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Influence of organic amendment on fate of acetaminophen and sulfamethoxazole in soil

Juying Li [a, c, *], Qingfu Ye [b], Jay Gan [c]

[a] College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China
[b] Institute of Nuclear Agricultural Sciences, Zhejiang University, Hangzhou 310029, China
[c] Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

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ABSTRACT

Land application of biosolids or compost constitutes an important route of soil contamination by emerging contaminants such as acetaminophen and sulfamethoxazole. Using ^{14}C labeling, we evaluated the influence of biosolids and compost on individual fate processes of acetaminophen and sulfamethoxazole in soil. The amendment of biosolids or compost consistently inhibited the mineralization of both compounds but simultaneously enhanced the dissipation of their extractable residues or parent form. Immediately after treatment, the majority of ^{14}C-residue became non-extractable, reaching 80.3–92.3% of the applied amount at the end of 84-d incubation. Addition of biosolids or compost appreciably accelerated the formation of bound residue, likely due to the fact that the organic material provided additional sites for binding interactions or introduced exogenous microorganisms facilitating chemical transformations. This effect of biosolids or compost should be considered in risk assessment of these and other emerging contaminants.

1. Introduction

Studies to date have shown that pharmaceutical and personal care products (PPCPs) can exert adverse effects on non-target aquatic and terrestrial organisms at trace levels (Daughton and Ternes, 1999; Fent et al., 2006; Jjemba, 2006; McClellan and Halden, 2010). Many PPCPs are known to be recalcitrant to conventional water treatment processes and may enter the soil environment via reuse of treated wastewater for irrigation or biosolids as soil amendment (Xia et al., 2005). Because of their agronomic values, land application of biosolids and compost is an increasingly common practice in agriculture and urban gardening (Chang et al., 2002; Vorkamp et al., 2002). In addition, biosolids usually act as a significant route for soil contamination by PPCPs (Kinney et al., 2006). The U.S. Environmental Protection Agency estimated that more than 8 million dry tons of biosolids are produced each year in the United States (U.S. Environmental Protection Agency, 2006), and over 50% are eventually land applied (U.S. Environmental Protection Agency, 2015). Bonnin (2001) reported that 65% of the sewage sludge is land applied in France.

The incorporation of organic waste materials into soil drastically affects a soil's physical, chemical and biological properties, which may in turn alter the persistence and fate of PPCPs. Biosolids or compost amendment generally stimulates soil microbial activity because of the added nutrients and exogenous microbial populations (Barriuso et al., 1997; Saison et al., 2006). On the other hand, as organic matter may adsorb and sequester organic compounds, amendment of biosolids or compost may also inhibit the transformation of PPCPs due to the decreased bioavailability (Jacobsen et al., 2005; Wanner et al., 2005). The influence of organic amendment on environmental fate of pesticides and endogenous hormones has been investigated. For example, Wanner et al. reported that the addition of straw decreased the mineralization of the fungicide dithianon. However, most studies to date on the environmental fate of PPCPs in soil have focused on transformation or sorption processes (Brooks et al., 2009; Xu et al., 2009), and endogenous hormones (Jacobsen et al., 2005) and relatively little attention has been given to ascertain the effect of organic material amendment that often is integral to soil contamination by PPCPs.

In this study, we used acetaminophen and sulfamethoxazole as two model compounds of PPCPs and ^{14}C labeling to obtain an in-depth understanding of the influence of biosolids and compost amendment on different fate processes in soil, including

* Corresponding author. College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China.
E-mail address: jyli@szu.edu.cn (J. Li).

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mineralization, degradation of parent compound, dissipation of extractable residues, and formation of bound residues. Acetaminophen and sulfamethoxazole are two of the most frequently detected PPCPs in biosolids. For instance, acetaminophen was detected at 89% frequency with concentrations up to 1400 μg/kg dry weight in biosolids destined for land application, while sulfamethoxazole was found with a maximum concentration of 160 μg/kg dry weight (Hydromantis, 2010; Jelić et al., 2012; Kinney et al., 2006). To date a few studies have considered the transformation and persistence of acetaminophen and sulfamethoxazole in agricultural soils (Li et al., 2014b; Salvia et al., 2014; Srinivasan and Sarmah, 2014). These studies generally showed that acetaminophen and sulfamethoxazole degraded rapidly with half-lives ranging from a few hours to a few days. However, so far few researchers have mechanistically examined the influence of organic amendment on the fate of these and other PPCPs in soil. The derived information from this study will be valuable for obtaining a more holistic understanding of environmental risks of PPCPs, particularly in light of the widespread use of biosolids and compost in agricultural fields.

2. Materials and methods

2.1. Chemicals

^{14}C-Benzyl ring-labeled acetaminophen (radiochemical and chemical purity >99%, specific activity 48.7 mCi/mmol; see Fig. S1 for structure and ^{14}C labeling position) and [ring-^{14}C (U)] sulfamethoxazole (radiochemical and chemical purity >99%, specific activity 77 mCi/mmol; see Fig. S2 for structure and ^{14}C labeling position) were purchased from American Radiolabeled Chemicals (St Louis, MO). Non-labeled acetaminophen and sulfamethoxazole were purchased from Sigma–Aldrich (Sigma–Aldrich, Inc, USA).

A stock solution of ^{14}C-acetaminophen or ^{14}C-sulfamethoxazole was prepared in methanol by mixing the labeled and non-labeled acetaminophen or sulfamethoxazole to arrive at a final specific activity of 5 μCi/mg. All organic solvents and other chemicals used were of high-performance liquid chromatography (HPLC) grade.

2.2. Soils and soil amendments

Two agricultural soils taken from the top 10 cm at locations in California with no known history of biosolids or compost application were used in this study. San Emigdio fine sandy clay loam (University of California Research and Education Center, Irvine, CA) and Arlington sandy loam soil (University of California, Citrus Research Center and Agricultural Experiment Station, Riverside, CA) are abbreviated herein as soil A and soil B, respectively. The soils were air-dried, homogenized and sieved through a 2-mm mesh to remove plant debris and then stored at 4 °C in the dark until use. A sample of biosolids was obtained from a local wastewater treatment plant using primary, secondary, and tertiary treatment stages. The wet material was centrifuged and the dewatered sludge contained 21.7% dry solids. The compost was purchased from a local supplier (E.B. Stone & Son, Suisun, CA) and the product was prepared from redwood sawdust that was fortified with 0.5% nitrogen. To achieve a uniform soil-amendment mixture, all amendments were ground and passed through a 2-mm sieve before use.

Table 1
Physicochemical properties of soils and soil amendments used in this study.

Soil	Texture	Particle size analysis (%)			pH (H_2O)	Elemental analysis (%)	
		Sand	Silt	Clay		TOC (%)[c]	N (%)[d]
A[a]	Sandy clay loam	57	22	21	6.8	0.67	0.05
B[b]	Sandy loam	63	18	19	7.3	0.35	0.05
Biosolids						42.9	5.53
Compost						23.6	0.42

[a] Soil collected from Irvine, CA.
[b] Soil collected from Riverside, CA.
[c] Total organic carbon (%).
[d] Total nitrogen content (%).

The organic carbon (OC) contents of soils, biosolids and compost were measured by combustion of a subsample on a nitrogen/carbon analyzer (Thermo Finnigan, Woods Hole, MA) after digestion with HCl (1 M) to remove carbonates. Selected properties of the test soils and organic amendments are listed in Table 1.

2.3. Experimental setup

Incubation experiments were carried out using the prepared soils with or without organic amendment. To discern the influence of biosolids, subsamples of soil A or B were mixed with 10% biosolids (w/w, dry weight). In addition, soil A was also amended with biosolids at 5%, or compost at 5 or 10%. Soil samples in bulk were pre-incubated for 7 d after adjusting the soil moisture to 40% of the soil's water-holding capacity (WHC) by using deionized water to revive the activity of indigenous microorganisms. To minimize the potential effect of solvent, 20 μL ^{14}C-acetaminophen (4.44×10^5 dpm) or 20 μL ^{14}C-sulfamethoxazole (2.22×10^5 dpm) in methanol was dispensed separately onto a 1.0-g (dry weight equivalent) soil subsample in a 40-ml amber glass vial for the unamended soil treatments. The treated soil was mixed with a spatula in a fume hood until the solvent was completely evaporated and then mixed with 9.0 g (dry weight) of the same type of soil which has been pre-incubated. Similarly, for amended soils, the same amount of ^{14}C-acetaminophen or ^{14}C-sulfamethoxazole was spiked drop-wise to the biosolids or compost subsample (1.0 g, dry weight) and then homogenized with the soil. The initial acetaminophen and sulfamethoxazole concentrations were 4 mg kg^{-1}. Deionized water was added to adjust the soil moisture to about 60% WHC. All treated samples were mixed on a shaker at a low speed for 2 h to achieve uniform distribution. Three replicates were selected and the uniformity of ^{14}C distribution within the treated soil samples was verified by analyzing ^{14}C activity from combustion of soil subsamples (1.0 g) on a biological oxidizer (OX-500, R.J. Harvey Instrument, Hillsdale, NJ, USA) (recovery 92.5 ± 2.8%; n = 3). Blank amended and unamended soil samples without ^{14}C-acetaminophen or ^{14}C-sulfamethoxazole were similarly prepared and used as the matrix control.

To capture $^{14}CO_2$ from mineralization of ^{14}C-acetaminophen or ^{14}C-sulfamethoxazole during soil incubation, a 2-mL GC vial filled with 1.0 mL of 1.0 M sodium hydroxide (NaOH) solution was suspended under the septum of each sample vial. Each of thus constructed systems constituted a “respirometer” (Li et al., 2013). All respirometers were tightly sealed with septa and crimp caps, and then covered with aluminum foil for incubation at the room temperature (21 ± 1 °C). At 0, 1, 3, 5, 7, 14, 28, 42, 56 and 84 d after the treatment, three replicate respirometers from each treatment were removed and ^{14}C-activity in the used NaOH solution was measured on a PerkinElmer TriCarb liquid scintillation counter (LSC) (PerkinElmer, Waltham, MA) after mixing with 5 mL of UltimaGold liquid scintillation cocktail (PerkinElmer). Samples were kept for at least 24 h in the dark before counting to avoid potential chemiluminescence. The counting time was 6 min, and each sample was measured for 3 times, from which the mineralized amount at the given sampling interval was calculated. The remaining respirometers were also opened at the same sampling intervals and were