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Underestimation of Per- and Polyfluoroalkyl Substances in Biosolids: Precursor Transformation During Conventional Treatment

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Abstract

Wastewater treatment plants generate a solid waste known as biosolids. The most common management option for biosolids is to beneficially reuse them as an agricultural amendment, but because of the risk of pathogen exposure, many regulatory bodies require pathogen reduction before biosolids reuse. Per- and polyfluoroalkyl substances (PFAS) are well documented in biosolids, but limited information is available on how biosolids treatment processes impact PFAS. Furthermore, quantification of PFAS has focused on perfluoroalkyl acids (PFAAs) which are a small fraction of thousands of PFAS known to exist. The objective of this study was to quantify 92 PFAS in biosolids collected from eight biosolids treatment facilities before and after

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Supporting Information
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List of materials, sample collection information, previous studies, instrument parameters, extraction efficiencies, and complete data sets (PDF)

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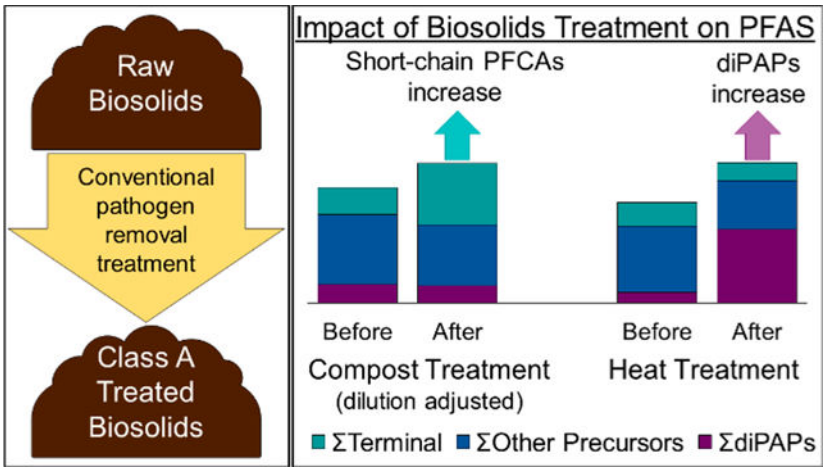
four pathogen treatment applications: composting, heat treatment, lime treatment, and anaerobic digestion. Overall, total PFAS concentrations before and after treatment were dominated by PFAA precursor species, in particular, diPAPs which accounted for a majority of the mass of the Σ_{92}PFAS. This differs from historic data that found PFAAs, primarily PFOS, to dominate total PFAS concentrations. Treatment options such as heat treatment and composting changed the ratio of PFAA precursors to PFAAs indicating a transformation of PFAS during treatment. This study finds that PFAA precursors are likely underrepresented by other studies and make up a larger percentage of the total PFAS concentration in biosolids than previously estimated.

Graphical Abstract



Keywords

Wastewater sludge; diPAP; PFAA; pathogen removal

INTRODUCTION

Municipal wastewater treatment plants (WWTPs) accept domestic and industrial wastewater before it is discharged or reused. The process of treating wastewater produces a solid waste referred to as wastewater treatment sludge or biosolids. Due to their high organic matter and nutrient content, biosolids are commonly used as an agricultural amendment in regions with advanced wastewater treatment. For example, in the United States, France, and Australia, 60%, 76%, and 83%, respectively, of biosolids generated are reused in agricultural applications.[1–3] The requirements placed upon biosolids for reuse are designed to prevent pathogen exposure and the environmental release of constituents of potential concern (COPC). Typically this includes a form of treatment, dewatering, demonstration of coliform reduction, and acceptable COPC concentrations.[2,4] In the U.S., biosolids application regulations require measures to reduce pathogen content and vector attraction and provide ceiling concentrations for 10 heavy metals (As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, and Zn) based on the type of application.[4] Constituents of emerging concern, including per- and polyfluoroalkyl substances (PFAS), are often not regulated in biosolids. The U.S. Environmental Protection Agency (EPA) has released regional

screening levels (RSLs) for perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorononanoic acid (PFNA), and hexafluoropropylene oxide dimer acid (HFPO-DA) in soil and groundwater matrices,[5] and in 2021, the EPA committed to finalize a risk assessment for PFOA and PFOS in biosolids in 2024.[6] Furthermore, 21 state-level regulatory agencies have promulgated PFAS regulations, and more have released provisional risk-based thresholds for soil, groundwater, and drinking water.[7–14] In Florida, where this study took place, provisional direct exposure risk-based thresholds, called Soil Cleanup Target Levels (SCTL), have been developed for PFOA and PFOS in commercial and residential applications.[15] Currently, regulations are emerging for PFAS in biosolids such as state-level government ordinances in Queensland, Australia, and Maine, U.S.,[16,17] but globally, there is a lack of federal regulation for PFAS in biosolids.

Due to their extensive use in consumer products and ongoing human exposure, PFAS have been found consistently in domestic wastewater for decades,[18–25] and there has been concern regarding the fate of PFAS during traditional wastewater treatment. Based on previous studies, a fraction of the PFAS load will pass through the wastewater treatment plant and be released to the environment as effluent, while a significant portion (especially larger molecular weight PFAS) partition to the solid fraction (i.e., biosolids).[26–28] Data from multiple countries have identified significant concentrations of PFAS in biosolids, and as analytical capabilities have improved, the variety of PFAS identified by these analyses has increased as well.[29–31] While PFAS in biosolids have been well studied, we hypothesize that existing research may underestimate the magnitude of PFAS in this waste stream as a result of two factors: analytical limitations which do not capture a significant fraction of PFAA precursors and sample selection which may not capture transformations which result from standard biosolids treatment processes, predominantly comprised of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), which are end products of the degradation of larger and less stable PFAA precursor species.[32,33] PFAA precursor species are susceptible to thermal and chemical decomposition and have been found to undergo biodegradation in standard environmental conditions.[32] Though certain PFAA precursors have been identified in biosolids,[34–40] there are a limited number of compounds that have been quantified, and even further, their explicit transformation during conventional treatment of biosolids is relatively unknown. Quantifying these precursors before and after treatment is important to understanding the true environmental risk posed by PFAS in biosolids.

In this study, 92 PFAS, including 72 PFAA precursors, were quantified in biosolids collected from eight treatment facilities which represent four conventional treatment types: composting, heat treatment, lime treatment, and anaerobic digestion. Samples were collected before and after treatment from each facility. Additionally, a laboratory-controlled heat treatment experiment was conducted on one sample of raw biosolids to corroborate transformations which were suspected to have resulted from heat treatment. This study is needed to address the remaining gaps in knowledge regarding PFAS in biosolids and to provide additional context for the interpretation of previous work. The quantitation of such a large suite of PFAS, including PFAA precursors of emerging concern, provides a more accurate estimate of the total abundance of PFAS in biosolids, and the collection of

samples before and after conventional treatment processes highlights the transformations which are likely occurring and the potential underestimation of total PFAS when these transformations are not taken into consideration. When treated biosolids are recycled as an agricultural amendment, the presence of precursor PFAS and transformations should be taken into consideration as part of an assessment of potential environmental risk.

MATERIALS AND METHODS

Sample Collection.

Biosolids are commonly transported from the WWTP to a separate facility for treatment. Here, all operations that treat biosolids to meet pathogen requirements will be referred to as biosolids processing facilities or simply “facilities.” In 2019 (the most recent year for which these data were available), the Florida Department of Environmental Protection (FDEP) identified 39 biosolids processing facilities which cumulatively generated over 200,000metric tons (mt) of Class A/AA treated biosolids.[41] Class A/AA biosolids are subject to the most stringent treatment standards and are approved for most distribution and marketing scenarios for land application.[42] An estimate of the types of biosolids treatment processes implemented at Florida facilities based on FDEP data and interviews with WWTP operators is included in Figure 1. Each fraction represents the fraction of biosolids, by mass, generated from each type of facility for which process information was available (corresponding to 93% of total Class AA biosolids). Aerobic composting was the most common treatment types used to treat 41% of Class AA biosolids, followed by lime treatment (27%), heat treatment (16%), anaerobic digestion (5%), and chemical oxidation (4%). Sixteen biosolid samples across Florida were collected from eight facilities which reflected the four most common treatment types: one sample before treatment and one treated sample. Additionally, two samples of material added during the composting process (animal bedding and yard waste) were collected from two facilities. All sample collections took place between June 2021 and August 2021.

Samples were collected in 23 L high-density polyethylene (HDPE) buckets using stainless steel shovels washed with methanol prior to and between collection. Samples were transported to the laboratory, aliquoted into 2 L HDPE bottles and stored at −20 °C until analysis (see Section 1 in the Supporting Information (SI) for detailed sample collection protocols). Facility information is presented below in Table 1, and a more detailed table including treatment details, samples collected, and facility information can be found in SI Table S1.

Laboratory Treatment Simulations.

To investigate the effects of heat treatment on a single sample, raw biosolids were subjected to heating processes meant to replicate holding times and temperatures reached during heat treatment. Homogenized raw biosolids collected from Facility 3 were heated to 115 °C for 2 h mixing frequently (like heat treatment used at Facilities 3 and 4). Subsamples collected before heat treatment and after heat treatment underwent the same sample extraction and analysis (including moisture content) as other samples.

Standards and Reagents.

Reagents used in these analyses include methanol, ammonium hydroxide, and water (all Optima grade) purchased from Fisher Scientific. A total of 92 PFAS standards (a mixture of PFCA-24PAR and individual standards) were used to quantify PFAS in biosolid samples. These include 71 standards purchased from Wellington Laboratories, Inc. (Guelph, ON, Canada), 26 standards donated by Synquest Laboratories, Inc. (Alachua, FL, USA; standards are abbreviated as Syn # hereafter), and 12 standards donated by Oakwood Products Inc. (Estill, SC, USA; standards are abbreviated as Oak # hereafter). In addition, 27 isotopically labeled standards (a mixture of MPFAC-24ES and individual standards) which were used as internal standards (IS) were also purchased from Wellington Laboratories, Inc. Details about the targeted PFAS abbreviation, chemical formulas, and corresponding IS used for quantification are summarized in the SI Table S3.

Sample Extraction and LC-MS/MS Analysis.

The sample extraction method is a modified version of a previously reported solid matrix extraction method.[43] Prior to extraction, biosolids samples were homogenized by rotating for 20 min at 70 rpm and air-dried in a fume hood for a period of 3 days. A subsample of air-dried biosolids was taken to complete dryness at 110 ± 5 °C according to ASTM D2216 to determine moisture content for calculating PFAS concentrations on a per dry mass basis (ASTM, 2019). Air-dried biosolids samples were divided into 10.0 ± 0.1 g subsamples, added to a 50 mL polypropylene tube, and spiked with 50 uL isotopically labeled PFAS IS mixture (see SI Table 3). Then, 8.5 mL of 0.3% ammonium hydroxide in methanol was added to the sample. The mixture was vortexed for 1 min, sonicated for 30 min, and rotated in an end-overend fashion for 30 min. The sample was centrifuged at 4000 rpm for 10 min, and the supernatant was removed using a pipet. An additional 8.5 mL of 0.3% ammonium hydroxide in methanol was added to the remaining sample, and the vortex, sonication, rotation, centrifugation, and supernatant removal steps were repeated. The combined extracts (17 mL) were concentrated to 10 mL under a gentle stream of high purity nitrogen gas (Biotage TurboVap II) at 35 °C. Evaporated extracts were aliquoted into 200 μL polypropylene autosampler vials for analysis by liquid chromatography and tandem mass spectrometry (LC-MS/MS).

PFAS analysis was performed using a Thermo Scientific Vanquish ultra high-pressure liquid chromatography (UHPLC) coupled to a TSQ Quantis triple quadrupole mass spectrometer (Thermo Scientific, San Jose, CA, USA). Chromatographic separation was achieved using a Phenomenex (Torrence, CA, USA) reverse phase column (Gemini C18 column, 100 mm × 2 mm; 3 μm). The LC was fitted with a Vanquish PFAS replacement kit, including an Acclaim 120 C18 delay column (2.1 mm × 50 mm, 5 μm, 120 Å), and PFAS-free plumbing and hardware to minimize background. Water (solvent B) and methanol (solvent A), both containing 5 mmol L^{-1} ammonium acetate, were used as the mobile phases at a flow rate of 0.5 mL min^{-1}. The gradient elution was set as follows: 0–1 min 90% B, 1–2.5 min 90%–35% B, 2.5–17.5 min 35%–5% B, 17.5–17.51 min 5%–0% B, 17.51–22.5 min 0% B, 22.5–22.51 min 90% B, and then equilibrated back to initial conditions in 37 min. The autosampler and the column compartment temperature were set to 4 and 40 °C, respectively. Data were acquired in selected reaction monitoring (SRM) mode in negative polarity with

the following parameters: ion source: HESI; ion spray voltage:, −3000 V; sheath gas flow, 60 arb; auxiliary gas flow, 5 arb; ion transfer tube temperature, 325 °C; and vaporizer temperature, 350 °C.

Calibration information for each PFAS in the sample extracts was derived and tailored using the prepared calibration levels. Each calibration level also contained a mixture of 27 mass-labeled PFAS internal standards (see SI Table S3) at a concentration of approximately 1000 ng L^{-1}. The mass of all reagents and standards was recorded to report the most precise concentration. The LC/MS/MS operation conditions are shown in SI Table S4. For quantification, a calibration curve (14 levels, spanning from 10 to 100,000 ng L^{-1}) was developed for all 92 PFAS (listed in SI Table S3) through serial dilutions of primary standard solutions.

Quality Control (QC) and Extraction Efficiency.

Fields blanks of deionized water (>18.2 MΩ cm) were prepared at each facility during sample collection. Three 10 mL deionized water extraction blanks underwent the sample extraction process and analysis to identify potential PFAS contamination or interference during the extraction. A solvent blank was included in the UHPLC-MS/MS sequence for every four samples to check for carryover. To monitor retention time (RT) shifting throughout the run, calibration levels (1–14) were included in the sequence randomly, and a midrange calibration level was analyzed frequently throughout the sample batch. Details on the method validation process are provided in SI Section 3.

Accuracy, extraction recovery, and matrix effects were evaluated using PFAS standards spiked into deionized water as well as pooled biosolids samples. Two pooled biosolids samples were created, one for untreated biosolids (a composite made with equal masses of eight raw biosolids samples) and one for treated biosolids (another composite, equal masses of eight treated biosolids samples). Each sample type was aliquoted into nine replicate 10.0 ± 0.1 g samples. To separate natively occurring PFAS in the pooled samples, three replicates (1–3) underwent extraction as described in the Sample Extraction and LC-MS/MS Analysis section, including the addition of 50 uL IS prior to extraction. To another three replicates (4–6), a 50 μL IS and a 20 μL mixture of nonmass-labeled PFAS standards were added before extraction; IS and nonmass-labeled PFAS standards were added to the remaining three replicates (7–9) after the evaporation step of extraction. For extraction efficiency calculations, the average mass-adjusted peak areas (peak area per gram of biosolids) of the PFAS in samples 1–3 were subtracted from the peak areas of the nonmass-labeled PFAS standards compounds and were compared between the samples where IS was added before any extraction (samples 1–3), after solid-phase extraction (samples 4–6), and after evaporation (samples 7–9). Results are included in SI Table S14.

RESULTS AND DISCUSSION

PFAS in Untreated Biosolids.

Of the 92 PFAS included in the analytical method, 25 were detected and quantified in samples collected from treatment facilities. Concentrations for PFAS on a per-dry-mass

basis in every sample are included in SI Tables S6–S13. The total concentration of PFAS (Σ_{92}PFAS) in biosolids before treatment ranged from 182 to 1650 ng g^{-1} (median, 385 ng g^{-1}; mean, 495 ng g^{-1}), within the range of other studies, with average concentrations of 138 ± 50 ng g^{-1} Σ_9PFAS[44] and 539 ± 224 ng g^{-1} Σ_{13}PFAS.[45] Concentrations of PFOS, a legacy PFAS which has been phased out of most applications over the past decades[46] ranged from 4.0 to 40 ng g^{-1}, which is lower than the ranges of 10 to 370 and 308 to 618 ng g^{-1} reported by the Gallen et al.[44] and Venkatesan and Halden[45] studies. These studies and many others did not analyze for PFAA precursors which accounted for an average of 82 ± 11% of the Σ_{92}PFAS for each sample in this study suggesting that historical characterization of biosolids may have underestimated the true mass of PFAS present (further comparison between the measurements reported in this study and previous studies are included in SI Section 2).

Fluorotelomer phosphate diesthers (diPAPs) represent the most significant class of PFAS among these biosolids samples and were quantified in 100% of raw biosolids samples. The sum of three diPAPs included in the analytical method, 6:2, 6:2/8:2, and 8:2 diPAP ($\Sigma_3$diPAP), ranged from 73 to 1400 ng g^{-1} making up 54% ± 15% of the Σ_{92}PFAS, on average, in raw biosolids. At all but one facility (Facility 8), $\Sigma_3$diPAP was greater than the sum of all PFAAs (Σ_{20}PFAA). Similar results were reported recently in Australian and U.S. studies where $\Sigma_3$diPAP contributed a majority of the total mass of PFAS in biosolids sampled.[40,47] Historically, however, most studies that have characterized PFAS in biosolids have focused on quantifying PFAAs and do not include PFAA precursors, such as diPAPs, suggesting they likely underestimate the total mass of PFAS present in biosolids.

PFAS in Treated Biosolids.

The treatment employed at each biosolids processing facility can be summarized into four groups: composting, heat treatment, lime treatment, and anaerobic digestion. In short, Facilities 1 and 2 employed composting, Facilities 3 and 4 heat treatment, Facility 5 lime treatment, Facility 6 a combination of lime and heat treatment, Facility 7 anaerobic digestion followed by belt press drying, and Facility 8 anaerobic digestion followed by heat drying. A more detailed description of each facility is found in SI Table S1.

Individual PFAS concentrations for Facilities 7 and 8 are included in the SI Tables S12 and S13, respectively. The Σ_{92} PFAS measured in the raw biosolids and biosolids treated with lime (Facility 5) were 182 and 112 ng g^{-1}, respectively. This represents a 38.5% decrease; however, the proportional fraction of PFAS classes remained consistent between biosolids before and after lime treatment. Concentrations of each PFAS for Facility 5 is detailed in SI Tables S10.

Two facilities (Facility 7 and Facility 8) used anaerobic digestion in their treatment process; however, the integrated treatment and dewatering processes differed between facilities in ways which appear to impact PFAS profiles in the treated biosolids. Facility 7 used anaerobic treatment to remove pathogens followed by belt-press dewatering, and Σ_{92}PFAS was 1650 ng g^{-1} in the raw biosolids and 584 ng g^{-1} (65% decrease) after treatment. At Facility 8, which followed anaerobic treatment with heat drying, the Σ_{92}PFAS values were 192 ng g^{-1} in the raw biosolids and 388 ng g^{-1} (102% increase) after treatment. A

possible explanation for this observation is that belt-press dewatering physically removes mobile PFAS with the water fraction, while heat drying removes water via evaporation, concentrating PFAS with the solid fraction and also potentially increasing the apparent concentration of PFAS as a result of PFAA precursor transformation. This suspected mode of PFAS transformation was explored further in a laboratory heat treatment simulation, described later in this section.

Biosolids underwent aerobic composting at Facilities 1 and 2. During the composting process, biosolids are mixed with other sources of organic matter such as animal bedding and yard waste. Individual PFAS concentrations for Facilities 1 and 2 are included in the SI Tables S6 and S7, respectively. In both cases, Σ_{92}PFAS concentrations were lower in composted biosolids compared to the corresponding raw biosolids. PFAS analysis of the composting material found all compounds below detection limits. Both facilities added composting material at approximately 2:1 ratio (composting material:biosolids, v:v), indicating a theoretical dilution of 67% (assuming similar moisture contents). Σ_{92}PFAS in composted biosolids decreased by 81% after treatment at Facility 1 and by 22% after treatment at Facility 2. While the overall reduction in Σ_{92}PFAS can be attributed to the dilution of biosolids with low-PFAS composting material, a dramatic shift in the ratio of PFAA precursors to terminal species was observed compared to the other treatment options explored in this study. This change is illustrated in Figure 2, which shows relative percent contributions from short and long chain PFCAs, short and long chain PFSAs, and PFAA precursors. Short chain PFCAs perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA) both increased after composting despite being diluted with low-PFAS composting material (Figure 2). PFPeA increased from 3.7 to 17 ng g^{-1} at Facility 1 and from 2.7 to 26 ng g^{-1} at Facility 2. PFHxA concentrations increased from 6.9 to 15 ng g^{-1} at Facility 1 and from 3.9 to 13 ng g^{-1} at Facility 2. These increases are believed to be attributed to the breakdown of PFAA precursors through microbial biodegradation. The PFAA precursor class diPAPs, which are a significant fraction of the PFAS measured in these samples, have been found to degrade into PFCA species through microbial breakdown of the phosphate ester to produce fluorotelomer alcohol (FTOH) species[48,49] and PFCAs.[49,50]

Heat treatment for pathogen removal was utilized at two of the facilities (Facilities 3 and 4), and heat drying was used in the dewatering process at two additional facilities (Facilities 6 and 8). Individual PFAS concentrations for Facilities 3, 4, 6, and 8 are included in SI Tables S8, S9, S11, and S13, respectively. For the facilities that utilized heat treatment or drying, Σ_{92}PFAS were sometimes slightly different, both higher and lower, after treatment or significantly higher. Facilities 3, 4, and 6 had slight increases or decreases from 519 to 501 ng g^{-1}, 422 to 451 ng g^{-1}, and 362 to 385 ng g^{-1}, respectively, while Facility 8 increased from 192 to 388 ng g^{-1}. There was no definitive trend in changes in PFAA concentrations among biosolids that underwent heat treatment. Facility 6 had a slight increase in average concentration for PFOS, from 15 to 19 ng g^{-1}, and a slight decrease in average concentration for PFOA, from 3.8 to 3.2 ng g^{-1}, while biosolids at Facilities 3, 4, and 8 decreased in average concentration for both PFOS and PFOA from 4.0 to 1.4 ng g^{-1} and 21 to 7.7 ng g^{-1} at Facility 3, 33 to 3.3 ng g^{-1} and 4.3 to 2.3 ng g^{-1} at Facility 4, and 30 to 14 ng g^{-1} and 6.3 to 4.9 ng g^{-1} at Facility 8. Most notably, concentrations of 6:2 diPAP increased in all heat treatment/drying samples after treatment, suggesting that heat treatment might

increase the concentration of diPAP species due to the breakdown of larger precursors not included in this analytical method. This finding is illustrated in Figure 3, where 6:2 diPAP concentrations in biosolids before and after treatment are compared for facilities which utilize heat treatment in any stage of their process, and those which do not utilize any form of heat treatment. The observed increase in 6:2 diPAP was unanticipated and is difficult to explain given the lack of available literature on polyfluoroalkyl phosphate esters (PAP) transformation and formation pathways. A possible explanation is the breakdown of triPAPs or larger homologues not included in the set of quantified PFAS. To further investigate this topic and to confirm that the observed increase in diPAPs was not due to artifacts during treatment, extraction, and analysis, a laboratory heat treatment experiment was conducted.

Raw biosolids collected from Facility 3 underwent controlled heat treatment to determine if the changes observed in the PFAS profile before and after treatment could be recreated in the laboratory as a result of the application of heat only. Concentrations of PFAAs, such as PFOA and PFOS, remained similar before and after treatment, changing from 9.4 to 10.6 ng g^{-1} and 4.9 to 4.3 ng g^{-1}, respectively. However, certain PFAA precursors increased or decreased, such as 6:2 diPAP, increasing from 123 to 224 ng g^{-1} or FPePA decreasing from 92 to 45 ng g^{-1}. Interestingly, when normalizing for the mass of florurine present, the combined concentration of measurable flourine increased by 30 ng $g^{-}1$ after treatment. The results of the experiment for 6:2 diPAP are included in Figure 3 alongside the samples collected before and after fullscale facility treatment. Concentrations of 6:2 diPAP increased significantly after the 2 h heat treatment at 115 °C, from 123 ± 7 to 224 ± 25 ng g^{-1}, remarkably similar to before and after facility treatment.

Reuse Implications.

Shorter chain species are less commonly found in raw biosolids due to their solubility in water; therefore, biosolids are typically dominated by long chain species that favor partitioning to the solid phase.[51] The presence of short chain PFCAs after treatment is likely due to the breakdown of 6:2 diPAP. The degradation of longer chain PFAS into shorter chain PFAAs has a significant impact on partitioning from solids into the aqueous phase. Higgins and Luthy[52] found that longer chain length PFAS are more likely to partition to soil, and each chain length of a CF_2 group has a 0.5 to 0.6 log increase of the partitioning coefficient. This provides a pathway for PFAS to leach out of land-applied biosolids and into the groundwater overtime as more PFAA precursors biodegrade. For example, transformation of 6:2 diPAP to PFHxA might increase the tendency for PFAS to partition from soil to water (i.e., the tendency to leach from biosolids into the surrounding environment) by a factor of 1000. The breakdown of PFAA precursors into terminal species has been demonstrated to take place during conventional treatment of biosolids and in soils that have had biosolids land applied to them.[32,40] If PFAS, and particularly short chain PFAAs, are to be regulated in biosolids, analytical protocols as well as when and where samples are taken will have an impact on the outcome of any monitoring program. For example, in this study, it was reported that aerobically composted biosolids increased in short chain PFCAs (i.e., PFHxA and PFPeA); if guidelines were in place to monitor the concentrations of these compounds, it would be theoretically possible to be below risk-based thresholds before treatment but exceed the same thresholds after treatment. Furthermore,

compounds such as large molecular weight PAP species which are not captured in even the most thorough targeted PFAS analysis may degrade into measurable precursor PFAS, and eventually PFAAs, as was observed by this study in heat treated biosolids. This implies that the mass release of short chain PFAAs in land-applied biosolids will be larger than what is initially measured through standard analytical characterization.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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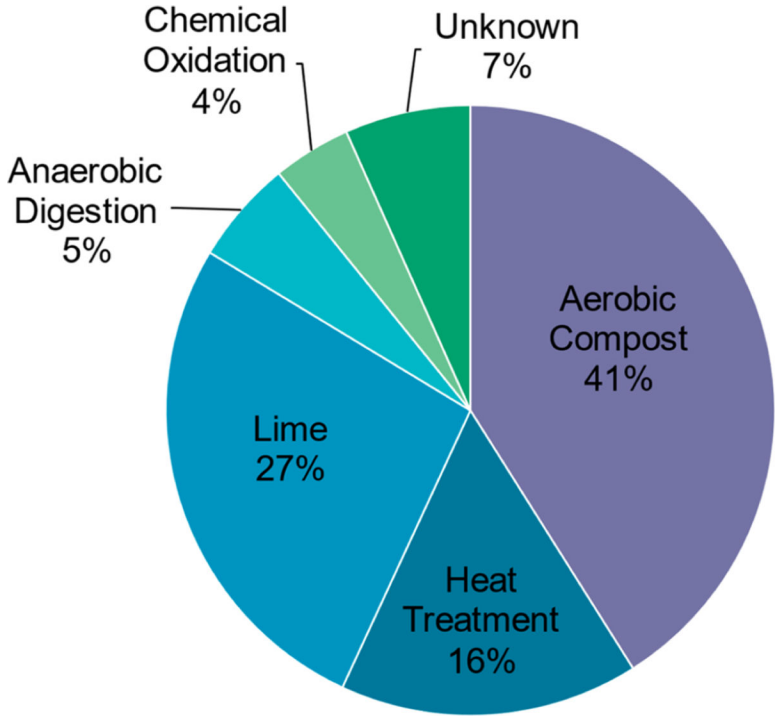

Figure 1.

Class A biosolids treatment types implemented across 39 facilities in Florida. Data collected from Florida Department of Environmental Protection and phone interviews with wastewater treatment plant operators from 2019 through 2021. Percentages reflect mass generated with each treatment type as a fraction of total Class A biosolids generated in Florida.

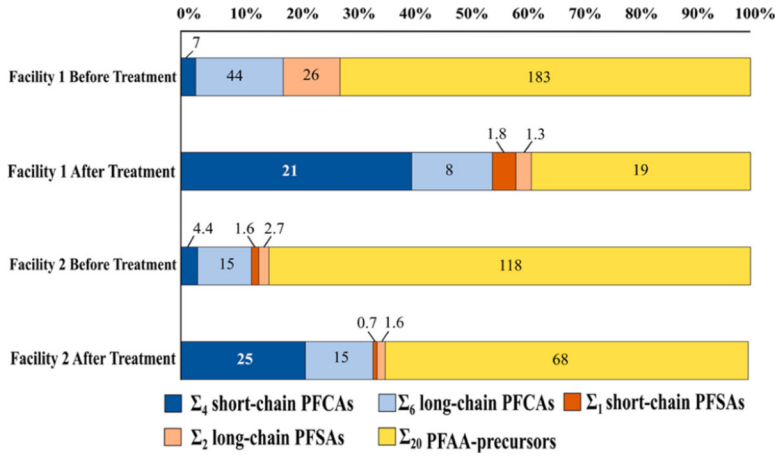

Figure 2.

Relative% contributions of each PFAS class to the average total PFAS concentration in biosolids undergoing aerobic composting normalized to the concentration of fluorine. The numbers in the bars represent the total mass of fluorine ng g^{-1} that each PFAS class contributed. PFAS classes are composed of short chain PFCAs (C4–C7), long chain PFCAs (C8–C12, C14), short chain PFSAs (C4), long chain PFSAs (C6, C8), and PFAA precursors. The total concentration of each class was divided by the Σ_{92}PFAS. Total class concentrations (e.g., $\Sigma_4$short chain PFCA, Σ_{20}PFAA precursor) are also included in the figure.

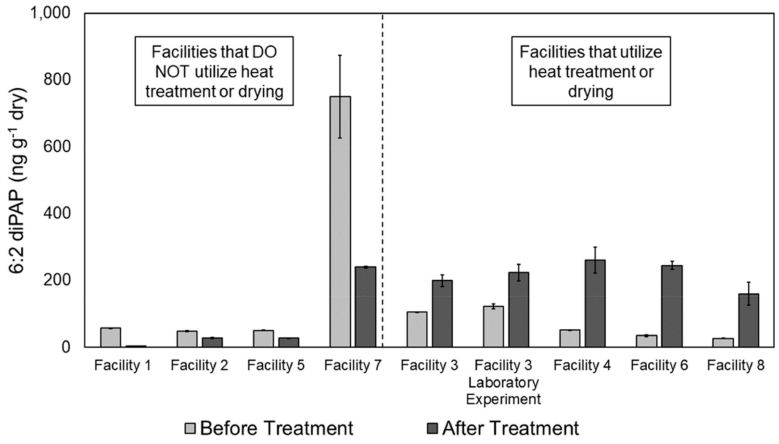

Figure 3.

6:2 diPAP concentrations measured in biosolids before and after treatment. Facilities 3, 3 (Laboratory experiment), 4, 6, and 8 employed heat treatment for pathogen reduction and/or drying, while Facilities 1, 2, 5, and 7 did not. Error bars represent one standard deviation in 6:2 concentrations between samples.

Table 1.

Information on Treatment Process Utilized by Facilities Sampled

Sample name	Treatment description	Treatment Type	Dry tonnes produced each year
Facility 1	1:2 Ratio of biosolids to yard waste/animal bedding. Windrows are left outside to weather for 45 days where internal temperatures can reach 60 °C. Piles are inoculated with thermophilic actinomycetes during initial mixing. Piles are screened to 3/4 in. for final processing.	Aerobic compost	2700
Facility 2	1:2 Ratio of biosolids to yard waste. Windrows are left outside to weather for 45 days where internal temperatures can reach 60 °C. Windrows are covered by an awning to shield the mixtures from rain. Piles are screened to 3/4 in. when aging is completed.	Aerobic compost	4000
Facility 3	Biosolids are solar dried for 14 days going from ~12% solids to ~60%. Then, biosolids go into a natural gas thermal chamber for pasteurization at 90–120 °C for 2 h and exit at a ~ 90% solids content.	Heat treatment	2700
Facility 4	Wet cake is centrifuged before entering a natural gas fueled dryer drum. Hot air is passed over the biosolids (90–120 °C) until they reach ~90% solids content and exit the drum via a cyclone separator.	Heat treatment	20,000
Facility 5	Dewatered sludge is mechanically mixed with CaO (quicklime) until a pH of 12 is reached. Sulfamic acid is added to the mix to decrease pH and increase the temperature to 60 °C for a 40 min retention time.	Lime treatment	8200
Facility 6	Lime is added as a stabilizing agent (pH < 12), while biosolids are dried by a combination of solar and a natural gas burner to reach a 90% solids content.	Lime treatment	4500
Facility 7	Belt filter pressed biosolids are fed into a two stage digestor: mesophilic (35 °C /thermophilic (50 °C) for a retention time of ~20 days. Post digestion biosolids are then dried by a belt filter press to reach 40% solids content.	Anaerobic digestion	6300
Facility 8	Belt filter pressed biosolids are fed into a two stage digestor: mesophilic (35 °C)/thermophilic (50 °C) for a retention time of ~20 days. Post digestion biosolids are then dried by natural gas burner (90–120 °C) until 90% solids content.	Anaerobic digestion	11,000