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Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils

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ABSTRACT

Pharmaceuticals and personal care products (PPCPs) are emerging contaminants in the environment, which have drawn popular concerns recently. Most studies on the environmental fate of PPCPs have focused on their behaviors during wastewater treatment processes, in aquatic environments, and in the sludge, however, little is known about their behavior in agricultural soils. In this study, adsorption and degradation of six selected PPCPs, including clofibric acid, ibuprofen, naproxen, triclosan, diclofenac and bisphenol A have been investigated in the laboratory using four US agricultural soils associated with reclaimed wastewater reuse. Adsorption test 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 triclosan > bisphenol A > clofibric acid > naproxen > diclofenac > ibuprofen. Retardation factor (R_F) suggested that ibuprofen had potential to move downward with percolating water, while triclosan and bisphenol A were readily retarded in soils. Degradation of selected PPCPs in soils generally followed first-order exponential decay kinetics, with half-lives ranging from 0.81 to 20.44 d. Degradation of PPCPs in soils appeared to be influenced by the soil organic matter and clay contents. Sterilization generally decreased the degradation rates, indicating 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.

1. Introduction

Effluents from wastewater treatment plants have been extensively employed for various purposes in many regions of the world, including agricultural and landscape irrigation, groundwater recharge to overdrawn aquifers, etc. (Pedersen et al., 2003; Levine and Asano, 2004; Miller, 2006). In 2006, an estimated $9.8 \times 10^6\ m^3\ d^{-1}$ of treated municipal wastewater (approximately 7–8% of the total generated) was reused in the United States (Miller, 2006). Many locations throughout the United States, including California, Florida, Colorado, and Arizona, have used reclaimed water to satisfy the demand for irrigation water to a relatively high extent. When enjoying the benefits of treated wastewater reuse, however, people have to face the adverse effects resulted from the effluent-derived organic contaminants. Some emerging organic contaminants, such as pharmaceuticals and personal care products (PPCPs) are reported present in the effluents (Kolpin et al., 2002; Wang et al., 2005; Loraine and Pettigrove, 2006). These contaminants, albeit at trace levels in the effluents, will probably accumulate in the soils if long-term irrigation occurs, which may result in environmental problems such as the contamination risk to groundwater (Kinney et al., 2006; Ternes et al., 2007; Xu et al., 2009a,b). In this respect, it necessitates the investigation on the fate, especially the persistence and adsorption capacity of these trace wastewater-borne contaminants in agricultural soils receiving reclaimed wastewater irrigation.

PPCPs consist of a wide range of compounds. Their adsorption behaviors vary from compound to compound, and are difficult to predict because their behavior is often controlled by interactions with specific functional groups or complicated pH-dependent speciation (Kibbey et al., 2007). Their degradation studies were mainly carried out in aqueous environments (for example biological degradation, photo degradation) (Richardson and Bowron, 1985; Buser et al., 1998; Zwiener and Frimmel, 2003; Lin and Reinhard, 2005; Yu et al., 2006), in sewage sludge (Kimura et al., 2007; Zhao et al., 2008), or in sediments (Ying and Kookana, 2003a). Few researches were conducted in agricultural soils (Ying and Kookana, 2005; Williams et al., 2006; Xuan et al., 2008). This study examines

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sorptive and degradation properties of six selected PPCPs, namely clofibric acid, ibuprofen, naproxen, triclosan, diclofenac and bisphenol A in four US agricultural soils with various physicochemical characteristics. The selected PPCPs were detected in agricultural runoff samples with reclaimed wastewater irrigation (Xu et al., 2009c), and in reclaimed wastewater irrigated turf grass field (Xu et al., 2009a), suggesting their introduction from sewage to soils. Degradation and adsorption as a function of soil types is also considered here, trying to find out the correlations between the adsorption/degradation and soil properties. Furthermore, the mechanism of degradation was investigated through comparative experiments using sterilized and nonsterile soils. Results from the present study can help to assess the environmental risks of PPCPs associated with reclaimed wastewater irrigation in agricultural soils.

2. Materials and methods

2.1. Chemicals and soils

Ibuprofen (99% of purity) was purchased from Acros Organics (Morris Plains, NJ, USA). Clofibric acid (>99% of purity), naproxen (>98% of purity), and diclofenac sodium salt (>98% of purity) were purchased from MP Biomedicals (Solon, OH, USA). Bisphenol A (>99% of purity), triclosan (>97% of purity), and the derivatizing reagent, *N*-tert-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Stock solutions of the reference compounds were prepared in ethyl acetate and stored at −20 °C. Acetone, ethyl acetate and dichloromethane (pesticide grade) 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. De-ionized water was prepared with a Milli-Q water purification system.

Four agricultural soils, Hanford loamy sand (HLS, mixed, superactive, nonacid, thermic Typic Xerorthents), Arlington sandy loam (ASL, mixed, thermic Haplic Durixeralfs), Imperial silty clay (ISC, semectitic, calcareous, hyperthermic Typic Torrifluvents), and Palouse silt loam (PSL, mixed, superactive, mesic Pachic Haploxerolls) were selected as the experimental media. Soil samples were collected from the 0 to 20 cm surface layer, air-dried, and ground to pass through a sieve with 2-mm openings. Particle size analysis was determined by the hydrometer method (Gee and Bauder, 1986) and organic matter (OM) content by the 450 °C combustion method (Davies, 1974). Soil pH values in 0.005 M $CaCl_2$ with soil to solution ratio of 1:1 were determined with a pH meter. Their mechanical composition and basic chemical properties are presented in Table 1.

Table 1
Textural and chemical properties of the four test soils.

Soil	Clay (%)	Sand (%)	Silt (%)	OM (%)	pH	f_{oc} (%)
HLS	3.6	95.6	0.8	0.58	7.54	0.44
ASL	12.5	70.9	16.6	1.93	7.06	0.55
ISC	42.5	10.8	46.7	2.46	7.48	1.43
PSL	18.1	32.2	49.7	5.45	7.14	3.16

2.2. Degradation study

In the laboratory experiments, five grams of soil were weighed into a 50-mL screw capped Teflon centrifuge tube. The concentration of individual PPCP applied to soils was 100 $\mu g\ kg^{-1}$ by adding into each vessel 50 μL of the mixed stock solution with a concentration of 10 $mg\ L^{-1}$ for each compound. De-ionized water was added to maintain moisture contents at 70% of the soil's water holding capacity. Centrifuge tubes were weighed, and water was added every other day for evaporation loss if necessary. The tubes were wrapped with aluminum foil to minimize any possible photo degradation. Other treatment experiments, including sterilization and higher initial soil concentration were conducted only on HLS soil. Sterilization was achieved by autoclaving HLS soil at 120 °C under 300 kPa pressure for 45 min three times in consecutive 3 d. Higher initial soil concentration of 1000 $\mu g\ kg^{-1}$ was used by adding into each vessel 50 μL of the mixed stock solution with a concentration of 100 $mg\ L^{-1}$ for each compound. The incubation temperature for all experiments was kept at 20 ± 2 °C, and concentrations of all PPCPs were monitored on day 0, 1, 3, 5, 8, 12, 16, 23, 30, and 45. All experiments were performed in triplicate.

2.3. Adsorption study

The batch adsorption experiments were performed with sterilized soils to avoid the influence of PPCPs degradation. Five grams (dry wt equivalent) aliquots of soils at the field moisture contents were each mixed with 10 mL of 0.01 M $CaCl_2$ solution containing chemicals at concentrations of 0, 0.5, 1.0, 2.5, 5.0, and 10 $mg\ L^{-1}$ in 50-mL Teflon centrifuge tubes. The soil suspensions were continuously mixed by shaking and equilibrated for 24 h at the room temperature (20 ± 2 °C). This period was selected as a result of a preliminary study showed that the adsorption equilibrium was achieved in 24 h. The contents were then centrifuged at 6708*g* for 10 min to separate the solid and aqueous phases. The decanted supernatants were extracted with dichloromethane. The organic dichloromethane phase was dried over anhydrous Na_2SO_4, concentrated, derivatized with MTBSTFA, and analyzed with gas chromatography–mass selective detector (GC/MSD) to obtain aqueous phase concentration, C_w ($mg\ L^{-1}$). Preliminary experiments showed that the recovery rate of liquid–liquid extraction procedure at least was 86% for the chemicals of concerns. The concentrations of sorbed 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.

2.4. Extraction and analysis

Determination of selected PPCPs in soils was carried out according to the procedures described by Xu et al. (2008). Briefly, 5 mL of acetone–ethyl acetate (1:1, v/v) were added into 50-mL Teflon centrifuge tube containing soil samples. The tube was ultrasonicated for 15 min, centrifuged at 6708*g* for 10 min, and decanted the supernatant. The soil was extracted three more times, and the supernatants were combined and were nitrogen-evaporated in a water bath at 40 °C to approximately 1 mL. The extract was re-dissolved in 500 mL of de-ionized water, and a solid-phase extraction (SPE) procedure was applied. The SPE cartridges were eluted with ethyl acetate, and the extracts were dried over anhydrous sodium sulfate, and reduced to 0.5 mL with a gentle stream of nitrogen at 40 °C, then transferred into the GC vial. Hundred microliter of MTBSTFA was added, and the volume was brought to 1 mL with ethyl acetate. The GC vials were put into GC oven at 70 °C for 60 min for derivatization. The limits of quantification (LOQ) of the method were 0.2 $\mu g\ kg^{-1}$ for ibuprofen, 0.4 $\mu g\ kg^{-1}$ for clofibric acid, naproxen, triclosan, and bisphenol A; and 1.2 $\mu g\ kg^{-1}$ for diclofenac sodium salt. The recoveries of ibuprofen, clofibric acid, naproxen, triclosan, bisphenol A and diclofenac sodium from soils were 103.4%, 63.9%, 110.7%, 95.7%, 104.3%, and 89.1%, respectively (Xu et al., 2008).

Target chemicals were determined using an Agilent 6890N GC with 5975C MSD equipped with an Agilent 7683B automatic liquid sampler and an HP-5MS GC column (30 m, 0.25 mm i.d., 0.25 μm

film thickness). Helium was used as the carrier gas, with a column flow rate of 1.2 mL $\min^{-1}$ in constant-flow mode. Injector temperature was 250 °C. The GC–MSD interface and the ion source temperatures were set at 280 and 230 °C, respectively. The GC oven temperature was kept at 50 °C for 1 min, followed by the first ramp at 20 °C $\min^{-1}$ to 120 °C, second ramp at 10 °C $\min^{-1}$ to 280 °C, and holding for 11 min. The mass spectrometer was operated in the selected ion monitoring (SIM) mode with electron impact ionization voltage of 70 eV. A 2-μL sample was injected in pulsed splitless mode.

2.5. Data analysis

For degradation experiments, data were fitted to the exponential decay model: $C = C_0\, e^{-kt}$ to obtain the degradation rate constant k. 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 $C_s = K_f\, C_w^n$ to 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 SigmaPlot v.10.0 was used for all model fitting in this study.

3. Results and discussion

3.1. Adsorption

Fig. 1 shows the adsorption isotherms of selected PPCPs in four agricultural soils. For all tested PPCPs, their adsorption could be well described with the Freundlich equation over the range of equilibrium concentrations, with the correlation coefficient R^2 ranging from 0.800 to 0.994 (Table 2). The individual Freundlich adsorption coefficients K_f were listed in Table 2. Generally, higher K_f values were associated with soils with higher OM content (except for clofibric acid in this study), which is consistent with the results from Pantelelis et al. (2006) and Xu et al. (2009b). K_f value derived from Freundlich equation reflects the adsorption affinity on soils, however, the K_f parameters cannot be compared among samples where the nonlinearity factors, n, are different (Chen et al., 1999). K_d was calculated for the tested PPCPs in the four soils for comparison purposes. Due to the fact that most n values derived from Freundlich equations were not close to 1, which meant the nonlinearity of adsorption isotherms, K_d values could not be attained by fitting adsorption data to the linear equation. Here K_d values were calculated with all measured data within tested concentrations, and the average of all individual points were displayed. Sorption coefficients on four different soils showed that ibuprofen had the lowest K_d values, with an average of 1.52 L kg^{-1}, while triclosan had the highest K_d, with an average of 116.86 L kg^{-1}. The average K_d of bisphenol A on the four soils was 25.76 L kg^{-1}, which was similar to the result from Ying and Kookana (2005), where they obtained the K_d value of 20 L kg^{-1} for bisphenol A on four different soils.

Analysis of variance showed significant differences of K_d values between the tested PPCPs and among the four soils ($p < 0.05$). 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 0.7328 to 0.9329, except for clofibric acid which had a very weak correlation coefficient of 0.0031. Our previous study also found that the adsorption coefficient for a non-steroidal anti-inflammatory drug, ketoprofen, was in a positive correlation with the OM contents in the soils (Xu et al., 2009b). The weak cor-

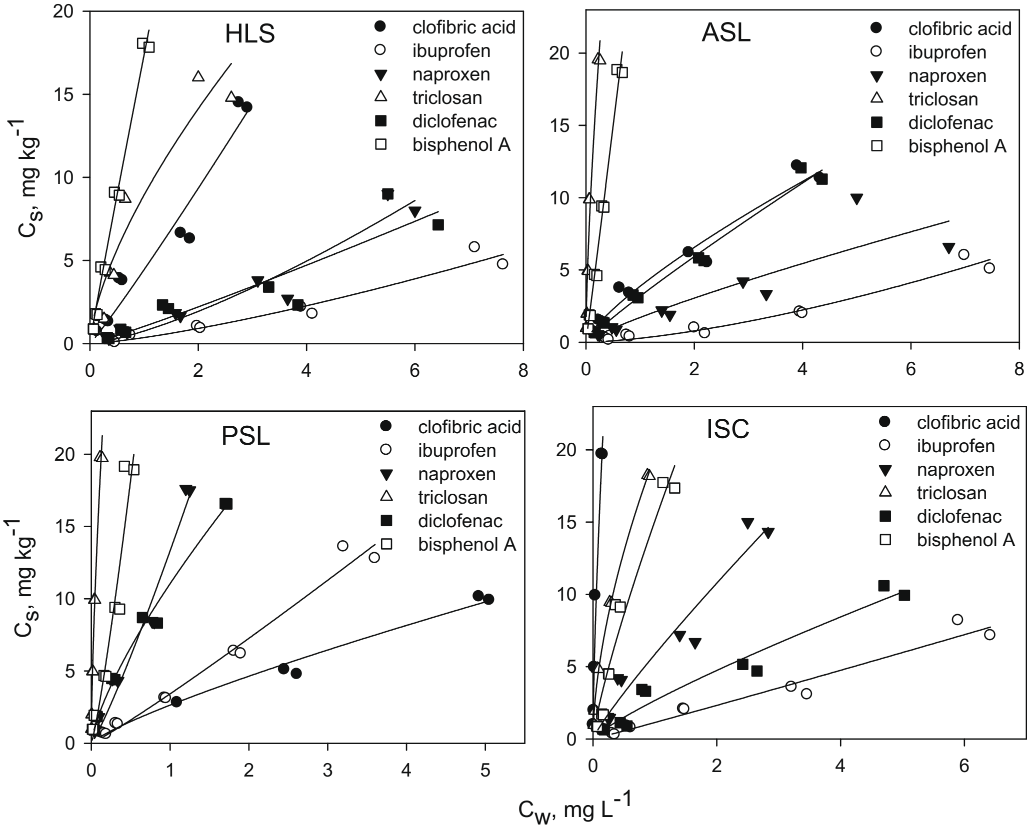

Fig. 1. Adsorption isotherms of selected PPCPs in four agricultural soils (20 ± 2 °C). Initial solutes concentrations ranged from 0 to 10 mg L^{-1}. Lines are fitted to the Freundlich equation weighted on $1/C_s$.

Table 2
Adsorption coefficients of selected PPCPs in four agricultural soils. K_f and n are Freundlich affinity coefficient and Freundlich linearity index respectively. The K_d and log K_{OC} values were calculated with all measured data points and shown as average values with standard deviation. Data in parenthesis show K_d and log K_{OC} ranges obtained in this study.

	HLS					ASL				
	K_f, mg^{1-n} L^n kg^{-1}	n	R^2	K_d, L kg^{-1}	log K_{OC}	K_f, mg^{1-n} L^n kg^{-1}	n	R^2	K_d, L kg^{-1}	log K_{OC}
Clofibric acid	4.44 ± 0.66	1.07 ± 0.16	0.947	5.36 ± 1.49 (3.41–8.00)	3.09 ± 0.12 (2.89–3.26)	3.87 ± 0.39	0.76 ± 0.08	0.963	4.54 ± 1.68 (2.46–7.09)	2.92 ± 0.17 (2.65–3.11)
Ibuprofen	0.36 ± 0.13	1.33 ± 0.19	0.948	0.56 ± 0.22 (0.17–0.94)	2.11 ± 0.20 (1.60–2.33)	0.27 ± 0.10	1.51 ± 0.19	0.962	0.56 ± 0.17 (0.27–0.86)	2.01 ± 0.14 (1.70–2.19)
Naproxen	0.76 ± 0.28	1.36 ± 0.22	0.933	1.24 ± 0.31 (0.74–1.64)	2.45 ± 0.12 (2.23–2.58)	1.71 ± 0.60	0.84 ± 0.22	0.800	1.65 ± 0.52 (0.99–2.55)	2.48 ± 0.14 (2.25–2.67)
Triclosan	8.93 ± 0.83	0.66 ± 0.10	0.886	9.72 ± 3.82 (5.66–18.00)	3.34 ± 0.16 (3.11–3.61)	51.15 ± 5.49	0.67 ± 0.06	0.970	132.83 ± 30.01 (74.92–164.67)	4.38 ± 0.11 (4.13–4.48)
Diclofenac	1.03 ± 0.47	1.10 ± 0.27	0.846	1.21 ± 0.36 (0.60–1.73)	2.44 ± 0.14 (2.14–2.59)	3.18 ± 0.26	0.90 ± 0.06	0.984	3.47 ± 0.73 (2.59–4.54)	2.80 ± 0.09 (2.67–2.92)
Bisphenol A	17.36 ± 0.56	0.96 ± 0.06	0.984	17.00 ± 3.05 (13.38–23.00)	3.59 ± 0.08 (3.48–3.72)	30.30 ± 1.88	1.03 ± 0.08	0.981	27.89 ± 3.93 (23.00–33.09)	3.71 ± 0.06 (3.62–3.78)
	PSL					ISC				
Clofibric acid	2.64 ± 0.23	0.81 ± 0.06	0.982	3.36 ± 1.55 (1.83–6.33)	2.03 ± 0.19 (1.76–2.30)	74.82 ± 12.37	0.70 ± 0.07	0.955	200.73 ± 59.93 (123–275.78)	4.15 ± 0.14 (3.93–4.29)
Ibuprofen	3.42 ± 0.32	1.09 ± 0.09	0.981	3.71 ± 0.46 (3.26–4.45)	2.07 ± 0.05 (2.01–2.15)	1.14 ± 0.24	1.03 ± 0.12	0.957	1.24 ± 0.26 (0.86–1.70)	1.94 ± 0.09 (1.78–2.08)
Naproxen	13.31 ± 0.60	1.14 ± 0.14	0.966	16.49 ± 5.17 (10.50–26.57)	2.72 ± 0.13 (2.52–2.92)	5.85 ± 0.63	0.88 ± 0.12	0.945	6.99 ± 2.33 (4.06–10.50)	2.69 ± 0.14 (2.45–2.87)
Triclosan	80.24 ± 8.96	0.68 ± 0.04	0.983	273.22 ± 78.43 (140.86–398)	3.94 ± 0.14 (3.65–4.10)	19.54 ± 0.41	0.59 ± 0.02	0.994	51.67 ± 24.37 (19.98–88.91)	3.56 ± 0.23 (3.15–3.79)
Diclofenac	11.04 ± 0.26	0.74 ± 0.04	0.991	17.72 ± 7.45 (9.63–29.25)	2.75 ± 0.19 (2.48–2.97)	2.66 ± 0.38	0.83 ± 0.10	0.952	2.83 ± 1.05 (1.64–4.33)	2.30 ± 0.16 (2.06–2.48)
Bisphenol A	41.90 ± 8.46	1.20 ± 0.22	0.922	42.22 ± 15.92 (25.03–74.92)	3.13 ± 0.16 (2.90–3.37)	15.08 ± 0.84	0.81 ± 0.09	0.948	15.93 ± 4.77 (9.98–25.78)	3.05 ± 0.13 (2.84–3.26)

relation between clofibric acid K_d and soil OM may be due to the chemical's low pK_a value. The adsorption of organic acid in soils is generally pH-dependent. Under soil pH conditions below their pK_a, organic acids are in general present in their neutral and undissociated form, which has a higher tendency to adsorb to soil organic matter compared with their more polar dissociated form. Clofibric acid in the four soils (pH values around 7) was highly dissociated because of its low pK_a value of 2.84 (Xu et al., 2009a), resulting in the weak adsorption to OM. Due to the diverse structures of PPCPs (polar or ionic), it is not easy to predict their adsorption behaviors in soils. 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 (Zhang and Cooper, 1996; Rai et al., 2000; Chen et al., 2006). K_d of clofibric acid was found to be highly correlated with soil clay contents, with correlation coefficient of 0.866, while for the other five chemicals the R^2 values were only between 0.0002 and 0.1051. To model the adsorption of pharmaceuticals in solid phases it is necessary to develop a method which considers the properties and the polarity of the functional groups of a molecule (Ternes et al., 2004).

Normalizing the adsorption coefficient K_d to the fraction of organic carbon 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 2.03 for ibuprofen to 3.81 for triclosan. Note that although adsorption of clofibric acid is not correlated to OM content, log K_{OC} values of clofibric acid in four soils are still presented here as a reference. The adsorption affinity of the six PPCPs on soil was in the following order: triclosan > bisphenol A > clofibric acid > naproxen > diclofenac > ibuprofen. Results suggest that ibuprofen is most mobile, and triclosan is the least mobile in soils. To estimate the travel time of the chemicals in soils, the retardation factor, R_F, was calculated using measured K_d values, as listed in Table 3. The R_F values of triclosan and bisphenol A were larger than 42 in all soils, while ibuprofen had low R_F values in soils. This indicated that adsorption substantially increased residence time of triclosan and bisphenol A in soils, while residence time for ibuprofen was low, which was in agreement with the adsorption results.

3.2. Degradation

PPCPs concentrations measured after different time intervals of incubation were plotted in Fig. 2, and the disappearance curves of each chemical were fitted to the exponential decay model to estimate the degradation rate constant k (d^{-1}) and half-life $t_{1/2}$ (d). As shown in Table 4, most of the fits were excellent with correlation coefficients $R^2 > 0.96$, except for three cases (clofibric acid in PSL and ISC soils, and diclofenac in ASL soil) with R^2 ranging from 0.89 to 0.93, suggesting that the degradation of selected PPCPs in agricultural soils could be well described with first-order exponential decay model.

Table 3
Retardation factors ($R_F = 1 + \rho_b K_d/\theta$) of six PPCPs in four soils.

	Soil property		Retardation factor					
	Bulk density, ρ_b	Porosity, θ	Clofibric	Ibuprofen	Naproxen	Triclosan	Diclofenac	Bisphenol A
HLS	1.60	0.38	24	3	6	42	6	73
ASL	1.55	0.40	19	3	7	516	14	109
PSL	1.42	0.43	12	13	55	903	60	140
ISC	1.33	0.48	557	4	20	144	9	45

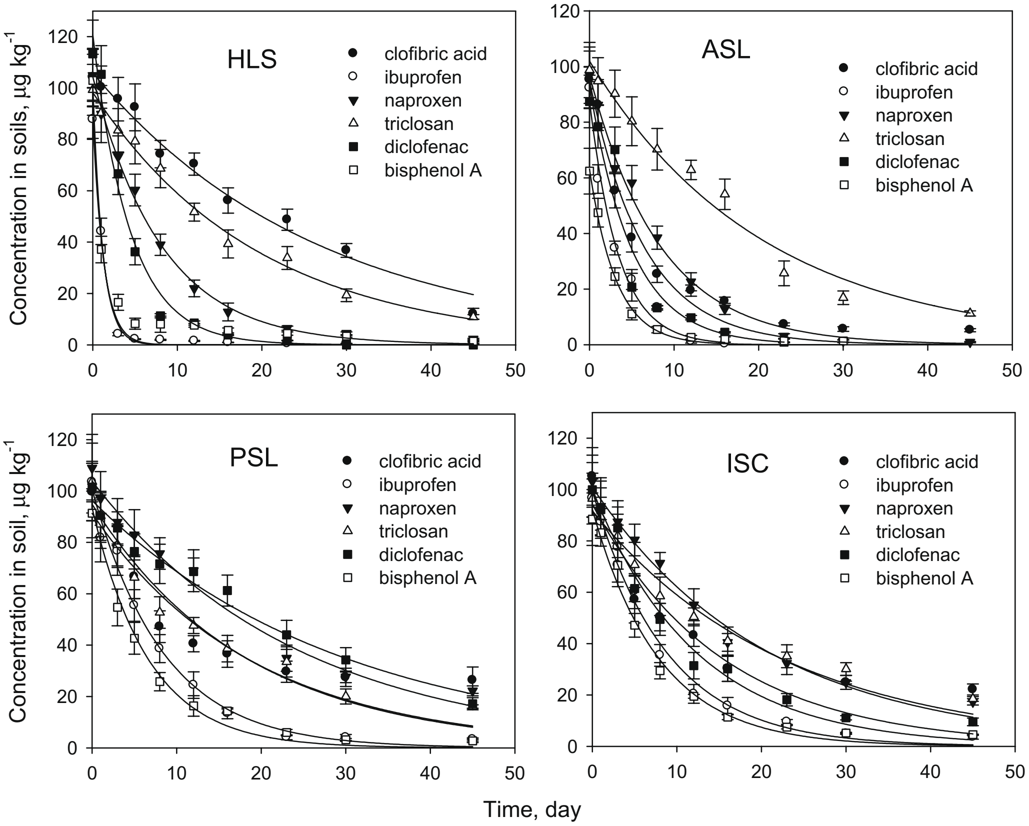

Fig. 2. Degradation curves of six PPCPs in four agricultural soils. Experiments were conducted at 20 ± 2 °C and lasted for 45 d, with moisture content at 70% of the soils water holding capacity. Lines are fitted to the first-order decay model.

Table 4
First-order degradation rate constants and correlation coefficients of PPCPs in four soils (spiking level is 100 µg kg^{-1}).

	HLS			ASL			PSL			ISC		
	k, d^{-1}	$t_{1/2}$, d	R^2	k, d^{-1}	$t_{1/2}$, d	R^2	k, d^{-1}	$t_{1/2}$, d	R^2	k, d^{-1}	$t_{1/2}$, d	R^2
Clofibric acid	0.0375	18.48	0.9838	0.1533	4.52	0.9770	0.0527	13.15	0.8921	0.0630	11.00	0.8945
Ibuprofen	0.7655	0.91	0.9948	0.2932	2.36	0.9858	0.1188	5.83	0.9902	0.1138	6.09	0.9884
Naproxen	0.1221	5.68	0.9973	0.1200	5.78	0.9950	0.0412	16.82	0.9809	0.0485	14.29	0.9886
Triclosan	0.0510	13.59	0.9922	0.0487	14.23	0.9776	0.0548	12.65	0.9619	0.0442	15.68	0.9729
Diclofenac	0.2256	3.07	0.9862	0.1995	3.47	0.9337	0.0339	20.44	0.9792	0.0818	8.47	0.9820
Bisphenol A	0.8511	0.81	0.9600	0.3167	2.19	0.9967	0.1497	4.63	0.9861	0.1260	5.50	0.9873

All six PPCPs in the four agricultural soils exhibited low to moderate persistence, with half-lives ranging from 0.81 to 20.44 d (Table 4). Within 16 d after treatment in this study, more than 50% of tested PPCPs were degraded in soils. For some pharmaceuticals, they undertook very fast degradation processes, showing low persistence in soils. For instance, over 45 d of incubation, soil concentrations of ibuprofen and diclofenac were below their detection limits in HLS and ASL soils. The percentages of degraded bisphenol A in all four agricultural soils were more than 95% (Fig. 2). It is found that degradation of bisphenol A was relatively faster in soils than in aquifer materials, whereas slower than in the acclimated activated sludge. Ying et al. reported that under the aerobic conditions, bisphenol A remained almost unchanged over 70 d in the aquifer media (Ying et al., 2003b), while the first-order biodegradation rate constant of bisphenol A in activated sludge was as fast as 0.80 h^{-1} at 20 °C (Zhao et al., 2008). The half-lives of bisphenol A in soils in present study were between 0.81 and 5.50 d, which were comparable to the results by Ying and Kookana, where they determined the half life of bisphenol A as 7 d in the nonsterile aerobic soil (Ying and Kookana, 2005).

The degradation behaviors of clofibric acid, ibuprofen, naproxen, diclofenac and triclosan in aquatic environments have been well addressed (Richardson and Bowron, 1985; Buser et al., 1998; Zwiener and Frimmel, 2003; Lin and Reinhard, 2005; Yu et al., 2006), to the best of our knowledge, however, no literature data on the degradation of these PPCPs in agricultural soils are available. Results from present study showed that degradation behaviors of selected PPCPs differed with compound and soil. As can be seen from Table 4, ibuprofen and bisphenol A were amenable to degradation, with half-lives ranging from 0.91 to 6.09 and 0.81 to 5.50 d, respectively, while the longest half lives of clofibric acid, naproxen, triclosan and diclofenac in soils were up to 18.48, 16.82, 15.68 and 20.44 d, respectively. For ibuprofen, naproxen and bisphenol A, the degradation rate constants in four soils followed the following order: HLS > ASL > PSL > ISC. For clofibric acid, the descending order was ASL > ISC > PSL > HLS. For diclofenac, the order of HLS > ASL > ISC > PSL was observed. Triclosan displayed similar degradation behaviors in the four agricultural soils, without significant difference ($p < 0.05$) between half lives. The different degradation rates of tested compounds in the different soils may

Table 5
First-order degradation rate constants and correlation coefficients of PPCPs in HLS soil with different treatments.

	100 μg kg^{-1}			100 μg kg^{-1}, sterile			1000 μg kg^{-1}		
	k, d^{-1}	$t_{1/2}$, d	R^2	k, d^{-1}	$t_{1/2}$, d	R^2	k, d^{-1}	$t_{1/2}$, d	R^2
Clofibric acid	0.0375	18.48	0.9838	0.0149	46.51	0.7725	0.0192	36.09	0.9605
Ibuprofen	0.7655	0.91	0.9948	0.0222	31.22	0.9645	0.3675	1.89	0.9891
Naproxen	0.1221	5.68	0.9973	0.0180	38.50	0.8815	0.0917	7.56	0.9896
Triclosan	0.0510	13.59	0.9922	0.0196	35.36	0.9361	0.0347	19.97	0.9822
Diclofenac	0.2256	3.07	0.9862	0.0099	70.00	0.8618	0.1607	4.31	0.9209
Bisphenol A	0.8511	0.81	0.9600	0.0689	10.06	0.8335	0.3646	1.90	0.9601

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). On the other hand, the physicochemical characteristics of soils may also have contributed to the difference in PPCPs degradation. For example, regression of the degradation rate constants k with soil properties showed that except for clofibric acid, degradation rate constants were negatively correlated with soil clay content (R^2 ranging from 0.42 to 0.56). Soil OM content also played an important role in the PPCPs degradation. For instance, the k values of diclofenac were inversely correlated with OM, with R^2 of 0.80. Previous studies have shown that high soil OM content may inhibit the organic compounds degradation, due to the increased adsorption of the chemical and reduced bioavailability (Johnson and Sims, 1993; Xu et al., 2009b), and the fact that soil organic matter may serve as an alternative nutrition source for the microorganisms involved in the degradation (Alvey and Crowley, 1995). For the other tested compounds, the negative correlation coefficients R^2 values ranged from 0.54 to 0.64 between k and OM contents, except for clofibric acid, which had a very poor regression with $R^2 = 0.014$.

Biodegradation of PPCPs has been reported to play a major role in the removal of these chemicals from environments (Kimura et al., 2007; Xu et al., 2009b). The comparative experiments conducted in the HLS soil showed that the sterilization treatment resulted in a decrease in the degradation rates of PPCPs (Table 5). Take clofibric acid as an example, after incubation for 45 d, the fraction of degraded clofibric acid in nonsterile and sterilized HLS were 88% and 43%, respectively. Diclofenac degradation showed even more pronounced differences between nonsterile and sterilized treatments. After 45 d incubation, almost all diclofenac was degraded in nonsterile HLS soil, while in the sterilized treatment, only 33% of the initial concentration disappeared. Degradation rates of clofibric acid, ibuprofen, naproxen, triclosan, diclofenac and bisphenol A in nonsterile soil were 2.5-, 34.5-, 6.8-, 2.6-, 22.8- and 12.4-fold faster than in the sterilized HLS soil. The inhibition by sterilization suggested that microbial transformations contributed to the overall degradation of PPCPs in the agricultural soils. From Table 5 we also found that increasing initial soil concentrations of tested compounds from 100 μg kg^{-1} to 1000 μg 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.

4. Conclusions

Results from 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. From the view of chemical mobility, short residence time was found for ibuprofen in different soils, indicating its high downward movement potential with percolating water, while triclosan and bisphenol A would be readily retarded in soils. From the view of persistence, soil properties were shown to correlate with the selected PPCPs degradation in present study. The higher the soil OM and clay contents, the lower the degradation rate constants. High initial soil concentrations also showed inhibitory effect on the PPCPs degradation. This indicates that for a given incubation time a higher percentage of PPCPs could be degraded in soils at a lower initial concentration than at a higher initial concentration.

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