



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.

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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 $9.8 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ 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.

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 $100\ \mu\text{g}\ \text{kg}^{-1}$ by adding into each vessel 50 μL of the mixed stock solution with a concentration of $10\ \text{mg}\ \text{L}^{-1}$ 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 $1000\ \mu\text{g}\ \text{kg}^{-1}$ was used by adding into each vessel 50 μL of the mixed stock solution with a concentration of $100\ \text{mg}\ \text{L}^{-1}$ for each compound. The incubation temperature for all experiments was kept at $20 \pm 2^{\circ}\text{C}$, 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 $10\ \text{mg}\ \text{L}^{-1}$ in 50-mL Teflon centrifuge tubes. The soil suspensions were continuously mixed by shaking and equilibrated for 24 h at the room temperature ($20 \pm 2^{\circ}\text{C}$). 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 6708g 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 ($\text{mg}\ \text{L}^{-1}$). 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 ($\text{mg}\ \text{kg}^{-1}$), 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 6708g 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 $0.2\ \mu\text{g}\ \text{kg}^{-1}$ for ibuprofen, $0.4\ \mu\text{g}\ \text{kg}^{-1}$ for clofibric acid, naproxen, triclosan, and bisphenol A; and $1.2\ \mu\text{g}\ \text{kg}^{-1}$ 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

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

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