

**Sorption behaviours and transport potentials for selected pharmaceuticals
and triclosan in two sterilised soils**

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Abstract

Purpose: Pharmaceuticals and personal care products (PPCPs) are emerging environmental pollutants, which in addition to direct deposition processes, can find their way into surface soils through the agricultural application of sewage sludge and irrigation practices using contaminated wastewater. Therefore, it is important to assess the extent to which soils are able to retain PPCPs and to prevent their downward migration towards groundwaters.

Materials and methods: To further our understanding in this area, batch sorption experiments and artificial rainwater leaching experiments have been performed using five compounds possessing a range of physicochemical properties (bezafibrate, carbamazepine, chloramphenicol, diclofenac and triclosan) in two soils with differing acidities and organic carbon contents.

Results and discussion: The determined K_{oc} values of triclosan and diclofenac consistently demonstrated their lower potential mobilities in both soils. The predicted high mobility of chloramphenicol is supported by its efficient leaching potential (89-100%) in both soils whereas bezafibrate, diclofenac and carbamazepine demonstrate slightly lower affinities for the leachate (61-96%) for soil A and are strongly retained (>99%) by soil B. The amount of PPCP in the leachate, the rate of leaching and the depth of soil penetration are explained in terms of the soil characteristics and the properties of the individual PPCPs (such as solubility and pK_a) with soil organic content being shown to be a critical factor controlling the ability of a soil to retain a PPCP in the surface layers.

Conclusions: The findings contribute to the scientific knowledge required by practitioners and regulators as they consider future sub-soil contamination by PPCPs and subsequent possible threats to groundwater resources and surface water habitats.

Keywords Batch sorption experiments • Distribution coefficients • Leaching potentials • Pharmaceuticals and personal care products • Soil depth distributions • Soil mobilities

1. Introduction

The release to the aquatic environment of pharmaceuticals and personal care products (PPCPs) is increasingly causing concern due to chronic sublethal effects (e.g. endocrine/hormonal disrupting activity) and due to the development of antimicrobial resistance (e.g. Daughton and Ternes 1999; Halling-Sorensen et al. 1998; Kasprzyk-Hordern et al. 2009a,b; Kummerer 2001; 2009a,b). PPCPs in sewage treatment plant effluents and landfill leachates have led to low concentrations (ng l^{-1} to $\mu\text{g l}^{-1}$) being detected in surface waters (Kasprzyk-Hordern et al. 2009c) and groundwaters (Heberer and Stan 1997; Holm et al. 1995; Sacher et al. 2001; Ternes et al. 2007). Studies of the environmental occurrence and fate of PPCPs have focused more on the aquatic environment and there is less information available on their levels and behaviours in soils although a range of veterinary medicines, including hormones, antibiotics, and parasiticides, have been detected in this environmental compartment (Hirsch et al. 1999; Kay et al. 2004). The widely differing physico-chemical properties of PPCPs, including hydrophobicity, have the potential to produce varying mobilities in the soil environment. This leads to an uncertainty regarding the associated risk posed to sensitive environmental compartments such as groundwater arising from potential soil migration and as such the sorption behaviour and potential transport of PPCPs in soils warrants further attention.

Soil and associated pore waters can be exposed to human pharmaceuticals through the use of digested sewage sludge as an agricultural fertilizer and through irrigation processes using treated or untreated wastewater (Borgman and Chefetz 2013; Calderon-Preciado et al. 2011; Siemens et al. 2010). Ternes et al. (2007) detected the presence of 54 different PPCPs in groundwater following arable crop irrigation with treated municipal wastewater, over a period of 45 years. Leakages from sewers and from sewage treatment plants or the flooding of fields with receiving waters containing appreciable proportions of treated wastewater can also result in PPCPs entering the soil environment (Oppel et al. 2004; Ellis 2006).

Sorption tests enable the affinity of PPCPs towards soil particles to be determined and the use of sterilised soils removes potential interferences due to biodegradation processes. This provides a situation in which the inherent chemical soil interactions and baseline behaviours of PPCPs in the soil environment can be better understood and against which subsequent potential transformation/biodegradation processes can be evaluated. Using a batch equilibrium method, Xu et al. (2009) observed that the behaviours of 6 selected PPCPs in 4 US agricultural soils, associated with reclaimed wastewater reuse, were well described by the Freundlich equation, with soil adsorption affinities in the order of triclosan > bisphenol A > clofibric acid > naproxen > diclofenac > ibuprofen. A strong affinity of carbamazepine for soil has been described by Williams and Adamsen (2006) with between 98 and 100% of the adsorption occurring within 1.75 h during a series of sorption and desorption batch equilibrium experiments at 17 °C.

The work described in this paper, investigates the fate of 5 compounds (bezafibrate, carbamazepine, chloramphenicol, diclofenac and triclosan) in terms of their sorption characteristics and transport processes in two different types of soil using both batch adsorption experiments and column leachate experiments. Bezafibrate is a widely used lipid regulator, which has been detected at median concentrations of $2.2 \mu\text{g l}^{-1}$ in sewage treatment plant effluents followed by a 5-10-fold decrease in the receiving waters (Ternes 1998). Carbamazepine is an anticonvulsant and mood stabilizing drug, which exhibits only limited removal efficiency in municipal wastewater treatment plants leading to discharged median concentrations of $2.1 \mu\text{g l}^{-1}$ (Ternes 1998; Zhang et al. 2008). Chloramphenicol is an

antimicrobial agent with roles in both human medical treatment and animal production prior to being banned for the latter purpose in the European Union (European Commission 1994). Diclofenac is a non-steroidal anti-inflammatory drug which is commonly detected in sewage with reported concentrations in treatment plant effluents in France, Greece, Italy and Sweden varying between 0.25 and 5.45 $\mu\text{g l}^{-1}$ (Ferrari et al. 2003). Triclosan is an antibacterial and antifungal agent, which has been measured in the concentration ranges of 13 to 82 $\mu\text{g l}^{-1}$ and 5 and 24 $\mu\text{g l}^{-1}$ in sewage treatment effluents and receiving rivers, respectively (Kasprzyk-Hordern et al. 2009c). The same authors identified the percentage removal efficiencies at two UK wastewater treatment plants of 53%, 58% and 83% for bezafibrate, diclofenac and chloramphenicol, respectively with carbamazepine being resistant to conventional sewage treatment processes. Given the incomplete breakdown of these PPCPs it is not surprising that they are frequently found in river waters at mean concentrations between 21 ng l^{-1} (chloramphenicol) and 328 ng l^{-1} (carbamazepine) (Kasprzyk-Hordern et al. 2009c) and also in groundwaters at concentrations as high as 900 ng l^{-1} for carbamazepine (Sacher et al. 2001).

Although PPCPs occur widely in the environment, their fate in soil matrices is not well understood. To extend the limited existing knowledge in this area, this paper investigates the sorption characteristics and leaching behaviour of selected PPCPs in different soils with the objective of assessing their potential removal in processes related to water quality protection, wastewater treatment and stormwater management. Soil filtration plays an important role in both agricultural and urban water cycles and therefore it is important to understand the interactions and fate of PPCP compounds in soil systems. In addition to contributing to scientific and technical knowledge this will provide relevant advice to regulators regarding possible future extensions to the list of xenobiotics specifically identified in the Water Framework Directive and to the European Medicines Agency which requires sorption studies to be carried out prior to the registration of medicinal products for human use (European Medicines Agency 2006; Williams et al. 2009).

2. Methodology

The two different soils (A and B) used in the batch adsorption experiments and the column leachate experiments differ in terms of their acidities and organic carbon contents but both contain over 70% of particle sizes associated with the sand fraction. The average $\text{pH} \pm$ standard deviation demonstrated by soil B (4.22 ± 0.01) is considerably lower than for soil A which is essentially neutral (7.22 ± 0.05). Soil B has a higher organic carbon content ($36.5 \pm 2.7 \text{ g kg}^{-1}$) than soil A ($8.3 \pm 0.3 \text{ g kg}^{-1}$). Further characteristics of these soils have been previously presented (Revitt et al. 2014). Both soils were sterilised to prevent biodegradation interfering with the sorption and leaching processes. Sterilisation was carried out by Isotron Ltd. (Swindon, UK) using gamma irradiation at a dosage level of 25-40 kGy to eliminate bacteria, actinomycetes and fungi whilst preserving the chemical composition of the soil (e.g. Getinga et al. 2004).

2.1 Batch adsorption experiments

Air dried sterile soil samples (5 g) were mixed with 10 ml of 0.01 M CaCl_2 solution (simulated rain water) containing a mixture of the PPCPs at concentrations of 0, 1, 5, and 10 mg l^{-1} in 50-ml centrifuge tubes. The soil suspensions were continuously mixed by shaking for 24 h at room temperature to enable equilibration to be achieved (Xu et al. 2009) after which the contents of the tubes were centrifuged at 4400 rpm for 10 min to separate the solid and aqueous phases from which the PPCPs were extracted as described in Section 2.3.

2.2 Column leachate experiments

Vertical soil column leaching experiments (OECD 2004) were performed using glass columns (200 mm, 50 mm diameter) packed with 200 g of sieved soil (<2 mm). Glass wool and glass beads (50 g, 3.5 mm) were placed in the bottom of each column to prevent soil loss and to filter the leachate samples. The soil was saturated from below and pre-equilibrated overnight with sterilised 0.01 M CaCl₂. 2 ml of a solution containing 10 mg/l each of bezafibrate, carbamazepine, chloramphenicol and diclofenac was applied to the top of each saturated column and sorption to the soil particles allowed for a period of 24 hours. For each soil, three columns were tested simultaneously together with a control column to which no PPCPs were added. A layer of glass wool and glass beads (25 g) placed on top of each column prevented soil disturbance by the incoming eluent. The comparable leaching potential of both soils has previously been validated using monuron as a reference compound (OECD 2004; Revitt et al 2014).

The leaching experiments were conducted over a period of 12 days by introducing 100 ml of 0.01 M CaCl₂ (artificial rainwater) each day. An average percolation rate, within each soil column, of approximately 4.2 ml h⁻¹ was maintained and after 7 days the leaching solution for one of the test columns and the control columns for each soil was changed to a 0.1M NaCl solution (in sterilised deionised water) in order to assess the impact of increasing the eluent ionic strength on the mobility of the tested PPCPs. Column eluents were collected daily and combined for consecutive 2 day periods prior to determination of PPCP levels and dissolved organic carbon (DOC) content (triplicate analysis using 20 ml aliquots in a Shimadzu TOC-V CPN instrument).

On completion of the leaching process, each soil column was carefully removed and divided into vertical segments corresponding to soil depths of 0-1 cm, 1-2 cm, 2-3 cm, 3-5 cm, 5-7 cm and greater than 7 cm. The soil samples were air dried for two days and subsequently stored at -10 °C until extraction of the PPCPs. The initial application of 20 µg of PPCP to each soil column ensured reliable detection in the soil segments above the determined LOQ of 20 ng g⁻¹ (see Section 2.3.3).

2.3 Sample extraction

2.3.1 Aqueous sample preparation

The aqueous phases from the batch adsorption experiments and the leachate samples were extracted and enriched using solid phase extraction (SPE). The filtered aqueous samples were passed through StrataX 3 ml SPE columns (200 mg, 8B-S100-FBJ, Phenomenex, UK) which had been previously solvated with methanol (3x2 ml) and washed with deionised water (3 ml). Following extraction, the SPE columns were washed with deionised water (3 ml) and then dried by vacuum aspiration for 30 min. The analytes were eluted with methanol (3x2 ml). The columns were saturated with methanol for 5 min before the methanol was allowed to run through the column at a flow rate of approximately 5 ml min⁻¹. Following elution, samples were reduced in volume to near dryness (<100 µl) under a nitrogen stream at 35 °C (TurboVap LV, Caliper) and stored at -80 °C. Immediately prior to LC-MS analysis, samples were taken to dryness and then reconstituted to 1 ml with 10% aqueous methanol. Samples were analysed in duplicate.

2.3.2 Ultrasonic extraction of solid samples

The air dried soils (5 g) were mixed with 25 ml methanol in screw-top centrifuge tubes (50 ml capacity) and ultrasonicated for 15 min. The solid particulates were separated by centrifuging at 4400 rpm for 5 min and the extraction process repeated twice with 25 ml methanol followed by ultrasonication for 15 min and centrifugation for 10 and 15 min respectively for each repetition. All supernatants were combined and reduced in volume to

approximately 1-2 ml using a rotary evaporator (Büchi Rotavapor R-114 coupled with Büchi Waterbath B480) at a water bath temperature of 30 °C. The concentrated extracts were transferred to 20 ml glass screw top bottles and stored at -80 °C. Immediately prior to LC-MS analysis, the concentrated extracts were treated as for the aqueous sample extracts with an additional centrifugation at 4000 rpm for 5 min to separate any remaining suspended solids. Samples were analysed in duplicate.

2.3.3 Validation of sample extraction procedures

A series of preliminary experiments were performed to validate the applied methodology and to assess the overall efficiency of the sample preparation stages. All compounds were stable in the aqueous phase (<5% losses) but slightly less so in the soil matrices (<20% losses) and therefore immediate extraction was introduced for this phase. The most efficient recoveries (>86%) from soil matrices were achieved for carbamazepine and chloramphenicol (Table 1). Due to its high affinity for soil particles, triclosan could not be extracted efficiently (<20%) from either soil and therefore this personal care product was not included in the leachate experiments. For the batch sorption experiments, the amount of triclosan sorbed on the soil was estimated from the difference between the starting concentrations and the final aqueous phase concentrations. The limit of quantification (LOQ) values for the extraction of bezafibrate, carbamazepine, chloramphenicol and diclofenac from the soil samples were consistently below 20 µg kg⁻¹.

The efficiency of the solid phase extraction of the PPCPs was assessed by repeated extractions of deionised water spiked with a mixture of the 5 compounds. The aqueous samples yielded excellent recoveries (>95%) for bezafibrate, carbamazepine, chloramphenicol and diclofenac with the average recovery for triclosan being slightly lower at 88% (Table 1). The reproducibilities based on analysing four 1 mg l⁻¹ mixed PPCP standard solutions 5 times each in a random order were within 5%. The LOQ for the solid phase extraction of aqueous samples process was consistently below 1.25 µg l⁻¹.

Table 1. Method validation results for the analysis of selected PPCPs.

PPCP	Soil A recovery % (RSD%) ^a	Soil B recovery % (RSD%) ^a	SPE recovery % ^b	Reproducibility RSD% ^c
Bezafibrate	49.9 (4.3)	65.1 (3.18)	>95	5.0
Carbamazepine	98.2 (4.5)	86.3 (2.8)	>95	3.6
Chloramphenicol	97.2 (4.8)	96.5 (3.8)	>95	2.2
Diclofenac	61.9 (6.1)	72.9 (8.4)	>95	3.7
Triclosan	<20	<20	88	3.3

RSD: Relative Standard Deviation

^a Recovery of PPCP compounds during the ultrasonic extraction process from soils A and B

^b Recovery of PPCPs from aqueous phase by solid phase extraction

^c Reproducibility of the chromatographic separation method (RSD values based on measured peak areas)

2.4 PPCP analysis

The five PPCPs were analysed by LC-MS using a Shimadzu LCMS-IT-TOF system equipped with LCMSsolution Version 3.50 software. The employed chromatographic conditions are presented in Table 2. The addition of formic acid to the mobile phase assisted peak separation and enhancement of peak signals due to increased PPCP ionisation (Kasprzyk-Hordern et al. 2007). PPCPs were detected using time of flight (TOF) mass

spectrometry (MS) combined with an electrospray ionisation interface (ESI). ESI-MS was performed in both positive and negative modes under the following operating conditions: probe voltage, 1.7 kV (absolute); nebulizer nitrogen gas, 1.5 l min⁻¹; curved desolvation line (CDL) temperature, 250 °C. The system was run in scan mode in the m/z range of 100 to 500 Daltons.

Table 2. Liquid chromatography conditions employed for PPCP analysis.

Column	Kinetex 2.6u C18 (50mm x 2.10mm)
Column temperature	35 °C
Mobile phase	Solvent A: 0.1% formic acid in water; Solvent B: 0.2 % formic acid in acetonitrile
Flow rate	0.3 ml/min
Injection volume	10µl
Solvent gradient	
Time (min)	B %
0.1	2
1.6	2
1.61	20
7	40
12	75
13	75
13.01	2

3. Results and discussion of sorption experiments

3.1 Derivation of sorption coefficients

The determined equilibrium concentrations in the aqueous and solid soil phases following the batch adsorption experiments fitted well to the Freundlich adsorption isotherm ($R^2 > 0.90$). The Freundlich adsorption coefficients (K_F) derived using Equations 1 and 2 are listed in Table 3.

$$C_s = K_F \times C_w^{1/n} \quad (\text{Eq 1})$$

$$\log C_s = \log K_F + 1/n \log C_w \quad (\text{Eq 2})$$

where: C_s is the sorbed amount (mg kg⁻¹),

C_w is the equilibrium concentration in the aqueous phase (mg l⁻¹), and

n is a dimensionless value which describes the isotherm curvature and indicates the correlation between K_F and the distribution coefficient (K_d); a value of $1/n = 1$ represents a linear distribution as shown in Equation 3:

$$C_s = K_d C_w \quad (\text{Eq 3})$$

Although the K_F value provides a measure of the soil adsorption affinity, where the values of n indicate non-linearity it is not appropriate to use this parameter for comparison between different samples (Chen et al. 1999). The K_d values have been used for this purpose and where n values deviate substantially ($n < 0.8$ or $n > 1.25$) from unity indicating nonlinearity, average K_d values have been derived using the range of measured data for a particular soil and PPCP combination. Subsequently, the organic carbon normalised adsorption coefficients

(Table 3) have been calculated using the measured organic carbon fractions for soils A and B of 0.008 and 0.036, respectively.

Table 3. Comparison of determined distribution coefficients for sterile soils A and B with literature reported values.

	Soil A			Soil B			log K_{oc} (predicted values)
	K_F (n value)	K_d ($l\ kg^{-1}$)	log K_{oc}	K_F (n value)	K_d ($l\ kg^{-1}$)	log K_{oc}	
Bezafibrate	0.37 (n=0.99)	0.39±0.13	1.64	20.23 (n=1.23)	22.84±4.16	2.80	2.62 ^a
Carbamazepine	0.14 (n=0.5)	0.54±0.39	1.78	4.52 (n=0.95)	4.56±2.10	2.10	2.71 ^a
Chloramphenicol	0.57 (n=1.24)	0.46±0.47	1.71	0.39 (n=0.94)	0.42±0.03	1.07	1.99 ^a
Diclofenac	1.23 (n=1.06)	1.17±0.09	2.11	33.07 (n=1.90)	77.42±36.55	3.33	2.39 ^b
Triclosan	12.92 (n=0.81)	12.11±5.92	3.13	22.25 (n=3.89)	119.77±101.5	3.52	3.54 ^b 4.06-4.20 ^c 3.99-4.04 ^d

^a estimated from K_{ow} ; Lyman, Reehl and Rosenblatt (1990)

^b agricultural soil; Barron, Havel, Purcell, Szpak, Kelleher and Paull (2009)

^c experimental; Wu, Spongberg and Witter (2009)

^d experimental; Karnjanapiboonwong, Morse, Maul, Anderson and Todd (2010)

The greatest discrepancies between K_d and K_F values, as indicated by large deviations of n from unity, exist for soil B (particularly diclofenac and triclosan) although carbamazepine shows a greater variability in soil A compared to soil B. Satisfactory agreement between the K_d and K_F values appears to hold for n values within the range $0.8 > n < 1.25$.

The sorption characteristics of PPCP compounds, as defined by K_d values, have not been extensively tested in soil matrices and therefore it is often necessary to rely on estimated values derived from octanol-water coefficients (K_{ow}). Comparison of the predicted log K_{oc} values with the experimental values (Table 3) shows the best agreement in the case of soil A for chloramphenicol and diclofenac and with the lower determined results for the other compounds indicating a greater mobility than would be predicted. For soil B, the closest similarity exists for bezafibrate with more efficient soil mobilities being indicated for carbamazepine, chloramphenicol and triclosan. The behaviour of diclofenac in soil B is unique for the tested soils in that the determined log K_{oc} value exceeds the predicted value. The associated reduced mobility may suggest that hydrophobicity-independent mechanisms, such as cation exchange, cation bridging at clay surfaces, surface complexation, and hydrogen bonding (Yamamoto et al. 2009; Tolls 2001) are additionally present as influencing parameters.

3.2 Environmental relevance of the determined sorption coefficients

Chefetz et al. (2008), Ternes et al. (2007), Williams and Adamsen (2006), Xu et al. (2009) and Yu et al. (2009) have identified soil organic matter (SOM) as being an important factor influencing the sorption of pharmaceuticals and thus their ultimate fate in the environment. The elevated sorption coefficients observed for the non-normalised K_d values clearly indicate

that this is the case for the more highly organic soil B compared to soil A. Drillia et al. (2005) determined the K_{oc} values for the sorption of carbamazepine and diclofenac to both high (7.1%) and low (0.37%) organic carbon content soils and found that the influence of organic carbon was much more pronounced for diclofenac which is replicated in this study. Chloramphenicol does not follow the preferential trend for sorption to a more highly organic soil indicating that other factors may be influencing the sorption process. In the case of chloramphenicol, it is possible that its high water solubility, combined with the hydrophobic nature of soil B results in reduced potential active surface sorption sites such that the majority of chloramphenicol remains in the aqueous phase.

Another influencing factor with regard to the sorption characteristics is the pK_a of the investigated compound relative to the pH of the soil. Where the soil pH is higher than the pK_a value, which is the case in soil A for bezafibrate ($pK_a = 3.3$) and diclofenac ($pK_a = 4.0$), these compounds tend to exist in the dissociated form and the resulting negatively charged species (> 99% composition in soil A) adsorb less strongly than their neutral counterparts (11% for bezafibrate; 39% for diclofenac in the more acidic soil B) and this is reinforced by the presence of a negative net surface charge on most subsurface soil particles. The considerably lower determined adsorption coefficients of these PPCPs in soil A compared to soil B are consistent with this phenomenon. For carbamazepine and chloramphenicol the pK_a values exceed the pH values of both soils producing predominantly positively charged species which increases the tendency for soil adsorption and, in the case of carbamazepine, reduces the difference in the sorption coefficients of the two soils. The higher K_{oc} value in soil A exhibited by chloramphenicol, may be a consequence of the higher clay/silt fraction in this soil (27%) compared to soil B (18%) which will encourage cation exchange processes to more strongly influence the otherwise prevalent organic carbon adsorption. In a series of controlled experiments, Shimizu et al. (1992) showed that the sorption of pentachlorophenol to a range of natural solids was more dependent on the expansive clay content and the cation exchange capacity than the organic carbon content. In the case of triclosan, a pK_a value of 7.9 indicates that 83% and >99% would exist as the more readily adsorbable positive ionised form in soils A and B, respectively. This is mirrored by the K_{oc} values although both soils demonstrate strong affinities for this compound. The log K_{oc} values are generally lower than the literature values which may be partly explained by the relatively high sand contents of both soils (>73%) (Karnjanapibeenwaong et al. 2010).

The derived K_{oc} coefficients for the selected PPCPs indicate different behaviours with respect to sorption and mobility in the two soils with triclosan and diclofenac consistently demonstrating the strongest soil affinities and hence potentially low or low/moderate mobilities. The adsorption order for soil A is bezafibrate < chloramphenicol < carbamazepine < diclofenac < triclosan with the similar values for carbamazepine, bezafibrate and chloramphenicol being representative of potentially moderate mobilities. In soil B, the order becomes chloramphenicol < carbamazepine < bezafibrate < diclofenac < triclosan with only chloramphenicol being potentially capable of a high mobility followed by decreases to moderate (carbamazepine), moderate/low (bezafibrate) and low mobilities (diclofenac and triclosan). The observed sorption behaviours predicted for diclofenac and triclosan are consistent with the K_{oc} values determined by Xu et al. (2009) from an investigation of four sterilised soils containing different percentages of organic carbon (0.44-3.16%).

4. Results and discussion of leachate experiments

Leachate experiments were conducted over a period of 12 days by introducing 20 μg of bezafibrate, carbamazepine, chloramphenicol and diclofenac to prepared soil columns. In addition to PPCP levels leaving the columns in the leachates and being retained within the

soil columns, the pH and dissolved organic carbon (DOC) in the leachate were determined. The pH of the introduced artificial rainwater (8.41 ± 0.09) showed the overall expected greater decrease of 4.5 for the more acidic soil B compared to a pH reduction of 1.0 for soil A. The measured leachate DOC concentrations were consistent with the differences in the soil organic contents and decreased over the period of the experiment from 57.7 ± 8.1 to $15.4 \pm 3.8 \text{ mg l}^{-1}$ in soil A and from 329.0 ± 12.6 to $67.3 \pm 5.4 \text{ mg l}^{-1}$ in soil B in the presence of CaCl_2 . Replacing the eluent by NaCl on day 7 slightly reversed this decreasing trend.

4.1 Concentrations and temporal distributions of selected PPCPs in the leachate samples

The leaching and soil retention behaviours of bezafibrate, carbamazepine, chloramphenicol and diclofenac in the two soils over 12 day experiments are illustrated in Fig. 1. The leachate histograms represent the relative average percentages of PPCPs that progressively leached through the soil columns. The lighter shaded bars represent the situation when the columns were continuously percolated with 0.01 M CaCl_2 and the darker bars indicate the impact of switching to 0.1 M NaCl after 7 days. The former are accompanied by standard deviations as these experiments were conducted in duplicate. The soil column histograms indicate the relative average percentages of PPCPs which were retained by the soils and are also differentiated in terms of whether the eluent was consistently 0.01 M CaCl_2 (lighter bars) or was changed to 0.1 M NaCl after 7 days (darker bars).

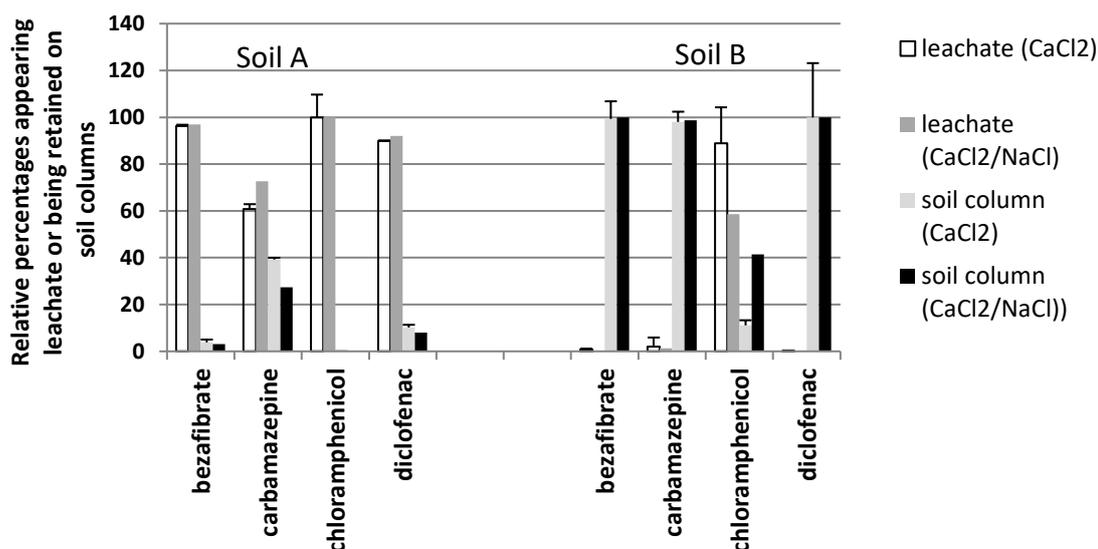


Figure 1. Relative percentages of PPCPs released in leachates and retained on columns for soils A and B.

It is clear that soil A exhibits a predominant potential for efficient leaching which is consistent with the lower organic content of this soil and the generally lower K_{oc} values determined for the PPCPs in this soil. Chloramphenicol, bezafibrate and diclofenac all show a high mobility in soil A with the overall preferential order of leaching being chloramphenicol > bezafibrate > diclofenac > carbamazepine (Fig. 1). This is not entirely consistent with the determined K_{oc} values in soil A which would have predicted similar mobilities for chloramphenicol, bezafibrate and carbamazepine with diclofenac expected to demonstrate a lower mobility. Hence the behaviours of carbamazepine and diclofenac in the

column leachate experiments do not follow those predicted by the K_{oc} values. The different pK_a values of diclofenac (4.0) and carbamazepine (13.4) are such that in the neutral pH environment provided by soil A, diclofenac will partially exist in the dissociated form which will generally adsorb less efficiently than its neutral counterpart. Schaffer et al. (2012) found that increasing the pH in columns packed with sandy sediments enhanced the mobility of naproxen, a weakly acidic pharmaceutical, due to the dissociation of a carboxylic acid group and demonstrated that this phenomenon became important in soils containing a low organic matter content. This may explain the unexpected behaviour of diclofenac compared to carbamazepine. It was also noticeable that carbamazepine was the only tested PPCP to show a significant behaviour change in the presence of 0.1M NaCl with the leachate content being elevated by 19% accompanied by a proportionate decrease in column retention. This is consistent with the results obtained from column leaching experiments reported by Navon et al. (2011) for carbamazepine in bulk clay soils and by Borgman and Chefetz (2013) for bezafibrate, carbamazepine and diclofenac in biosolids-amended soils due to an increased mobilisation of dissolved organic carbon (DOC). Field experiments have shown that the preferential mechanism for carbamazepine was sorption to a volcanic sandy soil (>99%) (Gielen et al. 2009) although there was the potential for leaching to occur at neutral pH in soils possessing low organic carbon content <1%. Similar results were observed by Calisto and Esteves (2012) for agricultural soils and by Fenet et al. (2012) who found that the parent compound was less mobile than two of its metabolites (carbamazepine-10,11-epoxide and 10,11-dihydro-10,11-dihydrocarbamazepine).

Only chloramphenicol demonstrated any tendency to leach from soil B which is consistent with the low $\log K_{oc}$ value (1.07) determined for this combination of soil and PPCP. Other characteristics of chloramphenicol which influence its preferential release from soil B relative to the other PPCPs are its higher solubility and lower K_{ow} values. However, the impact of changing the eluent to NaCl exerts a negative effect by reducing the relative amount of chloramphenicol leaving the columns from 89% to below 60% and the reason for this is not clear. The rates of leaching from both soils follow the decreasing order of chloramphenicol > bezafibrate > diclofenac, carbamazepine although the minimum amounts of bezafibrate, diclofenac and carbamazepine leaving the soil B columns makes this effect insignificant. A comparison of the observed leaching rates of chloramphenicol from both soils in the presence of $CaCl_2$ as eluent is shown in Fig. 2 demonstrating that the majority of the leached chloramphenicol leaves the soil A columns in the first 4 days (90%) followed by a rapid drop which results in a negligible presence in the leachate after 12 days. In soil B, the leachate behaviour of chloramphenicol is more protracted with only small amounts appearing after 2 days and the majority leaving the column in the 4-8 day period (78%). There is still a small amount of chloramphenicol in the soil leachate after 12 days. The temporal behaviour of bezafibrate in soil A leachates is similar to chloramphenicol in that there is an immediate release (74% after 4 days) followed by a progressive decrease which is still not fully exhausted after 12 days. The temporal patterns of diclofenac and carbamazepine leaching from soil A are similar with increases to day 4 followed by an exponential decrease to day 12. Although changing the eluent to 0.1M NaCl after 7 days increases the DOC content of the leachate, the effect on bezafibrate, chloramphenicol and diclofenac was minimal. This was probably because for soil A, the majority of the leaching had already occurred whereas for soil B, the leachate presence of these compounds was minimal, except for chloramphenicol.

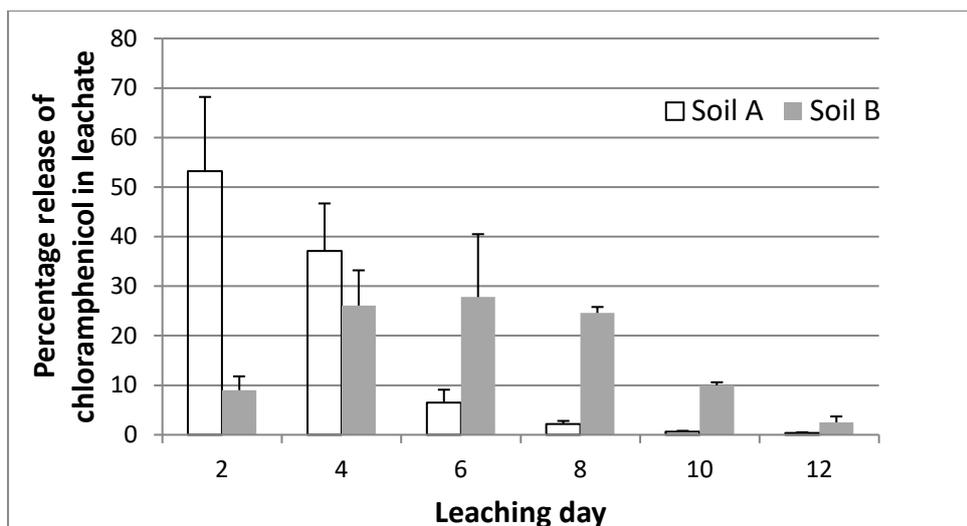


Figure 2. Temporal pattern of PPCP release in the leachate from soils A and B with 0.01M CaCl_2 as eluent.

4.2 Final soil distributions of applied PPCPs

As expected from the leachate behaviours, the predominant behaviour of soil B is retention of PPCPs on the soil column due to attachment to the particulate phase (>98% in the case of diclofenac, bezafibrate and carbamazepine) (Fig. 1). This is entirely consistent with the determined K_{oc} values and indicates that sorption to organic carbon is the predominant mechanism in this soil. Chloramphenicol exhibited the lowest K_{oc} value for soil B which identifies it as the most mobile PPCP in this soil. Only a low overall relative percentage (11%) was retained on the soil column after 12 days and this was mainly accumulated (78%) within the lowest soil layer (>7 cm) (Fig. 3). The PPCP distribution patterns in the soil B column were consistent with the determined K_{oc} values, with the majority of carbamazepine travelling into the deeper segments (peaking at 3-5 cm depth) compared to bezafibrate and diclofenac for which >90% was retained above 3 cm (Fig. 3). The ability of PPCPs to form complexes with dissolved organic matter (DOM) (Hernandez-Ruiz et al. 2012) illustrates their potential to penetrate organic rich soils, such as soil B, via pore water transport.

The small amounts of those PPCPs retained in soil A demonstrated abilities to penetrate to depths below 3 cm (Fig. 3). These results suggest that polarity of the PPCPs and the organic matter content of the soil are important factors affecting the mobility of the pharmaceuticals. Soil B has a higher organic matter content and polar compounds with less affinity for organic substances would pass through the soil quicker. This is in agreement with Chefetz et al. (2008), who suggest that carbamazepine and diclofenac can be classified as low mobility compounds in SOM-rich soil layers but that this mobility increases with decreasing SOM. This emphasizes the potential transport of pharmaceuticals to groundwater due to intensive irrigation with reclaimed wastewater in SOM-poor soils, such as soil A.

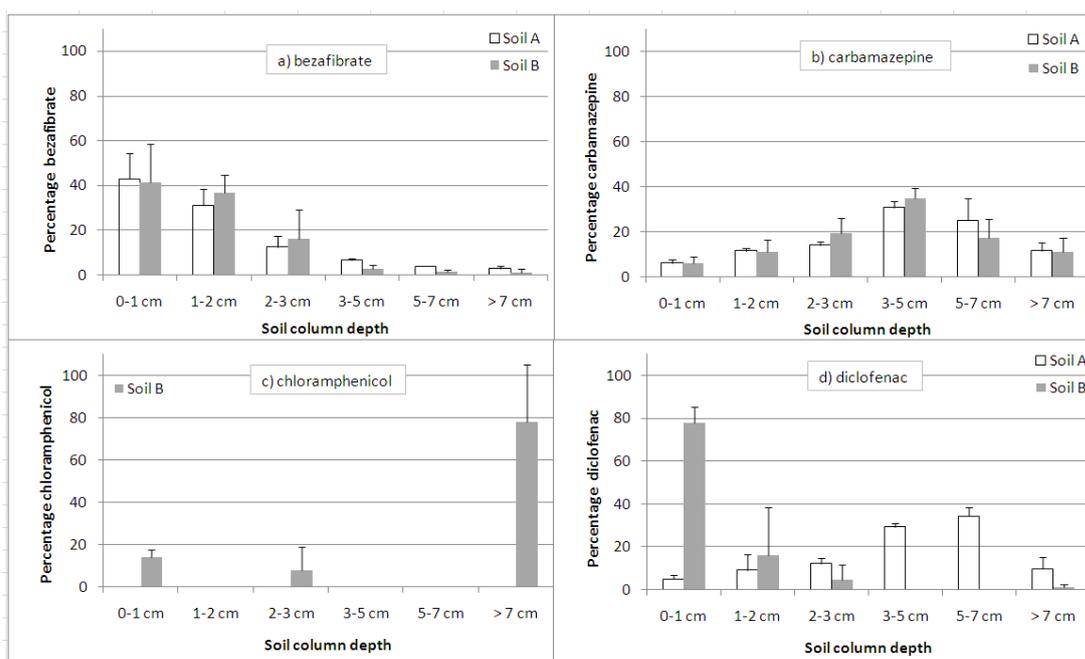


Figure 3. The percentage distributions of a) bezafibrate, b) carbamazepine, c) chloramphenicol and d) diclofenac by depth in columns containing soils A and B after leaching with 0.01M CaCl₂ for 12 days.

Despite the greater overall retention of carbamazepine within soil B, the soil depth profiles are similar with peak penetration after 12 days being attained at 3-5 cm followed by decreases to the >7 cm depth (Fig. 3). Similar migration patterns for both soils also exist for bezafibrate with a progressive decrease occurring with increasing depth. Diclofenac demonstrates different soil depth distributions with the elevated amounts in soil B being preferentially retained in the surface layer and no migration evident below 3 cm. Only 6% of bezafibrate reached depths below 3 cm in soil B (Fig. 3). The preferential accumulation of diclofenac in the upper layers of a biosolids-amended soil has been reported by Borgman and Chefetz (2013) during column leaching experiments.

The effect of changing the effluent to 0.1M NaCl was observable for soil B in terms of the overall amount retained and its movement to the lower soil layers. The influence of NaCl was not significant for soil A columns with the most strongly retained PPCP being carbamazepine followed by diclofenac and bezafibrate (Fig. 1). In this case the lack of exact agreement with the prediction derived from the determined K_{oc} values would indicate that additional factors to organic carbon sorption are also present. Although a change in the leaching solution from 0.01M CaCl₂ to 0.1M NaCl increased mobilisation of the dissolved organic carbon (DOC), this was not accompanied by an improved leaching efficiency of the compounds of interest. This is consistent with the results obtained from column leaching experiments reported by Navon et al. (2011) for carbamazepine in bulk clay soils and by Borgman and Chefetz (2013) for bezafibrate, carbamazepine and diclofenac in biosolids-amended soils.

Both tested soils predominantly consist of the sand fraction (70%) although soil B has a slightly lighter texture. However, it appears that the higher organic content and lower pH of soil B are responsible for the greater retention of the PPCP compounds. The ionic strength of the eluent can also play an important role but this was not observed in the reported experiments. The soil pH is particularly relevant for the sorption of weak acids and bases. At low pH values, weak bases in the cationic form are adsorbed to a higher extent than the free bases, as demonstrated by the behaviour of chloramphenicol exhibiting a greater retention in

soil B. Also weak acids such as bezafibrate and diclofenac have stronger sorption at low pH. In a pH environment higher than the pK_a (as in soil A), these compounds would partially exist in their dissociated forms and as anions they generally adsorb less strongly to organic carbon and clay than their neutral counterparts. However, soil properties such as pH have only a small effect on the sorption of these compounds to clay minerals except in soils with low organic matter content where this phenomenon is magnified. In soil B the organic matter content is over 3.6% and this appears to be the strongest factor affecting the sorption of PPCP compounds.

5 Conclusions

Widely contrasting behaviours have been observed for the interactions of PPCPs possessing different physico-chemical characteristics when exposed to soils varying in acidity and organic carbon content. Experimentally determined organic carbon distribution coefficients (K_{oc}) are shown to be more reliable than estimated values, based on octanol–water coefficients, for predicting PPCP soil mobilities, particularly for lower organic content soils. The controlling influence of hydrophobicity dependent mechanisms can be seen to be moderated by other factors such as the soil pH/pK_a relationship which results, for example, in an enhanced mobility for diclofenac in soil A. Only this soil, characterised by being neutral and possessing a low organic content allowed bezafibrate, carbamazepine, chloramphenicol and diclofenac to pass through soil columns efficiently over a 12 day period. Chloramphenicol demonstrated the most effective leaching potential, in terms of both amount and rate and also possesses the ability to leach through soil B although at a reduced rate. Therefore, PPCPs with similar properties to chloramphenicol are unlikely to be efficiently removed by soil filtration and have the potential to penetrate to much greater depths than those tested in these experiments. On the other hand, diclofenac, bezafibrate and carbamazepine were effectively retained by soil B with the majority being held in the top 5 cm which indicates the potential for a more highly organic soil of this type to be used for soil purification purposes. Where PPCPs are present in wastewaters being irrigated on to agricultural soils with low organic content, their mobility presents a potential risk of groundwater contamination and the use of organic amendments is recommended to assist the retention of the PPCPs in the upper soil layers. However, given the wide range of properties which exist for PPCPs and indeed for soil types it is evident that considerable further work is required before a fuller understanding of the risk posed by soils contaminated with PPCPs can be determined. Additionally, the role played by influencing factors, such as biodegradation in non-sterile soils needs to be further explored.

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