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Biosolids inhibit bioavailability and plant uptake of triclosan and triclocarban

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ABSTRACT

Biosolids from wastewater treatment are primarily disposed of via land applications, where numerous pharmaceuticals and personal care products (PPCPs) may contaminate food crops and pose a human exposure risk. Biosolids are rich in organic carbon and addition of biosolids can increase the sorption of certain PPCPs in soil, decreasing their bioavailability. This study tested the hypothesis that the relative plant uptake of PPCPs decreases with increasing biosolids amendment. Accumulation of triclosan and triclocarban was measured in roots of radish and carrot grown in soils with or without biosolids. Addition of biosolids significantly prolonged the persistence of triclosan in soil. When expressed in bioaccumulation factor (BCF), accumulation of triclosan drastically decreased in biosolids-amended soils, while the effect was limited for triclocarban. Compared to the unamended soil, amending biosolids at 2% (w/w) decreased BCF of triclosan in the edible tissues of radish and carrot by 85.4 and 89.3%, respectively. Measurement using a thin-film passive sampler provided direct evidence showing that the availability of triclosan greatly decreased in biosolids-amended soils. Partial correlation analysis using data from this and published studies validated that biosolids decreased plant uptake primarily by increasing soil organic carbon content and subsequently sorption. Therefore, contamination of food crops by biosolids-borne contaminants does not linearly depend on biosolids use rates. This finding bears significant implications in the overall risk evaluation of biosolids-borne contaminants.

1. Introduction

Biosolids are the byproduct of wastewater treatment operations. Agricultural land is increasingly used as the disposal destination of biosolids, as the beneficial reuse may improve soil health and increase crop yields. According to the U.S. EPA, about 8 million tons of biosolids are produced by 16,500 wastewater treatment plants (WWTPs) in the U.S., of which 60% is eventually applied to agricultural lands (United States Environmental Protection Agency, 2009; 1999). However, studies to date have shown that numerous trace organics such as pharmaceutical and personal care products (PPCPs) are present in biosolids, with levels ranging from $\mu g\ kg^{-1}$ to $mg\ kg^{-1}$. In particular, due to their high affinity for organic matter, heavily used antibacterial agents such as triclosan and triclocarban are enriched in biosolids and may reach several hundreds of $mg\ kg^{-1}$ in biosolids (Halden and Paull, 2005; Walters et al., 2010).

Once in agricultural fields, PPCPs in biosolids may be taken up by food crops, constituting a risk for human exposure through dietary intake (Aryal and Reinhold, 2011; Holling et al., 2012; Pannu et al., 2012; Prosser et al., 2014a, 2014b; Sabourin et al., 2012; Wu et al., 2012a; Wu et al., 2010, 2016). Several field studies have demonstrated the potential for plants to accumulate PPCPs. For example, Wu et al. (2010) found that soybean plants grown in biosolids-amended soils could accumulate triclosan, triclocarban, carbamazepine, fluoxetine, and diphenhydramine, with the maximum level of triclocarban at 168 ± 34 $ng\ g^{-1}$ (dry weight) in roots. Sabourin et al. (2012) also reported the occurrence of 24 PPCPs, 17 hormones, and 6 parabens at trace levels (0.33–6.25 $ng\ g^{-1}$) in tomatoes, potatoes, carrots, and sweet corn grown in a biosolids-amended field. In a comprehensive field study, we grew eight types of vegetables with treated wastewater irrigation and detected a range of PPCPs in the edible parts at harvest (Wu et al., 2014).

While biosolids serve as the main route for soil contamination of

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PPCPs, amendment of biosolids may also induce drastic effects on the soil-plant continuum, which can in turn influence the plant uptake of PPCPs. Most noticeably, biosolids are rich in organic matter and may contain up to 38% organic carbon on a dry mass basis (Kinney et al., 2006). Therefore, application of biosolids may greatly increase a soil's organic carbon content (OC), leading to enhanced sorption or reduced chemical bioavailability. It may be hypothesized that biosolids amendment has dual effects: while it introduces PPCPs into soil, it also simultaneously inhibits plant uptake of PPCPs due to reduced bioavailability. However, although a number of studies have considered plant accumulation of PPCPs from soil with or without biosolids (Carter et al., 2014; Macherius et al., 2012b; Pannu et al., 2012; Prosser et al., 2014a; Wu et al., 2012a), to date there lacks a clear understanding of how biosolids affect plant accumulation of PPCPs.

In this study, we used triclosan and triclocarban, two high-production-volume chemicals found in numerous household and healthcare products, as model PPCPs and tested the hypothesis that biosolids amendment had an inhibitory effect on their plant accumulation. Two root vegetables, i.e., radish (*Raphanus sativus*) and carrot (*Daucus carota* ssp. *satiuus*), were considered because they present a potentially greater risk for human exposure as the edible organ is in direct contact with soil (Prosser and Sibley, 2015). To substantiate that biosolids inhibited plant uptake by decreasing chemical bioavailability, we further used a thin film-based passive sampler to detect the bioavailable concentrations in soils. Given that application of biosolids is the primary route for PPCPs to contaminate food crops, findings from this study may bear significant implications for better understanding the overall risk of biosolids-borne contaminants.

2. Materials and methods

2.1. Chemicals

Standards of triclosan (CAS# 3380-34-5) and triclocarban (CAS# 101-20-2) with >98% purity were obtained from Alfa Aesar (Ward Hill, MA) and TCI America (Portland, OR), respectively. The isotope-labeled standards of triclosan-d_3 and triclocarban-d_4 were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). A stock solution was prepared by dissolving the standards in methanol and kept in amber glass vials at −20 °C before use. All organic solvents and other chemicals were of HPLC grade and obtained from Thermo Fisher (Fair Lawn, NJ).

2.2. Soils and biosolids

Plant accumulation of triclosan and triclocarban was determined in plants grown in different soils and biosolids-amended soils. Three soils (abbreviated as soil A, B, and C herein) with different physicochemical properties were collected from the surface layer (0–10 cm) in fields in Riverside, CA and Irvine, CA. The aerobically treated, dewatered biosolids were obtained from a local wastewater treatment plant. The soils and biosolids were sieved through a 2-mm mesh. The organic carbon content (OC) of the biosolids was determined to be 36.2% (dry weight basis). The field water holding capacity of each soil was determined using a standard method (Gardner, 1986). Biosolids-amended soils were prepared by incorporating biosolids to soil A at 2% (Soil A_2), 5% (Soil A_5), and 10% (Soil A_{10}) (dry weight basis), representing approximately 8, 20, and 40 tonnes/ha with a 25 cm depth of incorporation and a soil bulk density at 1.6 g/cm^3. Selected properties of soils and biosolids-amended soils used in this study are summarized in Table 1.

Table 1
Physicochemical properties of soils and biosolids-amended soils.

Soil no.	Soil type	pH (H_2O)	TOC[a] (%)	Sand (%)	Silt (%)	Clay (%)	CEC[b] Meq 100g^{-1}
A	Sandy loam	6.42	0.41	64	24	12	9.6
A_2[c]	Sandy loam	6.57	1.21	67	22	11	11.1
A_5[c]	Sandy loam	6.51	2.45	67	22	11	14.4
A_{10}[c]	Sandy loam	6.42	3.50	62	26	12	18
B	Sandy loam	7.67	0.50	73	13	14	18.5
C	Sandy Clay	7.39	1.25	57	23	20	27

[a] TOC: total organic carbon.
[b] CEC: cation exchange capacity.
[c] A_2: soil A applied with 2% of biosolids; A_5: soil A applied with 5% of biosolids; A_{10}: soil A applied with 10% of biosolids.

2.3. Plant cultivation and treatments

Radish and carrot were grown in soils with and without biosolids in a greenhouse (day/night: approximately 16/8 h, 25/20 °C; relative air humidity: 30–65%). Briefly, an aliquot of 100 g soil or biosolids-amended soil was spiked with 1.0 mL working solution containing triclocarban or triclosan in methanol and mixed thoroughly in a fume hood using a stainless steel blender. After the methanol was evaporated, the spiked soil was mixed thoroughly with the same type of soil (7900 g) using a motorized cement mixer. The nominal concentration of triclosan or triclocarban was 2 mg kg^{-1}. The background concentrations of triclosan and triclocarban in biosolids were determined to be 2.5 ± 0.54 and 1.5 ± 0.39 mg kg^{-1}, respectively. Therefore, even at the highest biosolids amendment rate (10%), the contribution of background triclosan or triclocarban to the overall chemical concentration in soil should be less than 12%.

The treated soils were then transferred to individual pots of 27 cm in diameter and 30 cm in height. Seeds of radish and carrot were directly sowed in the containers. After germination and establishment, 6 radish and 10 carrot seedlings were retained in each pot while the extra plants were thinned out. To maintain soil moisture, deionized water was added to each container twice daily. No drainage was visible during the experiment.

Subsamples of radish and carrot plants were removed after 35 and 70 d of cultivation, respectively. The leaves were separated from the roots, and the roots were carefully rinsed with deionized water, dried and divided into root skin (2 mm surface tissue) and root core. The soil in the container was mixed thoroughly using a stainless steel spatula and an aliquot of 10 g was removed. All samples (soil, root core, root skin, and leaf) were freeze-dried in a freeze dryer (Labconco, Kansas city, MO). After freeze-drying, plant tissues were ground into fine powder using a stainless steel coffee grinder (Hamilton Beach, Picton, Ontario, Canada) and stored at −20 °C before extraction and analysis.

2.4. Assessment of bioavailability using film-based passive sampler

Bioavailability of triclosan and triclocarban in soil A, soil A_2, soil A_5, and soil A_{10} was determined using a film-based sampling technique. Thin films of different polymers have been previously used to determine the freely dissolved concentration of organic compounds in water, sediment or soil as a measurement of bioavailability (Cornelissen et al., 2008; Haftka et al., 2013; Jia et al., 2012; Mayer et al., 2000). In this study, polymethylmethacrylate (PMMA) film (50 μm; Goodfellow, Coraopolis, PA) was selected through preliminary experiments. The PMMA film was cut into 2 × 1 cm pieces with a razor blade and cleaned with water/methanol (95:5, v/v). The PMMA strips were further swelled in ethyl ether for 30 min and dried overnight to increase their