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## Per- and Polyfluoroalkyl Substances (PFAS) in Treated Sewage Sludge from Michigan Wastewater Treatment Plants

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# PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN TREATED SEWAGE SLUDGE FROM MICHIGAN WASTEWATER TREATMENT PLANTS

Garrett W. Link, M.S.

Western Michigan University, 2023

Concentrations, compositions, and variability of Per- and Polyfluoroalkyl Substances (PFAS) in sewage sludge are characterized using an extensive dataset of 350 samples from 190 wastewater treatment plants (WWTPs) across Michigan. All samples are comprised of final treated sewage sludge generated at the end of the wastewater treatment process.

Concentrations of  $\Sigma_{24}$  PFAS are log normally distributed with a range of 1 to 3200 ng/g dry wt. and of average  $108 \pm 277$  ng/g dry wt. Compounds with carboxyl and sulfonic functional groups comprised 29% and 71% of  $\Sigma_{24}$  PFAS concentrations, respectively, on average. Primary sample variability is associated with long-chain PFAS with higher tendency for partitioning to sewage sludge. Short-chain carboxylic compounds, most notably PFHxA, are responsible for secondary variability and are highly detected in 77% of the samples with average concentrations of  $10 \pm 30$  ng/g dry wt. Sulfonamide precursor compounds, namely N-MeFOSAA, generally contribute more mass to total PFAS than PFOS on average, a well monitored and regulated compound. Trends in PFAS enrichment were found to generally increase with compound hydrophobicity; however, the partitioning of PFAS onto sewage sludge in WWTPs is a complex process not easily described nor constrained using experimentally derived partitioning coefficients.

PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN TREATED SEWAGE SLUDGE FROM  
MICHIGAN WASTEWATER TREATMENT PLANTS

by

Garrett W. Link

A thesis submitted to the Graduate College  
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2023

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Garrett W. Link

## TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
I. INTRODUCTION .....	1
II. METHODOLOGY .....	5
Data Procurement.....	5
Sample Collection and Laboratory Analytical Methods.....	6
Sample Population Retained: Quality Assurance/Quality Control .....	7
Statistical Analyses .....	8
III. RESULTS AND DISCUSSION .....	8
Summary Statistics .....	8
Distribution of Sulfonamide Compounds.....	12
Trends in Compound Variance .....	13
PFAS Enrichment in Sewage Sludge .....	14
Analyte Limitations.....	16
4. CONCLUSIONS.....	17
REFERENCES .....	20

## LIST OF TABLES

1. Compilation of Previous PFAS in Sewage Sludge Studies .....	31
2. Summary Statistics .....	33
3. Compound Specific Statistics .....	34

## LIST OF FIGURES

1. Sulfonamide and $\Sigma_{24}$ PFAS concentration distributions .....	36
2. Principal component analysis loading plot .....	37
3. PFAS in sewage sludge enrichment factor .....	39
4. Detection frequency of PFAS in sewage sludge and/or wastewater influent .....	40



## I. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a diverse class of highly persistent, organic environmental pollutants containing at least one carbon-fluorine bond and cause adverse human health impacts at parts-per-trillion concentrations. Polyfluorinated precursor PFAS, most of which are excluded from analytical suites used for regulatory compliance, can transform to terminal perfluoroalkyl acids (PFAAs) in the environment (Vo et al., 2020; Berhanu et al., 2023; Coffin et al., 2023; Pelch et al., 2023), which are detected. PFAS, PFAAs in particular, persist in the environment because the high strength of the carbon-fluorine bond resists natural degradation mechanisms (Buck et al., 2011; Liu et al., 2022; Sørmo et al., 2023). As a result, PFAS cycle between anthropogenic treatment activities, such as wastewater treatment plants (WWTPs) and landfills, and the natural environment (Renou et al., 2008; Gallen et al., 2016; Helmer et al., 2022; Winchell et al., 2022; Titaley et al., 2023). Of the thousands of species presently identified, Buck et al. (2021) identified 256 commercially relevant PFAS compounds. Only two PFAAs are widely regulated and monitored in drinking water and wastewater; perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) (USEPA, 2022b; EGLE, 2022; OECD, 2023). However, dozens of other PFAS compounds are detected worldwide in every environmental medium (Wang et al., 2020; Death et al., 2021; Lesmeister et al., 2021; Xu et al., 2021; Sims et al., 2022). In response, PFAS release mechanisms and pathways to the environment are receiving increased attention (Garg, et al., 2020; Evich et al., 2022; Titaley et al., 2023).

WWTPs receive PFAS from myriad sources and treated effluent and sewage sludge are an important pathway of PFAS release to the environment (Sepulvado et al., 2011; AECOM,

2021; Munoz et al., 2022; Helmer, et al., 2022; Johnson, 2022). Sources of PFAS in influent include consumer products, landfill leachate, aqueous film-forming foam (AFFF) from municipal, commercial, and military activities, and industrial waste streams (Schaidler et al., 2017; Vo et al., 2020; Whitehead et al., 2021; Thompson et al., 2023; Vitale et al., 2023). Many precursors are readily transformed to PFAAs in WWTPs (Lenka et al., 2021, Helmer et al., 2022), but not all precursors are fully transformed to PFAAs, and the PFAAs are not degraded in WWTPs. Due to their tendency to partition to the solid organic phase, multiple PFAS accumulate in final treated sewage sludge generated at WWTPs (Venkatesan and Halden 2013; Arvaniti et al., 2014; Ateia et al., 2019; AECOM, 2021; Coggan et al., 2019; Li et al., 2021; Moodie et al., 2021; Munoz et al., 2022). Partitioning of PFAS to the solid organic phase increases with increasing carbon chain length due to increasing hydrophobicity (Arvanti et al., 2014; Rovero et al., 2021).

Disposal of the large quantities of treated sewage sludge generated in wastewater treatment is one of the most expensive problems facing WWTPs. The least expensive and most sustainable option is the beneficial reuse of treated sewage sludge as a soil amendment in agriculture (biosolids). In 2019, roughly 2.44 million dry metric tons (51%) of biosolids generated in the U.S. were land applied (USEPA, 2022b). However, elevated concentrations of PFAS has recently led to regulations aimed at reducing PFAS loading to agricultural soils (EGLE, 2021; Hall et al., 2021; USEPA, 2022d). In 2022, the U.S. State of Maine introduced a complete ban of the application of biosolids due to concerns about PFAS (MDEP, 2019). Regulation of PFAS in land-applied biosolids helps limit the potential for PFAS contamination of soils, and subsequently crops, livestock, dairy products and shallow groundwater systems (De Silva et al., 2020; Johnson, 2022; Lesmeister et al., 2021). Sewage sludge that cannot be land-applied as

biosolids, are disposed of in landfills, which is a much more expensive option, or through incineration. As in WWTPs, the landfill environment transforms precursors to PFAAs, but does not break down PFAAs (Allred et al., 2015; Liu et al., 2021). As a result, PFAAs introduced to landfills via sewage sludges may contribute to PFAS concentrations in landfill leachates (Renou et al., 2007; Helmer et al., 2022). Because landfill leachate is often sent offsite to WWTPs for treatment, a cyclical transport pathway is created and increases potential for discharge into the environment.

Several studies have investigated the distribution and composition of PFAS in biosolids-amended soils (Washington et al., 2010; Yoo et al., 2010; Sepulvado et al., 2011; EGLE, 2021b; Johnson, 2022). However, few have characterized PFAS occurrence and distribution in sewage sludge prior to land application. Because every land-application site is unique in its soil composition and climate, it is laborious and often cost-prohibitive to compare and evaluate PFAS signatures of land-applied biosolids for a multitude of sites. Analyzing PFAS signatures of freshly generated samples of sewage sludge from WWTPs is a more practical approach because the results can be universally applied to different soils and climatic conditions.

Most previous investigations in the literature have concluded that long-chain sulfonate PFAS compounds, such as PFOS, tend to be the dominant analytes in sewage sludges (Higgins et al., 2005; Sepulvado et al., 2011; Venkatesan and Halden, 2013; Munoz et al., 2022). However, some short chain carboxylate PFAS, such as perfluorohexanoic acid (PFHxA), are increasingly detected in sewage sludge (Thompson et al., 2023; Gravesen et al., 2023). Microbial-facilitated transformation of precursor compounds to PFAAs in sludge at various stages in WWTPs has

been observed (Zhao et al., 2013; Guerra et al., 2014; D'Agostino and Mabury, 2017) and is expected to continue after land application or disposal in a landfill.

Higgins et al. (2005) pioneered the characterization of PFAS in solid matrices by investigating the presence of 12 PFAS compounds in sediments and sludges. Despite the rapid progression of PFAS research, the scope of Higgins et al. (2005) remains comparable to modern sewage sludge studies. However, along with the studies that succeed Higgins et al. (2005), investigations of PFAS in sewage sludge have largely been limited in sample population (Sepulvado et al., 2011; Zhang et al., 2013; Gallen et al., 2016; Coggan et al., 2019; Letcher et al., 2020; Moodie et al., 2021) and/or analyte suite (Sepulvado et al., 2011; Venkatesan and Halden, 2013; Zhang et al., 2013; Armstrong et al., 2016; Gallen et al., 2016) (table 1 and S1). One of the largest sample populations in the literature (4981 samples from 1165 WWTPs) was analyzed by Ulrich et al. (2013); however, the analytical suite was limited to only 11 PFAS compounds. Notably absent from the analyte list were several sulfonates, such as perfluorosulfonic acids (PFSA), fluorotelomer sulfonates (FTSA), and perfluoroalkane sulfonamido substances, particularly N-MeFOSAA. Many researchers have demonstrated that these sulfonic compounds, which are PFOS precursors, constitute a major portion of PFAS in sewage sludge (Higgins et al., 2005; Sepulvado et al., 2011; Kim et al., 2012; Munoz et al., 2022). Lastly, some studies included samples from storage banks which do not reflect the PFAS compositions and signatures of modern sewage sludges (Munoz et al., 2022).

This study investigates the composition, distribution, and variability of PFAS in sewage sludge from the largest known sample population collected in the U.S. to date, representing a geographically diverse range of WWTPs serving communities of various sizes and industrial

activity. Samples were taken from 190 Michigan WWTPs and analyzed a suite of 24-29 analytes (depending on the year) that represent 7 PFASs, 11 perfluorocarboxylic acids (PFCAs), 3 sulfonamide compounds (N-MeFOSAA, N-EtFOSAA, and FOSA), 3 FTSAAs, as well as HFPO-DA (GenX), ADONDA, 9Cl-PF3ONS, and 11Cl-PF3OUdS (table S2) (EGLE, 2023). Statistical analyses are used to assess trends in carbon chain length, determine concentration ranges and detection rates, and evaluate compound variability.

## II. METHODOLOGY

### Data Procurement

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) has performed several statewide sampling campaigns and investigations of WWTP influent, effluent, and solid treatment residuals (i.e., sewage sludge) (EGLE, 2020; AECOM and EGLE, 2021). The first of three major investigations, the 2018 Evaluation of PFAS in Influent, Effluent, and Residuals of WWTPs in Michigan, included 85 aqueous and 71 solids samples from 42 WWTPs (AECOM, 2021). A second investigation, the 2021 Statewide WWTP and Biosolids/Sludge Study, involving 22 of the same WWTPs as the first study, included 85 aqueous (influent and effluent) and 44 solids samples from 37 WWTPs. A third and ongoing sampling campaign, Land Application of Biosolids Containing PFAS Interim Strategy, was implemented in the summer of 2021 and requires WWTP operators intending to land apply biosolids to sample and submit PFAS results of biosolids generated at their facilities prior to land application (EGLE, 2022a). Results of sample analyses may limit or prohibit disposal method (e.g., land application) and/or lead to source investigations (EGLE, 2022a). WWTP sampling frequency is contingent on

treatment volume, permit, if the WWTP has an Industrial Pretreatment Program (IPP) and previous interim strategy PFAS results (EGLE, 2022a). At the time of procurement, the Land Application of Biosolids Containing PFAS Interim Strategy dataset contains nearly 300 samples from 181 WWTPs. Collectively, 406 solids samples were made available for analysis through a data sharing agreement between EGLE and the authors of this work.

### Sample Collection and Laboratory Analytical Methods

EGLE, their contractors, and WWTP operators sample sewage sludge in accordance with the state “Biosolids and Sludge PFAS Sampling Guidance” (EGLE, 2022b). This sampling procedure involves the use of PFAS-free equipment, decontamination between samples, collection of field and equipment blanks, and preservation of collected samples at temperatures  $\leq 6^{\circ}\text{C}$  prior to laboratory analysis. The “PFAS Minimum Laboratory Analyte List” developed by the state of Michigan outlines the recommended analytes for sewage sludge (EGLE, 2023). The minimum analyte list increased from 24 to 28 in 2019 (Merit, 2019). Due to very low detection rates of the more recently analyzed PFAS, we only analyzed the initial 24 compounds included in all sewage sludge samples. Laboratories using 537 Modified, a modified version of the USEPA 537 Rev. 1.1 but not approved by the USEPA, and ASTM D-7968 with isotope dilution are recommended for PFAS analysis for solid matrices (EGLE, 2022b).

The use of 537 Modified and ASTM D-7968 for PFAS quantification in solid matrices involves solvent (e.g., methanol) extraction from the solid matrix followed by liquid chromatography-tandem mass spectrometry (LC/MS-MS) analysis (Prakash et al., 2017). Sample preparation under 537 Modified uses solid-phase extraction prior to LC/MS-MS analysis, while ASTM D-7968 centrifuges each sample prior to filtering and adjusts pH using an acetic acid

solution (ASTM, 2017). To meet the state recommended analyte list, modified versions of these methods must include additional surrogate standards. Inconsistent analyte recovery due to matrix effects often leads labs to make corrections using isotopic dilution (Parkash et al., 2017).

Approximately 55% of samples were analyzed using ASTM D-7968 (modified to include surrogates for the additional PFAS analytes recommended by EGLE), 42% using Modified 537, and 3% either did not list or used other methods. Although variations between laboratories may exist, the greatest variability likely occurs during the methanol extraction process, as the participating laboratories employ proprietary procedures and do not disclose specifics. Approximately 82% of samples in this study were performed by laboratories utilizing isotope dilution to account for varying degrees of analyte recovery.

#### Sample Population Retained: Quality Assurance/Quality Control

Data collected in the initial 2018 sampling campaign have undergone internal quality assurance and quality control (QA/QC) measures taken by EGLE and their contractors during preparation for state reports (AECOM and EGLE, 2021). For this project, QA/QC was performed on samples from the 2021 Statewide WWTP and Biosolids/Sludge Study and Land Application of Biosolids Containing PFAS Interim Strategy by comparing the compiled concentrations of each sample to those of the original laboratory reports. Additionally, any solid samples not representative of final treated sewage sludge (e.g., sludge sampled from primary clarifiers) (n=30) were excluded from this study.

A small subset of samples (n=8) was rejected due to analytical methods that were unverifiable or not intended for sewage sludge analyses (table S2). PFAS detection rates were also evaluated between laboratories to further validate data quality. One laboratory was found

to exhibit substantially above average detection rates for all analytes (figure S1) and this led to the removal of all samples associated with this laboratory (n=11). Results from the six remaining labs were determined to be acceptable and were included for a total study population of 350 samples.

### Statistical Analyses

Standard statistical analyses were based on carbon-fluorine moiety (i.e., carbon chain length), functional group, total and individual PFAS constituent concentrations, and compound detection rates. Long and short chain classification is consistent with previous studies (Buck et al., 2011), where long chain compounds are  $\geq C6$  and  $\geq C8$  for PFAS with sulfonic and carboxyl functional groups, respectively. Conversely, short chain PFAS compounds consist of  $\leq C5$  for sulfonic functional groups and  $\leq C7$  for carboxyl functional groups (table S2). Where relevant, sample concentrations reported below the laboratory reporting limit (RL) were considered non-detect (ND) and were converted to 0 ng/g concentrations. This method for evaluating censored data generally biases analytical results low (Akritas et al., 1994); however, we consider it appropriate as RLs were typically  $\sim 1$  ng/g or less. Variances of PFAS compounds in the sample population were analyzed using principal component analysis (PCA) generated and plotted through the Factoshiny package from the FactoMineR library in Rstudio.

## III. RESULTS AND DISCUSSION

### Summary Statistics

Total PFAS ( $\Sigma_{24}$  PFAS) statistics from 190 WWTPs within Michigan are provided in table 2. Sample concentrations ranged between  $\sim 1$  and 3200 ng/g dry weight (dry wt.) with all analytes



(n=24) detected at least once (table 3). The greatest contribution to  $\Sigma_{24}$  PFAS is from long chain compounds which account for 88% of PFAS in sewage sludge on average. The most frequently detected chain lengths include C8, C10, and C6 which contribute 70%, 9.6%, and 8.9% to  $\Sigma_{24}$  PFAS, respectively. Between the two functional groups included in the 24-analyte suite, sulfonic compounds dominate samples with an average of 71%. Although landfill leachates are identified as a considerable source of PFAS entering some of the study WWTPs (Gallen et al., 2016; Helmer et al., 2022), the short chain carboxyl chemistry associated with leachate is distinct from the long chain sulfonic composition found in sewage sludge of this study as well as others (refer to table 1).

Concentrations of  $\Sigma_{24}$  PFAS reported here are found to have a lower mean than other studies, yet the maximum concentration of 3192 ng/g dry wt. appears to be consistent (table 1). Our mean concentration of  $108 \pm 277$  ng/g dry wt. (table 2) is considerably less than most of the  $\Sigma$  PFAS reported in other studies which are as high as 617 ng/g dry wt. (table 1). Higher  $\Sigma$  PFAS concentrations for studies with larger analyte suites, such as Moodie et al. (2021), Munoz et al. (2022), and Thompson et al. (2023) are expected due to the inclusion of more compounds. To better understand this discrepancy, data representing sewage sludge from the supplementary data of Munoz et al. (2022) and Thompson et al. (2023) were extracted and evaluated. In the case of Munoz et al. (2022), approximately 102 of the 160 analytes were detected at least once in the studies sewage sludge samples. Similar to what is found in Michigan (table 3), the greatest contributions to  $\Sigma$  PFAS in those samples include PFOS and EtFOSAA; however,  $\Sigma$  PFAS contributions from PFOSAmS and 6:2 FTAB are 18% and 13%, respectively, which are not included in our study analyte suite. Likewise, percent contribution to

$\Sigma$  PFAS of 36% and 12% were observed for 6:2 and 8:2 diPAP in samples from Thompson et al. (2023). Another reason for the lower mean  $\Sigma$  PFAS values in this study is the inclusion of samples from WWTPs of all sizes and industrial backgrounds. Unlike other studies which focus on sewage sludge samples from industrially impacted WWTPs, samples in this study are collected from a diverse set of 190 WWTPs that include facilities serving communities as small as 700 residents, providing a more realistic representation of PFAS concentrations in sewage sludge across an entire U.S. state.

Compound-specific concentration ranges reported in table 3 are also relatively consistent with other published values (table 1). Armstrong et al. (2016) suggested legacy 3M compounds (i.e., PFOS) in sewage sludge have not substantially increased or declined since the early 2000s which is consistent with our study data. The PFOS concentration range of ND-2150 ng/g dry wt.,  $40 \pm 179$  ng/g dry wt. mean concentration, and 95% detection rate indicates that it is consistently a leading constituent in 2018-2022 sewage sludge samples, comparable to many early studies (Higgins et al., 2005; Sepulvado et al., 2011; Venkatesan and Halden, 2013) despite the voluntary manufacturing phase out of PFOS and PFOA by 3M in the early 2000s (Buck et al., 2011). More recent studies report a narrower range in PFOS concentrations; however, many are sampled from Australian WWTPs which generally receive substantially less PFAS loading in wastewater influent than the U.S. (Coggan et al., 2019; Moodie et al., 2021; Munoz et al., 2022).

Munoz et al. (2022) identified FTSAAs as widespread legacy PFAS replacement compounds, but their findings are inconsistent with the data in this study as well as others (Schultz et al., 2006; Moodie et al., 2021). After isolating the sewage sludge data from Munoz et

al. (2021) (as it contains several organic waste products), we found  $\Sigma_{15}$  FTSA contribute just over 2% of total PFAS mass. We report a maximum concentration of 6:2 FTSA exceeding 2000 ng/g dry wt., but this was isolated to a single WWTP with heavy industrial inputs. Study data and those of past studies agree on the ubiquitous occurrence of sulfonamide compounds (i.e., N-MeFOSAA, N-EtFOSAA, and FOSA) in sewage sludge which are known PFOS precursors (Higgins et al., 2005; Sepulvado et al., 2011; Moodie et al., 2021; Munoz et al., 2022). These trends are explored further in the following section.

Long and short chain PFASs are most ubiquitously detected (96%) followed by sulfonamides (94%) and PFCAs (89%). This aligns well with many studies reporting 100% detection for several PFSA compounds – PFOS being most ubiquitously reported (Higgins et al., 2005; Sepulvado et al., 2011; Arvaniti et al., 2012; Venkatesan and Halden, 2013). As a legacy PFAS, PFOS detections are expected to decrease over time, leading to diminished detection rates. As previously mentioned, the presence of PFOS in wastewater treatment has not substantially declined. We report 5% less frequent detections for this compound than previous studies which is most likely attributed to the diverse nature of the WWTPs included in this study, many of which service small communities and do not receive industrial wastewater or landfill leachate.

Of the highly detected compounds, the short chain carboxyl chemistry of PFHxA appears out of place at 76% and is roughly on par with long chain carboxyls (79%). Some partitioning of PFHxA onto sewage sludge certainly occurs, but higher detection and concentrations of PFHxA than PFOA (a longer chain compound with stronger partitioning behavior) is unexpected. Sewage sludge samples with higher PFHxA concentrations may indicate WWTPs that receive

larger volumes of landfill leachate, which tends to abound in PFHxA (Gallen et al., 2016; Lang et al., 2017; Coffin et al., 2022; Helmer et al., 2022). Other studies have observed similar trends (Ma and Shih, 2010; Kunacheva et al., 2011; Venkatesan and Halden, 2013; Moodie et al., 2021; Munoz et al., 2022) and many suggest the high frequency of detection of PFHxA may be due to the release of this compound by the transformation of precursors (e.g., fluorotelomer alcohols (FTOHs), FTSAAs, and diPAPs), which is facilitated by microbial activity in activated sludge systems (Liu and Avendaño, 2013; Zhao et al., 2013; Guerra et al., 2014; D'Agostino and Mabury, 2017). Expanding the PFAS analyte suite to include known PFHxA precursors would provide further insight into the importance of precursor transformation as a mechanism impacting the detection and relative abundance of PFHxA.

#### Distribution of Sulfonamide Compounds

The sum of the three sulfonamide compounds measured ( $\Sigma_3$  sulfonamides = [FOSA+N-MeFOSAA+N-EtFOSAA]) is detected as ubiquitously in sewage sludge as PFOS (table 3). Further investigation of  $\Sigma_3$  sulfonamide concentration distribution (figure 1, a-c) reveals that these compounds collectively contribute greater mass to  $\Sigma_{24}$  PFAS than PFOS. Of these compounds, N-MeFOSAA is most ubiquitously detected (92%), with a maximum concentration of nearly 200 ng/g. N-EtFOSAA was the second most ubiquitously detected (87%), with a maximum concentration exceeding 460 ng/g dry wt. (table 3). Comparing the concentrations of sulfonamide compounds reported in early studies in the U.S. (Higgins et al., 2005; Schultz et al., 2006; Sepulvado et al., 2011) to those found in this study, with samples collected from 2018-2022, shows that sulfonamides are just as prevalent, if not more, than they were in the years 1998-2007.

Transformation of sulfonamide PFAS to terminal PFAAs, particularly PFOS, has been observed to be microbially mediated in both activated sludge (Rhoads et al., 2008) and in soils (Avendano and Liu, 2015). Given this, and the quantity of sulfonamide PFAS measured in the sewage sludge studied here (figure 1.b), suggests that PFOS generation likely occurs anywhere in the environment these precursors are found. Thompson et al. (2023) showed that the quantity of PFAAs in sewage sludge sampled as they are generated at WWTPs is biased low, because precursors not analyzed will continue to breakdown over time and form PFAAs. As mentioned in Section 3.1, expanding the analyte suite to include more intermediary precursors to PFOS (e.g., FOSAA and N-EtFOSE) would greatly improve the characterization of PFAS in sewage sludge and lead to more reliable estimates of PFAAs likely to be generated after disposal.

#### Trends in Compound Variance

Evaluation of the loading plot generated during principal component analysis (PCA) reveals several interesting trends regarding contributions of variance by each PFAS compound. Collectively, the first two dimensions, or principal components (PC1 and PC2, figure 2), describe approximately 35% of variance. The variation associated with PC1 is attributed largely to long chain carboxyl compounds of chain lengths C8-C12 (note  $\cos^2$  values in figure 2) which trend together along PC1 in quadrant 4. Almost perpendicular to this cluster ( $\sim 88^\circ$ ) is a tighter cluster which trends along PC2 in quadrant 1. The compounds which make the greatest contributions ( $\cos^2$ ) to PC2 are short chain carboxyl compounds (C4-C7) and PFOS. Although the physiochemical properties of PFOS differ from the other compounds in this group, it likely trends with this secondary variance due to the nearly ubiquitous detection of PFOS (95%).

Otherwise, there is a clear distinction between the long and short chain carboxyl chemistry of PC1 and PC2, respectively.

Munoz et al. (2022) performed PCA on PFAS in organic waste products (which included sewage sludge). Although their PC1 and PC2 describe more variance than this study (~47%), there are several important differences that may explain their higher variance and that make it impossible to directly compare the results of the two studies. Most importantly, Munoz et al. (2022) studied organic waste products which included sewage sludges, sludges mixed with compost of green waste, manures, and industrial sludges and ashes. Unlike this study, their PCA effectively describes variance of PFAS between multiple solid matrices – not of sewage sludge (i.e., final treated solid residuals from WWTPs). Additionally, unlike here, the waste products studied in Munoz et al. (2022) had been sampled over a period of several decades, which also imposes a temporal variability on the PCA captured. These factors, along with the limited sample size (n=47) in Munoz et al. (2022), means the variance captured in their PCA represents a substantially different statistical implication.

#### PFAS Enrichment in Sewage Sludge

To evaluate the partitioning behavior of PFAS between wastewater influent and sewage sludge, samples of aqueous influent were paired with samples of sewage sludge from the same facility and taken on the same date (n=73 pairs). The log ratio of sewage sludge concentration (converted to ng/kg, parts-per-trillion (ppt)) to influent aqueous concentration (ng/l, ppt) is plotted against two proxies for hydrophobicity (figure 3a-b). The degree to which a PFAS compound favors the solid phase over the liquid phase determines the degree to which that PFAS compound will be enriched in sewage sludge. Figure 3a plots the log ratio of sewage

sludge/influent concentration for each PFAS compound against log values of the experimental octanol-water partition coefficients ( $\log K_{ow}$ ) reported in the literature (Pancras et al., 2016). figure 3b plots the same ratio against carbon-fluorine units (i.e., the number of  $CF_2$  units, or carbons with  $\geq 2$  fluorine bonds). In both plots, the minimum ratio values for each compound/class exhibit the expected trend of longer-chain, more hydrophobic PFAS compounds partitioning to a greater extent to sewage sludge. Mean and maximum values do not depict this trend as strongly, likely due to a combination of detection limitations and sample size. However, such analyses are complicated by the fact that values for  $K_{ow}$  in the literature for individual PFAS compounds vary dramatically.

Several compounds have limited representation in the figure 3 plots, due to non-detection in either aqueous or solid matrices. This was observed most frequently for the less common, longer chain compounds with very low solubilities, which made non-detection in the aqueous phase more likely. As shown in figure 4c-d, many long chain compounds are below detection limits in the influent and are almost exclusively detected in sewage sludge. For example, PFUnDA was frequently detected in sewage sludge samples (~80% in this case, figure 4a) but was never detected in aqueous samples (figure 4c). This may be accounted for partially by the transformation of PFAS precursors not included in the analyte suite but is much more likely due to enrichment of these PFAS in sewage sludge. Although the concentration factor cannot be explicitly quantified, given that aqueous reporting limits are typically ~1 ppt, we can generally state that a compound such as PFUnDA concentrates from less than 1ppt in aqueous influent to  $\sim 1.4 \pm 5.2$  ppb in sewage sludge (table 3) – an enrichment of at least three orders of magnitude.

## Analyte Limitations

To our knowledge, this study compiles the largest sewage sludge sample population analyzed for PFAS in the United States, and on a global scale is second only to Ulrich et al. (2013). This sample size captures the diversity of WWTPs throughout the state of Michigan (i.e., industrial impacts and lack thereof, absence/presence of contributions from landfill leachate, and community size), and is also representative of PFAS signatures in modern (2018-2022) sewage sludge. PFAS detection and quantification is limited to the analyte suite recommended by EGLE and lacks several important PFAA precursors were shown in other studies to be frequently detected at appreciable concentrations.

The minimum PFAS analyte list increased from 24 to 28 analytes after the initial sampling campaign and is reflected in samples collected after 2019 (Merit, 2019). Newly added are HFPO-DA (GenX), ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS. PFECHS was also included in the EGLE 2021 Statewide WWTP and Biosolids/Sludge Study; however, it was detected only twice in samples taken from the same WWTP. Between the two samples, the mean concentration of PFECHS was only  $1.17 \pm 0.15$  ng/g and suggests the exclusion of this compound has a negligible impact on the scope of this work. HFPO-DA, 11Cl-PF3OUdS, 9Cl-PF3ONS, and ADONA (n=336, 96% of the samples) may be considered equally negligible with detection rates of 3.6%, 5.4%, 4.8% and 3.3%, respectively, with nearly all concentrations slightly above detection limit.

Perhaps less negligible are polyfluoroalkyl phosphate diesters (diPAPs), fluorotelomer alcohols (FTOHs), and fluorotelomer carboxylic acids (FTCAs). Although we are unable to determine their relevance in Michigan WWTPs, Yoo et al. (2010) detected FTOHs in biosolids-amended soils, suggesting their prevalence in raw sewage sludge. Moodie et al. (2021) reported



the presence of FTCAs and diPAPs in treated sewage sludge with each class having over 90% detection rate and mean concentrations of 24 and 140 ng/g, respectively. Similar findings are reported by D'eon et al. (2009), Fredriksson et al. (2022), and Thompson et al. (2023).

Although a 24-analyte suite is smaller than that used by Munoz et al. (2022), Moodie et al., (2021), and Thompson et al. (2023), this study contains a larger analyte suite than roughly 87% of the sewage sludge studies reviewed. Furthermore, many regulatory suites, including the upcoming USEPA Method 1633 (USEPA, 2022a), do not include many of the compounds missing from our suite (e.g., diPAPs and FTOHs). While this does not justify the absence of relevant PFAS compounds in this study, it brings to light the challenges facing this area of research going forward. We identify several instances where a more comprehensive analytical suite that includes FTOHs, FTCAs, and diPAPs would improve our characterization and understanding of PFAS in sewage sludge. Not only do these PFAS represent PFAA precursors, but quantifying their presence in WWTP matrices can improve mass balance estimates (Vitale et al., 2023). Currently, studies must attribute discrepancies between influent and effluent PFAS mass to error. Although it can be inferred that an increase in PFAA mass is due to transformations within WWTPs, including the aforementioned precursors would serve as quantitative evidence and aid in constraining error.

#### 4. CONCLUSIONS

The presence of PFAS in WWTP influent, effluent and sewage sludge has been well established for at least 2 decades, yet there is still considerable progress to be made. In this study, we developed a comprehensive baseline for the occurrence of PFAS in sewage sludge,

determined how these compounds vary throughout a geographically significant region (i.e., the state of Michigan), and address the need for additional analytes to better understand the implications associated with our results. The following are the key findings from this study:

- Sewage sludge studies relying on multiple data sources to form large sample populations require careful consideration of the contributing laboratories and the analytical methods to ensure comparability and statistical integrity of the data. Furthermore, it is crucial to exclusively focus on samples which represent fully processed sludges (i.e., biosolids) at the end of the wastewater treatment to best represent PFAS concentrations prior to disposal.
- Consistent with previous studies, sewage sludge from Michigan WWTPs are dominated by long-chain sulfonic PFAS compounds, although select short chain carboxyl compounds (namely PFHxA) are frequently detected. Terminal short chain carboxyl compounds may represent the occurrence of transformations in activated sludges and should receive additional attention in future investigations.
- PFOS remains a leading PFAS constituent in 2018-2022 sewage sludge throughout Michigan and was detected in 95% of the samples despite the voluntary phase-out in manufacturing in the early 2000s.
- Sulfonamide compounds substantially contribute to  $\Sigma_{24}$  PFAS and are as ubiquitously detected as PFOS. Considering the implications of sulfonamide transformations to PFOS after disposal, additional research and regulatory focus on these compounds is needed.

- State-wide variability of PFAS compounds in sewage sludge is primarily controlled by long-chain carboxyl compounds of chain lengths C8-C12, and secondarily controlled by short chain carboxyls and PFOS.
- Our data indicate trends in sewage sludge PFAS enrichment generally increase with compound hydrophobicity; however, the partitioning of PFAS onto sewage sludge in WWTPs is a complex process not easily described nor constrained using experimentally-derived partitioning coefficients (i.e.,  $K_{ow}$  and  $K_d$ ).

Despite the magnitude of the sample population included in this study, further work is necessary to fully develop our understanding of PFAS cycling and occurrence in WWTPs, sewage sludge, and the environmental compartments they impact. We encourage researchers, regulators, and the like to improve upon these findings through the addition of relevant precursors, such as diPAPs, FTCAs, and FTOHs, and to sample fully processed sludges as frequently as financially possible.

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TABLES

Table 1. Compilation of previous studies investigating PFAS in biosolids (n=30 studies) with select results relevant to the results of this study. A larger version of this table (which includes the full suite of analytes and number of samples) can be found in the supplementary information (table S4). All concentrations are in ng/g dry weight (or have been converted for comparability).

Study (Country)	No. of Analytes	Sampling Year(s)	Mean $\Sigma$ PFAS	$\Sigma$ PFAS Range	PFHxA	EtFOSAA	MeFOSAA	PFOS
Venkatesan and Halden, 2013 (U.S.)	13	2001	539	NA	3-12	NA	NA	308-618
D'eon et al., 2009 (Canada)	13	2002	NA	NA	NA	NA	NA	0.1-460
Higgins et al., 2005 (U.S.)*	12	1998-2004	617	176-3390	NA	ND-544	ND-154	14-2610
Schultz et al., 2006 (U.S.)	12	2004	NA	NA	NA	91-100	130-140	81-160
Sinclair et al., 2006 (U.S.)	15	2004-2005	NA	NA	NA	NA	NA	26-65
Loganathan et al., 2007 (U.S.)*	8	2005	166	17-382	NA	NA	NA	8.2-110
Sepulvado et al., 2011 (U.S.)	16	2004-2007	436	NA	NA	42-72	63-143	80-219
Yu et al., 2009 (Singapore)	2	2006-2007	NA	NA	NA	NA	NA	31-702
Armstrong et al., 2016 (U.S.)	12	2005-2013	NA	NA	ND-21	NA	NA	ND-68
Ma et al., 2010 (Hong Kong)	19	2008	NA	NA	0.3-28	NA	NA	3-7304
Zhang et al., 2013 (China)*	16	2009	19	6.8-66.7	NA	NA	NA	0.9-22.5
Kunacheva et al., 2011 (Thailand)	10	2009	NA	NA	0.3-100	NA	NA	396-526
Gómez-Canela et al., 2012 (Spain)	5	-	NA	0.5-39	NA	NA	NA	ND-5
Kim et al., 2012 (Korea)	15	2010	NA	NA	NA	NA	NA	15-260
Arvaniti et al., 2012 (Greece)	4	2009-2010	NA	NA	0-62	ND-11.2	ND-9.9	2-17
Yan et al., 2012 (China)	14	2010	NA	126-809	0.5-100	NA	NA	28-173
Ruan et al., 2015 (China)	16	2010-2011	NA	NA	NA	NA	NA	ND-218
Ulrich et al., 2016 (Germany)	11	2008-2013	NA	NA	ND-680	NA	NA	ND-7600
Sindikou et al., 2013 (Nigeria)	10	2012	NA	NA	ND-0.25	NA	NA	ND-0.5
Alder et al., 2015 (Switzerland)	10	2011	NA	NA	1-91	NA	NA	197-324

Chirikona et al., 2015 (Kenya)	9	2013	NA	NA	ND-0.56	NA	NA	ND-0.67
Navarro et al., 2016 (Spain)	20	-	NA	NA	ND-32	NA	NA	ND-84
Gallen et al., 2016 (Australia)*	14	2014	128	0-403	ND-12	NA	NA	0-370
Fredriksson et al., 2022 (Sweden)*	79	2004-2017	337	49.7-1124	ND-7.2	ND-49	ND-21	6.2-41
Stahl et al., 2018 (Germany)	14	2010-2016	NA	NA	ND-16	NA	NA	ND-698
Munoz et al., 2021 (Australia)**	160	1976-2017	307	13-900	0.6-3.2	1.9-582	2.2-41	0.35-284
Coggan et al., 2019 (Australia)	21	2017	34	2-130	ND-13	NA	NA	ND-90
Letcher et al., 2020 (Canada)*	24	2012-2017	30	3.4-53	0.2-4.7	NA	NA	0.49-50
Moodie et al., 2021 (Australia)*	44	2018	250	NA	ND-17	ND-50	ND-56	0.9-190
Thompson et al., 2023 (U.S.)***	92	2021	78-584	NA	15	3.9	6	19

NA – not analyzed

ND – non-detect (includes values <MDL, <RL, and <LOQ).

\*reported mean  $\Sigma$  PFAS and/or range

\*\*determined in this study using select samples classified as sewage sludge from supporting materials.

\*\*\* mean concentration used when range is unavailable



Table 2. Summary statistics of total PFAS in sample population (n=350). The % values refer to the percent of the samples in which each chain length and functional group were above detection. Mean concentrations include  $\pm$  standard deviation.

Chain Length		Functional Group		Concentration $\Sigma$ PFAS (ng/g dry wt.)			
Short	Long	Carboxyl	Sulfonic	Minimum	Mean	Median	Maximum
12%	88%	29%	71%	1.4	108 $\pm$ 277	49	3192
C4	C5	C6	C7	C8	C9	C10	C11
2.3%	3%	8.9%	0.3%	70%	1%	9.6%	1.1%
C12	C13	C14					
2.7%	0.2%	0.6%					

Table 3. Compound specific statistics in sample population (n=350) organized by PFAS class and sub-class (long and short chain designation). Class and sub-class rows describe collective statistics and are bolded. Concentrations are all on a dry-weight basis and mean values include  $\pm$  standard deviation.

Class	Homologue	Detection Rate (%)	Mean (ng/g dry wt.)	Median (ng/g dry wt.)	Maximum (ng/g dry wt.)
<b>PFSA</b>		<b>96</b>	<b>43 <math>\pm</math> 180</b>	<b>14</b>	<b>2158</b>
<b>Long chain</b>		<b>95</b>	<b>42 <math>\pm</math> 180</b>	<b>12</b>	<b>2158</b>
	PFDS	36	1.8 $\pm$ 5.6	0	54
	PFNS	1.7	0.0 $\pm$ 0.3	0	4.7
	PFOS	95	40 $\pm$ 179	10	2150
	PFHpS	1.4	0.0 $\pm$ 0.4	0	7.4
	PFHxS	14	0.3 $\pm$ 1.2	0	11
<b>Short chain</b>		<b>21</b>	<b>1.2 <math>\pm</math> 3.5</b>	<b>0</b>	<b>28</b>
	PFPeS	0.3	0.0 $\pm$ 0.1	0	1.9
	PFBS	21	1.2 $\pm$ 3.5	0	28
<b>PFCA</b>		<b>89</b>	<b>28 <math>\pm</math> 51</b>	<b>11</b>	<b>389</b>
<b>Long chain</b>		<b>79</b>	<b>18 <math>\pm</math> 35</b>	<b>6.5</b>	<b>298</b>
	PFTeDA	21	1.0 $\pm$ 11	0	200
	PFTTrDA	10	0.4 $\pm$ 2.5	0	35
	PFDoDA	62	2.4 $\pm$ 4.8	1.3	55
	PFUnDA	37	1.4 $\pm$ 5.2	0	78
	PFDA	73	6.8 $\pm$ 13	2.7	120
	PFNA	36	1.2 $\pm$ 3.8	0	40
	PFOA	63	4.8 $\pm$ 11	1.2	96
<b>Short chain</b>		<b>77</b>	<b>10 <math>\pm</math> 30</b>	<b>3.0</b>	<b>377</b>
	PFHpA	14	0.8 $\pm$ 5.4	0	74
	PFHxA	76	5.1 $\pm$ 12	2.5	162
	PFPeA	39	3.4 $\pm$ 11	0	114
	PFBA	15	1.1 $\pm$ 4.1	0	38
<b>Sulfonamide</b>		<b>94</b>	<b>25 <math>\pm</math> 45</b>	<b>14</b>	<b>605</b>

	MeFOSAA	92	$13 \pm 18$	8.5	190
	EtFOSAA	87	$10 \pm 30$	4.2	461
	FOSA	49	$1.7 \pm 4.6$	0	73
<b>Fluorotelomer</b>		<b>27</b>	<b><math>11 \pm 122</math></b>	<b>0</b>	<b>2186</b>
	8:2 FTSA	19	$1.2 \pm 8.0$	0	136
	6:2 FTSA	17	$9.8 \pm 114$	0	2050
	4:2 FTSA	0.3	$0.0 \pm 0.5$	0	9.3

## FIGURES

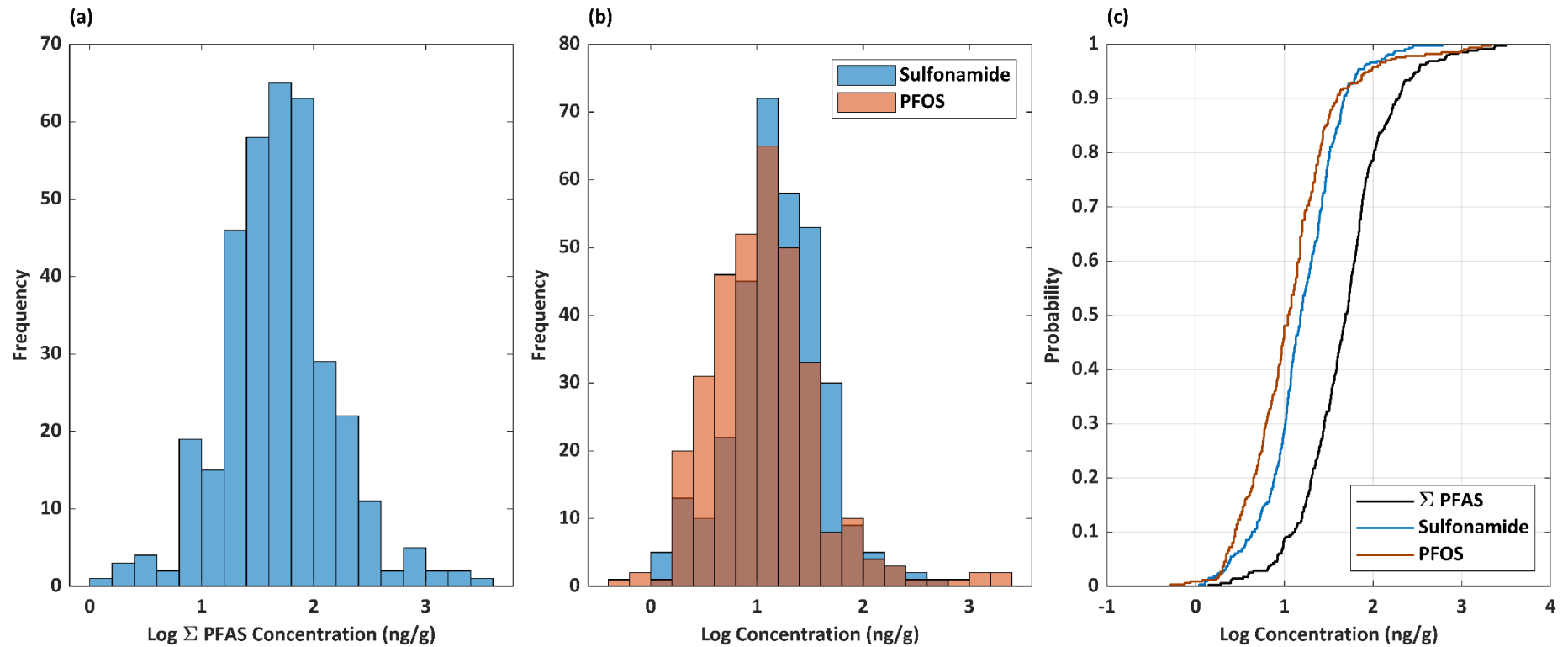


Figure 1. (a) Lognormal distribution of total PFAS concentrations ( $\Sigma$ 24 PFAS) in sample population (n=350), (b) lognormal distributions of Sulfonamide compounds (MeFOSAA, EtFOSAA, and FOSA) and PFOS in sample population (n=350), and (c) cumulative distribution function of all detected  $\Sigma$ 24 PFAS (n=350), Sulfonamide (n=328), and PFOS (n=333) values.

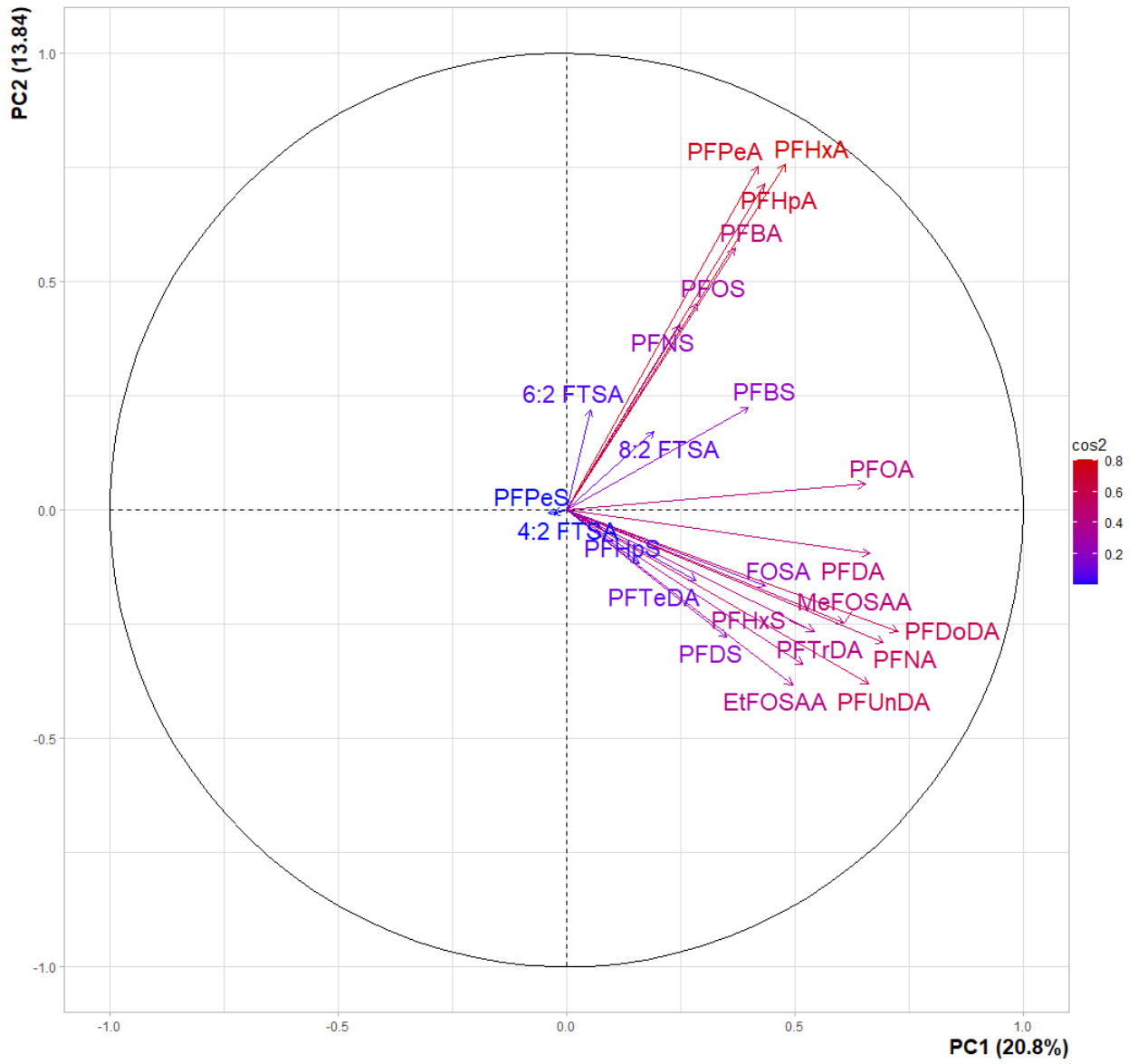


Figure 2. Loading plot of constituents contributing to principal component analysis (n=350). Vectors and  $\cos^2$  values describe contributions to principal components 1 and 2 (PC1 and PC2, respectively). Note the dominance of long-chained compounds along PC1 and shorter-chained compounds along PC2.

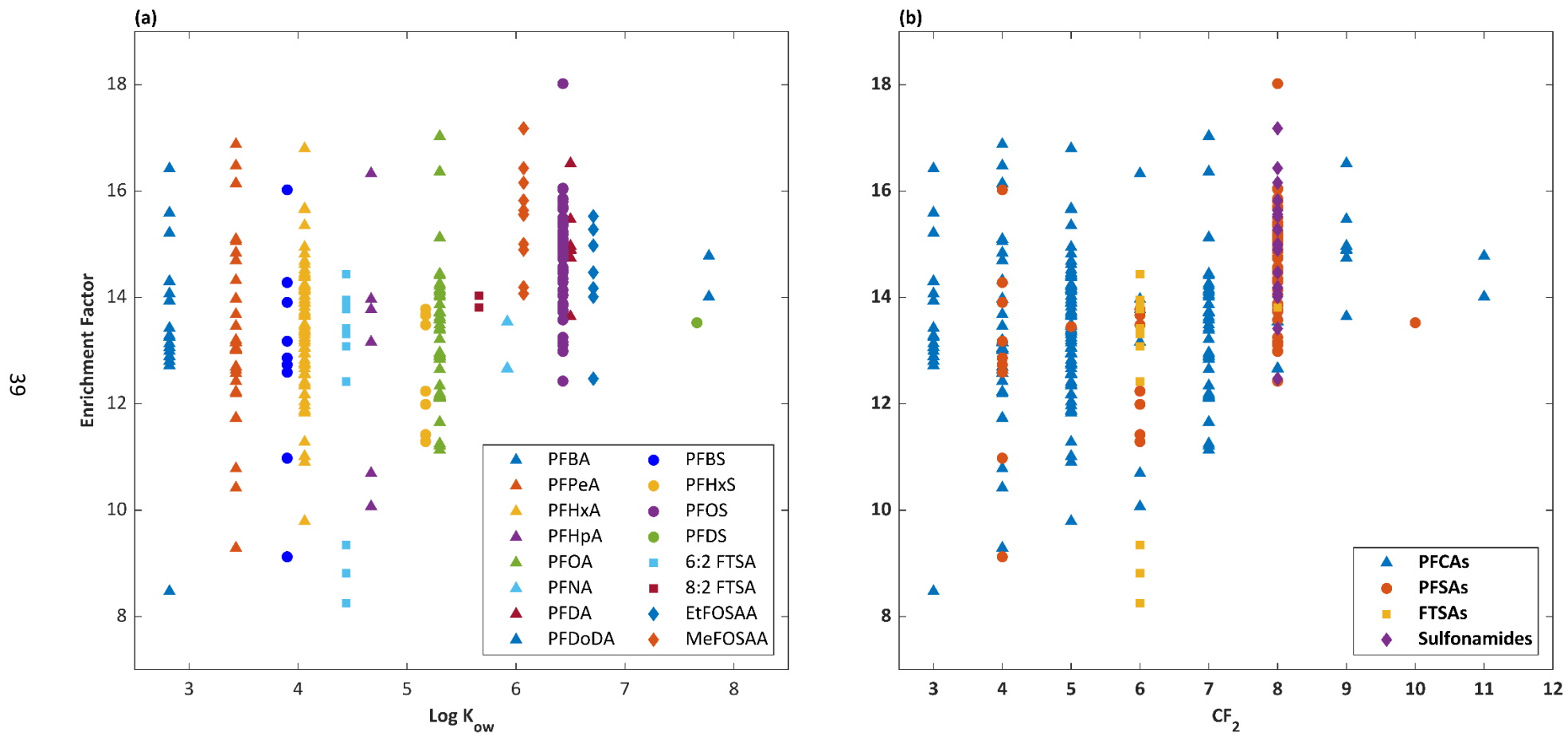


Figure 3. Ratio of biosolids concentration (ng/kg) to influent concentration (ng/l) on a logarithmic scale describing the enrichment of PFAS on biosolids versus (a) experimental log  $K_{ow}$  values and (b) carbon-fluorine units ( $CF_2$ ).

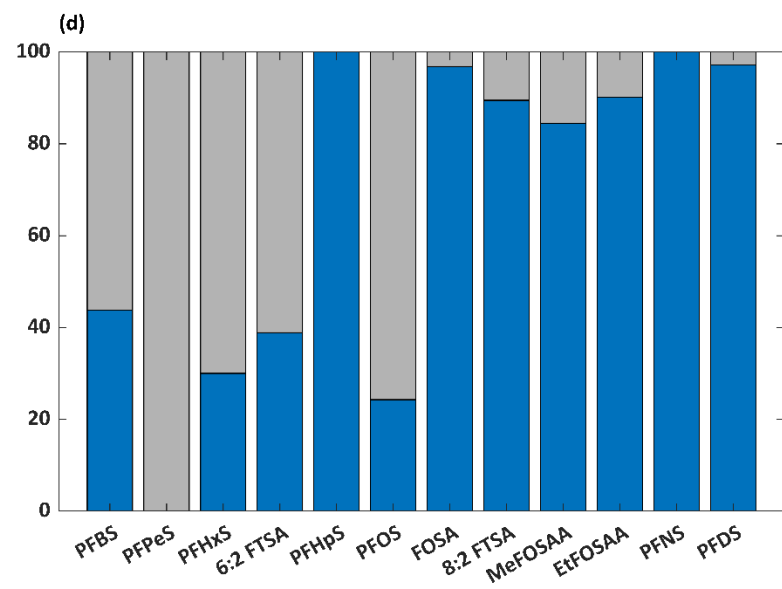
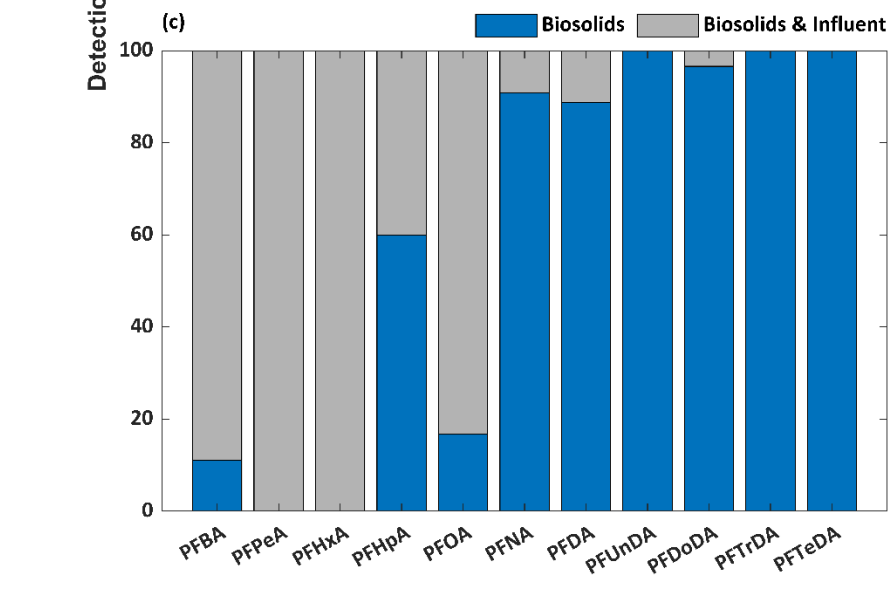
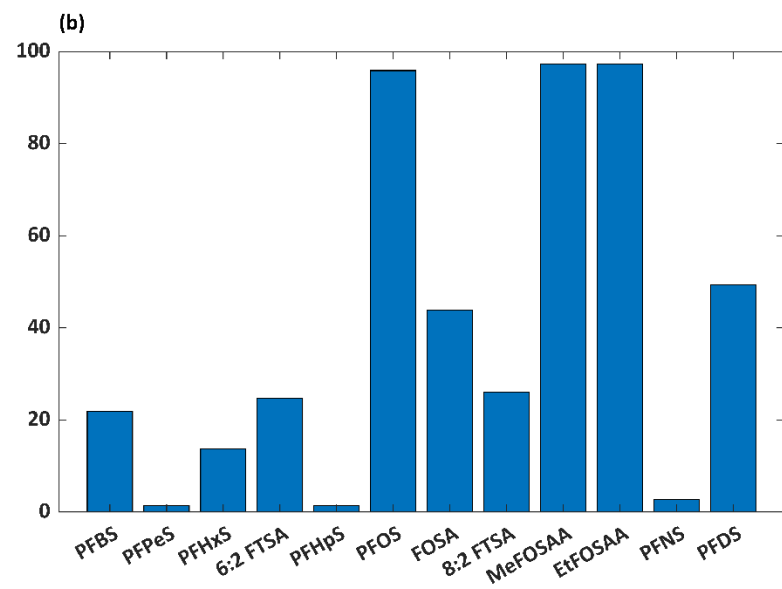
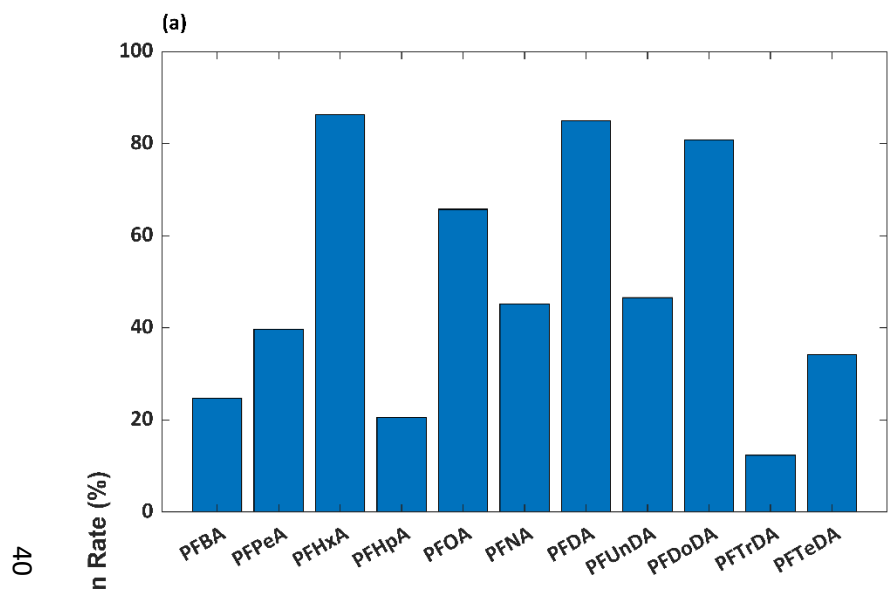




Figure 4. Detection rates of individual PFAS from select samples (n=73 pairs) categorized by (a) carboxylate and (b) sulfonic compounds. Plots (c) and (d) depict the frequency at which detections in (a) and (b) occur in both biosolids and wastewater influent (grey) or only in biosolids (blue).