Environmental Pollution 210 (2016) 137–144

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Meta-analysis of biosolid effects on persistence of triclosan and triclocarban in soil

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ARTICLE INFO

Article history:
Received 8 September 2015
Received in revised form
29 November 2015
Accepted 2 December 2015
Available online xxx

Handling Editor: Baoshan Xing

Keywords:
Biosolids
Triclosan
Triclocarban
PPCPs
Bioavailability

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 PPCPs 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.

1. Introduction

Biosolids are extensively used in agriculture as fertilizers, concurrently serving as an important mean 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. (United States Environmental Protection Agency, 1999; United States Environmental Protection Agency, 2009) However, studies show that many pharmaceuticals and personal care products (PPCPs), such as triclosan and triclocarban, are concentrated in biosolids. (United States Environmental Protection Agency, 2009; McClellan and Halden, 2010; Heidler et al., 2006; Cha and Cupples, 2009) 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. (Prosser et al., 2014; Wu et al., 2010; Sabourin et al., 2012) The potential for secondary pollution depends on a chemical's availability in soil, which is a function of dissipation or half-life ($t_{1/2}$). (Xu et al., 2009a; Semple et al., 2013; Roberts et al., 2007) Biosolid amendment may induce different effects on the persistence of PPCPs. On the 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

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http://dx.doi.org/10.1016/j.envpol.2015.12.003
0269-7491/

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. (Halden and Paull, 2005; Yueh et al., 2014; Kwon and Xia, 2012) Due to their widespread use, triclosan and triclocarban are frequently detected in biosolids, often in the mg kg^{-1} range. (United States Environmental Protection Agency, 2009; McClellan and Halden, 2010; Heidler et al., 2006; Cha and Cupples, 2009) Research shows that triclosan and triclocarban may induce developmental, carcinogenic or other chronic toxicities to human and other non-target organisms. (Udoji et al., 2010; Dinwiddie et al., 2014; Chung et al., 2011; Anger et al., 2013; Buth et al., 2010) 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. (Kwon et al., 2010) 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. (Wu et al., 2009) 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 (Xu et al., 2009a; Kwon et al., 2010; Wu et al., 2009; Cha and Cupples, 2010; Ying et al., 2007; Xu et al., 2009b; Waller and Kookana, 2009; Higgins et al., 2011; Lozano et al., 2012; Langdon et al., 2011; Waria et al., 2011; Agyin-Birikorang et al., 2010; Carter et al., 2014; Barron et al., 2009; Chen et al., 2014a,b; Al-Rajab et al., 2015; Karnjanapiboonwong et al., 2010; Butler et al., 2012) 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 A_2), 5% (Soil A_5), and 10% (Soil A_{10}) on a dry mass basis (w/w). The water holding capacity of each soil was measured using the pressure chamber method. (Gardner, 1986) 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. (United States Environmental Protection Agency, 1992; Huang et al., 2011) The higher rates were used to facilitate regressional 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. (Organization for Economic, 2000) 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 $CaCl_2$ solution containing 0.2% NaN_3 (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 2000 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. (Kwon et al., 2010; Cha and Cupples, 2010; Ying et al., 2007) 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-μm polytetrafluoroethylene (PTFE) filter membrane (Millipore, Carrigtwohill, Cork, Ireland) and then stored at −20 °C before instrumental analysis.