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Combined effects of biosolids application and irrigation with reclaimed wastewater on transport of pharmaceutical compounds in arable soils

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ABSTRACT

Pharmaceutical compounds (PCs) are introduced into the agricultural environment through irrigation with treated effluents and application of biosolids. Transport processes can determine the fate of PCs and the associated risks related to their exposure in the environment. The aim of this work was to evaluate the combined effects of biosolids application and irrigation with treated effluents on the mobility of PCs in soil and to elucidate the main mechanisms affecting their transport. Column-leaching experiments revealed that application of biosolids generally increased the retardation of PCs, whereas treated effluents increased the mobility of weakly acidic PCs in the biosolids-amended soils. Experiments conducted at environmentally relevant PC concentrations ($\sim 1 \mu\text{g/L}$) highlight the importance of irreversible sorption as a possible mechanism for low leachability. Data generated from this study suggest that (i) transport behavior of PCs can be affected by common biosolids application to arable land; (ii) treated effluents increase the mobility of weakly acidic PCs mainly by increasing of the soil solution pH and not due to complexation of the PCs with dissolved organic matter; and (iii) it is highly important to evaluate transport behavior at environmentally relevant concentrations and not to base modeling on data obtained from experiments conducted in high concentrations.

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1. Introduction

Pharmaceutical compounds (PCs) are frequently detected in a variety of environmental compartments (Calderón-Preciado et al., 2011; Loos et al., 2010). Some PCs are not fully metabolized in the body and thereafter not completely eliminated during conventional wastewater treatment. Thus, biologically active PCs are ubiquitous in treated effluents; these are discharged to surface water bodies, used to recharge groundwater, or used for irrigation (Jelic et al., 2011). Irrigation with effluents and the application of biosolids as soil amendment

facilitate the introduction of PCs into the agricultural environment (Pedersen et al., 2003, 2005; Kinney et al., 2006; McClellan and Halden, 2010).

Major concern has arisen regarding the presence of sewage-derived pollutants (e.g., PCs) in runoff and drainage water from cultivated fields due to irrigation with reclaimed wastewater and/or biosolids application (Stoob et al., 2007; Yang et al., 2012). Moreover, PCs' potential to enter the food chain through irrigation of edible plants with reclaimed wastewater has recently become a matter of concern (Shenker et al., 2011; Wu et al., 2010). This issue is of high importance

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due to the extensive use of reclaimed wastewater to irrigate farmlands, especially in arid and semiarid zones, and the common practice of applying biosolids (containing active PCs) to agricultural soils. Understanding the mobility and transport behavior of organic pollutants in soils can help quantify the overall environmental exposure and risks associated with the introduction of these compounds into the agricultural environment.

Transport processes control the migration of pollutants from soil to groundwater and fresh water reservoirs (Unold et al., 2009), and the availability of pollutants for biodegradation or plant uptake (Pot et al., 2011; Shenker et al., 2011). The transport of pollutants in soil results from multiple processes within the soil matrix (Mccarthy and Zachara, 1989). Several recent reports have emphasized the increased retardation of PCs in soil columns with higher loading of soil organic matter (SOM) (Arye et al., 2011; Chefetz et al., 2008; Kurwadkar et al., 2011; Majumdar and Singh, 2007). These results are consistent with batch sorption studies showing a positive correlation between PC sorption and SOM content (Chefetz et al., 2008; Figueroa-Diva et al., 2010; Xu et al., 2009). In addition to SOM, dissolved organic matter (often expressed as the amount of dissolved organic carbon, or DOC) has also been reported to influence the mobility of organic solutes in soils. Based on its properties, the properties of the solute and the soil's characteristics, DOC can enhance or reduce mobility of a contaminant (Ding et al., 2011; Haham et al., 2012). The application of biosolids to arable soils, and mainly to SOM-poor soils, increases the content of SOM (Brown et al., 2011) and therefore can potentially increase sorption and retardation of organic pollutants (Dolaptsoglou et al., 2007). On the other hand, biosolids can serve as a source of both pollutants and DOC in the soil environment, and thus might enhance the mobility of the organic pollutants.

Solution chemistry may also affect the transport of PCs in the soil. Since many PCs contain dissociating functional groups, their charge changes with solution pH and thus their transport behavior may be affected. Increasing the pH can enhance the transport of sulfonamide antibiotics, due to the increase in negatively charged sulfonamide species (Kurwadkar et al., 2011; Strauss et al., 2011). Likewise, increasing the pH in columns packed with sandy sediment enhanced the mobility of the weakly acidic PC naproxen, probably due to the dissociation of its carboxylic functional group (Schaffer et al., 2012a). Assuming nonlinear sorption behavior of some PCs (Navon et al., 2011; Kurwadkar et al., 2007), it is expected that applied concentrations will also affect their mobility. However, the effect of initial concentration on the transport of pharmaceutical compounds is not well known, and was not studied for a wide variety of compounds.

Though the mobility of PCs in soil has been studied, the multiple and combined effects of biosolids application and irrigation with reclaimed wastewater on their transport behavior are yet to be elucidated. Therefore, the aim of this work was to study the mechanisms affecting the mobility of PCs in SOM-poor soil under regime of compost application and irrigation with reclaimed wastewater. In addition, we compared the transport behavior of PCs at high (mg/L) versus environmentally relevant ($\mu\text{g/L}$) concentrations, providing new evidence regarding the effect of initial concentrations on

transport of the PCs and the overall behavior of these compounds in field conditions. We hypothesize that the retardation of the studied PCs will be affected both by the compost application (acting as a sorption domain) and the solution chemistry that will affect the PC-soil and PC-compost binding interactions.

2. Materials and methods

2.1. Pharmaceutical compounds (PCs) and analytical standards

The following PCs were used as analytes in the breakthrough experiments: the antibiotics sulfapyridine (SPD) and sulfamethoxazole (SMX), the anticonvulsant drugs carbamazepine (CBZ) and lamotrigine (LTG), the nonsteroidal anti-inflammatory drugs naproxen (NAP), diclofenac (DCF), ibuprofen (IBP) and ketoprofen (KTP), and the lipid regulators gemfibrozil (GFB) and bezafibrate (BZF). Structures and physicochemical properties of the target PCs are presented in Table 1. For LC-MS analysis, the following labeled internal standards were used: sulfapyridine-phenyl- $^{13}\text{C}_6$, sulfamethoxazole- D_4 , naproxen- D_3 , ibuprofen- D_3 , ketoprofen- D_3 , bezafibrate- D_4 , carbamazepine- $^{13}\text{C}-\text{D}_2$, diclofenac- D_4 , gemfibrozil- D_6 and lamotrigine- $^{13}\text{C}_3$. The labeled standards were supplied by Toronto Research Chemicals (Toronto, Canada) and Sigma–Aldrich Israel, Ltd. (Rehovot, Israel).

2.2. Sampling of soil and composted biosolids

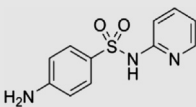
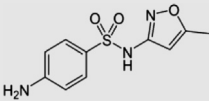
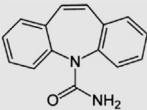
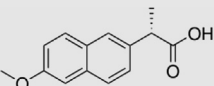
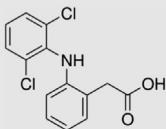
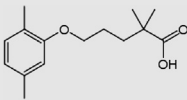
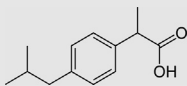
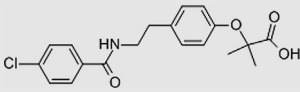
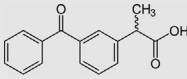
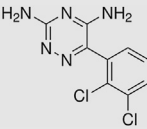
Loess soil was sampled from an agricultural field near Kibbutz Nir Oz, Israel. The soil was air-dried, manually crushed and sieved to obtain the <2 mm size fraction. Soil properties are presented in Table 2. Commercially available composted biosolids were sampled from Dlila Waste Recycling Center, Israel. The biosolids were sieved to obtain the <2 mm size fraction and kept freeze-dried until used. Organic matter content in biosolids was $55 \pm 1\%$ as measured by weight loss after ignition (400°C , 4 h).

2.3. Breakthrough experiments

2.3.1. Effect of biosolids loading

A glass column (4.7 cm i.d., 25 cm length) was packed with soil to a height of 15 cm. Soil was added to the glass column in small increments to prevent layering. Then another 5 cm layer of soil containing 0, 2.5, 5 or 10% (w/w) composted biosolids was added to the top for a total soil column length of 20 cm (experiments A, B, C and D in Table 3, respectively). Glass wool was placed at the bottom of the column to prevent soil leaching. Column experiments were initiated by saturating the column from the bottom with a background solution of 10 mM CaCl_2 . Then the columns were washed from the top, using a peristaltic pump, with 4 pore volumes of 10 mM CaCl_2 pulse solution containing 10 mg/L of bromide tracer (added as KBr) and 1 mg/L of each of the target PCs (SMX, NAP, SPD, GFB, CBZ and DCF). The accurate initial PC concentrations were measured in the pulse solution using HPLC-DAD. At the end of the pulse, the columns were washed with 4–10 pore volumes

Table 1 – Structures and physicochemical properties of the tested analytes.

Name and formula	Structure	Molecular weight (g/mol)	pK _a	log D ^l		Water solubility (mg/L)
				pH 7.4	pH 8.4	
Sulfapyridine C ₁₁ H ₁₁ N ₃ O ₂ S		249.3	2.28 ^a , 8.4 ^b	0.02	−0.32	246 ⁱ
Sulfamethoxazole C ₁₀ H ₁₁ N ₃ O ₃ S		253.3	1.83 ^c , 5.57 ^c	0.61	0.07	380 ^j
Carbamazepine C ₁₅ H ₁₂ N ₂ O		236.3	–	2.77	2.77	125±2 ^k
Naproxen C ₁₄ H ₁₄ O ₃		230.3	4.45 ^d	−0.16	−0.79	204 × 10 ³ (pH > 8.5) ^d
Diclofenac C ₁₄ H ₁₁ Cl ₂ NO ₂		296.2	4.14 ^d	0.96	0.42	10.2 × 10 ³ (pH > 8.5) ^d
Gemfibrozil C ₁₅ H ₂₂ O ₃		250.3	4.7 ^d	1.45	0.71	5.4 (pH > 7.5) ^d
Ibuprofen C ₁₃ H ₁₈ O ₂		206.3	4.4 ^f	1.31	0.43	120 × 10 ³ (pH = 8) ^f
Bezafibrate C ₁₉ H ₂₀ ClNO ₄		361.8	3.3 ^f	0.56	0.10	80 × 10 ³ (pH = 8) ^f
Ketoprofen C ₁₆ H ₁₄ O ₃		254.3	3.98 ^g	0.22	−0.26	51 ^e
Lamotrigine C ₉ H ₇ Cl ₂ N		256.1	5.7 ^h	1.91	1.93	480 (pH = 7.4) ^h

a (Lin et al., 1997a).

b (Kan and Petz, 2000).

c (Lin et al., 1997b).

d (Avdeef, 2007).

e (Gao and Deshusses, 2011).

f (Siemens et al., 2010).

g (Avdeef et al., 2000).

h (Mashru et al., 2005).

i (Reillo et al., 1995).

j (Zhang et al., 2007).

k (Chefetz et al., 2008).

l Values were calculated using MarvinSketch v5.9.3 software (<http://www.chemaxon.com>).

Table 2 – Selected properties of Nir Oz Loess soil.

Sand (%) ^a	82.5
Silt (%) ^a	5
Clay (%) ^a	12.5
Soil texture	Sandy loam
Organic matter content (% w/w)	0.84 ± 0.001
CaCO ₃ (% w/w) ^b	3.5 ± 0.01
Bulk density (g/cm ³)	1.471 ± 0.032
pH ^c	7.68
EC (mS/cm) ^c	2.45
Specific surface area (m ² /g) ^d	39.86 ± 2.17
Exchangeable cation capacity (meq/100 g) ^e	9.245 ± 0.782

a (Gee and Or, 2002).

b (Loeppert and Suarez, 1996).

c Measured in saturated paste extract.

d (Pennell, 2002).

e (Sumner and Miller, 1996).

of the same background solution without the PCs. Water flux varied between 0.172 and 0.252 cm/min in different experiments. The leachate was collected at the bottom of the column in 20 mL fractions, using an automated fraction collector. The columns were kept saturated throughout the leaching experiment by maintaining a thin film of water above the packed soil.

Leachate samples were analyzed for pH, electrical conductivity (EC), PC and bromide concentrations. Bromide concentrations were measured using ICP/AES-EOP (Spectro, Kleve, Germany), and PC concentrations were determined using HPLC-DAD or LC/MS as described in Section 2.4.3. The concentrations measured in the leachate were divided by the initial concentration measured in the pulse solution to obtain the relative concentration C/C_0 .

2.3.2. Effects of different background solutions

Experiments were performed using soil columns packed as described in Section 2.3.1, with 5% (w/w) composted biosolids in the top 5 cm of the columns and 1 mg/L of SMX, NAP, SPD, GFB, CBZ and DCF in the pulse. Pulse duration was 4 pore volumes, as before, and the duration of the wash phase was 10 pore volumes. Four different background solutions were used, with different salt composition and DOC content: (i) 10 mM CaCl₂, (ii) secondary treated wastewater (STWW), (iii) CaCl₂-

DOC solution and (iv) DOC-free STWW solution (experiments E, F, G and H in Table 3, respectively). STWW was collected from Ayalon Wastewater Treatment Plant, Israel. The STWW had a pH of 8.37, EC of 1.88 mS/cm and DOC level of 18.75 mg/L. The CaCl₂-DOC solution contained 10 mM CaCl₂ and 21 mg/L DOC which was extracted from composted biosolids (Navon et al., 2011). This solution had a pH of 6.2 and EC of 2.2 mS/cm; similar pH and EC values were measured in the 10 mM CaCl₂ solution. The DOC-free STWW solution was artificially prepared based on the ionic composition and strength of the STWW, excluding DOC. Concentrations of the principal cations in the DOC-free STWW solution were 3.8 meq/L Ca²⁺, 2.8 meq/L Mg²⁺, 13.7 meq/L Na⁺ and 0.7 meq/L K⁺, and concentrations of the principal anions were 12.9 meq/L Cl⁻, 9.9 meq/L CO₃²⁻ and 1.4 meq/L SO₄²⁻. The pH and EC of this solution were 8.43 and 1.79 mS/cm, respectively. At the end of the leaching experiment, soil columns were sliced into 5-cm segments and kept frozen (-20 °C) until analysis.

2.3.3. Application of PCs at environmentally relevant concentrations

In these experiments, we used soil columns with 0 or 5% biosolids in the top 5 cm with background solutions of 10 mM CaCl₂ or CaCl₂-DOC (see Section 2.3.2 for details on background solutions, and Table 3 for summary of experimental parameters). The PCs (SMX, SPD, LTG, NAP, DCF, IBP, KTP, and BZF; Table 1) were applied at an initial concentration of 0.4–1 µg/L. The experimental procedure was as described in Section 2.3.1, with 4 pore volumes of pulse solution applied to the columns followed by 10 pore volumes of washing with PC-free solution. Half of each eluted fraction (20 mL) was evaporated and then reconstituted in 0.5 mL of 30:70 (v/v) acetonitrile:water, giving a concentration factor of 20. Samples were then spiked with labeled PCs (as internal standards) and filtered (0.22 µm PTFE membrane) into 1.5-mL amber glass vials.

2.3.4. Physical characterization of water flow

To compare results from different experiments on the basis of changes in chemical interactions between the solutes and sorbents, the physical parameters of water flow in different soil columns must be similar (Strauss et al., 2011). Thus, breakthrough curves for the nonreactive tracer bromide were

Table 3 – Summary of parameters for different soil columns used for breakthrough curve experiments.

Column	% (w/w) of added compost	Background solution	PCs initial concentration	Leachate pH	Soil extracted for PCs
A	0	10 mM CaCl ₂	1 mg/L	7.4	No
B	2.5	10 mM CaCl ₂	1 mg/L	7.4	No
C	5	10 mM CaCl ₂	1 mg/L	7.4	No
D	10	10 mM CaCl ₂	1 mg/L	7.4	No
E	5	10 mM CaCl ₂	1 mg/L	7.4	Yes
F	5	STWW	1 mg/L	8.4	Yes
G	5	10 mM CaCl ₂ + DOC	1 mg/L	7.4	No
H	5	DOC-free STWW	1 mg/L	8.4	No
I	5	10 mM CaCl ₂	1 µg/L	7.4	No
J	5	10 mM CaCl ₂ + DOC	1 µg/L	7.4	No
K	0	10 mM CaCl ₂	0.4–1 µg/L	7.4	No

fitted to the one-dimensional convection–dispersion equation for non-reactive solutes using the CXTFIT code in inverse mode (Toride et al., 1999). Data for the bromide tracer in different column experiments are presented in Fig. S1. Bromide breakthrough curves were similar for the different experiments (Fig. S2). The calculated longitudinal dispersivity (λ) varied between 0.194 and 0.377, indicating the physical repeatability of our experimental setup. In addition, the obtained bromide breakthrough curves were symmetrical, showing that water flow is in physical equilibrium. Average flow parameters of dispersion coefficient (D), average pore-water velocity (v), pulse application time (T) and input concentration (C_0) of bromide in the pulse were used to generate a representative (average) breakthrough curve for bromide, using CXTFIT in direct mode (Toride et al., 1999). Average flow parameter values were $D = 0.171 \text{ cm}^2/\text{min}$, $v = 0.597 \text{ cm}/\text{min}$, $T = 140 \text{ min}$ and $C_0 = 1$. The average bromide breakthrough curve was used to compare the relative mobility of PCs in the different experiments. A detailed description of CXTFIT modeling is provided in the [Supplementary Information](#), where the physical parameters of water flow are provided in [Table S1](#).

2.3.5. Retardation factors

PC retardation factors (R_f) were calculated from breakthrough data based on the ratio between the pore volume needed for the reactive solute (i.e., PC) to reach half of its initial concentration ($C/C_0 = 0.5$), and the pore volume needed for the inert tracer (bromide) to reach $C/C_0 = 0.5$ (Widmer et al., 1995). Errors in R_f calculation (taking into account the contribution of both analytical and experimental errors) were less than 5% for the high concentration experiments (based on CBZ data) and 10% for the environmentally relevant concentration (based on NAP).

2.4. Analytical procedures

2.4.1. Extraction of PCs from soil-column samples

Soil samples were extracted following leaching experiments: (i) 5% biosolids and 10 mM CaCl_2 as background solution (experiment E, [Table 3](#)), and (ii) 5% biosolids and STWW as background solution (experiment F, [Table 3](#)). Soil samples were also extracted at the end of a step experiment with 5% biosolids and 10 mM CaCl_2 . All experiments were conducted at an initial PC concentration of 1 mg/L. Extraction solution was methanol and 0.05% NaOH in deionized water (1:1, v/v). Samples (10 g) from each column section (four sections per column, 5 cm each) were weighed in triplicate into 30-mL glass centrifuge tubes. After adding 15 mL of extraction solution, the tubes were agitated horizontally for 1 h and then centrifuged (4100g, 20 min). Next, 10 mL of the solution was decanted and replaced with fresh extraction solution, and the procedure was repeated. Concentrations of PCs in soil extracts were determined with HPLC as described in [Section 2.4.2](#), and were then used to calculate the levels of PCs in the different sections of the soil column. The values of PC levels in soil were then compared between different column sections using Tukey HSD all-pairs test ($\alpha = 0.05$) in JMP 7 software (SAS Institute Inc., Cary, NC, USA). Recovery values for the extraction method are provided in [Table S3](#).

2.4.2. Determination of PCs background levels in soil and compost

Soil and compost were intensively extracted using accelerated solvent extraction (ASE 350, Dionex, Sunnyvale, CA, USA). Freeze-dried soil samples (7 g) and compost samples (4 g) were packed on 1 g of florisil ($\text{Mg}_2\text{O}_4\text{Si}$, Alfa Aesar, Heysham, England) in 10 mL stainless steel extraction cells. Extraction procedure consisted of three static cycles of 15 min each with 70:30 acetonitrile:water solution at 100 °C and constant pressure of 10.34 MPa. Rinse volume was 60%. Extracts were evaporated to dryness under nitrogen stream and then reconstituted in 1 mL 30:70 acetonitrile water solution, sonicated for 10 min and spiked with labeled internal standards to a final concentration of 20 $\mu\text{g}/\text{L}$ and filtered, before LC-MS analysis. Levels of PCs detected in the composted biosolids ($n = 4$) were 3.1 ± 0.1 , 136.2 ± 5.7 , 261.1 ± 17.3 , 47.2 ± 3.8 and $4.6 \pm 0.1 \mu\text{g}/\text{kg}$ dry weight for SPD, GFB, CBZ, DCF and BZF, respectively. Soil samples did not contain detectable amounts of PCs.

2.4.3. PCs analysis

At high concentrations (0.05–1 mg/L), PCs were measured on a LaChrom D-7000 HPLC (Merck-Hitachi, Darmstadt, Germany) coupled to an L-7455 DAD detector (Merck-Hitachi). PCs were separated on an RP-18 column (LiChrospher 250 \times 4 mm, 5- μm particle size; Merck, Darmstadt, Germany) with binary gradient elution using acetonitrile (A) and 0.1% formic acid in deionized water (B). The initial solvent ratio was 25:75 (A:B); the level of solvent A was increased to 100% in 19 min, maintained at 100% for 2 min, then returned to 25% in 0.5 min and maintained at this ratio for an additional 4.5 min. Detection wavelengths were 270 nm for SPD and SMX, 285 nm for CBZ, 230 nm for NAP and 276 nm for DCF and GFB. Concentrations in the samples were determined using external standards.

PC concentration in the eluent samples obtained in experiments with an initial concentration of 0.4–1 $\mu\text{g}/\text{L}$ were determined using an Agilent 1200 Rapid Resolution LC system (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a Gemini C-18 column (150 \times 2 mm, 3- μm particle size; Phenomenex, Torrance, CA, USA), coupled to an Agilent 6410 triple quadrupole mass spectrometer with ESI ion source (Agilent Technologies Inc.). A binary gradient of 1.5% acetic acid in deionized water (A) and 0.05% acetic acid in acetonitrile (B) was used for separation of the PCs as follows: 0–3 min, 90:10 (A:B); B increased to 96% in 15 min; maintained at 4:96 (A:B) for 7 min; B decreased back to 10% in 0.1 min, and this constant solvent ratio was maintained until the end of the run, for a total time of 31 min. More details of LC-MS/MS analysis parameters are presented [Table S2](#).

3. Results and discussion

3.1. Effect of biosolids loading on PCs transport

The qualitative analysis of a breakthrough curve can provide a tool for comparing the behavior of different solutes. In general, stronger interactions of the solute with solid material in the soil will decrease its transport velocity and result in its

retardation. The pore volumes of solution needed for the leachate concentration of the solute to reach a certain level can be used to measure the solute's retardation. In addition, the area under the breakthrough curve can be used to calculate the recovery of the solute, and may indicate whether the solute is irreversibly retained in the column or maybe degraded. The shape of the breakthrough curve can be used to determine whether the system is in equilibrium. Symmetric breakthrough curve of an inert tracer is indicative of physical equilibrium, while an asymmetric breakthrough curve of a reactive solute indicates that the solute adsorption has not reached equilibrium (Gamerding et al., 1990).

All PCs, except for the sulfonamide antibiotic SMX, showed increased retardation with increased loading of biosolids (Fig. 1). The calculated retardation factors (R_f) followed the order: $SMX < NAP < SPD < GFB < CBZ < DCF$ for all biosolids loadings (Table 4). GFB, CBZ and DCF exhibited low eluted amounts even without adding compost to the soil column, and these amounts decreased even more with increasing compost application. On the other hand, the eluted amounts of SMX, NAP and SPD without compost addition were high (>95% of the amount applied with the pulse) and did not change markedly with the application of compost. As shown further on (Section 3.3), total mass balance of GFB, CBZ and DCF (eluted and soil-extracted) was around 100% in most cases, suggesting that the compounds were not degraded and/or transformed during the experiments. It is important to note that the R_f value calculated from the breakthrough data represents the sum of equilibrium, kinetic and irreversible sorption processes of a solute under constant flow (Gabriel et al., 1998).

The higher mobility of SMX compared to the other sulfonamide antibiotic, SPD, could be related to the former's lower pH-dependent partitioning ($\log D$ value) (Carda-Broch and Berthod, 2004). The higher mobility of SMX relative to other sulfonamide antibiotics has also been shown by others (Kurwadkar et al., 2011; Strauss et al., 2011). Similarly, other works have shown higher mobility of NAP compared to GFB, CBZ and DCF in soil columns (Chefetz et al., 2008; Siemens et al., 2010). As with the sulfonamide antibiotics, these differences in PCs mobility are generally attributed to the higher "hydrophobicity" of GFB, CBZ and DCF as compared to NAP, and are therefore positively correlated with the level of SOM. However, for most PCs, R_f values were not correlated with their general molecular properties, such as molecular weight, $\log D$ values or water solubility (Table 1). This implies that the prediction of sorption and mobility of PCs in soil cannot be based on a small and very general set of molecular descriptors, which mainly account for nonspecific sorbate–sorbent interactions. For this reason, modeling and prediction of the sorption of PCs and organic compounds to sewage sludge and SOM make use of an extensive set of physicochemical and structural characteristics of both the sorbents and the sorbates (Barron et al., 2009; Schuurmann et al., 2006; Bronner and Goss, 2011). In addition, Siemens et al. (2010) have suggested that dipole moment and charge distribution might explain the differences between the mobility of NAP and BZF in column experiments. Recently, Teixidó et al. (2011) suggested that H-bonding is a significant mechanism in the sorption of the antibiotic sulfamethazine to O functionalities of black carbon, emphasizing the role of specific interactions in the retardation of sulfonamide compounds.

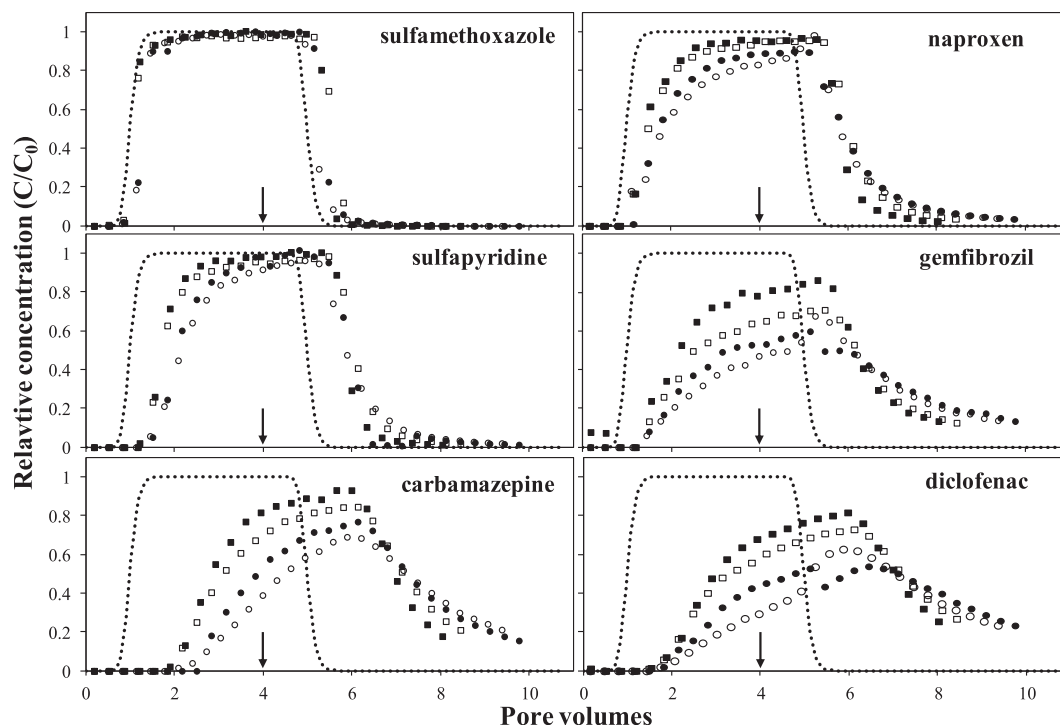


Fig. 1 – Breakthrough curves of sulfamethoxazole, naproxen, sulfapyridine, gemfibrozil, carbamazepine and diclofenac in soil columns containing 0% (■), 2.5% (□), 5% (●) and 10% (○) composted biosolids in the top 5-cm layer. Initial concentration (C_0) of the PCs was 1 mg/L. Arrow marks the end of the loading pulse; dotted line represents the average breakthrough curve of the inert tracer bromide.

Table 4 – Retardation factors as affected by loadings of composted biosolids and different eluent solutions – 10 mM CaCl₂ (CaCl₂), secondary treated wastewater (STWW), 10 mM CaCl₂ with 21 mg/L DOC (CaCl₂-DOC) and DOC-free STWW solution. The estimated error in retardation factor is < 5%.

	Different loading of composted biosolids 10 mM CaCl ₂ eluent solution			
	0%	2.5%	5%	10%
Sulfamethoxazole	1.05	1.04	1.29	1.25
Naproxen	1.45	1.48	1.75	1.84
Sulfapyridine	1.72	1.71	2.05	2.15
Gemfibrozil	2.17	2.51	3.25	4.63
Carbamazepine	2.81	3.08	3.84	4.45
Diclofenac	2.98	3.29	4.75	5.14
	5% loading of composted biosolids different eluent solutions			
	CaCl ₂	STWW	CaCl ₂ -DOC	DOC-free STWW
Sulfamethoxazole	1.26	1.21	1.28	1.16
Naproxen	1.85	1.52	1.91	1.44
Sulfapyridine	2.24	2.19	2.34	2.17
Gemfibrozil	3.69	1.74	3.04	1.64
Carbamazepine	4.16	4.29	4.33	4.00
Diclofenac	6.42	2.61	5.20	2.28

3.2. Effects of eluent solution chemistry

In this section we discuss the effects of the eluent solution's properties on the transport behavior of the studied PCs in soils with 5% compost in the top 5 cm of the column (Fig. 2). The initial pH of the solution (measured before loading to the column) and the final pH value (measured in leachate samples) are important factors in determining the PCs behavior.

The initial pH values of the STWW and (artificial) DOC-free STWW eluent solutions were 8.37 and 8.43, respectively. These values did not change considerably during the experiment, giving pH value of 8.4–8.5 in leachate samples from these experiments. In the non-buffered CaCl₂-based solutions (10 mM CaCl₂ and 10 mM CaCl₂-DOC solutions), the initial pH value for the two solutions was 6.2 and it increased after passing the soil columns to ~7.4 in leachate samples.

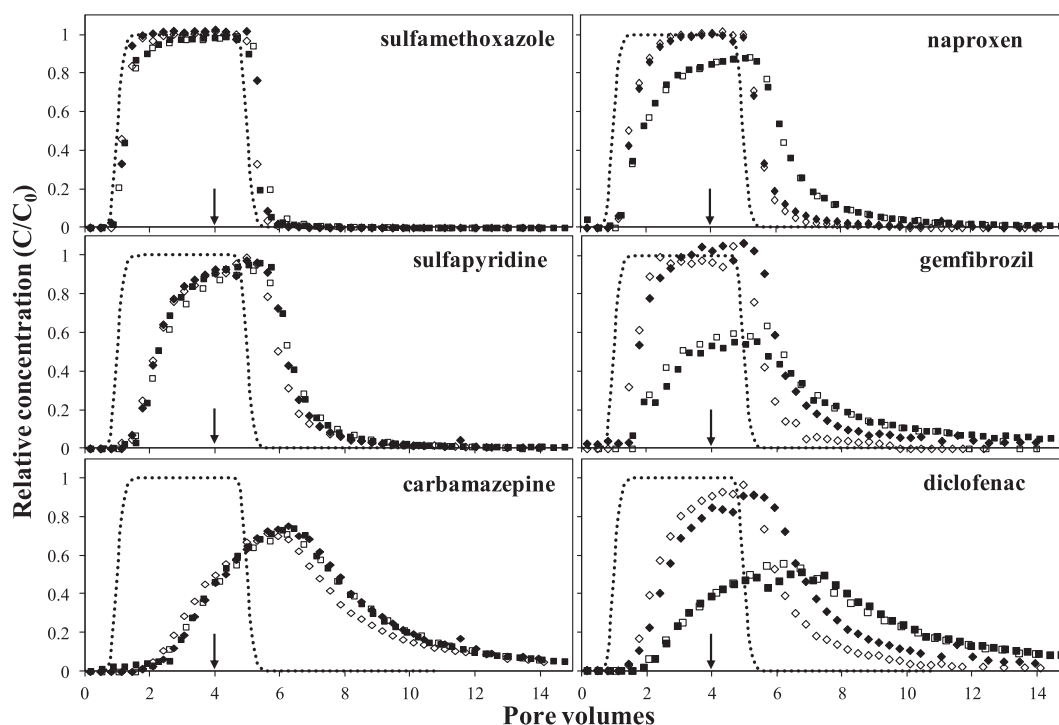


Fig. 2 – Breakthrough curves of sulfamethoxazole, naproxen, sulfapyridine, gemfibrozil, carbamazepine and diclofenac in soil columns containing 5% composted biosolids in the top 5-cm layer. Initial concentration (C_0) of the PCs was 1 mg/L. The following eluent solutions were used: 10 mM CaCl₂ (■), secondary treated wastewater (STWW) (◆), 10 mM CaCl₂ with 21 mg/L DOC (□) and DOC-free STWW salt solution (◇). Arrow marks the end of the loading pulse; dotted line represents the average breakthrough curve of the inert tracer bromide.

The breakthrough curves of the anticonvulsant drug CBZ and the two sulfonamide antibiotics (SMX and SPD) were not affected by the chemistry of the solution, i.e., breakthrough curves with STWW were similar to those with the 10 mM CaCl₂ solution. On the other hand, the mobility of the weakly acidic compounds NAP, GFB and DCF increased when STWW and DOC-free STWW solutions were applied. Consequently, retardation with the two latter eluents followed the order SMX < NAP < GFB < SPD < DCF < CBZ (Table 4). In addition, the eluted amounts of GFB and DCF increased from 76% for GFB and 86% for DCF with the 10 mM CaCl₂ solution, to around 100% of the applied amount for both PCs with the STWW-based solutions. With the DOC-free STWW solution, both GFB and DCF exhibited a lower degree of desorption hysteresis during the elution phase, as indicated by the decreased tailing of their breakthrough curves (Fig. 2).

Although interactions of PCs with DOC in solution have been documented (Hernandez-Ruiz et al., 2012; Maoz and Chefetz, 2010), DOC did not seem to be a significant factor in determining the mobility of the analytes in the current experimental setup. Instead, we hypothesize that pH was the dominant factor enhancing the mobility of NAP, GFB and DCF in both STWW and DOC-free STWW eluent solutions. This is supported by Schaffer et al. (2012a), who showed increased mobility of NAP in a sandy sediment column with increasing pH values. In this respect, the faster release (desorption) of DCF and GFB observed when DOC-free STWW solution was used as eluent, as compared to STWW, can be attributed to the slightly higher pH of the former. It should be noted, however, that the initial pH of the CaCl₂ solutions (6.2) was lower than that of the leachate samples, and the change in pH was probably gradual throughout the column (Strauss et al., 2011). Consequently, we assume that the effect of pH on mobility was more pronounced in the compost-containing top layer of the soil column, where most of the PC retardation was expected to occur. Contrary to our results, Kurwadkar et al. (2011) showed that pH variations of one or two units, in a range relevant to the current work, changed the mobility of sulfonamide antibiotics in soil columns. However, Kurwadkar et al. (2011) used only certain size fractions of the soil (between 2 mm and 0.15 mm) excluding most of the clay and SOM fractions, limiting the ability to compare their results and the current work.

As discussed in the previous section, the effect of specific interactions on the retardation of organic solutes cannot be explained using partition-based approaches, i.e., log *D* or log *K*_{OW} values. Nevertheless, in the experiments described in this section, variations in log *D* could explain the effect of pH on the mobility of the acidic analytes. It is important to note that the apparent partition (log *D*) of weak carboxylic acids can vary significantly with pH, even when pH values of the solution are 3–4 units above the carboxylic acids' p*K*_a (Berthod et al., 1999). This is also shown by the log *D* values given in Table 1. However, whereas the sulfonamide antibiotics' calculated log *D* values changed between the different experimental pH values, there was no change in the mobility of these compounds with the different eluent solutions (Table 4, Fig. 2). Thus, although the sorption mechanisms of the weak acid analytes probably included specific interactions, they were less dominant than partition-related mechanisms (non-specific interactions, i.e., van der Waals interactions and

hydrophobic effects). On the other hand, for the sulfonamide antibiotics, specific interactions were probably more important. The sulfonamide antibiotics tested in our work had more H-bond donor/acceptor sites than the other analytes, indicating the possibility of different sorption mechanisms for different PCs. However, our experimental system did not allow us to determine the explicit sorption mechanisms for each PC.

3.3. Residual levels of PCs in the soil columns

The profile of residual PCs in the soil column was determined at the end of a step experiment in which the soil column (with 5% biosolids in the top layer) was loaded with 4 pore volumes

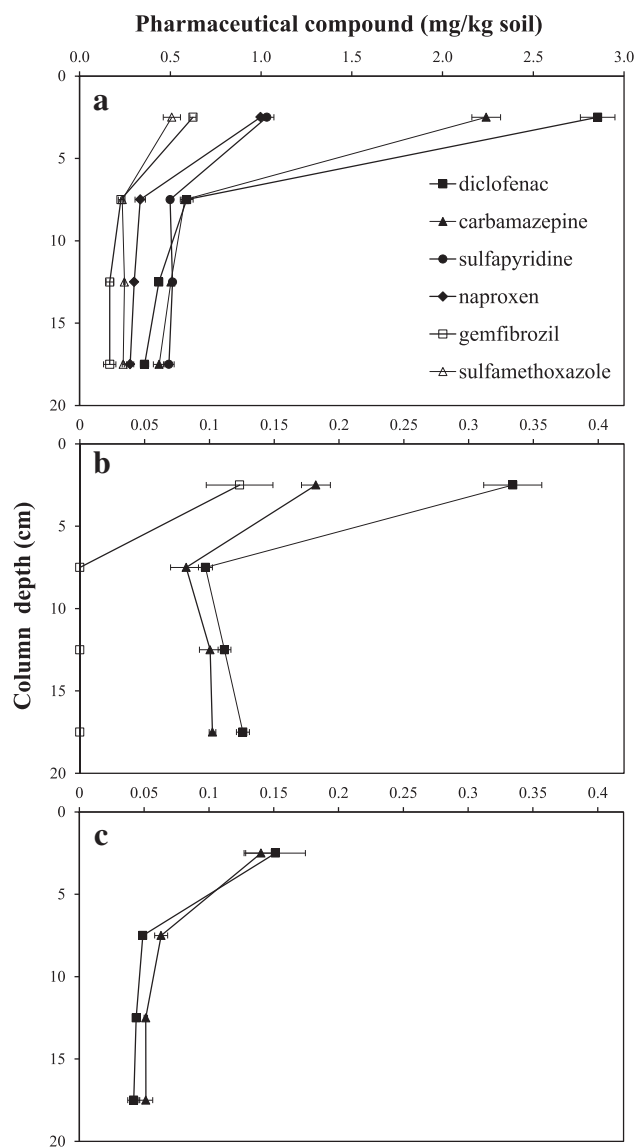


Fig. 3 – Residual levels of pharmaceutical compounds in soil columns, at the end of a step experiment with 10 mM CaCl₂ (a), and at the end of two pulse experiments, with 10 mM CaCl₂ (b) or secondary treated wastewater (c) eluent solutions. Bars represent standard deviation (*n* = 3). Initial concentration (*C*₀) of the PCs in the step and pulse solutions was 1 mg/L.

of 10 mM CaCl_2 solution containing 1 mg/L of the analytes (Fig. 3a). For all PCs, the amount in the top 5 cm of the column was significantly higher than in the lower soil layers, emphasizing the role of biosolids in PC sorption and retardation. In the lower parts of the column (5–10, 10–15 and 15–20 cm), the concentrations of each analyte were statistically similar. In the top 5 cm of the soil column, the levels of analytes followed the same order as the R_f values. In addition, PC levels were determined in the soil from two of the pulse (breakthrough) experiments described in the previous section, with eluent solutions of (i) 10 mM CaCl_2 and (ii) STWW (experiments E and F, Table 3). The profiles of PCs in the soil are presented in Fig. 3b and c, respectively, and the corresponding breakthrough curves are presented in Fig. 2. Only DCF and CBZ were detected in soil samples at the end of both leaching

experiments, whereas GFB was detected only in the top layer of the soil when 10 mM CaCl_2 was used as eluent. For both experiments, the levels of DCF and CBZ were significantly higher in the top 5 cm of the column than in the lower layers. Moreover, there were no significant differences between the levels of CBZ and DCF in the lower soil layers with either eluent. Levels of SMX, SPD and NAP in the soil were below detection limits. The effect of organic matter content on the distribution of CBZ in a soil column was also demonstrated by Arye et al. (2011). They showed higher levels of CBZ in the top layer of a sandy soil column corresponding to the higher amount of SOM in this section of the column.

The influence of the eluent solution properties on the distribution of the analytes in the profile was evident; the level of DCF in the top soil layer was significantly higher in the CaCl_2

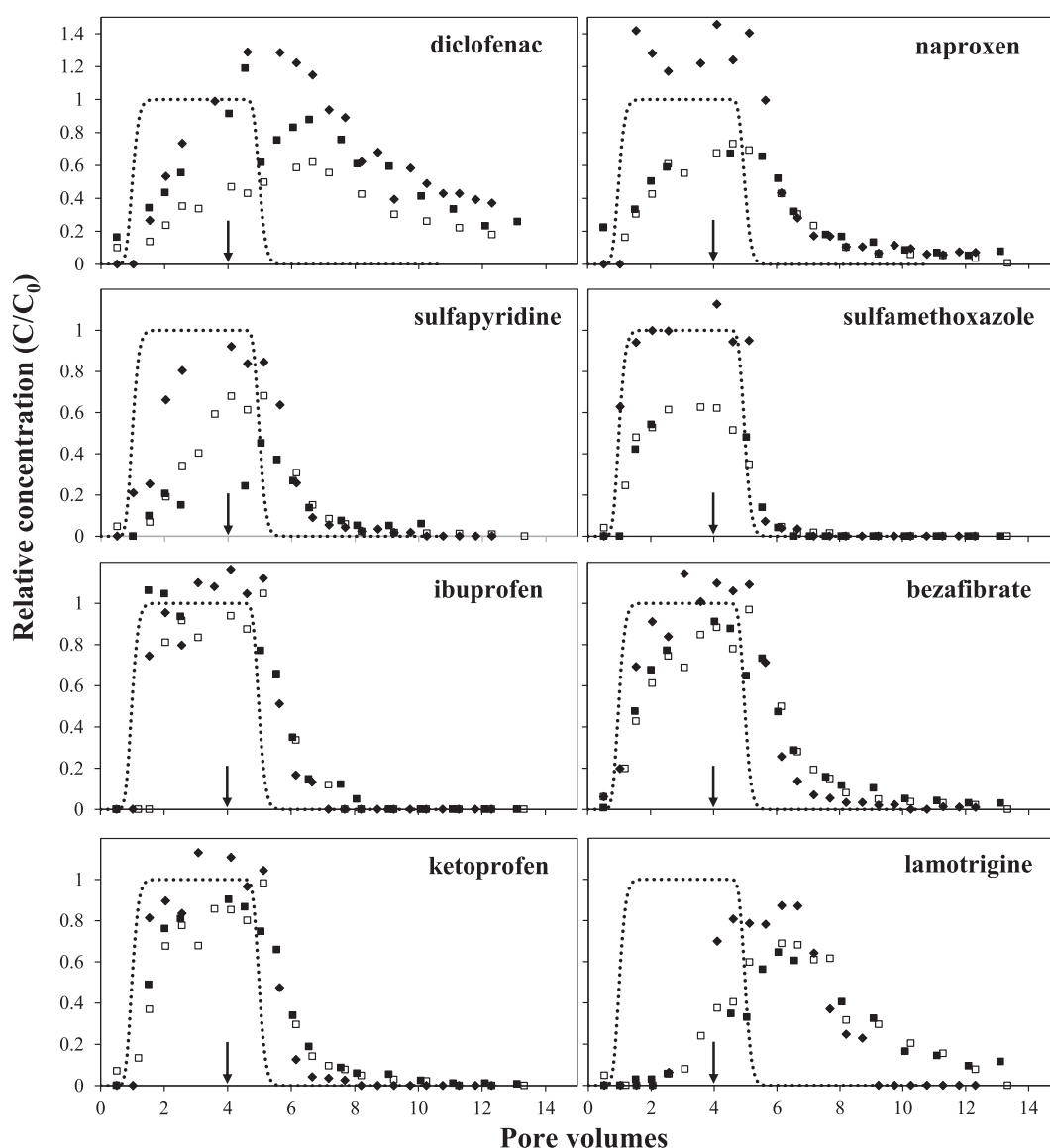


Fig. 4 – Breakthrough curves of diclofenac, naproxen, sulfapyridine, sulfamethoxazole, ibuprofen, bezafibrate, ketoprofen and lamotrigine at environmentally relevant concentrations ($C_0 = 0.4\text{--}1\ \mu\text{g/L}$), in different leaching experiments: (i) soil columns containing 5% composted biosolids in the top 5-cm layer and eluent solutions of 10 mM CaCl_2 (■) and 10 mM CaCl_2 with 21 mg/L DOC (□); and (ii) soil column with no compost addition and eluent solution of 10 mM CaCl_2 (◆). Arrow marks the end of the loading pulse; dotted line represents the average breakthrough curve of the inert tracer bromide.

experiment than in the STWW experiment, as expected from the increased mobility of DCF with STWW (Fig. 2, bottom right). As already suggested, the higher pH of the STWW eluent, compared to the CaCl₂ eluent, was probably the reason for the increased mobility of DCF with the former solution. On the other hand, the levels of CBZ in the soil were also significantly lower with the STWW eluent than with CaCl₂, even though the breakthrough curves from these two experiments did not show any difference in CBZ behavior (Fig. 2, bottom left). Therefore, we cannot rule out the effects of DOC present in STWW, which might have caused the increased release of sorbed PCs.

Total mass balance for the leachate and soil extractions was 94–114% of the applied amount for all analytes with both eluents, suggesting that microbial degradation and chemical transformation were insignificant in the soil columns. The only exception was GFB with the CaCl₂ eluent, which showed a total mass balance of only 81%. The residual (non-extracted) fraction of GFB was probably irreversibly sorbed to the soil and not microbially degraded, since contact time of the analytes was relatively short (~100 min).

3.4. Breakthrough experiments at environmentally relevant PCs concentrations

Fig. 4 illustrates the effect of compost amendment and DOC application on the breakthrough curves of the PCs SPD, SMX, NAP, IBP, BZF, KTP and LTG at their environmentally relevant initial concentrations (0.4–1 µg/L). Compost addition generally increased the retardation of PCs, similar to our observations from experiments with higher initial concentrations (Fig. 1). However, while the application of compost did not change SMX behavior at higher initial concentration (Fig. 1), breakthrough curves at environmentally relevant initial concentration have shown increased SMX retardation with the addition of compost (Fig. 4). This increased retardation of SMX may be attributed to its ability to form specific interactions with the compost added to the soil column, which were more prominent with the lower initial concentration. This effect is also evident, albeit to a lesser extent, in the breakthrough curves of SPD (Fig. 4), which also showed greater retardation

due to compost addition with low initial concentration. As mentioned before, the role of specific interactions was expected to be more significant in the retardation of the sulfonamide antibiotics (SMX and SPD) as compared to the other PCs (Tables 4 and 5).

Breakthrough curves of the PCs were not affected by the addition of DOC under our experimental conditions (5% composted biosolids in the top soil layer). On the other hand, breakthrough curves of DCF showed apparently decreased mobility with the addition of DOC to the eluent solution. However, DCF was also present in the composted biosolids at relatively high levels (47 µg/kg), therefore its behavior is influenced by its release from the compost in the top soil layer. It is important to note that in this experimental setup, the DOC concentration added to the eluent solution was 21 mg/L while the PC concentration was less than 7 µg/L (based on organic C level). Thus, the concentration ratio between DOC and PCs reached almost four orders of magnitude. These findings support our data obtained for the high PCs concentration that DOC is not a significant factor in determining the mobility of the investigated analytes. This is also supported by Navon et al. (2011) reporting that CBZ sorption at environmentally relevant concentrations to soil is not affected by DOC.

In a review of the current literature, we found only one similar comparison between mobility of polar organic contaminants with initial concentrations that vary by three orders of magnitude. Schaffer et al. (2012b) tested the mobility of the β -blocker atenolol in a sediment column at initial concentrations varying from 1 to 30,000 µg/L, and found no significant difference in its behavior. The authors determined that the main sorption mechanism of atenolol in their experiments was cation exchange; therefore its sorption was not affected by the change in initial concentration. Since previous works have shown concentration-dependent sorption of the tested analytes (Chefetz et al., 2008; Kurwadkar et al., 2007; Thiele-Bruhn et al., 2004), we expected retardation of the compounds to be higher for lower initial concentrations. However, the similar fronting and tailing of the SMX and NAP breakthrough curves (Figs. 1, 2 and 4) indicates that the magnitude and rate of equilibrium and kinetic sorption/desorption processes were the same with different C₀ values. For SPD, on the other hand, lower initial concentration changed the shape of the breakthrough curve, indicating higher sorption affinity but also higher desorption capability, resulting in decreased hysteresis compared with the higher C₀ value. In general, our data suggest that at lower initial concentrations, irreversible sorption is more apparent. Since physical interactions with pores and voids in organic matter can limit desorption of organic contaminants (Pignatello and Xing, 1996), an apparently irreversible sorption can be observed when sorption equilibrium is not reached. In addition, while some sorption processes have a negligible effect on experiments with high analyte concentration, they can dominate solute behavior at environmentally relevant concentrations.

Table 5 – Retardation factors obtained from soil column experiments at environmentally relevant initial concentrations. The estimated error in retardation factor is < 10%.

	CaCl ₂ 0% compost	CaCl ₂ 5% compost	CaCl ₂ -DOC 5% compost
Sulfamethoxazole	0.93	1.86	1.78
Naproxen	1.22	2.03	2.29
Sulfapyridine	1.87	n/a ^a	3.38
Diclofenac	2.01	2.32	5.23
Ibuprofen	1.39	0.99	1.88
Bezafibrate	1.36	1.59	1.76
Ketoprofen	1.36	1.55	1.78
Lamotrigine	3.67	5.48	4.93

^a Retardation factor could not be calculated since the maximum relative concentration (C/C₀) did not reach 0.5.

4. Conclusions

The application of organic amendments to agricultural fields with low SOM content can increase the retardation of PCs

originating from wastewater irrigation. However, our results show that the solution chemistry properties can still dominate transport processes, even when the amended soil contains relatively high levels of SOM (5% in the top layer). More specifically, solution pH can be an important factor in determining the mobility of PCs, and not necessarily DOC which is considered an important transport agent for more hydrophobic contaminants. In addition, for higher initial PC concentrations, most of the compounds could be eluted from the soil column when sufficient washing was applied, indicating that the involved sorption processes were mostly reversible. At environmentally relevant concentrations, the leaching of PCs was shown to be affected by processes that cannot be observed in experiments with higher concentrations. These processes may include binding to high-energy adsorption sites which are not abundant, and thus become more significant when the analyte is applied at low concentrations. Therefore, a better understanding of the fate of PCs in soil, and the underlying processes controlling it, can be achieved by using more relevant analyte concentrations.

The experiments described above were conducted on a laboratory scale with saturated soil and at constant flow, conditions that do not always prevail in the field. However, the phenomena observed in our work have environmental implications, and can help in understanding the processes and mechanisms that determine the environmental fate of PCs in soil and water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.03.045>.

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