuticals, are more complex to calculate and partition coefficients must be generated by predictive models (Bronner and Goss, 2011; Kah and Brown, 2006). Schaffer and Licha (2015) propose a systematic framework that allows the assessment of transport properties of organic molecule species by their chemical nature (neutral, acidic, basic, ampholytic). As a result, the inclusion of a pH-dependent n-octanol water distribution coefficient, log D, which accounts for the species distribution at a certain pH, leads to satisfying results. log D is then calculated from log KOW and the compound dissociation constant pKa for acids and bases. Beyond this theoretical standpoint, that briefly introduces the gaps and challenges in the scientific knowledge of organic contaminant sorption processes, batch and column experiments are still the most common and practical approaches to characterize site-specific sorption parameters for various hydrological conditions.

In summary, the assessment of pharmaceutical pollution of groundwater resources must rely on appropriate laboratory experiments that provide adequate reactive information based on the most realistic conditions. Admitting this premise, this paper presents the results of laboratory batch experiments using sediments and groundwater samples from two studied aquifers with the aim to provide suitable data for selected pharmaceuticals. Focusing on sorption processes, our goal is characterizing the appropriate sorption reactions and the subsequent coefficients that will control their migration in the subsurface. On the one hand, we contribute to the overall knowledge of pharmaceutical sorption in sediments; on the other hand, we look forward providing data to understand their spatial distribution at a regional scale based on these results.

In particular, selected compounds for this study comprise antipyrine, atenolol, caffeine, carbamazepine, ciprofloxacin, diclofenac, ketoprofen, ofloxacin, and sulfamethoxazole (Table 1). These and other pharmaceuticals have been found in groundwater in two distinct field sites: the Vistrenque alluvial aquifer (Sassine et al., 2016b, 2015, 2014) and the Baix Fluvià fluvio-deltaic aquifer (Boy-Roura et al., 2018). These compounds also meet the following criteria: (1) they represent different groups in terms of therapeutic use, and (2) they lay on a wide range of log KOW and pKa values. Among them, some are well-studied as carbamazepine, whereas a thorough understanding about others is missing, such as ciprofloxacin, although it is on the Watch List of the EU (Carvalho et al., 2015).

**Table 1.** Structures and physicochemical properties of the pharmaceuticals used in the batch experiments (data source: NCBI database)

1. **Materials and methods**
	1. *Chemicals*

Complete list of chemicals used in presented study can be found in the Supplementary Material (SM.1).

* 1. *Sediments*

Different sediment types were selected for the laboratory experiments: (1) technical quartz sand (G) (Dorsilit Nr. 5F, Quarzsande GmbH, Germany), (2) aquifer material from the Vistrenque Aquifer, France (V) and materials from distinct layers of the Baix Fluvià Aquifer, Spain (E1, E2, E3). Technical sand was selected as a reference material. It was assumed that its low organic carbon content TOC and clay content will result in low sorption. The Vistrenque aquifer is related to a shallow alluvial aquifer (Sassine et al., 2016b). The area is used for agriculture (vineyards, orchards, vegetables, and cereals). In the Vistrenque basin, pharmaceuticals in the water bodies are related to the infiltration of stream water receiving WWTP effluents, and such recharge is determined by surface water – groundwater interactions. Several compounds (antibiotics, anticonvulsant, beta-blockers and analgesics) were found in both surface waters and groundwater. The Baix Fluvià unconfined quaternary aquifer is constituted by of the upper layers of fluvio-deltaic deposits of Fluvià River. It consists of gravel and sand and is underlined by an aquitard of silt and loam. The study area is dominated by intense agricultural activities (corn and orchards). As a result, the occurrence of antibiotics is mainly attributed to agricultural fertilization inputs of slurry and manure (Boy-Roura et al., 2018).

Locations of sediment sampling sites (Table 2) were selected according to two criteria: (1) representativeness for each particular aquifer, and (2) no pollution by pharmaceuticals detected in the vicinity of sampling location (Boy-Roura et al., 2018; Sassine et al., 2016a). The distinct particle size distribution for each sediment is shown in Figure 1. Sediments particles mainly range from fine sand to coarse sand, according to USDA Soil Texture Classification, yet two of them show a significant percentage of silt (E2, and especially E1 with a silt content of nearly 75%). Additionally, selected sediments are diversified by their texture, clay and carbon content, assuring a broad spectrum of sediment-specific parameters known to affect sorption. Sediment characteristics are given in Table 2.

After sampling, sediments were air dried and sieved through 2 mm sieve. Larger fractions were discarded in the experiments. Texture was measured by sieve analyse (2-0.063 mm) and by sedimentary analyse for finer fractions (<0.063 mm) (ISO 17892-4). Sediment pH was measured in a 0.01M CaCl2 solution with a pH-meter (pH 3110, WTW, Welheim, Germany) (ISO 10390:2005). Total carbon (TC) and total organic carbon (TOC) contents were analysed using Shimadzu Total Organic Carbon Analyzer TOC-5050 (Shimadzu, Duisburg, Germany). To determine TOC the inorganic carbon was removed by adding a few drops of 8M HCl solution. Cation Exchange Capacity (CEC) and Specific Surface Area (SSA) were commercially analysed (Ingenieur-Büro Dr. agr. Werner Häusler). CEC for calcareous sediments (V, E1, E2, E3) was determined following the ISO 13536, by adding a buffered BaCl2 solution and for non-calcareous sediment (G) by applying NH4Cl solution (Handbuch Forstliche Analityk, method A3.2.1.1.). Specific surface area (SSA) was tested by BET analysis using Quantachrome Autosorb-a (Quantachrome Corporation, Greenvale, New York, USA) following ISO 9277:2003-05.

**Table 2.** Sediment properties

**Fig. 1.** Particle size distribution of examined sediments (G, V, E1, E2 and E3 – sediment type, explanation in text)

* 1. *Water*

Three types of water were used in the experiment: two collected from the field sites, and one withdrawn for practical reasons from the nearby well located in Neuherberg (by München) at the Helmholtz Zentrum München (Germany). Groundwater from the respective aquifers was obtained from selected, non-contaminated wells. These waters are characterised by different mineralisation and ionic composition that allows considering the natural local hydrogeochemistry and its actual influence on sorption. For instance, water from the Vistrenque aquifer presents a Ca-HCO3-SO4 facies and pH=6.9, and water from the Baix Fluvià area shows a Ca-SO4-HCO3-Ca facies, pH=7.3. Water in the experiments using sediment G, and is HCO3-Ca-Mg type, pH=7.5. Coordinates of the sampling points and physicochemical properties of each groundwater used in the batch experiments are listed in the Supplementary Material (SM.2).

* 1. *Experimental setup*

Experimental setup was planned according to OECD test Guideline 106 (OECD, 2000) and to the guideline of U.S. EPA (2008) with some modifications, as described below. Air-dried sediment aliquots were placed in 120 mL glass bottles. A volume of 45 mL of water was added and left overnight for equilibration by shaking. Afterwards, 5 mL of stock solution were added in order to achieve the final liquid volume of 50 mL. The experiments were conducted in constant pH of ca. 7.0-7.5, resulting in following ionic form of the selected compounds: (1) neutral: antipyrine, carbamazepine, caffeine; (2) anionic: diclofenac, ketoprofen, sulfamethoxazole; (3) cationic: atenolol; and (4) zwitterion: ciprofloxacin, ofloxacin. The bottles were closed with buthyl septum, crimped, and stored in the dark (wrapped in aluminium foil) to avoid photodegradation, at room temperature (20°C±1°C). In order to focus on sorption only and avoid biodegradation, abiotic conditions were achieved by adding sodium azide (NaN3) with final concentration 50 mg/L (1 mL of stock solution of 5 g/L for each 100 mL; Hillebrand et al., 2013). An aliquot of liquid was taken by syringe, filtrated on a 0.22 µm syringe filter, and transferred to vials. Batch-blanks were prepared the same way (but without sediment), and the concentration measured in these samples were taken as the initial ones.

Batch experiments were conducted in two steps: (1) first, sediment/solution ratio and time of exposition was tested (data not shown), and then (2) the main batch test was performed (of which results are presented).

Preliminary study was performed in the course of this study in order to select the optimum experiment conditions, using sediments G, V, and E1 and initial solute concentrations of about 400 µg/L. Selected liquid to solid ratios of: 1:1, 2:1, and 5:1 were tested. Parallel method was used in the experiment; i.e. triplicate samples with the same sediment/water ratio were prepared, as many as the time intervals at which it was desired to study the sorption kinetics. To determine the equilibrium time, samples were collected sequentially over few days (after 4, 8 h, 1, 2, 3, 4 d). The equilibration time was determined by aqueous concentration versus time plot estimation. Liquid to solid ratio was set on 5:1 for practical reasons, i.e. easier sampling of water phase (50 mL of liquid and 10 g of sediment). Equilibrium time was achieved after 4 days.

In the main batch experiment, five concentrations steps for determining the sorption isotherms were investigated as advised by U.S. EPA (2008). For each concentration step, a separate stock solution was prepared with concentrations ranging from ca. 500 up to ca. 7500 μg/L. Initial concentrations in respective bottles were than diluted and the final concentrations were about 10-times lower (Table 3). For double-checking the final initial concentration in the respective concentration step and sediment type, we prepared batch-blanks without sediment and the concentrations in these samples were assumed as initial values. Therefore, any analytical uncertainty can be indirectly accounted for and the actual used concentration was determined.

**Table 3.** Compound concentrations in [μg/L] in stock solution

* 1. *Quantification with LC-MS/MS*

Concentrations of pharmaceuticals were measured with a liquid chromatography – tandem mass spectrometry (LC-MS/MS) system which consisted of Agilent 1200 binary pump (Agilent Technologies, Böblingen, Germany) and AB Sciex API 2000 Q-Trap mass spectrometer (Applied Biosystems, Framingham, USA). Kinetex C18 column (2.6 µm, 150 x 3 mm) purchased from Phenomenex (Aschaffenburg, Germany) was used.

The method used was based on one by Gros et al. (2012) and is described in detail in the Supplementary Material (SM.3, SM.4, SM.5).

* 1. *Data analysis*

The mass of the test substances sorbed on the sediments at equilibrium, *S* [µg/kg] were calculated using following formula (U.S. EPA, 2008):

$S=\frac{(C-C\_{0})∙V}{m\_{S}}$ *(1)*

where *C0* – initial concentration, ML-3; *C* – residual concentration, ML-3; *V* – solute volume, L3; *mS* – sediment mass, M.

Data were modelled using using the most widely used equations to describe the relation between sorbed and dissolved concentration at a fixed temperature (Appelo and Postma, 2005; Limousin et al., 2007); namely the linear

$S=K\_{d}∙C$ *(2)*

Freundlich

$S=K\_{F}∙C^{η}$ *(3)*

and Langmuir isotherms

$\frac{S}{S\_{max}}=\frac{K\_{L}∙C}{1+K\_{L}∙C}$ *(4)*

where *C* – aqueous concentration of compound, ML-3; *S* – mass of compound sorbed to mass of adsorbent, MM-1, *Smax* – maximal sorption capacity, MM-3; *Kd*, *KF*, *KL* – partition coefficients, L3M-1; *η* – degree of isotherm nonlinearity.

Sorption isotherms were fitted in the software SigmaPlot 12.0 (Systat Software, San Jose, CA), using least squares regression. Correlation tests were performed using Sigma Plot 12.0 to evaluate the influence of sediment properties on sorption behaviour of individual pharmaceuticals. Fitting was conducted by the least square method and the Pearson Product Moment Correlation was considered as a measure of the linear correlation. Plots were prepared in Sigma Plot 12.0 and in R (R Core Team, Vienna, Austria).

Errors were indicated in the graphs presenting data and isotherms. Horizontal error bars point out the standard deviation of the batch-triplicates. Vertical error bars represent errors calculated basing on the error propagation methodology, as *S* is a quantity calculated (not measured directly) from several input quantities. Therefore, the uncertainty components from all components were taken into account, resulting in combined standard uncertainty (JCGM 100:2008). When error bars are not visible, they are smaller than the symbol size.

To judge about the fitting goodness of sorption isotherm to data, it was assumed either very good (R²≥0.9), satisfactory (0.9>R²≥0.8), or acceptable (0.8>R²≥0.6). In some cases, it was not possible to fit any particular isotherm to the observed values, meaning that calculations of parameters were mathematically possible but did not fulfil logical conditions (all numbers positive, R²≥0.6).

1. **Results**
	1. *Isotherm fitting*

Sorption coefficients were obtained from the batch experiments by fitting of theoretical sorption isotherms to experimental data (Table 4). An illustrative example of isotherms (obtained in Sediment E3), which are graphical presentations of the outcomes, is shown in Figure 2. The entire set of all calculated isotherms is presented as Supplementary Material (SM.6). Comparison of sorption isotherm of atenolol, caffeine and carbamazepine obtained for different sediments is presented in Figure 3.

Sorption distribution coefficients of studied compounds are represented by different sorption isotherms. The selection was done by comparing the R2-values; in case of similar fitting goodness, a “simpler” model was chosen. Freundlich or linear isotherms offered the best fit for most of the cases, independently of compound or sediment type. The highest sorption coefficients were normally observed for ciprofloxacin and ofloxacin, regardless of the sediment type. However, some results did not allow quantifying sorption parameters for these compounds, as the goodness of fit was not sufficient, so it may be qualitatively stated that Kd is high (>100 L/kg). For antipyrine, in particular, any fitting for the sediments from the field sites provided an acceptable isotherm (Tab. 4) due to little sorption which means that Kd is very low or close to zero. In general, compound specific sorption was found the smallest for antipyrine and the largest for ofloxacin and ciprofloxacin.

In Table 4 the most fitting isotherm is highlighted in bold. Some isotherms were discarded either due to low R2, η>1 (cell highlighted in light grey) or due to non-realistic values (<0) (highlighted in dark grey).

* 1. *Sorption*

For the G-sediment sorption of all compounds could be adequately fitted by a linear isotherm. The Kd values were as follows: antipyrine – 7.00 L/kg, atenolol – 4.51 L/kg, caffeine – 3.55 L/kg, carbamazepine – 4.73 L/kg, ciprofloxacin – 1.25 L/kg, diclofenac – 0.31 L/kg, ketoprofen – 0.66 L/kg, ofloxacin – 3.30 L/kg, sulfamehoxazole – 1.10 L/kg.

For the sediment V, a linear sorption offered the best fit for atenolol, carbamazepine, diclofenac, and ketoprofen with Kd of 2.15 L/kg, 0.48 L/kg, 2.39 L/kg, 0.07 L/kg, respectively; whereas Langmuir isotherm represented caffeine (KL = 0.01 L/kg, Smax = 444 μg/kg) and ciprofloxacin (KL = 0.06 L/kg, Smax = 5197 μg/kg). In the case of antipyrine, ofloxacin, and sulfamethoxazole no isotherm could be fitted.

For the sediment E1, the best fit by linear sorption was obtained for caffeine (Kd = 6.81 L/kg). Freundlich isotherm represented the sorption behaviour of carbamazepine (KF = 6.80 (L/kg)η, η = 0.68). Langmuir isotherm represented atenolol (KL = 0.01 L/kg, Smax = 2000 μg/kg), dicofenac (KL = 3.7E-3 L/kg, Smax = 286 μg/kg) and sulfamethoxazole (KL = 0.01 L/kg, Smax = 2225 μg/kg). For antipyrine, ciprofloxacin, ketoprofen and ofloxacin no isotherm was fitted.

For sediment E2 linear sorption was found to be the best fit for antipyrine (Kd = 0.43 L/kg), carbamazepine (Kd = 2.30 L/kg) and sulfamethoxazole (Kd = 0.30 L/kg), whereas a Freundlich isotherm was better fitted to atenolol (KF = 32.35 (L/kg)η, η = 0.59), caffeine (KF = 14.44 (L/kg)η, η = 0.81) and ciprofloxacin (KF = 820 (L/kg)η, η = 0.40). Ciprofloxacin was fitted by Langmuir isotherm (KL = 0.01 L/kg, Smax = 2225 μg/kg). For diclofenac, ketoprofen, and ofloxacin no isotherm was fitted.

For the sediment E3, linear sorption isotherm corresponds to caffeine (Kd = 2.05 L/kg), carbamazepine (Kd = 1.14 L/kg) and ofloxacine (Kd = 87.55 L/kg). For atenolol a Langmuir isotherm was an acceptable fit (KL = 0.02 L/kg, Smax = 573 μg/kg), satisfactory for sulfamethoxazole (KL = 1.3E-3 L/kg, Smax = 1967.2 μg/kg), and very good for ciprofloxacin (KL = 0.04 L/kg, Smax = 4114 μg/kg), diclofenac (KL = 0.01 L/kg, Smax = 7335 μg/kg), ketoprofen (KL = 0.01 L/kg, Smax = 2234 μg/kg). For antipyrine no isotherm was fitted.

**Table 4.** Sorption parameters obtained in the batch experiments

**Fig. 2.** Observed data and fitted sorption isotherms in Sediment E3. Black solid line: linear isotherm; red dashed line: Freundlich isotherm; green dotted line: Langmuir isotherm

**Fig. 3.** Comparison of sorption isotherms of A) atenolol, B) caffeine, C) carbamazepine obtained in different sediments

* 1. *Influential factors*

The sorption coefficients corresponding to the linear model were further used for statistical data evaluation, even when linear model was not chosen as the best fit. The correlations between sediment properties and sorption parameters are presented in Table 5; whereas all correlation plots are presented in the Supplementary Material (SM.7, 8). Correlation plots between sorption coefficient Kd and selected sediment properties identify the interactions that govern sorption of the respective different compounds (Figure 4). The sediment properties used in correlation included: Cation Exchange Capacity (CEC), clay and silt content (Clay), sediment pH (pH), Specific Surface Area (SSA), Total Carbon (TC), and Total Organic Carbon (TOC). In particular, antipyrine showed high correlation of K-coefficient with sediment pH. For caffeine, sulfamethoxazole and ciprofloxacin CEC and SSA were the most crucial factors. Ciprofloxacin also showed correlation of sorption to the presence of clay minerals. Sorption of carbamazepine presented moderate correlation to sediment pH, and atenolol to CEC and SSA. For diclofenac and ketoprofen no correlations were found

Sorption behaviour cannot be explained by the octanol/water partitioning coefficient KOW for any sediment (Table 6). For all sediments, any prove of correlation was found between these two coefficients, as the correlation coefficients R2 describing relationship between KOW and Kd were low.

**Table 5.** Correlation coefficients R2 describing relationship between sorption coefficient Kd and selected sediment properties

**Fig. 4.** Correlation graphs between sorption coefficient Kd and selected sediment properties

**Table 6.** Correlation coefficients R2 describing relationship between KOW and Kd

1. **Discussion**

A distinct range of sorption parameters have been obtained from batch experiments for the tested compounds in different sediment types, from low values (Kd = 0 L/kg) for antipyrine up to the high values for ciprofloxacin and ofloxacin (Kd >100 L/kg). Observed values were generally within the range reported in literature (Fig. 5), yet this figure illustrates the wide range of partition coefficient values for a single compound under distinct experimental setups.

In this work, determination of isotherm could not be determined in some cases due to too low initial concentrations and complete sorption of all compound, suggesting high K-coefficients (ciprofloxacin, ofloxacin). The problem in finding an appropriate isotherm appeared also for antipyrine or ketoprofen, where K-coefficients oscillated around 0, making it difficult to find more precise values. From this result, we anticipate that increasing the concentration range would improve the experimental determination of the isotherm. Admittedly, isotherms for sediment G could be attributed to the S-class with much lower K-values; however, this type of isotherm is rather rare (Hinz, 2001) and, therefore, was excluded from further analysis.

As stated in the introduction, literature review indicates that sorption of ionic compounds strongly depends on pH. In these experiments the ionic form of the compounds had stronger influence on sorption behaviour than sediment type. The experiments were conducted at constant pH of ca. 7.0 up to 7.5, and the selected compounds were in different ionic forms: (1) neutral: antipyrine, carbamazepine, caffeine; (2) anionic: diclofenac, ketoprofen, sulfamethoxazole; (3) cationic: atenolol; and (4) zwitterion: ciprofloxacin, ofloxacin. These differences were reflected in their sorption behaviour in the batch experiments, and are hereafter discussed.

**Fig. 5**. Sorption partition coefficients Kd and KF obtained in this study in comparison with the literature data

* 1. *Sorption of neutral compounds*

In this study, sorption of neutral compounds was negligible. Similar observations are present in the literature: for example Greenhagen et al. (2014) stated no retardation (due to sorption) in their column experiments.

Carbamazepine is the most documented compound among the pharmaceuticals included in this study and it is known to be persistent in the environment with negligible or low retardation due to sorption (Scheytt et al., 2005a). However, Banzhaf et al. (2012) observed apparent retardation of carbamazepine in a column experiment, that was explained by sorption as the dominating transport process. Chefetz et al. (2008) reported nonlinear sorption isotherms with KF values of 0.9 and 12.7 for sediment samples of respectively low (0.94%) and high (8.13%) organic carbon. Similar observations were described by Drillia et al. (2005), where the lowest values of KF =0.5 (L/kg)η were obtained for sediment with low organic content; otherwise, higher sorption was linked to sediments with high organic content, being the highest in sludge (KF =49 (L/kg)η). In the presented study, however, no correlation between TOC and sorption coefficient was found. Indeed, the observed Kd was between 0.5 L/kg and 4.7 L/kg. Antipyrine is reported by Burke et al. (2013) to show conservative transport behaviour (Kd = 0 L/kg). Similar results were corroborated by D’Alessio et al. (2015) and Henzler et al. (2014).

* 1. *Sorption of anionic compounds*

Negatively charged compounds (diclofenac, ketoprofen, and sulfamethoxazole) generally showed small sorption, since most sediments lack strong anion exchange sites (Manahan, 2017). However, anionic compounds diclofenac and ketoprofen were largely sorbed than neutral molecules in sediment E3.

* 1. *Sorption of cationic compounds*

Sorption of atenolol present in cationic form is relatively high. For example Schaffer et al. (2012b) and Yamamoto et al. (2009) reported the strongest retardation due to sorption for protonated molecules in their column experiments (atenolol, among the others).

* 1. *Sorption of zwitterions*

Sorption of ciprofloxacin is strongly pH-dependant and the most effective at lower pH, when the compound appears in cationic form (Vasudevan et al., 2009). In this study, even in a less-sorbing zwitterion form, ciprofloxacin and ofloxacin were the most sorbed among the tested compounds.

High sorption K-coefficients (even >1000 L/kg) of ciprofloxacin and ofloxacin has been reported in the literature, and their dependency on pH was also emphasized (Drillia et al., 2005; Vasudevan et al., 2009; Zhou et al., 2014). Similar observations were obtained in this study, with K-coefficients ranging from 4 up to more than 100 for both antibiotics. In general, high K-values should be treated with caution as it may be concluded that high loads of these compounds can be entirely sorbed, suggesting little threat for water quality deterioration. It is therefore puzzling, that ofloxacin and ciprofloxacin are present in the aquatic environments and have been reported in several field sites (also of the tested sediments) (e.g. Boy-Roura et al., 2018; López-Serna et al., 2013; Santos et al., 2013), reporting the paradox of why highly sorbing compounds in lab experiments occurring at considerable concentrations in groundwater. Discrepancies between lab data and field observations at a regional scale reflect the difficulty on tracing the fate of these pollutants in the subsurface and assessing their impact in groundwater quality.

* 1. *Choice of isotherm and reactions involved*

It is known, that the isotherm itself does not automatically provide information about the type of reaction involved (Limousin et al., 2007). For instance, it is known that linear sorption, that showed a good fit for most of the compounds and sediments used in the experiment, satisfactorily describes the sorption behaviour for low solute concentrations (Delle Site, 2001). This case actually corresponds well to the pharmaceuticals in groundwater, as these compounds are generally found at low concentrations (at ng/L level; Boy-Roura et al., 2018). Nevertheless, linear isotherm is considered as an easy-to-use approximation rather than an precise description of sorption mechanism (Limousin et al., 2007). Other sorption models used in this study take into account that sorption is not infinitely linear. The Freundlich isotherm is an empirical model, that assumes a progressive saturation of the sorption sites, whereas the Langmuir model assumes to have a limited sorption capacity. Usually the choice of isotherm has to be found experimentally, because it strongly depends on several (site specific) factors (as presented e.g. by Al-Khazrajy and Boxall, 2016; Paul et al., 2014). For example, Chefetz et al. (2008) observed that carbamazepine sorption was less linear in sample with high organic carbon content, whereas with low organic carbon content, isotherm became more linear. Conversely, the linear model accurately represented sorption of carbamazepine in the present study. Indeed, the simplest model is usually selected rather than the more complex ones (Limousin et al., 2007). Therefore, a careful selection of sorption model is critical for its further use in modelling approaches that predict solute mobility in groundwater (Hinz et al., 1994).

In our experiments, we have opted for selecting the isotherm with a best regression coefficient in the fitting process (Table 5), yet we are aware of the conceptual assumptions involved in this decision. This is the reason why all potential isotherms are also included as Supplementary Material (SM6).

* 1. *Other factors controlling sorption*

The impact of compound properties and sediment characteristics on sorption parameters has also been addressed by different authors (e.g. Al-Khazrajy and Boxall, 2016; Kodešová et al., 2015). However, any attempt to find a general relationship enabling calculating Kd based on other parameters has only been possible for specific (for the particular experiment) conditions and it was, therefore, biased. Although this work points out some dependencies of the K-coefficients of individual compounds and the sediment properties (Fig. 5), a clear, universal pattern for all compounds is missing. For example, for the tested compounds, sorption behaviour cannot be explained by KOW of the respective compounds or organic carbon content as previously proposed (Scheytt et al., 2005b). This standard concept to predict retardation by means of KOW could be improved by considering the charge of the species in dependence on pH value. The mechanistic understanding of the sorption behaviour of charged compounds has been recently highlighted, because in particular electrostatic interactions are not yet quantitatively predictable (Schaffer et al., 2012; Schaffer and Licha, 2015).

* 1. *Concentration range used in the experiment*

Used concentrations of all compounds (ca. 35-750 μg/L) are still higher comparing to the concentrations observed in the environment (range of ng/L), but lower compared to other laboratory studies which generally used high initial concentrations in batch studies. Fenet et al. (2012) used carbamazepine in concentrations of 250-3000 μg/L, and Calisto and Esteves (2012) performed their experiment at even higher input concentrations 2-10 mg/L. Kodešová et al. (2015) and Yamamoto et al. (2009) performed batch tests using different compounds in concentrations of 0.5-10 mg/L and 20-100 μg/L, respectively. We highlight the scale range of our experiments, as well as those referenced in literature, as an issue of concern when isotherms are applied to model field data.

1. **Conclusion**

Batch experiments sorption parameters of selected pharmaceuticals for distinct scenarios based on actual sediments and groundwater from previously studied field sites. Even though the underlying processes of the different sorption behaviour are difficult to assess due to several factors influencing sorption, we found that pharmaceuticals on selected sediments did not depend solely on KOW, organic carbon content, or any other parameter as proposed in the literature. More important was the ionic form of the compounds. Therefore, it is crucial to control pH during experiments, in order to be able to predict the behavior of examined chemicals. Further studies are also needed to advance our understanding about specific sorption processes (adsorption vs absorption), in particular the role of organic matter and clay minerals.

Batch experiments are and remain a reliable method to investigate sorption behaviour of contaminants in groundwater systems. They are easy to apply, relatively fast, enable to study site specific sorption, and give quantitative results, which may be further utilized e.g. in vulnerability analysis and modelling. Still, it needs to be kept in mind that laboratory batch experiments give information on sorption behaviour for equilibrium conditions and for initial concentrations of compounds exceeding concentration ranges (µg/L) typically found in aquifers (ng/L). Further, we showed that it is important to consider different isotherm types, because different compounds undergo different sorption mechanisms not necessarily described best by linear approximations even for pharmaceutical compounds with low environmental concentrations.

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