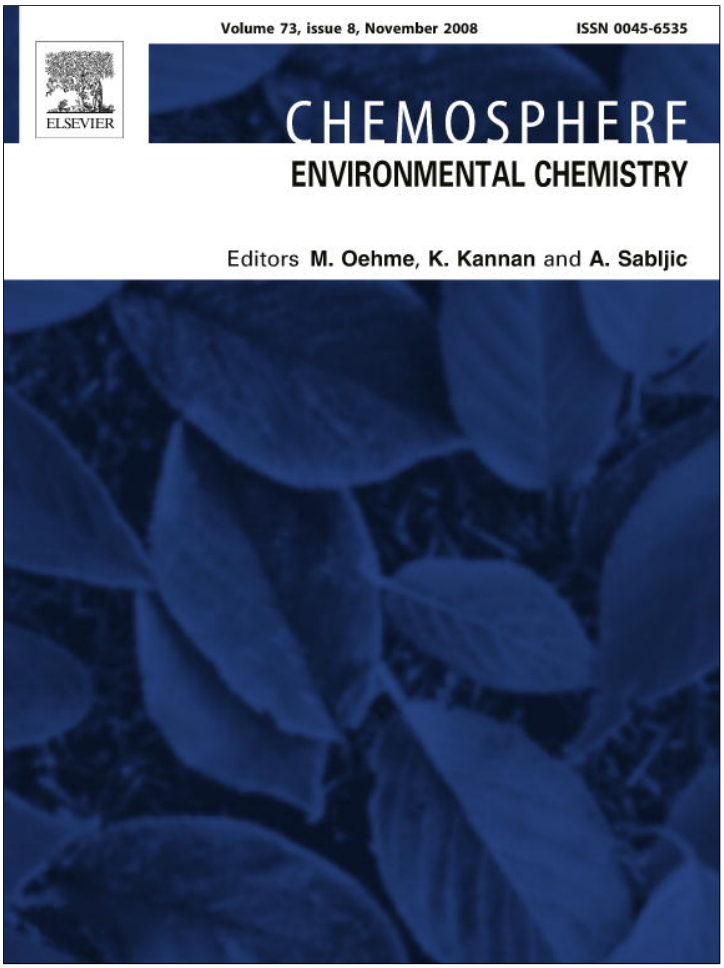

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Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater

Benny Chefetz *, Tamar Mualem, Julius Ben-Ari

Department of Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences, The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 76100, Israel

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ABSTRACT

Use of reclaimed wastewater for irrigation is an important route for the introduction of pharmaceutical compounds (PCs) into the environment. In this study, the mobility and sorption–desorption behavior of carbamazepine, naproxen and diclofenac were studied in soil layers sampled from a plot irrigated with secondary-treated wastewater (STWW). Carbamazepine and diclofenac were significantly retarded in the 0–5 cm soil sample rich in soil organic matter (SOM): carbamazepine was not affected by the water quality (freshwater versus STWW), whereas diclofenac exhibited a higher retardation factor (RF) in the freshwater system. Naproxen exhibited significantly lower RFs than diclofenac but with a similar trend – higher retardation in the freshwater versus STWW system. In the 5–15 cm soil sample containing low SOM, naproxen was highly mobile while carbamazepine and diclofenac were still retarded. In the 15–25 cm sample, all compounds exhibited their lowest RFs. Sorption data suggested that SOM governs the studied PCs' interactions with the soil samples. However, higher carbon-normalized sorption coefficients were measured for the PCs in the 15–25 cm sample, suggesting that both quantity and the physicochemical nature of SOM affect sorption interactions. While both naproxen and carbamazepine exhibited reversible sorption isotherms, diclofenac exhibited pronounced sorption–desorption hysteresis. This study suggests that carbamazepine and diclofenac can be classified as slow-mobile compounds in SOM-rich soil layers. When these compounds pass this layer and/or introduced into SOM-poor soils, their mobility increases significantly. This emphasizes the potential transport of PCs to groundwater in semiarid zones due to intensive irrigation with reclaimed wastewater in SOM-poor soils.

1. Introduction

Pharmaceutical compounds (PCs) have been introduced into the environment for many years with very little attention. Information concerning the concentration and environmental fate of these "emerging contaminants" has only been reported in the last decade (Halling-Sørensen et al., 1998; Ternes, 1998; Kummerer, 2001; Kolpin et al., 2002; Thiele-Bruhn, 2003; Moldovan, 2006; Sarmah et al., 2006; Duong et al., 2008). Many of the PCs are active at very low dosages and a large fraction of the consumed active compounds are extracted from the body after a short period of time. This results in the loading of bioactive substances into municipal sewage systems and wastewater-treatment plants (Ternes, 1998; Castiglioni et al., 2006; Loraine and Pettigrove, 2006; Reemtsma et al., 2006). Recently, reports have shown that many of the PCs do not fully degrade during municipal wastewater treatment (Halling-Sørensen et al., 1998; Buser et al., 1999; Kummerer, 2001; Castiglioni et al., 2006; Ellis, 2006; Yu et al., 2006; Al-Rifai et al., 2007). Retardation of PCs in sludge is a dominant process for the more hydrophobic compounds, whereas the persistent hydrophilic compounds are present mainly in the treated wastewater effluents. The release of reclaimed wastewater into surface and groundwater has resulted in the increasing ubiquity of these chemicals in surface water bodies (Kolpin et al., 2002) where they can re-enter the biosphere and the drinking water supply (Snyder et al., 2007).

Introduction of PCs to the environment (i.e., agricultural fields) via irrigation is a highly relevant exposure route in semiarid zones where recycled wastewater is an important source of irrigation water (Kumar et al., 2005; Kinney et al., 2006). Highly mobile PCs have the potential to leach to the groundwater, whereas strongly sorbing PCs can accumulate in the top soil layer. These compounds can subsequently affect the soil microbial community and may be taken up by plants (Thiele-Bruhn, 2003). Sorption of PCs to soils has been shown to be influenced by the solution chemistry and the type of mineral and organic sorbents (Tolls, 2001; Boxall et al., 2002; Drillia et al., 2005; Hari et al., 2005; Loffler et al., 2005; Williams et al., 2006; Blackwell et al., 2007). In addition to these factors, dissolved organic matter (DOM) originating

* Corresponding author. Tel.: +972 (8) 948 9384; fax: +972 (8) 947 5181.
E-mail address: chefetz@agri.huji.ac.il (B. Chefetz).

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from wastewater effluents can affect transport and sorption of organic compounds in soils (Kan and Tomson, 1990; Kögel-Knabner and Totsche, 1998; Nelson et al., 1998; Seol and Lee, 2001; Totsche and Kögel-Knabner, 2004). DOM can increase the solute's apparent solubility and therefore enhance its mobility. Alternatively, DOM can reduce mobility due to co-sorption and cumulative sorption to the soil's solid phases. These processes are controlled by the binding affinity of the organic contaminant to the DOM, the binding affinity of the DOM to the soil organic and inorganic matrices, and the sorption affinity of the DOM-organic contaminant complex to the soil solid phases.

In this study, the transport, sorption and desorption processes of selected PCs, which are frequently detected in wastewater effluents (Ternes, 1998; Joss et al., 2005; Ternes et al., 2007), were investigated in three soil samples and two types of irrigation water. Our major objective was to evaluate the effect of irrigation-water quality (freshwater versus secondary-treated wastewater; STWW) on the environmental behavior (mobility versus accumulation) of PCs in soils continuously irrigated with STWW.

2. Materials and methods

2.1. Soil samples

Soil (Rhodoxeralf) was sampled from a citrus orchard (Basra, Israel) which has been irrigated with treated wastewater for over 25 years. The top nondecayed organic layer was removed and samples were collected from depths of 0–5, 5–15 and 15–25 cm. Soil was sampled in four locations and mixed samples were prepared. The samples were air-dried and sieved through a 2-mm sieve. The bulk properties of the studied soil samples were measured by the standard soil-testing methods (Sparks et al., 1996). The soil properties at the different depths are presented in Table 1.

2.2. PC analysis in STWW

STWW samples (200 mL) were filtered (0.45 μm) and adjusted to pH 2. The samples (three replicates) were allowed to mix for 2 h before loading on a solid-phase extraction Oasis HLB cartridge (500 mg; Waters, The Netherlands). Then the cartridge was washed with 5 mL of double-distilled water and dried with N_2 for 30 min. The PCs were eluted from the cartridge using 5 mL of methanol (twice). The eluent was evaporated to dryness under a N_2 stream and dissolved in 100 μL of methanol. Recovery tests were run in parallel and indicated the following recovery values for the spiked compounds in STWW: carbamazepine (100 ± 2%), diclofenac (90 ± 2%), ibuprofen (104 ± 4%), naproxen (91 ± 10%), ketoprofen (70 ± 7%), bezafibrate (111 ± 17%), gemfibrozil (129 ± 8%), clofibric acid (101 ± 7%). The PCs were separated using an Agilent 1200 rapid resolution LC system equipped with a C-18 column (Thermo Hypersil Gold 100 mm × 2.1 mm, 1.9 μm). A binary gradient consisting of 0.05% acetic acid in both water (solvent A) and acetonitrile (solvent B) at a flow rate of 0.3 mL min^{-1} was used. The gradient was as follows: 30% B held for 2 min, increased linearly to 95% over 10 min and held for 8 min. The compounds were identified and quantified using an Agilent 6410 triple quadrupole MS equipped with electrospray ionization ion source. Ionization was achieved using following operating parameters: capillary voltage 4000 V, nebulizer pressure 40 psi, drying gas flow 10 L min^{-1} and gas temperature of 350 °C. The optimized MS parameters are presented in Table 2.

2.3. Column studies

The column experiments were carried out with the three soil samples (0–5, 5–15 and 15–25 cm) and two types of water samples (STWW and tap water). Selected chemical and physical properties of the studied PCs are summarized in Table 3. The STWW sample was collected from the Shafdan wastewater-treatment plant (Rishon LeZion, Israel) and the tap water (freshwater) from Rehovot, Israel. Selected properties of the water samples are presented in Table 4. Glass wool was packed at the bottom of a glass column (3 × 25 cm) to prevent leaching of soil particles. Then air-dried soil samples were manually packed into the column. The soil was added in increments during tapping to avoid obvious layering or segregation of the soil materials. Prior to the experiments, water was applied from the outlet below the column until the column was saturated. The solutions were spiked with KBr (10 mg L^{-1}) and the PC (1 mg L^{-1}) and left to equilibrate overnight before they were applied to the top of the column. Throughout the experiment, flow rates were kept at 2 mL min^{-1}, corresponding to an effective velocity of 0.28 cm min^{-1}. The column was eluted with approximately 12 exchanged pore volumes. The column was then washed with the same solutions without tracer or PC. The eluted solution

Table 1
Selected properties of Basra soil samples (±SD)

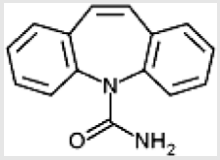
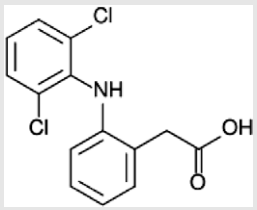
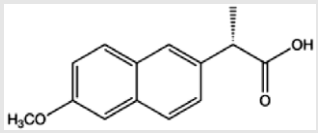
	Sample depth		
	0–5 cm	5–15 cm	15–25 cm
Sand (%)	80.6 ± 1.7	82.2 ± 0.2	82.4 ± 0.5
Silt (%)	14.2 ± 1.8	10.2 ± 0.1	5.0 ± 0.1
Clay (%)	5.2 ± 0.1	7.6 ± 0.1	12.6 ± 0.4
Texture[a]	Sand	Sandy loam	Sandy loam
Cation exchange capacity (meq 100 g^{-1})[b]	19.1	11.4	11.6
Exchange Na^+ (meq 100 g^{-1})	0.1	0.1	0.1
Exchange K^+ (meq 100 g^{-1})	0.7	0.6	0.5
Exchange Ca^{+2} (meq 100 g^{-1})	16.3	9.2	9.3
Exchange Mg^{+2} (meq 100 g^{-1})	2	1.5	1.7
Specific surface area (m^2 g^{-1})[c]	73.8 ± 8.6	90.9 ± 4.3	89.4 ± 9.1
pH[d]	7.7 ± 0.1	7.5 ± 0.2	7.4 ± 0.1
Organic carbon (%)[e]	8.13 ± 0.33	0.94 ± 0.04	0.40 ± 0.03
$CaCO_3$ (%)[f]	1.17 ± 0.06	0.16 ± 0.01	0.03 ± 0.01
Electrical conductivity (dS m^{-1})[d]	0.98	0.66	0.54

[a] Determined by hydrometer analysis.
[b] Determined by NH_4OAc procedure.
[c] Determined by the ethylene glycol mono-ethyl ether (EGME) method.
[d] Measured in saturated paste.
[e] Determined by loss on ignition at 400 °C for 8 h.
[f] Determined by reaction with acid in calcimeter.

Table 2
MS parameters for the analysis of pharmaceutical compounds in the secondary-treated wastewater

Compound	RT (min)	Polarity	MRM transitions	Fragmentor voltage (V)	MS/MS energy (eV)
Carbamazepine	6.2	Positive	237 → 194	110	15
Clofibric acid	7.9	Negative	213 → 127; 213 → 85	70	5
Ketoprofen	8.4	Positive	255 → 209; 255 → 105	110	10
Naproxen	8.5	Positive	231 → 185	110	7
Bezafibrate	8.7	Positive	362 → 316; 362 → 276	110	10
Diclofenac	9.9	Negative	294 → 250; 294 → 214	70	4
Ibuprofen	10.0	Negative	205 → 161	70	4
Gemfibrozil	10.7	Negative	249 → 121; 249 → 127	80	4

Table 3
Selected chemical and physical properties of the studied pharmaceutical compounds

Name	Formula	Structure	Molecular weight (g mol^{-1})	Aqueous solubility (mg L^{-1})	Log K_{ow}	pK_a
Carbamazepine	$C_{15}H_{12}N_2O$		236.27	125.0 ± 2	2.45[a]	
Diclofenac	$C_{14}H_{11}Cl_2NO_2$		296.16	360.0 ± 10[b]	4.51[c]	4.15[d]
Naproxen	$C_{14}H_{14}O_3$		230.27	60.1 ± 2	3.18[d]	4.15[d]

[a] Hanna et al. (1998).
[b] For sodium diclofenac at pH 7.4.
[c] Tixier et al. (2003).
[d] Avdeef et al. (2000).

was collected in 10-mL fractions using a fraction collector and kept refrigerated until analysis. The concentration of the bromide tracer was determined using ICP-OES (ARCOS, Spectro, Germany). The concentration of the PCs was determined using an L-7100 LaChrom HPLC (Merck-Hitachi, Darmstadt, Germany) equipped with a LiChrospher® RP-18 column (25 cm × 4.0 mm, 5 μm). The PCs were eluted at a flow rate of 1 mL min^{-1} using isocratic conditions of 55:45, 75:25 and 60:40 (acetonitrile/0.1% formic acid) for naproxen, diclofenac and carbamazepine, respectively. Diclofenac and carbamazepine were detected using a photodiode-array detector by absorbance at 276 and 286 nm, respectively. Naproxen was detected by fluorescence detector using 230 and 356 nm as the excitation and emission wavelengths, respectively. All PCs were quantified using external standards prepared in the background or STWW solutions.

2.4. Batch sorption–desorption studies

The soil samples 0–5 and 15–25 cm were used as sorbents; selected chemical and physical properties of the sorbates are summarized in Table 3. Sorption isotherms were obtained by batch equilibrium technique at 25 °C in Teflon® centrifuge tubes. Sorbate solutions (0.1–10 mg L^{-1}) were prepared by adding aliquots from concentrated methanol stock solutions to a background solution containing 50 mg L^{-1} $NaHCO_3$ (to buffer the pH), 5 mM $CaCl_2$ (to maintain a constant ionic strength) and 100 mg L^{-1} NaN_3 (to inhibit microbial activity) or to STWW solution spiked with 100 mg L^{-1} NaN_3. In all solutions, methanol concentration was maintained at less than 0.1% (v/v) to avoid co-solvent effects. The tubes (three replicates and a blank for each concentration) were agitated in the dark at 200 rpm for 72 h to reach equilibrium with carbamazepine and naproxen and for 48 h with diclofenac based on preliminary kinetics experiments. Desorption was performed by replacing 50% of the supernatant with fresh sorbate-free solution. Then the tubes were further agitated under the same conditions to perform desorption for the time determined in the kinetics tests (4, 7 and 5 days for carbamazepine, naproxen and diclofenac, respectively). Three sequential desorption steps were performed. An aliquot of the supernatant solution at every sorption or desorption step was used to determine the concentration of PCs using the above-described procedures. Mass-balance analyses ensured negligible sorption of the target analytes to the tubes or loss due to volatilization, and therefore sorption was calculated by mass differences.

2.5. Data analyses

The Freundlich parameters (K_F and N) were calculated using the Freundlich equation $q = K_F \times C_e^N$, where q is the sorbed amount (mg kg^{-1}), C_e is the equilibrium concentration (mg L^{-1}), K_F [(mg kg^{-1}) (mg L)$^{-N}$] is the Freundlich capacity coefficient, and N (dimensionless) describes the isotherm curvature. The Freundlich

Table 4
Analysis of the freshwater (tap water) and secondary-treated wastewater (STWW) used in the column experiments

	Tap water	STWW
Electrical conductivity (dS m^{-1})	0.91	1.6 (0.1)
pH	8.2	7.8 (0.1)
COD (mg L^{-1})		42 (3.5)
BOD (mg L^{-1})		11.5 (0.7)
TOC (mg L^{-1})		11.1 (2.4)
TSS (mg L^{-1})		2.6 (0.2)
Sodium adsorption ratio (cmol $L^{-1})^{0.5}$		4.5 (0.4)
$N - NO_3^-$ (mg L^{-1})	13.5	0.6 (0.3)
$N - NH_4^+$ (mg L^{-1})		1.6 (0.7)
P_{total} (mg L^{-1})		2.1 (0.7)
Cl^- (mg L^{-1})	105	286 (40)
HCO_3^- (meq L^{-1})	7.1	5.6 (0.4)
Na^+ (meq L^{-1})	2.0	7.6 (0.9)
Ca^{2+} (meq L^{-1})	5.5	3.7 (0.4)
Mg^{2+} (meq L^{-1})	1.9	2.0 (0.1)
K^+ (meq L^{-1})	1.7	15.0 (1.4)
Carbamazepine (μg L^{-1})		0.66 (0.01)
Diclofenac (μg L^{-1})		0.51 (0.05)
Ibuprofen (μg L^{-1})		0.24 (0.01)
Naproxen (μg L^{-1})		0.34 (0.01)
Ketoprofen (μg L^{-1})		0.08 (0.01)
Bezafibrate (μg L^{-1})		1.49 (0.06)
Gemfibrozil (μg L^{-1})		0.04 (0.01)
Clofibric acid (μg L^{-1})		0.01 (0.01)

Pharmaceutical compounds were detected in STWW sampled in March 2008. Mean results from three replicates are presented with STD in brackets.

equation parameter calculations and fitting were performed using an Excel spreadsheet (Bolster and Hornberger, 2007). Organic carbon-normalized sorption coefficients (K_{OC}) were calculated at C_e of 0.5 and 5 mg L^{-1}. Apparent sorption–desorption hysteresis was quantified for each of the isotherms using the hysteresis index (HI) defined by Huang et al. (1998) $HI = \frac{q_e^d - q_e^s}{q_e^s}$, where q_e^s and q_e^d are solid-phase solute concentrations for sorption and desorption experiments, respectively. Hysteresis indices at two C_e (0.5 and 5 mg L^{-1}) were calculated for each sorbent-sorbate pair. Higher HI values indicated increased difficulty of the sorbed analyte to desorb from the matrix. Retardation factor (RF) was calculated as the ratio of the time required for a PC to reach half-maximum concentration to that for the Br tracer (Widmer et al., 1995).

3. Results and discussion

Better understanding of PC sorption and transport is needed to identify the main processes influencing the fate and occurrence of PCs in agricultural soils irrigated with reclaimed wastewater. The studied STWW contained PCs (Table 4) in concentrations similar to those reported for wastewater effluents (Heberer, 2002; Ternes et al., 2004, 2007; Pedersen et al., 2005; Kinney et al., 2006).

3.1. Column experiments

3.1.1. Naproxen

Breakthrough curves of the tested PCs are presented in Fig. 1. Naproxen exhibited different behavior when introduced into the 0–5 cm soil sample in STWW versus freshwater. Although in both cases naproxen was retarded compared to the bromide tracer, when it was introduced into the column in freshwater solution, the RF was higher than the value calculated for STWW (3.0 versus 1.8, respectively). The recovery values for naproxen were 90 and 103% for the freshwater and STWW systems, respectively. The breakthrough curves obtained for naproxen in freshwater with the 5–15 and 15–25 cm soil samples were significantly different from the curves obtained with the 0–5 cm sample. With the 5–15 cm sample, the RFs were 2.0 and 1.6 for the freshwater and STWW, respectively. RFs of 1.6 and 1.2 were obtained with the 15–25 cm soil sample for the two solutions, respectively. With the 5–15 and 15–25 cm samples, the naproxen recovery values were >97%. The enhanced transport observed for naproxen in the 0–5 cm soil sample with STWW as compared to the freshwater system may have resulted from complexation of the naproxen with the DOM or with organic and inorganic suspended materials which were higher in the STWW solution than in the freshwater. These interactions can facilitate mobility (Totsche and Kögel-Knabner, 2004). However, the similar breakthrough curves exhibited for the two tested water types in the 15–25 cm soil system suggest that the solution chemistry and/or the presence of dissolved or suspended organic materials were not a major factor controlling retardation. This is probably due to the relatively low concentration of dissolved organic carbon (11 mg L^{-1}, Table 4). Under the experimental conditions (pH > 7.5), the carboxyl functional group of naproxen is deprotonated and therefore negatively charged. This is probably why naproxen was highly mobile in the soil samples having low SOM. In the 0–5 cm sample (8.13% organic carbon), naproxen probably interacted with the SOM, hindering its mobility; the low SOM content in the other samples probably did not promote these interactions. The higher mobility of naproxen with STWW in the 0–5 cm soil sample may have resulted from competition between the DOM and naproxen for binding sites in the SOM. Due to the higher concentration and molecular size of the DOM (as compared to naproxen), it competed efficiently for the sorption sites and therefore, naproxen's mobility was enhanced relative to the freshwater system. Due to the relatively high level of SOM in the 0–5 cm sample, naproxen was still able to interact with SOM and therefore exhibited higher retardation as compared to the 5–15 and 15–25 cm samples, which were poorer in SOM.

3.1.2. Carbamazepine

Unlike naproxen, carbamazepine exhibited pronounced retardation in the 0–5 cm soil sample, with no major differences between the STWW and freshwater solutions. In this case, the maximum normalized carbamazepine concentration ($C\ C_0^{-1}$) was 0.48 and the total eluted compound was only 46% (up to 10 pore volumes). The calculated RFs were 5.8 and 5.3 for the STWW and freshwater, respectively. In the freshwater experiment, the column was eluted with up to 14.5 pore volumes and carbamazepine recovery increased to 75.4%, with a normalized concentration of 0.13, after this long elution time. This supports the notion that carbamazepine is not likely to be degraded during the experiments (Scheytt et al., 2006a). Higher mobility of carbamazepine was obtained with the 5–15 and 15–25 cm soil samples containing lower levels of SOM. With the 5–15 cm soil sample, when carbamazepine was introduced into the freshwater system, high RFs were obtained (3.3). Although lower RFs were calculated with the 15–25 cm sample, carbamazepine still exhibited lower mobility in the freshwater system (RFs of 2.3 and 1.6 for freshwater and STWW systems, respectively). Scheytt et al. (2006a) reported higher carbamazepine mobility under unsaturated conditions with aquifer sediments containing 0.13% organic carbon. On the other hand, Mersmann et al. (2002) reported strong retardation of carbamazepine under saturated conditions in sediment containing 0.2% organic carbon. In the latter study, the RFs were similar to the values obtained in our study with the 15–25 cm sample containing 0.4% organic carbon. Unlike naproxen, carbamazepine is a neutral substance and is therefore quite likely to interact with the SOM. Therefore, a higher SOM content resulted in higher carbamazepine retardation.

3.1.3. Diclofenac

Similar to carbamazepine, diclofenac exhibited significant retardation with the 0–5 cm soil sample, and similar to naproxen, it exhibited a higher RF when introduced into the freshwater system

(4 and 5.3 for the STWW and freshwater systems, respectively). Under the experimental conditions (pH of 7.5–7.8), diclofenac is negatively charged (pK_a of 4.15), similar to naproxen. However, diclofenac is more hydrophobic than naproxen (Table 3) and therefore, its behavior was probably more affected by the interactions with the SOM. Similarly, Scheytt et al. (2006a,b) reported that diclofenac is significantly retarded under unsaturated conditions. However, they concluded that diclofenac was probably degraded under their experimental conditions. In our study, biotic degradation was prevented by using NaN_3 in all experiments and diclofenac recovery values with the 5–15 and 15–25 cm soil samples were all >96%. For the experiments with the 0–5 cm sample, diclofenac recovery values were 36 and 68% with freshwater and STWW, respectively. We therefore believe that the significant retardation of diclofenac observed with the 0–5 cm soil sample was mainly due to interactions (sorption) with the SOM and/or formation of non-extractable residues of diclofenac in the soil similar to carbamazepine. When the level of SOM was reduced (i.e., in the 5–15 and 15–25 cm samples), the transport behavior of diclofenac changed markedly: RFs of 2.2 and 2 were obtained for the 5–15 cm sample, and 1.3 and 1.4 for the 15–25 cm sample with STWW and freshwater, respectively. Similar to our results with the 5–15 and 15–25 cm samples, Mersmann et al. (2002) reported that diclofenac is transported more slowly than the tracer but significantly faster than carbamazepine.

3.2. Batch sorption–desorption experiments

Sorption and desorption are the major processes influencing the fate (uptake, biodegradation, chemical degradation, photodegradation and mobility) of organic contaminants in the environment. In this study, sorption–desorption interactions of carbamazepine, diclofenac and naproxen were measured with the 0–5 cm (8.13% organic carbon) and 15–25 cm (0.4% organic carbon) soil samples (Fig. 2).

3.2.1. Carbamazepine

All sorption isotherms of carbamazepine were nonlinear, exhibiting N values between 0.64 and 0.91 (Table 5). The isotherms with the 0–5 cm soil sample (high SOM content) were less linear than those with the 15–25 cm sample (low SOM content), and the isotherms measured with STWW were more linear than those measured in freshwater solution. Scheytt et al. (2005a) also reported nonlinear sorption isotherms of carbamazepine and Drillia et al. (2005) reported that carbamazepine isotherms were less linear with soil containing high SOM level. Due to the different N values, the K_F values from different isotherms cannot be directly compared. Therefore, the single-point organic carbon-normalized sorption coefficients (K_{OC}) were calculated at equilibrium concentrations of 0.5 and 5 mg L^{-1} (Table 5). The K_{OC} values with the 15–25 cm soil samples were all higher than those calculated for the 0–5 cm SOM-rich sample. With the latter sample, the K_{OC} values were independent of the solution properties (176 L kg^{-1} with STWW and 180 L kg^{-1} with freshwater), in accordance with the similar breakthrough curves exhibited for this sample with STWW and freshwater (Fig. 1). The higher retardation and sorption affinity of carbamazepine with the 0–5 cm soil sample was due to its higher level of SOM relative to the 15–25 cm sample (Table 1). We speculate that the lower affinity of carbamazepine to the SOM (i.e., K_{OC}) originated from the 0–5 cm sample is mainly governed

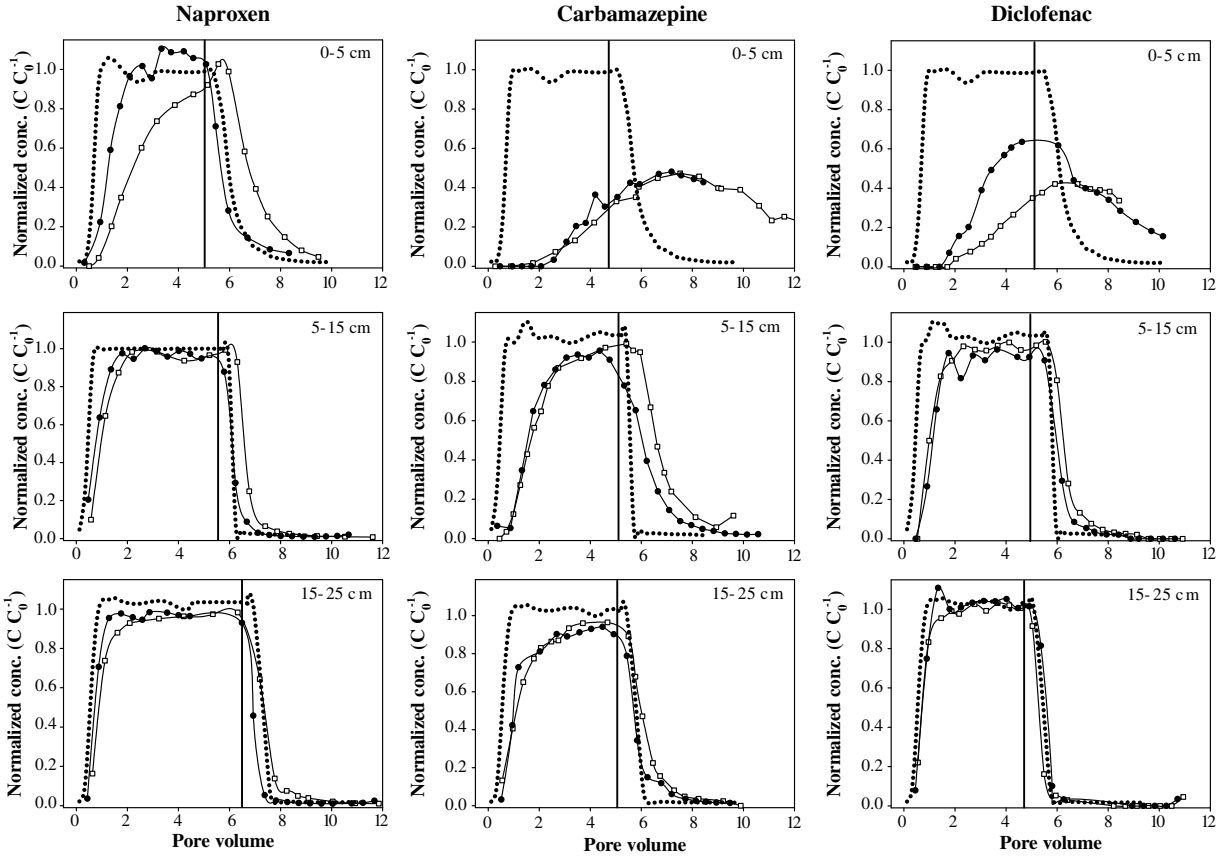


Fig. 1. Breakthrough curves of naproxen, carbamazepine and diclofenac in freshwater (open symbols) and secondary-treated wastewater (filled symbols). Dashed line is for bromide; end of spiking is indicated by solid vertical line.

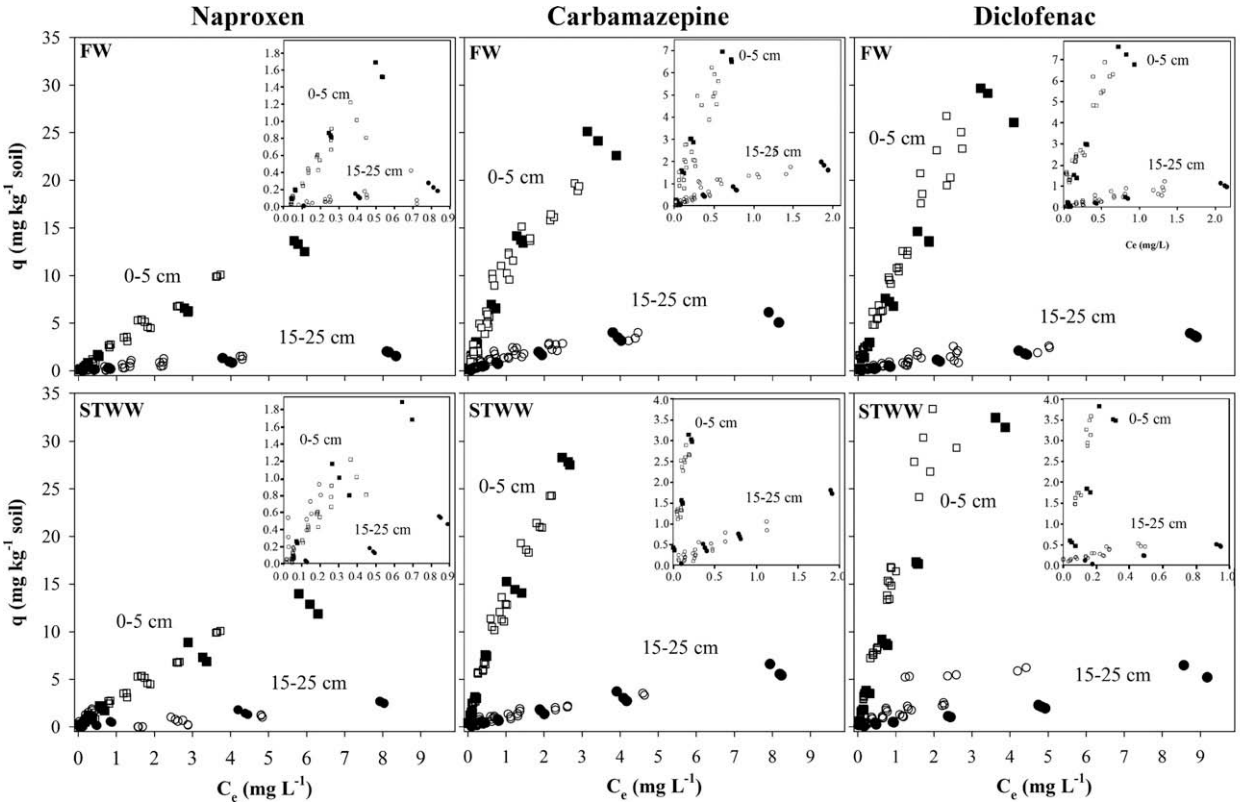


Fig. 2. Sorption–desorption isotherms for naproxen, carbamazepine and diclofenac with 0–5 cm (squares) and 15–25 cm (circles) soil samples in freshwater (FW, top) and secondary-treated wastewater (STWW, bottom) solutions. Sorption and desorption data are represented by filled and open symbols, respectively.

Table 5
Sorption coefficients of carbamazepine, diclofenac and naproxen with Basra soil samples

Sample	K_F[a]	N	E[b]	$K_{OC\ 0.5}$[c]	$HI_{0.5}$[d]	$K_{OC\ 5}$[e]	HI_5[f]
Solution: secondary-treated wastewater (STWW)							
Carbamazepine							
0–5 cm	12.63 ± 0.4	0.82 ± 0.04	0.99	176.0	0.08	116.3	0.14
15–25 cm	0.87 ± 0.1	0.91 ± 0.07	0.96	213.3	0.47	188.5	0.03
Diclofenac							
0–5 cm	11.90 ± 0.8	0.81 ± 0.06	0.97	167.3	0.35	107.3	0.86
15–25 cm	0.27 ± 0.07	1.13 ± 0.1	0.95	61.7	4.92	83.2	2.82
Naproxen							
0–5 cm	2.91 ± 0.3	0.82 ± 0.07	0.98	40.4	0.08	27.0	−0.08
15–25 cm	0.44 ± 0.06	0.84 ± 0.07	0.98	122.6	0.01	85.4	−0.03
Solution: freshwater							
Carbamazepine							
0–5 cm	11.46 ± 0.9	0.65 ± 0.07	0.91	180.2	−0.09	79.7	−0.05
15–25 cm	1.21 ± 0.01	0.73 ± 0.06	0.96	364.5	−0.05	196.2	0.48
Diclofenac							
0–5 cm	8.81 ± 0.7	0.89 ± 0.07	0.96	116.9	0.24	90.8	0.09
15–25 cm	0.49 ± 0.04	0.92 ± 0.04	0.99	129.1	0.55	108.4	0.62
Naproxen							
0–5 cm	2.44 ± 0.2	0.95 ± 0.04	0.99	31.0	0.11	27.8	0.11
15–25 cm	0.32 ± 0.06	0.84 ± 0.09	0.95	59.6	0.07	61.4	0.16

[a] $(mg\ kg^{-1})\ (mg\ L^{-1})^{-N}$.
[b] E characterizes the model efficiency. A model efficiency of 1 indicates a perfect fit to the data (Bolster and Hornberger, 2007).
[c] Single-point organic carbon-normalized distribution coefficients (K_{OC}) at an equilibrium concentration of 0.5 mg L^{-1}.
[d] Hysteresis index at an equilibrium concentration of 0.5 mg L^{-1}.
[e] Single-point organic carbon-normalized distribution coefficients (K_{OC}) at an equilibrium concentration of 5 mg L^{-1}.
[f] Hysteresis index at an equilibrium concentration of 5 mg L^{-1}.

by the nature of the SOM. The surface soil layer (0–5 cm) seems to contain mostly partially decomposed and relatively polar organic materials. With decomposition (i.e., increasing soil depth), the readily degradable materials such as carbohydrates decompose first, followed by decomposition of the phenolic functionalities. As a result, the SOM found in deeper soil layers (e.g., 15–25 cm soil sample) is characterized by more hydrophobic nature due to relatively higher level of aromatic and alkyl moieties (Chefetz et al.,

2000). Carbamazepine is believed to exhibit stronger sorption interaction with hydrophobic rather than polar SOM, thus lower K_{OC} values were obtained with the 0–5 cm sample.

In contrast to our data, Williams et al. (2006) reported higher carbamazepine K_{OC} values, and they reported higher K_{OC} values with soil amended with biosolids than with untreated soil (1250 and 885 L kg^{-1} organic carbon, respectively). They speculated that the higher salinity of the soil amended with biosolids was the main factor influencing sorption. In our case, salinity was probably not a major factor since carbamazepine exhibited similar sorption behavior with both solutions, which differed in salinity content (Table 4).

With the 15–25 cm sample, significantly lower K_{OC} values were obtained with the STWW solution at 0.5 mg L^{-1} carbamazepine, whereas at a 5 mg L^{-1} equilibrium concentration, the K_{OC} values were similar for both solutions. Such behavior can result from a competition effect of the DOM (originated from the STWW) on the solid-phase sorption sites or from complexation of carbamazepine with DOM which can reduce sorption of non-ionized organic compounds to the soil. Drori et al. (2005) reported that a DOM concentration of 60 mg L^{-1} organic carbon does not affect sorption of atrazine to soils and Seol and Lee (2000) reported that very high levels of DOM (>150 mg L^{-1} organic carbon) are needed to significantly reduce triazine herbicide sorption by soils. In our study, the DOM concentration was only 11 mg L^{-1} organic carbon, and thus was not expected to induce sufficient complexation of carbamazepine to reduce sorption to the soil matrix. We therefore believe that competition of DOM with carbamazepine was the major factor reducing its sorption affinity to the low-SOM-content sample at low solute concentrations in the presence of STWW. At high C_e (5 mg L^{-1}), competition was less pronounced and therefore the K_{OC} values were similar (188 and 196 L kg^{-1} organic carbon with and without DOM, respectively).

Carbamazepine exhibited reversible sorption isotherms with the SOM-rich 0–5 cm soil sample; with both solutions, HI values were low (Table 5). More pronounced hysteresis was observed with the 15–25 cm sample. It is important to note that the observed hysteresis for carbamazepine in our study was significantly lower than the hysteresis reported by Williams et al. (2006). In their study, most of the adsorbed carbamazepine did not desorb after two desorption steps (equilibrium time was 2 h for the sorption and desorption steps). Drillia et al. (2005) performed sorption–desorption experiments with carbamazepine in soils (equilibrium time was 24 h) in a concentration range similar to our study. In their study (Drillia et al., 2005), carbamazepine exhibited HI values lower than those obtained by Williams et al. (2006) but they were still higher than the values obtained in our study. Similar to the higher hysteresis observed for the 15–25 cm sample, Drillia et al. (2005) reported higher carbamazepine hysteresis in soil containing a lower level of SOM. The lower HI values recorded for carbamazepine in our study are probably related to the longer experimental period (4 d), during which carbamazepine reached equilibrium. The role of sorption–desorption kinetics is also highlighted by comparing the breakthrough curves (Fig. 1) of carbamazepine with the 0–5 cm sample (from which desorption hysteresis was expected). However, this was not observed in the sorption–desorption experiments (Table 5), probably due to the longer equilibrium time used in these experiments versus the 1-d column experiments.

3.2.2. Diclofenac

Based on the breakthrough curves of diclofenac in the 0–5 cm soil sample (Fig. 1), a lower sorption coefficient was expected in the presence of STWW. However, in the batch sorption experiments, a higher diclofenac sorption coefficient was recorded with the STWW solution (Table 5). Similar to carbamazepine, diclofenac sorption isotherms were nonlinear. Under the experimental conditions (pH > 7.5), diclofenac is negatively charged and therefore is expected to exhibit low affinity to the soil, similar to anionic herbicides (Grey et al., 1997). However, diclofenac exhibited sorption affinity values within the range of the values of carbamazepine (Table 5). Distribution coefficients, lower or on the same order as those of carbamazepine, have also been reported for diclofenac with natural sediments (Scheytt et al., 2005a). Similarly, Drillia et al. (2005) and Ternes et al. (2004) reported higher distribution coefficients for diclofenac than carbamazepine. We suggest that the high hydrophobicity of diclofenac facilitated its interactions with SOM. In agreement with this, Scheytt et al. (2005b) reported K_{OW} values (measured at pH 7) of 1.69 for diclofenac and 1.3 for carbamazepine. These values were better correlated with the sorption and transport data. The higher sorption coefficient of diclofenac with the 0–5 cm soil sample in the presence of STWW as compared to the system with freshwater results from co-sorption and/or cumulative sorption with DOM to the soil's solid matrix (mainly SOM) (Kögel-Knabner and Totsche, 1998; Totsche and Kögel-Knabner, 2004; Ling et al., 2006). With the 15–25 cm sample, diclofenac exhibited the opposite trend: higher sorption affinities were recorded with the freshwater versus STWW system. This supports the notion that with the 0–5 cm SOM-rich sample, diclofenac interacted mainly with SOM via co- and/or cumulative sorption. When the level of SOM is significantly lower, DOM acts as a competitor and therefore sorption affinities in the STWW system were lower (similar to the observation with carbamazepine).

Diclofenac exhibited significant sorption–desorption hysteresis which was more pronounced in the STWW system and with the low SOM content sample (15–25 cm; Fig. 2 and Table 5). Similarly, Drillia et al. (2005) reported higher diclofenac hysteresis with low-SOM content soil. It was suggested that diclofenac hysteresis is due to entrapment of the adsorbed molecules in the organic and inorganic matrices. The higher HI values obtained for the 15–25 cm sample than for the SOM-rich sample (0–5 cm) suggest that sorption and desorption processes may be affected by factors additional to SOM content. These factors include the humification (maturation) stage of the SOM as well as the level of clay and organo-clay complexes. It is also interesting to note that higher HI values were obtained with the STWW system which exhibited lower sorption-affinity values than the freshwater system for the 15–25 cm sample.

3.2.3. Naproxen

Naproxen exhibited the lowest sorption affinity to the studied soil samples, similar to its behavior in the column experiments, where it exhibited the highest mobility among the tested PCs. Like the other studied PCs, naproxen exhibited higher sorption affinity to the 0–5 cm sample than to the 15–25 cm sample. An opposite trend was observed for the K_{OC} values. The values calculated for the 15–25 cm sample were significantly higher (more than twice) than the values for the SOM-rich 0–5 cm sample. This trend was much more pronounced than for diclofenac or carbamazepine. Similar to diclofenac, naproxen was ionized (negatively charged) under the experimental conditions, suggesting that the inorganic soil matrix (clays) was not a major factor influencing sorption. On the other hand, naproxen has an aromatic skeleton similar to naphthalene which can facilitates π–π interactions with aromatic moieties of the SOM. These interactions were probably more pronounced with the more mature and humified SOM present in the 15–25 cm sample. Therefore, higher K_{OC} values were calculated with this sample relative to the SOM-rich sample. Desorption hysteresis of naproxen was low, suggesting that it was mainly adsorbed to soil organic and inorganic surfaces and was readily desorbed.

4. Conclusions

Based on the results obtained in this study (column and batch sorption–desorption experiments), we suggest that carbamazepine and diclofenac can be classified as slow-mobile compounds in SOM-rich soil layers. When these compounds pass this layer and/or are introduced into SOM-poor soils, their mobility increases significantly. Naproxen was highly mobile and exhibited the lowest sorption affinities to the studied samples. Our data suggest that in semiarid soils (consisting of low SOM), PCs can potentially be transported to the groundwater in fields irrigated with reclaimed wastewater. For example, carbamazepine is considered highly stable in water/sediment and sewage-treatment systems (Ternes, 1998; Loffler et al., 2005; Ternes et al., 2007) and therefore is not expected to degrade in soils; it is therefore not surprising that it has been found in the groundwater (Ternes et al., 2007). Both diclofenac and naproxen exhibit relatively high degradation potential during sewage treatment (Ternes, 1998; Tixier et al., 2003) and therefore, although they exhibited high mobility in our study, they were probably degraded (or sorbed to in the case of diclofenac) in the soils and therefore have lower potential to reach the groundwater in areas irrigated with reclaimed wastewater, as was observed by Ternes et al. (2007). Nevertheless, the higher mobility of naproxen and diclofenac in freshwater column systems suggests that their residues in soils irrigated with STWW can leach from the root zone and be transported to the groundwater after rain events.

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