1 **Meta-Analysis of Biosolid Effects on Persistence of Triclosan and Triclocarban in Soil**

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ABSTRACT

Biosolids are extensively used in agriculture as fertilizers while offering a practical solution for waste disposal. Many pharmaceutical and personal care products (PPCPs), such as triclosan and triclocarban, are enriched in biosolids. Biosolid amendment changes soil physicochemical properties, which may in turn alter the persistence of PPCPs and hence the risk for secondary contamination such as plant uptake. To delineate the effect of biosolids on PPCP persistence, triclosan and triclocarban were used as model compounds in this study and their sorption (K_d) and persistence ($t_{1/2}$) were determined in different soils before and after biosolid amendment. Biosolids consistently increased sorption of triclosan and triclocarban in soil. The K_d of triclosan increased by 3.9-21 times following amendment of a sandy loam soil with biosolids at 2-10%. The persistence of both compounds was prolonged, with $t_{1/2}$ of triclosan increasing from 10 d in the unamended soil to 63 d after biosolid amendment at 10%. The relationship between $t_{1/2}$ and K_d was further examined through a meta-analysis using data from this study and all relevant published studies. A significant linear relationship between $t_{1/2}$ and K_d was observed for triclosan ($r^2 = 0.69$, $p < 0.01$) and triclocarban ($r^2 = 0.38$, $p < 0.05$) in biosolid-amended soils. On the average, when biosolid amendment increased by 1%, $t_{1/2}$ of triclosan was prolonged by 7.5 d, while $t_{1/2}$ of triclocarban was extended by 4.7 d. Therefore, biosolid amendment greatly enhances persistence of triclosan and triclocarban, likely due to enhanced sorption or decreased chemical bioavailability. This finding highlights the importance to consider the effect of biosolids when evaluating the environmental risks of these and other biosolid-borne PPCPs.

Capsule: Amendment of biosolids significantly inhibited degradation and increased persistence of triclosan and triclocarban, likely due to decreased bioavailability.

Keywords: Biosolids; Triclosan; Triclocarban; PPCPs; Bioavailability.

1. INTRODUCTION

Biosolids are extensively used in agriculture as fertilizers, concurrently serving as an important means for municipal waste disposal. In the United States, about 8 million dry tons of biosolids are produced annually, of which over 60% are land-applied.^{1,2} However, studies show that many pharmaceuticals and personal care products (PPCPs), such as triclosan and triclocarban, are concentrated in biosolids.²⁻⁵ Once in soil, PPCPs may accumulate into edible parts of plants or move offsite to contaminate groundwater or surface water, constituting a risk for secondary pollution.⁶⁻⁸ The potential for secondary pollution depends on a chemical's availability in soil, which is a function of dissipation or half-life ($t_{1/2}$).⁹⁻¹¹ Biosolid amendment may induce different effects on the persistence of PPCPs. On one hand, addition of biosolids may introduce exogenous microbes and increase a soil's microbial population density and diversity, which can lead to enhanced biotic degradation or decreased $t_{1/2}$. On the other hand, biosolid amendment may alter a soil's physical and chemical properties by adding a significant external source of organic carbon to the soil, which may result in enhanced sorption (K_d) or inhibited degradation of PPCPs due to decreased bioavailability. Given that biosolid amendment is a primary pathway for PPCPs to enter soil, it is of great importance to quantitatively evaluate how biosolids change the persistence of commonly occurring PPCPs.

In this study, triclosan and triclocarban were used as two model PPCPs to understand the effect of biosolids on the persistence of PPCPs. Triclosan and triclocarban are two anti-bacterial agents found in numerous household and healthcare products, such as soaps, toothpaste, cosmetics, shampoo, and textiles, and are designated as high-production-volume chemicals by the U.S. EPA.¹²⁻¹⁴ Due to their widespread use, triclosan and triclocarban are frequently detected in biosolids, often in the mg kg^{-1} range.²⁻⁵ Research shows that triclosan and triclocarban may

induce developmental, carcinogenic or other chronic toxicities to human and other non-target organisms.^{15–19} To date, a number of studies have considered degradation or persistence of triclosan and triclocarban in soil with or without biosolid amendment. However, there lacks a clear conclusion as to how biosolids affect the persistence of triclosan and triclocarban in soil. For instance, Kwon et al. observed that $t_{1/2}$ of triclosan increased from 2 d in a fine loam to 50 d after application of biosolids, and from 13 d to 108 d in a coarse loam, while smaller increases were noticed for triclocarban under the same conditions.²⁰ In contrast, Wu et al. did not find any appreciable change in $t_{1/2}$ of triclosan or triclocarban in a silt clay soil and a sandy loam soil after addition of biosolids.²¹ The inconsistent observations may be attributed to the use of different experimental conditions or a limited number of soils or biosolids in a given study, highlighting the need for considering all available studies in order to identify a clear effect pattern.

In addition to K_d and $t_{1/2}$ values measured in four soils with or without biosolid amendment in this study, relevant available literature data^{9,20–37} were also included in meta-analysis to discern the interactions between $t_{1/2}$, K_d and biosolid application. The correlation analysis was further used to test the hypothesis that biosolid amendment increases persistence of triclosan and triclocarban and that the increased persistence is mainly due to enhanced sorption. With a holistic analysis of the measured and literature data, results from this study also provide unified information on K_{oc} and $t_{1/2}$ for these two important PPCPs in soil before and after biosolid amendment. The findings provide justification to consider the effect of biosolids when predicting the fate and risks of PPCPs resulting from biosolid applications.

2. Materials and methods

2.1. Chemicals.

Triclosan (purity $\geq$ 99%, CAS# 3380-34-5) and triclocarban (purity $\geq$ 98%, CAS# 101-20-2) were purchased from Alfa Aesar (Ward Hill, MA), and TCI America (Portland, OR), respectively. The isotope labeled triclosan- d_3 and triclocarban- d_4 were obtained from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). The stock solutions of these compounds were prepared in methanol and the working solution was prepared by diluting the stock solution with methanol. All stock and working solutions were stored in amber glass vials at -20 °C. All organic solvents and other chemicals were of HPLC grade and purchased from Thermo Fisher (Fair Lawn, NJ).

2.2. Soils and biosolids.

Soil samples of different textures (abbreviated herein as soil A, B, C, and D) were collected from the surface layer (0-10 cm) at two different locations. Soil A (sandy loam) was taken from the Experimental Station of University of California in Riverside, CA, while soils B, C, and D were taken from fields at the University of California Research and Education Center in Irvine, CA. Dewatered biosolids (moisture, 78%) were collected from a local wastewater treatment plant (Riverside, CA). The biosolids were sieved through 2-mm sieve before use. All soils were air dried and sieved using a 2-mm sieve before use. The organic carbon content of biosolids was determined to be 36.2% by using the loss-on-ignition method. Biosolids was added to soil A at 2% (Soil A₂), 5% (Soil A₅), and 10% (Soil A₁₀) on a dry mass basis (w/w). The water holding capacity of each soil was measured using the pressure chamber method.³⁸ Other physicochemical properties of soils and biosolids were determined using standard methods by the UC Davis Analytical Laboratory at University of California Davis, CA, and are summarized in Table 1.

2.3. Sorption experiments.

The batch equilibration method was used to construct sorption isotherms of triclosan and

triclocarban in four soils as well as in soil A after the addition of biosolids at 2, 5, and 10% (w/w). The lowest biosolid amendment rate was based on the U.S. EPA's recommendations corresponding to a typical biosolid application rate of 20 tons per hectare to the top 15-20 cm soil.^{39,40} The higher rates were used to facilitate regression analysis and also to account for scenarios such as repeated biosolid applications. The protocol of sorption experiments was similar to OECD's Guideline Test 106.⁴¹ Briefly, 1.0 g of soil (dry weight, with or without biosolids) was placed in a 50-mL glass centrifuge tube, followed by the addition of 40 mL of 0.01 M CaCl₂ solution containing 0.2% NaN₃ (to suppress microbial activity). The soil samples were mixed on a mechanical shaker at 150 rpm for 24 h, after which the soil slurry was spiked with triclosan and triclocarban to achieve a nominal concentration of 0.2, 0.4, 0.8, 1.6, and 2.0 mg L⁻¹. In preliminary experiments, sorption kinetics were examined by monitoring the aqueous phase concentration from 2 to 120 h, and it was observed that after 48 h, the aqueous phase concentration was essentially unchanged (variation less than 6%). Therefore, 48 h was chosen as the time interval for attaining equilibrium after chemical addition.

After 48 h of mixing, samples were centrifuged at 2,000 rpm for 30 min to separate the solid and aqueous phases. Aliquots (0.5 mL) of supernatant were transferred to 2-mL amber auto-sampler vials and mixed with 0.5 mL methanol. The solid phase was freeze-dried and extracted three times using a previously published method.^{20,22,23} Briefly, 1.0 g (dry weight) of soil sample was spiked with 50 µL of 10 mg L⁻¹ triclosan-*d*₃ and 1.0 mg L⁻¹ triclocarban-*d*₄ stock solution and then extracted with 20 mL acetone under sonication condition for 20 min, followed by centrifugation for 30 min at 2000 rpm. The supernatant was transferred into 60-mL glass vials and evaporated to dryness under nitrogen gas. The extraction was repeated for a total of three times. The final residue was recovered in 1.0 mL methanol and transferred to a 2-mL

autosampler vial. All samples were filtered through a 0.22- μ m polytetrafluoroethylene (PTFE) filter membrane (Millipore, Carrigtwohill, Cork, Ireland) and then stored at -20 °C before instrumental analysis.

2.4. Degradation experiments.

Degradation of triclosan and triclocarban was measured in the four soils as well as in soil A amended with biosolids at 2, 5, and 10%. The incubation was carried out under aerobic conditions at room temperature (25 °C). An aliquot of 200 g (dry weight) soil was placed in a 500-mL glass jar. The soil moisture was adjusted to 30% of the soil water holding capacity using deionized water. After a 7-d pre-incubation, 200 μ L of triclosan or triclocarban stock solution (2000 mg L⁻¹ in methanol) was spiked to the soil to arrive at a nominal spiked concentration of 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 biosolid amendment rate (10%), the contribution of background triclosan or triclocarban to the overall chemical concentration in soil was less than 12%. After spiking, the jars were left open in a fume hood until the solvent was evaporated. Deionized water was then added to adjust the soil moisture to 60% of the water holding capacity. The soil samples were mixed thoroughly with a stainless steel spatula. The soil jars were loosely covered with aluminum foil and kept in the dark. To maintain the aerobic conditions during the incubation experiment, each jar was opened every other day for aeration. The soil moisture was maintained by adding deionized water every two days. At 0, 5, 11, 29, and 46 d after treatment, aliquots of 10 g soil (in triplicate) were removed from each jar and used for analyzing the triclosan or triclocarban concentration remaining in the soils.

Soil samples collected at different time intervals were freeze-dried, and 1.0 g soil

subsamples (dry weight) were extracted three times using the same method as described above. The extracts were condensed to near dryness under a gentle nitrogen stream, re-dissolved in 1.0 mL methanol and then filtered into 2-mL amber glass vials through a 0.22- μ m PTFE filter membrane. All final samples were stored at -20 °C prior to instrumental analysis.

2.5. Instrumental analysis.

Instrumental analysis was performed on a Waters ACQUITY ultra-performance liquid chromatography (UPLC) combined with a Waters Micromass electrospray ionization tandem mass spectrometer (ESI-MS/MS) (Waters, Milford, MA). Separation was achieved with an ACQUITY UPLC BEH C18 column (2.1 mm x 100 mm, 1.7 μ m particle size, Waters). Pure methanol and 5% methanol in water (containing 0.001% formic acid) were used as the mobile phases B and A, respectively, which was programmed (with respect to mobile phase A) as below: 0-5 min, 90% to 0%; 5-6 min, 0 to 90%; and 6-8 min, 90 to 10%, at a flow rate of 0.2 mL min⁻¹. The injection volume was 5 μ L and the column temperature was 40 °C. The mass data was acquired under the multiple reactions monitoring (MRM) in the negative ESI mode. The MRM transitions of target compounds were optimized as 287>35 for triclosan, 290>35 for triclosan-*d*₃, 313>160 for triclocarban, and 317>160 for triclocarban-*d*₄. The specific instrument settings were: capillary voltage 3.2 kV, cone voltage 30 V, collision gas (Argon, 99.99%) 0.2 mL min⁻¹, dwell time 0.02 s, source temperature 120 °C, desolvation temperature 350 °C, desolvation gas 600 L h⁻¹ and cone gas 50 L h⁻¹. The cone voltage (V) and collision energy (eV) were 30 and 8, respectively, for triclosan, and 25 and 10, respectively, for triclosan-*d*₃. The corresponding values were 30 and 20 for triclocarban, and 30 and 10 for triclocarban-*d*₄.

2.6. Quality assurance and quality control.

Identification of triclosan and triclocarban was based on the MRM transition in mass

spectrometry as well as comparison of the retention time to the corresponding standard in UPLC. Deuterated compounds (i.e., triclosan- d_3 and triclocarban- d_4) as surrogates were spiked in each sample before extraction to account for the potential analyte loss during sample preparation, matrix effect and variations in UPLC-MS/MS response. The average recoveries of target compounds including their deuterated compounds from all the sample matrices were generally varied from 80% to 105%. Three method blanks (i.e. extraction procedure control blank) were included with every sample batch to check possible background or contamination. No target compounds were detected in the blanks. All data were expressed as the mean and standard deviation of triplicates. One-way ANOVA test was performed at $\alpha=0.05$ to evaluate the significance of difference between treatments. Statistical analyses were completed using the SPSS 19.0 software (IBM SPSS Statistics, Armonk, NY).

3. Results and discussion

3.1. Sorption in soils and biosolid-amended soils.

In this study, sorption of triclosan and triclocarban was measured in soils with different physicochemical properties as well as in biosolid-amended soils (Table 1). Addition of biosolids did not appreciably change the pH in soil A (Table 1). It was estimated that 92 - 95% of triclosan ($pK_a = 7.9$) was in its neutral form in soil A with or without biosolid amendment, while all triclocaban ($pK_a = 12.7$) should be in the neutral form. The OC contents of the four soils were relatively low, ranging from 0.41% in soil A to 1.25% in soil C. However, addition of biosolids substantially increased the OC content, and as expected, the increase was generally proportional to the rate of biosolid amendment. (**Table 1**).

The measured concentrations of triclosan or triclocarban in the aqueous phase (C_w , $\mu\text{g L}^{-1}$)

and the solid phase (C_s , $\mu\text{g kg}^{-1}$) at equilibrium were first fit to the Freundlich equation:

$$C_s = K_f C_w^n$$

where K_f is the Freundlich sorption coefficient, and n is the linearity constant (Figure S1). A good fit was obtained for all soils, including biosolid-amended soils, with $r^2 \geq 0.93$. Since the average n from the regression was close to 1 (**Table 2**), the isotherms were subsequently fit to a linear equation to derive the linear partition coefficient K_d (L kg^{-1}), from which the OC-normalized partition coefficient K_{oc} (L kg^{-1}) was further calculated (Figure S2, **Table 2**).

In soils without biosolids, K_d ranged from 35 to 170 for triclosan, and from 771 to 1477 for triclocarban (Table 2). For both compounds, the smallest K_d values were observed in soil A, while the largest K_d in soil C, likely due to its relatively higher OC content. The correlation between K_d and soil OC content was generally linear for triclosan ($r^2 = 0.93$, $p < 0.01$) and triclocarban ($r^2 = 0.82$, $p < 0.01$), suggesting that organic carbon played a dominant role in the sorption of triclosan and triclocarban in soil. The average K_{oc} was $1.01 (\pm 0.25) \times 10^4$ for triclosan, and $1.63 (\pm 0.38) \times 10^5$ for triclocarban. Therefore, sorption of triclocarban in the same soil was substantially stronger than that of triclosan.

After the addition of biosolids to soil A, K_d increased for both triclosan and triclocarban, but the increase was more pronounced for triclosan (Table 2). The increase in K_d was also proportional to the biosolid amendment rate. For example, after addition of biosolids at 2%, K_d of triclosan increased from 35.1 to 137.6, representing a 3.9-fold increase. When biosolids were amended at 5 or 10%, K_d of triclosan further increased to 311 or 731, reflecting about 9 or 21-fold increase (Table 2). Biosolids-induced increases in K_d for triclocarban were smaller than that

for triclosan. Compared to the unamended soil A, K_d of triclocarban increased by 1.7-7.0 times in the amended soils. Sorption to biosolids was further calculated by subtracting K_d in the biosolid-amended soil by K_d in the unamended soil. The derived K_{oc} for biosolids was $1.6 (\pm 0.54) \times 10^4$ for triclosan, and $9.9 (\pm 0.46) \times 10^4$ for triclocarban. Therefore, K_{oc} values of triclosan and triclocarban for the biosolids were generally similar to those observed for the unamended soils.

Sorption of triclosan and triclocarban in soils was also studied in several previous studies. In Wu et al., K_d was 178-231 for triclosan and 763-1029 for triclocarban in soils containing 1.56-1.61% OC, and these values overlap with those in the current study.²¹ Karnjanapiboonwong et al. determined K_d of triclosan in three soils (sand, sandy loam, and silt loam), and the observed K_d values ($9.8-282 \text{ L kg}^{-1}$) were also similar to those in the present study.³⁶ In general, organic carbon is believed to contribute greatly to the sorption of triclosan and triclocarban in soil, though exceptions were observed in some studies. For example, Xu et al. measured K_d of triclosan in four soils, and found the highest K_d (132.8 L kg^{-1}) in a soil with lower organic matter content (1.9%), whereas K_d was only 51.7 L kg^{-1} in a soil with higher organic matter content (2.5%).⁹ Waller et al. found K_d of triclosan to be similar (17.6 and 17.8 L kg^{-1}) in two soils with different OC contents (0.85 and 1.85%).²⁵ The lack of a clear dependence of sorption on the soil OC content may be attributed to the fact that the properties of soil organic carbon vary in different soils.

3.2. Relationship between K_d and soil OC content.

To better delineate the relationship between K_d and soil OC content and increase the power of this study, a meta-analysis was conducted by systematically combining results from 19 independent previous studies. A significant linear correlation ($r^2 = 0.94$, $p < 0.01$, $n = 29$) was observed between soil OC content and K_d of triclosan in biosolid-amended soils,^{9,20-22,24-37,43} but

there was no significant correlation in unamended soils ($r^2 = 0.01$, $p > 0.05$, $n = 30$).^{9,20,21,24,25,30–32,36,43} For triclocarban, a linear relationship between soil OC and K_d was observed in both unamended ($r^2 = 0.49$, $p < 0.05$, $n = 10$)^{9,20,21,24,25,30,32,43} and biosolid-amended soils ($r^2 = 0.38$, $p < 0.01$, $n = 24$).^{9,20–22,24–37,43} Again, the lack of a strong dependence on the OC content for triclosan in unamended soils may be attributed to the fact that soil organic carbon is qualitatively different among different soil types.

The OC normalized partition coefficient K_{oc} reflects the affinity of a compound to soil organic carbon. The K_{oc} derived in this study ranged from 8.9×10^3 to 2.1×10^4 for triclosan and from 9.4×10^4 to 2.0×10^5 for triclocarban. To estimate the effect of biosolids on the sorption of triclosan and triclocarban, K_{oc} values from this and other studies were further calculated for three solid matrices: soils without biosolid amendment, soils amended with biosolids, and biosolids (**Figure 1**). Sorption to biosolids was estimated by subtracting K_d in biosolid-amended soil from that in the original soil, from which K_{oc} was then calculated. The estimated K_{oc} for biosolids ranged from 9.1×10^3 to 2.4×10^4 L kg⁻¹ for triclosan,^{9,21,22,24,25,30} and from 6.1×10^4 to 3.1×10^5 L kg⁻¹ for triclocarban (Figure 1).^{21,30} The variation in these values suggested that biosolids from different sources were drastically different in their physicochemical properties and hence their affinity for these compounds. The estimated K_{oc} in soils ranged from 939 to 4.1×10^4 L kg⁻¹ for triclosan, and from 4.5×10^3 to 2.0×10^5 L kg⁻¹ for triclocarban, while K_{oc} in biosolid-amended soils ranged from 4.0×10^3 to 2.4×10^4 L kg⁻¹ for triclosan, and from 5.9×10^3 to 1.5×10^5 L kg⁻¹ for triclocarban. After compiling the literature K_{oc} values and data from the current study, the median and mean K_{oc} values in both soils and biosolid-amended soils were 1.6×10^4 L kg⁻¹ and 1.5×10^4 L kg⁻¹, respectively, for triclosan, and 6.1×10^4 L kg⁻¹ and 7.6×10^4 L kg⁻¹, respectively, for triclocarban (**Figure 1**). Therefore, the median and mean K_{oc} values were generally similar

for each compound, suggesting a normal distribution of K_{oc} values across different studies.

It should be further noted that K_{oc} of triclosan in biosolid-amended soils was significantly higher ($p < 0.01$) than that in soils, while the difference was not significant ($p > 0.05$) for triclocarban, suggesting that amendment of biosolids generally would have a more pronounced enhancement in sorption of triclosan than triclocarban. The difference in sorption between triclosan and triclocarban may be attributed to differences in their hydrophobicity and pKa. The stronger hydrophobicity of triclocarban and higher pKa likely contribute to stronger interactions of triclocarban with soil minerals and organic matter than triclosan. It is likely that the stronger sorption of triclocarban to soil leaves relatively less chemical available for sorption by biosolids as compared to triclosan. However, the overall strong enhancement effect of biosolids on soil sorption implies that addition of biosolids to soil may result in lower chemical bioavailability and thus inhibit microbial degradation of these compounds in biosolid-amended soils.

3.3. Persistence in soils and biosolid-amended soils.

Degradation of triclosan and triclocarban was measured in the four soils and in soil A amended with biosolids at different rates. The dissipation of chemicals over time was well described by the first-order decay model and good fit ($r^2 \geq 0.88$) was consistently found for all treatments. In the four soils, $t_{1/2}$ ranged from 7 to 10 d for triclosan and from 74 to 101 d for triclocarban (Figure S3, **Table 2**), suggesting that each compound had similar stability in these soils and that triclocarban was much more persistent than triclosan under the same conditions. The $t_{1/2}$ in soils was generally in agreement with the findings from earlier studies^{9,21,23,24,31} where $t_{1/2}$ varied from 11.5 to 58 d for triclosan and from 87 to 231 d for triclocarban.

The addition of biosolids inhibited degradation of triclosan and triclocarban in soil and prolonged their persistence, and the inhibition was more pronounced for triclosan (Table 2). In

the soil with 2% biosolid amendment, $t_{1/2}$ of triclosan almost doubled, increasing from 9.7 d to 18.1 d. When the amendment rate was increased to 5 and 10%, $t_{1/2}$ of triclosan further increased to 31 d and 63.6 d, respectively. The persistence of triclocarban also increased with the rate of biosolid amendment, although the inhibition was more gradual and the effect of biosolids was statistically significant only in the soil amended with 10% biosolids. Inhibitory effects of biosolids were also observed in previous studies. For example, Kwon et al. conducted a microcosm study to determine the degradation of triclosan and triclocarban in a Marinetta fine loam and a McLaurin coarse loam. The $t_{1/2}$ of triclosan in the fine loam and coarse loam soils were 3 and 13 d, respectively, but increased to 50 and 108 d after addition of biosolids at 3.3%. The $t_{1/2}$ of triclocarban was not calculated in that study because more than 50% of the initial amount still remained after 100 d of incubation.²⁰ However, Wu et al. found that biosolid application had no appreciable effect on the degradation of triclosan or triclocarban.²¹ The difference may be attributed to the types of biosolids used in the studies. While Kwon et al. used solid biosolids, Wu et al. used liquid biosolids that contained organic carbon at relatively low levels.

The group comparison is summarized in Figure 2. Paired t -test of $t_{1/2}$ values from this and all published studies to date showed that biosolid amendment significantly enhanced the persistence of triclosan ($p < 0.01$), while the enhancement was not significant ($p > 0.05$) for triclocarban.^{9,20–24,26–29,31,33–35,37} When all available data were considered, the mean $t_{1/2}$ of triclosan is 13 d in soil or 50 d in a biosolid-amended soil, while an average $t_{1/2}$ for triclocarban is 84 d in soil.

3.4. Meta-analysis of biosolid effect on persistence.

To explore the dependence of persistence of triclosan and triclocarban on soil properties and

discern the influence of biosolids, linear regression analysis was performed on data from this and all relevant published studies. Previously published studies on triclosan and triclocarban did not always report $t_{1/2}$ and the corresponding soil OC (or OM) content, limiting the use of some published studies in this analysis. A weak, but statistically significant linear relationship ($r^2 = 0.16$, $p < 0.05$, $n = 25$)^{21,22,26–29,33,35,37} was observed between $t_{1/2}$ of triclosan and soil OC content in biosolid-amended soils, while no association ($r^2 = 0.06$, $p > 0.05$, $n = 16$)^{9,20,21,23,24,31} was detected in the unamended soils. For triclocarban, a significant correlation was found between $t_{1/2}$ and soil OC content in both unamended ($r^2 = 0.50$, $p < 0.05$, $n = 8$)^{20,21,23} and biosolid-amended soils ($r^2 = 0.37$, $p < 0.01$, $n = 18$)^{21,22,26,33–35}. Therefore, results from this and previous studies together demonstrated that biosolids generally exhibited a significant effect in inhibiting degradation or prolonging persistence of both triclosan and triclocarban in biosolid-amended soils, and that the change was underlined by increases in soil OC content brought upon through biosolid addition.

A meta-analysis was further performed on the interaction of $t_{1/2}$ and K_d before and after biosolid amendment. Correlation between $t_{1/2}$ and K_d values from this study showed a significant linear relationship ($p < 0.05$) in biosolid-amended soils for both compounds, while the relationship in the unamended soils appeared to be less apparent (Figure 3). After integrating data from this and all published studies, a significant relationship remained for both triclosan ($r^2 = 0.69$, $p < 0.01$)^{9,21,22,24,31} and triclocarban ($r^2 = 0.38$, $p < 0.05$)^{21,22} for biosolid-amended soils (Figure 3). The scattering may be partially attributed to the use of different experimental conditions, different biosolid types (e.g., solid vs. liquid), and different soil types in the range of studies considered. With increasing K_d due to biosolid addition, $t_{1/2}$ of both triclosan and triclocarban consistently increased, suggesting that the prolonged persistence in biosolid-amended soils was a

result of biosolid-induced increases in K_d , or that biosolids likely decreased the bioavailability of these compounds to soil microorganisms due to enhanced sorption.^{45,46}

Assuming typical biosolids contain 24% organic carbon,⁴⁷ amending soil with biosolids at 1% would result in an increase of 0.24% in soil OC content. Using the average K_{oc} values for triclosan (5.0×10^4) and triclocarban (2.5×10^5) in biosolids, addition of biosolids at 1% would increase a soil's K_d by 126 L kg^{-1} for triclosan, and 629 L kg^{-1} for triclocarban. When these K_d increments were used in the regression lines in Figure 3, changes in $t_{1/2}$ of triclosan and triclocarban were predicted (Figure 4). On the average, with every 1% increase in biosolid application rate, $t_{1/2}$ of triclosan would increase by 7.5 d, while that of triclocarban would be prolonged by 4.7 d. Given its relatively short persistence in unamended soils (average soil $t_{1/2} = 13 \text{ d}$), the enhancement effect of biosolids on the persistence of triclosan is extremely substantial.

4. Conclusions

Results from this and other studies together show that addition of biosolids greatly alters a soil's physicochemical properties, especially the soil OC content. Because of the dominant role of soil organic carbon in the sorption of triclosan and triclocarban, biosolid amendment consistently enhanced the sorption of these compounds in soil, and the effect was more pronounced for triclosan than triclocarban. As a consequence of the enhanced sorption from biosolid addition, degradation was inhibited or persistence was prolonged for these compounds in biosolid-amended soils, and the effect was also greater for triclosan. For triclosan, biosolids may increase $t_{1/2}$ from about two weeks in soil up to several months. The increased persistence in biosolid-amended soils implies an elevated potential for secondary pollution, including increased

plant accumulation, a higher leaching risk or a greater tendency for surface runoff. Such effects should be further evaluated and validated under field conditions using standard agronomic practices. In addition, the increased persistence due to biosolid amendment should be considered when assessing ecotoxicological risks or human exposure of triclosan and triclocarban. Moreover, as PPCPs vary greatly in their structures and properties, the overall validity of the inhibitory effect of biosolids should be considered also for other biosolid-borne PPCPs.

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Table 1. Physicochemical properties of different soils and biosolid-amended soils used in this study

Soil No.	Soil type	pH (H ₂ O)	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	Sandy loam	6.51	2.45	67	22	11	14.4
A ₁₀	Sandy loam	6.42	3.5	62	26	12	18
B	Sandy loam	7.67	0.5	73	13	14	18.5
C	Sandy clay loam	7.39	1.25	57	23	20	27
D	Sandy loam	7.23	0.86	71	15	14	18.2

^aTOC: total organic carbon; ^bCEC: cation exchange capacity; ^cA₂: soil A applied with 2% of biosolids; A₅: soil A applied with 5% of biosolids; A₁₀: soil A applied with 10% of biosolids.

Table 2. K_d (L kg⁻¹), K_{oc} , K_f (L kg⁻¹) and $t_{1/2}$ (d) of triclosan and triclocarban in different soils and biosolid-amended soils in this study

Soil	Triclosan					Triclocarban				
	K_d	K_{oc}	$t_{1/2}$ (d)	K_f	n	K_d	K_{oc}	$t_{1/2}$ (d)	K_f	n
A	35±4	0.89×10 ⁴	10±0.2	36	0.94	771±88	1.9×10 ⁵	74±34	689	0.95
A ₂	137±24 ^a	1.1×10 ⁴	18±2.25 ^a	128	0.85	1326±57	1.1×10 ⁵	90±1	1377	1.01
A ₅	311±31 ^b	1.3×10 ⁴	31±2.4 ^b	270	0.97	2318±201 ^a	0.94×10 ⁵	109±5	2204	0.97
A ₁₀	731±46 ^c	2.1×10 ⁴	63±8 ^c	668	0.95	5449±1330 ^b	1.5×10 ⁵	133±29 ^a	1685	0.71
B	46±4	0.93×10 ⁴	8±0.3	48	1.00	964±284	1.9×10 ⁵	82±20	970	1.00
C	170±13	1.4×10 ⁴	9±0.6	169	1.01	1476±109	1.2×10 ⁵	101±30	1516	1.02
D	65±3	0.76×10 ⁴	7±0.1	64	0.98	1248±82	1.5×10 ⁵	81±5	1195	0.99

^aSignificant at $p < 0.05$ as compared with unamended Soil A; ^bSignificant at $p < 0.01$ as compared with unamended Soil A; ^cSignificant at $p < 0.001$ as compared with unamended Soil A

Figure captions:

Figure 1. Distribution of K_{oc} values of triclosan and triclocarban in soils, biosolid-amended soils, and biosolids. (A) K_{oc} distribution of triclosan in soils ($n=22$),^{9,21,24,25,30,32,36} biosolid-amended soils ($n=24$),^{21,22,30} and biosolids ($n=9$);^{21,22,24,25,43} and (B) K_{oc} distribution of triclocarban in soils ($n=11$),^{21,30,32} biosolid-amended soils ($n=24$),^{21,22,30} and biosolids ($n=11$).^{9,21,30}

Figure 2. Distribution of half-life ($t_{1/2}$) values of triclosan and triclocarban in soils and biosolid-amended soils. (A) $t_{1/2}$ distribution of triclosan ($n=16$) in soils^{9,20,21,24,31,43} and biosolid-amended soils ($n=25$);^{20-22,26-29,33,35,37} (B) $t_{1/2}$ distribution of triclocarban in soils ($n=16$)^{20,21,24,43} and biosolid-amended soils ($n=18$).^{21,22,26,33-35}

Figure 3. Correlation of half-life ($t_{1/2}$) and K_d of triclosan and triclocarban in soils and biosolid-amended soils. (A) Triclosan in soils ($n=21$);^{9,21,24,31} (B) Triclosan in biosolid-amended soils ($n=14$);^{21,22} (C) Triclocarban in soils ($n=14$);^{21,22} and (D) Triclocarban in biosolid-amended soils ($n=14$).^{21,22}

Figure 4. Predicted response of persistence (half-life $t_{1/2}$) to biosolid amendment rate (% , w/w) of triclosan and triclocarban in biosolid-amended soils.

Figure 1

Figure 2

Figure 3

Figure 4