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# Influence of Microbial Weathering on the Partitioning of Per- and Polyfluoroalkyl Substances (PFAS) in Biosolids

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## Abstract

Per- and polyfluoroalkyl substances (PFAS) are a large group of man-made fluorinated organic chemicals that can accumulate in the environment. In water resource recovery facilities (WRRFs), some commonly detected PFAS tend to partition to and concentrate in biosolids where they can act as a source to ecological receptors and may leach to groundwater when land-applied. Although biosolids undergo some stabilization to reduce pathogens before land application, they still contain many microorganisms, contributing to the eventual decomposition of different components of the biosolids. This work demonstrates ways in which microbial weathering can influence biosolids decomposition, degrade PFAS, and impact PFAS partitioning in small-scale, controlled laboratory experiments. In the microbial weathering experiments, compound-specific PFAS biosolids-water partitioning coefficients ($K_d$) were demonstrated to decrease, on average, 0.4 logs over the course of the 91-day study, with the most rapid changes occurring during the first 10 days. Additionally, the highest rates of lipid, protein, and organic matter removal occurred during the same time. Among the evaluated independent variables, statistical analyses demonstrated that the most significant solids characteristics that impacted PFAS partitioning were organic matter, proteins, lipids, and molecular weight of organics. A multiple linear regression model was built to predict PFAS partitioning behavior in biosolids based on solid characteristics of the biosolids and PFAS characteristics with a $R^2$ value of 0.7391 when plotting predicted and measured log $K_d$. The findings from this work reveal that microbial weathering can play a significant role in the eventual fate and transport of PFAS and their precursors from biosolids.

## Keywords

PFAS; Biotransformation; Fate and Transport; Microbial Weathering; Biosolids; Sludge Stabilization

## Environmental Significance Statement

Per- and polyfluoroalkyl substances (PFAS) have extensively contaminated the environment through land applications of biosolids, resulting in potential dietary exposure routes to human and ecological receptors. Water resource recovery facilities (WRRFs) receive PFAS-contaminated influent; partitioning to the biosolids causes subsequent re-release to the environment. Currently, evaluations of PFAS contamination in biosolids can vastly underestimate the total PFAS release due to analytical limitations and transformations of precursor PFAS. The results of this investigation demonstrate that when biosolids are allowed to weather, microbial processes can rapidly decompose the quality and organic composition of the biosolids, transform precursor PFAS, and impact the compound-specific biosolids-water partitioning factors.

## Funding Sources

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large and diverse family of organofluorine chemicals that resist degradation, accumulate in various environmental solids, and can be soluble in aqueous matrices.(1–3) Over the past 60 years, PFAS have been frequently used in household consumer products and wide scale industrial processes, commonly having waste streams that can enter water resource recovery facilities (WRRFs) as influent.(4–8) PFAS are widely used in various applications due to their high thermal and chemical stability, amphiphilic nature, and surfactant properties.(1,9,10) As a result, an extensive range of environmental matrices have been contaminated leading to persistent exposures to humans, wildlife, and other components of the environment. WRRFs concentrate PFAS from their influent and have been demonstrated to be a pathway of PFAS release to the environment through their liquid and solid effluents, where they can behave quite differently depending on their specific chemical and physical properties.(11,13–15) To date, multiple major literature reviews have been conducted investigating occurrence, fate, transformation, and removal of PFAS during wastewater treatment.(16–20) Major findings from these reviews show that PFAS in the WRRFs influent can accumulate in solid effluent where the extent of accumulation is largely dependent on compound characteristics. Through a United States National Sewage

Sludge Survey, it was found that most abundant PFAS compound detected was perfluorooctanesulfonic acid (PFOS) 403 ± 127 ng/g dry weight (dw), and the mean average load of 13 targeted PFAS compounds was 2749-3450 kg/year.(21) Another major finding is that frequently there are higher concentrations of perfluoroalkyl acids (PFAAs) in the effluents compared to the influent due to a combination of abiotic and microbial degradation that can transform PFAS precursors to recalcitrant PFAAs.

WRRFs produce solid effluents that are typically nutrient rich materials with high organic matter content which can be land-applied after stabilization processes, as a fertilizer to improve or maintain soil quality for agriculture.(22) Sewage sludges produced in WRRFs go through sludge stabilization methods such as anaerobic digestion, aerobic digestion, thermal drying, lime stabilization, composting, and more before the dewatering and stabilization steps that produce regulated biosolids which can be spread on agricultural land. Biosolids are defined as stabilized products of solids treatment in WRRFs that meet current regulatory requirements for beneficial use (e.g., land application), and this terminology will be used throughout the work presented as it is the most commonly used term globally.(23–25) Biosolids have high organic matter content, active and changing microbial communities, and are applied in a variety of different settings; all factors that impact decomposition rates that have the potential to be closely related to PFAS fate and transport. For example, frequent use of biosolids applied to the surface favors the production of dissolved organic carbon that can be transported to deeper soil horizons.(26) Specifically related to components of the organic matter, proteins and lipids have been demonstrated to substantially decrease during digestion of biosolids due to increases in methanogenic populations.(27) Protein specifically is closely related to nitrogen mineralization in biosolids, and decomposition is often rapid over the first 14 days of storage if preventative measures are not taken to reduce bioavailable protein.(28,29) The organic matter components of biosolids and their decomposition all can play roles in PFAS behavior when land applied.(30,31)

Following land application, PFAS partition among surface soil, biosolids, groundwater, air, and biota. Sludge stabilization methods that generate sludge have been demonstrated to impact the extent of transformation of PFAS precursors and the partitioning of the compounds in the biosolids, therefore potentially impacting the accumulation of PFAS in these products.(21,32–34) Specifically, stabilization processes can have direct impacts on PFAS in biosolids, impacting PFAA concentrations and partitioning.(15,33,34) While treatment processes do not have as much of an impact on PFAS mass load in biosolids as PFAS sources to WRRFs(15), secondary treatment processes and stabilization methods have been shown to impact PFAS sorption and leaching potential.(33) In the surface soil, vadose zone, and groundwater, PFAS have been demonstrated to be positively correlated with biosolid mass loading, with steady leaching to groundwater where some compounds have been found at one to two times higher orders of magnitude than the soil.(20) In biosolids specifically, sustained PFAS leaching has been demonstrated through six months with precursors leaching and transforming similarly to biosolids land application.(35) Since PFAS are present in biosolids and groundwater, Pepper et al. looked at groundwater and biosolid contamination of agricultural soils and found that biosolids applications resulted in greater PFAS soil concentrations than groundwater application.(36) PFAS have been demonstrated to accumulate in plant tissues in PFAS contaminated soils in a variety of crops such as wheat, lettuce, and tomatoes.(37–39) PFAS may also accumulate in those organisms that consume soil, such as earthworms(40), larger animals (livestock and game animals) that may feed on crops or be exposed via water, soil, and air, and through inhalation of dust particle sized biosolids.(41,42)

Application of biosolids as a recycling method of macronutrients is a sustainable practice but is constantly challenged by the increasing presence of metals and persistent organic pollutants.(43,44) Currently, in the United States, there are no federal minimum standards for PFAS concentration in biosolids for land applications(16), even though a report from 2013 calculated substantial loads of total PFAS to the environment from biosolids.(21) Since this work, many agricultural lands with historical applications of biosolids have been demonstrated to contain PFAS in soil, crops, and groundwater.(36,45,46) As a result of these findings, there have been little response on the regulatory end, with only Maine requiring testing since March 2019 for four PFAS compounds.(47) Michigan and Wisconsin have made efforts to reduce PFAS in WRRF influent and develop educational information directed towards the farmers using these products to reduce exposure risks.(48) The United States Environmental Protection Agency has released a PFAS Strategic Roadmap(49) which intends to determine if regulation is appropriate by 2024 and if so, which regulations and restrictions would improve environmental and public health protection. A recent review by Hall et al., compiled all of the known international regulations regarding PFAS in biosolids and found that only Germany and Maine have set limits for PFAS in biosolids for land application and other countries, such as Norway, Finland, and Australia are using risk-based approaches similar to Wisconsin and Michigan.(50) Due to the lack of regulation of PFAS in biosolids and the negative impacts associated, there is a great need to improve the understanding of the fate and transport of PFAS once land applied as biosolids to further develop knowledge on the potential impacts on environmental and human health over time during weathering processes.

Biosolids can be exposed to different weathering processes that can be broken down simply into abiotic and microbial (biotic) processes, similar to soils.(51,52) The work presented here aims to examine how microbial weathering, such as microbial decomposition of organic biopolymers, like lipids and proteins, can impact PFAS leaching potential from biosolids over time as the solid characteristics change. For these microbial weathering experiments, biosolids were collected from WRRFs (aerobic digestion, anaerobic digestion, and composting) and placed in an environmentally controlled chamber for three months to investigate the impacts of microbial weathering. Samples were characterized by their solid characteristics, a range of enzyme activities, PFAS sorption behavior, and PFAA precursors to realize the impacts of microbial activity on PFAS leaching potential and precursor PFAS transformation. To date, there is a modest number of studies that look at the impacts of PFAS leaching from soils and only a few studies on PFAS leaching from biosolids. This study investigated a selected range of PFAS in biosolid samples over time, providing insight to how microbial weathering influences biosolids characteristics, PFAS structure, PFAS fate and transport, and which specific biological and geochemical factors may impact PFAS partitioning to different matrices to the greatest extent.

## 2. Materials and Methods

### 2.1 Chemicals

Sodium nitrate (>99%) was obtained from GFS Chemicals (Columbus, OH, USA). Methanol (>99%) was obtained from Fisher Scientific (Hampton, NH, USA). Sodium hydroxide, (>97%), sodium azide (>99.5%) and formamide (>99%) were obtained from Sigma-Aldrich, Co. (St. Louis, MO, USA). Chloroform (>99.8%) was obtained from MilliporeSigma (Burlington, MA, USA). PFAS compounds used in this study included 7 perfluoroalkyl carboxylic acids (PFCA), 4 perfluoroalkyl sulfonic acids (PFSA), and 2 fluorotelomer sulfonic acids (FtS). In total, 13 technical-grade PFAS compounds with 95% purity or higher were used in partitioning experiments, of which C4- C10 PFCA and C4- C6- C8- and C10 PFSA were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). 6:2 and 8:2 FtS were purchased from Toronto Research Chemicals (Toronto, ON, Canada). Native and mass-labelled standards were purchased from Wellington Labs, Inc. (Whitby, ON, Canada). PFAS concentrations were reported for 13 analytes, perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorounanoic acid (PFUnA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS), perfluorodecanesulfonic acid (PFDS), 6:2 fluorotelomer sulfonic acid (6:2 FtS), and 8:2 fluorotelomer sulfonic acid (8:2 FtS).

### 2.2 Sample Collection, Preparation, and Storage

WRRFs representing sludge stabilization methods were recruited for biosolid samples. Collected biosolid samples encompassed stabilization methods of aerobic digestion (n=2), anaerobic digestion (n=1), and composting (n=3). Recruited WRRFs were provided instructions to collect samples to minimize contamination, with more detail found in a previous study.(33) Upon arrival, biosolid samples were stored at 4 ºC for a maximum duration of one month before the beginning of the study. When all samples of a specific stabilization method were received, a portion of the sample was set aside and had 1 g/L of sodium azide added as a control for microbial weathering, before compositing. After this step, all biosolid samples from each WRRF were dried at 105 ºC to remove moisture. Composite samples of each solids treatment type (treatment and sodium azide controls) were created by adding equal portions, if applicable, of dry weight from each WRRF in that type (aerobic digestion, anaerobic digestion, and composting), and stored at -20ºC. A schematic of the sample collection and processing can be found in the Supplementary Information (S1).

### 2.3 Experimental Set-Up and Design

To investigate the microbial weathering of the various biosolids, samples were placed into a controlled relative humidity chamber (77% ± 1%) with the temperature at 21.4 ºC ± 3.1 ºC, with both parameters measured once a week (i.e., 13 measurements across the experimental duration). These conditions were selected to represent typical United States growing season conditions, while controlling temperature and humidity as variable that may impact biosolids-water $K_d$.(53) While conditions were at set values mirroring this climate, the design does not mirror real conditions (variable temperature, humidity, and light/dark cycles), but allows for more controlled data analysis. Humidity was controlled by creating a saturated solution of sodium nitrate inside of the chamber.(54) To minimize effects from solar irradiation, the entire chamber was covered with cardboard to prevent light from weathering the biosolid samples. Biosolid samples were expected to be contaminated with PFAS prior to reception, since they were received from the same WRRFs as a previous publication by Ebrahimi et al., therefore no PFAS were added during the weathering experiments to allow for better understanding of the microbial weathering in a representative sample. (33) Each composited treatment type was separated into uncovered 50 mL polypropylene vials with 30 g ± 0.5 g of biosolids for sacrificial samples throughout the course of the experiment. For each treatment type, there was one sample with sodium azide for each collection day as inactivated with sodium azide and triplicate samples without sodium azide. The biosolid samples were allowed to weather in the humidity chamber for 91 days with routine collections at days 1, 4, 10, 32, and 91.

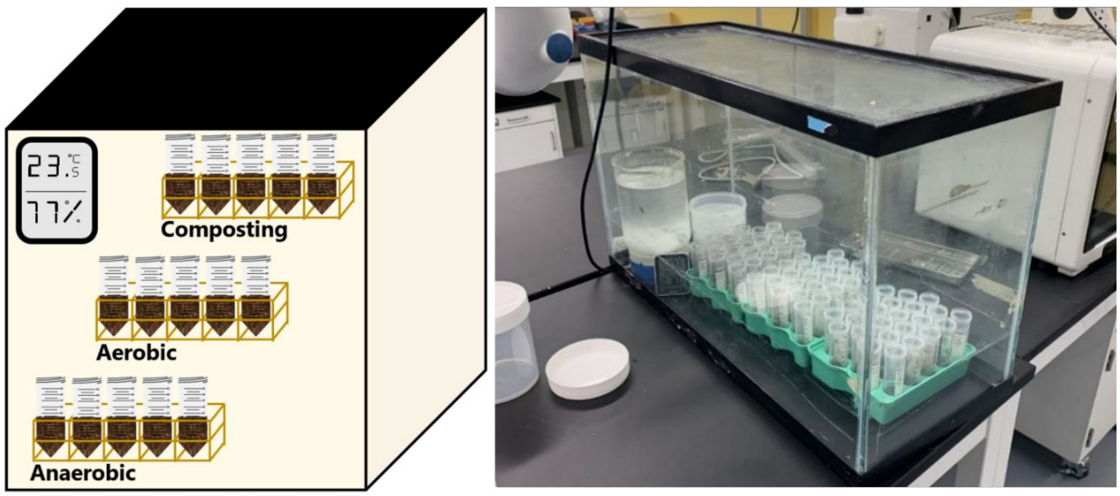


**Figure 1.** Schematic of the environmentally controlled chamber for observation of the microbial weathering of biosolids (left) and photo of uncovered experimental set-up (right). The chamber was kept in darkness to prevent solar irradiation effects, humidity was controlled through a fully saturated sodium nitrate salt solution placed inside the chamber, and temperature was set at room temperature and monitored.

### 2.4 Analytical Methods

#### 2.4.1 Biosolid Characterization

For solids characterization, analyses were conducted for hydrophobicity, organic matter molecular weight, organic matter content (loss-on-ignition), proteins, and lipids. To characterize hydrophobicity and organic matter molecular weight, a modified extraction procedure was followed that involved an additional grinding step and extraction with formamide and sodium hydroxide.(55) Once extracted, hydrophobicity was measured via a reverse-phase HPLC method(56) to characterize the polarity distribution of biosolids extracts. This was achieved by calibrating eleven organic compounds with known octanol-water partitioning coefficients ($K_{ow}$) versus the elution time in an isocratic method with methanol. Organic matter molecular weight was measured by size exclusion chromatography (SEC) which estimates the molecular weight distribution of organic molecules(57) using polystyrene sulfonate standards (33400, 16000, 7540, 5180 g/mole) and acetone (58 g/mole) as size calibration standards. To measure protein content of the samples, a procedure was followed(58) and determined using a modified Lowry Protein Assay Kit from Thermo-Fisher Scientific (Waltham, MA, USA). Lipids were measured through an extraction process that used chloroform and methanol, washed with Milli-Q UltraPure water, and determined gravimetrically.(59) Organic matter content was determined by loss-on-ignition at 450ºC for 8 hours.(60)

Indicators of solids characteristics measured include DOC, DON, and pH. DOC and DON followed an extraction method using potassium chloride, water, and centrifugation(61) and then extractable DOC and DON were analyzed with the 680°C combustion catalytic oxidation method (Shimadzu TOC-L Series analyzer) with a measurement range from 5 µg/L to 30,000 mg/L. Microbial activity analyses included lipase activity, protease activity, acid phosphatase activity, and oxygen consumption rate (OCR), and were all determined using a Molecular Devices Filtermax™ F5 Multi-Mode Microplate Reader (Molecular Devices, San Jose, CA, USA). Lipase activity was measured using a Lipase Activity Assay Kit (Catalog No. MAK046, Sigma-Aldrich, Co. (St. Louis, MO, USA)). Protease activity was measured using a Protease Activity Fluorometric Assay Kit (Catalog No. K781-100, Biovision Inc. (Milpitas, CA, USA)). Acid phosphatase activity was measured using an Acid Phosphatase Activity Fluorometric Assay Kit (Catalog No. MAK087, Sigma-Aldrich, Co. (St. Louis, MO, USA)). Oxygen consumption rate was measured using an Oxygen Consumption Rate Assay Kit (Item No. 600800, Cayman Chemical (Ann Arbor, MI, USA)).

### 2.4.2 Partitioning Experiments, PFAS Analysis, and Precursor Quantification

Partitioning experiments to determine compound-specific PFAS biosolid-water partitioning coefficients ($K_d$) were conducted in polypropylene tubes and included 49.8 mL aqueous solution (10 mM ammonium nitrate, 5 mM ammonium bicarbonate, and pH 7) and 200 mg (dry weight) solids, using a previously demonstrated method by Ebrahimi et al.(33) All sample vials were amended with 200 ng of a 14 compound PFAS and mixed end-over-end at room temperature for seven days to achieve equilibrium.

PFAS analysis followed methods presented by Ebrahimi et al., where liquid fractions were subsampled, and then amended with methanol containing an internal standard suite (2 µg/L). PFAS extraction from solids consisted of internal standard addition, followed by a basic methanol extraction and EnviCarb clean-up.(62) Total Oxidizable Precursors (TOP) assay(63) was also performed on the solid extracts by implementing a modified version of TOP assay for biosolids, without any spiking with technical grade PFAS.(64) Extractions used to determine precursor concentrations followed the same procedures as those extractions described for the partitioning experiments. Quantification of targeted PFAS for both the partitioning experiments and the TOP assay was achieved by LC-QTOF-MS (Sciex x500r). The details of the PFAS analytical methods and QA/QC procedures can be found in the SI of Ebrahimi et al.(33)

### 2.5 Data Analysis and Statistical Data Analysis Methods

Calculation of various PFAS concentrations (total PFAA, PFCA, PFSA, precursor PFAS) is described in Supplementary Information (S2). Partitioning experiments analyzed 13 PFAS compounds while TOP assay results analyzed 24 PFAS, 18 PFAAs and 6 known precursor compounds (S3,S4). $K_d$ is calculated by the solids PFAS concentration (mg/kg) divided by the aqueous PFAS concentration (mg/L) data, resulting in L/kg units. Delta log $K_d$ was calculated by subtracting the final value by the initial value (Day 91-Day 1). If PFAS concentration in either the liquid or solid-extracted sample was below limit-of-quantitation (<LOQ), then a partitioning coefficient was not calculated (i.e., not considered quantitative) and omitted from final data analysis and visualization. Statistical analyses were performed to relate the biosolid-water partitioning coefficients determined throughout the course of the experiment to the solids, chemical, and physical characteristics of the biosolids. The effect of each parameter measured was looked at through single variable linear regressions, single Spearman's rank correlations, and multiple linear regressions to build a predictive model for $K_d$ depending on PFAS compound characteristics and biosolids characteristics. Single variable linear regressions were run in R using lm(), Spearman's rank correlations were run in R using cor.test(), multiple linear regressions were run in R using the package "olsrr" and specifically "ols_step_all_possible" to determine most significant environmental factors, and then a linear regression model was built in R using lm().

# 3. Results and Discussion

## 3.1 Impacts of Microbial Weathering on PFAS Partitioning in Biosolids

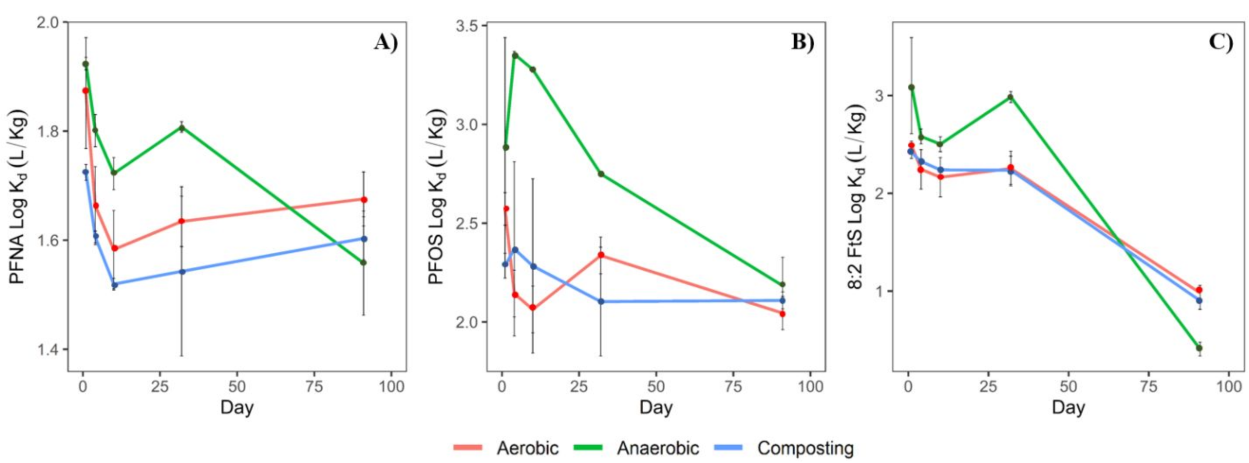

**Figure 2**. Time series for change in PFAS biosolids-water log $K_d$ (L/Kg) for PFNA (Figure 2A), PFOS (Figure 2B), and 8:2 FtS (Figure 2C). n = 3 (experimental triplicate). Error bars represent standard deviation.

Thickened sludge can go through various sludge stabilization methods such as composting, anaerobic digestion, and aerobic digestion, to transform this material into stabilized biosolids(65), which have been found to have significant effects on resultant biosolids-water $K_d$ values.(33) These stabilization methods produce biosolids that can have quite variable solids characteristics and microbial communities, impacting the partitioning coefficients of organic contaminants, like PFAS. In the study presented here, similar trends were observed where biosolids-water $K_d$ values varied between stabilization methods upon receipt before any laboratory microbial weathering took place. In Figure 2, which depicts the change of biosolids-water log $K_d$ over time for compounds with equal perfluoroalkyl chain lengths (n=8) and varying head groups, perfluorononanoic acid (PFNA), perfluorooctanesulfonic acid (PFOS), and 8:2 fluorotelomer sulfonic acid (8:2 FtS), it can be observed that the starting values, at day 1, were quite variable among stabilization methods. For example, PFOS had log $K_d$ values of 2.87 ± 0.57, 2.57 ± 0.08, and 2.28 ± 0.06 for aerobic, anaerobic, and composting digestion, respectively. A more comprehensive figure presenting all PFAS compounds analyzed can be found in the supplementary information (S4,S6). Once microbial weathering experiments commenced, $K_d$ values were shown to significantly change even within 4 days (Figure 2). Greater decreases in $K_d$ were observed over the first 10 days of the experiment than the following 81 days (Figure 2). This suggests that the microbial activity present in the samples is most active over the first 10 days and is impacting those solid characteristics responsible for PFAS sorption to the biosolids and subsequently changing the values reflected in the biosolids-water $K_d$. Sodium azide deactivation of the microbial activity in the biosolids was insufficient – as evidenced by the fact solids characteristics still changed significantly over the course of the study, suggesting that newer methods should be investigation for microbial deactivation of biosolids without impacting the solids characteristics (S5). Sodium azide deactivation of sludge has been effective in other matrices without impacting the solid characteristics, but it has been evidenced to be essentially ineffective in sewage sludges.(66,67) While the microbial activity was only slightly inhibited, if at all, through the addition of sodium azide for deactivation in biosolid samples, it is important to demonstrate that other methods need to be developed for microbial studies of biosolids decomposition.

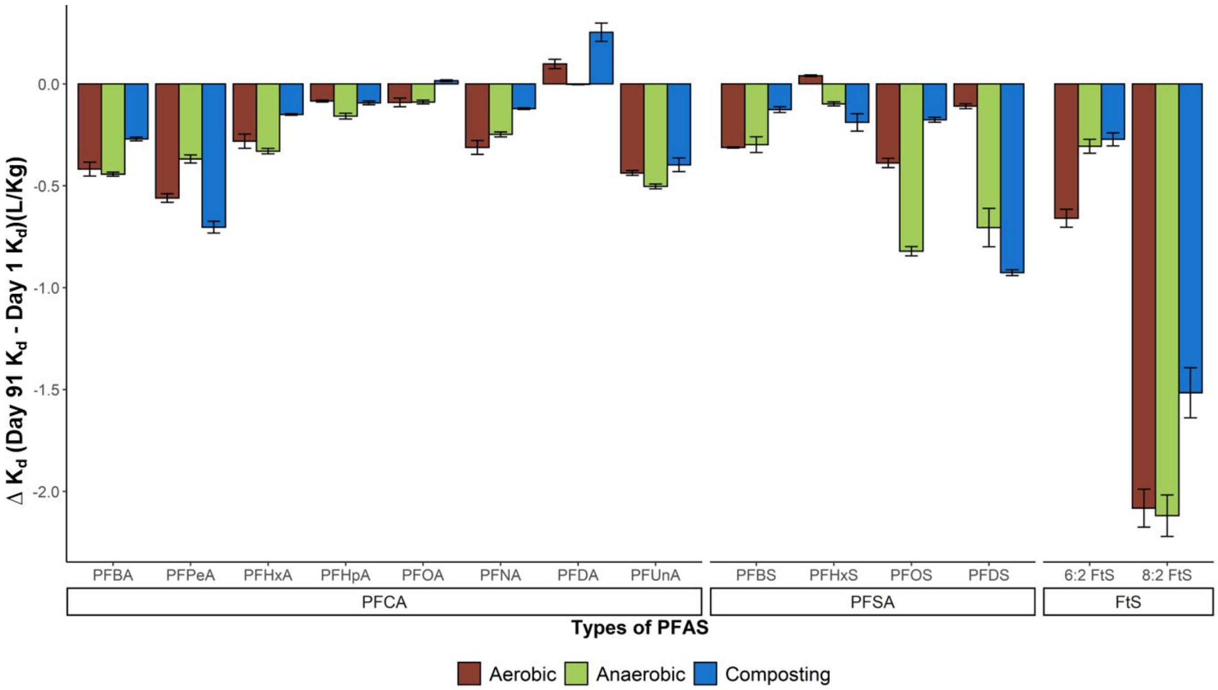


**Figure 3.** Change (Δ) in log PFAS biosolids-water $K_d$ over the course of the microbial weathering experiment. n=6 for all data points (experimental replicates). Error bars represent standard deviation.

Throughout the course of the microbial weathering experiment, significant changes in partitioning constants were observed for the majority of the PFAS compounds investigated across all sludge stabilization methods. As seen in Figure 3, change in biosolids-water log $K_d$ (Δ log $K_d$) values ranged from insignificant to 2.2 but on average were around 0.4 Δ log $K_d$, when comparing $K_d$ values on days 1 and 91. Because of the decreases in the biosolids-water $K_d$, once biosolids are land-applied there is increased potential of leaching to groundwater as weathering processes occur to both the biosolids and the PFAS precursors. Historically, land application of biosolids is a source of pollution to the crops, soils, and groundwater for a range of contaminants, namely metals, polychlorinated biphenyls (PCBs), and other persistent organic pollutants (POPs).(68,69) Once biosolids are land-applied, they are exposed to varying environmental conditions that may impact the partitioning of certain compounds and impact microbial activities.(70,71) For PFAS specifically, historical land application of biosolids have PFAS soil concentrations and groundwater concentrations at 1 to 2 orders of magnitude higher than background soils and groundwater just offsite that were not impacted by biosolids application(46,72,73), suggesting possible leaching. On top of leaching potential, PFAS tend to accumulate in the vadose zone at high concentrations, likely due to their tendency to partition to the air-water interface, across the world.(74) PFAS accumulation in the soil is concerning because it can act as a sink for continual bioaccumulation through biota as well as continual leaching to the groundwater. More mobile PFAS compounds, or short-chain compounds, have lower $K_d$ values (S4), and therefore may have greater potential to leach to groundwater. In addition to changes in partitioning behavior over-time, precursor PFAS may be biotransformed through the microbial activity in the biosolids, impacting the mobility of the distribution of PFAS.

### 3.2 Changes in PFAA Precursors during Microbial Weathering – Indicative of Precursor Biotransformation

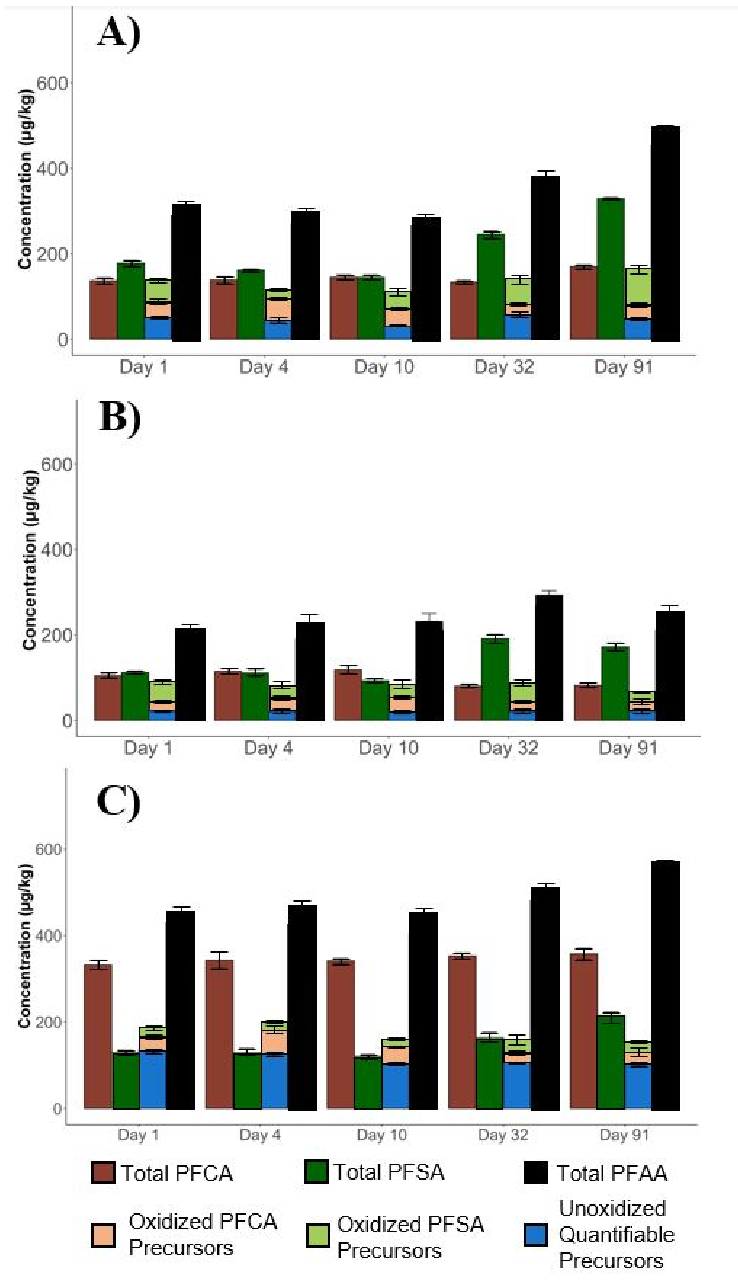


**Figure 4.** PFAS concentration change overtime for aerobic digestion (4a), anaerobic digestion (4b), and composting (4c) broken down into Total PFCA (PFBA, PFPeA, PFHxA, PFHpA,

PFOA, PFNA, PFDA, PFUnA), Total PFSA (PFBS, PFHxS, PFOS, PFDS), Precursors (broken down into those that oxidized into PFCA (light orange), those that oxidized into PFSA (light green), and unoxidized quantifiable precursors (blue) (4:2 FtS, 6:2 FtS, 8:2 FtS, N-MeFOSAA, N-EtFOSAA, and PFOSA)), and total PFAA (Total PFCA and PFSA summed). n=3 (experimental replicates). Lighter shaded PFCA and PFSA represent compounds identified in the oxidized samples during TOP assay. Error bars represent standard deviation.

Throughout this study, the TOP assay was performed to gain a general understanding of the PFAAs and the PFAA precursors present in each dried sample (Figure 4). Specific information on how total PFAAs, total PFCAs, total PFSAs, and precursor compounds were calculated can be found in Supplementary Information (S2). It is important to note that precursor compounds were either characterized as those that oxidized into PFCAs or PFSAs or those that were unoxidized by the TOP assay but were detected and quantified (i.e., 4:2 FtS, 6:2 FtS, 8:2 FtS, N-MeFOSAA, N-EtFOSAA, and PFOSA). As shown in Figure 4, across all stabilization methods there is an increase in total PFAAs over the 91 day experiment conducted, suggesting that PFAA precursors were being transformed. The increase in total PFAAs, as evidenced by the TOP assay, indicates that some of the precursor PFAS are being biotransformed.(75) For example, for aerobically digested samples, there was a large increase in total PFAA concentration from 312.7 µg/kg to 498.5 µg/kg. For anaerobically digested samples, there was a slight increase in total PFAA concentration from 198.3 µg/kg to 217.3 µg/kg. Finally, for composted samples, there was an increase from 476.7 µg/kg to 588.3 µg/kg. Since the biosolids for each stabilization method originated from different wastewater treatment plants, the change in total PFAAs over the 91 days could be influenced not only by the type of stabilization method but also differences in the precursors that were present in the biosolids from each treatment plant. These results are in agreement with other studies that have also shown that precursor PFAS in biosolids, such as methylperfluorooctanesulfonamidoacetic acid (MeFOSAA), can undergo biotransformation after being land-applied.(36),(72) For example, one study looking at the impacts of long-term applications of PFAS contaminated biosolids on agricultural lands and detected high levels of on the precursor PFAS methylperfluorooctanesulfonamidoacetic acid (MeFOSAA) in the biosolid but no detection in the soils post-application, suggesting rapid biotransformation.(36) Another study on MeFOSAA in land-applied biosolids and biosolids amended soils also reported significant decreases in MeFOSAA concentrations but not significant increases in PFOS, a known transformation product.(72) In our work, over the 91 day study, we also observed significant decreases in the quantifiable precursor PFAS in unoxidized samples investigated (4:2 FtS, 6:2 FtS, 8:2 FtS, Me-FOSAA, Et-FOSAA, and PFOSA) (S3), which could have been the cause of the increases in PFSAs seen in Figure 4.

Within the total PFAA concentrations, total PFCAs and total PFSAs were investigated to see if precursor PFAS in each sample were precursors for PFCAs or PFSAs and if there were differences between sludge stabilization methods. Across all sludge stabilization methods, significant increases in PFSA concentrations were observed: aerobically digested samples increased 84.8%, anaerobically digested samples increased 53.2%, and composted samples increased 64.8%. Increases in PFCA concentrations varied between samples and if increased, was at a lesser magnitude than PFSAs: aerobically digested samples increased 24.1%, composted samples increased 7.9%, but by contrast anaerobically digested samples decreased 21.3%. These data suggest that there are significant PFSA precursors in the biosolid products that are metabolized by microbes in the samples, a more common process in biological than chemical transformations.(76) In fact, precursors of PFOS, MeFOSAA, EtFOSAA and PFOSA, were all shown to decrease over the 91 day study (S3). For PFCAs, it was observed that there were slight increases in concentrations for composted and aerobically digested samples, while there was a slight decrease in the anaerobically digested sample). It is uncertain whether PFCA precursors are easily transformed in the WRRF processes (i.e., prior to collection) or underwent biotransformation processes more slowly than the PFSA precursors in the experimental set-up. While it is likely that this difference came from sampling and analysis variation or other losses, there is some evidence that terminal PFAS (PFAS that are regarded to not further degrade, which includes PFAAs) have potential to transform in anaerobic conditions.(77–79)

Although there is evidence that precursors of PFAAs are being generated, upon a closer look at the data presented in Figure 4 it becomes apparent that there were inefficiencies in the oxidation step of the TOP assay that complicate interpretation of this data, and it is suggested to follow a hydrogen peroxide pretreatment for future work.(80) In the data presented in Figure 4, the precursor concentrations determined from the TOP assay remained relatively constant while the total PFAA concentration increased, suggesting ineffectiveness. In theory, the TOP assay is expected to only create PFCAs but it was observed that PFSAs were formed as well. In addition, it was also expected that total PFAA concentration should remain constant across the 91 days if the TOP assay is 100% efficient in oxidizing the precursors but this was not the case (as shown in Figure 4), indicating inefficiencies in the TOP assay conducted for the biosolid samples in this study . TOP assay inefficiencies have also been demonstrated in other work involving PFAS in biosolids.(35) Other work has found extensive contamination of biosolids by precursor PFAS (other than the six quantified in this study) (S3)), such as perfluorophosphinates (PFPiAs), polyfluoroalkyl phosphoric acid diesters (diPAPs), and perfluorophosphonates (PFPAs), providing a potential explanation for the increase in total PFAAs in this study but relatively consistent concentrations of precursor PFAS.(35,81,82) In our TOP assay results, the diPAPs (or other associated precursors) likely have been unaccounted for due to the chemical behavior and/or matrix issues associated with the biosolids extracts.(35)

Influents to WRRFs containing PFAS can contain a range of PFAS from a diverse set of precursor PFAS to the recalcitrant terminal PFAAs that do not degrade under typical environmental conditions.(83) This diversity of precursor compounds in influent can lead to different proportions of PFCAs and PFSAs in biosolids, depending on the contamination sources are. While it is not fully understood whether transformation to PFCAs or PFSAs are most common, it is likely that the most important concept is understanding the extent of precursor PFAS presence in the biosolids to understand the level of PFAS leaching potential from land-applied biosolids.(35) Throughout WRRF processes, it has been demonstrated that precursor PFAS can be transformed and that the effluents can contain high concentrations of terminal PFAS. (17,84,85) In wastewater, precursor PFAS can account for up to 63% of total PFAS concentrations.(86) While degradation may occur, full transformation to terminal PFAS does not occur, shown by the present of precursor PFAS in effluents from WRRFs, like Class B biosolids.(36) As a result, PFAS contaminated biosolids that are land-applied will have a distribution of both terminal PFAS (PFAAs) and precursor PFAS.

The various stabilization methods can also play a role in the extent of biotransformation of the precursors in the final biosolid products that were received. Composting and aerobically digested samples have been demonstrated to have high microbial activities leading to increased precursor PFAS transformation rates(87,88), which is in agreement with the results shown in Figure 4a and 4c from the present study. Anaerobically digested samples, Figure 4b, did not show as great of a transformation to terminal PFAS throughout the experiment. This observation could be a result of limited precursor biotransformation in anaerobic conditions compared to that which occurs in aerobic conditions at WRRFs.(89–91)

As demonstrated in Figure 4, there is little to no change in total PFAA concentrations in Days 1, 4, and 10 and clear increases in total PFAA concentrations in the Day 32 and 91 samples. For days 1-10 the rate change in total PFAA are -4.41 µg/kg/day, -0.78 µg/kg/day, and -2.95 µg/kg/day for aerobic digestion, anaerobic digestion, and composting, respectively. For days 10-91 the increase rates for total PFAA are 2.78 µg/kg/day, 5.64 µg/kg/day, and 1.36 µg/kg/day, for aerobic digestion, anaerobic digestion, and composting, respectively. Calculations used to determine these values can be found in Supplementary Materials (S7). The first 10 days had negative values of rate change for total PFAA possibly due to partial biotransformation of precursor PFAS to transient products and the last 81 days had positive values of rate change related to further transformations to terminal PFAS. These data suggest that any biotransformation of precursor PFAS is slow to occur in the beginning of the weathering experiment. The microbial activity in the samples may target more easily digestible carbon sources until they are depleted or inaccessible before metabolizing any part of the precursor PFAS, especially in the anaerobic samples. The anaerobic samples had the highest OCR (Figure 5) and the greatest organic matter content (S5) when received, providing further evidence of easily digestible carbon sources and why the change to total quantifiable PFAS may not be as significant as in the aerobic and composting samples. The microbial environment has been demonstrated to play a significant role in the rate and extent of biotransformation in soils and biosolids, however the body of work looking at microbial weathering specifically related to agricultural practices is limited. In biosolids specifically, there has been few studies on the transformation products over-time, but the work done on PFAS contaminated soils, specifically those of biosolids-amended soils(92,93), can give insight into the mechanisms responsible for transformations.

### 3.3 Changes in Solids Characteristics and Biological Activity During Microbial Weathering of Biosolids

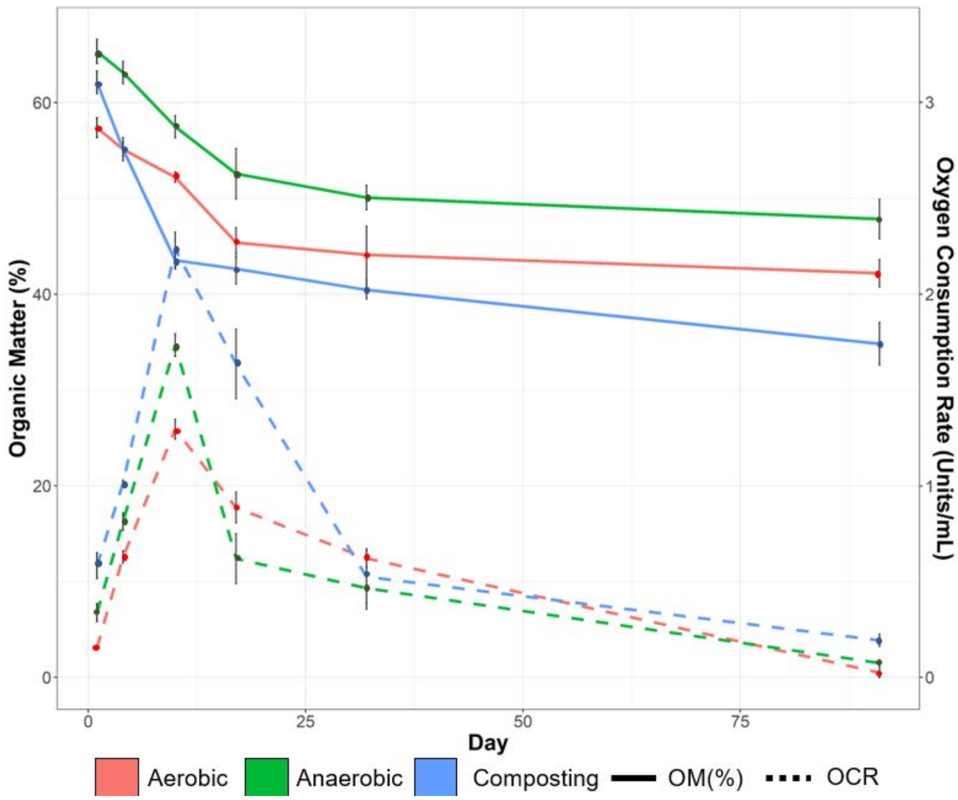


**Figure 5.** Oxygen consumption rate (OCR) and organic matter (%) over time. n=3 for each data point for days 1, 4, 10, 17, 32, and 91. Error bars represent standard deviation.

By looking at general oxygen consumption rate (OCR) and organic matter (Figure 5) throughout the experiment, we can observe the impacts of microbial activity in the sample at each time point. While this does not bring insight into the differences in microbial communities between stabilization methods, it provides information on the microbial activity throughout the experiment and can infer what may happen to the solids characteristics and environments that may help facilitate the biotransformation of precursor PFAS. The greatest rate change (S5) in organic matter occurs between days 4 and 17 for anaerobic and aerobic samples, which also coincides with the greatest OCRs. For composting samples, the greatest rate change in organic matter occurs initially, and the peak OCR may have been between days 1 and 4. After day 17, changes in organic matter and OCRs begin to decrease slowly. Since the peak OCR generally coincides with the greatest changes in organic matter it suggests that the greatest degradation of organics occurs when microbial activity is highest in these samples. Interestingly, composting samples had the highest peak OCR (Figure 5) and the lowest percent rate of generation of terminal PFAS (Figure 4), suggesting that there is more easily digestible organic material in the biosolid product and there may be a lag period before precursor PFAS may be digested compared to aerobic digestion and composting samples.

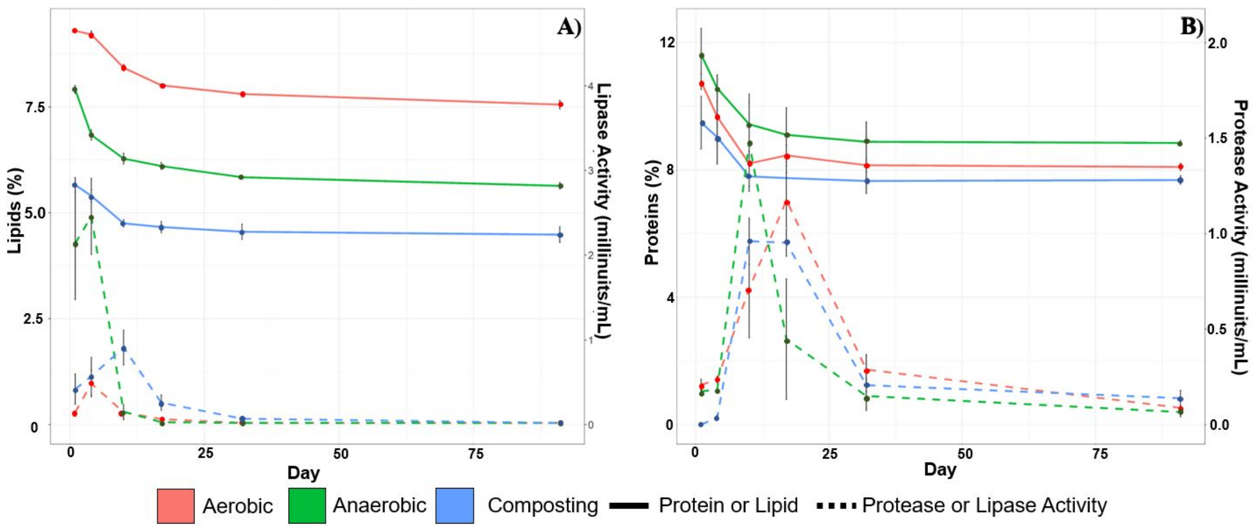


**Figure 6.** Lipase activity and lipids (Figure 3a) and protease activity and lipids (Figure 3b) over time. n=3 for each data point for days 1, 4, 10, 17, 32, and 91. Error bars represent standard deviation.

Organic matter consistently decreased over the course of the experiment but at different rates. Proteins, lipids, and their associated enzyme activities were also investigated for components of the organic matter (Figure 6). Here, similar trends to Figure 5 can be observed where peak enzyme activity occurs when the specific biopolymer is being degraded (proteins and lipids). However, protease activity and protein decomposition appeared to peak between days 10 and 17 while lipase activity and lipid decomposition occurred earlier on, between days 4 and 10. Anaerobic digestion has a relatively steep change in lipid content over the first 10 days and a high initial peak lipase activity, likely due to the heavy presence of lipids (volatile fatty acids) commonly found in these digesters and produced biosolids. (94) Since PFAS have been shown to interact with proteins and lipids, it was important to study how it changes throughout the course of the experiment. To fully investigate the solids characteristics, a wider variety of factors were sampled for at each time point throughout the course of the experiment (days 1, 4, 10, 17, 32, and 91), as shown in Supplementary Information (S5), and comparisons of the characteristics between stabilization methods are presented.

Among the biosolids stabilization methods there were significant differences in many of the general characteristics, specifically organic matter, lipids, and proteins. For example, organic matter was 57.37% in aerobic samples, 65.33% in anaerobic samples, and 62.12% in composting samples. Organic matter content decreased during the 91 days microcosm weathering as follows: aerobic samples decreased 15.19%, anaerobic samples decreased 25.25%, and composting samples decreased 27.3%. Aerobic samples had the highest protein content while anaerobic samples had the highest lipid content; composting samples were consistently the lowest for proteins and lipids across all time points. Interestingly, composting samples had the lowest extractable DOC and increased throughout the experiment while aerobic and anaerobic samples extractable DOC decreased. Since PFAS have been demonstrated to associate with DOC(95), this suggests that the weathering of composted biosolids may lead to increased leaching compared to aerobically and anaerobically digested samples through this mechanism.

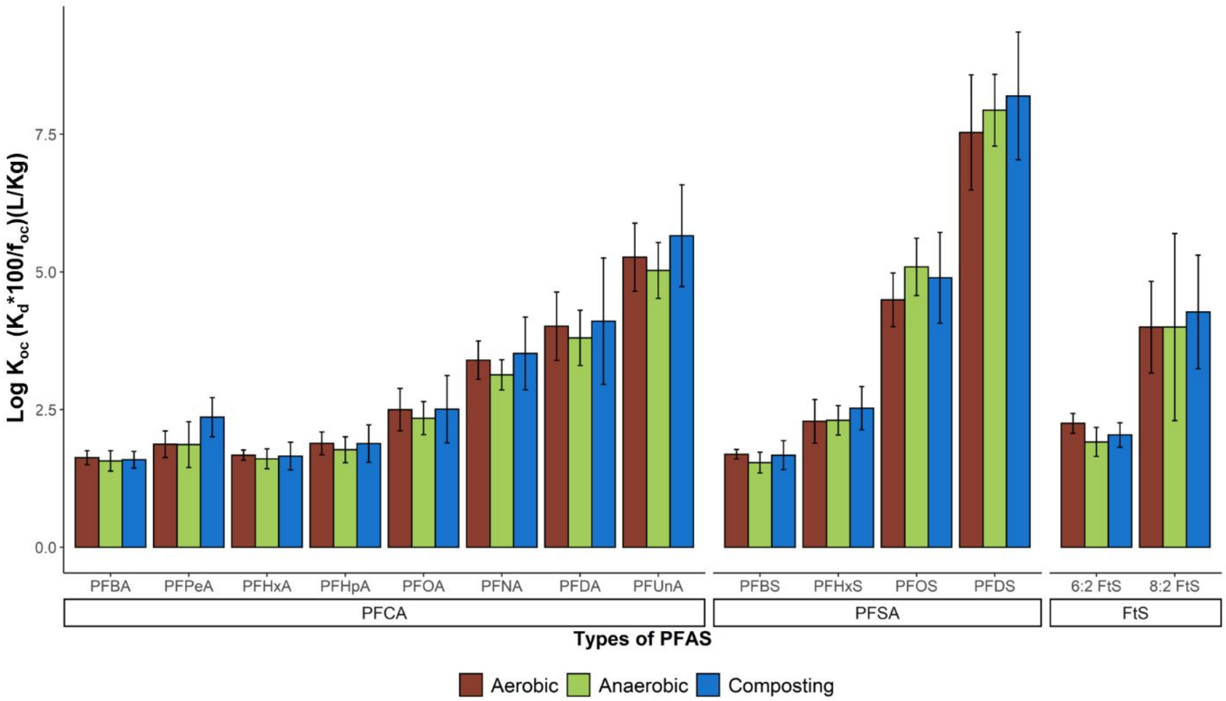


**Figure 7.** Log $K_{oc}$ vs PFAS. n=15 (experimental replicates) for each compound. $K_{oc}$ values were calculated by multiplying the $K_d$ times 100 and dividing by the fraction of organic carbon (%) (assumed 50% of mass from loss-on-ignition is carbon) for sampling days 1 and 91 of the microbial weathering experiment. Error bars represent standard deviation.

Many PFAS have been demonstrated to be associated with organic matter in solid matrices and are commonly removed from water through adsorption processes to organic material, like granular activated carbon. In Figure 7, it can be observed that when biosolids-water log $K_d$ values are adjusted for the fraction of organic carbon ($f_{oc}$), then the values are relatively consistent, suggesting that the $f_{oc}$ of these biosolids is a dominant variable affecting PFAS sorption, further explored in section 3.4. $K_{oc}$ is a soil organic carbon normalized adsorption coefficient and may not directly capture contributions from electrostatic interactions. While this may be the case, there is considerable variability in some of the values that suggests there are secondary explanatory variables that are responsible for change in $K_d$, for each compound. Some PFAS have been demonstrated to be amphiphilic, leading to partitioning to interfaces(96,97) since the PFAS tail is hydrophobic and the head group often polar and hydrophilic.(1) The main three mechanisms believed to be responsible for PFAS sorption to solids include hydrophobic effects (associations with organic carbon), electrostatic interactions (charge of functional group) (98), and interfacial partitioning. To date, the literature has demonstrated PFAS sorption to be most closely correlated with organic carbon content and pH.(99) Many of the sorption studies work under the assumption that there is equilibrium and sorption is reversible, while sometimes this is not the case depending on the compound and matrix.(100) Additionally, PFAS sorption can be concentration dependent, where they tend to sorb more strongly at low concentrations.(101) Lower pH has been shown to enhance sorption as well, and increases in ionic strength and the valency of the cations can actually increase PFAS partitioning to solids.(98,102) A recent study has shown that increased cation valency and ionic strength increase the sorption through a mechanism that increases the hydrophobic interactions between PFAS and solids.(103)

While microbial weathering has been demonstrated to play a key role in changing the quality of soils and biosolids, other environmental conditions such as rainfall, solar irradiation, and physical disturbances impact soil weathering, all which would be relevant in real-life weathering situations, but this study looks specifically at microbial weathering. As these solids are weathered, leaching potential can be altered and PFAS may be transported to the groundwater or be bioaccumulated. The microbial community may vary between stabilization methods but also over-time in weathering processes, which may impact how biosolids are decomposed and could lead to favorable environments for both PFAS and precursor PFAS transformations.

### 3.4 Linking PFAS $K_d$ to Factors that Changed during Microbial Weathering

It has been demonstrated that the biosolids characteristics, the PFAS compound-specific biosolids-water partitioning coefficients, and precursor PFAS have changed throughout the course of the experiment. To better explore the relationships between change in PFAS partitioning factors and the characteristics of the solid biosolid matrix they interact with, a few statistical tests were conducted. For each compound, single linear regressions were run for each environmental factor to explore the significance of each and to which level (S8-20). It became apparent through the single linear regressions that some environmental factors had significant relationships with $K_d$ values, but many were insignificant, not linearly related, and had non-normally distributed relationships. As a result, non-parametric Spearman's Rank Correlation Coefficients were calculated for each relevant environmental characteristic and $K_d$ values (Figure 8).

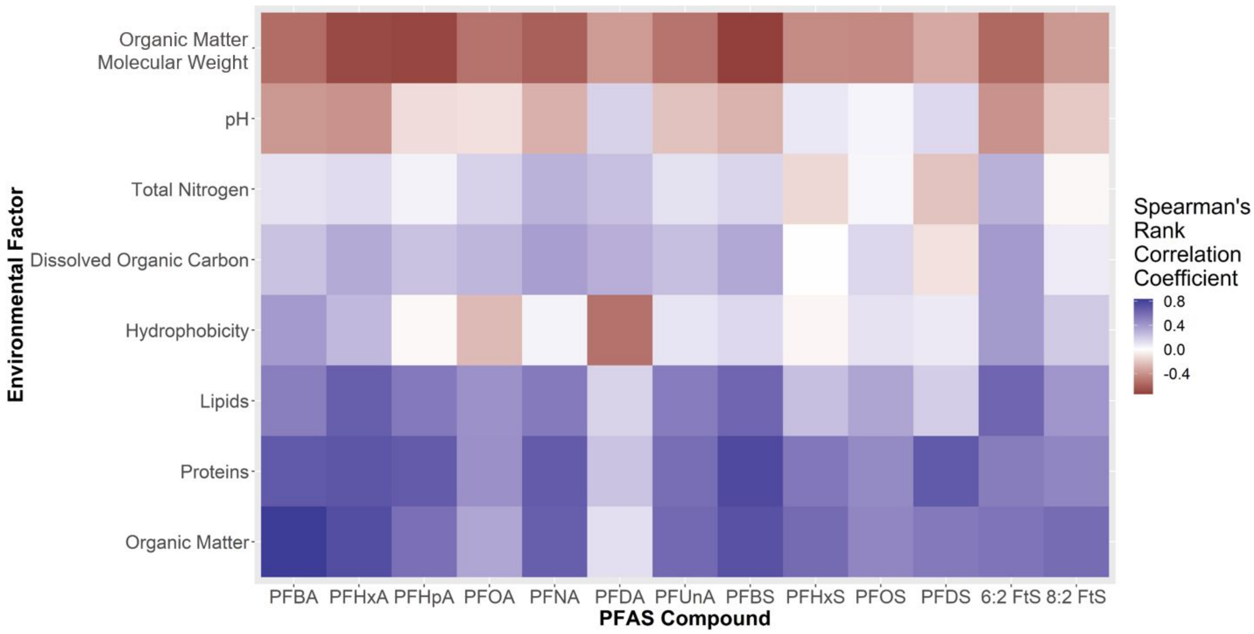


**Figure 8.** Results from Spearman's Rank Correlation Coefficients for relevant environmental factors related to the PFAS biosolids-water $K_d$ values. Strongly positively correlated factors are presented as dark blue and strongly negatively correlated factors are presented as dark red. PFPeA was analyzed for, but omitted, due to potential cross-contamination.

Spearman's rank correlation coefficient tests indicated that for the majority of the PFAS compounds, the most significant environmental factors that were positively correlated with the biosolids-water partitioning coefficient were proteins, lipids, and organic matter, while organic matter molecular weight was negative correlated with $K_d$, as indicated in Figure 8, with the full results in Supplementary Information, S22. Positively correlated results suggest that increases in the magnitude of those increased the PFAS partitioning to the solids (increased log $K_d$ value), while negatively correlated results had a nonlinear response or decrease in $K_d$ values. For organic matter molecular weight, there has been evidence that the organic matter molecular weight has a bimodal distribution with the smallest and largest particle sizes binding the greatest percentage of organic contaminant.(104) . Multiple linear regressions were run with "ols_step_all_possible", in R to calculate the adjusted-$R^2$ values for for the environmental factors of organic matter, organic matter molecular weight, proteins, and lipids (S23) for each compound. Since the adjusted $R^2$ resultant values were variable and $K_d$ values have been demonstrated to be strongly impacted by perfluorinated carbon chain length, head groups containing sulfur (PFSAs and FtSs), and compounds with unfluorinated regions (FtS)(33,105) , multiple linear regression model was built to include these variables. Since the multiple linear regressions varied greatly when PFAS characteristics were not built in (S23), the complete model was built with the significant environmental factors ($\rho > \pm 0.4$) determined using the compound-specific Spearman's Rank Correlation Coefficients, perfluorinated carbon chain length, presence of sulfur in the head group, and unfluorinated carbon chain sections, to allow for $K_d$ to be predicted for each PFAS compound from these environmental factors and compound characteristics in biosolids.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_{Sulf} X_{Sulf} + \beta_{Unfluor} X_{Unfluor} \tag{1}$$

The multiple linear regression model (Equation 1) was built using only the environmental factors that were determined to have significant linear relationships with PFAS partitioning ($K_d$) (Supplementary Materials, S8-23). In Formula 1, y = log biosolids-water biosolid-water partitioning coefficients $K_d$, $\beta_0$ = y-intercept, $\beta_{1-5}$= slope coefficients for explanatory variables (organic matter (%), lipids (%), proteins (%), Log organic matter molecular weight (Da), and perfluorinated alkyl chain length), $\beta_{Sulf}$ = slope coefficient for compounds with sulfur containing moiety, $x_{1-4}$= explanatory variables (solids characteristics), x5 = perfluorinated chain length, $X_{Sulf}$= dummy variable for compounds with sulfur containing moiety, and $X_{Unfluor}$ = dummy variable for compounds with unfluorinated region.

**Table 1.** Results from multiple linear regression model for slope coefficients, variables, intercept, and dummy variables.

| **Slope Coefficient ($\boldsymbol{\beta}_x$)** | **Explanatory Variable ($\boldsymbol{x}_x$)** |
|---|---|
| $\boldsymbol{\beta_0}$ = -1.52 | |
| $\boldsymbol{\beta_1}$ = -0.0255 | $x_1$ = Lipids (%) |
| $\boldsymbol{\beta_2}$ = 0.125 | $x_2$ = Proteins (%) |
| $\boldsymbol{\beta_3}$ 0.0024 | $x_3$ = Organic Matter (%) |
| $\boldsymbol{\beta_4}$ = -0.0637 | $x_4$ = Log Organic Matter Molecular Weight |
| $\boldsymbol{\beta_5}$ = 0.370 | $x_5$ = Perfluorinated Chain Length |
| $\boldsymbol{\beta}_{Sulf}$ = 0.423 | $X_{Sulf}$ = Sulfur Containing Moiety |
| $\boldsymbol{\beta}_{Unfluor}$ = 0.234 | $X_{Unfluor}$ = Unfluorinated Region (two carbon) |

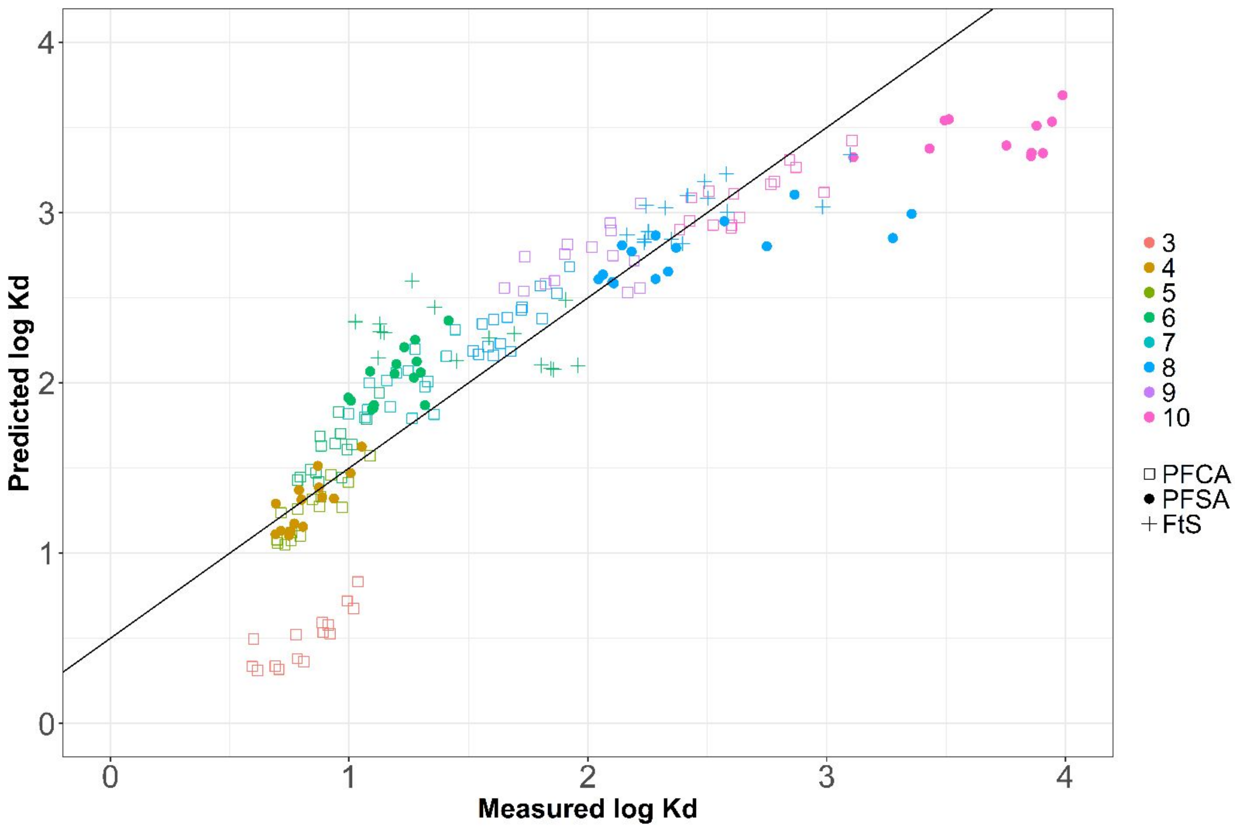


**Figure 9.** Predicted biosolids-water log $K_d$ against measured biosolids-water log $K_d$ values for multiple linear regression model. The shape of the marker signifies the class of PFAS defined by the headgroups and the number refers to the perfluorinated chain length of the compound. Adjusted $R^2 = 0.7941$, F-statistic = 107.1 on 7 and 187 DF, p-value <2.2e-16 values for the predicted multiple linear regression. 1:1 line with y-intercept of 0.5 is also displayed to show goodness-of-fit.

The purpose of the multiple linear regression built was to evaluate the impact that PFAS compound characteristics and environmental factors have on PFAS distribution throughout environmental biosolid samples between water and solids. Figure 9 presents the measured log $K_d$ values for each PFAS compound and the predicted log $K_d$ values for each compound through the multiple linear regression model. The adjusted $R^2$ value between the predicted and measured values was 0.7941, suggesting that this built model can predict $K_d$ for PFCAs, PFSAs, and FtS compounds by knowing the organic matter, proteins, lipids, and organic matter molecular weight in biosolids combined with the known compound characteristics. The practical results that come from this model build off what is already known about PFAS partitioning in the environment, that the compound characteristics have the most significant effects.(106) In this model, the most important drivers of partitioning for compound characteristics are sulfur containing moiety ($\beta = 0.423$), perfluorinated carbon chain length ($\beta = 0.370$), and unfluorinated chain length region ($\beta = 0.234$), in that order. For environmental drivers, the order of significant on partitioning impact was proteins ($\beta = 0.125$), log organic matter molecular weight ($\beta = 0.0637$), organic matter ($\beta = 0.0637$), and lipids ($\beta = 0.0225$). The results suggests that while PFAS compound characteristics impact PFAS partitioning behavior the greatest, changes in environmental conditions can have significant impacts as well and can be modeled. While the model shows a close connection between predicted partitioning coefficients and measured partitioning coefficients, there are outliers in the model. The outliers for the compounds study are PFBA, a short-chain PFAS compound, and the long-chain PFSA compounds. Lab-based modeling studies have established that there are limitations to modeling PFAS using equilibrium sorption parameters due to rate-limited sorption considerations.(107,108) PFBA sorption has a greater influence of ionic interactions than other PFAS compounds and long-chain PFAS compounds, specifically PFSAs can have non ideal sorption/desorption behavior during partitioning experiments.(109)

Microbial activity directly impacts the solids characteristics and can be monitored but understanding the PFAS interactions with the solids characteristics can provide more detailed insight into how PFAS partitioning in the environment and what components have the greatest effects. Ebrahimi et al. looked at solids characteristics of biosolids (proteins, lipids, and organic matter) through single variable linear regressions and a multiple linear regression and determined all three to have significant impacts on PFAS partitioning.(33) The model in this study however, includes organic matter molecular weight and PFAS characteristics, allowing for a more comprehensive and better fit model. A closer look at Figure 9 reveals that the log $K_d$ values of PFAS in biosolids end up grouping by the perfluorinated chain length and head group, shown by color and shape, as previously demonstrated. The significance of the results of the linear regression model is that if site characteristics are known and PFAS are believed to impact a site, then the PFAS partitioning and environmental impact can be better understood before measuring PFAS across all the matrices at the site, which can help to understand which environmental matrices will be affected by which PFAS and improve knowledge on their fate and transport.

## 4. Conclusions

This work provides evidence that microbial weathering processes that lead to degradation of organic matter and biopolymers (as indicated by lipase activity, protease activity, and oxygen consumption rate, as well as changes in lipid, protein, and organic content) can impact PFAS partitioning and increase leaching potential in biosolids. In addition to microbial decomposition of organic compounds, biotransformation of PFAS during microbial weathering was observed, with the extent of PFAA formation depending on the amount and presence of precursor-PFAS in the sample. In addition to increased PFAA concentrations, PFSAs or PFCAs can dominate the transformation products depending on the distribution of PFAS in the sample, however the exact mechanisms of these transformation are not well understood. The multiple linear regression model showed that it is possible to accurately predict compound-specific PFAS biosolids-water partitioning coefficients ($K_d$) values from the PFAS characteristics (perfluorinated alkyl chain length and sulfur containing moieties) and key characteristics of the biosolids (lipids, proteins, organic matter, and organic matter molecular weight) for a limited range of PFAS, although commonly detected. While the results from this work demonstrated that microbial activity impacts PFAS partitioning and we were able to predict $K_d$ values in these specific biosolid samples, future work is needed to predict $K_d$ values for a wider range of PFAS compounds (varying head groups, extent of fluorination, able to be biodegraded) in other environmental matrices and develop more knowledge on the mechanisms of the biotransformation processes occurring in the biosolids.

## Credit Author Statement

**Asa J Lewis:** Conceptualization; Methodology; Investigation; Data Curation; Writing – Original Draft, Writing – Review & Editing. **Farshad Ebrahimi:** Conceptualization; Methodology; Investigation; Data Curation: Writing – Review & Editing. **Erica R. McKenzie:** Funding Acquisition; Supervision; Conceptualization; Writing - Review & Editing. **Rominder Suri:** Funding Acquisition; Writing - Review & Editing; Supervision. **Christopher M. Sales:** Funding Acquisition; Supervision; Conceptualization; Writing - Review & Editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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