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Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes

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HIGHLIGHTS

- Sludge stabilization significantly affected PFAS K_d in biosolid.
- Secondary treatment did not significantly affect PFAS K_d in sludge.
- Biosolids generally had significantly lower PFAS K_d compared to secondary sludge.
- Protein was stronger predictor of PFAS K_d than organic matter or lipid fraction.
- Elevated mono- and divalent cations increased PFAS K_d, while high pH decreased it.

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have gained increasing attention due to the potential health risks that they present. Secondary sludge and biosolids are known as notable PFAS emission routes to the environment. In this study, partitioning behavior of 14 PFAS were investigated across four secondary wastewater treatment types (activated sludge, trickling filter, biological nutrient removal, and rotating biological contactor; n = 10) and three sludge stabilization methods (composting, aerobic digestion, and anaerobic digestion; n = 6). Batch experiments were conducted to evaluate how PFAS sorption to secondary sludge and biosolid was affected by various treatment methods, solid properties, and solution chemistry parameters. Insignificant differences in compound-specific partitioning coefficients (K_d) were observed among the four secondary treatment methods. However, sludge stabilization resulted in significantly different partitioning behavior among biosolid samples, in which anaerobically digested biosolids generally had significantly higher K_d values compared to aerobically digested and composted biosolids (anaerobic digestion > aerobic digestion > composting). Multiple linear regression models were developed to explain analyte-specific K_d values across the biosolid samples and identified that solid-specific property significance was as follows: protein fraction > organic matter fraction > lipid fraction. Stabilization generally decreased the PFAS sorption capacity relative to the secondary sludge samples. Furthermore, PFAS K_d increased with elevated calcium concentrations and ionic strengths and decreased with increasing pH values in sludge and biosolid samples. These findings could inform the decision-making process to reduce the release of PFAS to the environment.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of diverse man-made chemicals which include a non-polymeric subgroup that is often characterized by a hydrophobic fluorinated carbon chain attached to an ionic headgroup (Kumar, 2005). The strong C—F bonds in PFAS make them thermally and biologically stable while the surfactant characteristics result in partitioning to interfaces and comparatively high mobility; more detailed discussion of PFAS sources, physio-chemical properties, fate, transport, and effects can be found elsewhere (Arvaniti and Stasinakis, 2015; Giesy

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and Kannan, 2002; Kannan, 2011; Kumar, 2005). These unique characteristics justify their extensive use in many consumer products such as cookware, personal-care products, and food packaging (Giesy and Kannan, 2002). PFAS have increasingly gained attention from the public, scientific, and regulatory sectors due to the carcinogenic, reproductive, and endocrine disruptive effects that they present (Ahrens, 2011; Gorrochategui et al., 2014).

Previous research has illustrated that water resources recovery facilities (WRRF[1]; also known as wastewater treatment plants) are notable PFAS emission routes to the environment, reflecting both liquid and solid discharge routes. According to Northeast Biosolid and Residual Association, more than seven million dry tons of sewage solids were produced at WRRF in 2004, of which 55% were land applied as soil quality enhancing additives (biosolids) and the remaining 45% were discarded through incineration and landfill disposal options. These sewage solids management practices have resulted in the release of approximately 3000 kg PFAS per year to agricultural lands and landfills (Venkatesan and Halden, 2013). PFAS may be taken up by plants and find their way into the agricultural products and foods, constituting a noteworthy human exposure route. PFAS compounds may accumulate within shallow depths of soil or leach into the soil and make it to groundwater (Blaine et al., 2013; Ghisi et al., 2019; Wen et al., 2014). PFAS pollution in groundwater can be mostly correlated to the flux of short chain PFAS compounds on land. One study found short chain PFAS (<C8) at depth of 1.2 m and more following a land application of biosolids as a soil amendment (Washington et al., 2010). Considering the significant quantities of PFAS-contaminated sewage solids (i.e., sludge and biosolid) generated by WRRF and the overall resistance of PFAS to degradation in conventional treatment trains (Deng et al., 2010; Lewis et al., 2020; Rayne and Forest, 2009; Ross et al., 2018), PFAS partitioning to sewage solids is considered a major removal pathway in WRRF and, consequently, a significant contributor to the release of such chemicals to the environment.

WRRF unit processes and treatment trains, including secondary treatment processes and sludge stabilization methods, can affect the sewage solids physical and chemical characteristics (Guerra et al., 2014; Stasinakis, 2012). For example, anaerobic digestion was found to reduce the fraction of volatile solids and increase sorption capacity of hydrophobic contaminants (Stasinakis, 2012). Another study reported that considerably higher concentrations of longer chain length perfluoroalkyl acids were found in digested sludge samples compared to non-digested samples (Guerra et al., 2014). Additionally, previous research has illustrated that PFAS concentrations were affected by type of treatment process (e.g., primary vs. secondary treatment) and type of unit process (e.g., aerobic biological vs. advanced biological nutrient removal) (Guerra et al., 2014; Schultz et al., 2006). Furthermore, operational parameters associated with the secondary treatment methods such as hydraulic retention time (HRT) and temperature have been found to be correlated with the conversion of PFAS precursors, with higher precursor conversion levels reported at higher HRT and temperatures (Guerra et al., 2014). Perfluoroalkyl acid (PFAAs; the stable terminal transformation products) formation through biotransformation of fluorinated precursors is a notable mechanism affecting the PFAA load in the WRRFs effluent, sometimes resulting in higher post-treatment concentrations relative to the influent concentrations (Arvaniti et al., 2012; Schultz et al., 2006; Stasinakis, 2012). These findings suggest that the treatment trains adopted in WRRF could impact the mass flow and PFAS concentration profiles as well as their sorption capacity to sewage solids.

A review of past studies illustrates a wide range of PFAS partitioning coefficients in various environmental media. Thus, it is not yet clear how solid properties and solution chemistry parameters affect PFAS sorption behavior in sewage solids (secondary sludge and biosolid) resulting from various treatment processes. Additionally, while previous research have investigated the effects of various treatment processes on the fate of PFAS in WRRF (Chen et al., 2012; Guerra et al., 2014; Lazcano et al., 2019; Wang et al., 2016), to our knowledge, no previous studies have linked PFAS partitioning behavior in secondary sludge and biosolids to treatment methods and few studies have compared PFAS sorption capacity of secondary sludge with their associated biosolids. Therefore, the objectives of this study were to investigate the effects of a variety of solution-specific characteristics (pH, mono- and polyvalent cation concentration), solid characteristics (organic matter, protein, and lipid content), PFAS characteristics (chain length, head group), and treatment methods (secondary treatment and sludge stabilization methods) on the sorption of PFAS to sewage solids.

2. Materials and methods

2.1. Chemicals and materials

The evaluated PFAS are anions under environmentally relevant conditions (circum-neutral pH values), so the anionic names are employed throughout the current research. The complete list of PFAS products and manufactures can be found in the supplementary information (Table S1 and section 1.1, respectively), which included eight perfluorocarboxylate (PFCA)[2], four perfluorosulfonate (PFSA)[3], and two fluorotelomer sulfonate (FtS)[4] compounds.

2.2. Sewage solid sampling

Municipal WRRF, with sizes spanning from 2 to 37 million gallons per day, were selected to reflect the most widely used secondary treatment and sludge stabilization methods. Ten WRRF provided sludge samples: activated sludge (AS),[5] trickling filter (TF),[6] biological nutrient removal (BNR),[7] and rotating biological contactor (RBC).[8] Among the recruited WRRF, six WRRF produced biosolids from which samples were obtained; stabilization processes included anaerobic digestion (ANA),[9] aerobic digestion (AER),[10] and composting (COM).[11] Sludge and biosolid sample labeling reflect both the treatment process type and the WRRF from which the sample was collected (WRRF details in Table S3). Recruited WRRF were provided instructions on appropriate sampling methodologies to minimize contamination. WRRF employees collected the solid samples in 1-liter high-density polyethylene bottles and shipped them to Temple University on cold packs. Sewage sludge and biosolid samples were solicited in Fall 2019 and were received over a six-week time period (~10/1/2019–11/15/2019).

Upon arrival at Temple University, sludge and biosolid samples

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[1] Water resources recovery facilities.

[2] Perfluorocarboxylate

[3] Perfluorosulfonate

[4] Fluorotelomer sulfonate

[5] Activated sludge.

[6] Trickling filter.

[7] Biological nutrient removal.

[8] Rotating biological contactors.

[9] Anaerobic digestion.

[10] Aerobic digestion.

[11] Composting.

were processed separately based on stability considerations. Sludge samples were amended with sodium azide (1 g into the 1-L sample), centrifuged at 3000 g for 20 min, and the liquid fraction was decanted. Dewatered and azide-amended sludge samples were stored at 4 °C prior to the experiments. Batch isotherm experiments and solid quantitation efforts (e.g., Fig. S2) for secondary sludge were initiated within 72 h of sample arrival to the laboratory. Biosolid samples were amended with sodium azide (1 g into the 1-L sample) and were stored at −20 °C. Batch isotherm experiments were conducted within 60 days of biosolid collection. Sludge samples were separated into two groups – (1) intensive investigation (seven-point isotherm and three-point edge experiments) and (2) limited investigation (single-point K_d assessment in the reference solution) as illustrated in Table S3. The selection reflected intensive evaluation of each secondary treatment method and their paired biosolid samples.

2.3. Isotherm experiments

Isotherm treatments were prepared in polypropylene tubes, including 49.5 mL isotherm solution (10 mM ammonium nitrate, 5 mM ammonium bicarbonate, and pH 7), 200 mg (wet-weight) azide-amended solids, and PFAS amendments as appropriate; care was taken to ensure that the same volume of methanol was added to every vial to avoid potential co-solvency artifacts. The seven-point isotherm solution included PFAS amendments of 0, 50, 100, 150, 200, 250, and 500 ng of 14 PFAS. The sludge and biosolid samples in the limited analysis category were evaluated with a 200 ng amendment of the PFAS suite (single-point partitioning experiment), which is referred to as the reference solution hereafter; this was done to reduce the overall laboratory workload. All treatment conditions were evaluated in triplicate. Isotherm vials were mixed end-over-end at room temperature for seven days, which is longer than values employed in literature, to ensure equilibrium was achieved in both sludge and biosolid samples. Attention was paid to create identical and well-mixed batch systems, with a goal of limiting uncertainty in the derived K_d values. During the experiments, the experiment vials were well-mixed and good dispersion of the solid particles in the solution was achieved to promote an equilibrated system. Head space in the experimental batch vessels (nominal 50 mL) was present, but only less than 1 mL; the end-over-end mixing was sufficient to maintain full mixing, but not so energetic to create foam. Following this mixing step, the samples were processed for liquid- and solid-associated PFAS quantification.

2.4. Edge experiments

Edge experiments were conducted to explore the effects of solution pH and cation effects (ionic strength) on PFAS partitioning coefficients. Edge experiments were prepared in polypropylene tubes, and each included 200 mg (wet-weight) azide-amended sludge, 49.5 mL edge solution, and 0.5 mL PFAS suite solution (equivalent to 200 ng suite of PFAS). The baseline edge solution included 5 mM ammonium bicarbonate and was modified to meet the experimental design needs where the treatment values were selected to simultaneously explore mechanistic effects and to be environmentally relevant. To evaluate pH effects, the edge solution pH was adjusted to 6, 7, and 8 via hydrochloric acid and ammonium hydroxide addition. Cation concentration effects were evaluated at 0.33, 3.33, and 33.33 mM calcium nitrate and 1, 10, and 100 mM ammonium nitrate; the calcium nitrate and ammonium nitrate concentrations were selected to create equivalent ionic strength solutions with monovalent and divalent cations. All experiments were conducted in triplicate.

2.5. Biosolid characterization

Biosolids were characterized for their organic matter, lipid, and protein fractions. More detailed description of each procedure is included in SI (section 1.2).

2.6. Sample processing and analytical methods

Equilibrated isotherm and edge samples were centrifuged at 3000 g for 20 min to separate the liquid and solid fractions. Batch solutions were subsampled for PFAS analysis by transferring 300 μL to poly propylene microcentrifuge tubes amended with 300 μL methanol containing internal standard suite (2 μg/L), which was then vortexed for 10 s and subsequently centrifuged at 13000 g for 20 min. The remaining batch supernatant was subsampled for pH, conductivity, and metal analysis, and the remaining solution was decanted. PFAS extraction from solids followed the methods detailed in literature (Higgins et al., 2005). In brief, internal standards were added (10 ng in 0.1 mL 70:30 methanol-water) followed by a basic methanol extraction and EnviCarb cleanup. Quantitation of targeted PFAS was achieved by LC-QTOF-MS (Sciex x500r). The details of the analytical methods and QA/QC[9] procedures are included in SI (section 1.3).

2.7. Data analysis

Isotherm data were fit with two models – linear and Freundlich – to determine sorption capacity of sewage solids and to gain insight on the sorption interactions. Samples were included in the analyses if both aqueous and solid phase concentrations met all quality assurance/quality control criteria. These isotherm models are represented as follows:

$$C_s = K_{lin} C_w \qquad \text{linear model} \tag{1}$$

$$C_s = K_f C_w^n \qquad \text{Freundlich model} \tag{2}$$

where $C_s \left[\mathrm{g\ kg^{-1}}\right]$ and $C_w \left[\mathrm{g\ L^{-1}}\right]$ are the concentrations of PFAS in the dry-weight solid and aqueous phases, respectively. K_{lin} $[\mathrm{L\ kg^{-1}}]$ is the linear model partitioning coefficient, $K_f\,[(\mathrm{g\ kg^{-1}}).(\mathrm{g\ L^{-1}})^{-n}]$ is the Freundlich model coefficient, and n is the Freundlich model exponent which represents the degree of non-linearity. Isotherm models were employed to fit the isotherm experiment data points from intensive evaluation experiments (seven-point isotherm experiments) and the adjusted coefficient of determination (R^2) was used to evaluate their goodness-of-fit.

Statistical analysis was performed on the solid-water partitioning coefficient values determined in the reference solutions. The effect of each solution chemistry parameter was quantified by a linear regression approach, as outline in the following equation:

$$\begin{aligned} Log(K_d) = \alpha_0 + \alpha_1 \times Treatment(RBC) + \alpha_2 \times Treatment(AS) \\ + \alpha_3 \times Treatment(TF) + \alpha_4 \times Chemistry \end{aligned} \tag{3}$$

where α_0 is the intercept of the model, α_1, α_2, and α_3 are coefficients of the secondary treatment methods, which are statistically included as dummy variables that can be either zero or one, depending on the type of treatment. BNR method was selected to be the reference treatment method and hence not included in the model; a similar approach was employed for biosolids and composting was selected as the reference. The reference selection is merely a statistical approach to avoid introducing excessive variables to the models. The solution chemistry variable, α_4, can be log (Ca [mM]), log (ammonium [mM]), or pH. Similarly, the effect of solid-specific parameters was quantified by a linear regression approach, where solid properties (protein, lipid, organic matter fractions) were treated as independent variables in a single-variable regression approach, as outlined in the following equation:

$$Log\ (K_d) = \alpha_0 + \alpha_1 \times f_i \tag{4}$$

where α_0 is the intercept of the model, and α_1 is the coefficient of the solid property (f_i), where i can be lipid, protein, and organic matter fraction, depending on the type of analysis.

3. Results

3.1. Secondary sludge

3.1.1. Partitioning behavior in secondary sludge

Evaluation of isotherm fitting efforts for 14 PFAS across the secondary sludge samples revealed mixed results on whether the linear or Freundlich model better fit the data (full fitting details in Tables S4–S19). Generally, these samples exhibited both isotherm forms, as exemplified by RBC_J in Fig. 1, though the distribution of best-fit was sample-dependent (Fig. 1b). The linear model generally fit all isotherm data moderately to very well ($R^2 > 0.9$) and generally prevailed as the best fit for short to mid chain-length compounds across all samples (e.g., PFOA and PFNA in Fig. 1 part1). Linear partitioning behavior of PFAS can occur as a result of substantially porous texture of the solids where the inner sorption sites enable access to abundant equal-energy sorption sites (Kennedy et al., 1992; Milinovic et al., 2015). However, the isotherm linearity generally decreased as the alkyl chain length of PFAS increased; for example, the Freundlich model fit PFDA and PFUnA (fluoroalkyl chain length of 9 and 10, respectively) well across all the samples. As the PFAS fluoroalkyl chain length increases, the hydrophobic interactions between sorbent and sorbate increase, which in turn can result in elevated PFAS sorption (e.g., as exemplified in Fig. 1 and discussed further below). However, less desirable sites may be utilized under higher sorption capacity cases (i.e., heterogeneous site energies) as reflected in the empirical Freundlich model. Additionally, long fluoroalkyl chains might hinder PFAS penetration into the preferable sites located in the interior of the solid (i.e., size exclusion), thereby preventing them from accessing equal-energy sites within the pores, resulting in non-linear partitioning behavior. However, exceptions to this trend were observed in PFSA compounds; for instance, PFDS, as a long-chain PFSA, exhibited linear isotherms in many cases, which can be explained by the higher sorption propensity of the sulfonate head group compared to carboxylate, which might make PFDS less sensitive to concentration effects.

Relatively high variability among PFAS sorption capacities were seen across secondary treatment methods (AS, TF, BNR and RBC; Fig. 3); however, one-way ANOVA analysis (significance level = 0.05) of the data revealed no significant difference among these treatment processes. Similar K_d values among the secondary treatment sludges indicates that sludge sorption capacity is insensitive to secondary treatment method, and that other sources of variability may be more important; potential contributors to the variability may include factors such as variable influent constituents and sludge compositions. Some AS samples exhibited lower K_d values, but the high variability in AS was observed (Fig. 2 and Fig. S3), both among the samples from WRRF that employ AS as secondary treatment (i.e., inter-sample variability) and also within replicate samples, which can be associated with the heterogeneities in the sludge or inconsistent moisture content of the dewatered sludge samples. The inconsistency of PFAS sorption capacities

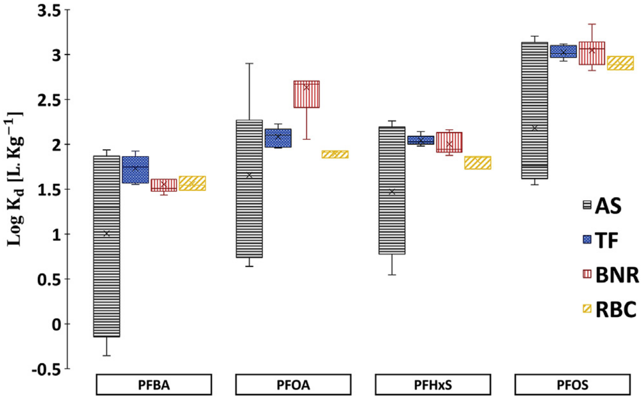

Fig. 2. PFBA, PFOA, PFHxS, and PFOS partitioning coefficients across different secondary treatments (n = 10 sludge samples with experiments conducted in reference solution).

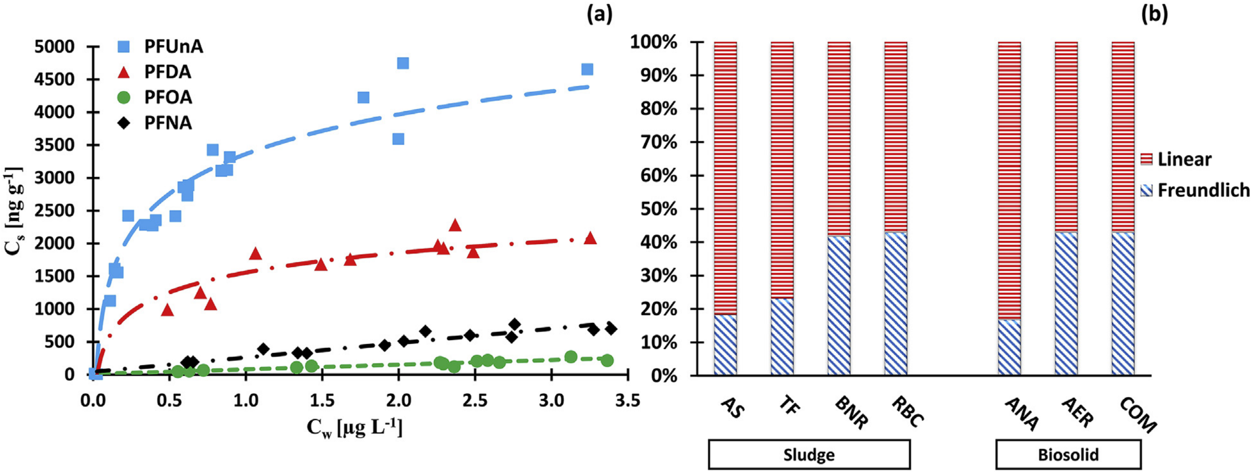

Fig. 1. a. Examples of isotherm model fittings (linear and Freundlich) in RBC_J sludge sample; PFOA (linear), PFNA (linear), PFDA (Freundlich), and PFUnA (Freundlich). **b.** Distribution of best-fit isotherm models across sludge and biosolid samples based on their secondary sludge and biosolids stabilization processing methods.

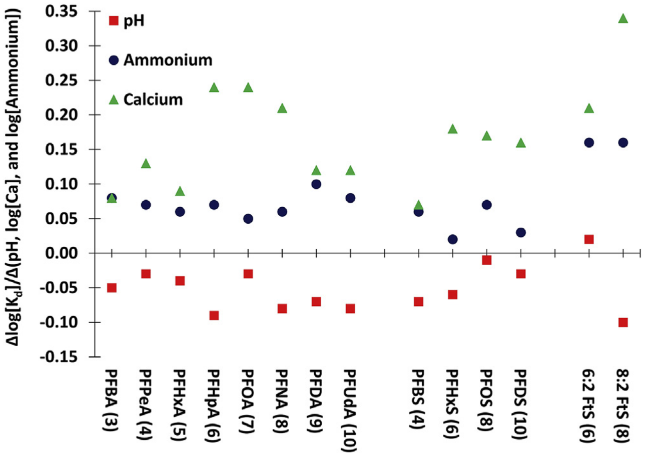

Fig. 3. Coefficient of analyte-specific linear regression to assess the effects of pH, mono-valent cation (ammonium), and di-valent cation (calcium) on PFAS sorption in TF_D sludge sample.

across activated sludge plants was previously observed (Zhou et al., 2010), and emphasizes the need for a representative sampling approach.

3.1.2. Solution chemistry effects: impacts of pH, mono- and divalent cations in sludge

3.1.2.1. pH effects. Partitioning behavior of the anionic PFAS was evaluated at three different pH values (6, 7, and 8) and linear regression of the data indicated that the effects of pH within the studied range was generally small but significant across the four secondary treatment methods. Minor pH-based differences in the log K_d data suggest that PFAS sorption may increase with decreasing pH (Fig. 3); on average, the difference between the pH 8 and 6 treatments resulted in a 0.05 log K_d difference (Table S23). Increased sorption is attributed to a decrease in the negative surface charge of the sludge at lower pH values (Johnson et al., 2007), since the PFAS will be overwhelmingly present as anions in the pH range evaluated. More substantial difference might be encountered if a wider range of pH values are considered. Previous studies have reported significant differences in PFAS partitioning coefficients in sludge when pH values from 2 to 9 were investigated and it was observed that PFAS sorption increased under more acidic conditions (Zhang et al., 2013; Zhou et al., 2010). Alternatively, a significant increase in PFOS partitioning coefficients has been reported with increasing solution pH from 7 to 8 in sediment (You et al., 2010). By contrast, pH (4.6–8) did not affect sorption of PFOS, PFOA, and PFBS onto six different sediments (Milinovic et al., 2015).

3.1.2.2. Mono- and divalent cation effects. Ammonium and calcium were evaluated as mono- and divalent cations, respectively, and were generally found to impact PFAS partitioning coefficients (e.g., log K_d related to log cation concentration; Fig. 3). Cation-concentration dependent trends could be observed in the sludge data (Table S24 and Table S25), suggesting that sorption increases at elevated cation concentrations and that this impact is greater for calcium than for ammonium (average increase of 0.17 and 0.08 log K_d, respectively, per order of magnitude increase in cation concentration). Despite the slightly higher system pH values due to the addition of NH_4NO_3 (e.g., Δ pH up to 0.5 units), the pH-dependent effect is expected to be minimal based on the results presented in section 3.1.2.1 (e.g., $\Delta \log K_d < 0.05$). Elevated sorption capacity of sludge at higher salinities could be associated with decreased negative charge on their surface (i.e., more neutral) due to electrostatic sorption of ammonium cations onto the sludge surface. Previous research indicated that monovalent cations resulted in insignificant bridging effects in water-sediment partitioning systems (Higgins and Luthy, 2006). Calcium was positively correlated with anionic PFAS sorption onto soil, sediment, and sewage sludge, with a typical slope of 0.3–0.5 log K_d per log [Ca] increase (Chen et al., 2012; Higgins and Luthy, 2006; You et al., 2010; Zhang et al., 2013) though this is not universally observed (Kwadijk et al., 2013). This relationship could be attributed to a bridging phenomenon, where a divalent cation electrostatically interacts with both the negatively charged surface of the sludge and the anionic PFAS head group. The enhanced sorption due to Ca^{2+} was observed to have a greater impact on carboxylate-PFAS. Carboxylate moieties are known to present higher propensity for cation-complexation compared to sulfonates which are comparatively weak ligands (Schwarzenbach et al., 2016). Therefore, PFCA were expected to be more noticeably impacted. Additionally, elevated salinities can reduce the solubility of organic molecules (i.e., salting-out) such as PFAS and enhancing their sorption propensity to sludge (Turner and Rawling, 2001). Overall, both mono- and divalent cations may result in increased partitioning coefficients, although increased sampling number and concentration range may more clearly reveal trends. Based on the findings in this study, other factors more substantially impact PFAS sorption to sewage solids.

3.2. Biosolid

3.2.1. Partitioning behavior in biosolids

Partitioning behavior of PFAS in biosolids were similar to that of secondary sludge in which the linear partitioning behavior was dominant as shown in Fig. 1b. However, statistically significant differences were observed in the analyte-specific partitioning coefficients based on stabilization method. The sorption capacity generally conformed to the following trend (highest to lowest) for biosolids: anaerobically digested biosolid > aerobically digested biosolid > composted biosolids, as shown in Fig. 4. One-way ANOVA at 0.05 significance level with post Tukey test indicated that for the PFAS studied here, except PFOS and 6:2 FtS, significant differences in partitioning coefficients exist among the sludge stabilization methods. Anaerobically digested biosolids generally had statistically higher partitioning coefficients compared to aerobically digested and composted biosolids across the PFAS suite except partitioning coefficients of PFBA, PFHxA, PFBS, PFOS, and 6:2 FtS in aerobically digested biosolids, as wells as PFOS, PFDS, and 6:2 FtS in composted biosolids, which did not differ significantly from those of anaerobically digested biosolids. Moreover, aerobic digestion had statistically higher partitioning coefficients than the composting method except for PFOS, PFDS, and 6:2 FtS, which showed insignificant differences. The differences in partitioning coefficient values across sludge stabilization methods may be due to the organic matter quality of the biosolids. For example, aerobic microorganisms thriving in aerobic digestion and composting methods, such as fungi, were found to be capable of degrading the organic matter to a greater extent compared to the anaerobic systems (Hubbe, 2014), which in turn can impact the sorption propensity of PFAS to such solids. Additionally, anaerobic digestion was found to reduce the volatile solid fraction and improve sorption capacity of hydrophobic contaminants (Stasinakis, 2012), which can also affect PFAS sorption capacity of anaerobically digested solids. It should be noted that the importance of the original PFAS concentrations in both sludge and biosolids has been considered in the current study. It has previously been found that sludge stabilization could convert some of the PFAS precursors into more stable PFAS compounds (Lazcano et al., 2019; Stasinakis, 2012; Wang et al., 2011). Therefore, the difference in the profile and composition of

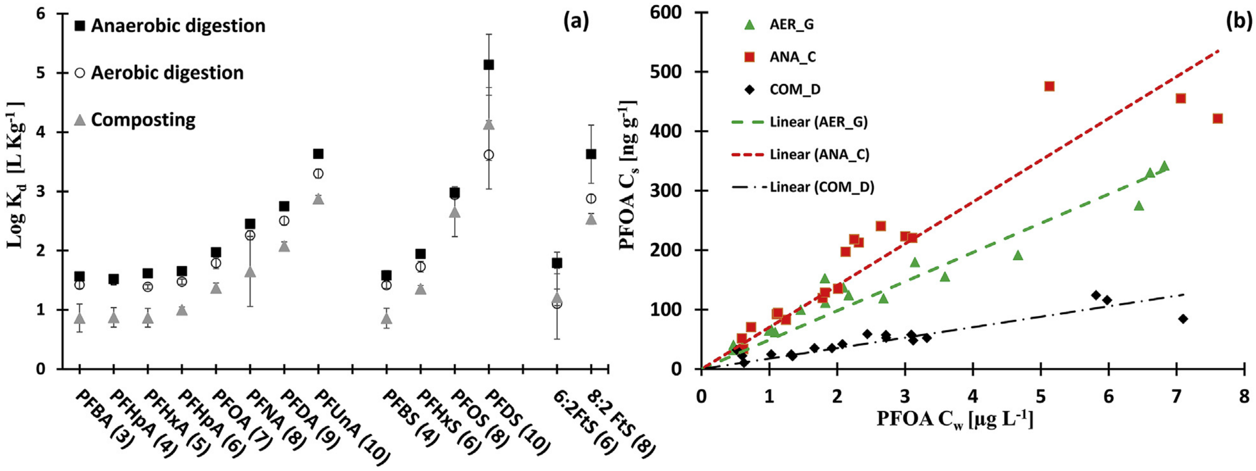

Fig. 4. a. PFAS (alkyl chain length) partitioning coefficients across different sludge stabilization methods (6 biosolid samples with partitioning experiments conducted in reference solution). **b.** PFOA partitioning coefficients, fit by linear model, across anaerobic, aerobic, and composting sludge stabilization methods.

PFAS in secondary sludge and biosolids is also acknowledged in this research, but is not expected to impact the K_d values that are determined in this study, which are based on measured liquid and solid concentrations. At the WRRF, shorter chain PFAS may be produced and sorb on the sludge and/or biosolids. Results in this study suggest that the concentration effects on the isotherms were mostly insignificant (i.e., most isotherms were linear), which in turn minimizes the importance of the original PFAS in the samples.

3.2.2. Solution chemistry effects: impacts of pH, mono- and divalent cations in biosolid

Similar to the secondary sludge, pH, ammonium and calcium were found to impact PFAS partitioning coefficients in biosolids as well (Fig. S10). Linear regression analysis was performed to quantify the effects of these solution chemistry parameters as outlined in equation three (details are provided in Table S26-S28). In summary, PFAS sorption in biosolids increased at elevated calcium and ammonium concentrations (average increase of 0.12 log K_d and 0.09 log K_d per order of magnitude increase in cation concentration of calcium and ammonium, respectively). However, pH decreased the PFAS sorption capacity by 0.06 log K_d per pH unit increase.

3.2.3. Biosolid characterizations: Impacts of protein, lipids, OM on partitioning

Significant differences in the sorption capacity of the stabilized biosolids was observed (i.e., 6 biosolid samples, 14 analytes, conducted in reference solution), which warranted further statistical of solid characteristics impacts on K_d. Three biosolid characteristics (protein, lipid, and organic matter fractions) and one WRRF-specific parameter (sludge stabilization methods) were included in a multiple linear regression model and the significant predictors were selected according to their p-values, as shown in Table S21. This analysis was performed in RStudio 1.3 software using the package olsrr. In summary, stepwise addition and removal of the predictors (protein, lipid, organic matter fraction, and treatment methods) was performed for each PFAS until all variables tested for the model. The final output of the analysis only retained statistically significant variables (p-value < 0.05).

Additional single variable linear regression models were also developed to assess the impact of each predictor individually (Table S22). It was found that sludge stabilization methods were important predictors across most analytes based on their frequency of appearances in the final models (Table S21). The significance of solid properties varied across the analytes; the importance of such properties conformed to the following order in multi-variable regression approach: protein > organic matter fraction > lipid. It is noteworthy to mention that the organic matter fraction encompasses both protein and lipid fractions. While organic matter can be a better predictor for PFAS partitioning coefficient than lipid fraction, protein outperformed both the organic matter and the lipid fractions. Single-parameter linear regression analysis revealed that both solid- and WRRF-specific parameters were significant predictors (confidence level = 0.05) for PFAS partitioning coefficients. The goodness of these predictive models based on individual solid-specific properties conformed to the following order: organic matter fraction (average R^2 across 14 PFAS: 0.61) > lipid fraction (average R^2 across 14 PFAS: 0.29) > protein fraction (average R^2 across 14 PFAS: 0.19).

3.3. Sorption capacity analysis of paired sludge-biosolid samples

Analysis of partitioning behavior of the PFAS suite in paired sludge and biosolid samples collected from plants C, D, F, G, H, and I revealed that sludge samples had higher K_d values (average 0.36 log K_d across 14 analytes in all six plants) in most cases (e.g., plant D in Fig. 5). Statistical analysis (two-sample *t*-test at 0.05 significance level) of these partitioning coefficients generally indicated significant differences in partitioning for paired sludge-biosolid samples.

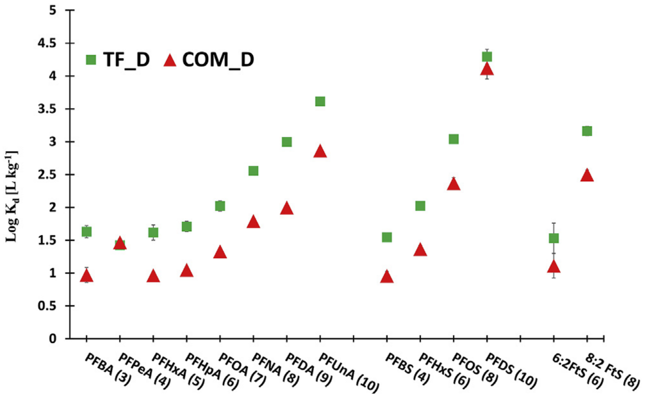

Fig. 5. comparison among paired-biosolid sludge samples in plant D. Partitioning experiments conducted in reference solution (200 ng spiking of suite of PFAS).

However, exceptions to this trend were observed in some cases; plant G (only PFNA, PFDA, PFHxS, and PFOS showed significantly different partitioning coefficients), PFPeA (showed significantly different partitioning coefficients in plants C, and H), 6:2 FtS (showed significantly different partitioning coefficients in plants C, F, G, H and I) and PFDS (showed significantly different partitioning coefficients in plants C, F, and H). Lower K_d values in biosolid samples compared to secondary sludge were previously reported (Arvaniti et al., 2014). Also, a significant difference in partitioning coefficients between primary sludge and secondary sludge (for PFDA, PFUnA, and PFOS), and between primary sludge and digested sludge (PFUnA and PFOS) were reported in previous research (Arvaniti et al., 2014).

3.4. PFAS-specific trends

3.4.1. Chain length and headgroups

Partitioning coefficients increased with increased fluoroalkyl chain length across all sewage solid samples, as demonstrated in Fig. S11. PFSA compounds had higher sorption capacities compared to PFCA compounds with the same fluoroalkyl chain length (i.e., the carbon in the carboxylate head was not counted) across both sludge and biosolid samples, as shown in Figs. 4a and 5 and S11. Evaluation of partitioning coefficients associated with FtS and PFSA compounds of identical alkyl chain length (8 and 10) revealed that PFOS and PFDS presented higher partitioning coefficients compared to 6:2 and 8:2 FtS, as shown in Fig. S11b, indicating that the methylene groups decrease sorption for equivalent alkyl chain length sulfonates. Similarly, PFNA and PFUnA, with 8 and 10 fluoroalkyl chain lengths, presented higher partitioning coefficients compared to 6:2 and 8:2 FtS, indicating that the reduction in the sorption capacity associated with $(CH_2)_2$ was greater than the increase associated with the sulfonate head group. More detailed discussion of the PFAS-specific trends can be found in section 2.2 of the supplementary information.

4. Conclusions

The results of the current study can lead the efforts on minimizing the release of PFAS through the solid effluents of WRRF. Even though PFAS-specific parameters such as their total mass, profile, and composition are not expected to vary significantly through the treatment processes, solution chemistry, solid characteristics, and stabilization methods can change the leaching potential of the sewage solids and hence can impact the release of PFAS to the environment. Since controlling the influent mass burden of PFAS to WRRF is not viable in most cases, more attention should be given in optimizing the treatment process within the WRRF. These efforts can include monitoring solution chemistry parameters proactively and maintaining a lower pH (<7) in wastewater as well as adding di-valent cations to both secondary treatment and sludge stabilization steps. Monitoring protein levels in the solid effluent of WRRF can also be another useful way to control PFAS leaching. Finally, more research should be conducted on the effects of sludge stabilization on PFAS leaching of the biosolids. Our results showed that different biosolid stabilization methods can lead to different PFAS leaching capacities in the solid effluent. However, more research is needed to understand how various operational parameters within these units (e.g., temperature and solid retention time) can alter the PFAS leaching capacity. This can potentially help optimize these sludge stabilization units and can impact the release of PFAS through the solid effluents of WRRF. It is important to note that quantification of 14PFAS is by no means indicative of the entire PFAS family partitioning behavior. Future research efforts may include employing the Total Organic Fluorine (TOF), Total Oxidizable Precursor (TOP), and non-targeted analytical approaches, which would provide more evidence on other possible PFAS compounds. These bulk PFAS family assessments can be useful for understanding general PFAS leaching, it will not be useful in understanding specific PFAS solid-water distribution coefficients and the effects of molecular features on this parameter. Future work should consider both determination of an expanded range of quantifiable PFAS compounds as well as leaching of the broader PFAS family, particularly considering how treatment process impacts each consideration.

Authors contributions

Farshad Ebrahimi: Investigation, Writing – original draft, Visualization, Formal analysis, Methodology. Asa Lewis: Investigation, Writing – review & editing. Christopher M. Sales: Conceptualization, Resources, Writing – review & editing, Funding acquisition. Rominder Suri: Conceptualization, Writing – review & editing, Funding acquisition. Erica R. McKenzie: Supervision, Funding acquisition, Resources, Writing – review & editing, Conceptualization, Methodology

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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Appendix A. Supplementary data

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