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Dissipation of triclosan, triclocarban, carbamazepine and naproxen in agricultural soil following surface or sub-surface application of dewatered municipal biosolids

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HIGHLIGHTS

- We characterized the soil fate of four organic contaminants carried in biosolids.
- Biosolids were placed on the soil surface or incorporated within the soil profile.
- Naproxen, triclosan and triclocarban were dissipated more rapidly when incorporated.
- Depth of placement did not influence the rate of carbamazepine dissipation.
- Soil incorporation of biosolids will result in more rapid dissipation of contaminants.

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ABSTRACT

In many jurisdictions land application of municipal biosolids is a valued source of nutrients for crop production. The practice must be managed to ensure that crops and adjacent water are not subject to contamination by pharmaceuticals or other organic contaminants. The broad spectrum antimicrobial agents triclosan (TCS) and triclocarban (TCC), the anti-epileptic drug carbamazepine (CBZ), and the nonsteroidal anti-inflammatory drug naproxen (NAP) are widely used and are carried in biosolids. In the present study, the effect of biosolids and depth of placement in the soil profile on the rates of TCS, TCC, CBZ, and NAP dissipation were evaluated under semi-field conditions. Aggregates of dewatered municipal biosolids (DMBs) supplemented with ^{14}C-labeled residues were applied either on the soil surface or in the subsurface of the soil profile, and incubated over several months under ambient outdoor conditions. The dissipation of TCS, TCC and NAP was significantly faster in subsurface than surface applied biosolid aggregates. In contrast the dissipation rate for CBZ was the same in surface applied and incorporated aggregates. Overall, the present study has determined a significant effect of depth of placement on the dissipation rate of biodegradable molecules.

1. Introduction

Municipal biosolids contain a wide range of pharmaceuticals and personal care products (PPCP) that persist and that partition into the organic fraction during the wastewater treatment process (McClellan and Halden, 2010; USEPA, 2009). Many jurisdictions permit the use of biosolids as a source of crop nutrients and valued soil conditioner in commercial agriculture (O'Connor et al., 2005; Requirements for application of prescribed materials, 2013; Service Ontario *eLaws*, 2014). Following application to land, there is potential for transport of PPCP residues to adjacent surface or shallow groundwater through surface runoff, leaching, or preferential flow (Edwards et al., 2009; Gottschall et al., 2012; Topp et al., 2008b). There is also a potential for crop uptake of PPCPs, although management practices such as a one-year delay between application and harvest of crops for human consumption result in negligible uptake (Prosser et al., 2014; Sabourin et al., 2012). Contamination of water or crops with PPCP residues is of concern with respect to human and environmental health (Boxall et al., 2012).

The persistence of PPCP residues in soil following biosolid application is the key factor limiting the opportunity for the contamination of

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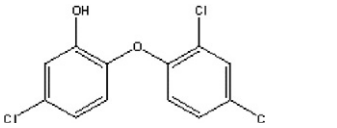
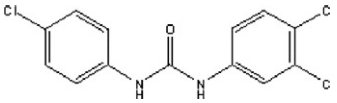
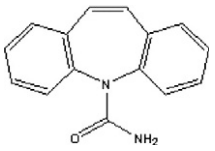
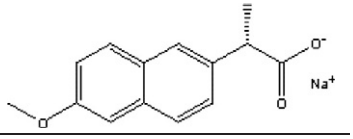
Table 1
Structure and key properties of the chemicals evaluated in this study (Chu and Metcalfe, 2007; Sabourin et al., 2009; Ying et al., 2007).

Compound CAS # formula	M.W	Solubility (mg L^{-1})	Log K_{ow}	p*Ka*	Structure
Triclosan 3380-34-5 5-chloro-2-(2,4-dichlorophenoxy)-phenol	289.5	4.621	4.7	8.1	
Triclocarban 101-20-2 3,4,4′-trichlorocarbanilide	315.6	0.6479	4.9	n/a	
Carbamazepine 000298-46-4 5H-dibenzo[b,f]azepine-5-carboxamide	236.3	17.7	2.45	14	
Naproxen 022204-53-1 (2S)-2-(6-methoxynaphthalen-2-yl)propanoic acid	230.3	15.9	3.18	4.15	

crops or adjacent water. Persistence of a PPCP is governed by its inherent recalcitrance, soil composition and physical and chemical properties, and climate factors such as moisture and temperature. Another key set of factors are the composition of the biosolids PPCP residues are entrained in, and how they are applied and incorporated into soil. Biosolids vary widely in their moisture content, ranging from slurry (liquid municipal biosolids; LMBs) with over 95% moisture content to dewatered cake (dewatered municipal biosolids; DMBs) with typically about 70% moisture content. The former is handled and applied as a liquid, whereas the latter is applied as a solid. The LMB is typically surface applied followed by incorporation, or injected directly into the soil profile (Topp et al., 2008b). The DMB is typically surface applied followed by incorporation, but equipment exists (Terratec Environmental Ltd., dewatered biosolids direct injection system) that can deposit extruded DMB directly into the soil profile (Edwards et al., 2009).

In previous semi-field studies we found the application matrix to have very significant effects on the dissipation kinetics and pathways of triclosan (TCS) and triclocarban (TCC) added directly to soil in water, carried in LMB, or carried in DMB (Al-Rajab et al., 2009). These two biocides are typically carried in biosolids at mg per kg dry weight concentrations (McClellan and Halden, 2010; Sabourin et al., 2012; USEPA, 2009). The dissipation of ^{14}C-triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol; Table 1), was found to be significantly more persistent when carried in aggregates of dewatered biosolids applied to the soil surface, than when incorporated into soil via application of either liquid municipal biosolids or water (Al-Rajab et al., 2009). In contrast, ^{14}C-triclocarban (3,4,4′-trichlorocarbanilide; Table 1) was found to be equally persistent regardless of how it was applied to soil (Al-Rajab et al., 2009). It was hypothesized that TCS is amenable to biodegradation by soil microorganisms and therefore incorporation promoting contact with soil was a key factor in the kinetics of dissipation. In contrast, TCC is inherently more recalcitrant to biodegradation, and therefore dissipation will not be influenced by the degree of incorporation and enhanced soil contact.

The present study sought to further explore the effect and significance of soil–biosolids contact on experimentally determined persistence kinetics and pathways. In a typical DMB application, the bulk of the aggregates is incorporated within the soil profile by tillage within 24 h of application. Inevitably some DMB aggregates will be left on the soil surface where they are vulnerable to weathering and precipitation-driven surface runoff. We thus evaluated the impact of surface versus sub-surface aggregate placement on PPCP persistence using radioisotope methods. In addition to ^{14}C-TCS and ^{14}C-TCC, we evaluated the dissipation of ^{14}C-carbamazepine (5H-dibenz(b,f)azepine-5-carboxamide; CBZ; Table 1) and ^{14}C-naproxen (2-(6-methoxy-2-naphthyl)propionic acid; NAP; Table 1). The anti-seizure medication CBZ is a commonly prescribed drug for the treatment of epilepsy, and is used in the treatment of bipolar disorder (WHO, 2013). In Canada, an estimated 21–25 tons are prescribed annually (McLaughlin and Belknap, 2008). The nonsteroidal anti-inflammatory drug NAP is widely used for the treatment of pain and swelling associated with arthritis, gout, and other inflammatory conditions. In Canada, an estimated 53–62 tons are sold annually (McLaughlin and Belknap, 2008). Based on previous experience, we anticipated that CBZ would be persistent, and NAP rapidly dissipated in soil under permissive conditions (Li et al., 2013; Topp et al., 2008a).

Our specific objectives in the present study were to: 1. Determine the impact of surface or subsurface soil placement of DMB aggregates on the dissipation kinetics of several PPCPs that commonly occur in biosolids (TCS, TCC, CBZ, and NAP) in outdoor conditions. 2. By using radioisotope methods, measure various dissipation pathways including non-extractable residue formation. 3. Determine if the rate of dissipation in surface-applied aggregates was rate-limited by mass loss through weathering.

2. Materials and methods

2.1. Chemicals

Triclosan, triclocarban, carbamazepine, naproxen, 3,4-dichloroaniline and 3-chloroaniline, carbamazepine10,11-epoxide, radiolabeled TCS (4′-chloro-2′-hydroxyphenyl-UL-^{14}C; purity >99%, specific activity 74 MBq $mmol^{-1}$), radiolabeled TCC (3,4-dichlorophenyl-ring-UL-^{14}C; purity >99%; specific activity 828.8 MBq $mmol^{-1}$), and radiolabeled CBZ (Carbamazepine-carbonyl-^{14}C; purity >99%; specific activity 836.2 MBq $mmol^{-1}$) were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). Radiolabeled NAP (naproxen[O-methyl-^{14}C]; purity >99%; specific activity 2035 MBq $mmol^{-1}$) was purchased from ARC (St. Louis, MO, USA). Methyltriclosan (Me-TCS; 5-chloro-2-(2,4-dichlorophenoxy)anisole) was purchased from Wellington Laboratories Inc. (Guelph, ON). Stock solutions of ^{14}C-labeled (final radioactive concentrations were 10.14; 12; 19.01 and 9.15 KBq 100 μL^{-1} for TCS, TCC, CBZ and NAP respectively) and unlabeled (1 mg mL^{-1}) chemicals were prepared in methanol and stored at 4 °C until used in experiments.