

**PERFLUOROALKYL ACIDS AND OTHER TRACE ORGANICS IN WASTE-
DERIVED ORGANIC PRODUCTS: OCCURRENCE, LEACHABILITY, AND PLANT
UPTAKE**

by

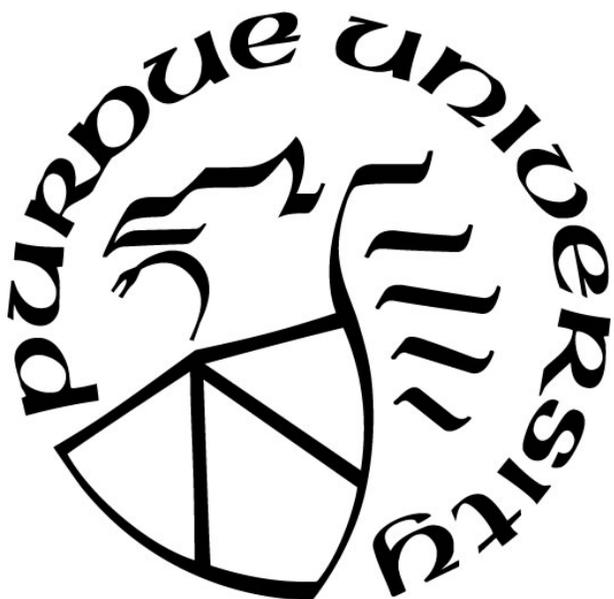
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To my family for unconditional love and support

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ABSTRACT

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Title: Perfluoroalkyl Acids and Other Trace Organics in Waste-Derived Organic Products:
Occurrence, Leachability, and Plant Uptake

Committee Chair: Dr. Michael L. Mashtare

Waste-derived organic products are nutrient-rich materials often applied to agricultural land as a fertilizer to enhance agricultural production and soil quality. Commercially available biosolid-based products, which are sold and distributed in bags or bulk, are rapidly gaining popularity for urban and suburban use. Although biosolid-derived products have many benefits, they may contain trace organic contaminants such as per- and polyfluoroalkyl acids (PFAAs) and pharmaceutical and personal care products (PPCPs), in varying levels, depending on waste source composition. These organic compounds have been used in a variety of consumer and industrial products and are known to accumulate in biosolids due to their recalcitrance in conventional wastewater treatment processes. Thus, the application of commercially available biosolids-based products on urban and suburban gardens may lead to transfer and accumulation of organic contaminants into food crops, raising food safety concerns. Most studies to date have focused on municipal biosolids application on agricultural lands with very few studies focused on commercial products available for home and urban gardens. For the latter, the evaluations of bioavailability and subsequent plant uptake of organic contaminants from biosolids have also often been conducted by adding organic contaminants to the growing media (e.g., soil or hydroponic) at a concentration that greatly exceed environmentally relevant concentrations. Moreover, there are currently no studies evaluating leaching and plant uptake potential of contaminants from commercially available (e.g., local stores) biosolids. The research described in this dissertation 1)

assessed the occurrence of PFAAs and representative PPCPs in commercially available biosolid-based products and their porewater concentrations in saturated media as a measure of bioavailability and leachability; 2) investigated how heat-treatment, composting, blending and thermal hydrolysis processes on biosolids to convert them to commercial biosolid-based products affect PFAA concentrations in the production of commercial biosolid-based product; and 3) assessed the bioavailability and plant uptake of PFAAs and targeted PPCPs by kale and turnips grown in soil-less potting media amended with Milorganite (a commercially available biosolids-based fertilizer product) at the recommended rate and four times the recommended rate.

The biosolid-based products displayed varying levels of organic contaminants. Higher PFAA concentrations were detected in biosolid-based products compared to nonbiosolid-based products. The common treatment processes used in taking biosolids to commercially available products were ineffective in reducing PFAA levels in the products except for blending with other essentially PFAA-free materials, thus served as a simple dilution. Porewater concentrations of PFAAs and PPCPs as an indicator of leachability and bioavailability were higher for the less hydrophobic compounds (e.g., short-chain PFAAs and diphenhydramine and carbamazepine with lower octanol-water partition coefficient). Leachability alone did not explain the observed plant uptake potential of PFAAs and PPCPs. With similar leachability and molecular weight/size between diphenhydramine and carbamazepine, higher uptake was observed with a positively charged compound (diphenhydramine compared to a neutral compound (carbamazepine). However, not all positively charged compounds were taken up by the plant. Azithromycin, a positively charged compound, had lower uptake than other contaminants which may be due to its large molecular size compared to diphenhydramine. Higher concentrations of miconazole, triclosan, and triclocarban were found in the biosolids-fertilizer; however, these compounds had

low leachabilities and limited uptake by plants. Also, for PPCPs, the application rates of biosolid-based products did not necessarily correlate with the higher uptake and translocation of contaminants to the above-ground portion of plants.

This study provides an evaluation of commercially available waste-derived organic products under condition comparable to home and urban garden setting. Although biosolids-based products can serve as alternatives to synthetic fertilizers, they contain higher levels of trace organic contaminants than nonbiosolid-organic products. Common biosolids treatment processes are ineffective for reducing the levels of trace organic contaminants in biosolids, particularly for PFAAs. Thus, it is critical to control the sources contributing to the higher level of these contaminants in biosolids-based products. Also, regulations (e.g., triclosan and triclocarban) and replacements (e.g., longer-chain PFAAs to short-chain PFAAs) of persistent trace organic chemicals have led to a reduction in their levels in biosolids-based products. Although longer chain PFAAs are more likely to bioaccumulate and persistent than the replacement short-chain alternatives, the current study has shown that the short-chain PFAAs are more readily taken up to edible parts of plants than longer-chain PFAAs even when applying at the recommended fertilizer rate. Thus, the current movement to replace longer chain PFAAs with short chains has the potential to result in higher total PFAA concentrations being bioavailable for plant uptake, thus increasing the risk of food contamination by PFAAs.

CHAPTER 1. INTRODUCTION

1.1 Introduction

The global urban population is expected to rapidly increase to 8.5 billion by 2030. More than half of the worldwide population is expected to live in urban areas (United Nations, 2015). While urbanization can promote social and economic development, including better access to healthcare, education, and employment (Meacham, 2014), it can also lead to environmental pollution, food insecurities, and natural resource limitations. Increased urbanization, along with population growth and improved economic status, is putting more pressure on available water and natural resources for food production and distribution. Exploring alternatives for growing food is necessary to alleviate pressure on natural resources to meet current and future food demand.

Biosolids are increasingly recognized as important resources in food production. Land application of biosolids has been demonstrated to be a viable method of waste disposal by adding organic matter and nutrients, and thus improving soil quality and supporting plant health (Sánchez-Monedero et al., 2004). A previous study by McIvor et al., (2012) showed that commercially available biosolids-based fertilizer and composts can be an important resource for improving urban soil for urban agriculture (McIvor et al., 2012). Despite these benefits, the beneficial use of biosolids are constantly challenged by questions related to contaminants remaining after wastewater treatment processes. Urbanization has resulted in rapid increases in the historical and projected influent wastewater flow from the U.S. population (**Figure 1-1**). This is leading to increased effluent discharge into the environment and an increase in the amount of biosolids and associated loads of organic contaminants (often referred to as trace organic) that have to be managed (Lu et al., 2012; Sato et al., 2013). Therefore, while biosolids have the potential to

facilitate more local food production, alleviating food insecurity in urban areas, research on the occurrence and impacts of trace organics on human and ecosystem health is needed.

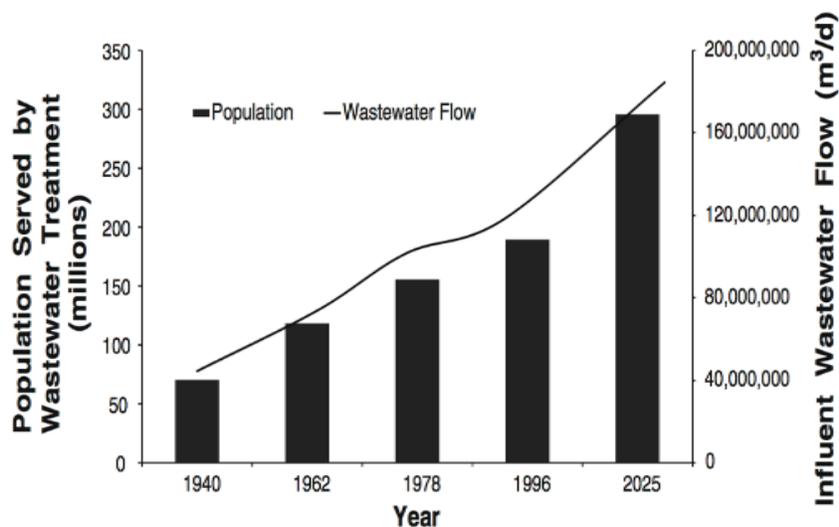


Figure 1-1. Historical and projected influent wastewater flow from the U.S. population by wastewater treatment. Adapted from Richard et al. (2009).

A number of studies have reported that organic contaminants, such as pharmaceutical and personal care products (PPCPs) and per- and polyfluoroalkyl substances (PFAS), have been detected in biosolids (Andrade et al., 2015; Brose et al., 2019; Eriksson et al., 2017; Semblante et al., 2015; Venkatesan & Halden, 2013). For example, the survey results of 72 PPCPs in municipal biosolids analysis from 94 wastewater treatment plants in 32 states (total 110 biosolids sample) showed that azithromycin (838 $\mu\text{g}/\text{kg}$), carbamazepine (238 $\mu\text{g}/\text{kg}$), diphenhydramine (1,740 $\mu\text{g}/\text{kg}$), miconazole (777 $\mu\text{g}/\text{kg}$), triclosan (12,640 $\mu\text{g}/\text{kg}$) and triclocarban (36,060 $\mu\text{g}/\text{kg}$) were present in relatively high concentrations and frequently detected in municipal biosolids (McClellan & Halden, 2010) (**Figure 1-2**). Also, the targeted PPCP contaminants are persistent in the environment with reported half-lives range from 187 days to more than 1,000 days in soils amended with biosolids (Walters et al., 2010).

In biosolids composite samples representing 32 U.S. States and the District of Columbia, perfluorooctane sulfonate (PFOS) was detected in the highest concentration (403 $\mu\text{g}/\text{kg}$), followed by perfluorooctanoic acid (PFOA; 34 $\mu\text{g}/\text{kg}$) and other PFAAs (3.4-9.2 $\mu\text{g}/\text{kg}$) (Venkatesan & Halden, 2013).

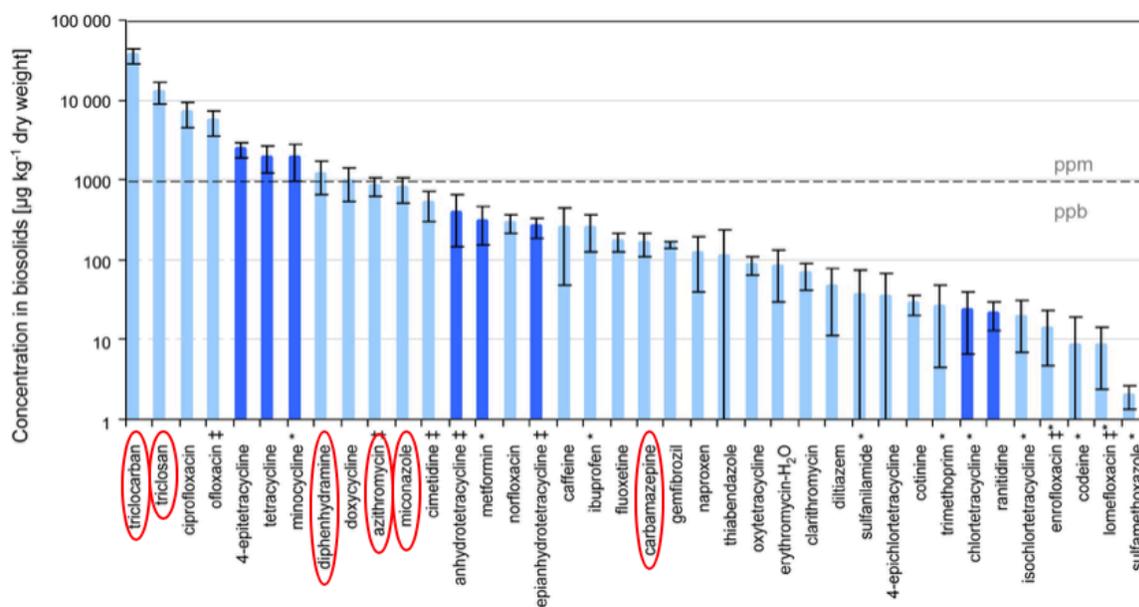


Figure 1-2. The rank order of mean concentration of pharmaceuticals in composites of a total 110 biosolids samples from 94 wastewater treatment plants in 32 states and the District of Columbia in the U.S. Adapted from McClellan and Halden (2010). Circles indicate PPCPs targeted in this study.

A 3-year outdoor mesocosm study of biosolids-soil mixtures showed ‘half-lives’ of PFAAs ranging from 385 to 866 days (Venkatesan & Halden, 2014). PFAAs are very persistent in the environment with no known natural degradation pathway; therefore, half-life in this context does not mean degradation but dissipation, which includes leaching, volatilization, and irreversible binding processes (Venkatesan & Halden, 2014). Due to their occurrence and persistence in biosolids and their unique physiochemical properties (e.g., high mobility), these organic contaminants have been detected in food crops grown in agricultural soil amended with municipal

biosolids (Blaine et al., 2014; Navarro et al., 2017; Sabourin et al., 2012). Examples of plant uptake for a representative set of organic compounds found in biosolids and are summarized in **Table 1**.

While many studies have addressed the environmental and human health impact of using municipal biosolids in an agricultural setting, studies on the occurrence, leachability and plant uptake potential of PFAS and PPCPs from waste-derived organic products used in home or urban gardens are not available. Application of biosolids in urban and suburban gardens may lead to higher risks of uptake and accumulation of PFAS and PPCPs in food crops because less soil or soilless media may be used in these settings. Therefore, there is a need to evaluate if they pose a risk to the urban ecosystem and human health, and if so, how they can be managed such that biosolids-based products may continue to serve beneficial purposes.

Among a myriad of trace organic contaminants, including a subset of PFAS (17 PFAAs, C4-C18) and PPCPs (Azithromycin, carbamazepine, diphenhydramine, miconazole, triclosan, and triclocarban) were selected for this dissertation research based on relatively high concentrations in biosolids and persistence after entering the environment (McClellan & Halden, 2010; Walters et al., 2010). Also, target compounds include neutral, anionic and ionizable in the environmentally relevant pH range. Ionizable compounds can exist in neutral, positively or negatively charged species depending on the pK_a (the acid dissociation constant) of the compound and the pH of the environmental matrix. For example, azithromycin (dicationic with pK_a of 8.74 or 9.45), diphenhydramine (pK_a of 9.0) and miconazole (pK_a of 6.65) are partially cationic and neutral while triclosan (pK_a of 7.8) is partially anionic at pH 7. Physiochemical properties, structures, reported half-lives (Tables 1-2 and 1-3) and concentrations reported in influent, effluent and biosolids of contaminants (Tables 1-4) assessed in this study are summarized in tables from literature reviews. These compounds have been shown to affect aquatic or terrestrial organisms adversely. In the case

of antibiotics and antimicrobials, the development of microbial resistance, as well as growth inhibition, has been exemplified (**Table 1-4**). Research on the risk of long-term exposure of contaminants (or a mixture of contaminants) to human and wildlife, including aquatic species is still limited and ongoing.

Table 1-1. Concentration of the example organic contaminants reported in plants grown in a subset of greenhouse and field studies using biosolids to enhance nutrients and organic matter.

Compound	Experimental setting (Initial concentration)	Concentration (μgkg^{-1}) in plant or soil (d.w.)	Refs.
Azithromycin	Field study Biosolids application (228 μgkg^{-1})	Winter wheat, $\text{kernel} < 15^*$	(N. Gottschall et al., 2012)
Azithromycin	Field study Biosolids application (213 μgkg^{-1})	Corn, $\text{kernel} < 1.92^*$; Carrot, $\text{root} < 2.43^*$; Tomato, $\text{fruit} < 4.22^*$; Potato, $\text{fruit} < 1.19^*$	(Sabourin et al., 2012)
Carbamazepine	Greenhouse - Pot study Biosolids-amended soil (93.1 μgkg^{-1})	Cabbage, $\text{aerials} : 317.6$ Cabbage, $\text{root} : 416.2$	(Holling et al., 2012)
Carbamazepine	Greenhouse - Pot study 1. Spiked Hoagland solution (10 μgL^{-1}) 2. Spiked biosolids (10 mgkg^{-1} d.w.)	Irrigation: First/second harvesting (60, 120 days) Soil = 0.7/1.1; Soybean, $\text{root} = 3.3/2.4$; Soybean, $\text{stem} = 1.37/0.6$; Soybean, $\text{leaf} = 3.4/1.9$; Soybean, $\text{fruit} = \text{not collected/n.d.}$ Biosolids application: First/second harvesting (60, 120 days) Soil = 49/44.2; Soybean, $\text{root} = 153/127$; Soybean, $\text{stem} = 27.3/33.5$; Soybean, $\text{leaf} = 216/110$; Soybean, $\text{fruit} = \text{not collected/n.d.}$	(C. Wu et al., 2010)
Carbamazepine	Spiked pot study (1 mgkg^{-1})	Radish, $\text{leaf} = 43,000$; Radish, $\text{bulb} = 8,000$; Ryegrass = 30,000	(Carter et al., 2014)
Carbamazepine	Field study Biosolids application (183 μgkg^{-1})	Winter wheat, $\text{kernel} < 1.5^*$	(N. Gottschall et al., 2012)
Carbamazepine	Field study Biosolids application (213 μgkg^{-1})	Corn, $\text{kernel} < 1.92^*$; Carrot, $\text{root} < 2.43^*$; Tomato, $\text{fruit} < 4.22^*$; Potato, $\text{fruit} < 1.19^*$	(Sabourin et al., 2012)

Diphenhydramine	Greenhouse - Pot study 1. Spiked Hoagland solution (10 µg ^L ⁻¹) 2. Spiked biosolids (10 mgkg ⁻¹ d.w.)	Irrigation: First/second harvesting (60, 120 days) Soil = 0.8/0.9; Soybean, root = 2.0/1.8; Soybean, stem = n.d/n.d; Soybean, leaf = n.d/n.d; Soybean, fruit = not collected/n.d. Biosolids application: First/second harvesting (60, 120 days) Soil = 43.0/46.6; Soybean, root = 26.2/17.8; Soybean, stem = 7.8/4.8; Soybean, leaf = 6.3/7.2; Soybean, fruit = not collected/n.d.	(C. Wu et al., 2010)
Diphenhydramine	Field study (research station) Biosolids application Spiked (100 mgkg ⁻¹ d.w.)	Pepper, root = 12; Pepper, shoot = 15; Pepper, fruit = 16 Collard, root = 8; Collard, shoot = 7; Collard, fruit = 0 Lettuce, root = 10; Lettuce, shoot = 8; Lettuce, fruit = 0 Radish, root = 5; Radish, shoot = 8; Radish, fruit = 0 Tomato, root = 5; Tomato, shoot = 9; Tomato, fruit = 22	(Choi et al., 2019; C. Wu et al., 2012)
Miconazole	Field study Biosolids application (n.a.)	Corn, stalk <0.76*; Corn, kernel <0.76*; Wheat, stalk <0.76*; Wheat, kernel <0.76*; Soil = 5.3	(Chen et al., 2013b)
Miconazole	Field study Biosolids application (341 µgkg ⁻¹)	Winter wheat, kernel <1.5*	(N. Gottschall et al., 2012)
Miconazole	Field study Biosolids application (213 µgkg ⁻¹)	Corn, kernel <2.17*; Carrot, root < 2.52*; Tomato, fruit <9.50*; Potato, fruit <1.19*	(Sabourin et al., 2012)
Triclocarban	Greenhouse - Pot study 1. Spiked Hoagland solution (10 µg ^L ⁻¹) 2. Spiked biosolids (10 mgkg ⁻¹ d.w.)	Irrigation: First/second harvesting (60, 120 days) Soil = 1.4/2.4; Soybean, root = 7.4/7.1; Soybean, stem = 7.06/4.8; Soybean, leaf = 5.9/14.9; Soybean, fruit = not collected/4.0 Biosolids application: First/second harvesting (60, 120 days) Soil = 73.9/82.5; Soybean, root = 126/168; Soybean, stem = 35.57/16.5; Soybean, leaf = 7.1/37.6; Soybean, fruit = not collected/2.6	(C. Wu et al., 2010)
Triclocarban	Field study Biosolids application (213 µgkg ⁻¹)	Corn, kernel <3.84*; Carrot, root < 4.87*; Tomato, fruit <8.43*; Potato, fruit <2.38*	(Sabourin et al., 2012)

Triclocarban	Field study Biosolids application (4,940 μgkg^{-1})	Winter wheat, kernel <3*	(N. Gottschall et al., 2012)
Triclosan	Greenhouse - Pot study Biosolids-amended soil (433.7 μgkg^{-1})	Cabbage, aerals = 41.1; Cabbage, root = 1519.7	(Holling et al., 2012)
Triclosan	Spiked pot study (1 mgkg^{-1})	Radish, leaf = 900; Radish, bulb = 1,000; Ryegrass = 2,000	(Carter et al., 2014)
Triclosan	Greenhouse - Pot study 1. Spiked Hoagland solution (10 μgL^{-1}) 2. Spiked biosolids (10 mgkg^{-1} d.w.)	Irrigation: First/second harvesting (60, 120 days) Soil = nd/nd; Soybean, root = 16.9/24.2; Soybean, stem = 10.1/58; Soybean, leaf = 13.7/80.1; Soybean, fruit = not collected/35.8 Biosolids application: First/second harvesting (60, 120 days) Soil = 12.8/13.2; Soybean, root = 28.9/76.8; Soybean, stem = 17.1/120; Soybean, leaf = 7.1/37.6; Soybean, fruit = not collected/12.6	(C. Wu et al., 2010)
Triclosan	Field study Biosolids application (10,900 μgkg^{-1})	Winter wheat, kernel <60*	(N. Gottschall et al., 2012)
Triclosan	Field study Biosolids application (213 μgkg^{-1})	Corn, kernel <78.80*; Carrot, root < 100.10*; Tomato, fruit <174.25*; Potato, fruit <48.83*	(Sabourin et al., 2012)
PFAAs (12 compounds)	Greenhouse – Pot study Biosolids-amended soil (PFOS: 28.20 μgkg^{-1} ; PFHxA: 4.77 μgkg^{-1} ; PFBA: 34.25 μgkg^{-1})	PFOS: Tomato, root = 1.17; Tomato, stem = 0.24; Tomato, leaf = 0.65; Tomato, fruit = 0.03 PFHxA: Tomato, root = 1.75; Tomato, stem = 3.11; Tomato, leaf = 12.14; Tomato, fruit = 6.39 PFBA: Tomato, root = N.D.; Tomato, stem = 6.19; Tomato, leaf = 38.07; Tomato, fruit = 12.45	(Navarro et al., 2017)

PFAAs (12 compounds)	Field study Biosolids application (total PFAAs: 41.4 - 220 μgkg^{-1})	Wheat, _{root} = 140-472; Wheat, _{straws} = 36.2-178; Wheat, _{husks} = 6.15-37.8; Wheat, _{grains} = 7.32-35.6 (Total PFAAs)	(Wen et al., 2014)
PFAAs (10 compounds)	Greenhouse – Pot study Biosolids-amended soil (PFOS: 319.49 μgkg^{-1} ; PFHxA: 2.40 μgkg^{-1} ; PFOA: 14.91 μgkg^{-1})	PFOS: Celery, _{shoot} = 17.21; Radish, _{root} = 21.03; Pea, _{fruit} <0.14 PFHxA: Celery, _{shoot} = 7.19; Radish, _{root} = 7.30; Pea, _{fruit} <0.71 PFOA: Celery, _{shoot} = 1.99; Radish, _{root} = 8.11; Pea, _{fruit} <0.07	(Blaine et al., 2014)

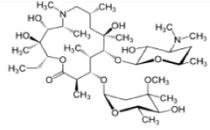
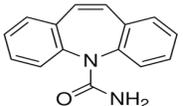
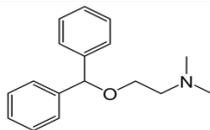
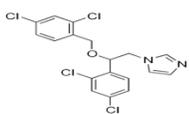
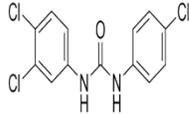
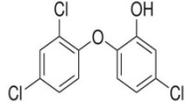
*Detected lower than the detection limits

d.w. = dried weight

n.d = not detected.

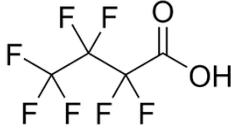
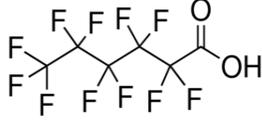
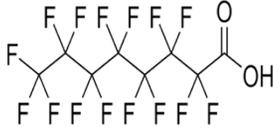
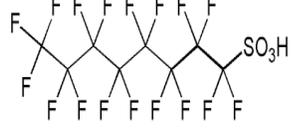
n.a = not applicable

Table 1-2. Physicochemical properties of selected PPCPs in this study.

	Azithromycin	Carbamazepine	Diphenhydramine	Miconazole	Triclocarban	Triclosan
Structure						
Formula	C ₃₈ H ₇₂ N ₂ O ₁₂	C ₁₅ H ₁₂ N ₂ O	C ₁₇ H ₂₁ NO	C ₁₈ H ₁₄ Cl ₄ N ₂ O	C ₁₃ H ₉ Cl ₃ N ₂ O	C ₁₂ H ₇ Cl ₃ O ₂
Use	Antibiotics	Anticonvulsant	Antihistamine	Antifungal	Antimicrobial	Antimicrobial
MW (g/mol)	748.996	236.269	255.355	416.14	315.582	289.542
pK _a	8.74 ^a	13.9 ^b	9.0 ^m	6.65 ^d	12.7 ^e	7.8 ^e
Log K _{ow}	4.02 ^f	2.45 ^g	2.94 (at pH 8) ^m	6.25 ^d	4.90 ^h	4.76 ^g
Log K _{oc} (L/kg)	3.496 ⁱ	3.6 ^j	3.92 ^m	4.834 ^k	3.732 ^l	4.265 ^l
Vapor pressure (mmHg, 25 °C)	-	1.8 x 10 ^{-7g}	3.6 x 10 ⁻² (at 20 °C) ^c	1.77 x 10 ⁻¹⁰ⁿ	3.61 x 10 ^{-9l}	6.45 x 10 ^{-7g} 4.65 x 10 ^{-6l}
Henry's Law Constants (atm*m ³ /mole)	5.3 x 10 ⁻²⁹ⁱ	1.08 x 10 ^{-10o}	-	-	4.52 x 10 ^{-11h}	2.13 x 10 ^{-8h}
Solubility (mgL ⁻¹ , 25 °C)	0.062 ⁱ	112 ^g	362.7 ^m	<1.03 ^p	0.648 ^l	10 ^g 4.621 ^l
Half-life (Dissipation)	85.52 ± 56.64 d in aerobic soil ^q 770 ± 181 d in biosolids-amended soil ^r	126 d ^j & 60 d in soil ^s ; 495 ± 36 in biosolids-amended soil ^r	88 ± 28 in clay loam soil ^u 335 ± 145 in loam soil ^u	1156 ± 198 d ^r ; 347 d ^t in biosolids-amended soil	108 d ^l & 87-231 d ^v in soil; >1,000 d in biosolids-amended soil ^r	18 d ^l , 120 d ^j & 20-58 ^v in soil; 187 ± 6 d in biosolids-amended soil ^r

^a (McFarland et al., 1997); ^b (Bui & Choi, 2010); ^c (Prosser et al., 2014); ^d (Bossche et al., 1987); ^e (T. R. Miller et al., 2008); ^f (Jank et al., 2014); ^g (Herklotz et al., 2010); ^h (Aryal & Reinhold, 2013); ⁱ (Lin et al., 2018); ^j (Muñoz et al., 2009); ^k (Chen et al., 2013a); ^l (Ying et al., 2007); ^m (Bayen et al., 2013); ⁿ (Chad A Kinney et al., 2012); ^o (Tixier et al., 2003); ^p (Kovács et al., 2009); ^q (Vermillion Maier & Tjeerdema, 2018); ^r (Walters et al., 2010); ^s (Monteiro & Boxall, 2009); ^t (N. Gottschall et al., 2012); ^u (Topp et al., 2012); ^v (C. Wu et al., 2009)

Table 1-3. Physiochemical properties of selected perfluoroalkyl acids.

	PFBA	PFHxA	PFOA	PFOS
Structure				
Formula	C ₄ F ₇ O ₂ H	C ₆ F ₁₁ O ₂ H	C ₇ F ₁₅ COOH	C ₈ F ₁₇ SO ₃ H
MW (g/mol)	214.039	314.06	414.07	500.13
pK _a	0.4 ^a	0.14 ^b	0.5 ^a	-3.27 ^b
Log K _{ow}	2.32 ^b	3.12 ^b	4.14 ^a 4.59 (estimated) ^b	4.49 ^a 5.26 (estimated) ^b
Log K _{oc} (L/kg)	1.88 (experimental, soil) ^f	1.61 (experimental, soil and sediment) ^e 1.31 ^f	2.1 (experimental, soil and sediment) ^{c†} 2.96 (experimental, biosolids) ^d 2.31 (experimental, soil and sediment) ^e	3.0, 3.34 (experimental, soil and sediment) ^{c†e} 3.79 (experimental, biosolids) ^d
Vapor pressure (mmHg at 25 °C)	6.4 ^a	2 ^a	0.52 ^a	0.001 ^a
Henry's Law Constants (atm/m ³ mole)	0.00012 ^a	0.0033 ^a	0.091 ^a	0.011 ^a
Solubility (mgL ⁻¹ , 25 °C)	-	15,700 ^b	3,400 ^b	570 ^b
Half-life (Dissipation)	385 d in biosolids- amended soil ^a	408 d in biosolids- amended soil ^a	693 d in biosolids- amended soil ^a	-

^a (Venkatesan & Halden, 2014); ^b (Deng et al., 2012); ^c (Zareitalabad et al., 2013); ^d (Arvaniti et al., 2014); ^e (Sepulvado et al., 2011);

^f (Guelfo & Higgins, 2013)

† Average of different experimental logK_{oc} values for different soils and sediment.

Table 1-4. The mean concentration of the target contaminants in wastewater influent, effluent and biosolids, and some ecotoxicity.

Contaminants	Wastewater influent (ngL ⁻¹)	Wastewater effluent (ngL ⁻¹)	Biosolids (µgKg ⁻¹ dw)	Ecotoxicity**
Azithromycin	2,272 ^a	935 ^a	838-1220 ^b 228 ^c	Unspecified amphipod: LC ₅₀ >120 mgL ⁻¹ Daphnia spp.: EC ₅₀ = 120 mgL ⁻¹
Carbamazepine	1,694 ^e 482 ^a	2,499 ^e 461 ^a	160 ± 60 ^b 183 ^c 15 – 1200 ^f	D. magna: EC ₅₀ , mobility inhibition, 48h > 13.8 mgL ⁻¹ m; C. dubia: EC ₅₀ , mobility inhibition, 48h = 77.7 mgL ⁻¹ m; C. vulgaris: EC _{50,24h} = 117.3 mgL ⁻¹ n
Diphenhydramine	426 ^g 222 ^g	194 ^g 86 ^g	444 ^g 293 ^g	D.magna: LC _{50-48h} = 0.374 mgL ⁻¹ h P.promelas: LC _{50-48h} = 2.09 mgL ⁻¹ (pH 8.5) & 59.28 mgL ⁻¹ (pH 6.5) h
Miconazole	32 ⁱ	3 ⁱ	777-1,100 ^b 341 ^c 238 ⁱ	D. magna: LC ₅₀ =0.3 mgL ⁻¹ ; LOEC, morality = 0.064 mgL ⁻¹ ; LOEC, feeding = cannot measure due to high toxicity to <i>D. magna</i> o
Triclocarban	6,700 ^j	110 ^j	36,000 ^b 4,940 ^c	M. mecenaria (larvae): LC ₅₀ =0.03 mgL ⁻¹ p A. salina: LC _{50-24h} =0.0178 mgL ⁻¹ q
Triclosan	2,500 ^k 6,100 ^j 8,700 ^e 22,800 ^e	35 ^j 2,500 ^e 5,700 ^e	13,000 ^b 10,900 ^c 800 ^f 5,140 ^k	A. salina: LC _{50-24h} =0.171 mgL ⁻¹ q D. magna: EC ₅₀ , 48h=0.39 µgL ⁻¹ r P. promelas: LC ₅₀ , 96h=0.26 µgL ⁻¹ r L. macrochirus: LC ₅₀ , 96h=0.37 µgL ⁻¹ r
PFAAs	PFOA 14.1-638.2 ^s PFOS 7.9 -374.5 ^s	PFOA 15.3-1057.1 ^s PFOS 7.3-461.7 ^s	PFOA 34 ^t PFOS 403 ^t	D. magna: LOEC _{immobility, 48h} = 0.5 mgL ⁻¹ (PFOS) u L. gibba: IC ₅₀ growth inhibition = 31.1 mgL ⁻¹ (PFOS) u

***S.vacuolatus* (green algae), *D.magna* (water flea), *A.salina* (brine shrimp), *P. promelas* (fathead minnow), *M. mecenaria* (saltwater clam), *Daphnia* (water flea), *C. vulgaris* (algae), *L.gibba* (macroalgae)

^a(Margot et al., 2013); ^b(Walters et al., 2010); ^c(N. Gottschall et al., 2012); ^e(Kasprzyk-Hordern et al., 2009); ^f(Chad A. Kinney et al., 2006); ^g(Subedi & Kannan, 2015); ^h(Berninger et al., 2011); ⁱ(Huang et al., 2010); ^j(Halden & Paull, 2005); ^k(Gardner et al., 2013); ^l(Brausch et al., 2012); ^m(Ferrari et al., 2003); ⁿ(Jos et al., 2003); ^o(Furuhagen et al., 2014); ^p(Davis & Hidu, 1969); ^q(Xu et al., 2015); ^r(Orvos et al., 2002); ^s(Yu et al., 2009); ^t(Venkatesan & Halden, 2013); ^u(Boudreau et al., 2003)

To date, the application of municipal biosolids on agricultural lands has been extensively studied in lab and greenhouse settings as well as a few field studies. Leaching and plant uptake studies have been frequently conducted by adding organic contaminants to growing media (e.g., soil or hydroponic) and often with unrealistic concentrations of organic contaminants. These approaches often result in overestimates of leaching and plant uptake potential of biosolids-borne contaminants when applied as a source of nutrients. Moreover, there are currently limited studies evaluating leaching and plant uptake potential of contaminants from commercially available biosolids such as Milorganite. When municipal biosolids are applied to an agricultural field, the rules and requirements (e.g., the Part 503 rule) are strictly placed so that it may ensure the safe application of biosolids. However, in an urban garden setting, only recommended rates are provided to the consumer; thus, if the potential risk of using commercial biosolids are not known, it may increase the potential risk to urban food safety and human health. With increasing interest in an urban farming (e.g., growing one's own food, buying locally produced food) (Mok et al., 2014) as well as beneficial use of waste-derived organic products, it is necessary to examine the potential risk of using waste-derived organic products in an urban garden setting to ensure urban food safety and human health. Therefore, the overarching goal of my research is to assess the level of organic contaminants (17 PFAAs and 6 PPCPs) in waste-derived organic products and their leachability as well as the plant uptake potential of these contaminants.

1.2 Objectives

1. Quantity concentrations and lability of seventeen PFAAs in a suite of commercially available waste-derived organic products and assess the leachability.

2. Compare PFAA concentrations in four commercially available biosolid-based products that received different types of processing: heat-treatment, composting, blending, and thermal hydrolysis.
3. Evaluate potential plant uptake of PFAA and PPCPs from commercial biosolid-based fertilizer-amended potting media in a controlled greenhouse study.

1.3 Organization

This thesis consists of five chapters including this introduction and the following four remaining chapters:

- CHAPTER 2: PFAA concentrations in a suite of commercially available waste-derived organic products (e.g., biosolid-based) were quantified and compared with nonbiosolid-based organic products. The porewater concentration of PFAAs were measured to assess their leachability. Kim Lazcano, Choi, Y., Mashtare, M.L. and Lee, L.S. 2019. Characterizing Per- and Polyfluoroalkyl Substances in Commercially Available Biosolid-versus Nonbiosolid-based Organic Fertilizers. Preparing for submission in *Environmental Science & Technology*.
- CHAPTER 3: To understand how different treatment process affect PFAA concentration in waste-derived fertilizers, PFAA concentrations were measured and compared in four commercially available biosolid-based products that received different processes: heat-treatment, composting, blending, and thermal hydrolysis. [Published: R. Kim Lazcano, C. de Perre, M.L. Mashtare and L.S. Lee. 2019. Per- and Polyfluoroalkyl Substances in Commercially Available Biosolid-Based Products: The Effect of Treatment Processes,

Water Environ. Research. Just released, DOI: 10.1002/WER.1174. Reproduced with permission from John Wiley & Sons, Inc, Copyright 2019; Kim Lazcano, R., C. de Perre, M.L. Mashtare and L.S. Lee. 2019. Per- and Polyfluoroalkyl Substances in Commercially Available Biosolid-Based Fertilizers: The Effect of Post-treatment Processes, WEFTEC Biosolids 2019, Proceedings, May 2019. Reproduced in part or whole with permission from WEFTEC, Copyright 2019]

- CHAPTER 4: The uptake of PFAAs and PPCPs by kale and turnip from a waste-derived organic fertilizer (Milorganite) amended in a soilless-media (Miracle-Gro) was examined in order to assess the bioavailability of the target contaminants, and the potential food contamination related to their leachability and level of contaminants. [Rooney Kim Lazcano et al., 2019. Plant Uptake of Perfluoroalkyl Acids and Pharmaceutical and Personal Care Products from a Commercially Available Biosolid. Preparing for submission in *Environmental Science & Technology*.]
- CHAPTER 5: The major conclusions of this dissertation research and future needs in evaluating the level, leachability and the plant uptake potential of PFAAs and PPCPs of waste-derived organic products.

CHAPTER 2. CHARACTERIZING PER- AND POLYFLUOROALKYL SUBSTANCES IN COMMERCIALY AVAILABLE BIOSOLID-VERSUS NONBIOSOLID-BASED ORGANIC FERTILIZERS

2.1 Abstract

Sales in commercially available biosolid-based products have been increasing over the last two decades. These organic products are a rich nutrient source used in urban agriculture (e.g., home and community gardens) and turf (e.g., golf courses, parks, lawns). Concerns around the presence of per- and polyfluoroalkyl substances (PFAS) in biosolids have been increasing among both public and regulatory entities. The objective of this study was to quantify and compare 17 perfluoroalkyl acids (PFAAs) concentrations in 11 commercially available biosolid-based products versus 7 nonbiosolid-based organic products (composted mushroom, manure, food or yard wastes) collected primarily from 2014. The biosolid-based products displayed higher total PFAA concentrations (9 – 199 $\mu\text{g}/\text{kg}$) than the nonbiosolid organic products (0.1 – 19 $\mu\text{g}/\text{kg}$). A total oxidizable precursors (TOP) assay revealed the significant presence of precursors in some of the biosolid-based products. Using time-of-flight mass spectrometry for precursor screening identified three sulfonamides, 6:2 and 8:2 fluorotelomer sulfonates and some polyfluoroalkyl phosphate diesters. PFAA porewater concentrations were measured as an indicator of leachability, which showed higher concentrations of short-chain PFAAs compared to the long-chains.

2.2 Introduction

Recently, commercially available biosolid-based products, which are sold in bags or bulk, have gained popularity for use in urban and suburban setting for gardens, golf courses, public parks, and lawns (Z. Liu et al., 2018; McIvor et al., 2012). Based on data available for TAGRO products, sales have increased over the last two decades (500 % increase in the gross revenue) (Fig. S1 in

Appendix A) and future sales are projected to increase. Biosolid-based products contain many beneficial components such as organic matter and macro- and micronutrients, thus an alternative to synthetic products. Also, the land application of biosolids can reduce the need to landfill or incinerate urban waste (Alvarenga et al., 2017). Despite the benefits of biosolid-based products, their use is continuously challenged by questions related to the presence of contaminants of concern such as per- and polyfluoroalkyl substances (PFAS). PFAS include different subclasses such as perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), perfluoroalkyl sulfonamides (FOSAs), fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphate esters (PAPs), which are known as perfluoroalkyl acid (PFAA) precursors (Z. Wang et al., 2017). PFAA precursors can be transformed to PFAAs in the environment via a natural process such as atmospheric oxidation (Dreyer et al., 2009) and microbial degradation with PFAAs being terminal metabolites (Houtz & Sedlak, 2012). PFAAs include all PFCAs and PFSAs. PFAS have been frequently detected in municipal biosolids due to their recalcitrant nature and widespread use in various industrial application and consumer products (Giesy & Kannan, 2002; Kissa, 2001). For example, agricultural farmland that has received municipal biosolids for more than 10 years contained higher PFAA concentrations, e.g., perfluorodecanoic acid (PFDA) $\leq 990 \mu\text{g/kg}$; perfluorododecanoic acid (PFDoA) $\leq 530 \mu\text{g/kg}$; perfluorooctanoic acid (PFOA) $\leq 320 \mu\text{g/kg}$ and perfluorooctane sulfonic acid (PFOS) $\leq 410 \mu\text{g/kg}$ than the background field soil without biosolids application (PFAA concentrations $\leq 0.243 \mu\text{g/kg}$) (Washington et al., 2010). A similar study also showed the elevated PFAA concentrations in crops, and the nearby surface and well water from the biosolids-applied field (Lindstrom et al., 2011). Thus, biosolids application to agricultural fields can potentially introduce PFAAs into the soil (N Gottschall et al., 2010; Sepulvado et al., 2011; Washington et al., 2010), water (Lindstrom et al., 2011), and food crops (Blaine et al., 2013).

For home or urban gardens, the application of biosolid-based products can lead to exposure of PFAS via consuming the fresh food crop grown in biosolid-amended plots as well as dust inhalation and dermal contact during organic product amendments. Despite the increased usage of biosolid-based products in home and urban gardens, and other urban and suburban land applications, no research has yet evaluated the occurrences and bioavailability of PFAS in commercially available biosolid-based products.

The objective of this study was to quantify and compare the concentrations and lability of seventeen PFAAs in commercially available biosolid-based products and non-biosolids based organic products. Potential PFAA precursors were evaluated using a total oxidizable precursor (TOP) assay followed by screening for 30 individual PFAA precursors in a subset of products identified to most likely contain PFAA precursors. As an assessment of PFAA leachability and bioavailability, PFAA porewater concentrations in water-saturated products were quantified. Relative PFAA distribution between porewater and the organic products were evaluated across products as well as PFAA loads that would be applied based on nitrogen recommendations.

2.3 Materials and Methods

Reagents and Standard Solutions

All 17 PFAAs were purchased as standard mixtures (PFCA-MXB) from Wellington Laboratories (Guelph, Canada), containing 13 PFCAs (C4 - C18) and 4 PFSAs, (C4 - C10). Isotopically mass-labeled compounds (7 PFCAs and 2 PFSAs) for use as internal standards were also purchased as mixtures (MPFAC-MXA) from Wellington Laboratories. Details are provided in Appendix A along with all other reagents used in the extraction of PFAAs, PFAA porewater concentrations, the TOP assay, and chromatographic analysis.

Organic Products

All organic products were obtained in 2014 from different states within the United States and consisted of eleven biosolid-based products and seven organic (nonbiosolid-based) products (**Table 1**) except for two obtained later from one vendor (Milorganite, Product J). Most organic products were available in bags from major retailers across the U.S., in bags at regional stores or via truckloads directly from the vendors (see **Table 1**). The additional samples from Milorganite (Product J) were those prepared for sale in 2016 and 2018 to examine if PFAA concentrations were declining in response to the early phase-out of PFOS (for most uses) and subsequently PFOA (Alder & van der Voet, 2015; USEPA, 2006).

Sample Preparation and Extraction.

Before extraction of PFAAs, all products were freeze-dried (Labconco, Kansas City, MO) for 72 h. The five heat-treated products (Products H-L) appeared homogenous as received. All other freeze-dried products were sieved (< 2 mm, Table S1 in Appendix A) to remove larger particles (primarily plant debris and rocks) and make them more homogeneous. The < 2 mm particle size fraction ranged from 36% to 80% of the total mass (Table S1 in Appendix A). In a previous study, we evaluated the PFAA levels in the < 2 mm versus > 2 mm particle size fraction for a subset of similar composted and blended biosolid-based products (Kim Lazcano et al., 2019). In this study, PFAA concentrations extracted from the > 2 mm fraction were highly variable (high standard deviations) with some replicates having negligible PFAA levels. It was concluded that the source of PFAA loads in this larger fraction was a result of the finer particles (< 2 mm) clinging to the larger particles (> 2 mm). Likewise, extracted co-composting and the woody materials used in some of the blended products which were all > 2 mm also had negligible total PFAA concentrations (< 2 µg/kg).

Table 2-1. Details for the other organic products (A-G) and biosolid-based products (H-R) used in the study.

ID	Brand	Description	Available form to consumer
<i>Non-biosolid organic products</i>			
A	Undisclosed source	Food and yard compost	Truck loads at vendors
B	EKO Organic Compost	Compost with untreated wood products	Bags at any national retailer
C	Gardener's Pride Composted Manure	Manure compost	Bags at any national retailer
D	New Plant Life Manure	Manure and peat compost	Bags at any national retailer
E	New Plant Life Mushroom	Mushroom compost	Bags at any national retailer
F	Country Soil Mushroom Compost	Mushroom compost	Bags at any national retailer
G	Promix Ultimate Organic Mix	Peat/compost based growing mix	Bags at any national retailer
<i>Biosolid-based products</i>			
H	Bay State Fertilizer	Heat-treated granular biosolids	Bags at local stores
I	Hou-Actinite	Heat-treated granular biosolids	Bags at local stores
J	Milorganite	Heat-treated granular biosolids	Bags at any major stores
K	OceanGro	Heat-treated granular biosolids	Bags at local stores
L	Undisclosed source	Heat-treated granular biosolids	Local vendor
M	TAGRO Potting Soil	Biosolids blended with maple sawdust and aged bark	Bags and truck loads at local vendor
N	Undisclosed source	Composted biosolids with woodchips	Truck loads at vendor
O	Undisclosed source	Composted biosolids with woodchips	Truck loads at vendor
P	Undisclosed source	Composted biosolids with municipal solid waste	Truck loads at vendors
Q	Dillo Dirt	Composted biosolids with residential yard trimmings	Bags at local stores
R	Elite Lawn	Composted biosolids with plant materials	Bags at local stores

The organic products were extracted in triplicate using a method described by Choi et al. (2019), which involves extracting three times sequentially with a methanol/200 mM ammonium hydroxide solution by sonicating for one hour followed by a 2-h end-over-end rotation. Before analysis, all solvent extracts were combined and concentrated under nitrogen using a RapidVap Vacuum

Evaporation System (Labconco, Kansas City, MO). The residuals were reconstituted with 99:1 v/v methanol/glacial acetic acid and cleaned with ENVI-Carb to reduce matrix effects that may affect quantitation. Additional details provided in Appendix A.

Total Oxidizable Precursor (TOP) assay

Analytical standards or individual chemical stocks are only available for a small fraction of the currently > 4730 PFAS potentially in production (Houtz & Sedlak, 2012; OECD, 2018). The TOP assay, which is a heat-activated persulfate treatment at initial pH values > 12, allows for estimating the level of potential PFAA precursors in complex environmental samples (Houtz & Sedlak, 2012) by converting them to PFAAs for which standards are readily available. The TOP assay was performed similarly to that described by Houtz & Sedlak (2012) after completing a solvent exchange except we evaluated the TOP assay response to extracts. Houtz et al. (2013) showed that TOP assay results were similar between ENVI-carb treated extracts versus untreated extracts; however, the extracts of the materials in the current study are likely much dirtier than previous samples published to date using the TOP assay. For assays prior to the ENVI-carb cleanup, the solvent extract (500 μ L) was transferred to a 2-mL microcentrifuge tube and evaporated to dryness under nitrogen. The dried extract was resuspended with 500 μ L of Nanopure water followed by sequentially adding 1.2 M sodium hydroxide (125 μ L) and 160 mM potassium persulfate (375 μ L) for final initial concentrations of 150 mM and 60 mM, respectively. Samples were vortexed for 1 minute and incubated in a temperature-controlled water bath between 80 °C to 85 °C for six hours. After incubation, samples were immediately placed in an ice bath to cool. Final sample pH values were measured using pH-indicator strips due to the small sample volumes (< 1 mL) (Table S7 in Appendix A). Samples were neutralized with glacial acetic acid. A 500- μ L sample aliquot was added to a 1.5-mL microcentrifuge tube containing 20 to 40 mg of ENVI-Carb

sorbent that was pretreated with 20 μL glacial acetic acid before adding 500 μL of methanol (final matrix 1:1 v/v $\text{H}_2\text{O}:\text{MeOH}$). The sample was vortexed and centrifuged at 17,000 RCF for 30 minutes, and the supernatant (~ 1000 μL) was transferred to a HPLC injection vial. The final sample was vortexed for 30 seconds before analysis.

Porewater Concentrations

Except for nonbiosolid-based products B-G which had negligible PFAA loads, PFAA pore-water concentrations were measured in triplicate after 48 h of being saturated with an electrolyte in 24-mL polypropylene (PP) syringes similarly to the method described by Choi et al. (2019). Briefly, PP syringes were rinsed with acetone and air-dried before packing with the organic products. The bottom of the syringe was fitted with a syringe cap and a stainless-steel mesh was placed inside of the syringe in order to retain liquid and solid materials, respectively. The organic products (~ 3 g) were packed into the syringe and then saturated (1:2 g:mL ratio) with an electrolyte solution (0.5 mM calcium chloride at pH 6.5) containing 3.08 mM sodium azide to minimize potential microbial degradation. The plunger was gently inserted into the syringe to reduce evaporation during incubation. No-organic product controls were prepared to assess any background PFAA concentrations. After 48 h incubation, the syringe was placed in a 50-mL PP tube and centrifuged at 1,613 RCF for 1 h to separate the liquid (collected in the tube) and solid materials (retained in the syringe). Pore-water pH was measured (Table S8 in Appendix A) followed by PFAA pore-water concentrations using a previously published solid-phase extraction (SPE) method (Yoo et al., 2009) with hydrophilic-lipophilic balance (HLB) SPE cartridges. Although weak-anion exchange (WAX) SPE cartridges have been used more frequently to clean PFAAs extracts, we found similar PFAA recoveries between HLB- and WAX SPE cartridges (Figure S2 in Appendix A) consistent with previous observations (Yoo et al., 2009). Additional

SPE method details are summarized in Appendix A. The spent-solids were weighed before and after the 72-h freeze-drying process to account for the PFAA concentrations in the residual moisture after centrifugation. The freeze-dried spent-products (~0.5 g) were extracted for evaluating mass balance.

Instrumental Analysis

All samples were analyzed for seventeen PFAAs using a liquid chromatography-mass spectrometry (LC-MS/MS) system coupled to a SCIEX triple quadrupole time-of-flight (QToF) 5600 (Framingham, MA). PFAA analysis was performed based on the method described by Choi et al. (2019). In addition to the quantifying 17 PFAAs, methanol extracts of the products were screened for 30 PFAA precursors (Table S11 in Appendix A) using LC-QToF/MS in SWATH™ acquisition mode. The PFAA precursor data was also acquired, as described by Choi et al. (2019). The detailed method is described in Appendix A.

Analytical QA/QC

A stable-isotope dilution with nine mass-labeled standards was used to correct for the matrix effects and extraction recovery. A six- to eight-point calibration curve ranging from 0.1 to 15 µg/L was prepared to cover the entire range of the sample concentrations and run at the beginning and the end of each batch run. A continuing calibration verification standard (CCV) was injected every 12 injections to monitor the calibration. An instrument blank was injected before a CCV injection to monitor potential carryover between injections. Values below the quantification limit (LOQ) were assumed to be 0 when calculating concentrations. The extraction recoveries (%) for 17 PFAAs were previously determined by Choi et al. (2019) and ranged from 78% to 126 % except for perfluorotridecanoic acid (PFTrDA, 142% ± 20). The standard reference material for sludge (SRM 2781) was also extracted and analyzed for the PFAAs as a confirmation of the

adequacy of the extraction method used in this study. Results were compared with those summarized in Reiner et al. (Reiner et al., 2015) (Table S7 in Appendix A).

Statistical Analysis

Statistical analyses were performed using R software (version 3.4.3). Normality and homogeneity of the variances were tested with the Shapiro-Wilk test and Levene's test, respectively. One way-analysis of variance (ANOVA) followed by Tukey's post hoc tests ($p < 0.05$) was performed to determine the statistical differences of the concentrations of the temporal variability.

2.4 Results and Discussions

PFAA Concentrations in the Organic Products

The PFAA concentrations ($\mu\text{g}/\text{kg}$) detected above LOQs are summarized in **Figure 2-1** and detailed in Tables S4 and S5 in Appendix A. Total PFAA concentrations ranged from 9 to 178 $\mu\text{g}/\text{kg}$ for the biosolid-based products (the < 2 mm particle size fraction) with all containing 8 PFAAs above the LOQ: perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluorohexanoic acid (PFHxA), PFOA, PFOS, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUDA) and perfluorododecanoic acid (PFDDoA). For the nonbiosolid-based products, the total PFAA concentrations are relatively low to negligible ranging from 0.1 to 19 $\mu\text{g}/\text{kg}$. Product A (food and yard compost) contained the highest total PFAA among the nonbiosolid-based products, which is consistent with the result from a recent study by Choi et al. (2019), showing higher PFAA levels in composts with food waste (29 – 76 $\mu\text{g}/\text{kg}$) and food packaging than composts without food (2 – 8 $\mu\text{g}/\text{kg}$). Of the short-chain PFAAs (PFCAs $\leq C7$ and PFSAs $\leq C5$) in the biosolid-based products, PFHxA (0.5 – 61.0 $\mu\text{g}/\text{kg}$) and PFBS (0.4 – 23.71

$\mu\text{g}/\text{kg}$) were dominant. PFOA (1.4 – 12.6 $\mu\text{g}/\text{kg}$) and PFOS (2.0 – 88.5 $\mu\text{g}/\text{kg}$) were the dominant long-chain PFAAs.

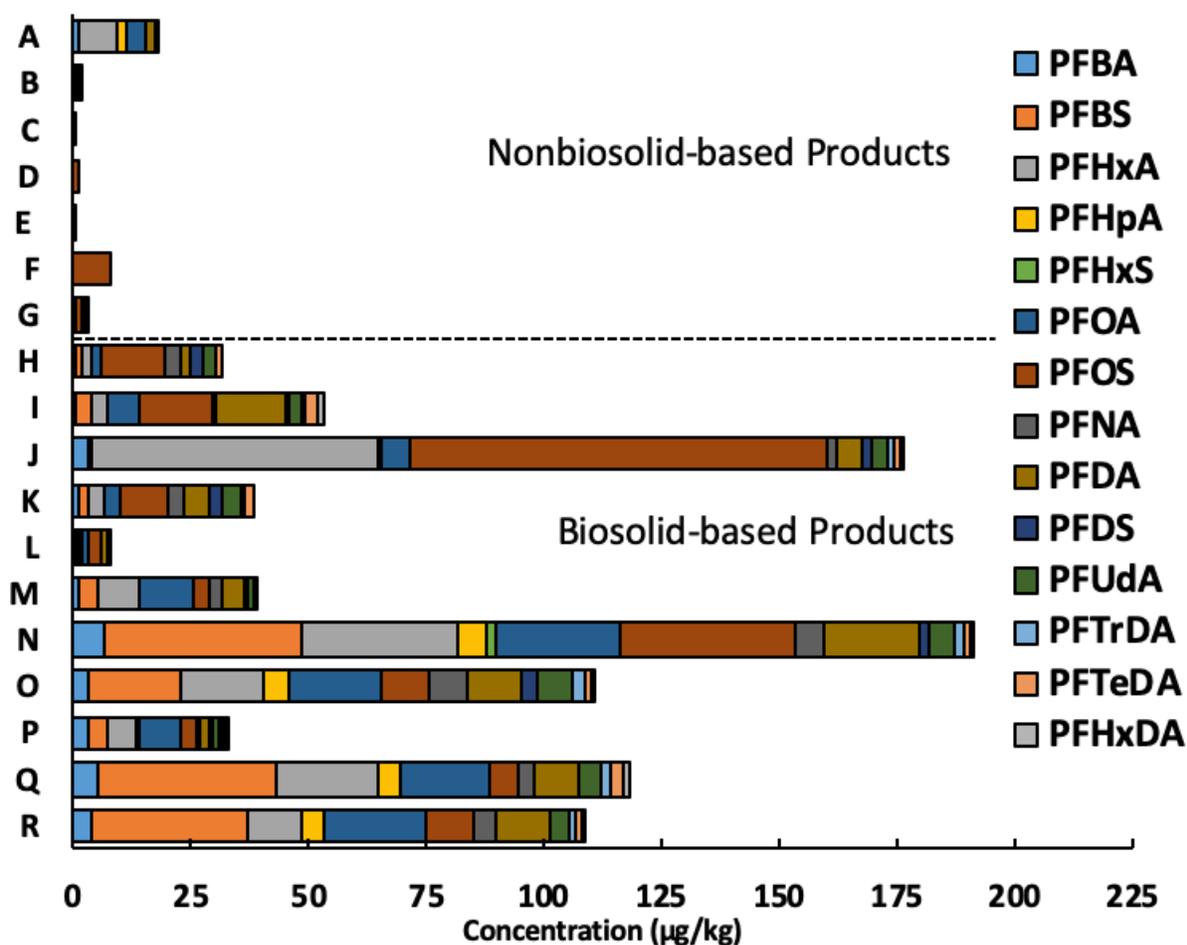


Figure 2-1. PFAA concentrations in the < 2 mm particle size fraction of products A-G and M-R. The granular heat-treated products H-L were not sieved.

For most biosolid-based products, PFOS was generally detected at the highest level compared to other PFAA levels despite the voluntary phase-out of PFOS and its related products in 2002 (Alder & van der Voet, 2015). The presence of PFOS is likely associated to its presence in long-lived consumer products such as outdoor textiles, ski wax, and clothing (Kotthoff et al., 2015). The concentrations of PFAAs in the heat-treated biosolid-based products ranged from 9 to

185 µg/kg, while the concentrations of PFAAs in the composted or blended biosolid-based products ranged from 34 to 209 µg/kg. The differences in PFAA concentrations among the products is likely due to differences in the sources coming into the different wastewater treatment plants from which the biosolids originated. Although different sludge and biosolids treatment processes may affect PFAA concentrations, Kim Lazcano et al. (2019) found that heat-treatment and composting did not significantly impact PFAA concentrations, only blending with materials (e.g., sawdust, aged bark, etc.) which just serve to dilute the PFAA loads. Since PFAAs are not degraded microbially, composting will not reduce PFAA loads, but may increase them due to the presence of PFAA precursors that can degrade microbially to PFAAs (Chad A. Kinney et al., 2006; Mejia-Avenidaño et al., 2016; Zhang et al., 2017).

Temporal Variation of PFAA Concentrations (2014, 2016 and 2018)

For Milorganite (Product J), which had the highest total PFAA load almost half of which was from ‘legacy’ PFOS (88 µg/kg), additional samples were obtained for material released for use in 2016 and 2018. Total PFAA concentrations decreased from 185 µg/kg to 77 µg/kg from (reduced from 115 µg/kg to 27 µg/kg) (**Figure 2-2**), Of the total PFAA reduction, 67% was due to 2014 to 2018, which was most likely due to the major reduction in the total long-chain PFAAs reduced PFOS loads from 2014 to 2018 ($F_{2,6} = 424.5$, $P < 0.01$). Decreases over time are statistically significant for total PFAA concentrations ($F_{2,6} = 388.9$, $p < 0.05$) as well as for both the short-chain PFAAs ($F_{2,6} = 9.58$, $p < 0.05$) and the long-chain PFAAs ($F_{2,6} = 603.1$, $p < 0.05$). When comparing significant differences between two years (2014 and 2016, 2016 and 2018 and 2014 and 2018), both the total concentration of PFAAs ($p < 0.05$) and the long-chain ($p < 0.05$) significantly decreased for all pairwise comparisons. For the short-chain PFAAs, changes were only statistically significant between 2014 versus 2018 ($p < 0.05$) with the decrease accounting for

≈15 % of the reduction in total PFAAs. Although temporal variations were only assessed for one product, decreases in PFOS concentration leading to an overall reduction in PFAA loads present in Milorganite (Product J) is consistent with recent studies reporting decreases in PFOS concentrations in municipal biosolids (Alder & van der Voet, 2015; Ulrich et al., 2016) blood samples from adults (Olsen et al., 2012) and wildlife (Sedlak et al., 2017).

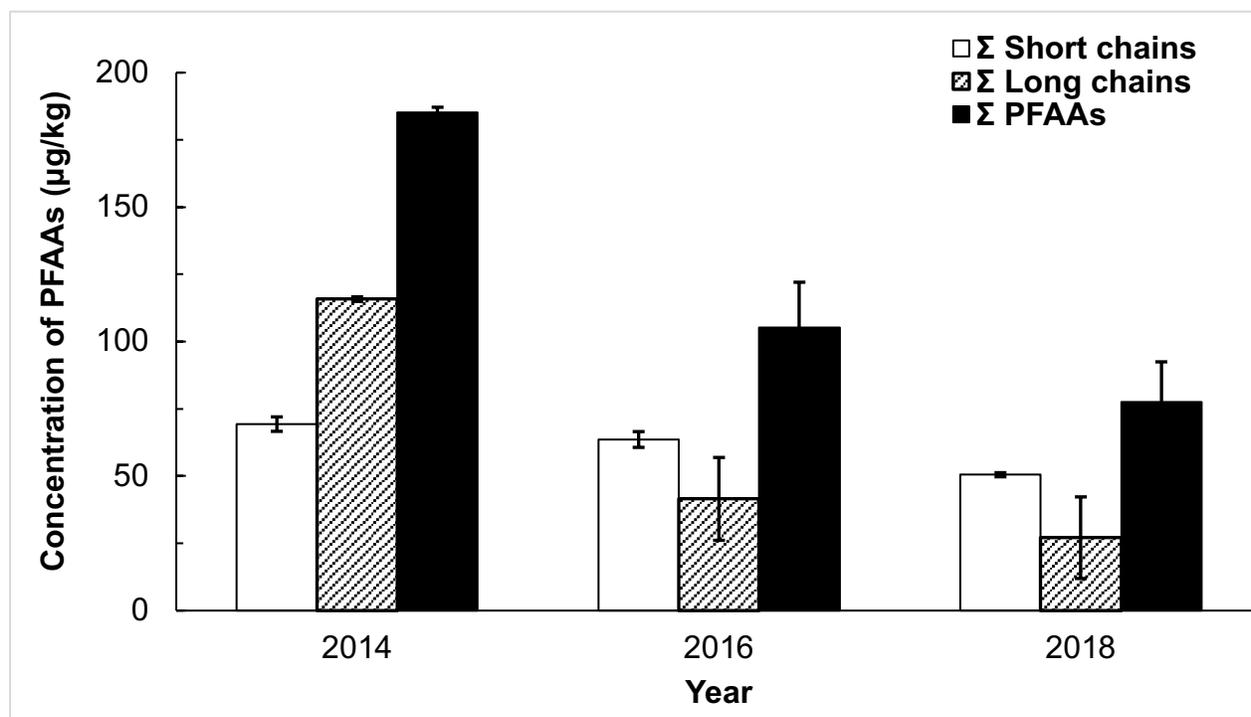


Figure 2-2. Temporal changes in PFAA concentrations (total short chain, total long chain and total PFAAs) for Milorganite released for consumer use in 2014, 2016 and 2018. The error bars represent the standard error of the mean.

Total Oxidizable Precursor (TOP) Assay

The TOP assay is a useful way to estimate levels of potential PFAA precursors in complex environmental samples (Houtz & Sedlak, 2012); however, there are some differences between what occurs in the TOP assay and what happens naturally in the environment. The TOP assay converts PFAA precursors to PFCAs from both PFCA and PFSA precursors (Houtz & Sedlak, 2012) which is different than microbial and biological transformation of PFSA precursors to PFSAs (Avendaño & Liu, 2015; Zhang et al., 2017). For example, sulfonamide-containing PFAA

precursors, e.g., *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE), *N*-ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), perfluorooctane sulfonamide (FOSA), and perfluorooctane sulfonamidoacetic acid (FOSAA), can transform to PFOA (major) (Houtz & Sedlak, 2012; Martin et al., 2019; Zhang et al., 2017) and PFHpA (minor) (Martin et al., 2019) via the TOP assay while the major transformation product is known to be PFOS (Avendaño & Liu, 2015; Zhang et al., 2017). The total concentration of PFCAs in the product extracts before and after the TOP assay are summarized in **Figure 2-3** and Table S6 in Appendix A.

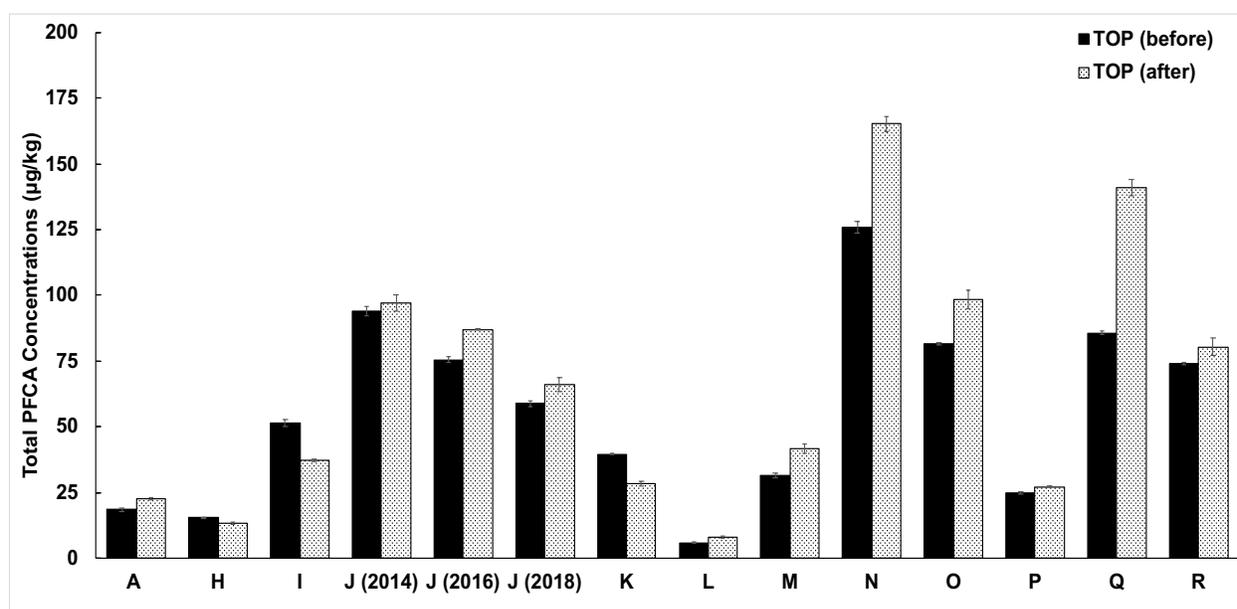


Figure 2-3. Total PFCA concentrations ($\mu\text{g}/\text{kg}$) before and after the TOP assay in the biosolid-based products except for Product A. The error bars represent the standard error of the mean ($n=3$).

The TOP assay results on the nonbiosolid-based products were excluded in the graph due to the low concentration in the extract as well as negligible changes in the concentrations. Increases in the total PFCAs after the TOP assay was observed only in Products J, N and Q. This indicating that a significant level of PFAA precursors is present, which may lead to increases in PFAA loads after application. For Products I and K, total PFCA concentrations were lower in the TOP assay which may be due to the degradation of PFCAs by the sulfate radicals as pH decreased during the

reaction time combined with a low to negligible level of PFAA precursors. The sample pH range at the end of the TOP assay was $4 < \text{pH} < 10$ (Table S8 in Appendix A). The oxidation of PFOA to shorter chain PFCAs by persulfate was observed at our similar pH, and temperature conditions at pH 7.1 at 85 °C (CS Liu et al., 2012) and the rate of oxidation is higher at lower pH (Park et al., 2016). Although the pH of Product I and K was not significantly lower than the other products, PFCAs can be degraded into the ultra-short chains ($< C_4$) (Park et al., 2016) under the acidic condition, which was not analyzed in this study. The rest of the products did not exhibit a significant change before and after the TOP assay, which does not necessarily mean that these products have low PFAA precursors. High level of organic matters and other contaminants can act as radical scavengers, affecting the oxidation rate of PFAA precursors (Casson & Chiang, 2018). Also, solvent-enhanced hydrolysis of some fluorotelomer-based PFAS (e.g., monoPAP) and loss of volatile PFAS (e.g., FTOH) can occur during the extraction and the sample preparation prior to the TOP assay (Chen Liu & Liu, 2016; Robel et al., 2017), which may lead to the underestimation of total PFAS concentration.

Screening Analysis of PFAS precursors.

In order to screen potential PFAA precursors, the three products that the TOP assay indicated a significant presence of potential PFAA precursors were screened for the 30 PFAA precursors (Table S10 in Appendix A) that are frequently detected in environmental samples (e.g., wastewater, biosolids, landfill leachate or food packaging) (Eriksson et al., 2017; Houtz et al., 2016; Lang et al., 2017). Nine out of the 30 PFAA precursors targeted in the screening were detected and identified, including sulfonamide-containing PFAA precursors (EtFOSAA, FOSA and FOSAA), fluorotelomer sulfonates (6:2 and 8:2 FTSA) and polyfluoroalkyl phosphate diesters (6:2/6:2-, 6:2/8:2-, 8:2/8:2-, 8:2/10:2 diPAPs) (Table S12 in Appendix A).

PFAA Pore-water Concentrations

C4 to C10 PFAAs were detected in the pore-water of water-saturated products. The most frequently detected PFAAs were PFBA and PFHxA with a concentration ranges of 155 to 4072 ng/L and 256 to 6215 ng/L, respectively. PFHxS was detected in only one product pore-water and at a low concentration (30 ng/L). Among the longer chains (C8 - C10), PFOA was detected most frequently at the highest concentration (100 to 800 ng/L). PFOS and PFNA were detected in some products with the concentration < 200 ng/L, whereas PFDA and PFDS were detected in two products with the concentration below 0.04 $\mu\text{g/L}$. All other longer chains (> C11) were not detected or < LOQ. The pore-water concentrations (ng/L) versus PFAA loads ($\mu\text{g/kg}$) in the biosolid-based products are plotted on a log-log scale (**Figure 2-4**) and pore-water concentrations generally increased with increasing loads.

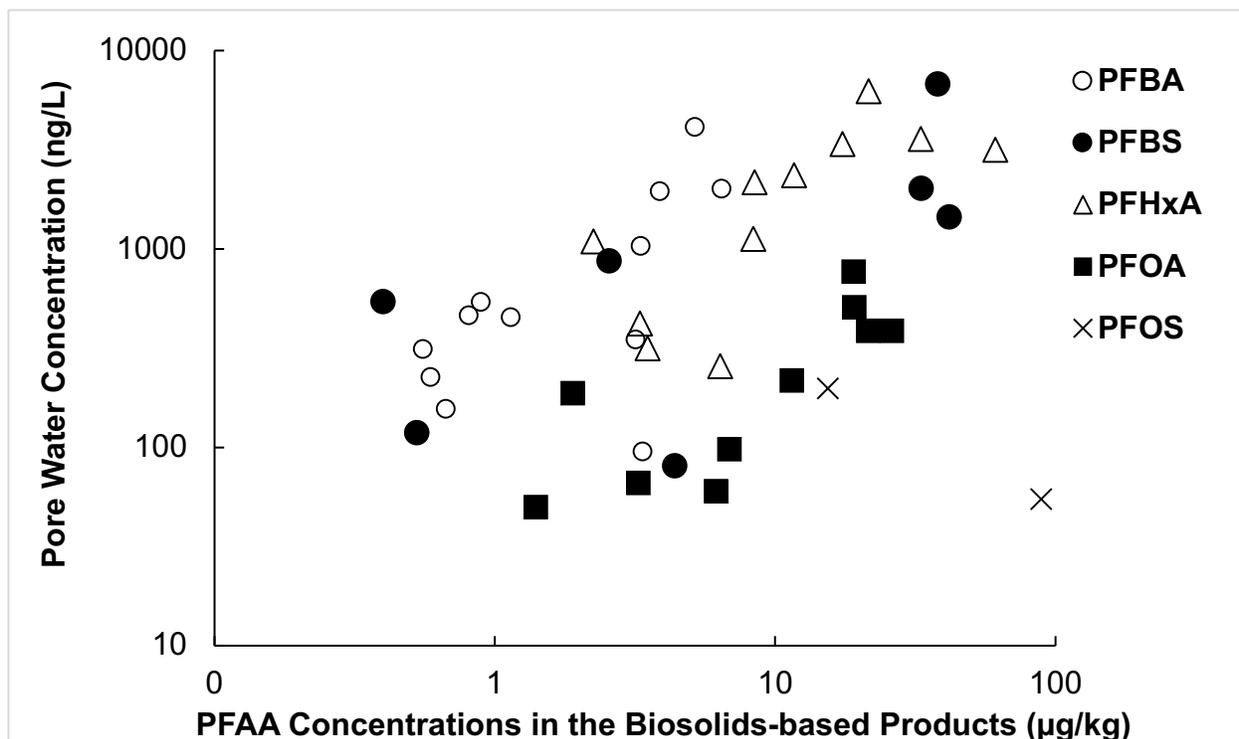


Figure 2-4. A log-log plot of PFAA pore-water concentrations (ng/L) and loads ($\mu\text{g/kg}$) in the biosolid-based products for five PFAAs (PFBA, PFBS, PFHxA, PFOA and PFOS).

Organic carbon (OC) normalized organic product-water partition coefficients (K_{oc}) were calculated using PFAA pore-water concentration (ng/L) and the PFAA loads remaining in the spent-sample ($\mu\text{g}/\text{kg}$).

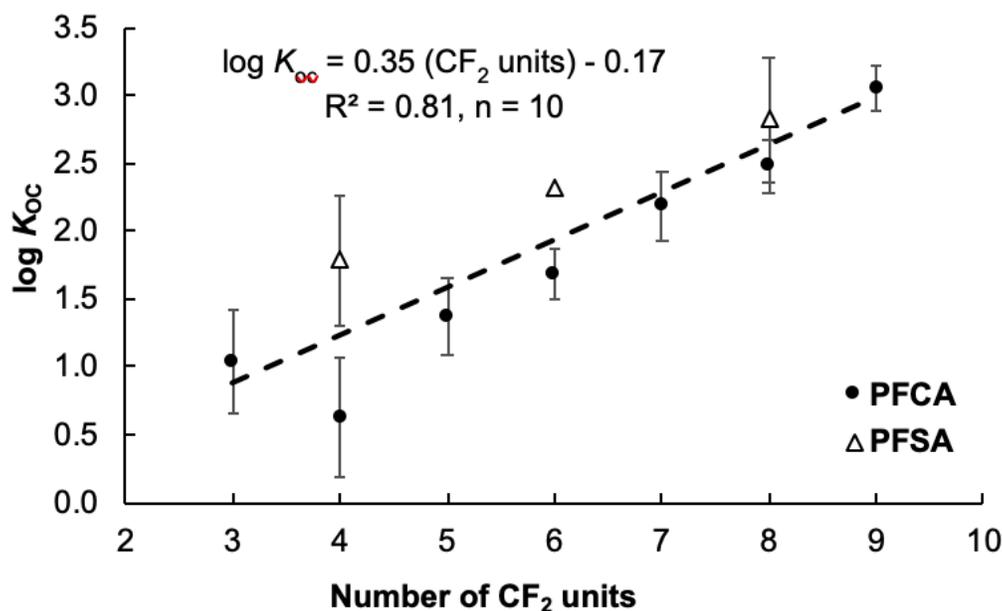


Figure 2-5. Average log of the OC-normalized partition coefficient ($\log K_{oc}$) for the biosolid-based product versus the number of CF_2 units for each PFAA.

OC was assumed to be 58% of the measured organic matter (Table S2 in Appendix A) for soils (Lyman et al., 1990). A good correlation ($R^2 = 0.81$) is observed between the $\log K_{oc}$ increased with increasing CF_2 units (**Figure 2-5**) similar to what Choi et al. (2019) found for municipal organic solid waste composts. Both **Figures 2-4** and **2-5** exemplify the higher leaching potential of shorter chain PFAAs. The similar trends were reported from batch leaching results from soil/water (Bräunig et al., 2019; Hale et al., 2017), a column study (Gellrich et al., 2012), a long-term lysimeter experiment (Stahl et al., 2013) and field measurements (Lindstrom et al., 2011; Sepulvado et al., 2011).

The current movement to replace longer chain PFAAs with the alternative short chains has a potential to result in higher total PFAA concentrations to be bioavailable for plant uptake, increasing the risk of food contaminations with PFAAs.

2.5 Conclusions

This study found that the commercially available biosolid-based products contain higher PFAA levels than nonbiosolid organic products. When considering how much fertilizer product a person may choose to use is typically based on nitrogen (N) content. Therefore, it is of interest to consider the total PFAA loads that may be applied with given fertilizer based on its N content (Table S2 in Appendix A), which is summarized in **Figure 2-6**.

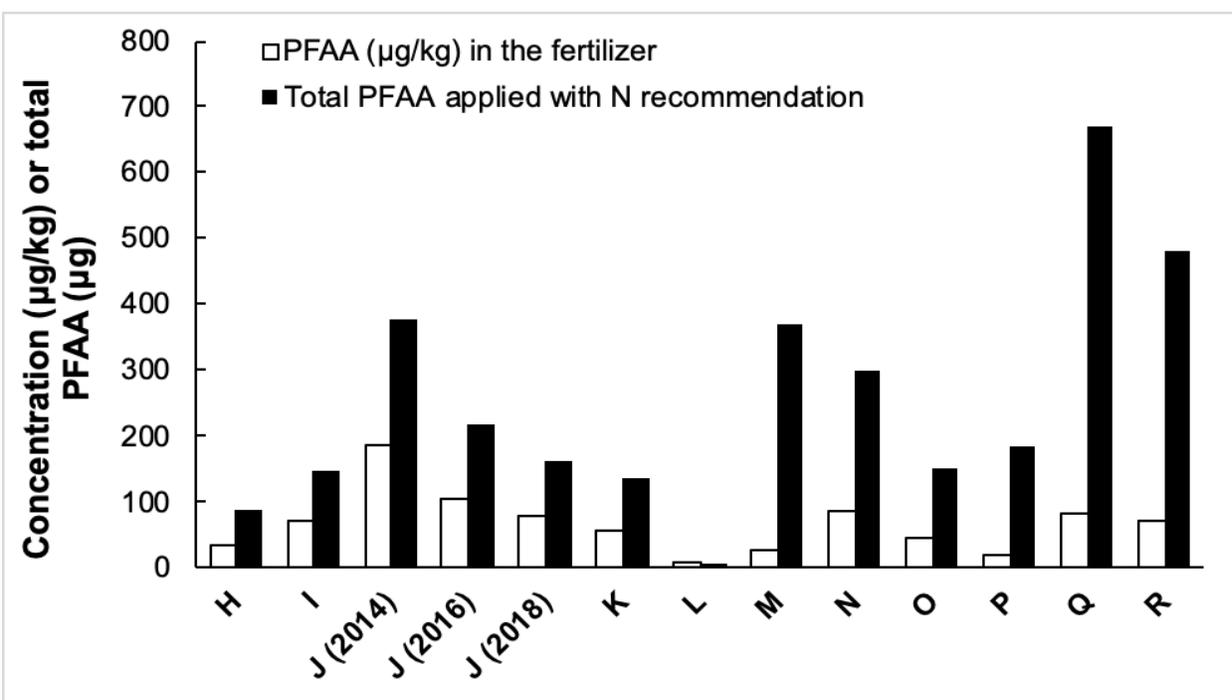


Figure 2-6. Total PFAA applied (µg) based on N recommendation rate by Product J compared with total PFAA concentration (µg/kg) in Products (H – R).

In some cases, organic product with a low level of N and low total PFAAs exceeded the total PFAA loading of fertilizer products with high total PFAA level. To avoid high PFAA loadings when using biosolid-based products or other PFAA-containing organic fertilizers such as composted food packaging (Choi et al., 2019) supplementing with inorganic nitrogen should be considered. Due to the lack of regulations, home-users may also inappropriately apply biosolid-based products. This may lead to unsafe practices such as not using proper personal protective equipment and/or using an excess amount of fertilizer products, which could potentially increase their exposure to PFAAs. Thus, it is crucial to assess what PFAA levels in products may be considered non-threatening to urban growers with regards to direct exposure via dust and hands, and PFAS contaminated food consumption.

2.6 Acknowledgements

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CHAPTER 3. PER- AND POLYFLUOROALKYL SUBSTANCES IN COMMERCIALLY AVAILABLE BIOSOLID-BASED PRODUCTS: THE EFFECT OF TREATMENT PROCESS

Reproduced from

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3.1 Abstract

Per- and poly fluoroalkyl substances (PFAS) have been used in a variety of consumer and industrial products and are known to accumulate in sewage sludge due to sorption and their recalcitrant nature. Treatment processes ensure safe and high-quality biosolids by reducing the potential for adverse environmental impacts such as pathogen levels; however, they have yet to be evaluated for their impact on the fate of PFAS. The objective of this study was to compare PFAS concentrations in four commercially available biosolid-based products that received different types of treatments: heat-treatment, composting, blending, and thermal hydrolysis. Seventeen perfluoroalkyl acids (PFAAs) were quantified using liquid chromatography with tandem quadrupole time-of-flight mass spectrometry followed by screening for thirty PFAA precursors. Treatment processes did not reduce PFAA loads except for blending, which served only to dilute concentrations. Several PFAA precursors were identified with 6:2 and 8:2 fluorotelomer phosphate diesters in all samples pre- and post-treatment.

3.2 Introduction

Biosolids are nutrient-rich materials from the treatment of domestic wastewater in a water resource recovery facility (WRRF) are applied to agricultural land as a fertilizer to enhance agricultural production and maintain soil quality. Although biosolid-derived products have many benefits, they may contain per- and polyfluoroalkyl substances (PFAS) of varying levels depending on sources entering WRRFs. PFAS are a group of man-made chemicals with both water and oil repellent properties, thus widely used in industrial and commercial products, such as paper, textiles, fire retardants, food packaging, pesticides and other (Buck et al., 2011). PFAS contain variable carbon chain lengths with covalently bonded fluorine atoms, making them chemically and thermally stable. Hence, PFAS are difficult to degrade via chemical and biological processes (Kissa, 2001). PFAS include numerous subclasses such as fluorotelomer alcohols (FTOHs), and perfluoroalkyl sulfonamides, which are known to be precursors to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAAs) (Z. Wang et al., 2017). PFCAs and PFSAAs together are referred to as perfluoroalkyl acids (PFAAs) and thus, their precursors will be herein referred to as PFAA precursors. Due to their ubiquitous usage and recalcitrant nature, PFAS are persistent in the environment and frequently detected in various environmental matrices such as water (Appleman et al., 2014; Guelfo & Adamson, 2018; Hu et al., 2016), biosolids (Alder & van der Voet, 2015; Armstrong et al., 2016; Navarro et al., 2018; Venkatesan & Halden, 2013), soil (Munoz et al., 2018), plant (Scher et al., 2018) and wildlife (Sedlak et al., 2017). In addition, PFAS including some long-chain PFCAs and PFSAAs can bioaccumulate in aquatic organisms (Babut et al., 2017; Gewurtz et al., 2014; Hong et al., 2015), and may transfer to the food chain. Several animal toxicity studies have shown that PFAS exposure might lead to hepatotoxicity, developmental toxicity, immunotoxicity, and hormonal disruption (Lau et al., 2007).

Conventional activated sludge processes are ineffective at removing PFAS in wastewater (Sinclair & Kannan, 2006). In some cases, PFAS concentrations in the effluent have been higher than observed in the influent (Filipovic & Berger, 2015; Guerra et al., 2014; Sinclair & Kannan, 2006). This has been attributed to the biodegradation of PFAA precursors to PFAAs (Arvaniti et al., 2012; Dauchy et al., 2017; Schultz et al., 2006), which are terminal degradation products of PFAS (Arvaniti et al., 2012; Z. Wang et al., 2017). PFAAs can be produced from the breakdown of PFAA precursors or can be directly used in commercial and industrial products (Benskin et al., 2012; Favreau et al., 2017). Furthermore, since PFAS degradation typically leads to other PFAS subclasses, any decrease in the total PFAS load in the wastewater will be primarily due to partitioning into the sludge during wastewater treatment processes (D'eon, 2012; Higgins et al., 2005; Sinclair & Kannan, 2006). Although some PFAS such as FTOHs are volatile (Ross et al., 2018), in the presence of high organic matter solids such as sludge, loss due to volatility will be low compared to degradation (J. Liu et al., 2007; N. Wang et al., 2011).

Treatment of sludge is necessary to meet the EPA Part 503 Biosolids regulations that require the reduction of pathogens, vector attraction, and heavy metals in order to use biosolids as nutrient sources and soil conditioners (USEPA, 1994). Depending on these levels, biosolids are categorized to Class A or Class B. Class A biosolids meet stringent pathogen and VAR standard (no restricted use) while Class B biosolids contain a higher level of pathogens than Class A biosolids (restricted use) (USEPA, 1994). Composting and heat-treatment are the most common methods to improve the stability of organic matter and decrease pathogen levels (Fernández et al., 2007; Marttinen et al., 2004). Currently, different types of commercially available biosolid-based products are available on the market. The most common types of fertilizers are biosolids co-composted with woody materials and heat-treated biosolids in a pelletized form. Other types may

include a biosolid product blended with woody materials and a liquid fertilizer that has undergone thermal hydrolysis processes. Although treatment processes can improve the quality of commercially available biosolid-based products, the effects of these processes on the fate of PFAS have not been evaluated.

The objective of this study was to compare PFAA concentrations in four commercially available biosolid-based products that received different treatments: heat-treatment, composting, blending, and thermal hydrolysis process. To evaluate PFAA loads before (pre) and after (post) various treatment processes, Class A or B biosolids (pre-treatment) and its final product (post-treatment) were obtained from four different processing facilities in the United States and Canada. Seventeen PFAAs were quantified, and qualitative analyses of PFAA precursors were assessed using a total oxidizable precursor (TOP) assay as well as target screening of 30 PFAA precursors with time-of-flight mass spectrometry.

3.3 Materials and Methods

Standards and Reagents

All 17 PFAAs were purchased as mixtures (PFCA-MXB) from Wellington Laboratories (Guelph, Canada), containing 13 perfluorocarboxylic acids (PFCAs, C4-C18, perfluoro-n-butanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA), perfluoro-n-hexanoic acid (PFHxA), perfluoro-n-heptanoic acid (PFHpA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-nonanoic acid (PFNA), perfluoro-n-decanoic acid (PFDA), perfluoro-n-undecanoic acid (PFUdA), perfluoro-n-dodecanoic acid (PFDoA), perfluoro-n-tridecanoic acid (PFTrDA), perfluoro-n-tetradecanoic acid (PFTeDA), perfluoro-n-hexadecanoic acid (PFHxDA) and perfluoro-n-octadecanoic acid (PFODA)), and 4 perfluorosulfonic acids (PFSAs, potassium perfluoro-1-butanesulfonate (PFBS), sodium perfluoro-1-hexanesulfonate (PFHxS), sodium perfluoro-1-

octanesulfonate (PFOS), sodium perfluoro-1-decanesulfonate (PFDS)). Isotopically labeled compounds were also purchased in premixed ampules from Wellington Laboratories (MPFAC-MXA), containing 1,2,3,4-¹³C₄-labeled perfluorobutanoic acid (MPFBA), 1,2-¹³C₂-labeled perfluorohexanoic acid (MPFHxA), 1,2,3,4-¹³C₄- labeled perfluorooctanoic acid (MPFOA), 1,2,3,4,5-¹³C₅- labeled perfluorononanoic acid (MPFNA), 1,2-¹³C₂-labeled perfluorodecanoic acid (MPFDA), 1,2-¹³C₂-perfluoro undecanoic acid (MPFUdA), 1,2-¹³C₂-labeled perfluorododecanoic acid (MPFDoA), ¹⁸O₂- labeled sodium perfluoro-1-hexanesulfonate (MPFHxS) and 1,2,3,4-¹³C₄-labeled sodium Perfluoro-1-octanesulfonate (MPFOS). The reagents used in the solvent extraction, TOP assay and chromatographic analysis are described in Appendix B.

Biosolid-based Product Collection

All biosolid-based products were obtained between August 2018 and September of 2018 from four WRRFs (nutrient analysis and other parameters in Table S1 in Appendix B) The treatment processes include heat-treatment, composting, blending, and thermal hydrolysis as detailed in **Table 3-1**. The Class A or B biosolids before treatment (pre), final biosolid-based products (post-treatment) and co-composting materials that were added during the treatment process (sawdust or aged bark) were obtained from the different WRRFs (**Table 3-1**). In addition, one facility supplied three additional samples where thermal hydrolysis processes were used to assess if different pH values (pH 9.5 - 10 versus >12) as well as if lagoon storage had additional impacts on PFAS levels, which was assessed for the pH 9.5 - 10 treatment process. For composted Class B biosolids, the composted material included biosolids from four different WRRFs at two different times (2016 and 2018); whereas, the 2018 Class B biosolids that were to be representative of PFAS loads prior to composting were from one WRRF in 2018. Therefore, data for the

composting process will be discussed differently, given a direct comparison is limited. Additional information associated with each of four WRRFs is in **Table 3-1** (last column).

Table 3-1. Description of the biosolid-based products used in the study.

Post-treatment process	Sample	Sample name	WRRF information
Heat-treatment (Rotary drying at 480 – 650 °C for 45 min)	Class B biosolids Heat-treated biosolids	Heat-treatment (pre) Heat-treatment (post)	~1.1 million people served Average flow: ~95 million gallon per day (MGD) Activated sludge process Aerobic and anaerobic digestion
Blending with maple sawdust and aged bark (20 % of Class A-EQ biosolids + 20 % sawdust + 60 % aged bark)	Class A-EQ biosolids Blended biosolids Sawdust Aged bark	Pre-Blend Post-Blend Sawdust (Blending material) Bark (Blending material)	~90,000 people served Average flow: ~ 27 MGD Activated sludge process Aerobic and anaerobic digestion
Thermal hydrolysis process (A high shear mixing between 800 to 1000 rpm at 70 – 75 °C, 15 psi and pH 9.5 – 10 for 1 h) ¹	Class B biosolids Liquid biosolids (regular process) Liquid biosolids (stored in a lagoon for 2 to 8 months after process at pH 9.5-10) Liquid biosolids (high pH condition)	Pre-Thermal hydrolysis Post-Thermal hydrolysis (pH 9.5-10) Post-Thermal hydrolysis (pH 9.5-10, lagoon) Post-Thermal hydrolysis (> pH 12)	1.5 million people served Average flow: ~150 MGD Activated sludge process Anaerobic digestion
Composting with sawdust (Windrow technology, 55 °C Active composting/curing for ~84 days, 20 % biosolids and 80 % sawdust)	Class B biosolids (2018) ² Composted 2016 biosolids ³ Composted 2018 biosolids ³ Sawdust	Class B biosolids from 2018 Composted 2016 biosolids Composted 2018 biosolids Co-composting material (sawdust)	~800,000 people served Average flow: ~70 MGD Activated sludge process Anaerobic digestion

¹ This hydrolysis process used for this product was conducted at lower pressure (as well as lower temperature) than is typically used (typically > 140 °C) in thermal hydrolysis processes (McNamara et al., 2012; Strong et al., 2011). ² Biosolids from a single municipal water resource recovery facility (WRRF); ³ Class B biosolids from four different WRRFs.

Upon receipt, samples were weighed and transferred to 50-mL polypropylene (PP) tubes and frozen (- 20 °C) until freeze-drying. Prior to extraction, all biosolid-based products were freeze-dried for 72 hours using a freeze dryer (Labconco, Kansas City, MO). The freeze-dried samples were sieved (< 2 mm) to obtain homogeneous samples (Table S1 in Appendix B). Organic product solution pH was measured (Accumet research AR20, Fisher Scientific, Hampton, NH) for a 0.5-g sample to 5-mL deionized water after a 24-h equilibration (Table S1 in Appendix B).

Biosolid-based Product Extraction

For all samples, PFAA analysis was done on subsamples from the < 2 mm fraction. In addition, the > 2 mm fraction of the post-composted 2016 biosolids product and post-blend product, as well as the blending and co-composting materials, were evaluated for PFAA loads, which we hypothesized would not contribute significantly to the overall PFAA loads in the final product. Freeze-dried samples (five replicate subsamples from each sample) were extracted for 17 PFAAs using a method modified from (Sepulvado et al., 2011). Briefly, 0.5-g samples were added to a 15-mL polypropylene (PP) tubes immediately followed by the addition of isotopically labeled surrogate mixtures (10 ng each). Samples were extracted with 7-mL 99/1 v/v methanol/200 mM ammonium hydroxide aqueous solution and vortexed for 1 minute. The samples were then sonicated in a heated sonication bath at 30 °C for one hour followed rotating end-over-end for 2 hours. The samples were centrifuged (1,613 RCF) for 30 minutes and the supernatant transferred to a clean 50-mL PP tube. This process was repeated two more times. Prior to analysis, all solvent extracts were combined and concentrated under nitrogen using a RapidVap Vacuum Evaporation System (Labconco, Kansas City, MO) and reconstituted with 1000 µL of 99:1 (v/v) methanol and glacial acetic acid. A fraction of the extract (500 µL) was saved for PFAA precursor screening analysis. The remaining extract (500 µL) was cleaned with 20 - 30 mg of ENVI-Carb to reduce

matrix effects that may affect quantitation. An aliquot of cleaned extract (400 μL) was transferred to a 1.5-mL injection vial containing 400 μL of 0.003% ammonium hydroxide in nanopure water (1:1, MeOH:H₂O, v/v). The samples were stored in a refrigerator at 4°C until analysis.

PFAA Analysis

All samples were analyzed for 17 PFAAs by liquid chromatography with tandem mass spectrometry (LC-MS/MS) using a Shimadzu system coupled to a SCIEX TripleToF 5600+ (Framingham, MA). PFAA analysis was performed based on the method described by Choi et al. (2019). Briefly, Analyst TF1.7 software (SCIEX) was used to control the instrument. Target analytes (15 μL) were separated using a Kinetex[®] EVO C18 column (100 Å, 100 x 2.1 mm, 5 μm , Phenomenex) with a gradient at a flow rate of 0.75 mL/min. A delay column (Luna C18, 100 Å, 30 x 4.6 mm ID, 3 μm , Phenomenex, Torrance, CA) was installed between the mobile phase mixer and autosampler injection port to separate PFAS background contamination from the system. The gradient used 0.15% acetic acid in water (A) and 20 mM ammonium acetate in methanol (B) mobile phases with the following gradient profile (total 11 min): 0 – 0.5 min: 30%B; 0.5 – 3 min: 30 – 70%B; 3 – 6.5 min: 70 – 100%B; 6.5 – 8.5 min: 100%B; 8.5 – 9 min: 100 – 30%B and 9 – 11 min: 30%B. All data were processed with MultiQuant software 3.0.1 (SCIEX). Precursor to product ions are summarized in Table S2 (Appendix B).

PFAA Precursor Screening Analysis

The potential presence of PFAA precursors in the biosolid-based products that are subject to generate PFAAs in the future was explored by screening for 30 known PFAA precursors (see Table S3 in Appendix B) using LC-QToF/MS in SWATH[™] acquisition mode. The PFAA precursor data were acquired on the SCIEX 5600 QToF as described by Choi et al. (2019), which used the same column and mobile phases as noted for the PFAA quantification except with a

different gradient at 0.5 mL/min as follows (total 18.20 min): 0 – 0.1 min: 10 %B; 0.1 – 10 min: 10 – 100 %B; 10 – 15 min 100 %B; 15.00 – 15.20 min: 10 %B and 15.20 – 18.20 min: 10%B. Biosolid-based product extracts in methanol, the procedural blank and a standard mixture of analytical PFAA precursors (EtFOSE, EtFOSAA, EtFOSA, MeFOSA, FOSA, FOSAA, 6:2 FTOH, 6:2 FTCA and 5:3 FTCA) were processed with a 30- μ L injection volume. PeakView 2.2 software with MasterView (SCIEX) was used to analyze SWATHTM data. Only [M-H]⁻ was considered. PFAA precursors were identified using a comparison of MS/MS spectra with the mixture of analytical standards or the Fluorochemical High-Resolution MS/MS Spectral Library (SCIEX) database.

Analytical QA/QC

A stable-isotope dilution with nine mass-labeled standards was used to correct for the matrix effect and the extraction recovery. A six-to eight-point calibration curve (0.01 to 15 μ g/L) to cover the entire range of the sample concentrations was prepared and performed at the beginning and the end of a sample batch. A continuing calibration verification standard was injected every 12 injections immediately after an instrument blank, which was used to monitor potential carryover between injections. The limit of detection (LOD) and quantification (LOQ), as well as recoveries and other analytical details, are included in Table S2 (Appendix B).

Statistical Analysis

Statistical analyses were performed using R software (version 3.4.3). Normality and homogeneity of the variances were tested with the Shapiro-Wilk test and Levene's test, respectively. One way-analysis of variance (ANOVA) followed by Tukey's post hoc tests ($p < 0.05$) were performed to determine the statistical differences.

3.4 Results

PFAA Concentrations in Pre and Post Samples

PFAA composition and loads ($\mu\text{g}/\text{kg}$ dry weight) in the < 2 mm particle size fraction before (pre) and after (post) heat-treatment, blending or thermal hydrolysis are summarized in **Figure 1** (additional details in Tables S4 and S5 in Appendix B).

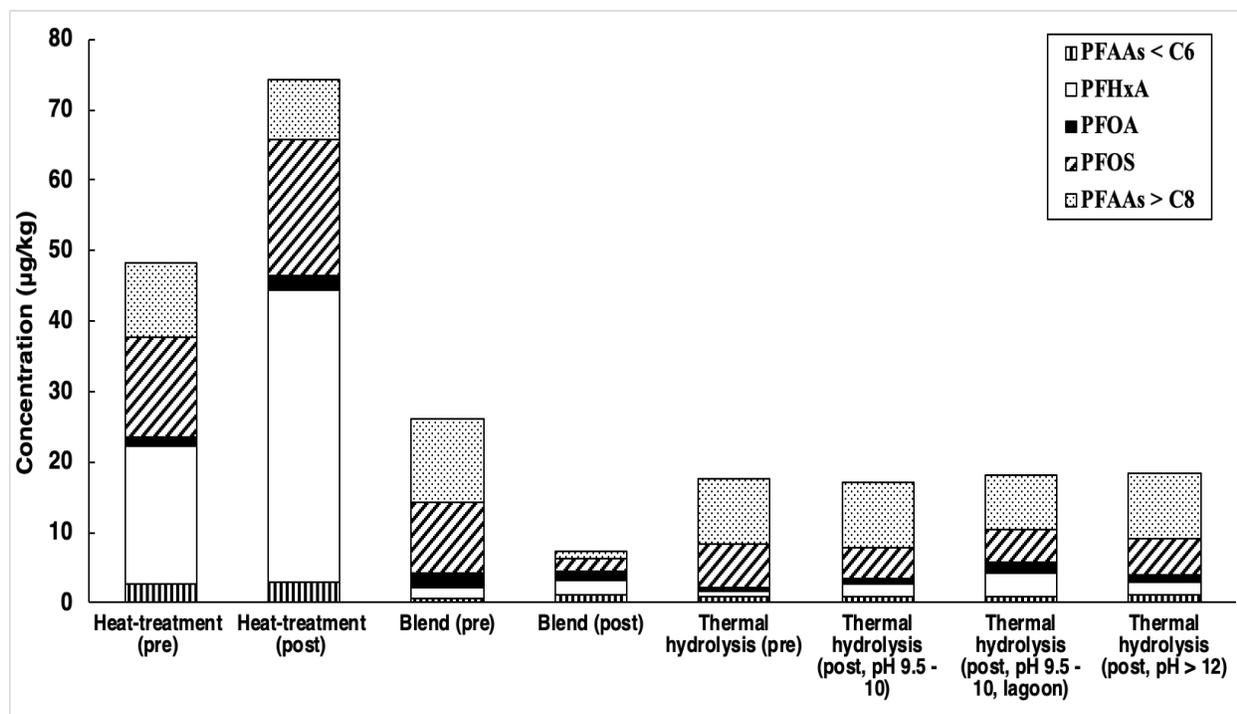


Figure 3-1. PFAA loads ($\mu\text{g}/\text{kg}$, dry wt.) for the < 2 mm particle size fraction of the samples. Pre: before post-treatment process (Class A or B biosolids) and post: after post-treatment process. PFAAs $< C6$ include PFBA, PFBS, and PFAAs $> C8$ include PFNA, PFDA, PFUdA, PFD_oA, PFTrDA and PFTeDA.

PFAAs ranged from 18 to 49 μg total PFAAs/kg (PFHxA: 0.4 – 19 $\mu\text{g}/\text{kg}$, PFOA: 0.7 – 1.3 $\mu\text{g}/\text{kg}$ and PFOS: 6.1 - 14.3 $\mu\text{g}/\text{kg}$) prior to treatment process. The ranges are generally within the range of PFAS detected in wastewater solids (Armstrong et al., 2016; N Gottschall et al., 2017; Navarro et al., 2017). After treatment, samples ranged from 8 to 123 μg total PFAAs/kg. Individual PFAA concentrations are summarized in Figure S3 (Appendix B). Heat-treatment (45 minutes at

480 to 650 °C) led to an increase in the total PFAA concentrations by 53% (49 to 75 µg/kg), which was mainly due to increased PFHxA concentrations (19 to 42 µg/kg) (**Figure 3-2**).

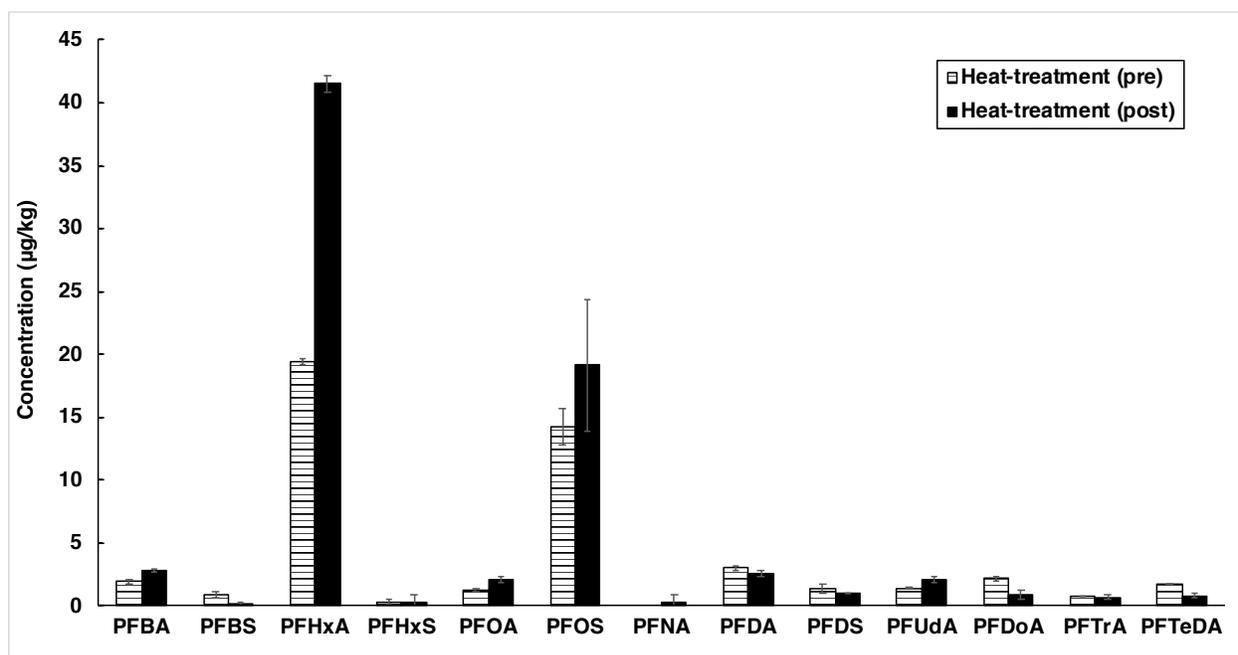


Figure 3-2. Individual PFAA concentrations (µg/kg, dry wt.) in biosolid-based products (< 2 mm fraction) pre and post heat treatment. Error bars represent the standard error of the mean (n = 4 – 5).

Increases in PFHxA indicates that some PFAA precursors with a C6 perfluorinated alkyl chain were degraded during the heat-treatment. Although PFAS are known to be thermally stable, limited thermal degradation of PFAS data is currently available. However, a few studies have suggested that certain fluoropolymers such as polytetrafluoroethylene (PTFE) and FTOHs can thermally (~500 °C) degrade to PFCAs (Ellis et al., 2001; Ellis et al., 2004). Based on the other degradation studies, fluorotelomer-based PFAA precursors, which contain a CH₂CH₂-linkage between the fluoroalkyl chain and polar functional group, break down to PFCAs via aerobic biotransformation (Chen Liu & Liu, 2016; N. Wang et al., 2011) and heat-activated chemical oxidation (Park et al., 2016). The blending process reduced the total PFAA concentrations by 72 %

(27 to 8 $\mu\text{g}/\text{kg}$), which is a dilution effect from blending of biosolids (20 %) with 80 % woody products (20 % sawdust and 60 % aged bark) (**Table 3-1**).

For the thermal hydrolysis treatment process (70 – 75 °C), there were no significant differences in total PFAAs before and after the pH 9.5 – 10 for 1-hour treatment even after lagoon storage or after the pH >12 treatment (**Figure 3-1**). However, PFHxA and PFOA concentrations ($\mu\text{g}/\text{kg}$) did increase after 2 to 8 months of lagoon storage after the pH 9.5 - 10 thermal hydrolysis treatment (**Figure 3-3**). PFAS breakdown under anaerobic conditions such as anaerobic sludge digestion (Sun et al., 2011) and landfills (Benskin et al., 2012) have been reported although degradation rates are slower than those observed in aerobic conditions (Sáez et al., 2008).

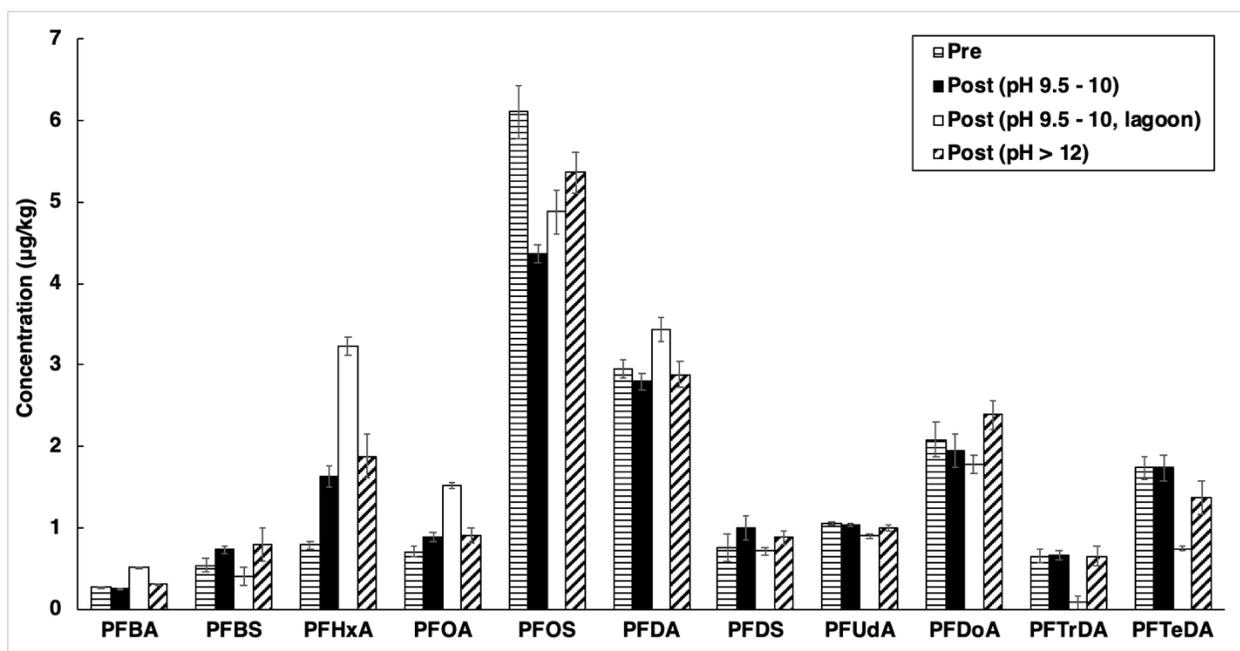


Figure 3-3. Individual PFAA concentrations ($\mu\text{g}/\text{kg}$, dry wt.) in the biosolid-based products (< 2 mm particle size fraction) treated by thermal hydrolysis. Pre: Class B biosolids before thermal hydrolysis; Post (pH 9.5 – 10): thermal hydrolyzed at pH 9.5 – 10; Post(pH 9.5 – 10, lagoon): lagoon storage after thermal hydrolysis at pH 9.5 – 10; and Post (pH > 12): thermal hydrolyzed at higher pH (> 12). Error bars represent the standard error of the mean (n = 4 - 5).

For composting, PFAA concentrations were higher in the composted 2018 biosolids compared with the untreated Class B biosolids from 2018 (**Figure 3-4**); however, the differences cannot be automatically assumed to be from the composting process.

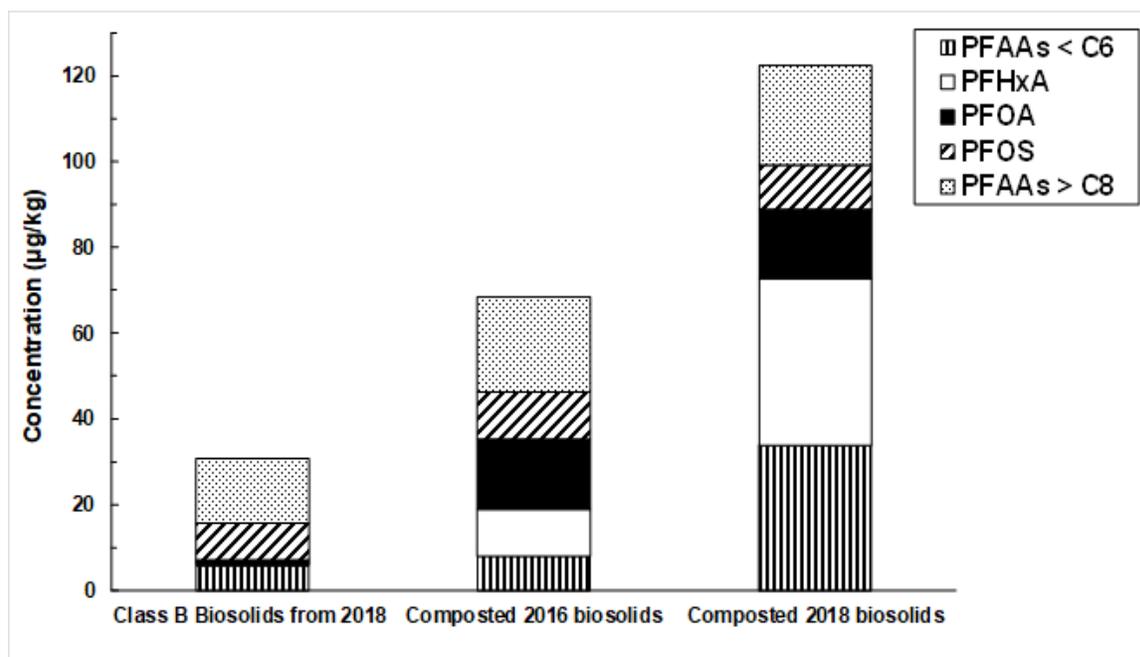


Figure 3-4. PFAA loads ($\mu\text{g}/\text{kg}$, dry wt.) for the < 2 mm particle size fraction of the Class B Biosolids from 2018 from a single municipal water resource recovery facility (WRRF) and final composted 2016 and 2018 fertilizer products that contained Class B biosolids from different WRRFs. Only one source of the Class B biosolids from 2018 was obtained and analyzed. PFAAs $< C6$ include PFBA, PFBS, and PFAAs $> C8$ include PFNA, PFDA, PFUdA, PFDoA, PFTrDA and PFTeDA.

As noted earlier, the uncomposted biosolids came from one WRRF whereas the biosolids that had been composted were a mix of biosolids from three additional WRRFs, which constituted approximately 40 % of the total biosolids that were composted in both 2016 and 2018. Without knowing the PFAAs level in the unanalyzed sources of the actual Class B biosolids that were used in the composting process prior to composting, it is difficult to evaluate the effect of composting on PFAS fate. The potential reasons for elevated PFAA concentrations in the composted samples can be attributed to higher PFAA levels in the other Class B biosolid sources or breakdown of

PFAA precursors to PFAAs during composting process. Also, it was noticed that there are several nearby manufacturing facilities that may use PFAS in their processes which may be potential sources of contamination to the composting site, which could occur through air transport or possibly contaminated water. Some volatile PFAS such as FTOHs can be transported and oxidized in the atmosphere yielding PFCAs (Ellis et al., 2004). For example, the primary product of 8:2 FTOH degradation and atmospheric oxidation is PFHxA (Ellis et al., 2004; J. Liu et al., 2007). However, PFHxA concentrations are three times higher in the composted 2018 biosolids compared to the composted 2016 biosolids whereas there are negligible differences in PFOA and PFOS. Therefore, increases in PFHxA is more likely to be a direct response to its use as a replacement of PFOS and PFOS precursors in 2002 and PFOA and PFOA-related chemicals in 2015 (Alder & van der Voet, 2015; USEPA, 2006). Even with the phase-outs, PFOS is still used in the chrome plating industry and many previously purchased consumer products containing PFOA-based materials are still in use (Briels et al., 2018; United Nations Environmental Program, 2009). Although dilution could occur in a composting process if co-composting materials such as plant materials are added as part of the process, others have shown that composting biosolids is ineffective at reducing contaminant levels in sludge or other types of biosolids product (Chad A. Kinney et al., 2006).

Variation in PFAA Levels between the < 2 mm and > 2 mm Particle Size Fractions

In the larger particle size fractions (> 2 mm), which were evaluated for the composted 2016 biosolids, > 2 mm) and the blend (post > 2 mm), the total PFAA concentration were 35 and 17 $\mu\text{g}/\text{kg}$, respectively, but with high standard deviations (SD) among the 5 replicates ($\pm 15 \mu\text{g}/\text{kg}$ and $\pm 16 \mu\text{g}/\text{kg}$, respectively). This high variation may be due to the clinging of the finer material (< 2 mm) to the larger particles (> 2 mm). It was difficult to separate the two fractions unless a

washing process was used, which could have leached out some of the PFAAs. For the bark blend, sawdust blend, and sawdust compost materials total PFAAs were $< 2 \mu\text{g}/\text{kg}$ (**Table 3-2**). Therefore, when PFAA concentrations determined for the $< 2 \text{ mm}$ particle size fraction are normalized to the whole product, overall PFAS loads per mass of product decreases (a dilution effect) with 32 % of the blended and 39 - 47 % of the composted 2016 and 2018 product consisting of the particle size $> 2 \text{ mm}$. Although these blending materials for these products were low in PFAAs, previously reported PFAS levels in wood building materials ranged from 1.39 to 18.3 $\mu\text{g}/\text{kg}$ with a median concentration of 4.9 $\mu\text{g}/\text{kg}$ (Bečanová et al., 2016). For these wood-based materials with higher PFAA levels, residual sealants and other adhesive products may serve as the PFAS source (Bečanová et al., 2016).

Table 3-2. A summary of ΣPFCAs , ΣPFSA s, $\Sigma\text{Short chains}$, $\Sigma\text{Long chains}$ and ΣPFAAs concentrations ($\mu\text{g}/\text{kg}$) of the $> 2 \text{ mm}$ particle size fraction and blending and co-composting materials from the Blend and Compost products ($n = 5$). The value in parenthesis is the standard error of the mean.

Sample	ΣPFCAs	ΣPFSA s	ΣShort^1	ΣLong^2	ΣPFAAs
Blended (post)	11.0 (5.5)	6.0 (1.5)	8.5 (2.9)	9.5 (4.1)	16.9 (6.9)
Composted 2016 biosolids	25.3 (5.3)	9.6 (1.5)	16.8 (2.8)	19.9 (4.1)	34.9 (6.8)
Bark (Blending material)	1.1 (0.5)	0.2 (0.1)	1.6 (0.4)	0.2 (0.1)	1.3 (0.4)
Sawdust (Blending material)	0 (0)	0 (0)	0 (0)	0 (0)	0.1 (0)
Co-composting material (sawdust)	0.1 (0)	0 (0)	0.2 (0)	0 (0)	0.2 (0)

¹Short chains include PFCAs $\leq C7$ and PFSAAs $\leq C5$

²Long chains include PFCAs $\geq C8$ and PFSAAs $\geq C6$.

Screening for PFAA Precursors

A summary of the PFAA precursors found in the biosolid-based products is summarized in **Table 3-3**. Of those found, 6:2 and 8:2 fluorotelomer phosphate diesters (diPAPs) were detected in all samples pre- and post-treatment. 6:2 and 8:2 fluorotelomer sulfonates (FTSA) and 5:3 fluorotelomer carboxylic acid (FTCA) were detected in the heat-treatment (pre and post), the 2018

Class B biosolids (from one WRRF) and the composted 2018 biosolids (represented Class B biosolids from several WRRFs). The 5:3 FTCA is a metabolite unique to degradation of fluorotelomers (J. Liu & Avendaño, 2013). Also detected in only the composted biosolids was perfluorooctane sulfonamide (FOSA), which is an intermediate metabolite prior to the formation of PFOS for *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) (Zhang et al., 2017) and mono/diPAPs (Benskin et al., 2013). The half-lives reported for microbial degradation of FTSA are > 3 months and vary widely for PAPs (J. Liu & Avendaño, 2013). The detection of diPAPs, FTSA and FTCA in biosolids was consistent with previous studies (Eriksson et al., 2017; Lee et al., 2013).

Table 3-3. PFAA precursors identified in the screening of 30 targeted PFAS (see Table S5 in Appendix B).

	Heat-treatment	Blending	Thermal hydrolysis¹	Composting²
Pre	5:3 FTCA 6:2 FTSA 8:2 FTSA 6:2/6:2 diPAPs 6:2/8:2 diPAPs 8:2/8:2 diPAPs	5:3 FTCA 6:2/6:2 diPAPs 6:2/8:2 diPAPs 8:2/8:2 diPAPs 8:2/10:2 diPAPs	5:3 FTCA 6:2/6:2 diPAPs 6:2/8:2 diPAPs 8:2/8:2 diPAPs 8:2/10:2 diPAPs	5:3 FTCA 6:2/6:2 diPAPs 6:2/8:2 diPAPs 8:2/8:2 diPAPs
Post	5:3 FTCA 6:2 FTSA 8:2 FTSA 6:2/6:2 diPAPs 6:2/8:2 diPAPs	6:2/6:2 diPAPs 8:2/8:2 diPAPs 8:2/10:2 diPAPs	5:3 FTCA 6:2/6:2 diPAPs 6:2/8:2 diPAPs 8:2/8:2 diPAPs	FOSA 5:3 FTCA 6:2 FTSA 8:2 FTSA 6:2/8:2 diPAPs 8:2/8:2 diPAPs 8:2/10:2 diPAPs

¹ For the materials processed with the standard thermolysis process at pH 9.5 - 10; ² Composting (pre) sample represents Class B biosolids from a single source in 2018 whereas the Composting (post) sample represents the composted 2018 Class B biosolids from different municipal water resource recovery facilities (WRRFs).

3.5 Conclusions

This study examined the effect of the treatment processes on the level of PFAS in commercially available biosolid-based products. The post-treatment processes either increased the

PFAA concentrations due to the breakdown of PFAA precursors or had no significant effect on the level of PFAAs with one exception. The blending process by dilution reduced the overall concentration of PFAAs. The QToF/MS screening revealed that some PFAA precursors remained after the treatment processes, which can degrade to PFAAs after application of biosolid-based products. Due to the ineffectiveness of common post-treatment processes on PFAS concentrations in biosolid-based products, it is important to control sources contributing to PFAS levels in biosolids. Implementation of control measures can rapidly reduce loads coming in our wastewater treatment plants. For example, Krogh et al. (2017) and Brose et al. (2019) found statistically significant decreases in triclosan and/or triclocarban concentrations in wastewater influent in 2014 compared to previous years, which could be attributed to a policy change by the U.S. FDA affecting the source of these compounds in consumer products (Brose et al., 2019; Krogh et al., 2017). Likewise, Andrade et al. (2015) showed a decrease in brominated diphenyl ether (BDE)-47 and BDE-49 concentrations in wastewater influent that could be attributed to the phase-out of these compounds in manufacturing (Andrade et al., 2015). Additional control measures are needed such as pretreatment of high PFAS level containing WRRF influent to reduce PFAS loads that may partition into materials used in producing biosolid-based products. These are critical points in the PFAS discussion as it relates to wastewater treatment given their persistence.

It is also important to inspect potential points of contamination in the biosolid treatment process such as equipment used in the treatment process that may contain PFAS. PFAS deposition from the area surrounding the composting facility can occur, especially when placed amidst other industry and manufacturing facilities that may use PFAS in their production line. Although biosolid-based products are beneficial to plant health and reduce wastes by recycling, thus diverting materials from incineration or landfilling, the presence of PFAS in biosolid-based

products is a rapidly growing concern among the public and within regulatory agencies. Recently, the Maine Department of Environmental Protection (DEP) has established screening standards for 3 PFAS (1,900 $\mu\text{g}/\text{kg}$ for PFBS, 2.5 $\mu\text{g}/\text{kg}$ for PFOA and 5.2 $\mu\text{g}/\text{kg}$ for PFOS) that products from all biosolids/sludge program licenses and biosolids/sludge composting facilities must meet to be land-applied. In our study, only three samples meet all three screening levels among all pre and post samples (a total of 11). These types of regulations will put an enormous amount of pressure on composting facilities along with additional costs. This research is an important first look at understanding how different treatment processes affect PFAS concentrations in final biosolid-based products. In addition to controlling PFAS sources entering our WRRFs, research is needed to find ways to minimize the PFAS in biosolids and reduce PFAS leachability from biosolids-based products to reduce PFAS loads entering the environment and risks to human and ecosystem health.

3.6 Acknowledgments

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CHAPTER 4. PLANT UPTAKE OF PERFLUOROALKYL ACIDS AND OTHER TRACE ORGANICS FROM A COMMERCIALY AVAILABLE BIOSOLID-BASED FERTILIZER

4.1 Abstract

While commercially available biosolids-based fertilizers have gained popularity for personal use in urban and suburban gardens, they contain trace organic chemicals such as perfluorinated alkyl acids (PFAAs) and pharmaceutical and personal care products (PPCPs). Here, the potential uptake of 17 PFAAs and 6 PPCPs by common garden plants (kale and turnip) grown in a Miracle-Gro potting mix amended at different rates (0X, 1X, and 4X) of Milorganite, a biosolids-based fertilizer, was determined. Plant roots, leaves, stems, and fruits at maturity were harvested and analyzed for the target organic chemicals along with the growing media. A measure of bioavailability was evaluated as well by quantifying the target contaminants in the pore-water of water-saturated Milorganite. Chemical concentrations were determined using liquid chromatography-tandem mass spectrometry. The plant uptake and pore-water concentrations of the PPCPs largely depended on the chemical's hydrophobicity, with chain length the most significant factor for PFAAs and for the PFAAs. The rate of application affected the level of the target contaminants more in the growing media than in the plant. The results of this study provide information on the potential bioavailability, plant uptake, and translocation of contaminants from the amendment of biosolids-based fertilizers to food crops in urban and residential gardens. This information will improve our understanding of the potential risk food safety and subsequent risk to ecological and human health.

4.2 Introduction

Sales in commercially available biosolid-based products have been increasing over the last two decades. These fertilizers are a rich source of nutrients and organic matter often used in urban agriculture (e.g., home and community gardens) and recreational areas (e.g., golf courses, parks, lawns). However, A number of studies have reported that organic contaminants, such as per- and polyfluoroalkyl substances (PFAS) and pharmaceutical and personal care products (PPCPs), have been detected in biosolids (Andrade et al., 2015; Brose et al., 2019; Eriksson et al., 2017; Semblante et al., 2015; Venkatesan & Halden, 2013). Thus, the potential risk of food contamination can increase when biosolids are applied to produce food crops.

Several studies have evaluated plant accumulation of target contaminants such as azithromycin, carbamazepine, miconazole, diphenhydramine, triclosan, and triclocarban from liquid or solid media by the plant's root and translocation to different parts of a plant (Table 1-1). While hydroponic experiments can be useful for understanding uptake mechanisms, they do not account for the interaction between compounds and soil, which can alter contaminant bioavailability, thus plant uptake (Pan & Chu, 2017). Therefore, the factors controlling plant uptake may also be different between hydroponic and field studies. Greenhouse pot studies better represent what may be taken up by plants in the field compared to hydroponic studies, but many studies either use unrealistic contaminant concentrations of interest or add the contaminants to the growing media artificially (Pan & Chu, 2017). As a result, uptake in such studies is more likely to overestimate the levels of plant uptake that may occur in the field or garden. A few studies have been conducted at the field-scale in which biosolids were applied to the soil; however, low contaminant concentrations and other processes (e.g., sorption or degradation) have led to difficulty in detecting or quantifying contaminants (N. Gottschall et al., 2012; Sabourin et al., 2012).

Therefore, the objective of this study was to better evaluate the potential plant uptake of organic contaminants from biosolid-amended fertilizer-amended growing media in suburban and urban gardens. We chose a greenhouse pot experiment using common garden crops (kale and turnip) grown in potting media (Miracle-Gro) and amended with a commercially available biosolids-based fertilizer (Milorganite). Among a myriad of trace organic contaminants, a subset of PFAS (17 PFAAs) and PPCPs (azithromycin, carbamazepine, miconazole, diphenhydramine, triclosan, and triclocarban) were selected for this research based on relatively high concentrations in biosolids and their persistence after entering the environment. Physiochemical properties, structures, reported half-lives, and the concentration range of target contaminants assessed in this study are shown in Table 1-2 (PPCPs) and 1-3 (PFAAs). The target compounds for this research have been shown to adversely affect aquatic or terrestrial organisms including endocrine disruption. In the case of antibiotics and antimicrobials, the development of microbial resistance, as well as growth inhibition, has been exemplified (Table 1-4).

4.3 Materials and Methods

Reagents and Standard Solutions

All 17 PFAAs, isotopically mass-labeled compounds for use as internal standards and solvents for LC-MS/MS analysis are described in Chapter 2. Azithromycin ($\geq 98\%$), miconazole and diphenhydramine ($\geq 98\%$) were purchased from Sigma-Aldrich (St. Louis, MO). Carbamazepine (98%) and triclosan (99%) were purchased from Alfa Aesar (Ward Hill, MA). Triclocarban ($> 98\%$) was purchased from TCI America (Portland, OR). Azithromycin-13CD₃, carbamazepine-d₁₀, diphenhydramine-d₃ were purchased from Toronto Research Chemicals (North York, Ontario, Canada). Miconazole-d₅, triclosan-d₃ and triclocarban-d₄ were purchased from C/D/N Isotopes Inc. (Pointe-Claire, Quebec, Canada). Formic acid, acetonitrile, tetra-butyl

ammonium hydrogen sulfate, sodium carbonate, sodium bicarbonate, methyl tert-butyl ether, and acetone were purchased from Fisher Scientific (Hampton, NH).

Biosolid-based Fertilizer Product

Milorganite, a biosolid-based fertilizer product, used in this greenhouse study, was obtained in 2016. The product contained 65.1 % organic matter, 60870 mg/kg total N, 704 mg/kg P, 1062 mg/kg K, 780 mg/kg Mg, 1850 mg/kg Ca, pH of 6.0 and cation-exchange capacity of 23.3 cmol/kg (determined by A&L Great Lakes Laboratories, Fort Wayne, IN). Although the Milorganite product from 2016 was used for this study, additional products for sale in 2014 and 2018 were also obtained to evaluate the temporal variation of these targeted trace organic chemicals. The temporal profile for PFAAs was reported previously in Chapter 2, but not for the PPCPs which are discussed in this chapter.

Greenhouse Experimental Design

A commercial potting mix (Miracle-Gro) was selected as the 'soil' media and weighed into plastic pots (8" Elite Azalea Pot, 20 cm diameter x 14 cm deep, 3100 cm³ capacity) at 1600 g Miracle-Gro per pot for the uptake studies. Miracle-Gro contained 50-60 % of forest product, compost, sphagnum peat moss, perlite, wetting agent and fertilizer (21000 mg/kg Total N, 305 mg/kg P, and 1,162 mg/kg K) (according to the accompanying fertilizer level). Milorganite (2016) was mixed into the top 1 inch of Miracle-Gro at 1 and 4 times the recommended application rate (1X, 9.4 g Milorganite/kg Miracle-Gro; 4X, 37.5 g Milorganite/kg Miracle-Gro). Control pots included a no Milorganite applied control treatment (0X) and no-plant controls for each of the two treatments. All treatments and controls were prepared in triplicate and arranged in a randomized-block design.

Kale (*Brassica oleracea*, Johnny's, Winslow, ME) and turnip (*Brassica rapa*, Johnny's, Winslow, ME) were selected for the plant uptake studies as representative leafy and root vegetables to examine potential differences in plant uptake. Seedlings were transplanted to each container. Plants were grown in a controlled greenhouse environment at 26 °C (day) and 22 °C (night) to provide a 12-hour day and 12-hour night cycle. Plants were watered every 3 days with Nanopure water (100-150 mL), which was 50-60% water-holding capacity to minimize water loss (no excess of water) until 30 days and then changed to every 2 days until harvest.

After 60 days, all plant samples were harvested, weighed, washed with Nanopure water, and dried. Plant samples were separated into leaves, roots, bulbs (turnip) and peels (the outer layer of bulbs, turnip), chopped and stored in a 50 mL polypropylene (PP) tube at -20 °C until freeze-drying. All samples (root, bulb, leaf, and stem) were freeze-dried (Labconco, Kansas City, MO) at -50 °C for 72 hours, ground into a fine powder using a stainless coffee grinder (KitchenAid, Benton Harbor, MI) and stored at 4 °C until extraction.

Extraction Methods for Milorganite, Miracle-Gro and Mixed Growing Media and Plants

PFAAs

Miracle-Gro, Milorganite, and the mixed media (varied with treatment) were extracted using the method described by Zhu et al. (2019) (Zhu & Kannan, 2019). Miracle-Gro (1 g) and the mixed media (1 g) were spiked with surrogate standards and extracted three times sequentially with 10 mL methanol on a 24-h end-over-end rotation. The combined extracts were concentrated under nitrogen using a RapidVap Vacuum Evaporation System. The residuals were reconstituted with 1-mL methanol.

Kale and turnip samples were extracted for 17 PFAAs using the method described by Zhao et al., (Zhao et al., 2018). Plant samples (0.5 g) were added to a PP tube along with 2-mL Nanopure

water and vortexed. Surrogate standards were added followed by 1 mL of the ion-pairing agent 0.5 M tetrabutylammonium hydrogen sulfate (pH adjusted with sodium hydroxide to 10 prior to addition) and 2 mL 0.25 M sodium carbonate/sodium bicarbonate buffer sequentially. After vortexing, 5-mL MTBE was added to the sample, rotated end-over-end for 20 minutes, and centrifuged at 3,000 rpm. The MTBE supernatant layer was decanted to a clean PP tube. The MTBE extraction step was repeated two more times and the combined MTBE extracts were concentrated under nitrogen using the RapidVap vacuum evaporator. The extraction recovery efficiencies are summarized in Table S1 (Appendix C).

PPCPs

Milorganite, Miracle-Gro, and growing media were extracted using the method described by Higgins et al. (2011) (Higgins et al., 2011). Milorganite (0.5 g), Miracle-Gro and the mixed media (1 g) were spiked with surrogate standards and extracted with 20 mL of 1:1 v/v acetone and methanol solution for 20 min in an ultrasonic bath (Branson, Danbury, CT). Samples were centrifuged at 1,400 rpm for 30 min and decanted to a new 40-mL glass tube. The extraction process was repeated twice, and the combined extract was concentrated under nitrogen gas.

Kale and turnip tissue were extracted for PPCPs (azithromycin, carbamazepine, diphenhydramine, miconazole, triclosan, and triclocarban) using the method of Wu et al. (2012) (X. Wu et al., 2012). Briefly, 0.3 g of plant sample (dry weight) was added to a 40-mL glass centrifuge tube, spiked with surrogate standards and extracted with 20 mL of MTBE with ultrasonication (5800 Branson, Danbury, CT) for 20 min. Samples were then centrifuged at 1,400 rpm for 30 minutes and the supernatants transferred into 40-mL glass tubes. The extraction process was repeated one more time and the combined extract was concentrated to near dryness under nitrogen using RapidVap N₂ at 30 °C. Samples were reconstituted with 1- mL methanol and diluted

with 20 mL of Nanopure water before loading onto an SPE cartridge (200 mg HLB, Waters, Milford, MA) for clean-up. Before clean-up, SPE cartridges were conditioned with 5 mL of methanol followed by 5 mL of Nanopure water. Samples were loaded at a flow rate of 1-5 mL/minute. After drying the cartridges for 20 minutes under vacuum, samples were eluted with 10 mL of methanol. The eluents were concentrated to near dryness under nitrogen using RapidVap N₂ Evaporator at 30 °C followed by addition of 1 mL of methanol, vortexing and sonicating for 1 min. The extraction recovery efficiencies and the matrix effect result are summarized in Table S2 (Appendix C).

Pore-Water Concentration Measurement

Pore-water concentrations of target contaminants were measured using the method described by Choi et al. (2019) as detailed in Chapter 2 for the PFAAs. For PPCPs, a similar approach was used except a glass syringe and glass wool were used to retain biosolids instead of a PP syringe and stainless-steel mesh and the SPE clean-up procedure used is as described for PPCP extraction from the media. The 48-h equilibrium time was selected to be sufficient based on kinetic studies (1 d, 7 d, 14 d, and 21 d), and the detailed desorption percent of selected PPCPs and PFAA are summarized in Table S3 (Appendix C).

Statistical Analysis

Statistical analyses were performed using R software (version 3.4.3). Normality and homogeneity of the variances were tested with the Shapiro-Wilk test and Levene's test, respectively. One way-analysis of variance (ANOVA) followed by Tukey's post hoc tests ($p < 0.05$) was performed to determine the statistical differences of the concentrations of the temporal variability.

Analytical Method: LC/MS-MS Instrumentation

PFAA

All samples were analyzed for seventeen PFAAs using a liquid chromatography-mass spectrometry (LC-MS/MS) system coupled to a SCIEX triple quadrupole time-of-flight (QToF) 5600 (Framingham, MA) using the method described by Choi et al. (2019) and detailed in Chapters 2 and 3.

PPCPs

A stable-isotope dilution with a mass-labeled standard for each PPCP was used to correct for the matrix effects and extraction recoveries. A six-to-eight-point calibration curve ranging from 0.01 to 150 µg/L was prepared to cover the entire range of the sample concentrations and run at the beginning and the end of each batch run.

LC-MS/MS analysis was performed using an LCMS-8040 tandem quadrupole mass spectrometer (Shimadzu, Kyoto, Japan). LabSolutions (Shimadzu) was used to control the instrument and process the data. Samples were separated using a reversed-phase column (Kinetex[®] EVO C18 column, 100 x 4.6 mm ID, 2.6 µm particle size, Phenomenex). The LC conditions for the target compounds are summarized in **Table 4-1**. For MS detection, electrospray ionization (ESI) was performed in both negative (ESI-) and positive (ESI+) mode. The MS conditions were optimized using a 2 L min⁻¹ nebulizing gas flow, 15 L min⁻¹ drying gas flow-, 250 °C desolvation line (DL) temperature, and 400 °C heat block temperature. Quantitative analysis of target contaminants was performed in multiple reaction monitoring modes (MRM), presented in **Table 4-2**.

Table 4-1. Chromatographic conditions for the target PPCP compounds.

LC Conditions	Azithromycin	Carbamazepine, diphenhydramine and miconazole	Triclocarban and Triclosan
Column	Phenomenex Kinetex EVO C ₁₈ , 100 mm x 4.6 mm (2.6 μm)		
Mobile phase	A: 0.1% Formic acid in H ₂ O B: 0.1% Formic acid in methanol	A: 0.1% Formic acid in H ₂ O B: Acetonitrile	A: 0.15% Acetic acid in H ₂ O B: Methanol
Flow-rate (mLmin⁻¹)	0.4	0.4	0.3
Gradient	1%B: 0-0.5 min 30%B:0.5-1.5 min 75%B: 1.50-5 min 99%B: 5-5.1 min 99%B: 5.1-10 min 1%B: 10-10.5 min 1%B: 10.5-16 min	20%B: 0-0.5 min 100%B: 0.5 -6.5 min 100%B: 6.5 -10 min 20%B: 10 – 10.5 min 20%B: 10.5 -15 min	5%B: 0-0.5 min 40%B: 0.5-1 min 100%B: 1-8 min 100%B 8-11 min 5%B: 11.5 min 5% B: 11.5 – 15 min
Column temperature (°C)	40	40	40
Injection vol.(μL)	5	5	10

Table 4-2. Detailed MS/MS information (transitions, retention times, positive or negative ion mode, Q1, CE and Q3).

Compound	Transitions	RT (min)	Mode	Q1 Pre Bias (V)	CE (V)	Q3 Pre Bias (V)
Azithromycin	749.40 > 116.25	2.845	+	-28	-49	-22
	749.40 > 591.30			-31	-40	
Azithromycin-13CD3	753.30 > 595.20	2.851	+	-28	-31	-40
	753.30 > 116.20			-26	-51	-22
Carbamazepine	236.80 > 194.10	2.790	+	-16	-19	-18
	236.80 > 192.05			-16	-24	-40
Carbamazepine-d10	249.90 > 204.25	2.745	+	-17	-21	-20
Diphenhydramine	265.05 > 167.20	2.689	+	-17	-12	-17
	256.05 > 164.90			-17	-44	-29
Diphenhydramine-d3	259.40 > 168.20	2.691	+	-18	-13	-16
Miconazole	416.75 > 159.10	3.180	+	-28	-34	-32
	416.75 > 124.15			-28	-61	-44
Miconazole -d5	421.75 > 164.00	3.157	+	-15	-30	-30
Triclocarban	313.10 > 160.10	5.187	-	21	12	26
	313.10 > 126.05			10	22	19
Triclocarban -d4	319.05 > 162.05	5.149	-	15	14	23
Triclosan	287.10 > 35	5.206	-	21	8	14
	289.10 > 35			18	10	29
Triclosan -d3	290.05 > 34.90	5.168	-	29	8	14

4.4 Results

Fertilizer product and potting media

Before the greenhouse study, the trace organic contaminants of interest were determined for the biosolid-based fertilizer (Milorganite) and the potting media (Miracle-Gro). The trace organic contaminants in Miracle-Gro were all below the limit of the quantification (LOQ). Total PFAA concentration in the 2016 Milorganite was 101 µg/kg. Among the 17 PFAAs, PFHxA (53 µg/kg) was the highest followed by PFOS (30 µg/kg). All other PFAAs ranged between the LOQs and 4 µg/kg. The detailed concentration profile is summarized in Table S5 (Appendix B).

For the PPCPs, triclocarban had the highest concentration in Milorganite ($1,328 \pm 64 \mu\text{g} / \text{kg}$) followed by triclosan ($955 \pm 26 \mu\text{g} / \text{kg}$), miconazole ($143 \pm 10 \mu\text{g} / \text{kg}$), diphenhydramine ($68 \pm 4 \mu\text{g} / \text{kg}$), azithromycin ($14 \pm 2 \mu\text{g} / \text{kg}$) and carbamazepine ($5 \pm 0.5 \mu\text{g} / \text{kg}$). These concentrations are comparable to the values reported in previous studies (summarized in Table 1-4). As discussed in Chapter 2, Milorganite was obtained for material released for use in 2016. Although Milorganite from 2016 was used for this study, the temporal variation of these compounds was assessed from 2014 to 2018 for PFAAs in Chapter 2 for both long-chain and short-chain PFAAs declined over time but the substantial drop in total PFAAs was mostly due to the decline in long-chain PFAAs.

For the PPCPs, noticeable temporal changes were observed in miconazole from 2014 to 2018 (66% increase, $p < 0.001$) and triclosan from 2014 to 2016 (60% decrease, $p < 0.001$). (Figure 4-1).

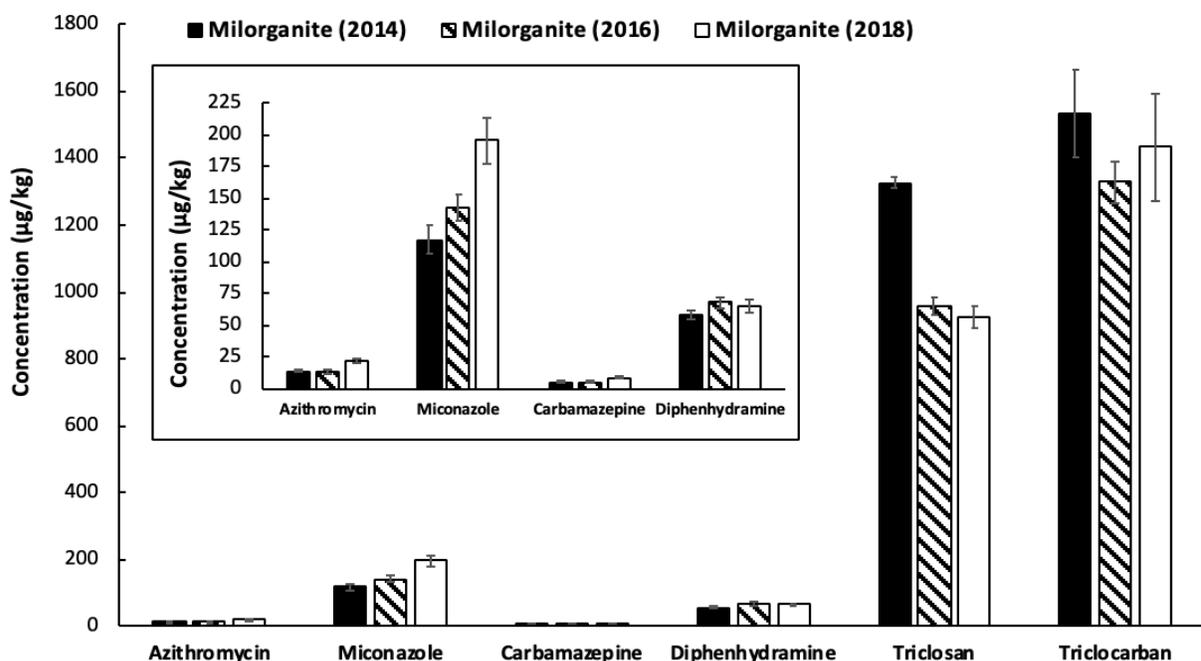


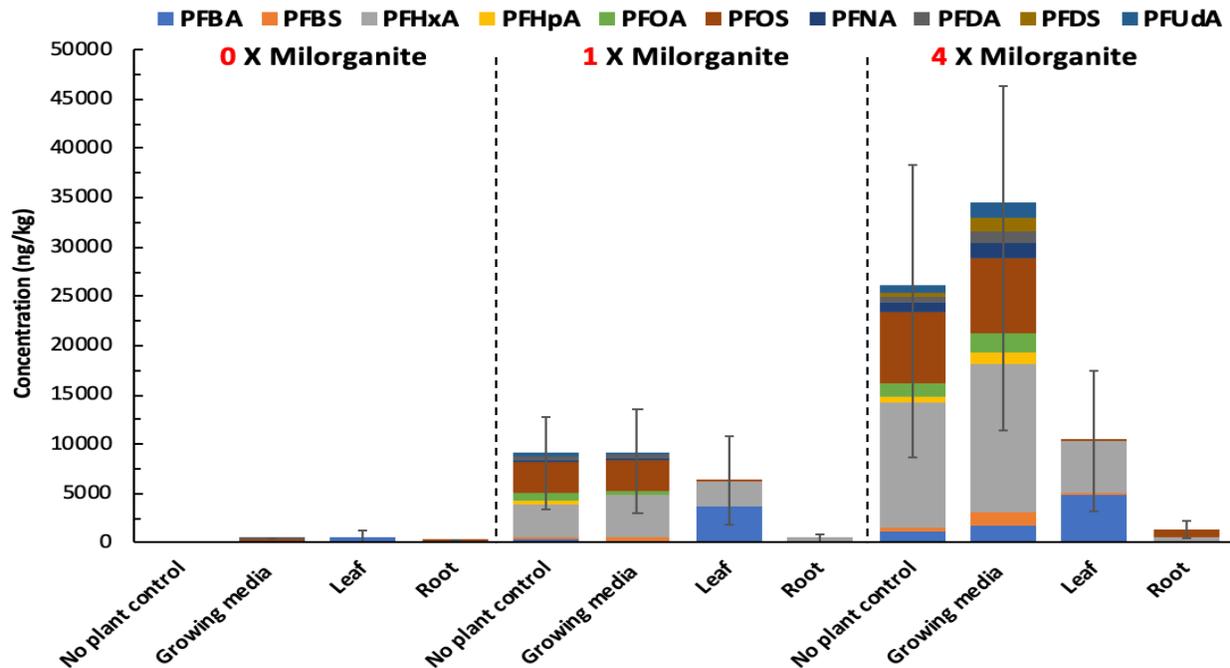
Figure 4-1. PPCP concentrations ($\mu\text{g} / \text{kg}$) in Milorganite samples obtained from 2014, 2016 and 2018. Milorganite (2016) was used for the greenhouse study. The error bars are the standard error of the mean ($n = 3$).

The decreasing trend of triclosan in biosolids from 2012 to 2017 was also reported by Brose et al. (2019) because of the FDA proposed rulemaking in 2013, the prohibiting use of antibacterial ingredients in soaps (Brose et al., 2019). Brose et al. (2019) also reported the decreased level in triclocarban; however, there were no significant changes in triclocarban from 2014 to 2016 ($p > 0.05$) in our samples. The temporal variations of the other PPCPs were not significant. The decreased PFAA levels were observed from 2014 to 2018, which was previously discussed in Chapter 2 (**Figure 2-2**).

Plant uptake

For the PFAAs, the C4-C6 PFAAs were the primary contaminants taken up by the plants while the $> C6$ PFAAs remained primarily in the growing media or plant roots (**Figure 4-2a and 4-2b**). Total PFAA concentrations (average \pm SE) in the growing media after harvest was 9000 ± 760 ng/kg (1X) and 35000 ± 7540 ng/kg (4X) in the kale pots and similar for the turnip pots (1X- 9200 ± 310 ng/kg and 4X- 19000 ± 3100 ng/kg). For kale, the total PFAAs concentrations (average \pm SE) in leaves were approximately 10 times higher than in roots for both 1X (6400 ± 550 vs 500 ± 150 ng/kg) and 4X treatment (10400 ± 5900 vs 1300 ± 620 ng/kg). The short-chain PFAAs were dominant in leaves (1X- 6200 ± 600 ng/kg and 4X- 10000 ± 5900 ng/kg) compared to the long-chain PFAAs (1X- 72 ± 80 ng/kg and 4X- 120 ± 70 ng/kg). For turnip, the leaves contained the highest total PFAAs (1X- 7700 ± 280 ng/kg and 4X- 12000 ± 1100 ng/kg) followed by the peels (1X- 3600 ± 340 ng/kg and 4X- 8400 ± 2000 ng/kg) and the bulbs (1X- 1300 ± 60 ng/kg and 4X- 2500 ± 700 ng/kg). The short-chain PFAAs were dominant in all plant parts.

(a)



(b)

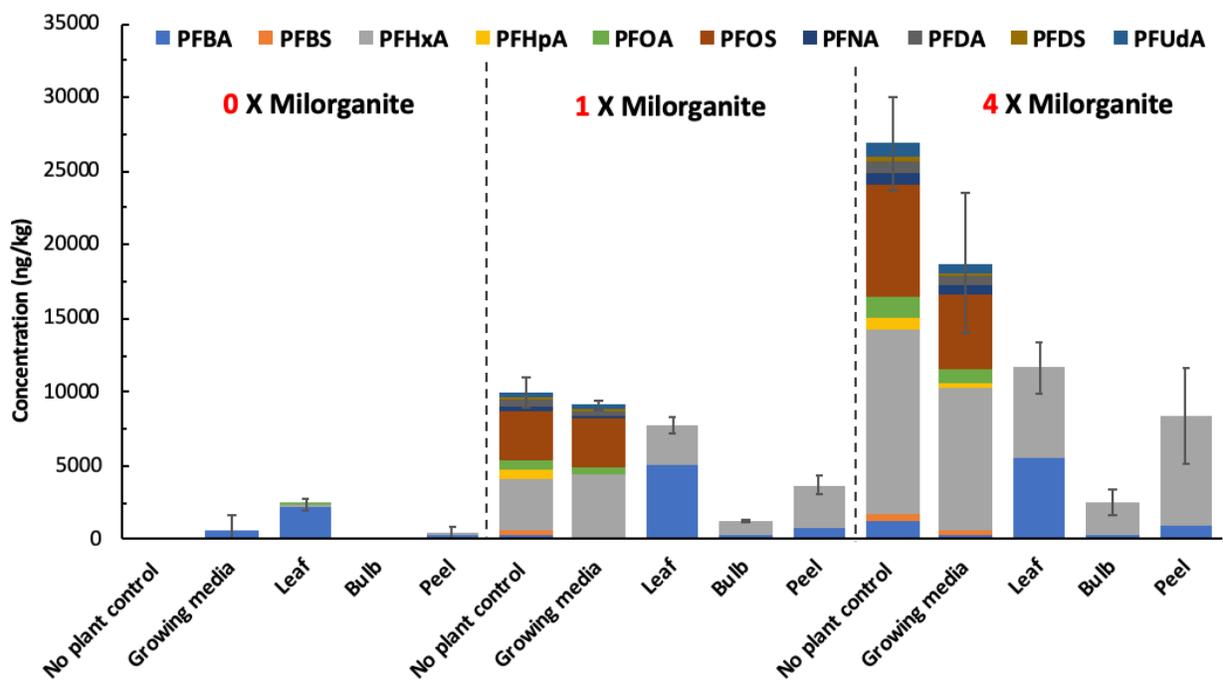
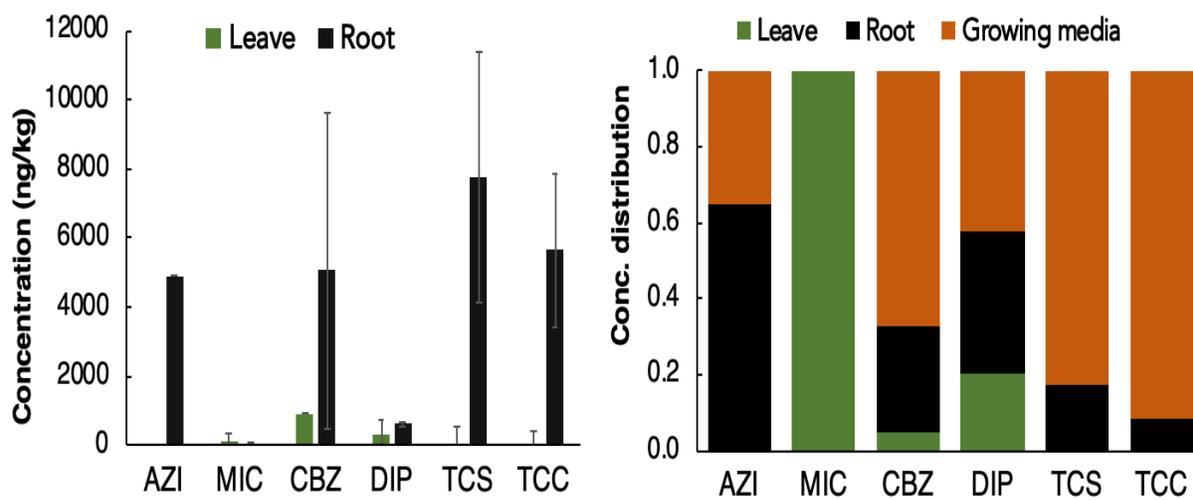


Figure 4-2. Figure 2. PFAA concentrations (ng/kg) in different plant tissues and the growing media at harvest: (a) kale and (b) turnip. The error bar represents the standard deviation of the mean (n=3).

For PPCPs in kale, most concentrations are higher in roots except for diphenhydramine (**Figure 4-3**). For turnip, it was difficult to conclude the difference in PPCP uptake between plant parts (leaves, bulb, or peel) except for diphenhydramine (**Figure 4-4**). For diphenhydramine, concentrations are highest in leaves (1X-800 ng/kg and 4X- 2400 ng/kg) compared to the bulb (1X- 250 ng/kg and 4X- 280 ng/kg) and the peel (1X - <LOQ and 4X- 100 ng/kg). For turnip roots, the mass was insufficient for extraction. Surprisingly, the 4X Milorganite application rates did not result in greater plant uptake than the 1X rate. PPCP concentration details are summarized in **Table 4-3**.

(a)



(b)

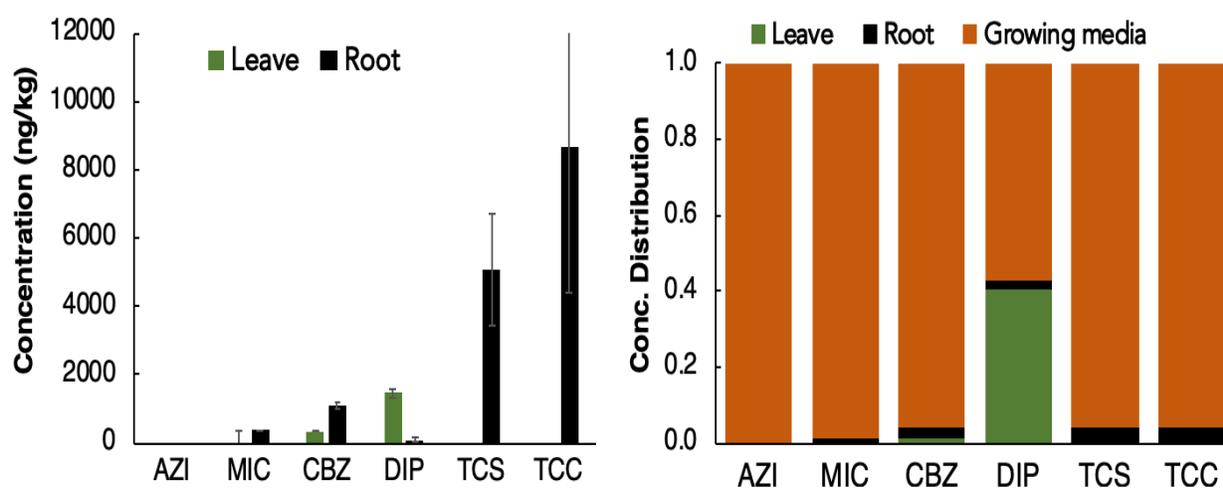
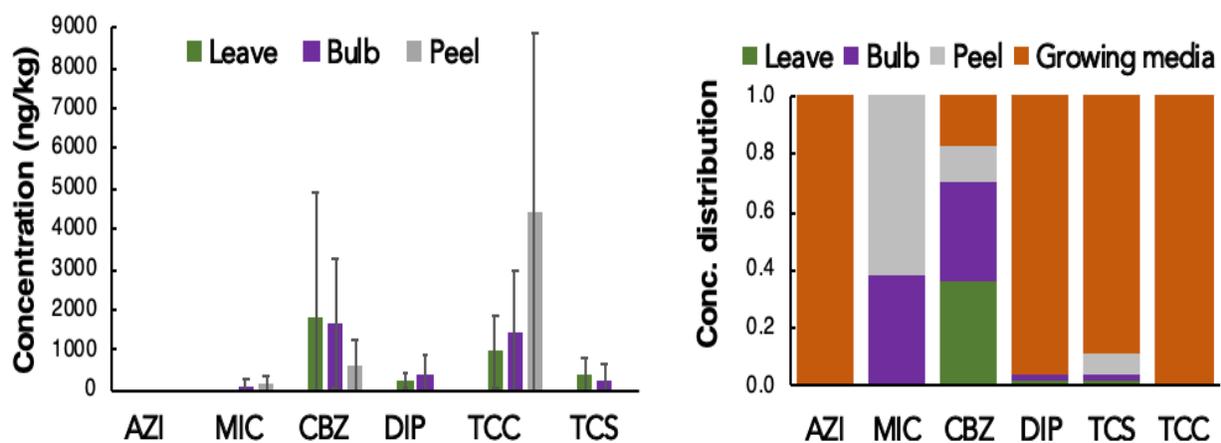


Figure 4-3. PPCP concentration (ng/kg) in kale and growing media at harvest (a) 1X and (b) 4X. The error bars are the standard error of the mean ($n = 3$).

(a)



(b)

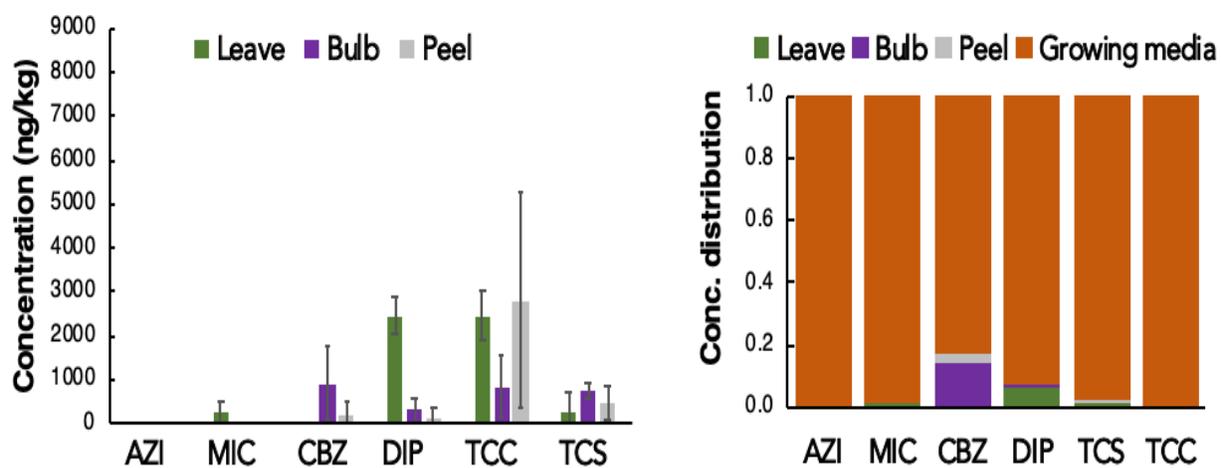


Figure 4-4. PPCP concentration (ng/kg) in turnip and growing media at harvest (a) 1X and (b) 4X. The error bars are the standard deviation of the mean ($n = 3$).

Table 4-3. PPCP concentrations (ng/kg) and SD (ng/kg) in growing media and plants. (a) turnip (b) kale.

(a)		AZI		MIZ		CBZ		DPH		TCS		TCC	
Part	Level	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD
No plant control	0X	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	305	249
Growing media	0X	<LOQ	<LOQ	3795	6573	245	136	64	111	1255	801	191	104
Leaf	0X	<LOQ	<LOQ	<LOQ	611	<LOQ	<LOQ	<LOQ	<LOQ	2493	407	329	1648
Bulb	0X	<LOQ	<LOQ	2360	746	356	199	180	180	3304	678	1067	681
Peel	0X	<LOQ	<LOQ	620	620	178	178	<LOQ	<LOQ	4447	3667	<LOQ	<LOQ
No plant control	1X	3317	934	17174	2452	28593	1850	1639	883	60285	1688	149281	11025
Growing media	1X	1497	<LOQ	<LOQ	<LOQ	14873	2313	827	202	52161	548	104798	9052
Leaf	1X	<LOQ	<LOQ	3091	1784	<LOQ	<LOQ	216	125	885	511	398	230
Bulb	1X	<LOQ	<LOQ	1573	908	192	111	444	256	1533	885	427	247
Peel	1X	<LOQ	<LOQ	935	540	<LOQ	<LOQ	<LOQ	<LOQ	1474	851	628	363
No plant control	4X	7493	1190	48760	24368	78399	16480	3248	688	167316	44308	396341	126758
Growing media	4X	2194	834	23503	12520	34872	3604	5392	5208	210373	84220	213743	47001
Leaf	4X	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	127	1228	247	<LOQ	328	566	251
Bulb	4X	<LOQ	<LOQ	838	484	<LOQ	<LOQ	254	146	706	408	<LOQ	<LOQ
Peel	4X	<LOQ	<LOQ	312	180	<LOQ	<LOQ	200	116	2454	1417	401	232

AZI: Azithromycin; MIZ: Miconazole; CBZ: Carbamazepine; DPH: Diphenhydramine; TCS: Triclosan; TCC: Triclocarban; LOQ: Limit of quantification.

LOQ (ng/kg): AZI (833.3), MIZ (166.7), CBZ (83), DPH (16.7), TCS (250) and TCC (166.7)

(b)		AZI		MIZ		CBZ		DPH		TCS		TCC	
Part	Level	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD	Conc.	SD
No plant control	0X	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	305	249
Growing media	0X	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	140	30	1451	2342	260	<LOQ
Leaf	0X	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2493	1108	329	329
Root	0X	<LOQ	<LOQ	<LOQ	<LOQ	187	<LOQ	8364	10153	<LOQ	<LOQ	1420	1565
No plant control	1X	3317	934	17174	2452	28593	1850	1639	883	60285	1688	149281	11025
Growing media	1X	2653	1541	<LOQ	<LOQ	716	189	12283	2077	36427	15260	62747	32902
Leaf	1X	<LOQ	<LOQ	142	465	344	142	928	173	<LOQ	<LOQ	<LOQ	<LOQ
Root	1X	4900	<LOQ	<LOQ	217	623	99	5082	7914	7773	6304	5642	3870
No plant control	4X	7493	1190	48760	24368	78399	16480	3248	688	167316	44308	396341	126758
Growing media	4X	2527	1262	36152	31407	2083	696	34151	20787	111281	73737	196921	235122
Leaf	4X	<LOQ	<LOQ	<LOQ	336	1473	<LOQ	336	123	<LOQ	<LOQ	<LOQ	<LOQ
Root	4X	<LOQ	<LOQ	370	<LOQ	83	117	1070	174	5069	2810	8660	7408

Contaminant porewater concentrations are important because only the dissolved fraction of a chemical will be available for plant uptake (E. L. Miller et al., 2016). Porewater of the target PPCPs and PFAAs (data available in Chapter 2) were measured, and the desorption percent was calculated using Eq. 3.

$$\text{Desorption \%} = \frac{\text{Total mass desorbed in water (g)}}{\text{Total mass present in Milorganite (g)}} \times 100 \quad (3)$$

The porewater results show that the % carbamazepine and diphenhydramine desorbed were greater than for the other PPCPs (Table 4-5).

Table 4-4. Comparison of the total amount ($\mu\text{g}/\text{kg}$) of the PPCPs and the pore-water concentration ($\mu\text{g}/\text{L}$) after 48 h incubation (1:2 g:mL mass:volume).

	Total amount in Milorganite 2016 (ng)	Mass in pore-water (ng)	% desorbed \pm SE
Miconazole	427	Not detected	0.0
Carbamazepine	15	2	14.7 ± 1.0
Diphenhydramine	204	23	11.3 ± 1.2
Triclosan	2867	2	0.1 ± 0.1
Triclocarban	3983	4	0.1 ± 0.02

The percent desorbed of diphenhydramine was the highest overall, which may explain the higher level of diphenhydramine in leaves among other PPCPs. Likewise, the higher % desorption of the short-chain PFAAs compared to the long-chain PFAAs paralleled the higher uptake of short-chain PFAAs compared to the long-chains.

4.5 Discussion

Several factors, including soil and chemical properties and various transport mechanisms, can affect the accumulation and translocation of contaminants in plants (Pan & Chu, 2017). Plant uptake greatly depends on the physicochemical characteristic of the chemicals, including water solubility, hydrophobicity which is often characterized by a compound's octanol-water coefficient

(K_{ow}) as well as characteristics of the plant growing media (e.g., pH and soil organic matter content). For ionizable contaminants, pH-dependent octanol-water partition coefficients (D_{ow}^{pH}) should be considered rather than K_{ow} to evaluate their likely behavior and interactions with plants and the growing media particularly (X. Wu et al., 2013). For non-ionizable contaminants or ionizable compounds that are neutral at environmentally relevant pH values, the K_{ow} and D_{ow}^{pH} are equivalent (Wells, 2007). K_{ow} and D_{ow}^{pH} values of the target contaminants are summarized in **Table 4-5**. Degree of ionization and D_{ow} was calculated for a pH = 7 using Eq. (1) and (2), respectively.

$$f_n = \frac{1}{1+10^{i(pH-pK_a)}} \quad (1)$$

where pK_a is the dissociation constant, f_n is the neutral fraction and i is 1 for acids and -1 for bases.

$$\text{Log } D_{ow}^{pH} = \text{Log } K_{ow} + \log \frac{1}{1+10^{i(pH-pK_a)}} \quad (2)$$

Table 4-5. The fraction of neutral molecule (f_n) and the pH-dependent octanol-water partition coefficient ($\log D_{ow}$) for the target PPCPs.

Compound	Acid/base	pK_a	Log K_{ow}	f_n (pH=7)	Log D_{ow} (pH=7)
Azithromycin	Base	8.74	4.02	0.02	2.27
Miconazole	Base	6.65	6.25	0.69	6.09
Carbamazepine	Base	13.9	2.45	1	-
Diphenhydramine	Base	8.98	3.27	0.01	1.29
Triclocarban	Acid	12.7	4.9	1	-
Triclosan	Acid	7.8	4.76	0.86	4.69

Among the target contaminants, miconazole has the highest Log D_{ow} value at pH 7 followed by triclocarban (K_{ow}), triclosan, carbamazepine (K_{ow}), azithromycin and diphenhydramine. Compounds with high D_{ow} or K_{ow} values are considered very hydrophobic (miconazole, triclocarban, and triclosan (in this study), and relatively low D_{ow} or K_{ow} values are considered less hydrophobic (azithromycin, carbamazepine, and diphenhydramine).

PFAAs are negatively charged at pH 7 due to their very low pK_a values (**Table 1-3**). Although measurement of $\log K_{ow}$ for PFAAs are tenuous due to their surfactant properties, a few studies using estimated $\log K_{ow}$ values showed that values increased with increasing perfluoroalkyl chain length (Ghisi et al., 2018; Higgins & Luthy, 2006). In a review by Ghisi et al., (2018), they also highlight that plant uptake of PFAAs largely depends on the chain-length and functional group (PFCAs vs. PFSAs). The short-chain PFCAs with ≤ 7 tend to translocate and accumulate in above-ground parts of plants while the long-chain PFCAs with > 7 tend to accumulate in roots or remain in growing media as observed in this study. The uptake of PFCAs was higher than the same length of PFSAs (Ghisi et al., 2018).

A previous study by Wu et al. (2014) suggested that hydrophobic contaminants are more likely to accumulate in roots and not translocate easily when treated wastewater was applied to soils. Intermediate hydrophobic contaminants are frequently detected in leaves, stems, and fruits (X. Wu et al., 2014). Another study concluded the similar result that neutral contaminants with intermediate hydrophobicity (e.g., carbamazepine and diphenhydramine) showed much greater transport. (Tanoue et al., 2012; C. Wu et al., 2010). For ionizable contaminants at environmentally relative pH, ionization can decrease the uptake to the shoots due to a decrease in its membrane permeability (Briggs et al., 1987; Trapp, 2000). Usually, ionized molecules cross membranes at a slower rate than neutral molecules (Trapp, 2000). Also, there are other mechanisms such as ion trap, an electrical attraction or repulsion may affect the uptake of ionized compounds by the root (E. L. Miller et al., 2016). For example, negatively charged contaminants (e.g., triclosan, partially negatively charged at pH 7) are known for poor uptake by root because the plant cells have a negative charge at the cell membrane. This leads to an electrical repulsion between negatively charged contaminants and the cell membrane (E. L. Miller et al., 2016). On the other hands,

positively charged contaminants can enhance the plant uptake due to an electrical attraction (X. Wu et al., 2013), which also explains the higher uptake of diphenhydramine. Also, the size of contaminants may possibly affect the uptake process as well; the large size may decrease mass flow or active transport (Kumar et al., 2005). This may hinder the uptake of cationic azithromycin along with high sorption to cation exchange sites.

In addition to the physicochemical properties of contaminants, plant species can vary in lipid content, and different plant types vary in places where contaminants may go (e.g., bulb, leafy, fruiting or root vegetables) (Carter et al., 2014). Also, how contaminants are introduced (e.g., biosolids-amendment, wastewater irrigations) may influence the bioavailability of compounds for plant uptake (Holling et al., 2012). Thus, uptake of contaminants by plants is complex and may be influenced by multiple factors (e.g., soil, plant, or chemical properties).

4.6 Conclusions

The uptake study revealed that short-chain PFAAs and PPCPs with less hydrophobic and cationic compounds were more readily taken up by the plant and translocated to the plant leaves compared to long-chain PFAAs and more hydrophobic compounds. In addition, the leachability of compounds affect the uptake rate. Diphenhydramine with the highest % desorption led to a higher level of diphenhydramine in leaves among other PPCPs. Likewise, the higher % desorption of the short-chain PFAAs compared to the long-chain PFAAs paralleled the higher uptake of short-chain PFAAs compared to the long-chains. Over-application the fertilizer product (4X) led to a higher level of PFAAs in all plant parts compared to the recommended rate of application (1X). Uptake of contaminants by plants is influenced by various factors such as soil, plant type, and physicochemical properties of organic contaminants.

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The current study investigated the occurrence and leachability of PFAAs and PPCPs in waste-derived organic products, and plant uptake of PFAAs and PPCPs from one of the waste-derived products (Milorganite) added as an amendment in a greenhouse pot study. The major findings of this study were:

1. Total PFAA concentrations in commercially available biosolids-based products were higher than nonbiosolid-based organic products. The temporal trend in PFAA concentrations (2014-2018) was observed with a 58% decrease in total PFAAs. This reduction was due to a reduced load of the legacy long-chain PFAAs (e.g., PFOS and PFOA) from 2014 to 2018.
2. The total oxidizable precursor (TOP) assay revealed that biosolid-based products contain PFAA precursors, which can be degraded to produce PFAAs after land application. A QToF/MS screening analysis confirmed that some PFAAs precursors (6:2 and 8:2 fluorotelomer sulfonates and some polyfluoroalkyl phosphate diesters) were present in some of the biosolid-based products.
3. The log K_{oc} values calculated from the PFAA pore-water concentrations and spent biosolid-based increased with increasing CF_2 units ($R^2 = 0.81$).
4. Fertilizers are typically applied based on N recommendations. Therefore, in some cases, biosolid-based products with a low level of N and low total PFAAs would exceed the total PFAA loads from other fertilizers that had higher levels of total PFAAs especially if they also had elevated N content.

5. The different treatment processes (heat-treatment, composting, blending and thermal hydrolysis process) either increased the PFAA concentrations due to the breakdown of PFAA precursors or had no significant effect on the level of PFAAs with one exception. The blending process by dilution reduced the overall concentration of PFAAs.
6. Short-chain PFAAs (C4-C6) accumulated in the leaves of kale and turnip while PFAAs with longer than C6 chain remained primarily in the growing media.
7. PPCPs remained mostly in the growing media rather than taken up by for kale and turnip. For kale plant parts, PPCP levels were higher in roots except for diphenhydramine. For turnip plant parts, there was no difference in PPCP uptake levels among plant parts (leaves, bulb or peel) except for diphenhydramine. Diphenhydramine was the highest level in leaves (1X-800 ng/kg and 4X- 2400 ng/kg) compared to the bulb (1X- 250 ng/kg and 4X- 280 ng/kg) and the peel (1X - <LOQ and 4X- 100 ng/kg. Diphenhydramine is cationic at pH 7 and has the lowest partition coefficient, leading to a higher pore-water concentration than other PPCPs.

5.2 Recommendations for future study

1. This study focused on the quantitative analysis of 17 PFAAs and some qualitative analysis of selected PFAA precursors in various types of waste-derived organic fertilizers. Currently, more than 4730 PFAS are potentially used in industrial processes. To obtain a more accurate estimation of PFAA loads after the application of the fertilizers, both screening PFAA precursors and quantitative analysis of PFAAs precursors should be conducted.
2. In Chapter 3, composting treatment was included in the study; however, the proper samples were not received to examine the composting effect on the level of PFAS. Composting is

one of the major processes used to produce commercially available waste-derived organic products. More study is needed to evaluate the effect of composting process on PFAS.

3. Plant uptake study was assessed in only one type of potting media (Miracle-Gro) in this study. Different types of potting media with various organic carbon contents should be used to evaluate the bioavailability of PFAAs and PPCPs from biosolid-amended potting media.
4. This study covered a suite of organic compounds that were persistent and frequently detected in biosolids. More study is needed to focus on grouping the compounds that behave similarly and understand the uptake behavior as a group rather than an individual chemical.

APPENDIX A. SUPPLEMENTAL INFORMATION: CHARACTERIZING PER- AND POLYFLUOROALKYL SUBSTANCES IN COMMERCIALY AVAILABLE BIOSOLID- VERSUS NONBIOSOLID-BASED ORGANIC PRODUCTS

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Table S11. List of the PFAA precursors.

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Figure S1. Historical annual gross revenue of a commercially available biosolid-based product (TAGRO, Product M).

Figure S2. The result of the recovery efficiency of PFAAs using two different SPE cartridges (HLB vs WAX). Error bars represent the standard error of the mean ($n = 3$).

A. Standards and Reagents

All 17 perfluoroalkyl acids were purchased in premixed ampules (PFCA-MXB) from Wellington Laboratories (Guelph, Canada), containing 13 perfluorocarboxylic acids (PFCAs, perfluoro-n-butanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA), perfluoro-n-hexanoic acid (PFHxA), perfluoro-n-heptanoic acid (PFHpA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-nonanoic acid (PFNA), perfluoro-n-decanoic acid (PFDA), perfluoro-n-undecanoic acid (PFUdA), perfluoro-n-dodecanoic acid (PFDoA), perfluoro-n-tridecanoic acid (PFTrDA), perfluoro-n-tetradecanoic acid (PFTeDA), perfluoro-n-hexadecanoic acid (PFHxDA) and perfluoro-n-octadecanoic acid (PFODA)), and 4 perfluorosulfonic acids (PFSAs, potassium perfluoro-1-butanefluorobutanesulfonate (PFBS), sodium perfluoro-1-hexanesulfonate (PFHxS), sodium perfluoro-1-octanesulfonate (PFOS), sodium perfluoro-1-decanesulfonate (PFDS)). Isotopically labeled compounds were also purchased in premixed ampules from Wellington Laboratories (MPFAC-MXA), containing 1,2,3,4-¹³C₄-labeled perfluorobutanoic acid (MPFBA), 1,2-¹³C₂-labeled perfluorohexanoic acid (MPFHxA), 1,2,3,4-¹³C₄-labeled perfluorooctanoic acid (MPFOA), 1,2,3,4,5-¹³C₅-labeled perfluorononanoic acid (MPFNA), 1,2-¹³C₂-labeled perfluorodecanoic acid (MPFDA), 1,2-¹³C₂-perfluoro undecanoic acid (MPFUdA), 1,2-¹³C₂-labeled perfluorododecanoic acid (MPFDoA), ¹⁸O₂-labeled sodium Perfluoro-1-hexanesulfonate (MPFHxS) and 1,2,3,4-¹³C₄-labeled sodium perfluoro-1-octanesulfonate (MPFOS). Individual PFAS precursors including 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (EtFOSE, > 98%), N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA >98%), N-ethylperfluoro-1-octanesulfonamide (EtFOSA, >98%), N-methylperfluoro-1-octanesulfonamide (MeFOSA, >98%), perfluoro-1-octanesulfonamide, (FOSA, >98%), perfluoro-1-octanesulfonamide acetic acid (FOSAA, >98%) were purchased from Wellington Laboratories. 5:3 fluorotelomer carboxylic

acids (5:2 FTCA), 6:2 fluorotelomer carboxylic acids (6:2 FTCA) and 8:2 fluorotelomer alcohol (8:2 FTOH, 99%) were provided by DuPont (Wilmington, DE).

Methanol ($\geq 99.9\%$, HPLC grade) and acetic acid ($\geq 99.7\%$ Certified ACS grade) were purchased from Fisher Scientific (Hampton, NH). Ammonium acetate (98%, ACS grade) was purchased from Mallinckrodt (St Louis, MS). Ammonium hydroxide (28-30 %, ACS grade), Supelclean™ ENVI-Carb (SPE bulk packaging), calcium chloride (anhydrous, $\geq 96\%$, ACS grade) and sodium azide ($\geq 99\%$) were purchased from Sigma-Aldrich (St. Louis, MO). Sodium hydroxide ($\geq 98.0\%$, ACS grade) was purchased from Macron Fine Chemicals (Center Valley, PA). Potassium persulfate ($\geq 99.0\%$, ACS grade) was purchased from Fluka Chemicals (Morris Plains, NJ). Nanopure water was prepared using a Barnstead Nanopure water purification system with 0.2- μm filter (Lake Balboa, CA). Hydrophilic-lipophilic balanced (HLB) and weak anion-exchange (WAX) solid-phase extraction cartridges were purchased from Waters (Milford, MA). Standard reference material for sludge (SRM 2781) was obtained from the National Institute of Standards and Technology.

B. Organic Product Extraction

Samples were extracted using the method described by Choi et al. (2019).(Choi et al., 2019) Freeze-dried product (0.5 g) were added into 15-mL polypropylene (PP) conical tubes and spiked with 40 μL of 250 $\mu\text{g}/\text{L}$ (10 ng) of isotopically labeled surrogates before adding extraction solvent. Samples were extracted with 7-ml methanol/200 mM ammonium hydroxide (99:1, v/v) and mixed by vortexing for 1 min. The mixtures were then sonicated in a heated sonication bath at 30 °C for 1 h followed by placing in an end-over end rotator for 2 h. After 2 h, the samples were centrifuged at 1,613 RCF for 30 minutes and decanted into a clean 50-ml PP tube. The extraction was repeated two more times, and the extracts were combined in to the 50-mL PP tube. The combined extracts

were evaporated to dryness under nitrogen and reconstituted with 1000 μL of 99:1 (v/v) methanol and glacial acetic acid. The fraction of extract (500 μL) was saved for a total oxidizable precursor (TOP) assay. The rest of extract (500 μL) was transferred into a microcentrifuge tube containing 30 mg of ENVI Carb sorbent with 20 μL glacial acetic acid, and was mixed by vortexing for 30 sec. The mixture was centrifuged at 17,000 RCF for 30 min. An aliquot of each cleaned extract (400 μL) was transferred to a 1.5 mL glass injection vial containing 400 μL of 0.003% ammonium hydroxide in nanopure water (1:1, MeOH:H₂O, v/v). The samples were stored in a refrigerator at 4°C until analysis.

C. Solid Phase Extraction

The samples were cleaned using a published method (Yoo et al., 2009). SPE vacuum manifolds (Supelco Visiprep 24, Sigma Aldrich, St. Louis, MO) and needles were cleaned with acetone, and the residual acetone was evaporated using vacuum. Prior to loading samples, a SPE cartridge (HLB) was preconditioned with 5 mL of methanol and 5 mL of Nanopure water, sequentially. The sample was acidified with 20 μL of glacial acetic acid and then loaded to the cartridge at the flow rate of 1-2 mL/min under very low vacuum. The cartridge was washed with 5 mL of acidified Nanopure water with 20 μL of glacial acetic acid, and then with 5 mL of a solution mixture (25:75, MeOH:H₂O, v/v). After drying the cartridge for 30 min under vacuum, the cartridge was eluted with 10 mL of methanol by gravity. The eluent was concentrated to near dryness under nitrogen at 30 °C using RapidVap N₂ Evaporation Systems (Labconco, Kansas City, MO). The dried sample was reconstituted with 1000 μL of 99:1 (v/v) methanol and glacial acetic acid, vortex-mixed for 1 min and sonicated for 1 min. The samples were analyzed as previously described for the product extracts.

D. Instrumental Analysis for PFAAs and screening of selective PFAA precursors (Choi et al., 2019)

All samples were analyzed for 17 PFAAs using a liquid chromatography-mass spectrometry (LC-MS/MS) system coupled to a SCIEX triple quadrupole time-of-flight (QToF) 5600 (Framingham, MA). Analyst TF1.7 software (SCIEX) was used to control the instrument. Target analytes (15 μ L injection volume) were separated using a reverse-phase column (Kinetex[®] EVO C18, 100 Å, 100 x 2.1 mm, 5 μ m, Phenomenex, Torrance, CA) on a Shimadzu LC instrument (LC30AD) at a flow rate of 0.75 mL/min. A delay column (Luna C18, 100 Å, 30 x 4.6 mm ID, 3 μ m, Phenomenex, Torrance, CA) was installed between the mobile phase mixer and autosampler injection port to separate PFAS background contamination from the system. The LC was operated using a gradient elution of 0.15% acetic acid in water (A) and 20 mM ammonium acetate in methanol (B). The gradient profile was used as following (total 11 min): 0-0.5 min: 30%B; 0.5-3 min: 30-70%B; 3-6.5 min: 70- 100%B; 6.5-8.5 min: 100%B; 8.5-9 min: 100-30%B and 9-11 min: 30%B. All samples were diluted 1:1 with water prior to the injection (1:1, MeOH:H₂O, v/v). All data were processed with MultiQuant software 3.0.1 (SCIEX).

SWATH-MS/MS data was acquired on the 5600+ QToF coupled with LC using different chromatography conditions of the 17 PFAA analysis. 30 μ L of the product extracts (1:1 MeOH:H₂O, v/v) were injected onto the same C18 column at a flow rate of 0.5 mL/min. In addition, the extract procedural blank and mixture of analytical PFAA precursors (EtFOSE, EtFOSAA, EtFOSA, MeFOSA, FOSA, FOSAA, 6:2 FTOH, 6:2 FTCA and 5:3 FTCA) were injected. The same mobile phases were used with a different gradient profile as follow (total 18.20 min): 0 - 0.1 min: 10 %B; 0.1- 10 min: 10- 100 %B; 10- 15 100 %B; 15.00- 15.20 min: 10 %B and 15.20 – 18.20 min: 10%B. In SWATH mode, a TOF-MS full scan was acquired at m/z 30-2000 with 50

millisecond accumulation time, followed by 17 MS/MS scans (m/z 100 to 1250) with predefined consecutive variable Q1. The MS/MS ions were acquired at m/z of 30-1250 for 50 millisecond accumulation time. PeakView 2.2 software with MasterView (SCIEX) was used to analyze the SWATH data. Only [M-H]⁻ was considered as potential adducts. PFAA precursors were identified using either MS/MS spectrum from the individual analytical standards or MS/MS spectrum from MS/MS spectrum database and LibraryView (SCIEX).

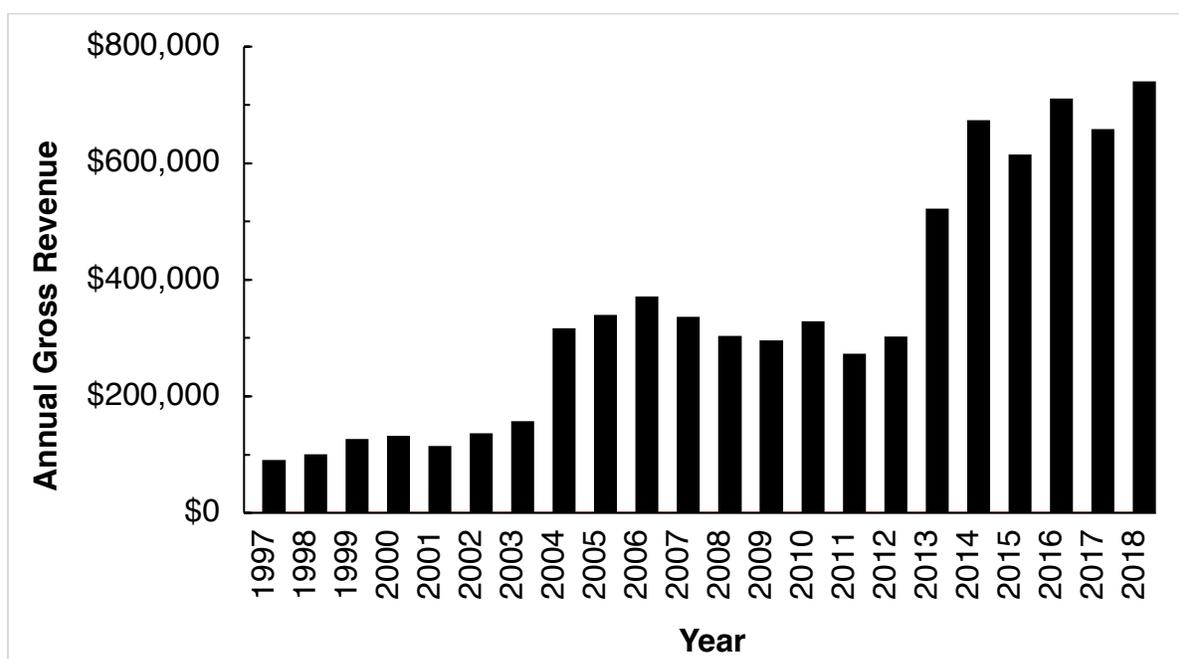


Figure S1. Historical annual gross revenue of a commercially available biosolid-based product (TAGRO, Product M).

Table S1. Average % mass < 2 mm and standard deviation (SD) for each product after freeze-drying. Heat-treated products H-L were granular and appeared uniform; thus, were not sieved.

Product	% < 2 mm, average (n = 2)	SD
A	61.4	2.2
B	80.0	2.6
C	62.9	3.4
D	59.7	8.0
E	48.0	1.9
F	76.2	5.5
G	50.4	4.7
M	63.9	1.6
N	40.0	3.5
O	36.4	2.4
P	56.6	4.6
Q	62.0	1.5
R	61.7	1.7

Table S2. The product nutrient contents including organic matter, total N, P, K, Mg, Ca, pH and CEC determined by A&L Great Lakes Laboratories (Fort Wayne, IN)

	H	I	J	J (2016)	J (2018)	K	L	M	N	O	P	Q	R
Organic matter (%)	64.1	67.7	67.3	65.1	68.9	64.6	63.4	39.0	59.0	64.5	64.2	22.0	37.0
Total N (%)	4.78	6.12	6.21	6.09	5.02	5.12	15.9	0.90	3.66	3.61	1.36	1.53	1.82
Phosphorus (mg/kg-P)	858	2492	827	704	1369	1414	86	876	1595	2133	464	362	2032
Potassium (mg/kg)	339	2819	1495	1062	2154	599	9776	486	1469	1271	1032	1647	1977
Magnesium (mg/kg)	550	1260	905	780	1210	1175	1055	430	1145	980	320	1235	1020
Calcium (mg/kg)	2600	3600	2700	1850	2650	4450	1900	1650	3200	3900	3650	23400	7450
pH	5.9	6.0	6.0	6.0	5.9	6.4	4.2	4.9	6.8	7.2	7.0	6.6	6.8
CEC (meq/100g)	23.3	42.9	30.9	23.3	36.1	38.4	55.4	29.9	30.2	30.9	23.6	99.9	52.4

Table S3. PFAA common names, acronyms, mass transitions and other MS associated parameters.

Target analytes	Acronym	P (m/z)	LOQ (µg/L)	D (m/z)	ISVF	CE	CES	DP	IRD	IRW	AcT (ms)	Surrogate
Perfluorobutanoic acid	PFBA	212.98	0.1	168.98	3900	-10	0	-100	43.514	17.184	300	MPFBA
Perfluoropentanoic acid	PFPeA	262.98	0.25	68.97	3900	-30	0	-80	27.799	10.978	300	MPFHxA
Perfluorohexanoic acid	PFHxA	312.97	0.1	268.95	3800	-30	0	-70	54.898	21.680	300	MPFHxA
Perfluoroheptanoic acid	PFHpA	362.97	0.1	62.98	3800	-10	0	-80	59.783	23.609	200.1	MPFHxA
Perfluorooctanoic acid	PFOA	412.96	0.1	218.96	3800	-25	0	-80	64.297	25.932	600	MPFOA
Perfluorononanoic acid	PFNA	462.96	0.5	418.95	3800	-15	0	-60	68.515	27.058	150	MPFNA
Perfluorodecanoic acid	PFDA	512.96	0.1	268.95	3900	-25	0	-80	72.488	28.626	400	MPFDA
Perfluoroundecanoic acid	PFUdA	598.92	0.1	568.95	3900	-20	0	-70	76.254	30.114	250	MPFUdA
Perfluorododecanoic acid	PFDoA	612.95	0.1	568.90	3800	-25	0	-80	79.843	31.531	400	MPFDoA
Perfluorotridecanoic acid	PFTTrDA	662.95	0.1	618.93	3800	-25	0	-70	83.277	32.887	300	MPFDoA
Perfluorotetradecanoic acid	PFTeDA	712.95	0.1	668.93	3800	-20	0	-70	83.277	32.887	300	MPFDoA
Perfluorohexadecanoic acid	PFHxDA	812.94	0.1	768.92	3800	-20	0	-80	92.820	36.656	300	MPFDoA
Perfluorooctadecanoic acid	PFODA	912.93	0.1	568.94	3800	-30	0	-80	83.277	32.887	300	MPFDoA
Perfluorobutane sulfonate	PFBS	298.94	0.1	79.95	3800	-40	0	-80	29.932	11.821	300	MPFHxA
Perfluorohexane sulfonate	PFHxS	398.93	0.1	82.95	3800	-45	0	-80	29.932	11.821	600	MPFHxS
Perfluorooctane sulfonic acid	PFOS	498.93	0.1	98.94	4300	-50	0	-80	29.932	11.821	150	MPFOS
Perfluorodecane sulfonate	PFDS	598.92	0.1	98.94	3900	-55	0	-80	29.932	11.821	250	MPFOS
Perfluoro[1,2,3,4- ¹³ C ₄]butanoic acid	MPFBA	216.99	-	171.98	3900	-10	5	-100	43.514	17.184	150	-
Perfluoro[1,2- ¹³ C ₂]hexanoic acid	MPFHxA	314.98	-	269.96	3800	-20	10	-70	55.102	21.760	300	-
Perfluoro[1,2,3,4- ¹³ C ₄]octanoic acid	MPFOA	416.98	-	371.97	3800	-20	0	-80	64.297	25.392	200	-
Perfluoro[1,2,3,4,5- ¹³ C ₅]nonanoic acid	MPFNA	467.98	-	422.97	3800	-20	10	-80	68.515	27.058	100	-
Perfluoro[1,2- ¹³ C ₂]decanoic acid	MPFDA	514.97	-	469.95	3900	-20	5	-80	72.488	28.626	200	-
Perfluoro[1,2- ¹³ C ₂]undecanoic acid	MPFUdA	564.96	-	268.96	3900	-25	5	-80	72.488	28.626	100	-
Perfluoro[1,2- ¹³ C ₂]dodecanoic acid	MPFDoA	614.96	-	569.95	3800	-15	10	-80	79.843	31.531	200	-
Sodium Perfluoro-1-hexane[¹⁸ O ₂]sulfonate	MPFHxS	402.95	-	102.95	3800	-40	15	-80	29.932	11.821	100	-
Sodium Perfluoro-1-[1,2,3,4- ¹³ C ₄]octane sulfonate	MPFOS	502.94	-	98.94	3800	-45	15	-80	29.932	11.821	100	-

P: Precursor; D: Daughter Ion; ISVF: Ion Spray voltage floating; CE: Collision Energy; CES: Collision Energy Spread; DP: Declustering Potential; IRD: Ion release delay; IRW: ion release width and AcT: accumulation time.

Table S4. The measured concentration ($\mu\text{g}/\text{kg}$) of PFAAs in the heat-treated biosolid-based products (H-L) and the < 2 mm particle fraction of biosolid-based (M-R) products and other organic (A-G) products. Values in parenthesis are the standard error of the mean (n=3). PFOA for all products < LOQ.

Name	PFBA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFDS	PFuDA	PFDoA	PFTrDA	PFTeDA	PFHxDA
A	0.8 (0.04)	<LOQ	8.4 (0.5)	2.3 (0.3)	<LOQ	4.1 (0.2)	<LOQ	<LOQ	1.7 (0.1)	<LOQ	<LOQ	0.9 (0.03)	<LOQ	0.4 (0.03)	<LOQ
B	0.6 (0.01)	<LOQ	<LOQ	<LOQ	<LOQ	0.5 (0.02)	<LOQ	0.2 (0.2)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
C	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.6 (0.02)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
D	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.2 (0.02)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
E	0.1 (0.1)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
F	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.1 (8.1)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
G	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.5 (0.05)	<LOQ	1.6 (0.6)	<LOQ	<LOQ	0.15 (0.1)	<LOQ	0.4 (0.02)	<LOQ	<LOQ
H	0.6 (0.03)	1.1 (0.2)	2.3 (0.1)	<LOQ	<LOQ	1.9 (0.06)	3.9 (0.1)	13.4 (0.9)	1.4 (0.1)	3.2 (0.2)	2.1 (0.03)	1.9 (0.2)	<LOQ	1.6 (0.3)	<LOQ
I	0.6 (0.01)	3.0 (0.2)	3.5 (0.3)	<LOQ	<LOQ	6.9 (0.2)	0.8 (0.5)	15.4 (0.9)	14.9 (0.5)	0.6 (0.2)	2.9 (0.2)	7.7 (0.3)	1.0 (0.1)	2.4 (0.3)	1.6 (0.07)
J (2014)	3.3 (0.07)	0.4 (0.04)	61.0 (2.53)	<LOQ	0.42 (0.01)	6.1 (0.1)	2.3 (1.3)	88.5 (0.6)	5.5 (0.3)	1.8 (0.4)	3.5 (0.2)	4.1 (0.1)	1.2 (0.1)	1.3 (0.1)	1.1 (0.04)
J (2016)	2.8 (0.1)	<LOQ	53.10 (1.8)	3.75 (0.3)	<LOQ	2.7 (0.04)	<LOQ	29.7 (2.7)	2.9 (0.1)	<LOQ	4.1 (0.4)	1.7 (0)	<LOQ	0.6 (0.3)	<LOQ
J (2018)	2.5 (0.1)	<LOQ	41.63 (1.3)	3.02 (1.7)	<LOQ	2.72 (0.1)	<LOQ	18.7 (1.5)	2.6 (0.4)	<LOQ	2.4 (0.04)	1.42 (0.06)	<LOQ	<LOQ	<LOQ
K	0.9 (0.03)	2.6 (0.1)	3.3 (0.1)	<LOQ	<LOQ	3.3 (0.2)	3.3 (0.4)	10.3 (0.1)	5.5 (0.2)	2.3 (0.3)	4.3 (0.1)	3.7 (0.2)	0.7 (0.4)	1.5 (0.2)	<LOQ
L	0.7 (0.04)	0.5 (0.04)	0.5 (0.04)	<LOQ	<LOQ	1.4 (0.1)	<LOQ	2.6 (0.1)	1.7 (0.2)	<LOQ	0.6 (0.1)	1.1 (0.04)	<LOQ	<LOQ	<LOQ
M	1.1 (0.03)	4.4 (0.1)	8.3 (0.2)	0.4 (0.4)	<LOQ	11.4 (0.7)	2.8 (0.5)	3.0 (0.2)	4.9 (0.2)	0.67 (0.2)	1.3 (0.1)	1.1 (0.1)	0.1 (0.1)	<LOQ	<LOQ
N	6.5 (0.1)	41.9 (2.4)	33.0 (0.5)	6.5 (0.8)	1.90 (0.2)	26.0 (1.1)	6.1 (1.0)	37.5 (1.6)	20.5 (0.1)	1.87 (0.3)	5.6 (0.5)	7.3 (0.6)	1.7 (0.1)	1.6 (0.2)	0.7 (0.1)
O	3.4 (0.1)	19.7 (1.5)	17.3 (0.2)	5.3 (0.1)	0.45 (0)	19.1 (0.4)	8.1 (0.7)	10.4 (0.1)	11.7 (0.02)	2.8 (0.15)	8.0 (0.1)	4.6 (0.01)	2.3 (0.02)	1.2 (0.04)	0.8 (0.1)
P	3.2 (0.1)	3.8 (0.2)	6.4 (0.1)	<LOQ	0.82 (0.03)	8.6 (0.4)	0.7 (0.7)	3.5 (0.1)	2.2 (0.02)	0.6 (0.2)	1.0 (0.06)	1.0 (0.01)	0.6 (0.02)	0.7 (0.04)	0.6 (0.1)
Q	5.2 (0.1)	38.1 (2.9)	21.5 (0.6)	4.4 (0.5)	<LOQ	19.0 (0.7)	3.6 (0.6)	5.9 (0.2)	9.6 (0.2)	0.2 (0.2)	4.2 (0.6)	6.3 (0.2)	2.5 (0.1)	2.7 (0.1)	1.3 (0.1)
R	3.9 (0.1)	33.2 (4.1)	11.6 (0.4)	4.1 (0.6)	0.47 (0.01)	21.5 (0.2)	4.9 (0.3)	10.1 (0.6)	11.5 (0.1)	<LOQ	4.0 (0.3)	4.8 (0.1)	1.3 (0.04)	1.2 (0.04)	0.5 (0.01)

Table S5. Summary of the Total PFAAs, PFCAs and PFSAAs concentrations ($\mu\text{g}/\text{kg}$) and relative compositions for PFCAs and PFSAAs as well as short and long chain PFAAs in the heat-treated biosolid-based products (H-L) and the < 2 mm particle fraction of biosolid-based products (M-R) and other organic products (A-G). Long chains refer to PFCAs \geq C7 and PFSAAs \geq C6.

Products	Σ PFCAs ($\mu\text{g}/\text{kg}$)	Σ PFSAAs ($\mu\text{g}/\text{kg}$)	Σ PFCAs (%)	Σ PFSAAs (%)	PFCAs/ PFSAAs	Σ Long ($\mu\text{g}/\text{kg}$)	Σ Short ($\mu\text{g}/\text{kg}$)	Σ Long (%)	Σ Short (%)	Long/ Short	Σ Total ($\mu\text{g}/\text{kg}$)
A	18.5	0.0	100	0.0	-	7.0	11.5	37.9	62.1	0.6	18.5
B	1.0	0.2	83.2	16.8	5.0	0.7	0.5	56.3	43.7	1.3	1.2
C	0	0.6	0	100	0	0.6	0	100	0	-	0.6
D	0	1.2	0	100	0	1.2	0	100	0	-	1.2
E	0.1	0	100	0	-	0.0	0.1	0.0	100	0	0.1
F	0	8.1	0	100	0	8.1	0	100	0	-	8.1
G	1.1	1.6	40.7	59.3	0.7	2.7	0	100	0	-	2.7
H	15.6	17.8	46.7	53.3	0.9	29.4	3.9	88.3	11.7	7.5	33.3
I	42.2	19.0	69.0	31.0	2.2	54.1	7.1	88.4	11.6	7.6	61.1
J (2014)	89.4	91.1	49.5	50.5	1.0	115.8	64.7	64.1	35.9	1.8	180.5
J (2016)	71.6	29.7	70.7	29.3	2.4	41.5	59.7	41.0	59.0	0.7	101.2
J (2018)	55.5	18.7	74.8	25.2	3.0	27.1	47.1	36.5	63.5	0.6	74.2
K	26.4	15.2	63.4	36.6	1.7	34.9	6.7	83.8	16.2	5.2	41.6
L	5.9	3.1	65.7	34.3	1.9	7.3	1.7	81.0	19.0	4.3	9.0
M	31.5	8.0	79.7	20.3	3.9	25.3	14.2	64.1	35.9	1.8	39.5
N	115.5	83.1	58.2	41.8	1.4	110.8	87.8	55.8	44.2	1.3	198.6
O	81.6	33.4	71.0	29.0	2.4	69.4	45.6	60.3	39.7	1.5	115.0
P	24.8	8.7	74.0	26.0	2.9	20.1	13.4	60.1	39.9	1.5	33.5
Q	80.2	44.2	64.5	35.5	1.8	55.2	69.2	44.4	55.6	0.8	124.4
R	69.3	43.8	61.3	38.7	1.6	60.2	52.9	53.2	46.8	1.1	113.1

Table S6. The concentration ($\mu\text{g}/\text{kg}$) of PFAAs in the heat-treated biosolid-based products (H-L) and the < 2 mm particle fraction of biosolid-based products (M-R) and one organic product (A) after TOP assay 150 mM NaOH in which NaOH and persulfate- final concentration 60 mM- were added sequentially to extract residues prior to ENVI-carb clean-up. Values in parenthesis are the standard error of the mean (n=3).

	Concentration ($\mu\text{g}/\text{kg}$)												
	PFBA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA
A	1.2 (0)	<LOQ	10.6 (0.4)	<LOQ	<LOQ	6.1 (0.5)	<LOQ	<LOQ	2.4 (0.3)	<LOQ	1.5 (0.1)	<LOQ	<LOQ
B	<LOD	1.3 (0)	<LOD	<LOD	1.4 (0)	1.3 (0)	<LOD	2.6 (2.0)	<LOD	<LOD	<LOD	<LOD	<LOQ
C	<LOD	<LOD	<LOD	<LOD	0.4 (0.7)	1.5 (0.9)	<LOD	2.3 (0.9)	<LOD	<LOD	<LOD	<LOD	<LOQ
D	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.2 (1.4)	<LOD	<LOD	<LOD	<LOD	<LOQ
E	<LOD	0.0	<LOD	<LOD	<LOD	<LOD	<LOD	0.6 (0.2)	0.1 (0.1)	<LOD	<LOD	<LOD	<LOQ
F	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
G	<LOD	<LOD	<LOD	<LOD	<LOD	1.2 (0)	<LOD	1.5 (0.3)	<LOD	7.1 (12.3)	<LOD	<LOD	<LOQ
H	1.1 (0.1)	1.1 (0.3)	4.1 (0.3)	<LOQ	<LOQ	3.1 (0.2)	<LOQ	12.3 (1.3)	1.7 (1.3)	2.1 (0.1)	1.9 (0.4)	<LOQ	<LOQ
I	1.0 (0.1)	0.9 (0.3)	4.6 (0.3)	<LOQ	<LOQ	7.1 (0.4)	<LOQ	12.1 (1.3)	14.6 (1.5)	2.6 (0.2)	6.8 (0.5)	0.7 (0)	0.9 (0)
J (2014)	5.5 (0.7)	1.2 (0.1)	60.0 (7.6)	<LOQ	<LOQ	9.1 (0.1)	4.2 (0)	120.1 (32.4)	5.7 (1.5)	4.2 (0.1)	5.0 (0.7)	<LOQ	<LOQ
J (2016)	4.3 (0.1)	0.9 (0.1)	61.4 (1.0)	<LOQ	<LOQ	5.1 (0.5)	<LOQ	29.4 (3.5)	3.5 (0.4)	5.3 (0.6)	2.4 (0.7)	<LOQ	<LOQ
J (2018)	3.7 (0.2)	0.8 (0)	48.6 (6.6)	<LOQ	<LOQ	4.0 (0.8)	<LOQ	22.4 (2.4)	<LOQ	2.6 (0.7)	2.0 (0.3)	0.9 (0)	<LOQ
K	1.9 (0.1)	<LOQ	5.3(0.4)	<LOQ	<LOQ	5.8 (0.5)	<LOQ	10.9 (1.5)	6.0 (0.3)	4.8 (0.2)	4.2 (0.6)	0.9 (0)	<LOQ
L	0.9 (0)	<LOQ	<LOQ	<LOQ	<LOQ	2.5 (0.1)	<LOQ	2.7 (0.7)	2.7 (0.8)	1.1 (0.5)	1.1 (0.3)	<LOQ	<LOQ
M	2.1 (0.3)	4.1 (0.5)	9.4 (1.1)	2.2 (0)	<LOQ	13.6 (0.6)	4.2 (0)	2.8 (0.6)	5.6 (1.0)	1.9 (0.1)	1.9 (0.7)	<LOQ	<LOQ
N	8.6 (0.2)	46.0 (1.0)	37.3 (3.8)	5.9 (1.2)	3.3 (0.1)	40.5 (0.9)	8.4 (3.4)	49.5 (3.3)	31.6 (3.1)	8.2 (0.6)	11.4 (0.5)	1.3 (0.1)	1.2 (0)
O	5.1 (0.2)	7.4 (0.7)	20.7 (1.4)	4.2 (0.5)	<LOQ	25.9 (1.0)	11.9 (4.7)	12.3 (0.9)	14.8 (3.6)	10.1 (0.2)	5.9 (1.5)	<LOQ	<LOQ
P	3.9 (0.2)	2.5 (0)	7.7 (0.3)	2.4 (0.3)	<LOQ	7.5 (0.4)	<LOQ	3.2 (0.1)	3.3 (0.3)	1.1 (0.2)	1.3 (0.1)	<LOQ	<LOQ
Q	10.8 (0.6)	71.1 (2.6)	32.8 (2.6)	6.1 (2.2)	0.9 (0.1)	31.2 (1.3)	6.4 (0)	14.9 (1.4)	17.8 (0.5)	5.9 (1.3)	11.9 (2.3)	<LOQ	<LOQ
R	5.3 (0.6)	28.6 (4.4)	14.1 (1.1)	2.9 (0.3)	<LOQ	24.0 (5.7)	<LOQ	8.6 (1.3)	15.0 (3.0)	6.1 (1.5)	6.4 (0.8)	<LOQ	<LOQ

Table S7. Concentration of PFAAs ($\mu\text{g}/\text{kg}$) measured in SRM 2781 by different laboratories using different method. Values represent the mean and standard deviation. *The table was adopted and modified from Reiner, J. et al (2015).(Reiner et al., 2015)

	NIST method 1 (n = 6)*	NIST method 2 (n = 9)*	NIST method 3 (n = 6)*	3M (n = 9)*	EPA Athens (n = 4)*	Inst. Marine Resources Eco. (n = 2)*	CO School mines (n = 8)*	This study (n = 3)
PFBA	23.3 \pm 1.4	18.9 \pm 2.4	23.4 \pm 1.9	3.34 \pm 0.47	35.9 \pm 5.7	NM	12.5 \pm 1.0	4.83 \pm 0.16
PFPeA	4.12 \pm 0.61	< 2.99	3.98 \pm 0.33	9.56 \pm 1.00	< 3.50	NM	5.65 \pm 1.13	10.2 \pm 2.6
PFHxA	9.97 \pm 1.61	12.1 \pm 1.8	11.4 \pm 1.1	13.9 \pm 0.7	16.9 \pm 1.8	NM	16.4 \pm 1.8	9.64 \pm 2.5
PFHpA	6.23 \pm 0.86	7.76 \pm 2.31	7.57 \pm 0.47	7.38 \pm 0.75	8.23 \pm 0.52	NM	4.83 \pm 0.54	5.98 \pm 3.2
PFOA	30.8 \pm 4.6	24 \pm 3.3	30.3 \pm 1.6	25.7 \pm 2.0	31 \pm 4.4	21.8-23	18.7 \pm 1.8	17.1 \pm 1.5
PFNA	3.2 \pm 0.55	6.59 \pm 1.05	<30.8	2.56 \pm 0.27	3.47 \pm 0.62	NM	2.82 \pm 0.55	3.66 \pm 0.32
PFDA	2.98 \pm 0.48	5.85 \pm 1.19	3.42 \pm 0.21	5.33 \pm 0.45	6.05 \pm 1.38	NM	2.67 \pm 0.54	20.7 \pm 8.9
PFUdA	2.74 \pm 0.56	7.13 \pm 1.75	23.6 \pm 2.6	2.89 \pm 0.32	< 1.5	NM	2.43 \pm 0.13	2.51 \pm 0.12
PFDoA	2.02 \pm 0.19	2.6 \pm 0.36	2.2 \pm 0.16	2.01 \pm 0.23	< 1.5	NM	4.81 \pm 2.3	1.63 \pm 0.13
PFTTrDA	1.37 \pm 0.39	3.25 \pm 0.99	24.4 \pm 2.4	NM	< 1.5	NM	NM	1.13 \pm 0.12
PFTeDA	0.556 \pm 0.11	< 0.631	1 \pm 0.2	NM	< 3.5	NM	NM	1.14 \pm 0.69
PFBS	<0.186	< 0.353	< 0.405	< 1.25	< 1.5	NM	34.9 \pm 4.0	2.01 \pm 0.48
PFHxS	7.34 \pm 1.09	9.7 \pm 2.89	10 \pm 0.4	5.04 \pm 1.67	NM	NM	9.28 \pm 1.0	4.64 \pm 0.37
PFOS	166 \pm 14	205 \pm 23	263 \pm 13	219 \pm 11	373 \pm 25	227-234	218 \pm 30	154 \pm 27.1
PFDS	NM	NM	NM	NM	NM	NM	290 \pm 50	250 \pm 30.8

NM: not measured

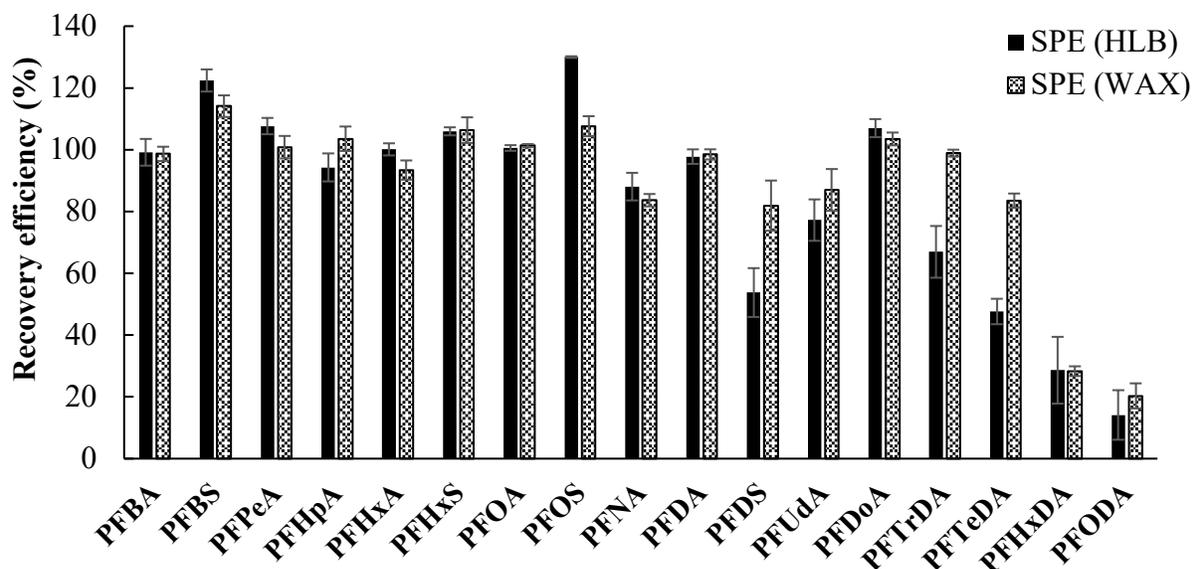


Figure S2. The result of the recovery efficiency of PFAAs using two different SPE cartridges (HLB vs WAX). Error bars represent the standard error of the mean ($n = 3$).

Table S8. The pH using pH-indicator strips at the end of the TOP assay immediately after cooling in an ice bath for the heat-treated biosolid-based fertilizer products (H-L) and the < 2 mm particle fraction of biosolid-based (M-R) products and one organic (A) product after TOP assay. pH-indicator strips were used due to the small sample volumes used in the TOP assay.

Fertilizer	pH
A	7-8
H	4-5
I	6-7
J (2014)	5-6
J (2016)	5-6
J (2018)	5-6
K	7-8
L	6-7
M	9-10
N	7-8
O	7-8
P	7-8
Q	6-7
R	7-8

¹ For the TOP assay using 150 mM NaOH in which NaOH and persulfate (the final concentration 60 mM) were added sequentially to extract residues prior to ENVI-carb clean-up.

Table S9. The pH of the pore-water after 48 h incubation for the heat-treated biosolid-based products (H-L) and the < 2 mm particle fraction of biosolid-based (M-R) products and one organic product (A).

Products	pH
A	8.26
H	6.31
I	5.75
J (2014)	5.81
J (2016)	5.99
J (2018)	5.78
K	6.64
L	4.42
M	4.91
N	6.56
O	7.14
P	6.71
Q	7.08
R	7.03

Table S10. The concentration of PFAAs ($\mu\text{g}/\text{kg}$) in the spent-samples for heat-treated biosolid-based products (H-L) and the < 2 mm particle fraction of biosolid-based products (M-R) and one organic product (A). These concentrations were accounted for the concentration of PFAAs in the moisture remained in the spent-sample prior to freeze-drying.

Products	PFBA	PFPeA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	PFDS	PFUdA	PFDoA	PFTTrDA	PFTeDA	PFHxDA
A	0.24	0	0	3.58	0	0	5.26	1.28	0.00	2.38	0.00	0.29	2.01	0.00	0.52	0
H	0.27	0.85	0	1.78	0	0	2.26	6.61	14.44	0.00	4.62	2.66	2.11	0.96	1.96	0.89
I	0.35	0.73	1.45	3.10	0	0	7.63	5.66	21.85	19.24	1.78	4.05	11.18	2.23	6.47	0.92
J (2014)	1.20	6.29	14.78	33.05	0	0.45	6.58	4.48	132.40	0	4.78	5.70	4.46	2.19	3.26	0.57
J (2016)	0.98	0.81	4.75	33.18	5.95	0	2.78	5.07	47.97	2.73	2.57	6.44	2.30	2.09	2.81	0.15
J (2018)	1.06	0.38	4.55	26.84	3.49	0	2.05	2.12	26.57	2.82	1.93	3.48	1.85	0.92	1.00	0.00
K	0.20	4.39	0	2.93	0	0	4.61	8.32	13.47	0	4.67	5.90	4.70	2.19	5.03	0.89
L	1.72	2.49	0	1.45	0	0	4.85	4.89	9.80	7.83	1.14	3.18	4.80	0.69	0.61	0
M	0.19	0	2.42	4.78	0	0	10.42	5.91	2.73	5.33	0.62	1.67	1.50	0.16	0.51	0
N	2.83	151.67	5.57	22.26	4.20	3.83	39.55	20.23	69.59	36.95	2.80	10.67	14.41	2.21	2.74	0
O	1.25	10.32	0.00	8.18	4.91	0.51	24.49	29.78	12.56	15.57	3.90	12.05	5.31	2.74	1.49	0
P	1.19	0.77	0.00	4.19	1.31	0.77	7.24	5.03	2.90	2.95	0.55	1.45	1.23	0.67	0.69	0
Q	1.28	57.13	3.91	15.55	7.66	0.84	35.16	13.64	20.44	18.58	0.73	6.74	12.11	2.79	3.37	0
R	0.38	23.54	0.00	6.00	1.82	0.51	19.75	11.36	10.06	13.66	0.83	4.99	6.81	1.70	1.62	0

Table S11. List of PFAA Precursors.

Precursors	Formula	Name
FOSA	C ₈ F ₁₇ SO ₂ NH ₂	Perfluorooctane sulfonamide
MeFOSA	C ₈ F ₁₇ SO ₂ NH(CH ₃)	<i>N</i> -Methyl perfluorooctane sulfonamide
EtFOSA	C ₈ F ₁₇ SO ₂ NH(C ₂ H ₅)	<i>N</i> -Ethyl perfluorooctane sulfonamide
MeFOSE	C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ CH ₂ OH	<i>N</i> -Methyl perfluorooctane sulfonamidoethanol
EtFOSE	C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)CH ₂ CH ₂ OH	<i>N</i> -Ethyl perfluorooctane sulfonamidoethanol
FOSAA	C ₈ F ₁₇ SO ₂ NHCH ₂ COOH	Perfluorooctane sulfonamidoacetic acid
MeFOSAA	C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ COOH	<i>N</i> -Methyl perfluorooctane sulfonamidoacetic acid
EtFOSAA	C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)CH ₂ COOH	<i>N</i> -Ethyl perfluorooctane sulfonamidoacetic acid
4:2 FTOH	C ₄ F ₉ CH ₂ CH ₂ OH	4:2 Fluorotelomer alcohol
6:2 FTOH	C ₆ F ₁₃ CH ₂ CH ₂ OH	6:2 Fluorotelomer alcohol
7:1 FTOH	CF ₃ (CF ₂) ₆ CH ₂ OH	7:1 Fluorotelomer alcohol
8:2 FTOH	C ₈ F ₁₇ CH ₂ CH ₂ OH	8:2 Fluorotelomer alcohol
10:2 FTOH	C ₁₀ F ₂₁ CH ₂ CH ₂ OH	10:2 Fluorotelomer alcohol
5:3 FTCA	C ₅ F ₁₁ (CH ₂) ₂ COOH	5:3 Fluorotelomer carboxylic acid
6:2 FTCA	C ₆ F ₁₃ CH ₂ COOH	6:2 Fluorotelomer carboxylic acid
7:3 FTCA	C ₇ F ₁₅ CH ₂ COOH	7:3 Fluorotelomer carboxylic acid
8:2 FTCA	C ₈ F ₁₇ CH ₂ COOH	8:2 Fluorotelomer carboxylic acid
10:2 FTCA	C ₁₀ F ₂₁ CH ₂ COOH	10:2 Fluorotelomer carboxylic acid
6:2 FTUA	C ₅ F ₁₁ CF=CHCOOH	6:2 Fluorotelomer unsaturated carboxylic acid
8:2 FTUA	C ₇ F ₁₅ CF=CHCOOH	8:2 Fluorotelomer unsaturated carboxylic acid
10:2 FTUA	C ₉ F ₁₉ CF=CHCOOH	10:2 Fluorotelomer unsaturated carboxylic acid
4:2 FTSA	C ₄ F ₉ CH ₂ CH ₂ SO ₃ H	4:2 Fluorotelomer sulfonate
6:2 FTSA	C ₆ F ₁₃ CH ₂ CH ₂ SO ₃ H	6:2 Fluorotelomer sulfonate
8:2 FTSA	C ₁₀ H ₃ F ₁₇ O ₃ S	8:2 Fluorotelomer sulfonate
6:2 monoPAP	(O)P(OH)(OCH ₂ CH ₂ C ₆ F ₁₃) ₂	6:2 Fluorotelomer phosphate monoester
8:2 monoPAP	(O)P(OH)(OCH ₂ CH ₂ C ₈ F ₁₇) ₂	8:2 Fluorotelomer phosphate diester
6:2/6:2 diPAPs	(O)P(OH)(OCH ₂ CH ₂ C ₆ F ₁₃)(O CG ₂ CG ₂ C ₆ F ₁₃)	6:2/6:2 Fluorotelomer phosphate diester
6:2/8:2 diPAPs	(O)P(OH)(OCH ₂ CH ₂ C ₆ F ₁₃)(O CH ₂ CH ₂ C ₈ F ₁₇)	6:2/8:2 Fluorotelomer phosphate diester
8:2/8:2 diPAPs	(O)P(OH)(OCH ₂ CH ₂ C ₈ F ₁₇)(O CH ₂ CH ₂ CH ₂ C ₈ F ₁₇)	8:2/8:2 Fluorotelomer phosphate diester
8:2/10:2 diPAPs	(O)P(OH)(OCH ₂ CH ₂ C ₈ F ₁₇)(O CH ₂ CH ₂ C ₁₀ F ₂₁)	8:2/10:2 Fluorotelomer phosphate diester

Table S12. The summary of the PFAA precursor screening results.

Product J	Product N	Product Q
FOSA	FOSA	FOSA
6:2 FTSA	6:2 FTSA	FOSAA
8:2 FTSA	8:2 FTSA	EtFOSAA
6:2/6:2 diPAPs	6:2/8:2 diPAPs	6:2 FTSA
6:2/8:2 diPAPs		
8:2/8:2 diPAPs		
8:2/10:2 diPAPs		

APPENDIX B. SUPPLEMENTAL INFORMATION: PER- AND POLYFLUOROALKYL SUBSTANCES IN COMMERCIALY AVAILABLE BIOSOLID-BASED PRODUCTS: THE EFFECT OF TREATMENT PROCESSES

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Standards and Reagents

Individual PFAS precursors including 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (EtFOSE, > 98 %), N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA, > 98 %), N-ethylperfluoro-1-octanesulfonamide (EtFOSA, > 98 %), N-methylperfluoro-1-octanesulfonamide (MeFOSA, >98%), perfluoro-1-octanesulfonamide, (FOSA, > 98%), perfluoro-1-octanesulfonamide acetic acid (FOSAA, > 98 %) were purchased from Wellington Laboratories. DuPont (Wilmington, DE) provided 5:3 fluorotelomer carboxylic acids (5:2 FTCA), 6:2 fluorotelomer carboxylic acids (6:2 FTCA) and 8:2 fluorotelomer alcohol (8:2 FTOH, 99%).

Methanol ($\geq 99.9\%$, HPLC grade) and acetic acid ($\geq 99.7\%$ Certified ACS grade) were purchased from Fisher Scientific (Hampton, NH). Ammonium acetate (98 %, ACS grade) was purchased from Mallinckrodt (St Louis, MO). Ammonium hydroxide (28 - 30 %, ACS grade),

Supelclean™ ENVI-Carb (SPE bulk packaging), calcium chloride (anhydrous, $\geq 96\%$, ACS grade) and sodium azide ($\geq 99\%$) were purchased from Sigma-Aldrich (St. Louis, MO). Sodium hydroxide ($\geq 98.0\%$, ACS grade) was purchased from Macron Fine Chemicals (Center Valley, PA). Nanopure water was prepared using a Barnstead Nanopure water purification system with 0.2- μm filter (Lake Balboa, CA).

Table S1. Nutrient analysis, organic matter, moisture, fraction (< 2 mm) and pH of the biosolid-based products.

Post-treatment	Type	Measured			Provided by vendors					
		pH	Moisture (%)	Fraction < 2 mm (%)	Organic matter (%)	Total N	Available N (%)	Organic N (%)	P	K (as K ₂ O)
Heat-treatment	Pre	6.89	86.1	100	-	-	-	-	-	-
	Post	6.35	1.2	100	-	6.0 %	2.5	3.5	4.0 %	0 %
Blend	Pre	7.18	76.7	100	-	-	-	-	-	-
	Post	7.15	12.6	68.4	-	10,400 mg/kg, dry (TKN)*	-	-	5,670 mg/kg, dry (total)	1,590 mg/kg dry
	Sawdust	-	12.6	-	-	-	-	-	-	-
	Bark	-	49.1	-	-	-	-	-	-	-
Thermal hydrolysis	Pre	6.89	71.2	100	-	-	-	-	-	-
	Post (pH 9.5-10)	8.11	83.0	100	9.67	4.02 %	1.03	2.99	5.26 % (as P ₂ O ₅)	2.25 %
	Post (post, pH 9.5 - 10, lagoon)	8.02	86.4	100	-	-	-	-	-	-
	Post (post, > pH 12)	9.32	83.4	100	-	-	-	-	-	-
Compost	Class B biosolids from 2018 ¹	7.55	77.9	100	-	-	-	-	-	-
	Composted 2018 biosolids ²	6.86	68.9	52.7	85.6	1.24 %	0.24	1.00	2.04 % (as P ₂ O ₅)	0.19 %
	Composted 2016 biosolids ²	7.05	67.6	61.1	-	-	-	-	-	-
	Sawdust	-	38.2	-	-	-	-	-	-	-

¹Biosolids from a single municipal water resource recovery facility (WRRF); ² Class B biosolids from four different WRRFs.

-: Either not measured or provided by vendors.

* TKN: Total Kjeldahl Nitrogen

Table S2. Target analytes, acronym, mass transitions and other parameters (Choi et al., 2019)

Analyte	Acronym	LOQ ($\mu\text{g/L}$)	RT (min)	Precursor (m/z)	Daughter (m/z)	Surrogate	Recovery (%)
Perfluorobutanoic acid	PFBA	0.0137	1.96	213.10	168.98	MPFBA	94 (4)
Perfluoropentanoic acid	PFPeA	0.0363	4.70	263.10	68.97	MPFHxA	113 (28)
Perfluorohexanoic acid	PFHxA	0.0372	6.54	313.10	268.95	MPFHxA	93 (6)
Perfluoroheptanoic acid	PFHpA	0.8271	7.83	363.10	62.98	MPFHxA	101 (27)
Perfluorooctanoic acid	PFOA	0.0102	8.79	413.10	218.96	MPFOA	93 (7)
Perfluorononanoic acid	PFNA	0.0456	9.59	463.20	418.95	MPFNA	78 (17)
Perfluorodecanoic acid	PFDA	0.0014	10.26	513.10	268.95	MPFDA	97 (5)
Perfluoroundecanoic acid	PFUdA	0.2150	10.85	562.80	568.95	MPFUdA	115 (13)
Perfluorododecanoic acid	PFDoA	0.0008	11.36	612.80	568.90	MPFDoA	116 (19)
Perfluorotridecanoic acid	PFTriDA	0.0097	11.80	663.00	618.93	MPFDoA	142 (20)
Perfluorotetradecanoic acid	PFTeDA	0.0041	12.20	713.00	668.93	MPFDoA	122 (30)
Perfluorohexadecanoic acid	PFHxDA	0.3680	12.86	813.00	768.92	MPFDoA	126 (52)
Perfluorooctadecanoic acid	PFODA	0.0886	13.37	912.90	568.94	MPFDoA	185 (86)
Perfluorobutanesulfonate	PFBS	0.1677	5.36	299.10	79.95	MPFHxA	128 (39)
Perfluorohexanesulfonate	PFHxS	0.0046	7.97	398.80	82.95	MPFHxS	94 (7)
Perfluorooctane sulfonic acid	PFOS	0.0154	9.63	499.10	98.94	MPFOS	97 (5)
Perfluorodecanesulfonate	PFDS	0.0625	10.84	599.00	98.94	MPFOS	90 (7)
Perfluoro[1,2,3,4- $^{13}\text{C}_4$]butanoic acid	MPFBA	-	1.94	217.10	171.98	-	-
Perfluoro[1,2- $^{13}\text{C}_2$]hexanoic acid	MPFHxA	-	6.54	315.20	269.96	-	-
Perfluoro[1,2,3,4- $^{13}\text{C}_4$]octanoic acid	MPFOA	-	8.80	417.10	371.97	-	-
Perfluoro[1,2,3,4,5- $^{13}\text{C}_5$] nonanoic acid	MPFNA	-	9.58	468.10	422.97	-	-
Perfluoro[1,2- $^{13}\text{C}_2$]decanoic acid	MPFDA	-	10.26	515.05	469.95	-	-
Perfluoro[1,2- $^{13}\text{C}_2$]undecanoic acid	MPFUdA	-	10.84	565.05	268.96	-	-
Perfluoro[1,2- $^{13}\text{C}_2$]dodecanoic acid	MPFDoA	-	11.35	615.05	569.95	-	-
Sodium Perfluoro-1-hexane[$^{18}\text{O}_2$]sulfonate	MPFHxS	-	7.98	403.05	102.95	-	-
Sodium Perfluoro-1-[1,2,3,4- $^{13}\text{C}_4$] octane sulfonate	MPFOS	-	9.63	503.10	98.94	-	-

Table S3. PFAA precursors targeted in screening analysis

Precursors	Formula	Name
FOSA	$C_8F_{17}SO_2NH_2$	Perfluorooctane sulfonamide
MeFOSA	$C_8F_{17}SO_2NH(CH_3)$	<i>N</i> -Methyl perfluorooctane sulfonamide
EtFOSA	$C_8F_{17}SO_2NH(C_2H_5)$	<i>N</i> -Ethyl perfluorooctane sulfonamide
MeFOSE	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	<i>N</i> -Methyl perfluorooctane sulfonamidoethanol
EtFOSE	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	<i>N</i> -Ethyl perfluorooctane sulfonamidoethanol
FOSAA	$C_8F_{17}SO_2NHCH_2COOH$	Perfluorooctane sulfonamidoacetic acid
MeFOSAA	$C_8F_{17}SO_2N(CH_3)CH_2COOH$	<i>N</i> -Methyl perfluorooctane sulfonamidoacetic acid
EtFOSAA	$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	<i>N</i> -Ethyl perfluorooctane sulfonamidoacetic acid
4:2 FTOH	$C_4F_9CH_2CH_2OH$	4:2 Fluorotelomer alcohol
6:2 FTOH	$C_6F_{13}CH_2CH_2OH$	6:2 Fluorotelomer alcohol
7:1 FTOH	$CF_3(CF_2)_6CH_2OH$	7:1 Fluorotelomer alcohol
8:2 FTOH	$C_8F_{17}CH_2CH_2OH$	8:2 Fluorotelomer alcohol
10:2 FTOH	$C_{10}F_{21}CH_2CH_2OH$	10:2 Fluorotelomer alcohol
5:3 FTCA	$C_5F_{11}(CH_2)_2COOH$	5:3 Fluorotelomer carboxylic acid
6:2 FTCA	$C_6F_{13}CH_2COOH$	6:2 Fluorotelomer carboxylic acid
7:3 FTCA	$C_7F_{15}CH_2COOH$	7:3 Fluorotelomer carboxylic acid
8:2 FTCA	$C_8F_{17}CH_2COOH$	8:2 Fluorotelomer carboxylic acid
10:2 FTCA	$C_{10}F_{21}CH_2COOH$	10:2 Fluorotelomer carboxylic acid
6:2 FTUA	$C_5F_{11}CF=CHCOOH$	6:2 Fluorotelomer unsaturated carboxylic acid
8:2 FTUA	$C_7F_{15}CF=CHCOOH$	8:2 Fluorotelomer unsaturated carboxylic acid
10:2 FTUA	$C_9F_{19}CF=CHCOOH$	10:2 Fluorotelomer unsaturated carboxylic acid
4:2 FTSA	$C_4F_9CH_2CH_2SO_3H$	4:2 Fluorotelomer sulfonate
6:2 FTSA	$C_6F_{13}CH_2CH_2SO_3H$	6:2 Fluorotelomer sulfonate
8:2 FTSA	$C_{10}H_3F_{17}O_3S$	8:2 Fluorotelomer sulfonate
6:2 monoPAP	$(O)P(OH)(OCH_2CH_2C_6F_{13})_2$	6:2 Fluorotelomer phosphate monoester
8:2 monoPAP	$(O)P(OH)(OCH_2CH_2C_8F_{17})_2$	8:2 Fluorotelomer phosphate diester
6:2/6:2 diPAPs	$(O)P(OH)(OCH_2CH_2C_6F_{13})(O$ $CG_2CG_2C_6F_{13})$	6:2/6:2 Fluorotelomer phosphate diester
6:2/8:2 diPAPs	$(O)P(OH)(OCH_2CH_2C_6F_{13})(O$ $CH_2CH_2C_8F_{17})$	6:2/8:2 Fluorotelomer phosphate diester
8:2/8:2 diPAPs	$(O)P(OH)(OCH_2CH_2C_8F_{17})(O$ $CH_2CH_2CH_2C_8F_{17})$	8:2/8:2 Fluorotelomer phosphate diester
8:2/10:2 diPAPs	$(O)P(OH)(OCH_2CH_2C_8F_{17})(O$ $CH_2CH_2C_{10}F_{21})$	8:2/10:2 Fluorotelomer phosphate diester

Table S4. The concentration ($\mu\text{g}/\text{kg}$) of PFAAs in the samples (< 2 mm particle size fraction). Values in parenthesis are the standard error of the mean ($n = 4 - 5$). The value $< \text{LOQ}$ were changed to 0 for calculation.

Sample Name	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS	PFNA	PFDA	PFDS	PFUdA	PFDoA	PFTTrDA	PFTeDA
Heat-treatment (pre)	1.9 (0.2)	0.9 (0.2)	19.4 (0.2)	0.3 (0.1)	1.3 (0.1)	14.3 (1.5)	0 (0.1)	3.0 (0.2)	1.4 (0.3)	1.4 (0.1)	2.2 (0.2)	0.8 (0)	1.8 (0)
Heat-treatment (post)	2.8 (0.1)	0.1 (0.2)	41.5 (0.6)	0.3 (0.6)	2.1 (0.2)	19.1 (5.3)	0.3 (0.7)	2.6 (0.3)	1.1 (0)	2.1 (0.3)	0.9 (0.4)	0.7 (0.1)	0.8 (0.1)
Blend (pre)	0.3 (0.1)	0.3 (0)	1.6 (0.1)	0.3 (0.3)	2.1 (0.3)	9.9 (0.4)	0.3 (0.3)	3.2 (0.2)	5.3 (0)	0.4 (0.2)	1.2 (0)	0.3 (0)	1.4 (0.2)
Blend (post)	0.4 (0.5)	0.9 (0)	2.0 (0.2)	0.1 (0)	1.3 (0.1)	1.8 (0.3)	0 (0.1)	0.6 (0.1)	0.4 (0.1)	0.2 (0.1)	0 (0)	0 (0)	0 (0)
Thermal hydrolysis (pre)	0.3 (0.1)	0.5 (0.5)	0.8 (0)	0.1 (0.3)	0.7 (0.1)	6.1 (0.5)	0 (0.1)	2.9 (0)	0.8 (0.3)	1.1 (0.1)	2.1 (0.4)	0.7 (0)	1.7 (0)
Thermal hydrolysis (post, pH 8-9)	0.3 (0.2)	0.7 (0.6)	1.6 (0.1)	0.1 (0.2)	0.9 (0.1)	4.4 (0.2)	0 (0.1)	2.8 (0.1)	1.0 (0.3)	1.0 (0.1)	2.0 (0.6)	0.7 (0)	1.7 (0)
Thermal hydrolysis (post, pH 8-9, lagoon)	0.5 (0.1)	0.4 (0.6)	3.2 (0)	0.1 (0.1)	1.5 (0.1)	4.9 (0.7)	0 (0.1)	3.4 (0.2)	0.7 (0.1)	0.9 (0.1)	1.8 (0.3)	0.1 (0)	0.8 (0)
Thermal hydrolysis (post, pH > 12)	0.3 (0.1)	0.8 (1.3)	1.9 (0.1)	0.1 (0.4)	0.9 (0.2)	5.4 (2.2)	0 (0.4)	2.9 (0.2)	0.9 (0)	1.0 (0.2)	2.4 (0.3)	0.7 (0)	1.4 (0.1)
Class B biosolids from 2018	0.2 (0)	5.6 (0.2)	0.4 (0)	0.1 (0.3)	0.9 (0.2)	8.5 (0.4)	0 (0.2)	4.2 (0.2)	2.2 (0)	1.4 (0.2)	3.3 (0)	1.2 (0)	3.0 (0.1)
Compost, post-2016 biosolids	2.8 (0.4)	5.2 (0.2)	11.0 (0.2)	0.4 (0)	16.4 (0.4)	11.0 (0.2)	1.9 (0.3)	12.2 (0.7)	0.8 (0.3)	1.9 (0.1)	3.7 (0.3)	0.7 (0.1)	0.9 (0.1)
Compost, post-2018 biosolids	5.1 (0.2)	29.0 (1.8)	38.8 (0.9)	0.5 (0.1)	16.1 (0.4)	10.5 (0.4)	2.6 (0.1)	9.6 (0.5)	0.6 (0.1)	4.3 (0.2)	3.1 (0.1)	2.4 (0.1)	0.7 (0.1)
Compost, post-2016 biosolids > 2 mm	2.1 (0.4)	4.5 (0.8)	8.4 (2.2)	0.2 (0.2)	7.9 (2.0)	4.5 (1.7)	0.2 (0.3)	4.5 (0.3)	0.4 (0)	0.7 (0.3)	1.2 (0.5)	0.1 (0)	0.2 (0.1)
Blend (post > 2 mm)	1.0 (0.4)	2.4 (0.9)	4.0 (2.4)	0.1 (0.1)	3.2 (2.0)	3.0 (0.8)	0.1 (0.3)	1.8 (0.4)	0.4 (0)	0.4 (0.1)	0.3 (0.2)	0 (0)	0.1 (0.1)
Blend (bark)	0.8 (3)	0.1 (0.1)	0.1 (0.1)	0 (0.2)	0.1 (0.2)	0.1 (1.1)	0 (0.2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Blend (sawdust)	0 (0)	0 (0.1)	0 (0.1)	0 (0)	0 (0.3)	0 (0.3)	0 (0.2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Compost (sawdust)	0.1 (0.1)	0 (0.1)	0 (0.5)	0 (0.3)	0 (0.1)	0 (0.2)	0 (0.2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)

Table S5. Σ PFCAs, Σ PFSA, Σ Short chains, Σ Long chains and Σ PFAs concentrations ($\mu\text{g}/\text{kg}$) in the samples (< 2 mm particle size fraction). Values in parenthesis are the standard error of the mean ($n = 4 - 5$). The value < LOQ were changed to 0 for calculation.

Sample Name	Σ PFCAs	Σ PFSA	Σ Short*	Σ Long**	Σ PFAs
Heat-treatment (pre)	31.7 (0.5)	16.9 (0.8)	23.7 (0.5)	26.4 (0.6)	48.6 (0.7)
Heat-treatment (post)	53.9 (1.2)	20.6 (2.8)	45.6 (1.0)	30.1 (2.7)	74.5 (2.1)
Blend (pre)	10.7 (0.2)	15.8 (0.9)	2.3 (0.1)	24.3 (1.0)	26.5 (1.1)
Blend (post)	4.4 (0.4)	3.1 (0.3)	3.3 (0.2)	4.3 (0.4)	7.5 (0.6)
Thermal hydrolysis (pre)	10.2 (0.3)	7.5 (0.5)	1.6 (0.1)	16.1 (0.7)	17.7 (0.7)
Thermal hydrolysis (post, pH 8 – 9)	11.0 (0.9)	6.1 (0.9)	2.6 (0.1)	14.5 (1.1)	17.1 (1.1)
Thermal hydrolysis (post, pH 8-9, lagoon)	12.2 (0.4)	6.1 (0.3)	4.2 (0.1)	14.2 (0.6)	18.3 (0.6)
Thermal hydrolysis (post, pH > 12)	11.4 (0.6)	7.1 (0.2)	3.1 (0.3)	15.5 (0.7)	18.5 (0.7)
Class B Biosolids from 2018	14.5 (0.2)	16.4 (0.7)	6.2 (0.2)	24.7 (0.7)	30.9 (0.8)
Compost, post-2016 biosolids	51.4 (1.5)	17.4 (0.5)	22.1 (0.3)	49.8 (1.9)	68.7 (1.9)
Compost, post-2018 biosolids	82.5 (0.7)	40.4 (2.4)	74.7 (2.4)	50.3 (3.6)	123.0 (2.9)

*Short chains include PFCAs \leq C7 and PFSA \leq C5

**Long chains include PFCAs \geq C8 and PFSA \geq C6

APPENDIX C. SUPPLEMENTAL INFORMATION: PLANT UPTAKE OF PERFLUOROALKYL ACIDS AND OTHER TRACE ORGANICS FROM A COMMERCIALY AVAILABLE BIOSOLID-BASED FERTILIZER

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Table S1. The extraction recovery efficiency (%) of the targeted PFAAs in solvent-spiked samples, plants, growing media and solid phase extraction.

Table S2. The extraction recovery efficiency (%) and matrix effect (%) of the targeted PPCPs in solvent-spiked samples, plants, growing media and solid phase extraction.

Table S3. The desorption percent of selected PPCPs and PFAAs over 21 days.

Table S1. The extraction recovery efficiency (%) of the targeted PFAAs in solvent-spiked samples, plants, growing media and solid phase extraction.

	PFBA	PFBS	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFDA	PFDS	PFUdA
Solvent Spiked (growing media)	93 ± 2	102 ± 2	93 ± 4	103 ± 3	93 ± 0	90 ± 2	91 ± 3	89 ± 3	93 ± 1	94 ± 2
Solvent spiked (plant)	95 ± 1	51 ± 2	99 ± 3	98 ± 2	96 ± 1	97 ± 2	94 ± 3	94 ± 5	82 ± 3	96 ± 1
Growing media	97 ± 2	106 ± 5	89 ± 4	93 ± 4	93 ± 1	100 ± 2	96 ± 2	89 ± 1	106 ± 9	103 ± 2
Kale (leave)	94 ± 2	67 ± 6	93 ± 5	95 ± 7	94 ± 2	98 ± 2	93 ± 2	90 ± 1	79 ± 4	92 ± 3
Kale (Root)	90 ± 2	82 ± 3	77 ± 8	96 ± 4	92 ± 2	100 ± 1	103 ± 6	81 ± 8	69 ± 3	96 ± 2

Table S2. The extraction recovery efficiency (%) and matrix effect (%) of the targeted PPCPs in solvent-spiked samples, plants, growing media and solid phase extraction.

Sample	Part	Azithromycin		Carbamazepine		Miconazole		Diphenhydramine		Triclosan		Triclocarban	
		EXT RE	Matrix	EXT RE	Matrix	EXT RE	Matrix	EXT RE	Matrix	EXT RE	Matrix	EXT RE	Matrix
Kale	Leave	110 ± 4	82 ± 17	191 ± 3	198 ± 10	73 ± 0	78 ± 6	50 ± 1	58 ± 5	96 ± 1	118 ± 7	92 ± 1	98 ± 7
	root	102 ± 2	78 ± 14	161 ± 8	134 ± 9	83 ± 1	83 ± 5	69 ± 21	83 ± 4	108 ± 3	107 ± 3	87 ± 2	96 ± 4
Turnip	Leave	107 ± 3	95 ± 16	206 ± 15	213 ± 13	84 ± 13	79 ± 7	55 ± 1	64 ± 5	109 ± 1	102 ± 8	98 ± 1	86 ± 9
	Bulb	102 ± 4	97 ± 6	164 ± 7	151 ± 9	72 ± 1	77 ± 2	54 ± 2	58 ± 3	98 ± 5	104 ± 6	91 ± 1	92 ± 5
Growing media	-	97 ± 8	91 ± 22	200 ± 7	203 ± 13	75 ± 7	83 ± 6	50 ± 1	56 ± 5	97 ± 7	111 ± 7	103 ± 7	108 ± 7
Solvent spike	-	97 ± 1	-	141 ± 9	-	90 ± 4	-	89 ± 7	-	100 ± 1	-	103 ± 7	-
Solid phase extraction	-	99 ± 1	-	104 ± 11	-	94 ± 1	-	100 ± 1	-	98 ± 5	-	101 ± 4	-

Table S3. The average desorption percent of selected PPCPs and PFAAs over 21 days.

Compound	Average \pm SD %			
	Day 1	Day 7	Day 14	Day 21
Carbamazepine	5.72 \pm 0.7	6.40 \pm 0.5	7.88 \pm 1.2	6.51 \pm 0.1
Miconazole	0.02 \pm 0.01	0.03 \pm 0.03	0.03 \pm 0.04	0.03 \pm 0.03
Triclocarban	0.07 \pm 0.06	0.06 \pm 0.03	0.05 \pm 0	0.05 \pm 0
Triclosan	0.07 \pm 0.05	0.10 \pm 0.02	0.08 \pm 0.02	0.09 \pm 0
PFOA	0.04 \pm 0.04	0.02 \pm 0.01	0.01 \pm 0	0.04 \pm 0.02

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