

## Interactions of Carbamazepine in Soil: Effects of Dissolved Organic Matter

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Pharmaceutical compounds (PCs) and dissolved organic matter (DOM) are co-introduced into soils by irrigation with reclaimed wastewater. We targeted carbamazepine (CBZ) as a model compound to study the tertiary interactions between relatively polar PCs, DOM, and soil. Sorption–desorption behavior of CBZ was studied with bulk clay soil and the corresponding clay size fraction in the following systems: (i) without DOM, (ii) co-introduced with DOM, and (iii) pre-adsorption of DOM before CBZ introduction. Sorption of the DOM to both sorbents was irreversible and exhibited pronounced sorption–desorption hysteresis. Carbamazepine exhibited higher sorption affinity and nonlinearity, and a higher degree of desorption hysteresis with the bulk soil than the corresponding clay size fraction. This was probably due to specific interactions with polar soil organic matter fractions that are more common in the bulk soil. Co-introduction of CBZ and DOM to the soil did not significantly affect the sorption behavior of CBZ; however, following pre-adsorption of DOM by the bulk soil, an increase in sorption affinity and decrease in sorption linearity were observed. In this latter treatment, desorption hysteresis of CBZ was significantly increased for both sorbents. We hypothesize that this was due to either strong chemical interactions of CBZ with the adsorbed DOM or physical encapsulation of CBZ in DOM–clay complexes. Based on this study, we suggest that DOM facilitates stronger interactions of polar PCs with the solid surface. This mechanism can reduce PC desorption ability in soils.

IN THE LAST FEW DECADES, the use of pharmaceutical compounds (PCs) for human and veterinary applications has increased. Due to incomplete removal of PCs during conventional wastewater treatment, both treated effluents and sludge contain active PCs (Díaz-Cruz et al., 2009; Ternes, 1998). In most countries, treated wastewater is released to natural water bodies. Therefore, until a few years ago, most studies on this subject were aimed at evaluating the fate of PCs in aquatic environments and not in soils. However, in semiarid zones, reclaimed wastewater is used for irrigation. For example, in Israel about 50% of the total irrigation water in 2010 was reclaimed wastewater. Thus, introduction to agricultural soils is a highly relevant route of exposure to PCs in many regions. Once in the soil, PCs might be retained by the solid matrix or mobilized by percolating water: the highly mobile PCs have the potential to leach to the groundwater, whereas strongly sorbed PCs can accumulate in the top soil layer (Chefetz et al., 2008).

Soil adsorption of PCs is influenced by the physicochemical properties of the molecule and by the soil characteristics, such as pH and the quantity and quality of both soil organic matter (SOM) and minerals (Drillia et al., 2005; Tolls, 2001). The organic pollutant–soil interactions are also influenced by the presence of dissolved organic matter (DOM) (Barriuso et al., 1992; Totsche et al., 1997). In general, interactions between DOM and organic pollutants in solution and competition of DOM for sorption sites on soil particles result in reduced sorption of the solute. In contrast, cumulative sorption and cosorption processes will enhance sorption to the solid phase (Celis et al., 1998; Totsche et al., 1997). The net effect of DOM on the sorption of organic pollutants to soils is the sum of the abovementioned processes, which are all controlled by the binding affinity of the organic pollutant to the DOM, the binding affinity of the DOM and the organic pollutant to the soil matrix, and the sorption affinity of the DOM–organic pollutant complex to the soil solid phase.

In this study, we targeted carbamazepine (CBZ) as a model compound to study the tertiary interactions between a relatively polar organic compound, DOM, and soil. Carbamazepine is a drug used for the treatment of epilepsy, bipolar affective disorder, and acute mania. This compound has great environmental

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**Abbreviations:** CBZ, carbamazepine; DOM, dissolved organic matter; HI, hysteresis index; HPLC, high-performance liquid chromatography; LC/MS, liquid chromatography-mass spectrometry; OC, organic carbon; OM, organic matter; PC, pharmaceutical compound; SOM, soil organic matter.

significance due to its limited removal efficiency during wastewater treatment processes (Joss et al., 2005; Radjenovic et al., 2009) and its high stability in the environment (Clara et al., 2004; Tixier et al., 2003). Carbamazepine has been detected in treated wastewater and in soils irrigated with treated wastewater effluents, in the groundwater and surface water, and even in drinking water (Miao et al., 2005; Stackelberg et al., 2004; Tixier et al., 2003; Zhang et al., 2007). Several recent reports have described a variety of different sorption–desorption behaviors of CBZ in soils (Chefetz et al., 2008; Scheytt et al., 2005; Yu et al., 2009). However, the effects of DOM on soil adsorption of CBZ are still unclear.

## Materials and Methods

Carbamazepine (5*H*-dibenzo[*b,f*]azepine-5-carboxamide, 98% w/w) was purchased from Sigma-Aldrich (Rehovot, Israel). The aqueous solubility of CBZ is 125 mg L<sup>-1</sup> and the reported log  $K_{ow}$  value is 2.45. D<sub>3</sub>-<sup>13</sup>C-labeled carbamazepine (Toronto Research Chemicals, North York, ON, Canada) was used as an internal standard for the liquid chromatography–mass spectrometry (LC/MS) analysis.

### Soil Sampling, Isolation of Clay Fraction, and Characterization

Soil (Vertisol) was sampled from a crop field (Kfar Baruch, Israel). Six subsamples were collected from a depth of 0 to 25 cm and combined to form a composite sample. The soil was air-dried and sieved through a 2-mm sieve. To isolate the clay fraction, the soil was dispersed in deionized water (50 g L<sup>-1</sup>). The clay-sized particles (<2 μm; hereafter termed clay fraction) were separated by sedimentation and then freeze-dried. The bulk properties of the studied soil and its clay fraction (Table 1) were measured by standard soil testing methods (Dane and Topp, 1996; Sparks, 1996). Basal spacing of the clay fraction (before and after DOM adsorption) was measured using an X-ray diffractometer (XRD; PW1830/3710/3020, Philips Analytical, Almelo, Netherlands) with Cu Kα radiation at λ = 1.526 nm.

### Dissolved Organic Matter Extraction and Characterization

Municipal sewage sludge and yard waste (1:1 v/v) compost was collected from a commercial composting facility. The DOM

was extracted by shaking (200 rpm) the compost overnight in distilled water (1:10 compost-to-water ratio). The suspension was centrifuged (25,000 × *g* for 20 min) and filtered (0.45 μm). To remove salts from the DOM, the solution was filtered by Prep/Scale-TFF cellulose cartridge (1000 Da, Millipore, Billerica, MA) and then freeze-dried.

High-performance liquid chromatography (HPLC)–size exclusion chromatography analysis was performed using an HPLC (Waters 600, Waters, Milford, MA) equipped with two stainless steel (8 by 300 mm) columns (MCX GPC 1000 and 100,000 Å, PSS Polymer Standard Service-USA, Warnick, RI) connected in line to achieve a good linear molecular weight relationship over the elution time of the standards. The mobile phase was a sodium phosphate buffer with final pH of 7.6 and electrical conductivity of 1250 μS cm<sup>-1</sup>. Molecular weight standards were composed of polystyrene sulfonate standards (910–48,600 Da) and 4-ethylbenzenesulfonic acid (186 Da). The concentration of the DOM and standards was 30 mg L<sup>-1</sup>, injection volume was 100 μL, and an isocratic flow rate of 1 mL min<sup>-1</sup> was used. The DOM and standard samples were detected by photodiode array set at 280 nm. The weighted-average molecular weight ( $M_w$ ) was calculated by Empower Pro software program (Waters 2002, Medford, MA).

### Sorption of Dissolved Organic Matter to Soil and Clay Fraction

Sorption was obtained by batch-equilibrium technique at 25°C in polypropylene centrifuge tubes at a solid-to-solution ratio of 1:5. Dissolved organic matter solutions (25–500 mg L<sup>-1</sup> for the soil and 75–500 mg L<sup>-1</sup> for the clay fraction) were prepared by dissolving the freeze-dried DOM samples in background solution containing 5 mM CaCl<sub>2</sub> (to maintain a constant ionic strength) and 100 mg L<sup>-1</sup> NaN<sub>3</sub> (to inhibit microbial activity) (Chefetz et al., 2006). The solutions were stirred overnight before being added to the sorbents. The tubes (three replicates for each concentration) were agitated in the dark at 200 rpm for 4 d to reach equilibrium (based on preliminary kinetic experiments). Blanks without sorbent or without DOM were used to determine the initial organic carbon (OC) concentration and the level of native OC released from the sorbents. Desorption was performed by replacing 80% of the supernatant with fresh DOM-free background solution. The tubes were then further agitated under the same conditions for 4 d. Two sequential desorption steps were performed. Concentrations of OC in the supernatant at every sorption or desorption step were determined using total organic carbon analyzer (Shimadzu Scientific Instruments, Kyoto, Japan).

### Sorption of Carbamazepine to Soil and Clay Fraction

Sorption isotherms were obtained by batch-equilibrium technique at 25°C in Teflon centrifuge tubes at a solid-to-solution ratio of 1:5. Carbamazepine solutions (0.5–100 μg L<sup>-1</sup>) were prepared by adding aliquots from a concentrated methanol stock solution to a background solution. In all solutions, methanol concentration was maintained at <0.001% (v/v) to avoid cosolvent effects. The tubes (in triplicate) were agitated in the dark at 200 rpm for 4 d to reach equilibrium (based on preliminary kinetic experiments). In addition, a set of blanks

**Table 1. Selected properties of the bulk soil and clay size fraction (± SD).**

Property	Soil	Clay fraction
Clay (%)	68.0 ± 1.6	–
Silt (%)	16.5 ± 0.0	–
Sand (%)	15.5 ± 1.6	–
Cation exchange capacity (meq 100 g <sup>-1</sup> )	19.7 ± 2.1	29.9 ± 0.8
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	373 ± 4	583 ± 9
Organic carbon (%)	1.04 ± 0.07	0.71 ± 0.04
DOC† concentration in 1:5 extract (mg L <sup>-1</sup> )	7.3 ± 0.9	22.4 ± 1.1
CaCO <sub>3</sub> (%)	6.3 ± 0.5	3.3 ± 0.1
Total iron oxide (Fe <sub>p</sub> ) (g kg <sup>-1</sup> )	13.97 ± 0.19	16.51 ± 0.49

† DOC, dissolved organic carbon.

(without sorbent or without CBZ) were agitated under the same conditions to determine the initial CBZ concentration and native CBZ release from the sorbents. Desorption was performed by replacing 80% of the supernatant with fresh CBZ-free background solution. The tubes were then further agitated under the same conditions for an additional 4 d. Three sequential desorption steps were performed.

The effects of DOM on CBZ sorption and desorption behavior were studied in two ways. (i) CBZ (0.5–100  $\mu\text{g L}^{-1}$ ) was allowed to equilibrate with DOM before introducing into the sorbent. In these experiments, a constant DOM equilibrium concentration of 107 mg OC  $\text{L}^{-1}$  was maintained during the entire experiment. (ii) The sorbents were allowed to interact with the DOM before CBZ was applied. After 4 d, the suspensions were centrifuged and 80% of the supernatant was replaced with CBZ solution free of DOM. For this treatment, all desorption steps were performed with DOM-free solutions. Carbamazepine concentrations in the supernatant at every sorption or desorption step were determined by LC/MS analysis. Mass balance analyses ensured negligible sorption of CBZ to the tubes or loss due to volatilization or degradation. Therefore, sorption was calculated by mass differences.

### Liquid Chromatography–Mass Spectrometry Analysis

The samples (1 mL) were spiked with 10  $\mu\text{L}$  of  $\text{D}_3$ - $^{13}\text{C}$ -labeled CBZ. Chromatographic analysis was performed using the Agilent 1200 Rapid Resolution LC system (Agilent Technologies Inc., Santa Clara, CA). Separation of CBZ was achieved under isocratic conditions (methanol/water 70:30 with 0.05% v/v acetic acid) using a Thermo Hypersil Gold C18 HPLC column (2.1 by 100 mm, particle size 1.9  $\mu\text{m}$ ). The LC was coupled with the Agilent 6410 triple quadrupole mass selective detector equipped with an electrospray ionization ion source. The MS was operated in positive ionization mode. The ion-source parameters were: capillary voltage, 3000 V; drying gas,  $\text{N}_2$  at 10  $\text{L min}^{-1}$ ; temperature, 350°C; nebulizer pressure, 241,316 Pa;  $\text{N}_2$  (99.999% purity) was used as the collision gas. The LC/MS system was controlled and data analyzed by MassHunter software (Agilent Technologies Inc., Santa Clara, CA). Quantitative analysis of CBZ was performed in multiple reaction monitoring (MRM) mode. The MRM parameters for CBZ were: fragmentor voltage, 110 V; collision energy, 15 eV for transitions 237→194 (241→197 for CBZ  $\text{D}_3$ - $^{13}\text{C}$ ); collision energy, 35 eV for transitions 237→179 m/z (241→181 for CBZ  $\text{D}_3$ - $^{13}\text{C}$ ). In all analyses, injection volume was 10  $\mu\text{L}$ , and limit of detection and limit of quantification achieved for CBZ were 40 and 75 ng  $\text{L}^{-1}$ , respectively.

### Data Analysis

Dissolved organic matter sorption curves were fitted to the Langmuir equation and CBZ sorption isotherms were fitted to the Freundlich equation. The parameters  $K_L$  (sorption affinity),  $q_{\text{max}}$  (sorption capacity),  $K_p$  and  $N$  were calculated using SigmaPlot 10 (Systat Software Inc., Richmond, CA). For CBZ, the sorption coefficient  $K_d$  was calculated at equilibrium concentrations ( $C_e$ ) of 0.5, 5, and 50  $\mu\text{g L}^{-1}$  using the equation  $K_d = K_f C_e^{N-1}$ . The OC-normalized sorption coefficient ( $K_{oc}$ ) was calculated for the above concentrations by dividing the  $K_d$  values by the fraction of OC in the sorbent. Apparent desorp-

tion hysteresis was quantified using the hysteresis index (HI), defined as the ratio of the Freundlich exponents for desorption and sorption ( $N_D/N_S$ ) isotherms. Statistical analysis (All Pairs, Tukey–Kramer,  $p = 0.05$ ) was performed by JMPIN software, version 7.0.2 (SAS Institute Inc., Cary, NC).

## Results and Discussion

### Binding of Dissolved Organic Matter to Soil and Clay Fraction

Adsorption of DOM to soils is typically characterized by non-linear binding curves (Kothawala et al., 2008; Vandenbruwane et al., 2007). Therefore, isotherms of DOM to the soil and clay fraction were fitted to the Langmuir equation. The sorption and desorption isotherms of DOM to the soil and clay fraction are presented in Fig. 1. The calculated  $K_L$  values were similar for the two sorbents (0.0013  $\text{L kg}^{-1}$ ), whereas the two sorbents exhibited different  $q_{\text{max}}$  values ( $2428 \pm 812$  and  $1928 \pm 471$  mg OC  $\text{kg}^{-1}$  for the soil and the corresponding clay fraction, respectively). In general,  $q_{\text{max}}$  values for soil binding of DOM are positively correlated with the amount of Fe and Al oxides and hydroxides and the level of the clay fraction, and negatively correlated with the indigenous organic matter (OM) content (Benke et al., 1999; Jardine et al., 1989). In our system, the bulk soil exhibited higher OM content and lower levels of clay and Fe oxide than the corresponding clay fraction (Table 1). However, these differences did not result in significantly different  $q_{\text{max}}$  values. Kothawala et al. (2008) reported  $K_L$  values for DOM with 52 mineral soils ranging from  $0.0003 \pm 0.0001$  to  $0.0432 \pm 0.029$   $\text{L kg}^{-1}$  and  $q_{\text{max}}$  values ranging from  $105 \pm 51$  to  $1968 \pm 1984$  mg  $\text{kg}^{-1}$ . Ling et al. (2006) reported  $K_L$  values of 0.011 to 0.191  $\text{L kg}^{-1}$  and  $q_{\text{max}}$  values of 298 to 700 mg  $\text{kg}^{-1}$  for DOM sorption to 10 soils. We assume that the relatively low  $K_L$  values obtained in the current study (0.0013  $\text{L kg}^{-1}$ ) are due to weak binding interactions (i.e., cation or water bridging and van der Waals interactions) of the DOM with the sorbents (Kothawala et al., 2008). On the other hand, the high  $q_{\text{max}}$  values obtained for both samples are probably resulted from the relatively high content of sorbing agents (i.e., Fe oxides and clay minerals; Table 1).

Size exclusion chromatography revealed that the DOM is fractionated during the sorption process. The  $M_w$  of the bulk DOM was  $5908 \pm 729$  Da, whereas that of the nonsorbed DOM was only  $2477 \pm 128$  Da. This suggests preferential binding of the higher-molecular-weight DOM molecules to the soil. Similarly, Guo and Chorover (2003) reported the preferential sorption of high-molecular-weight components to soil. This phenomenon is usually attributed to the sorption of DOM to Fe oxides (Gu et al., 1995). In some studies, DOM has been reported to be fractionated by clay minerals as well (Specht et al., 2000). In addition, sorption of DOM can facilitate the release of native low-molecular-weight SOM to the solution (Kaiser and Zech, 1998). These processes result in differences between solids and solution with respect to DOM amount and properties. These changes might affect the behavior of the sorbed DOM and the fate of organic pollutants in the soil.

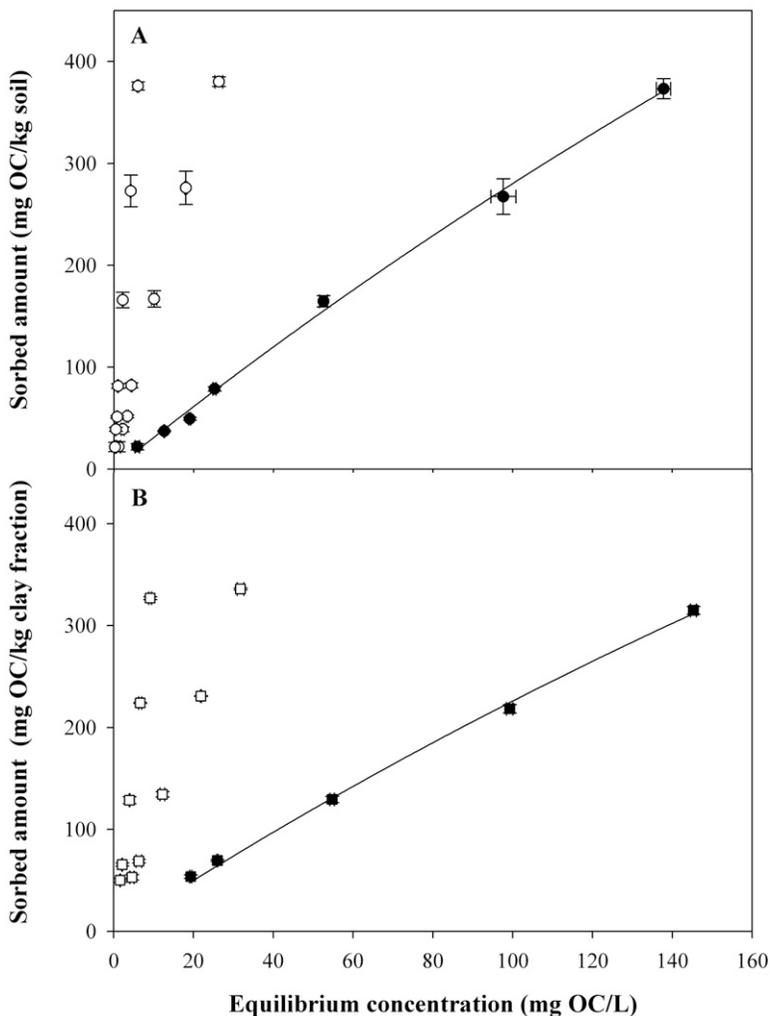


Fig. 1. Sorption–desorption isotherms for dissolved organic matter with the (A) bulk soil and (B) clay size fraction. Sorption and desorption data are represented by filled and open symbols, respectively. OC, organic carbon.

Although many studies have reported data on DOM sorption to soils and minerals, reports on its desorption behavior are scarce. In our study, sorption of the DOM to both studied sorbents was irreversible and exhibited strong sorption–desorption hysteresis (Fig. 1). Similarly, Benke et al. (1999) and Kahle et al. (2003) reported that after sorption of DOM to soil, only 11 to 25% of the DOM is released, and Kaiser and Zech (1999) reported negligible desorption (<3%) of DOM from a subsoil (containing a low level of OM). Pronounced sorption–desorption hysteresis of DOM has been reported mainly with Fe and Al oxides due to strong chemical binding such as ligand exchange, electrostatic interactions, and H-bonding (Benke et al., 1999; Gu et al., 1995; Kaiser and Zech, 1999). In addition, DOM may adsorb to the oxide surfaces via multiple binding sites, and desorption requires detachment from all sites simultaneously (Kaiser and Zech, 1999). In contrast, adsorption of DOM to clay minerals has been reported to be governed mainly by weak interactions, such as water and cation bridging and van der Waals forces, and it is therefore reversible (Baham and Sposito, 1994).

In our clay-rich system, a possible explanation for the irreversible adsorption of DOM might be its physical entrapment within the clay mineral layers. However, this mechanism

was ruled out because our XRD analysis revealed that DOM sorbed mainly to external surfaces of the expandable clay minerals (i.e., d-spacing did not change due to DOM adsorption). Nevertheless, we also suggest that at least part of the measured hysteresis was due to interactions (such as ligand exchange, H-bonding, cation bridging) of polar moieties of the DOM with the solid interface, forming stable clay–DOM aggregates. Arnarson and Keil (2000) reported the relative contribution of ligand-exchange interactions to the overall sorption of DOM to montmorillonite as approximately 35%. This suggests that chemisorption to clay minerals may also have contributed to the apparent sorption–desorption hysteresis of DOM in our study.

### Sorption of Carbamazepine to Soil and Clay Fraction

Carbamazepine exhibited different sorption–desorption behavior with the clay fraction as compared to the corresponding bulk soil, although the former made up about 68% of the soil mass (Fig. 2A and 3A). The  $K_d$  values of CBZ with the bulk soil were higher than with the clay fraction. After normalizing the sorption coefficient data to the OC content of the sorbent ( $K_{oc}$ ), the differences between the two sorbents were reduced; however, sorption to the soil was still significantly higher than to the clay fraction (Table 2). The CBZ isotherms exhibited desorption hysteresis and a higher degree of nonlinearity with the bulk soil, whereas with the clay fraction, CBZ exhibited linear and almost reversible sorption. The HI calculated for the CBZ–clay fraction system was  $0.91 \pm 0.05$ . The HI value for CBZ in the bulk soil system was much lower ( $0.64 \pm 0.04$ ), indicating more difficulty in releasing the adsorbed molecules from this matrix. Stein et al. (2008) reported that CBZ exhibits reversible sorption

with one sediment and pronounced desorption hysteresis with another. They speculated that hysteresis was caused by either slow desorption kinetics from the solids (equilibrium time was only 1 d) or sorption-induced OM deformation. In another study (Williams et al., 2006), CBZ exhibited strong sorption–desorption hysteresis with two soil samples. However, in that study the sorption and desorption steps were performed in 2-h intervals. In both abovementioned studies, short equilibrium time was used, thus suggesting that the observed hysteresis might be considered as artificial desorption hysteresis. In our study, the desorption equilibrium time was 4 d and the recovery of CBZ was high (98.9 and 93.0% for the clay fraction and the bulk soil, respectively). Therefore, the differences observed in the sorption–desorption behavior of CBZ between the two sorbents were likely due to the different nature of the SOM in the various size fractions of the soil. The sorption–desorption behavior of CBZ with the bulk soil (i.e., higher affinity, nonlinearity, and desorption hysteresis) might reflect binding by polar interactions with polar moieties which are present in larger amounts in this sorbent. On the other hand, the SOM in the clay fraction seems to act as a partitioning domain for

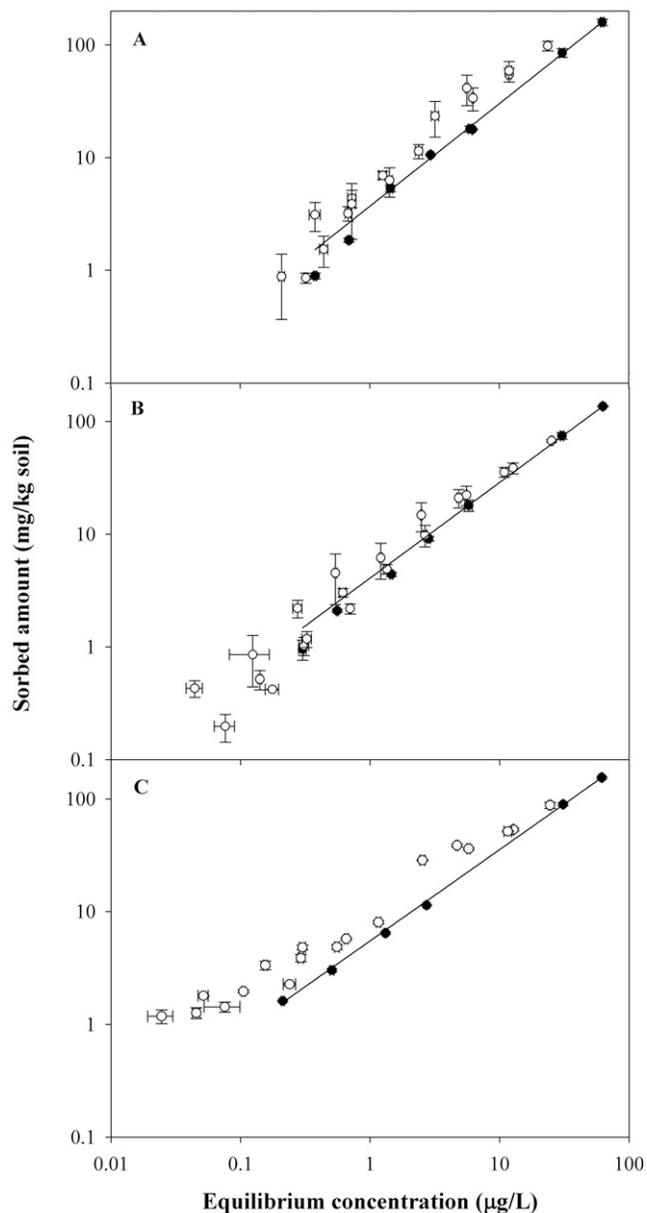


Fig. 2. Sorption–desorption isotherms for carbamazepine with the bulk soil: (A) no dissolved organic matter (DOM) added, (B) co-introduced with DOM, and (C) pre-adsorbed DOM. Sorption and desorption data are represented by filled and open symbols, respectively; fitted lines for the sorption curves are presented.

CBZ, exhibiting linear and nonhysteretic sorption. In general, the mature and humified OM in soil has been found to exhibit a higher affinity for nonpolar organic pollutants than the fresh OM present in the coarser size fractions (Chefetz and Xing, 2009; Sun et al., 2008). Therefore, the OM in the clay fraction is thought to play a major role in the sorption of nonpolar organic pollutants. We studied the behavior of the CBZ molecule (which contains polar functionalities), and therefore polar interactions, such as hydrogen bonding and  $\pi$ - $\pi$  interactions, might be significant to the overall sorption interactions. Thus, unlike hydrophobic organic pollutants, CBZ might exhibit higher affinity to polar SOM in the coarser size fractions of the soil, facilitating binding by polar interactions. This is in contrast to other studies that concluded that sorption of CBZ to soils is controlled mainly by the quantity of SOM,

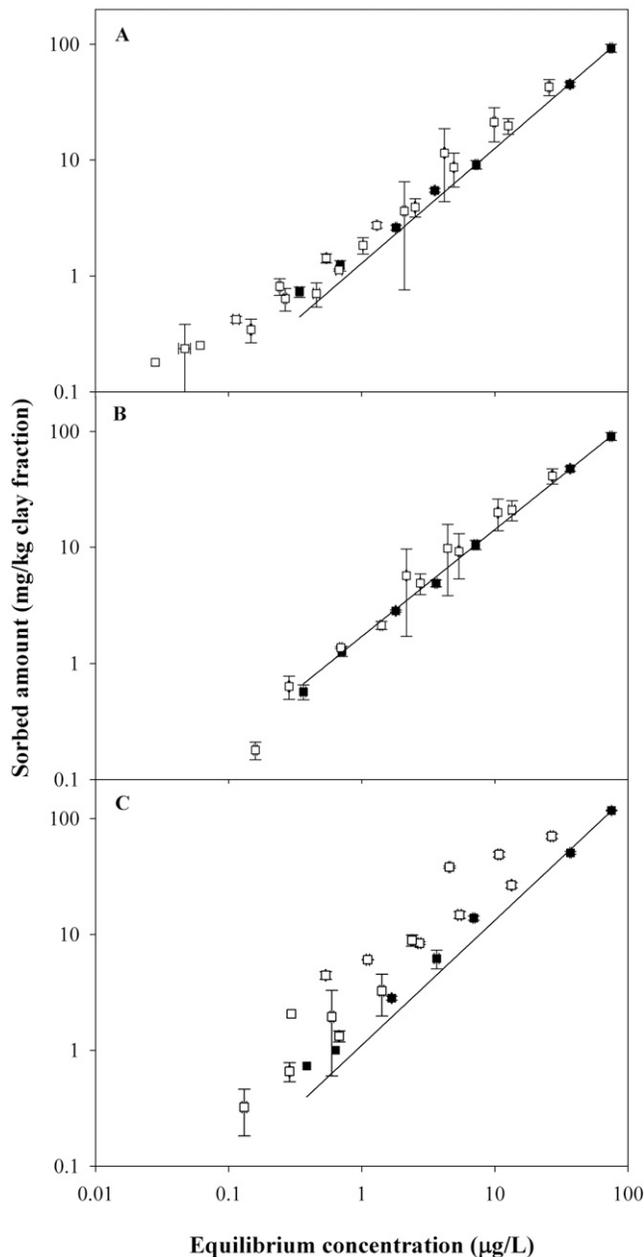


Fig. 3. Sorption–desorption isotherms for carbamazepine with the clay size fraction: (A) no dissolved organic matter (DOM) added, (B) co-introduced with DOM, and (C) pre-adsorbed DOM. Sorption and desorption data are represented by filled and open symbols, respectively; fitted lines for the sorption curves are presented.

and less by its quality, and that nonspecific interactions are the dominant sorption interaction (Chefetz et al., 2008; Scheytt et al., 2005; Stein et al., 2008). We hypothesize that specific and polar interactions of CBZ are highly important and, therefore, control its fate in the environment.

### Effect of Dissolved Organic Matter on Sorption and Desorption Behavior of Carbamazepine

Co-introduction of CBZ and external DOM did not significantly affect the sorption curves of CBZ to the soil or clay fraction (Fig. 2B and 3B and Table 2). In contrast, other studies have shown a pronounced effect of DOM on the sorption of organic compounds with properties similar to CBZ. For

**Table 2. Sorption parameters of carbamazepine with the bulk soil and the clay size fraction ( $\pm$  SE).**

Sample	Freundlich			$K_d$			$K_{oc}$		
	$K_f$	$N$	$R^2$	$0.5 \mu\text{g L}^{-1}$	$5 \mu\text{g L}^{-1}$	$50 \mu\text{g L}^{-1}$	$0.5 \mu\text{g L}^{-1}$	$5 \mu\text{g L}^{-1}$	$50 \mu\text{g L}^{-1}$
Soil									
No DOM† added	4.03 $\pm$ 0.70	0.89 $\pm$ 0.04	0.990	4.36 $\pm$ 0.77	3.37 $\pm$ 0.63	2.60 $\pm$ 0.64	419.4 $\pm$ 75.8	324.1 $\pm$ 62.1	250.5 $\pm$ 62.0
Co-introduction with DOM	4.10 $\pm$ 0.35	0.85 $\pm$ 0.02	0.997	4.55 $\pm$ 0.39	3.20 $\pm$ 0.29	2.25 $\pm$ 0.27	438.5 $\pm$ 41.1	308.3 $\pm$ 30.4	216.8 $\pm$ 27.1
Pre-adsorbed DOM	5.52 $\pm$ 0.42	0.81 $\pm$ 0.02	0.999	6.30 $\pm$ 0.49	4.06 $\pm$ 0.34	2.61 $\pm$ 0.28	607.0 $\pm$ 52.1	390.8 $\pm$ 35.3	251.6 $\pm$ 28.7
Clay fraction									
No DOM added	1.32 $\pm$ 0.27	0.98 $\pm$ 0.05	0.991	1.34 $\pm$ 0.28	1.29 $\pm$ 0.28	1.24 $\pm$ 0.35	188.1 $\pm$ 39.5	181.2 $\pm$ 40.1	174.5 $\pm$ 49.4
Co-introduction with DOM	1.74 $\pm$ 0.30	0.92 $\pm$ 0.04	0.992	0.84 $\pm$ 0.32	1.52 $\pm$ 0.28	1.26 $\pm$ 0.30	259.0 $\pm$ 45.8	213.9 $\pm$ 40.0	176.6 $\pm$ 42.2
Pre-adsorbed DOM	1.10 $\pm$ 0.23	1.08 $\pm$ 0.05	0.996	1.04 $\pm$ 0.22	1.25 $\pm$ 0.27	1.50 $\pm$ 0.42	146.4 $\pm$ 30.7	175.7 $\pm$ 38.9	210.8 $\pm$ 59.4

† DOM, dissolved organic +matter.

example, Flores-Céspedes et al. (2006) reported that addition of DOM (15–100 mg OC L<sup>-1</sup>) increases the sorption of herbicides, probably due to cumulative sorption; and Barriuso et al. (1992) reported that sorption of atrazine to soil is reduced, possibly due to formation of stable complexes with the DOM in the solution. The insignificance of the effects of DOM on the sorption of CBZ in the current study could be due to negligible interactions of CBZ with the studied DOM in solution (data not shown) and the fact that the bound level of DOM did not significantly increase the level of SOM in the system (following adsorption of DOM, the soil OC level only increased by up to 3.5%). Based on this, we conclude that solution interactions, cosorption, and cumulative sorption are not significant processes in our system. In addition, the DOM molecules probably do not compete with CBZ for sorption sites.

Following pre-adsorption of DOM, an increase in  $K_d$  values was observed only for the bulk soil (Fig. 2C). This increase was considerably higher than the increase in OM content, and probably resulted from a qualitative change in OM properties following the adsorption of DOM (Drori et al., 2005). Gao et al. (2007) suggested that binding of DOM to soil might occur through hydrophobic regions of the macromolecules, while the more hydrophilic and ionizable groups are oriented toward the solution. As a result, the soil–water interfaces become more hydrophilic and thus facilitate polar interactions with CBZ. Following pre-adsorption of DOM to the soil, a decrease in sorption linearity was observed ( $N$  decreased from 0.89 to 0.81). This finding, along with the observed increase in sorption affinity for this treatment, further suggests a putative surface modification following DOM sorption that facilitates sorption via specific interactions.

Another interesting observation was that following pre-adsorption of DOM, desorption hysteresis of CBZ was significantly increased for both sorbents. For the clay fraction, the HI value decreased from 0.91  $\pm$  0.05 to 0.52  $\pm$  0.05. For the bulk soil, the degree of hysteresis exhibited a concentration-dependent profile: HI values were 0.16, 0.28, 0.39, 0.50, 0.57, and 0.69 for the increasing initial concentrations (0.5–100  $\mu\text{g L}^{-1}$ ), while the HI of the bulk soil was 0.64  $\pm$  0.04. As previously stated, in the current work, CBZ and DOM did not compete for the same sorption sites and DOM–CBZ complexes did not form in solution. Therefore, we hypothesize that the increased hysteresis following adsorption of DOM was caused by either strong chemical interactions between CBZ and the adsorbed DOM or by physical encapsulation of CBZ in DOM–clay

complexes. Recently, Maoz and Chefetz (2010) reported that CBZ has significantly different affinities to different structural fractions of DOM. Therefore, it is possible that during the sorption process of DOM to the soil, the DOM fractions that are able to specifically bind CBZ were preferentially sorbed. These fractions are probably the hydrophobic acid and hydrophilic acid fractions which are rich in polar functionalities. Thus, when adsorbed they can facilitate specific interactions (such as multiple H-bonding) of the solid phase with CBZ. Moreover, adsorption of DOM to the solid surface might change it to more rigid conformation. These changes might contribute to the formation of specific sorption interactions, and therefore to increase sorption nonlinearity and hysteretic behavior. All of these processes probably facilitated specific interactions between CBZ and the solid phase via adsorption of DOM, which in turn reduced the desorption ability of the sorbed CBZ.

## Conclusions

Our data suggest that CBZ behavior in soils is influenced not only by the content of SOM, but also by its properties. We suggest that the coarser fractions of the SOM are more important as binding domains for CBZ, and probably for other polar PCs, which are introduced into soils via irrigation with reclaimed wastewater. Due to the polar nature of the PCs, the effect of DOM on the adsorption by soils is lower than that observed for highly hydrophobic pollutants. However, DOM may facilitate stronger interactions of polar PCs with the solid surface, thereby reducing their desorption ability. In deeper soil horizons (subsoils) with low SOM content and high sorption potential for DOM, the addition of external DOM (from the application of biosolids and/or irrigation with reclaimed wastewater) might have a more pronounced effect on both CBZ sorption and desorption.

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