

Sorption and degradation of wastewater-associated pharmaceuticals and personal care products in agricultural soils and sediment

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ABSTRACT

Pharmaceuticals and personal care products (PPCPs) have drawn popular concerns recently as an emerging class of aquatic contaminants. In this study, adsorption and degradation of four selected PPCPs, metronidazole, tinidazole, caffeine and chloramphenicol, have been investigated in the laboratory using two agricultural soils in China and sediment from Changjiang River. Adsorption tests using a batch equilibrium method demonstrated that adsorption of all tested chemicals in soils could be well described with Freundlich equation, and their adsorption affinity on soil followed the order of chloramphenicol > caffeine > tinidazole > metronidazole. Generally, higher K_f value was associated with soils which had higher organic matter contents (except for caffeine acid in this study). Degradation of selected PPCPs in soils generally followed first-order exponential decay kinetics, and half-lives ranging from 0.97 to 10.21 d. Sterilization generally decreased the degradation rates, indicating that microbial activity played a significant role in the degradation in soils. The degradation rate constant decreased with increasing initial chemical concentrations in soil, implying that the microbial activity was inhibited with high chemical loading levels.

Key words | agricultural soil, degradation, pharmaceuticals and personal care products (PPCPs), reclaimed water, sediment, sorption

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INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) have recently received much attention as organic micro-pollutants in aquatic environments (Kolpin *et al.* 2002). A wide range of PPCPs have been detected in a variety of environmental samples such as river water and drinking water at levels ranging from ng/L up to g/L (Yu *et al.* 2006; Serrano *et al.* 2010). Many of the PPCPs do not fully degrade during municipal wastewater treatment (Ellis 2006; Al-Rifai *et al.* 2007; Serrano *et al.* 2010).

Effluents from wastewater treatment plants have been extensively used in many regions of the world, including agricultural and landscape irrigation, groundwater recharge to overdrawn aquifers, etc. (Miller 2006). The contaminants of effluents, although at low level, will probably accumulate in the soils if long-term irrigation occurs, which may result in environmental problems such as the contamination risk to groundwater (Xu *et al.* 2009a, b). In this respect, understanding PPCP sorption and degradation behavior in

agricultural soils and sediment is important for assessing their environmental risks.

PPCPs comprise a large group of compounds. Their behavior is often controlled by interactions with specific functional groups or complicated pH-dependent speciation, therefore their adsorption behaviors have their own characteristics among different compounds and are difficult to predict (Kibbey *et al.* 2007). Their degradation research was mainly carried out in aqueous environments, such as biological degradation, photo degradation (Lin & Reinhard 2005; Yu *et al.* 2006), and in sewage sludge (Serrano *et al.* 2010), or in sediments (Ying & Kookana 2003). But few studies focus on agricultural soils (Xuan *et al.* 2008).

As the key process, sorption is controlling the fate of PPCPs because of their low solubility in water (Zhang *et al.* 2010). Sorption and degradation are processes expected to play a key role in the downward movement of PPCPs in soil that receives treated wastewater via irrigation or

groundwater recharge. This study is timely, because sorption of PPCPs has not been well investigated in sediments and agricultural soils.

In this study, four PPCPs (metronidazole, tinidazole, chloramphenicol as most commonly used antibiotics and caffeine as central nervous system stimulant) were selected to examine sorptive and degradation properties in two agricultural soils in China and Changjiang River sediment (CRS). Because of their toxic properties, to study the fate of them will be necessary. The primary objective of this study was therefore to investigate the equilibrium sorption behavior of PPCPs in sediments from the Changjiang River and the effect of irrigation-water quality (freshwater versus secondary-treated wastewater; STWW) on the environmental behaviors (mobility versus accumulation) of PPCPs in soils continuously irrigated with STWW. As a function of soil types, degradation and adsorption are also considered here. We tried to find out the correlations between the adsorption/degradation and soil properties.

EXPERIMENTAL PROCEDURES

Chemicals and soils

Metronidazole (>98%), tinidazole (>98%), caffeine (>98%) and chloramphenicol (>98%) were purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Acetone and ethyl acetate were purchased from Fisher (Fair Lawn, NJ, USA). Anhydrous sodium sulfate (Fisher) was analytical grade. It was baked at 400 °C for 4 h and stored in a sealed container. Deionized water was prepared with a Milli-Q water purification system. Stock solutions (200 mg L⁻¹) of the reference compounds were prepared in methanol and stored at -20 °C. A suite of working solutions containing all pharmaceuticals at 5.0, 10, 25, 50 and 100 mg L⁻¹ each was prepared by appropriate dilutions of the stock solutions in methanol.

CRS and two agricultural soils, Wuhan silt loam (WSL) and Jilin loamy sand soil (JLS), were selected as the experimental media. The surface sediment samples were collected from the river bank in Wuhan (WH, 30°59'7"N, 114°32'8"E) in April 2011. Agricultural soil samples were collected from the 0 to 20 cm surface layer and air-dried. The dry materials passed through a 2 mm sieve to remove the large particles and were then homogenized by grinding. Particle size analysis was determined by the hydrometer method (Gee & Bauder 1986) and organic matter (OM)

content by the 450 °C combustion method (Davies 1974). Soil pH values in 0.005 M CaCl₂ with soil to solution ratio of 1:1 were determined with a pH meter. Organic carbon (OC) were determined with potassium dichromate oxidation spectrophotometry. Their mechanical composition and basic chemical properties are presented in Table 1.

Adsorption study

Sorption of the selected pharmaceuticals in the soils was measured using a batch equilibrium method at room temperature (25 ± 2 °C). Briefly, 5.0 g soil (dry weight equivalent) were weighed into 50 mL Teflon centrifuge tubes and 9 mL of 0.01 M CaCl₂ solution. The soil samples were spiked with 1 mL working solutions to yield initial nominal concentrations of 0.5, 1.0, 2.5, 5.0, and 10 mg L⁻¹ for each compound in the aqueous phase. Sodium azide (5 mg) was added into each sample to suppress microbial activity during the equilibration. The sample tubes were closed with Teflon-lined caps, and continuously mixed by shaking and equilibrated for 24 h at room temperature (25 ± 2 °C). After shaking, the tubes were centrifuged for 10 min at 5,000 g, and the supernatant was removed by pipetting. An aliquot of the supernatant was passed through a Whatman 0.45 μm fiber microfilter and 1.0 mL of the filtrate was directly subjected to analysis with a high-performance liquid chromatograph (HPLC) (Dionex Summit U3000) to obtain the aqueous phase C_w (mg L⁻¹). The concentrations of adsorbed PPCPs, C_s (mg kg⁻¹), were calculated from the measured solution phase concentrations based on mass balance. Duplicate samples were performed for adsorption experiments.

Degradation experiments

In the laboratory experiments, 10 g of soil were weighed into a 50 mL screw capped Teflon centrifuge tube. The concentration of individual PPCPs applied to soils was 100 μg kg⁻¹ by adding into each vessel 100 μL of the mixed stock solution with a concentration of 10 mg L⁻¹

Table 1 | Textural and chemical properties of soils

Soil	Sand (%)	Silt (%)	Clay (%)	OM ^a (%)	pH	OC ^b (%)
CRS	40.7	44.5	6.0	5.58	7.80	3.22
WSL	38.7	50.2	1.2	6.23	7.92	3.67
JLS	69.6	25.6	0.4	4.91	7.85	2.89

^aOM = organic matter content, %.

^bOC = organic carbon content, %.

for each compound. The soil water content was maintained at 70% of maximum water-holding capacity by adding a given amount of deionized water. Centrifuge tubes were weighed, and water was added every other day for evaporation loss if necessary.

Other treatment experiments, including sterilization and higher initial PPCP concentration in soil were conducted only on WSL soil. Sterilization was achieved by autoclaving WSL soil at 120 °C for 45 min three times in consecutive 3 d. Higher initial soil concentration of 1,000 $\mu\text{g kg}^{-1}$ was used by adding each vessel 100 μL of the mixed stock solution to WSL soil with a concentration of 100 mg L^{-1} for each compound.

The treated samples were incubated in a dark and airy cabinet at room temperature (25 ± 2 °C). Concentrations of all PPCPs were monitored on day 0, 1, 2, 3, 4, 6, 8, 10, 12, 15 and 20. All experiments were performed in triplicate.

Extraction and analysis

Determination of selected PPCPs in soils was carried out according to the procedures described by Xu *et al.* (2009a). Briefly, 10 mL of methanol was added into 50 mL Teflon centrifuge tube containing soil samples. The tube was ultrasonicated for 15 min, centrifuged at 5,000 g for 10 min, and decanted the supernatant. The soils were extracted three more times. The supernatants were combined and nitrogen-evaporated in a water bath at 40 °C to 0.5 mL. After passing through a Whatman 0.45 μm fiber microfilter, the samples were analyzed with HPLC.

Initial and residual concentrations of target chemicals were analyzed by a Dionex Summit U3000 HPLC system equipped with a manual injector and a Photodiode Array Detector (PAD) (Dionex Technologies, USA). An amethyst-C18 column (4.6 mm \times 250 mm, 5 μm) from Sepax Technologies Inc. (Newark, USA) was connected with a guard column (cartridge 2.1 mm \times 12.5 mm, 5 μm , Agilent Technologies, Palo Alto, CA, USA) filled with the same packing material. Methanol/water (35:65 v/v; flow rate = 1.0 mL min^{-1}) was used for metronidazole, tinidazole and caffeine analysis. For chloramphenicol determinations, the mobile phase was 65:35 methanol/water (isocratic; flow rate = 1.0 mL min^{-1}). The UV detector was set at a wavelength of 320 nm for metronidazole and tinidazole analytes, and 270 nm for caffeine and chloramphenicol analytes. The limits of quantification (LOQ) of the method were 20.0 $\mu\text{g kg}^{-1}$ for metronidazole, tinidazole; 19.2 $\mu\text{g kg}^{-1}$ for caffeine, and 45.0 $\mu\text{g kg}^{-1}$ for chloramphenicol. The recoveries of metronidazole, tinidazole, caffeine and

chloramphenicol from soils were 98.9, 73.9, 63.7 and 84.3%, respectively.

Data analysis

For degradation experiments, the degradation rate constant k was calculated by the exponential decay model: $C = C_0 e^{-kt}$. Half lives ($t_{1/2}$) were calculated by the equation: $t_{1/2} = 0.693/k$. For the adsorption data, the C_w versus C_s were fitted to Freundlich equation $C_s = K_f C_w^n$ estimate K_f and n . The organic carbon adsorption coefficient K_{OC} values were calculated by the equation: $K_{OC} = K_d / f_{OC}$, where $K_d (=C_s/C_w)$ values were shown as the ranges within the tested concentrations for all measured data. Software Origin 8.0 was used for all model fitting in this study.

RESULTS AND DISCUSSION

Adsorption

In this study, control experiments were carried out and the results verified that concentration of compounds reduction were due to adsorption.

Figure 1 shows the adsorption isotherms of selected PPCPs in CRS and two agricultural soils. For four PPCPs, their adsorptions could be well described with the Freundlich equation over the range of equilibrium concentrations, with the correlation coefficient R^2 over 0.96 (Table 2). The individual Freundlich adsorption coefficients K_f which reflect the adsorption affinity on soils are listed in Table 2. It is evident from Figure 1 that sorption of the selected compounds was dependent on the types of pharmaceuticals and soil. Moreover, in general, the silt loam soil (WSL) had the greatest sorption capacity for all test compounds, while the JLS had the lowest sorption capacity. The K_f values of the selected PPCPs (except for caffeine) in soils had the order as follows: WSL > CRS > JLS. In soils, usually, the higher OM content (except for caffeine acid in this study) got the higher K_f values, which is consistent with the results from Pantelelis *et al.* (2006) and Xu *et al.* (2009b). They both studied adsorption properties of compounds with different structures in different soils.

K_d was calculated for the tested PPCPs in the three soils for comparison purposes. Sorption coefficients on different soils and sediments showed that metronidazole had the lowest K_d values, with an average of 1.74 L kg^{-1} , which

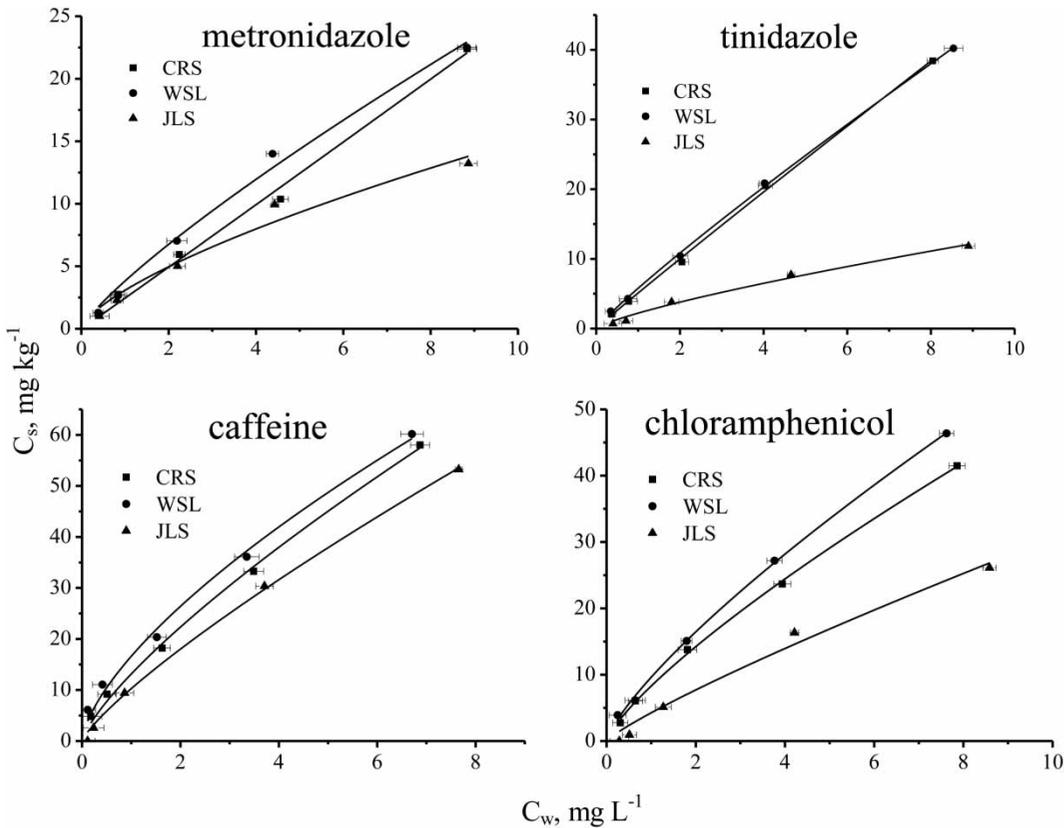


Figure 1 | Adsorption isotherms of four selected PPCPs in two soils and one sediment ($25 \pm 2^\circ\text{C}$). Initial solute concentrations ranged from 0 to 10 mg L^{-1} . Lines are fitted to the Freundlich equation weighted on $1/C_s$.

Table 2 | Adsorption coefficients of selected PPCPs in two agricultural soils and one sediment. K_f and n are Freundlich affinity coefficient and Freundlich linearity index, respectively. The K_d was calculated with all measured data points and shown as average values

Metronidazole						Tinidazole				
	$K_f, \text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$	n	R^2	$K_d, \text{L kg}^{-1}$	$\log K_{oc}$	$K_f, \text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$	n	R^2	$K_d, \text{L kg}^{-1}$	$\log K_{oc}$
CRS	3.15	0.77	0.9886	1.82	1.75	5.11	0.97	0.9884	4.78	2.17
WSL	3.82	0.82	0.9898	2.53	1.84	5.79	0.91	0.9921	4.63	2.10
JLS	1.33	0.84	0.9693	0.86	1.47	2.22	0.78	0.9873	1.31	1.66
Caffeine						Chloramphenicol				
	$K_f, \text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$	n	R^2	$K_d, \text{L kg}^{-1}$	$\log K_{oc}$	$K_f, \text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$	n	R^2	$K_d, \text{L kg}^{-1}$	$\log K_{oc}$
CRS	16.60	0.67	0.9899	5.01	2.19	8.28	0.78	0.9987	7.84	2.39
WSL	10.27	0.81	0.9973	5.78	2.20	9.61	0.78	0.9889	8.05	2.34
JLS	13.13	0.77	0.9961	3.17	2.04	4.25	0.86	0.9792	6.94	2.38

was similar to the result from Rabølle & Henrik (2000), where they obtained the K_d value of 0.60 L kg^{-1} for metronidazole on three different soils. Chloramphenicol had the highest K_d , with an average of 7.61 L kg^{-1} . The average K_d

of tinidazole and caffeine on the soils and sediments were 3.57 and 4.65 L kg^{-1} , respectively.

From the K_d data in Table 2 and soil property data in Table 1, we conducted the regression analysis between K_d

and soil properties, and concluded that K_d values of tested chemicals were positively correlated with soil OM contents, with correlation coefficients R^2 ranging from 0.7243 to 0.9954. Previous study also found that the adsorption coefficient for a non-steroidal anti-inflammatory drug, ketoprofen, showed a positive correlation with the OM contents in the soils (Xu *et al.* 2009b). The results are supportive of OM content playing a significant role in sorption of the test compounds.

As indicated above, the adsorption coefficients for some compounds increased with the OM contents in the soils, while in some other cases, adsorption behavior is dependent on soil clay contents (Chen *et al.* 2006). In this study, no evident relevance was found between the adsorption coefficients and soil clay contents, which suggested that inorganic soil matrix (clays) may not play a major role in the sorption of these four pharmaceuticals but surface charges may play important role.

Normalizing the adsorption coefficient K_d to the fraction of OC of the soils yields K_{OC} , and their logarithm forms were shown in Table 2. The log K_{OC} values for tested PPCPs on

average ranged from 1.69 for metronidazole to 2.37 for chloramphenicol. The adsorption affinity of the four PPCPs on soil was in the following order: chloramphenicol > caffeine > tinidazole > metronidazole. A chemical with strong sorption is usually less mobile in soil and has a limited leaching potential. The lack of appreciable sorption for four tested PPCPs implies a likely high mobility for these compounds in soil and hence a potential risk for groundwater contamination when treated wastewater is applied as irrigation water and used for groundwater recharge.

Degradation

Upon the control experiments of 15 d in the meantime, the four selected pharmaceuticals showed the decay by hydrolytic or thermal means was negligible during the degradation experiments.

The dissipation of the selected pharmaceuticals in the soils and sediment over time is plotted in Figure 2. Curves in Figure 2 represent the fit of the experimental data to the exponential decay model ($C_t = C_0 e^{-kt}$)

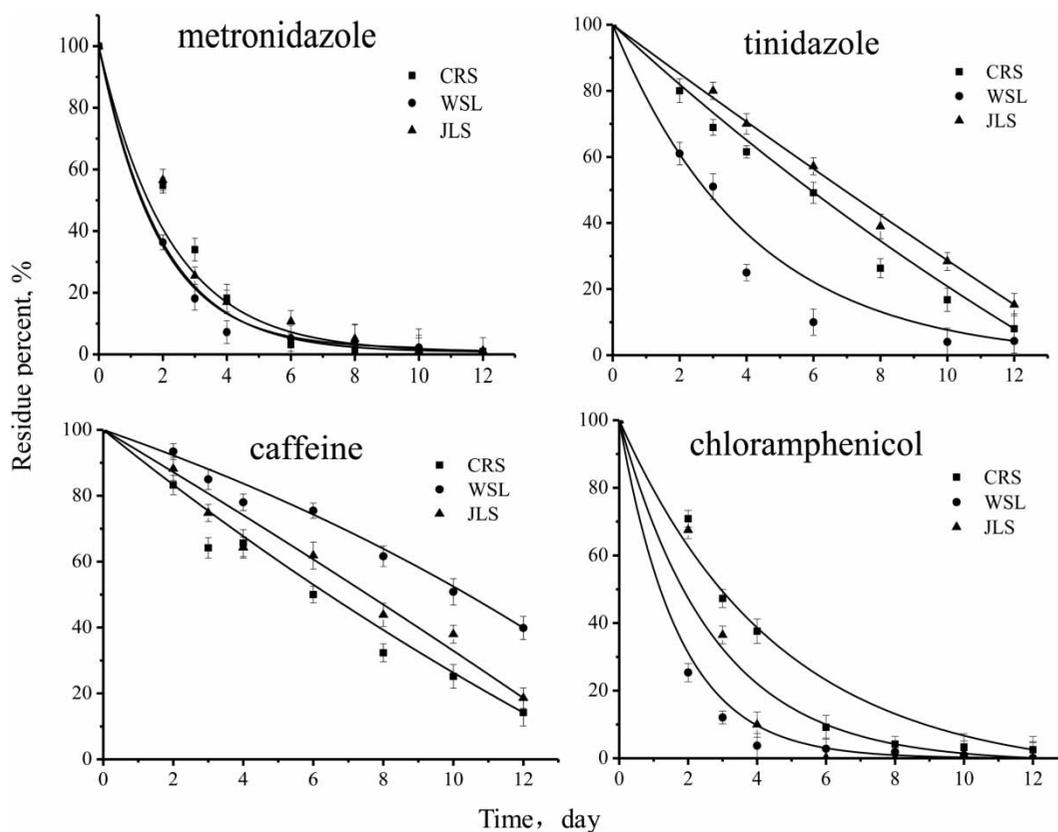


Figure 2 | Degradation curves of four PPCPs in two soils and one sediment. Experiments were conducted at 25 ± 2 °C and lasted for 20 d, with moisture content at 70% of the soils' water holding the capacity. Lines are fitted to the first-order decay model.

for those treatments that the regression was successful ($R^2 > 0.95$), suggesting that the degradation of selected PPCPs in agricultural soils could be well described with first-order exponential decay model. The corresponding values of degradation rate constant k (d^{-1}) and half-life $t_{1/2}$ (d) are listed in Table 3.

All four PPCPs in the agricultural soils and sediments exhibited low to moderate persistence, with half-lives ranging from 0.97 to 10.21 d (Table 3). Within 15 d after treatment in this study, all four tested PPCPs were degraded more than 60% in soils. For some pharmaceuticals, they undertook very fast degradation processes, showing low persistence in soils.

To the best of our knowledge, no literature data on the degradation of these PPCPs in agricultural soils and sediments are available. Results from present study showed that degradation behaviors of selected PPCPs differed with compound and soil. As can be seen from Table 3, metronidazole and chloramphenicol were amenable to degradation, with half-lives ranging from 1.25 to 1.92 and 0.97 to 2.79 d, respectively, while the longest half lives of tinidazole and caffeine in soils were up to 6.84 and 10.21 d, respectively. For metronidazole and chloramphenicol, the degradation rate constants in three soils followed the order: WSL > JLS > CRS. For tinidazole, the descending order was WSL > CRS > JLS. For caffeine, the order of CRS > JLS > WSL was observed. The different degradation rates of tested compounds in the different soils may be attributed to two reasons. First, different soils may have different

indigenous microbial populations, as seasonal and spatial variations could influence the microbial populations and activities in solid matrix (Lin *et al.* 2008; Xu *et al.* 2009a). On the other hand, the physicochemical characteristics of soils may also have contributed to the difference in PPCP degradation. For example, regression of the degradation rate constants k with soil properties showed that except for caffeine, degradation rate constants were positively correlated with soil OM content (R^2 ranging from 0.57 to 0.83). Previous studies have shown that soil OM may serve as an alternative nutrition source for the microorganisms involved in the degradation (Alvey & Crowley 1995). The negative correlation coefficients of caffeine between k and OM contents, could be due to the fact that high soil OM content may increase adsorption of the chemical and reduce bioavailability, thus inhibit the organic compounds degradation (Topp *et al.* 2006; Xu *et al.* 2009b).

Biodegradation is a significant factor in the removal of PPCPs from environments (Xu *et al.* 2009b). The comparative experiments conducted in the WSL soil showed that the sterilization treatment resulted in a decrease in the degradation rates of PPCPs (Table 4). Using metronidazole as an example, after incubation for 7 d, almost all metronidazole was degraded in non-sterile WSL soil, while in the sterilized treatment, only 22% of the initial concentration disappeared.

For all selected PPCPs, pronounced differences were observed between non-sterile and sterilized treatments. Degradation rates of metronidazole, tinidazole, caffeine

Table 3 | First-order degradation rate constants and correlation coefficients of PPCPs in three soils (spiking level is $100 \mu\text{g kg}^{-1}$)

	Metronidazole			Tinidazole			Caffeine			Chloramphenicol		
	k, d^{-1}	$t_{1/2}, \text{d}$	R^2									
CRS	0.3609	1.92	0.9830	0.1297	5.35	0.9922	0.1220	5.68	0.9819	0.2479	2.79	0.9645
WSL	0.5561	1.25	0.9929	0.2800	2.47	0.9632	0.0679	10.21	0.9843	0.7028	0.97	0.9986
JLS	0.3761	1.84	0.9737	0.1014	6.84	0.9958	0.0965	7.18	0.9679	0.3374	2.05	0.9231

Table 4 | First-order degradation rate constants and correlation coefficients of PPCPs in WSL soil with different treatments and different concentrations

	$100 \mu\text{g kg}^{-1}$			$100 \mu\text{g kg}^{-1}, \text{sterile}$			$1,000 \mu\text{g kg}^{-1}$		
	k, d^{-1}	$t_{1/2}, \text{d}$	R^2	k, d^{-1}	$t_{1/2}, \text{d}$	R^2	k, d^{-1}	$t_{1/2}, \text{d}$	R^2
Metronidazole	0.5561	1.25	0.9929	0.0352	19.66	0.9722	0.1231	5.63	0.9758
Tinidazole	0.2800	2.47	0.9632	0.0243	28.50	0.9631	0.1088	6.37	0.9822
Caffeine	0.0679	10.21	0.9843	0.0153	45.20	0.9564	0.0354	19.56	0.9230
Chloramphenicol	0.7028	0.97	0.9986	0.0477	14.52	0.9856	0.1889	3.67	0.6000

and chloramphenicol in non-sterile soil were 15.7-, 11.52-, 4.44- and 14.7-fold faster than in the sterilized WSL soil. The inhibition by sterilization suggested that microbial transformations contributed to the most degradation of PPCPs in the agricultural soils. From Table 4 we also found that increasing initial soil concentrations of tested compounds from 100 to 1,000 $\mu\text{g kg}^{-1}$ reduced the degradation rates, which is in agreement with the results by other researchers (Gan *et al.* 1996; Fogg *et al.* 2003). This increased persistence has been generally attributed to the inhibited activity of the degrading microorganisms.

Results from the present study may provide information on the likelihood for pharmaceuticals to reach groundwater due to irrigation or groundwater recharge with treated wastewater, and then can help to assess the environmental risks of PPCPs.

CONCLUSIONS

The results of the present study suggest that introduction of effluent-derived PPCPs into agricultural soils may cause potential soil pollution and thereby groundwater contamination, depending on soil type and chemical structures. Both metronidazole and chloramphenicol exhibit relatively high degradation potential in the surface soil, although they exhibited poor sorption in the soils and therefore have lower potential to reach the groundwater in areas irrigated with reclaimed wastewater. Nevertheless, the fact that caffeine and tinidazole exhibited slower degradation and poor sorption in the soils and sediments suggests that they can potentially be transported to the groundwater in fields irrigated with reclaimed wastewater, leading to an enhanced risk for groundwater contamination. From the view of persistence, soil properties were shown to correlate with the selected PPCP degradation in present study. The adsorption coefficient of select pharmaceuticals was in a positive correlation with the OM contents in the soils. High initial soil concentrations also showed inhibitory effect on the PPCP degradation. Additional studies, including lysimeter experiments and field monitoring experiments, should be considered in the future to better address such implied risks.

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