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Drying reduces the total PFAS concentration in biosolids and alters the PFAS profile†

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While per- and polyfluoroalkyl substances (PFAS) are not actually generated at water resource recovery facilities (WRRFs), utilities are being forced to consider PFAS in biosolids management plans due to mounting political pressure and pending regulations. Emerging thermal technologies including pyrolysis, gasification, and super critical water oxidation have garnered recent attention for PFAS destruction. Drying, however, is a conventional technology that might also be a tool for utilities to manage PFAS in biosolids, but research on the impacts of drying on PFAS in biosolids is scarce. The objective of this research was to determine how drying affected the fate of PFAS in biosolids. Full-scale sampling was paired with lab-scale oven drying experiments to understand the impact of drying on measurable PFAS in biosolids. Overall, drying substantially reduced the total PFAS concentration in biosolids. PFAS removal during a full-scale facility's drying process matched the removal achieved when solids were taken from that facility and dried in a lab-scale oven instead, with average PFAS removal being approximately 80%. Precursors to perfluoroalkyl acids (PFAAs), primarily 5 : 3 fluorotelomer carboxylic acid (FTCA) and 6 : 2 FTCA, as well as perfluorooctane sulfonic acid (PFOS) were substantially reduced between pre-drying and post-drying triplicate samples. Additional lab-scale oven drying experiments corroborated that measurable PFAS were removed from biosolids collected from three different utilities. Drying experiments at 30 °C and 105 °C revealed that the PFAS profiles were similar, but PFAS concentrations were lower in the 105 °C samples compared to 30 °C samples. While more research is necessary to determine and validate the removal mechanism, drying could be a viable technology to reduce measurable PFAS levels in biosolids to concentrations below guidelines for land application.

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Water impact

PFAS have substantially altered the biosolids management industry. Emerging technologies offer a means to reduce PFAS to non-detect levels in solid products such as biochar. Drying, however, is a widely employed technology that could sufficiently reduce PFAS levels to meet guidelines for land application.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have altered the biosolids management landscape. Though water resource recovery facilities (WRRFs) are not actually a source of PFAS, they receive and convey PFAS because of the widespread use of PFAS in society and consumer products.¹ PFAS are abundant in a range of products including cosmetics, water-proof clothing, carpets, and fast-food wrappers.^{2–5} PFAS are widely

detected in people, including breastmilk, blood, and urine samples, and therefore municipal sewage also contains PFAS.^{6–8} Moreover, consumer products laden with PFAS are sent to landfills where products degrade over time, and PFAS are released into leachate that is often sent to the head of a WRRF.^{3,9,10} The concentration in biosolids depends on any nearby industrial sources of PFAS discharged to the WRRF as well as the unit operations used at the WRRF.^{2,11–13} Some European countries, Australia, Canada, and states in the United States have set limits for PFAS concentrations in soil, and some states in the United States have set PFAS concentration limits for biosolids that can be land applied to minimize human health impacts.^{7,14–20}

Biosolids management requires an understanding of how biosolids handling technologies impact the fate of PFAS. Emerging technologies, in particular thermal processes, have

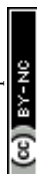
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garnered attention for their potential to reduce PFAS concentrations in solids.^{21,22} Indeed, pyrolysis has been shown to remove and transform PFAS at the lab and pilot scale.^{23–29} Incineration, a more established technology, also removes the majority of PFAS from the solid phase.³⁰ Pyrolysis and gasification are still emerging technologies in the biosolids marketplace, and both of these technologies require drying first.^{23,31} Drying, however, is already a widely used and established solids handling process. Aside from being useful when paired with emerging thermal technologies, drying offers the benefit of substantial mass reduction *via* removal of water. As numerous utilities already dry and land apply biosolids, it is important to understand the impacts of drying on the fate of PFAS in biosolids.

Limited studies have been conducted thus far regarding the potential impacts of drying on PFAS fate, and results have been mixed.^{32–34} Indeed, heat treatment of wastewater solids at 480–650 °C led to an increase in total perfluoroalkyl acids (PFAAs) by 53%, mainly due to perfluorohexanoic acid (PFHxA) increases.¹² In another study, heat drying at 90–120 °C was found to increase PFAS concentrations, in particular the concentration of fluorotelomer phosphate diesters (diPAPs).³² A lab study on drying at 115 °C at 2 hours found that 6:2 diPAP approximately doubled; perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were similar before and after heat treatment; and perfluoropentanoic acid (PFPeA) decreased by approximately 50%.³² One study on a full-scale dryer with a regenerative thermal oxidizer (RTO) found that 50–90% of PFAS were transferred from the biosolids to the gas phase, and 18 PFAS were detected in the gas phase headed for treatment in the RTO.³⁴ Despite widespread use of drying in the industry, limited studies are available that document the impacts of drying on the fate of PFAS in biosolids.

The objective of this research was to determine the impact of drying on PFAS in biosolids. As some government regulatory agencies move towards implementing concentration-based limits for PFAS in biosolids and soils, it is particularly important to know how drying processes impact measurable PFAS concentrations. This research combined sampling at a full-scale dryer with lab-scale oven drying experiments on the same full-scale pre-drying solids samples. Additionally, pre-drying solids samples provided by three different WRRFs were used for lab-scale oven drying experiments. Finally, lab-scale oven drying experiments were conducted on high moisture content (MC) samples at 30 °C and 105 °C.

2. Methods and materials

2.1. Comparison of full-scale drying to lab-scale oven drying on PFAS concentrations in biosolids

A WRRF agreed to provide pre-drying and post-drying samples from their full-scale dryer under conditions of anonymity. The average influent flow rate to this WRRF is over 50 million gallons per day (MGD). Liquid treatment steps include grit removal, primary clarification, conventional acti-

vated sludge, and chlorination. Solids undergo thickening and dewatering prior to drying. The total solids (TS) content for the pre-drying solids fed to the dryer was approximately 16% TS, and the TS content for the post-drying solids taken from the effluent of the dryer was approximately 90% TS. Triplicate pre-drying samples and triplicate post-drying samples were collected on-site from the full-scale dryer. In addition to full-scale sampling, pre-drying solids samples were dried in triplicate in a lab-scale oven at 105 °C for 5 hours to compare lab-scale oven drying to full-scale drying. All samples were sent to Eurofins Environment Testing USA (Eurofins) for PFAS extraction and analysis as described in section 2.4.

2.2. Lab-scale oven drying of solids from three different WRRFs

Solids from three different WRRFs were dried in a lab-scale oven to assess if PFAS removal was observed when drying different solids. The three WRRFs tested for this experiment were from different states than the WRRF described in section 2.1. Each WRRF requested to be kept anonymous and provided the following general information to provide context on their biosolids without revealing their identity. WRRF A receives less than 25 MGD of wastewater influent. Liquid processes include primary treatment and secondary treatment that has full nitrification and one train with anoxic zones for incidental denitrification. Primary sludge and thickened waste activated sludge (WAS) are sent to a mesophilic anaerobic digester. A portion of digested solids are sent to a screw press, and effluent samples from the screw press were collected for this work. The TS content was 18.3%. WRRF B is over 50 MGD and utilizes a two-stage anaerobic digestion process. The first stage is fed a mixture of primary sludge and WAS and has a solids retention time (SRT) of 2 days or less. The second stage has an SRT of 15–20 days. The digestate is processed through a centrifuge. Effluent samples from the centrifuge were collected for this work. The TS content was 20.8%. WRRF C is less than 10 MGD. The WRRF employs primary clarification, and solids from the primary clarifiers are pumped directly to anaerobic digesters. The WRRF employs activated sludge, and the WAS is thickened and then pumped directly to the anaerobic digesters as well. After anaerobic digestion, centrifuges are used for dewatering. Effluent samples from the centrifuges were collected for this work. The TS content was 24.2% TS.

The collected pre-drying solids samples were shipped to a laboratory at California State University-Bakersfield (CSU-B) for lab-scale oven drying. Samples were stored at 4 °C until used for the experiment. Storage was less than 7 days. “Pre-drying” refers to solids that were received from the WRRFs before undergoing any drying. “Post-drying” refers to solids after they were dried in the lab-scale oven. Approximately 20 g of pre-drying solids were placed in a drying tin. The samples were dried overnight (24 hours) at 105 °C in a conventional lab-scale oven with the fan mode on. After drying,



samples were transferred to containers that were provided by Eurofins for PFAS analysis. Dried samples were stored in the dark at room temperature until shipped to Eurofins. Pre-drying and post-drying samples were shipped to Eurofins for targeted analysis of PFAS as described in section 2.4.

2.3. Lab-scale oven drying experiments on high moisture content samples at 30 °C and 105 °C

High moisture content samples (99.8% MC, 0.2% TS) were dried to assess PFAS profiles in biosolids dried at two different temperatures. Triplicate biosolids drying experiments were conducted at 105 °C at the CSU-B laboratory and at the lower temperature of 30 °C. The 105 °C test was conducted overnight and the 30 °C test lasted 5 days. The 30 °C test was conducted in a lab-scale oven with the temperature lowered to 30 °C. These experiments were also conducted to assess the possibility of PFAS sticking to the drying tins. After the first set of experiments conducted in section 2.1 with results shown in section 3.1, it seemed feasible that PFAS previously associated with water could stick to the drying tin (and not the solids) as the water evaporated. This possibility was tested by employing a 'wipe kit' provided by Eurofins. This kit includes a methanol-soaked cloth that is used to wipe the tin after biosolids are completely removed for sampling following drying.

2.4. PFAS analysis

Sixty targeted PFAS analytes were measured. They are all listed by chemical class in the ESI document (ESI†), Table S1. The associated Isotope Dilution Analytes (IDAs), also known as isotopically labeled analogs, used for each PFAS analyte are also listed in ESI† Table S1. PFAS analyses were performed on a SCIEX 5500+ triple quad LC/MS/MS system operated in multiple reaction monitoring (MRM) mode. Biosolid samples were manually mixed in their collection containers and then subsampled (nominally 1 g for both pre-drying and post-drying samples). Each subsample was fortified with IDAs of the native target analytes, then extracted *via* sonication with basic methanol for one hour. The resulting extracts were re-constituted in water and then cleaned up *via* solid phase extraction (SPE) using a WAX SPE cartridge (Strata X-AW or equivalent), which retains the desired PFAS. The IDAs and target analytes were then eluted from the SPE cartridge with basic methanol and adjusted to a final extract volume of 10 ml in 80:20 methanol/water, after additional fortification with 13C2-PFOA as the internal standard (ISTD). Identical sample extraction procedures were applied to pre-drying and post-drying biosolid samples.

Accuracy of measurements for the reported list of 60 target analytes is ensured *via* initial and ongoing assessment of accuracy and precision *via* laboratory control sample aliquots, control sample duplicates, laboratory method blanks, method detection limit (MDL) studies, MDL verification aliquots, and performance testing studies. Each of these is performed as described in the associated laboratory Standard Operating Procedures (SOPs), and the results are monitored and validated *via*

3rd party laboratory accreditation bodies for the corresponding regulatory programs including the National Environmental Laboratory Accreditation Program and the United States Department of Defense Environmental Laboratory Accreditation Program.

Within each sample, additional measures of method performance are monitored, including IDA recovery, ISTD response, analyte retention times, analyte ion ratios, and analyte signal-to-noise ratios. Each of these sample-specific quality controls or identification elements must meet the criteria specified in the corresponding laboratory SOPs. PFAS concentrations are reported on a dry weight basis whereby dry weight is determined when moisture has been removed at 105 °C and the sample has been cooled to room temperature in a desiccator.

2.5. Analysis & Statistics

To conduct conservative statistical analyses on the fate of PFAS during drying, the reporting limits (RLs) provided in the Eurofins PFAS analysis report were used to fill in the gaps of the non-detects in the triplicate data before percent removal or significance of species removal was determined, *i.e.*, "zero" values were not used for statistics. Note that these RL data are not reflected in the figures; only species concentrations higher than the reporting limits are shown.

Statistical analysis was conducted using GraphPad Prism v10.3.1 (GraphPad Software, La Jolla, CA). The tests conducted for each experiment are listed in the ESI† Tables S5, S8, & S16. *P*-values < 0.05 were considered statistically significant. Concentrations of PFAS were normalized and reported in micromoles (μmol) of F per kg dry solids, where the F content stemmed from the moles of F present in the species of PFAS that were measured through targeted analysis. These concentrations were used to calculate percent removals.

3. Results

3.1. Impacts of full-scale drying and lab-scale oven drying on PFAS in biosolids

3.1.1. Full-scale dryer results. The full-scale dryer reduced the mass of detectable PFAS and changed the measurable PFAS profiles between the pre-drying and post-drying samples (Fig. 1 and ESI† Tables S2 & S3). Ten PFAS were detected across all three pre-drying samples for the full-scale dryer. The most abundant species in the pre-drying samples was 5:3 fluorotelomer carboxylic acid (FTCA), and 6:2 FTCA was the third most abundant species. These FTCA compounds are common precursors to short-chain PFAAs; 'precursors' are chemical species known to degrade and transform into other species of PFAS.^{35–37} PFOS was the second most abundant PFAS overall in the pre-drying samples, and the most abundant PFAA. Of the ten PFAS detected across all three pre-drying samples, seven were detected above RL in all three post-drying samples. 7:3 FTCA was detected in two of the three post-drying samples, perfluorodecanoic acid (PFDA) was detected in one of the three post-drying samples, and 6:2 FTCA was not detected in any of



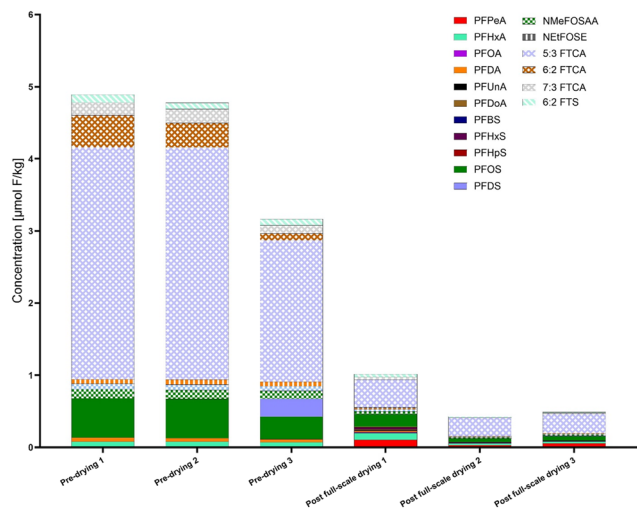


Fig. 1 Full-scale drying reduces measurable PFAS concentrations in biosolids. Samples were collected in triplicate ($n = 3$). Reprinted with permission. © The Water Research Foundation.³⁹

the post-drying samples (Fig. 1 and ESI† Tables S2 & S3). Two PFAAs, specifically perfluoropentanoic acid (PFPeA) and perfluorohexane sulfonic acid (PFHxS), were detected across all three post-drying samples, but not in any of the pre-drying samples. These two PFAAs were present at concentrations in the post-drying samples that were below the RLs for the pre-drying samples (ESI† Tables S3 & S4). Therefore, it is not possible to know if these two PFAAs appeared during the drying process due to a reaction or if they were already present in the pre-drying samples but could not be detected.^{12,38} In general though, the PFAS fraction attributed to precursor compounds, *i.e.*, FTCA, fluorotelomer sulfonic acids (FTS), perfluorooctane sulfonamido acetic acids (FOSAA), and perfluorooctane sulfonamido ethanols (FOSE), decreased significantly during drying (ESI† Fig. S1, Tables S7 & S8).^{35–37}

3.1.2. Lab-scale oven drying results. The solids samples collected before entering the full-scale dryer were also dried in a lab-scale oven at 105 °C to compare the impacts of lab-scale oven drying to full-scale drying on the PFAS profile in biosolids. The lab-scale oven data reflected similar trends as the full-scale dryer data. Total PFAS were reduced and the profile changed (Fig. 2). Of the ten PFAS detected across all three pre-drying samples, four were detected above RL in all three post-drying samples (ESI† Tables S3 & S4). One species, PFHxS, a terminal PFAA, appeared in all three lab-scale oven post-drying samples despite not being detected in the pre-drying samples. Similar to the full-scale dryer post-drying samples, PFOS was detected in all three lab-scale oven post-drying samples and was the second most abundant species detected after 5:3 FTCA. Together, 5:3 FTCA and PFOS accounted for, on average, more than half of the molar F as PFAS concentration in the lab-scale oven post-drying samples and full-scale dryer post-drying samples. There was no significant difference between the concentrations of these two species from the two drying methods (ESI† Table S5). Lab-scale

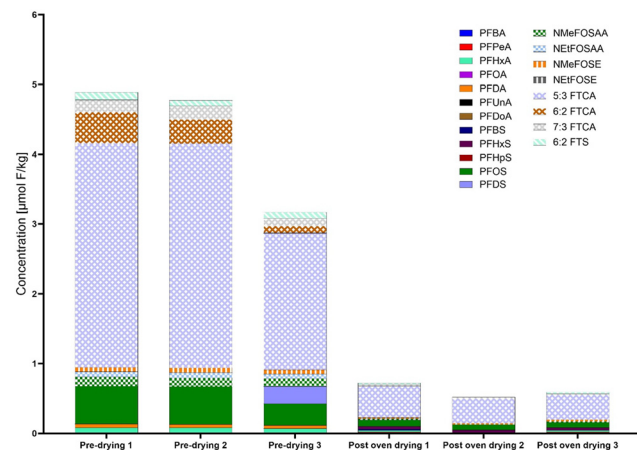


Fig. 2 Lab-scale oven drying at 105 °C reduces measurable PFAS concentrations in biosolids. Triplicate lab-scale oven drying experiments were conducted ($n = 3$). Reprinted with permission. © The Water Research Foundation.³⁹

oven drying also decreased the ratio of precursor species to total PFAS in biosolids (ESI† Fig. S1, Tables S7 & S8), which is consistent with the full-scale dryer sample data.

Overall, the full-scale dryer and lab-scale oven drying experiments revealed substantial reductions in measurable PFAS in the biosolids (Fig. 3). The average PFAS removal in the full-scale dryer was 84.9% and the average PFAS removal in the lab-scale oven was 81.9% (ESI† Table S9). Average removal of total PFAS was not significantly different between the full-scale dryer and the lab-scale oven (ESI† Table S8). These results indicate that drying biosolids could be a viable option to reduce the measurable PFAS concentration in biosolids, and, for these particular systems, the lab-scale oven setup can be used to help estimate removal percentage for the majority of detectable PFAS in biosolids in a full-scale system.

On a PFAS mass concentration basis, pre-drying total PFAS concentrations ranged from approximately 100–150 $\mu\text{g kg}^{-1}$ (ESI† Table S3). The full-scale dryer post-drying samples had a wider range of concentrations than the lab-scale oven post-drying samples. The full-scale dryer post-drying samples total PFAS concentration ranged from 13–31 $\mu\text{g kg}^{-1}$, and the lab-scale oven post-drying samples ranged from 16–23 $\mu\text{g kg}^{-1}$. Some states have employed interim guidelines for land application of biosolids that set 20 $\mu\text{g kg}^{-1}$ of PFOS and PFOA as a threshold wherein any concentrations below this level can be land applied.⁴⁰ The pre-drying biosolids samples had PFOS and PFOA concentrations already below this threshold.

3.2. Impact of lab-scale oven drying on PFAS in biosolids from three different utilities

Biosolids samples were collected anonymously from three WRRFs that were unique from the WRRF that provided samples for the results presented in section 3.1 above. The biosolids samples were collected from different WRRFs with varying



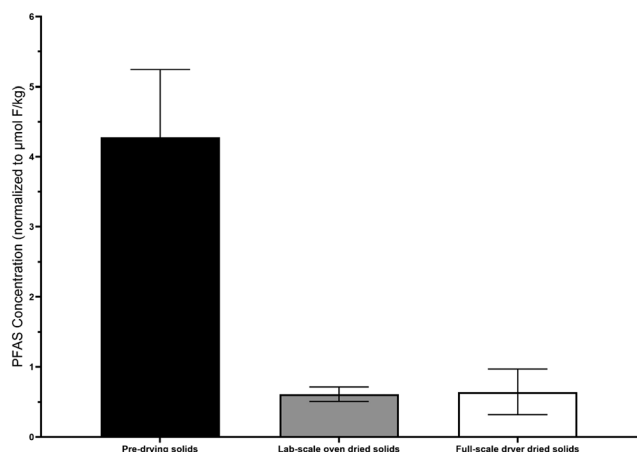


Fig. 3 Average total PFAS concentration (normalized to $\mu\text{mol F kg}^{-1}$) across pre-drying solids, lab-scale oven post-drying solids, and full-scale dryer post-drying solids. Samples taken in triplicate ($n = 3$) and error bars represent standard deviation. Reprinted with permission. © The Water Research Foundation.³⁹

influent flow rates and unit operations as described in the methods section. Regardless of biosolids sample, the total sum of measurable PFAS decreased after drying (Fig. 4, ESI† Tables S10 & S11). For all three pre-drying samples, 5:3 FTCA was the first or second most abundant PFAS. PFOS was one of the three most abundant PFAS in each pre-drying sample as well. These two PFAS were still detected in post-drying samples, but their concentrations decreased. Average PFAS removal across the three samples was 76% (ESI† Table S13). These results indicate that drying can reduce measurable PFAS in biosolids, but drying does not completely remove PFAS from biosolids.

3.3. Impact of drying temperature on PFAS profiles in samples with high moisture content

High moisture content samples (99.8%) were dried at 30 °C and 105 °C. Overall, the PFAS fingerprint and concentration

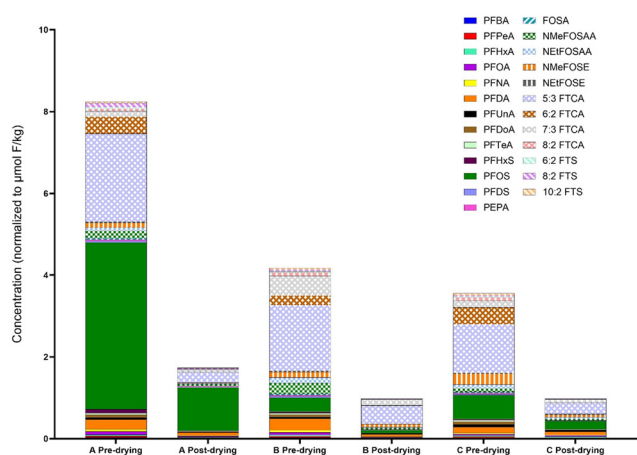


Fig. 4 Lab-scale oven drying reduced measurable PFAS in samples from three different WRRFs. Reprinted with permission. © The Water Research Foundation.³⁹

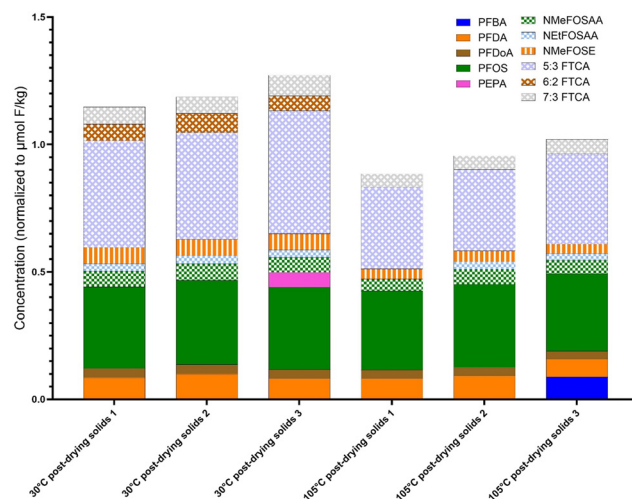


Fig. 5 Drying at 105 °C decreased total PFAS concentration by 16% compared to drying at 30 °C. Water content of pre-drying solids was 99.8%. 30 °C and 105 °C drying of samples were conducted in triplicate ($n = 3$). Reprinted with permission. © The Water Research Foundation.³⁹

profiles were similar for samples dried at 30 °C and samples dried at 105 °C (Fig. 5), but temperature did have some effect on PFAS profiles in the dried biosolids. Four of the eight PFAS detected in both post-drying samples across all triplicates (5:3 FTCA, 7:3 FTCA, *N*-methyl perfluorooctane sulfonamido ethanol (NMeFOSE), and perfluorododecanoic acid (PFDoA)) were significantly lower in biosolids dried at 105 °C compared to biosolids dried at 30 °C (ESI† Tables S14–S16). Similar to the other data sets, 5:3 FTCA and PFOS were the first and second most abundant PFAS in every sample (Fig. 5 and ESI† Tables S14 & S15). Overall, the total PFAS concentration was 16% lower in the 105 °C post-drying sample than the 30 °C post-drying sample, with a statistically significant p -value of 0.0058. A wipe kit was provided by Eurofins to wipe the drying tins and test for residual PFAS. The reporting limit was 1 ng PFAS per wipe. No PFAS detections were observed for any of the six wipes tested (three tins at each temperature). Either there were no residual PFAS in the tins, or the wipes were not able to absorb residual PFAS that may have been left in the tins. This test was conducted to observe any major experimental artifacts of PFAS residual in tins that could be absorbed with a methanol wipe.

3.4. Impact of moisture content on PFAS removal

Across the full-scale dryer and lab-scale oven data sets, moisture content was weakly correlated to total PFAS removal (Fig. 6, ESI† Table S18). The potential role of water in PFAS removal is discussed in more detail in the discussion section below. While certainly more data from a range of biosolids types and moisture contents are needed to validate this correlation, these data indicate that further study on the role of moisture content during drying of biosolids is warranted.



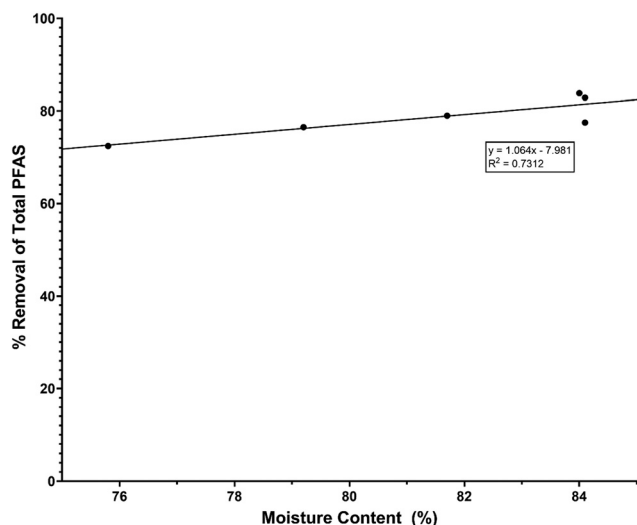


Fig. 6 Moisture content correlated to PFAS removal across sample sets. Reprinted with permission. © The Water Research Foundation.³⁹

4. Discussion

The effect of drying on the PFAS profile of biosolids has been largely overlooked in literature.³⁴ Due to the recognized thermal stability of PFAS and their high boiling points as pure substances, it has been posited that temperatures around 100 °C would be insufficient to remove them from biosolids.³³ The following three sections discuss possibilities to explain the observed PFAS removal with recognition that more research is required to determine the removal mechanism.

4.1. Potential role of water and removal with aerosols

It has been established that PFAS readily partition to the air-water interface (AWI), and, in fact, a reduction in the aqueous concentration of PFAS increases this tendency of PFAS to partition to the AWI.^{41–43} In the case of water-bearing biosolids, an accurate assessment of the AWI partitioning tendency of PFAS is complicated by the potential presence of air bubbles formed during the drying process as the temperature approaches 100 °C, at which point the water begins to boil.⁴⁴ As the boiling bubbles burst upon reaching the surrounding atmosphere of the biosolids, small water droplets may be flung into the air in what is referred to as the “bubble microtome effect”; these droplets, having existed as underwater pockets of air before bursting, may harbor significant quantities of PFAS that partitioned to their surface.⁴⁴ Furthermore, Hoff *et al.* suggest that the organic solutes most apt to partition to the interface of air bubbles have low vapor pressure and low solubility in water, and are typically polar; with polar functional groups and low Henry's constants, this characterization may apply to some PFAS, including PFAAs.^{44,45} In this way, the drying of biosolids may provide an avenue by which non-volatile PFAS may escape wet biosolids, *i.e.*, *via* attachment to bubbles that form during drying and subsequent re-

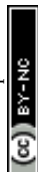
lease (and removal from biosolids) attributed to the bubble microtome effect.

Additionally, recent research by Nguyen *et al.* revealed that PFAS can be removed from wastewater aeration basins *via* attachment to aerosols.⁴⁶ Indeed, PFOS removal was over 75%, and the concentration of PFOS associated with aerosols was 100 to 1000-fold greater than the PFOS associated with the wastewater.⁴⁶ PFOA also exhibited similar removal *via* association with aerosols.⁴⁶ This finding is important for two reasons. First, the removal of PFAS to aerosols occurred at 20 °C, a temperature well below the boiling point of water as well as lower than the temperatures reported for volatilization of PFAS, indicating that it is possible for PFAS to leave a water matrix without volatilizing.^{46–50} Second, the PFAS that were removed *via* association to aerosols were not classically defined ‘volatile’ PFAS, *e.g.*, fluorotelomer alcohols (FTOH), that have been reported in landfill gas, for example.^{45,51} Therefore, this aerosol removal mechanism does not require a phase change of PFAS. As the agitation of water due to aeration within aeration basins may catalyze the aerosolization of water, the tendency of PFAS to partition to the AWI may increase their susceptibility to removal with these water molecules.^{43,52} This phenomenon of aerosolization of PFAS could also likely occur during tumbling of biosolids in rotary dryers.

In addition to these more nuanced potential mechanisms of removal, Hakeem *et al.* highlighted the need for more research to understand the impact of water vaporization on the fate of PFAS during the drying of biosolids; due to the complexity of interactions at the AWI, it may also be prudent to explore the impact of water content on removal.³³ As the PFAS concentration in the drying biosolids decreases, their tendency to partition to the AWI may increase, which may perpetuate the cycle of their removal during the above processes, despite the fact that they may occur at temperatures lower than the PFAS' boiling points.^{43,47–50} In order to validate this claim, an analysis of the atmospheres of the drying environments (both lab-scale ovens and full-scale dryers), as well as of any water droplets generated and expelled during heating processes would be necessary.^{45,53} Moreover, variations in moisture content may affect the consistency of PFAS extraction methods from solid samples due to the complex partitioning behavior of PFAS in multi-phase media. Further investigation on extraction methods and experimental artifacts is prudent for understanding the entire scope of the observed results.

4.2. Potential role of pure chemical volatilization

While PFAS are used in non-stick pans and fire-fighting foams because of their resistance to degradation, they still can volatilize as temperatures increase.⁴⁹ Sasi *et al.* observed PFOA weight loss at 100 °C *via* thermal gravimetric analysis (TGA), raising the possibility that some PFOA could be lost during drying *via* volatilization.⁴⁹ However, in the pure chemical studies by Sasi *et al.*, PFOS weight loss was not observed until temperatures were



above 400 °C.⁵⁴ The drying temperatures in these studies were below 400 °C, yet PFOS removal was still observed, indicating that loss *via* volatilization was unlikely, or at the least not the major removal mechanism.^{49,54}

4.3. Potential role of biotransformation

In addition to the concentration of PFAS changing during drying, the fingerprint, *i.e.* the specific PFAS present in each sample, changed after drying. FTCAs are a common class of precursors, and it is possible that biological enzymes converted FTCA precursors to terminal short-chain PFAAs such as perfluorobutanoic acid (PFBA), PFPeA, or PFHxA.⁵⁵ Research has been reported on the degradation of 5:3 FTCA to PFPeA and the more general theory that *n*:2 fluorotelomer carboxylic acids, *N*-alkyl perfluoroalkane sulfonamido acetic acids, and perfluoroalkane sulfonamido ethanols (*i.e.* 6:2 FTCA, NETFOSAA, NMeFOSAA, and NMeFOSE) transform into perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs).^{35–37} The fraction of total PFAS attributed to precursors decreased after drying for the majority of experiments (ESI† Fig. S2). To confirm biotransformation, microbial activity assays and microbial community analyses would need to be conducted. If transformation were the only mechanism occurring, then total targeted PFAS measurements would increase as undetectable precursors were converted to detectable terminal species. The total sum of PFAS went down, implying that other mechanisms are at play even if transformation partially explained a change in PFAS profiles.

5. Conclusions

Biosolids management plans that incorporate PFAS management considerations are imperative while regulatory agencies weigh risk assessments for allowable PFAS concentrations that are safe for land application of biosolids. Source reduction is still the most important and effective way to mitigate PFAS in wastewater solids. It is essential to recognize the impact that all treatment processes may have on altering the PFAS profile of biosolids. Current treatment technologies could be leveraged to achieve compliance. Drying of biosolids may serve as a method by which PFAS contaminated biosolids are treated and made to achieve regulatory compliance for land-application. However, it is essential to recognize that the reduction in concentration of PFAS in biosolids during drying might result in air-borne PFAS associated with water droplets. Additional studies are needed to assess the fate of PFAS to assist the industry and regulators in establishing appropriate management and treatment protocols. Both lab-scale oven drying and full-scale drying processes had significant impacts on the measurable PFAS profile of biosolids, thereby suggesting that drying is indeed an effective process for altering the PFAS profile of biosolids. Drying is a technology already widely used in the industry. While drying does not completely remove PFAS to below reporting limits, it does substantially reduce measurable PFAS concentrations. Future research is needed to confirm if PFAS are emitted with the

gas phase or if other mechanisms are responsible for these changes observed during drying.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

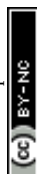
There are no conflicts to declare.

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