

# Characterizing and Comparing Per- and Polyfluoroalkyl Substances in Commercially Available Biosolid and Organic Non-Biosolid-Based Products

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**ABSTRACT:** There is increasing concern over the presence of per- and polyfluoroalkyl substances (PFAS) in biosolids, while sales in commercially available biosolid-based products used as soil amendments are also increasing. Here, the occurrence of 17 perfluoroalkyl acids (PFAAs) present in 13 commercially available biosolid-based products, six organic composts (manure, mushroom, peat, and untreated wood), and one food and yard waste compost were studied. The PFAA concentration ranges observed are as follows: biosolid-based products (9.0–199  $\mu\text{g}/\text{kg}$ ) > food and yard waste (18.5  $\mu\text{g}/\text{kg}$ ) > other organic products (0.1–1.1  $\mu\text{g}/\text{kg}$ ). Analysis of 2014, 2016, and 2018 bags produced from one product line showed a temporal decrease in the total PFAAs (181, 101, and 74  $\mu\text{g}/\text{kg}$ , respectively). The total oxidizable precursor (TOP) assay revealed the presence of PFAA precursors in the biosolid-based products at much higher levels, when the soluble carbon was removed by the ENVI-Carb clean-up prior to the TOP assay. Time-of-flight mass spectrometry confirmed the presence of three sulfonamides, two fluorotelomer sulfonates, and several polyfluoroalkyl phosphate diesters. Pore-water concentrations of water-saturated products were primarily of short-chain PFAAs and increased with increasing PFAA concentrations in the products. A strong positive log-linear correlation between organic carbon (OC)-normalized PFAA partition coefficients and the number of  $\text{CF}_n$  units indicates that OC is a good predictor of PFAA release concentrations.



## INTRODUCTION

Recently, commercially available biosolid-based products have gained popularity for urban and suburban applications in gardens, golf courses, public parks, and lawns.<sup>1,2</sup> For example, sales for TAGRO products, based out of Washington, have increased over the past 2 decades (500% increase in the gross revenue) (Figure S1), and future sales are projected to increase. Biosolid-based soil amendments contain many beneficial components, such as organic matter and macro- and micronutrients, which can be a useful organic growing medium, and for some products, an alternative to synthetic fertilizers. In addition, the land application of biosolids can reduce the landfilling and incineration of urban waste, which can add up to an order of magnitude in additional costs to the municipal customer.<sup>3</sup> Land application of biosolids is a widespread practice, but the percentage of biosolids that are land-applied varies with region. For example, in the United States,<sup>4</sup> Australia,<sup>5</sup> Canada,<sup>6</sup> and Europe,<sup>7</sup> on average, more than half the biosolids are reported to be land-applied, although the actual percentage is region-specific within a country, e.g., from <1% to >70% in different European states.<sup>8</sup> In Sweden, approximately 25% of the biosolids are land-applied,<sup>6</sup> whereas in China, <3% is reported to be land-applied for agricultural purpose but >80% is improperly dumped.<sup>9</sup> To

contextualize how this translates into the mass of biosolids applied, consider that over 7.18 million tonnes of dry biosolids were reported in 2004 to be produced annually for the United States alone.<sup>10</sup>

Despite the benefits of biosolid-based products, their use is constantly 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 acids, which include perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), and known perfluoroalkyl acid (PFAA) precursors, such as perfluoroalkyl sulfonamides (FOSAs), fluorotelomer alcohols (FTOHs), and polyfluoroalkyl phosphate esters (PAPs).<sup>11</sup> PFAA precursors can be transformed into PFAAs in the environment via natural processes such as atmospheric oxidation<sup>12</sup> and microbial degradation, with PFAAs being the terminal metabolites.<sup>13</sup> PFAS have been frequently detected in

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municipal biosolids due to their persistence and widespread use in various industrial applications and consumer products.<sup>14,15</sup> PFAS use in consumer products has also led to the presence of PFAS in composts (29–76  $\mu\text{g}/\text{kg}$  dw) produced from the urban collection of compostable paper wastes along with plant (tree and grass) clippings.<sup>16</sup>

Agricultural farmland that had received municipal biosolids for more than 10 years contained higher PFAA concentrations (e.g., perfluorodecanoic acid (PFDA)  $\leq 990$   $\mu\text{g}/\text{kg}$ , perfluorododecanoic acid (PFDoA)  $\leq 530$   $\mu\text{g}/\text{kg}$ , perfluorooctanoic acid (PFOA)  $\leq 320$   $\mu\text{g}/\text{kg}$ , and perfluorooctane sulfonic acid (PFOS)  $\leq 410$   $\mu\text{g}/\text{kg}$ ) than the background field soil without the biosolid application (PFAA concentrations  $\leq 0.243$   $\mu\text{g}/\text{kg}$ ).<sup>17</sup> A similar study also showed elevated PFAA concentrations in crops grown in a biosolid-applied field, as well as in the nearby surface and well water.<sup>18</sup> Thus, the application of biosolids to agricultural fields can potentially introduce PFAAs into the soil,<sup>10,17,20</sup> water,<sup>18</sup> and food crops.<sup>21</sup> For home or urban gardens, the application of biosolid-based products can lead to the exposure of PFAS via consumption of crops grown in biosolid-amended plots, as well as dust inhalation and dermal contact during the use of organic product amendments and gardening activities.

Despite the increasing use of biosolid-based products in home and urban gardens, as well as other larger-scale 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 17 perfluoroalkyl acid (PFAA) concentrations in 13 commercially available biosolid-based products (mostly obtained in 2014 except for one each in 2016 and 2018), six products consisting of composted natural organic materials (manure, mushroom, peat, or untreated wood), and the composted food and yard waste-based product. The presence of PFAA precursors was evaluated using a total oxidizable precursor (TOP) assay followed by screening for 30 precursors in a subset of products. The potential for underestimating the precursor presence with the TOP assay due to the presence of the dissolved organic carbon was also evaluated. In addition, PFAA leachability and bioavailability were assessed by quantifying the PFAA pore-water concentrations in water-saturated samples. The relative PFAA distribution between the pore water and organic products was evaluated across products as were the PFAA concentrations that would result when applied based on nitrogen recommendations.

## MATERIALS AND METHODS

**Reagents and Standard Solutions.** All 17 PFAAs were purchased as mixtures (PFCA-MXB) from Wellington Laboratories (Guelph, Canada), containing 13 PFCAs (C4–C18) and four PFSAs (C4–C10). Isotopically mass-labeled compounds (seven PFCAs and two PFSAs) for use as internal standards were also purchased as mixtures (MPFAC-MXA) from Wellington Laboratories. Details are provided in the Supporting Information (Sections A–D and Table S1) along with all other reagents used in the extraction of PFAAs, PFAA pore-water concentrations, the TOP assay, and chromatographic analysis.

**Soil Amendment or Fertilizer Products.** All organic products were obtained in 2014 from different states within the United States and consisted of 11 biosolid-based products and seven organic (non-biosolid-based) products (Table 1) except for two obtained later from one vendor (Milorganite, Product

**Table 1. Details for the Organic (All Natural Material) Products (A–G) and Biosolid-Based Products (H–R) Analyzed in the Study<sup>a</sup>**

ID	brand	description	available form
<b>Organic Non-Biosolid Products</b>			
A	undisclosed source	food and yard compost	truck loads at vendors
B	EKO Organic Compost Soil	composts of tree and grass clippings and discarded Christmas trees	bags at any major stores
C	Gardener's Pride Composted Manure	manure compost	bags at any major stores
D	New Plant Life Manure	manure and peat compost	bags at any major stores
E	New Plant Life Mushroom	mushroom compost	bags at any major stores
F	Country Soil Mushroom Compost	mushroom compost	bags at any major stores
G	Promix Ultimate Organic Mix	Canadian sphagnum peat moss, perlite, limestone, gypsum, soy-based natural fertilizer	bags at any major stores
<b>Biosolid-Based Products</b>			
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 vendors
M	TAGRO Potting Soil	biosolids blended with maple sawdust and aged bark	bags and truck loads at local vendors
N	undisclosed source	composted biosolids with woodchips	truck loads at vendors
O	undisclosed source	composted biosolids with woodchips	truck loads at vendors
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

<sup>a</sup>Products H–L are heat-treated.

J). Most organic products were available in bags from major retailers across the United States, in bags at regional stores, or via truck loads directly from the vendors (detailed in Table 1). The additional samples from Milorganite (Product J) were those prepared for sale in 2016 and 2018 and collected to examine if PFAA concentrations were declining in response to the early phase-out of PFOS (for most uses) and subsequently PFOA.<sup>22</sup> All products were freeze-dried (Labconco, Kansas City, MO) for 72 h. The freeze-dried samples of all composted and blended products were sieved (<2 mm; Table S2) to remove larger particles such as plant debris and rocks. The five heat-treated products (H–L) were granular and had a uniform appearance and thus were not sieved. The <2 mm particle size fraction of the composted and blended products ranged from 36 to 80% of the total mass (Table S2). The basic nutrient data provided by A&L Great Lakes Laboratories (Ft. Wayne, IN) are summarized in Table S3.

**Sample Preparation and Extraction.** The freeze-dried samples were extracted in triplicate using a method described by Choi et al.<sup>16</sup> Briefly, isotopically labeled surrogates (2–5 ng of each) were added to each sample followed by extracting

three times sequentially with a methanol/ammonium hydroxide solution with 1 h sonication followed by a 2 h end-over-end rotation. Prior to analysis, all solvent extracts were combined and concentrated under nitrogen using a RapidVap Vacuum Evaporation System (Labconco, Kansas City, MO). The combined extracts were evaporated to dryness under nitrogen, reconstituted with 1000  $\mu\text{L}$  of 99:1 (v/v) methanol/glacial acetic acid and transferred to a microcentrifuge tube containing  $\sim 40$  mg of the ENVI-Carb sorbent with 20  $\mu\text{L}$  glacial acetic acid, and vortexed for 30 s. The mixture was centrifuged at 17 000 RCF for 30 min. An aliquot of each cleaned extract (400  $\mu\text{L}$ ) was transferred to a 1.5 mL glass injection vial containing 400  $\mu\text{L}$  of 0.003% ammonium hydroxide in Nanopure water (1:1, MeOH/H<sub>2</sub>O, v/v) for analysis, while the remaining cleaned extract was used for the TOP assay. The samples were stored at 4 °C until analysis. Here the TOP assay was performed on the extracts after the ENVI-Carb clean-up, whereas Choi et al.<sup>16</sup> performed the TOP assay prior to the ENV-Carb clean-up step. For comparison, we repeated the extraction, in which the TOP assay was performed on a subsample after solvent exchange prior to the ENV-Carb clean-up step as described below.

**Total Oxidizable Precursor (TOP) Assay and Dissolved Carbon Effects.** Analytical standards or individual chemical stocks are only available for a small fraction of the currently >4730 PFAS potentially in production.<sup>23,24</sup> The TOP assay is a heat-activated persulfate treatment at initial pH values >12, which allows for estimating the level of potential PFAA precursors in complex environmental samples<sup>6</sup> by converting them to PFAAs for which standards are readily available. High levels of organic matter and other contaminants can act as radical scavengers, affecting the oxidation rate of the PFAA precursors.<sup>25</sup> In the TOP assay results on the extracts of composted plant and paper wastes, Choi et al.<sup>16</sup> indicated that only 3 of the 10 sources evaluated had significant levels of precursors. They performed the TOP assay prior to a clean-up step due to concerns that precursors may be lost in the clean-up; however, this may have inadvertently led to the underestimation of the precursor presence. Therefore, we explored whether the dissolved organic carbon released during extraction of the biosolids may significantly compete with the precursors for radicals generated in the TOP assay, thus underestimating the precursor presence. We performed the TOP assay on extracts with and without an ENVI-Carb clean-up treatment. In one set of samples, the TOP assay was performed as described by Houtz and Sedlak<sup>22</sup> after performing a solvent exchange and an ENVI-Carb clean-up step. In the second set of samples, the samples were reconstituted with 1000  $\mu\text{L}$  of 99:1 (v/v) methanol/glacial acetic acid followed by transfer of a 500  $\mu\text{L}$  aliquot to a 2 mL microcentrifuge, which was evaporated to dryness under nitrogen. The dried extract was resuspended with 500  $\mu\text{L}$  of Nanopure water followed by performing the TOP assay.

The TOP assay was performed on both sets of extracts by sequentially adding 1.2 M sodium hydroxide (125  $\mu\text{L}$ ) and 160 mM potassium persulfate (375  $\mu\text{L}$ ) for final concentrations of 150 and 60 mM, respectively. The samples were vortexed for 1 min and incubated in a temperature-controlled water bath at 80–85 °C for 6 h. After incubation, the samples were immediately placed in an ice bath to cool. The final sample pH values were measured using pH-indicator strips due to the small sample volumes (<1 mL). The samples were neutralized with glacial acetic acid. For extracts that had not been

previously cleaned up, a 500  $\mu\text{L}$  sample aliquot was mixed 1:1 by volume with methanol containing the internal standard into a 1.5 mL microcentrifuge tube containing 20 mg of the ENVI-Carb sorbent that was pretreated with 20  $\mu\text{L}$  glacial acetic acid. The sample was vortexed and centrifuged at 17 000 RCF for 30 min, and the supernatant ( $\sim 1000$   $\mu\text{L}$ ) was transferred to a high-performance liquid chromatography (HPLC) injection vial. The final sample was vortexed for 30 s prior to analysis.

**Pore-Water Concentrations.** Except for organic non-biosolid-based products (B–G), which had negligible PFAA concentrations, PFAA pore-water concentrations were measured in triplicate after 48 h of being saturated with an electrolyte solution (0.5 mM calcium chloride at pH 6.5) in 24 mL polypropylene (PP) syringes similar to the method described by Choi et al.<sup>16</sup> A 48 h equilibration time was selected based on a kinetic study on two different composts in which aqueous PFAA concentrations were found to be statistically the same between 1 and 7 days.<sup>16</sup> Briefly, PP syringes were rinsed with acetone and air-dried prior to packing with the organic products. The bottom of the syringe was fitted with a syringe cap and a stainless steel mesh was placed inside the syringe to retain the liquid and solid materials, respectively. The organic products ( $\sim 3$  g) were packed into the syringe and then saturated (1:2 g:mL ratio) with the electrolyte solution containing 3.08 mM sodium azide to minimize potential microbial degradation. The plunger was gently inserted into the syringe to reduce evaporation during incubation. Controls containing no product were prepared to assess any background PFAA concentrations. After a 48 h incubation, the syringe cap was removed and the syringe was placed in a 50 mL PP tube and centrifuged at 1613 RCF for 1 h to separate the liquid (collected in the tube) and solid materials (retained in the syringe due to the stainless steel mesh). The pore-water pH was measured followed by PFAA concentrations in the pore-water supernatant using a previously published solid-phase extraction (SPE) method<sup>26</sup> with hydrophilic–lipophilic balance (HLB) SPE cartridges. Although weak-anion exchange (WAX) SPE cartridges have been used more frequently to clean the PFAA extracts, we found similar PFAA recoveries between HLB and WAX (Figure S2) consistent with the previous observations.<sup>20</sup> Additional SPE method details are summarized in the Supporting Information. The spent-solids were weighed prior to and after the 72 h freeze-drying process to account for the PFAA concentrations in the residual moisture after centrifugation. The freeze-dried spent-samples ( $\sim 0.5$  g) were extracted for evaluating the mass balance.

**PFAS Analysis.** All samples were vortexed for 30 s and then analyzed for 17 PFAAs using a Shimadzu liquid chromatography (LC) system coupled to an SCIEX 5600 quadrupole time-of-flight (QToF) mass spectrometer (Framingham, MA), as previously described.<sup>16</sup> The sample extracts for a subset of samples were screened for 30 known PFAA precursors (Table S4) using LC-QToF/MS in SWATH acquisition mode confirmation with the MS/MS library or aged analytical standards (detailed in the Supporting Information).

**Analytical QA/QC.** Nine mass-labeled isotopes were used as internal standards to correct for the matrix effects and extraction recovery. A six- to eight-point calibration curve ranging from 0.1 to 15  $\mu\text{g/L}$  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

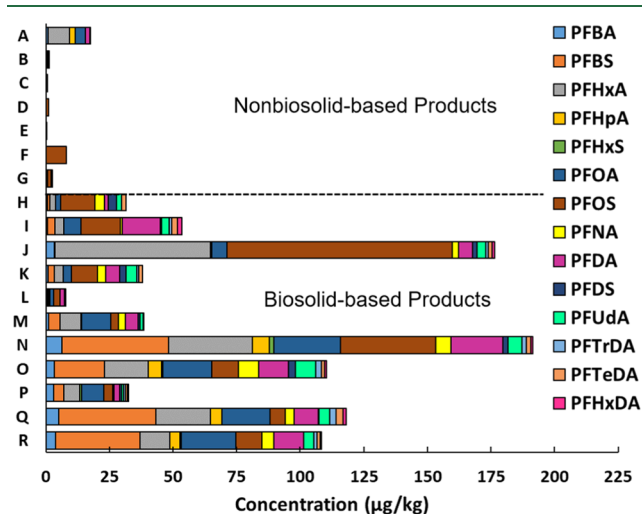
monitor the calibration. An instrument blank was injected before and after a CCV injection to monitor the potential carryover between injections. Values below the quantification limit (LOQ) were assumed to be 0 when calculating concentrations. PFAA extraction recoveries (%) were assumed to be similar to those previously reported for composted plant and paper wastes, which ranged from 78 to 126% except for perfluorotridecanoic acid (PFTrDA,  $142 \pm 20\%$ ).<sup>16</sup> We included the extraction and analysis of a sludge Standard Reference Material (SRM 2781), for which the results were compared well with those summarized in Reiner et al.<sup>27</sup> (Table S5), thus confirming the adequacy of the extraction method that we used.

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

## RESULTS AND DISCUSSION

### PFAA Concentrations in Soil Amendment Products.

The PFAA concentrations ( $\mu\text{g}/\text{kg}$ ) above LOQs are summarized in Figure 1 and detailed in Tables S6 and S7.



**Figure 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. Product A is a food and yard compost.

The total PFAA concentrations ranged from 9 to 199  $\mu\text{g}/\text{kg}$  in the biosolid-based products (the <2 mm particle) with all containing eight PFAAs > LOQs: perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluorohexanoic acid (PFHxA), PFOA, PFOS, perfluorodecanoic acid, perfluoroundecanoic acid (PFUdA), and perfluorododecanoic acid (PFDoA). For the non-biosolid-based products, the total PFAA concentrations were relatively low to negligible, ranging from 0.1 to 19  $\mu\text{g}/\text{kg}$ , with the high end being product A (food and yard compost), which was dominated by PFHxA. In the study by Choi et al.<sup>16</sup> on composts from primarily urban plant and paper wastes, composts with food or food packaging had higher PFAAs (8–76  $\mu\text{g}/\text{kg}$ ) than those with only yard trimmings (<2  $\mu\text{g}/\text{kg}$ ) and PFHxA was also the dominant PFAA. For the biosolid-based products, the dominant short-

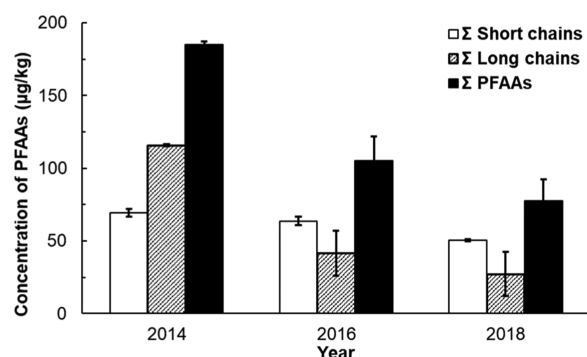
chain PFAAs (PFCAs  $\leq C7$  and PFSAs  $\leq C5$ ) were PFHxA (0.5–61.0  $\mu\text{g}/\text{kg}$ ) and PFBS (0.4–41.9  $\mu\text{g}/\text{kg}$ ), whereas PFOA (1.4–26.0  $\mu\text{g}/\text{kg}$ ) and PFOS (2.0–88.5  $\mu\text{g}/\text{kg}$ ) were the dominant long-chain PFAAs. PFOS was generally present at higher concentrations than other PFAAs in the biosolid-based products despite the voluntary phase-out of PFOS and its related products in 2002 from most uses.<sup>28</sup> The phase-out of PFOS-based mist suppressants came later (2012–2015 time frame)<sup>28</sup> and thus may have impacted the 2014 biosolid-based products in this study. Also, the PFOS presence is most likely associated with its presence in long-lived consumer products,<sup>29</sup> products imported from countries where PFOS is still being used, such as on carpets, clothing, paper and packaging, and plastics,<sup>30</sup> and legacy PFAS still entering our municipal facilities that receive landfill leachate.

The total PFAA concentrations in the heat-treated biosolid-based products ranged from 9 to 181  $\mu\text{g}/\text{kg}$ , while the PFAA concentrations in only the <2 mm fraction of the composted or blended biosolid-based products ranged from 34 to 199  $\mu\text{g}/\text{kg}$ . Of these composted or blended biosolid-based products, 36–64% of the material was >2 mm, which appeared to be primarily plant debris and rocks and likely had low PFAA levels. In one of our previous studies focused on the effect of treatment processes on PFAAs in biosolid-based products,<sup>31</sup> both the <2 mm and the >2 mm particles were extracted independently. The PFAA concentration in the >2 mm fraction had high standard deviations, including near-zero values, which from the observation was attributed to if and how many fine particles (<2 mm) were clinging to the larger particles (>2 mm). In the same study, we also extracted the unsieved co-composting and co-blending woody materials used in the treatment processes and found PFAA concentrations to be negligible (<2  $\mu\text{g}/\text{kg}$ ) relative to PFAA levels in the <2 mm fraction of the final products. If the same is assumed for the non-heat-treated biosolid-based products M–R, the range in the PFAA concentration normalized to the whole product decreases to 19–79  $\mu\text{g}/\text{kg}$  (Table S7). The heat-treated biosolid-based products (H–L) were not sieved. On a normalized basis, the 2014 heat-treated product J (Milorganite) had the highest total PFAA load across all products (181  $\mu\text{g}/\text{kg}$ ), with almost half being from PFOS (88  $\mu\text{g}/\text{kg}$ ). For non-biosolid products A–G, it is reasonable to assume that the PFAA concentrations are similar in the <2 mm and >2 mm fractions based on that found previously for the PFAA occurrence in composted urban plant and paper wastes.<sup>16</sup>

The differences in PFAA concentrations among the products are likely primarily due to the differences in the sources coming into the different wastewater treatment plants from which the biosolids originated. Even the heat-treated biosolid-based products (H–L) that were not sieved had a large range in the total PFAA concentrations (9–180.5  $\mu\text{g}/\text{kg}$ ; Table S7). Although different sludge and biosolid treatment processes may affect PFAA concentrations, Kim Lazcano et al.<sup>31</sup> did not find common treatments such as heat treatment and typical thermal hydrolysis processes to reduce the PFAA concentrations; only blending with materials (e.g., sawdust, aged bark, etc.) served to dilute the PFAA loads being applied. In addition, given that PFAAs are common terminal metabolites from microbial degradation, composting will not reduce PFAA loads but may increase them due to the presence of PFAA precursors that can degrade microbially to PFAAs.<sup>13</sup>

**Temporal Variation of PFAA Concentrations (2014, 2016, and 2018).** For Milorganite (Product J), additional

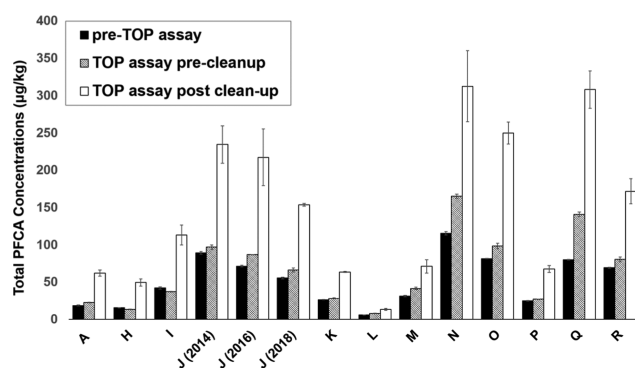
samples were obtained for the material released for use in 2016 and 2018. The total PFAA concentrations decreased from 185 to 77  $\mu\text{g}/\text{kg}$  from 2014 to 2018 due to the significant reduction in the long-chain PFAAs from 115 to 27  $\mu\text{g}/\text{kg}$  ( $F_{2,6} = 603.1$ ,  $p < 0.01$ ) (Figure 2). Of the total PFAA reduction, 67% was due



**Figure 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.

to reduced PFOS concentrations from 88.5  $\mu\text{g}/\text{kg}$  in 2014 to 29.7 and 18.7  $\mu\text{g}/\text{kg}$  in 2016 and 2018, respectively ( $F_{2,6} = 424.5$ ,  $p < 0.01$ ). Decreases over time are also statistically significant for the total PFAA concentrations ( $F_{2,6} = 388.9$ ,  $p < 0.01$ ), as well as for the short-chain PFAAs ( $F_{2,6} = 9.58$ ,  $p < 0.05$ ). When comparing significant differences between 2 years (2014 and 2016, 2016 and 2018, and 2014 and 2018), both the total concentration of PFAAs ( $p < 0.01$ ) and the long chain ( $p < 0.01$ ) significantly decreased for all pairwise comparisons. For the short-chain PFAAs, changes were only statistically significant between 2014 and 2018 ( $p < 0.05$ ), with the decrease accounting for only about 15% of the reduction in the total PFAAs. Although temporal variations were only assessed for one product, decreases in PFOS concentrations leading to an overall reduction in PFAA concentrations for Milorganite (Product J) are consistent with the recent studies reporting decreases in PFOS concentrations in municipal biosolids,<sup>32</sup> adult blood samples,<sup>33</sup> and wildlife.<sup>34</sup>

**Total Oxidizable Precursor (TOP) Assay and Effect of Dissolved Organic Carbon.** The  $\sum$ PFCA concentrations in the extracts of the biosolid-based products compared to that found in the TOP assay with and without the ENVI-Carb clean-up are summarized in Figure 3 and Table S8. TOP analysis is now shown for the non-biosolid-based products because extract concentrations were low and concentration changes were negligible. For all biosolid-based products, increases in  $\sum$ PFCA concentrations are statistically significant when the TOP assay was performed on the ENVI-Carb cleaned-up extracts (Figure 3), whereas only products N and Q had significant increases in  $\sum$ PFCA in the uncleaned extracts. This clearly exemplifies that many of the radicals produced in the TOP assay were consumed by the solubilized organic matter, thus the importance of a clean-up step prior to imposing the TOP assay. Houtz et al.<sup>35</sup> observed no statistical differences in PFAAs measured after the TOP assay was performed on extracts of two PFAS-contaminated media (surficial soil and aquifer solids) before and after the ENVI-Carb clean-up (Figure S6 in Houtz et al.<sup>35</sup>). However, biosolids and composted materials are much richer in organic



**Figure 3.** Total PFCA concentrations ( $\mu\text{g}/\text{kg}$ ) in the sample extracts (pre-TOP) and those resulting from the TOP assay before and after the ENVI-Carb clean-up prior to the TOP assay of the product extracts. The error bars represent the standard error of the mean.

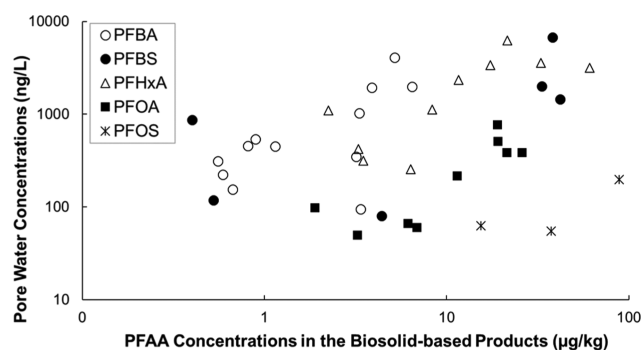
matter than in the media they evaluated, and as observed in the current study, TOP prior to clean-up can lead to underestimating the precursor presence. Therefore, it is highly likely that the TOP results performed on uncleaned extracts of the composted plant and paper wastes<sup>16</sup> underestimated both the magnitude of precursor presence and the number of samples that contained a significant level of precursors.

The TOP assay is a useful way to estimate the levels of potential PFAA precursors in complex environmental samples,<sup>23</sup> which is important since their presence indicates that PFAA concentrations from the products may increase after application to soil. There are, however, differences between the PFAAs that result in the TOP assay and what happens naturally in the environment. The TOP assay oxidizes both PFCA and PFSA precursors to PFCA,<sup>23</sup> whereas the microbial and biological (e.g., in vivo) transformation of PFSA precursors yields PFSA.<sup>36,37</sup> 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), oxidize to PFOA (major) and PFHpA (minor) via the TOP assay,<sup>23,38</sup> while the major microbial transformation product is known to be PFOS.<sup>37</sup> Note that PFSA in samples treated with the TOP assay remain intact, i.e., no conversion.

**PFAS Precursors.** Seven biosolid-based products (J, K, M, N, O, P, and Q) and one non-biosolid-based product (B) were screened for 30 PFAA precursors (Table S4) frequently detected in environmental samples (e.g., wastewater, biosolids, landfill leachate, or food packaging).<sup>39,40</sup> No precursors were identified in the non-biosolid-based EKO Organic Compost soil product (product ID B), but several were identified in the biosolid-based products. The greatest number of precursors were identified in Product J (Milorganite, 2014), which included three sulfonamide-containing PFAA precursors (EtFOSAA, FOSA, and FOSAA), fluorotelomer sulfonates (6:2 and 8:2 FTSA), and several polyfluoroalkyl phosphate diesters (6:2/6:2, 6:2/8:2, 8:2/8:2, and 8:2/10:2 diPAPs) (Table S10). Several of these precursors were also identified in all of the other biosolid-based products except for the TAGRO Potting Soil (Product M). The increase of approximately 3–8 times more PFOA in the TOP assay (with cleaned extracts) along with the average factor of 3 increase in PFHxA is reflective of the precursors identified in those biosolid products

(Tables S6 and S8.2). It should be noted that the solvent-enhanced enzyme hydrolysis of some fluorotelomer-based PFAS to FTOHs such as the monoPAPs can occur, thus potentially reducing their presence in the screening of the solvent extracts.<sup>41</sup> In addition, there could be several other PFAA precursors present in the biosolids that were not extracted using a methanol-based extractant. Letcher and Chu<sup>42</sup> investigated two 3M-derived side-chain sulfonamide-urethane polymers in a suite of biosolids from Canada, during which they had to use more aggressive solvents and temperatures (acetone/hexane at 45 °C) to extract these larger substances (1300–1650 g/mol range). These larger fluorinated polymers also require MS systems that can scan higher molecular weights. Most notably, these perfluorooctane and perfluorobutane side-chain substances were present at approximately 30 times higher concentrations than any of the commonly monitored PFAA and PFAS precursors. Although these large PFAS are likely to degrade slowly<sup>41,43</sup> and thus may not contribute significantly to PFAA concentrations mobilizing through the soil profile, they will serve as a long-term source in the root zone thus available for plant uptake.

**PFAA Pore-Water Concentrations.** C4–C10 PFAAs were detected in the pore water of water-saturated biosolid-based products (Table S11). The most frequently detected PFAAs were PFBA and PFHxA, with a concentration range of 155–4072 and 256–6215 ng/L, respectively. PFBS was only quantifiable in the pore water for five of the products evaluated, in which the concentrations reached up to 20 000 ng/L. Among the longer chains, PFOA was detected most frequently at the highest concentration (100–800 ng/L). PFOS and PFNA were detected in the pore water of some products, but at <200 ng/L. PFHxS, PFDA, and PFDS were each detected in the pore water of only two products (not necessarily the same products) and at low concentrations near the LOQs. For all other longer chains, pore-water concentrations were <LOD or <LOQ. PFAA pore-water concentrations (ng/L) generally increased with increasing PFAA concentrations ( $\mu\text{g}/\text{kg}$ ) in the biosolid-based products (Figure 4). Note that PFAA concentrations released from a soil

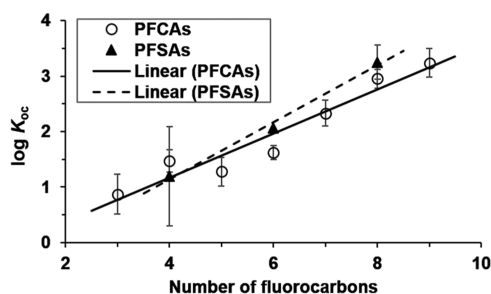


**Figure 4.** Log–log plot of PFAA pore-water concentrations (ng/L) and in biosolid ( $\mu\text{g}/\text{kg}$ ) in the unsieved heat-dried biosolids and the <2 fraction of the biosolid-based products for five PFAAs.

amendment will be highly attenuated as PFAA sorption to the surrounding soil particles occurs, as well as dilution with rain or irrigation water. The saturated-product pore-water pH values ranged from pH 4.4 to 8.3 (Table S12), which will also be moderated by the buffer capacity of the surrounding soil.

**PFAA Partition Coefficients.** Organic carbon (OC)-normalized product-water desorption partition coefficients

( $K_{oc}$ , L/kg<sub>oc</sub>) were calculated using PFAA pore-water concentration ( $\mu\text{g}/\text{L}$ ) (converted from ng/L, as summarized in Table S11) and the PFAA concentrations remaining in the spent-biosolids ( $\mu\text{g}/\text{kg}$ ) (Table S13). OC was assumed to be 58% of the measured organic matter (Table S3), as assumed for soils.<sup>44</sup> The resulting log  $K_{oc}$  values are highly positively correlated with increasing  $\text{CF}_n$  units (Figure 5), as observed for



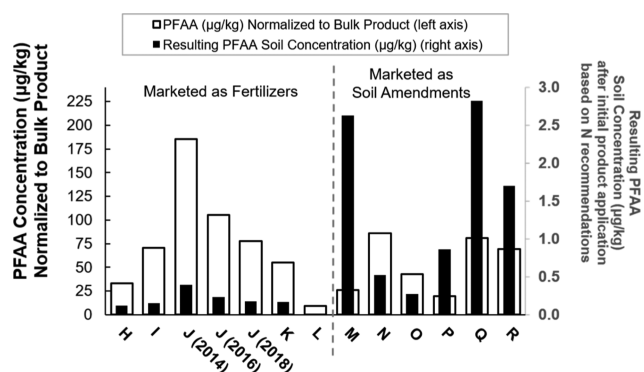
**Figure 5.** Average log of the OC-normalized partition coefficient ( $\log K_{oc}$ , L/kg<sub>oc</sub>) of PFCAs and PFSAs for the biosolid-based products versus the number of fluorocarbons and associated log-linear regressions as follows: PFCAs:  $\log K_{oc} = (0.40 \pm 0.05)(\text{CF}_n) - (0.41 \pm 0.32)$ ;  $R^2 = 0.927$ ,  $n = 7$ , and PFSAs:  $\log K_{oc} = (0.51 \pm 0.05)(\text{CF}_n) - (0.91 \pm 0.29)$ ;  $R^2 = 0.99$ ,  $n = 3$ .

composted urban plant and paper wastes.<sup>16</sup> Separate linear regressions of the average log  $K_{oc}$  values versus the number of  $\text{CF}_n$  units for the PFCAs and the PFSAs resulted in a higher slope for the PFSAs consistent with the observations of others for these two subclasses.<sup>45</sup> Although strong trends in PFAA sorption with the organic carbon have not been observed for soils across the globe,<sup>45</sup> the strong correlations observed with both biosolid-based fertilizers and the composted plant and paper wastes are likely due to the high OC content of these materials. This strong trend between PFAA desorption, PFAA concentrations, and OC content supports the use of such correlations for predicting PFAA release concentrations from organic amendments.

Both Figures 4 and 5 exemplify the higher leaching potential of shorter-chain PFAAs. Similar trends have been reported from soil/water batch studies,<sup>46</sup> a column study,<sup>47</sup> a long-term lysimeter experiment,<sup>48</sup> and field studies.<sup>18,19</sup> The current movement to use shorter-chain PFAS as alternatives to longer-chain PFAS has the potential to result in higher total PFAA concentrations being bioavailable for plant uptake, increasing the risk of food contamination with PFAAs.

**Implications and Perspective.** This study found that the commercially available biosolid-based products contain a range in the PFAA concentration similar to those found in composted urban plant and paper wastes and that these levels are substantially higher than the non-biosolid organic products marketed commercially. These commercial products are marketed as either a fertilizer (products H–L) or a soil amendment to enhance the soil's N and C contents, as well as other nutrients and water-holding capacity. For those marketed as fertilizers, the recommended application rates are typically based on the nitrogen (N) content. Biosolid-based soil amendments are typically blended with other materials (as exemplified in Table 1) and are often added at much larger amounts than those marketed as fertilizers. Therefore, products with lower PFAA levels that also have low N levels could contribute relatively higher PFAA loads to a garden compared to products with higher PFAA levels. Although each product

will come with application recommendations for different purposes (e.g., vegetables versus lawns, etc.), to exemplify the differences in PFAA loads added to a garden area, we used the Milorganite 2016 application recommendations for growing vegetables (e.g., tomatoes in this case at 4.5 lbs per 50 sq ft mixed throughout the root zone). We converted this rate to kilogram product per kilogram soil (detailed in the [Supporting Information](#)) and adjusted this recommendation for other products based on differences in their N content ([Table S3](#)) to compare across biosolid-based products. The results are summarized in [Figure 6](#), which shows the resulting PFAA



**Figure 6.** PFAA concentrations in soils ( $\mu\text{g}/\text{kg}$ ) (the right y-axis) after an initial application of commercially available organic-based fertilizer and soil amendments based on N needs compared to the total PFAA concentration ( $\mu\text{g}/\text{kg}$ ) in the bulk product (the left y-axis).

concentrations in the soils ( $\mu\text{g}/\text{kg}$ ) (the right y-axis) after making the initial application based on N needs, as well as the total PFAA concentration ( $\mu\text{g}/\text{kg}$ ) in the bulk product (the left y-axis). From this analysis, two things are apparent. Fertilizers are added at low amounts compared to the soil mass being amended; thus, the resulting PFAA concentrations are relatively low for the products in this study. Second, in some cases, soil amendments with lower N levels and low total PFAAs may result in higher total PFAA loading compared to fertilizers with a high total PFAA level. Product guidelines typically recommend a second application in the growing season if needed to maintain plant health. Recommended application rates for lawns are a magnitude lower, but up to four applications in a growing season are recommended in product guidelines depending on lawn health. The generation of additional PFAAs through precursor degradation once land-applied is not included in the estimates here. For example, Lee et al.<sup>49</sup> reported increases of PFHxA in plant tissues from the application of 6:2 diPAPs in biosolid-amended greenhouse studies, resulting from the slow transformation and release of PFHxA in the root zone, which is an area needing further investigation. Relative to the PFAS exposures we experience daily through the use of PFAS-containing products in our homes, cars, offices, etc., combined with their benefits to soil fertility and carbon sequestration, PFAS contribution from applying commercial fertilizer and soil amendment products from the residential organic materials noted here may not be that significant. However, to avoid high PFAA loadings when using materials that have relatively low N content, such as some biosolid-based products and other PFAA-containing soil amendments, including those containing composted food packaging<sup>16</sup> ([Table S3](#)), supplementing with inorganic nitrogen should be considered. Alternatively, given the known

persistence of PFAS and their presence in biosolid-based products, it may seem prudent to ban their land application. However, this places a heavy burden on public municipalities and could lead to numerous unintended consequences for which discussion is outside the scope of this work. One general approach would be to optimize the blending of biosolids for the purpose of keeping low PFAS loads. Blending to optimize the N content is already a frequent practice among applicators who receive biosolids from multiple sources. Meanwhile, efforts to ban all nonessential use of PFAS will go a long way in reducing PFAS burdens in municipal wastes from biosolids to municipal solid wastes.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b07281>.

Name, acronym, mass transitions, and other QAQC parameters; % of the product mass that was <2 mm; organic matter analysis of the products; list of PFAA precursors screened with QToF/MS; total PFAA, PFCA, and PFSA concentrations; pH of the extracts after the TOP assay; summary of the PFAA precursors identified in the QToF/MS screening; the average pore-water pH; historical annual gross revenue of a commercially available biosolid-based product; and the result of the recovery efficiency of PFAAs using two different SPE cartridges ([PDF](#))

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### Notes

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