Chemosphere 341 (2023) 140081

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effective stabilization of per- and polyfluoroalkyl substances (PFAS) precursors in wastewater treatment sludge by surfactant-modified clay

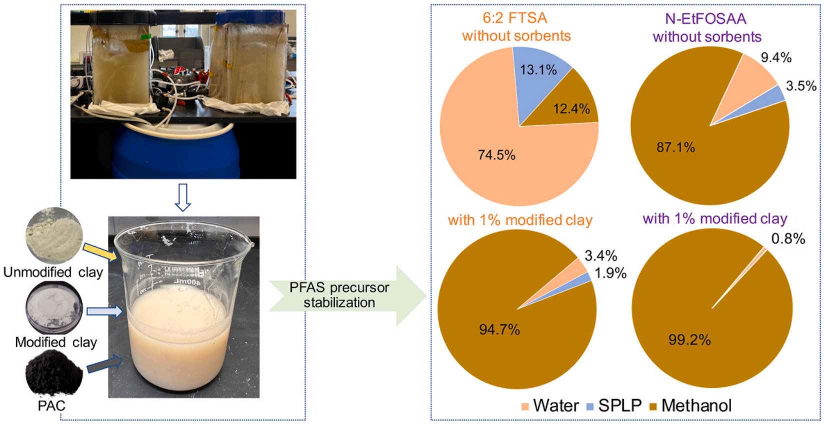
Tao Jiang [a,*], Md. Nahid Pervez [a], Monica M. Quianes [a], Weilan Zhang [a], Vincenzo Naddeo [b], Yanna Liang [a]

[a] *Department of Environmental and Sustainable Engineering, University at Albany, State University of New York, Albany, NY, 12222, USA*
[b] *Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno, Fisciano, 84084, Italy*

HIGHLIGHTS

- Physicochemical properties of precursors are critical for stabilization behaviors.
- Modified clay exhibited the best PFAS stabilizing performance in sewage sludge.
- Water leachability of N-EtFOSAA was reduced by 91.5% by the modified clay.
- Modified clay decreased water leachability of 6:2 FTSA by 95.4%.

GRAPHICAL ABSTRACT



Sludge preparation and treatment by sorbents

Leachability of PFAS precursors on Day 47

ARTICLE INFO

Handling Editor: Antonis A. Zorpas

Keywords:
Poly- and perfluoroalkyl substances (PFAS)
PFAS precursors
Stabilization
Surfactant-modified clay
Sewage sludge

ABSTRACT

The application of biosolids or treated sewage sludge containing per- and polyfluoroalkyl substances (PFAS) in agricultural lands and the disposal of sludge in landfills pose high risks to humans and the environment. Although PFAS precursors have not been regulated yet, their potential transformation to highly regulated perfluoroalkyl acids (PFAAs) may enable them to serve as a long-term source and make remediation of PFAAs a continuing task. Therefore, treating precursors in sewage sludge is even more, certainly not less, critical than treating or removing PFAAs. In this study, a green surfactant-modified clay sorbent was evaluated for its efficacy in stabilizing two representative PFAA precursors in sludge, e.g., N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) and 6:2 fluorotelomer sulfonic acid (6:2 FTSA), in comparison with unmodified clay and powdered activated carbon (PAC). Results showed N-EtFOSAA and 6:2 FTSA exhibited distinct adsorption behaviors in the sludge without sorbents due to their different physicochemical properties, such as hydrophobicity and functional groups. Among the three sorbents, the modified clay reduced the water leachability of N-EtFOSAA and 6:2 FTSA

---

* Corresponding author. 1400 Washington Avenue, Albany, NY, 12222, USA.
E-mail address: tjiang2@albany.edu (T. Jiang).

https://doi.org/10.1016/j.chemosphere.2023.140081
Received 15 June 2023; Received in revised form 22 August 2023; Accepted 4 September 2023
Available online 5 September 2023
0045-6535/© 2023 Elsevier Ltd. All rights reserved.

by 91.5% and 95.4%, respectively, compared to controls without amendments at the end of the experiment (47 days). Within the same duration, PAC decreased the water leachability of N-EtFOSAA and 6:2 FTSA by 60.6% and 37.3%, respectively. At the same time, the unmodified clay demonstrated a poor stabilization effect and even promoted the leaching of precursors. These findings suggested that the modified clay had the potential for stabilization of precursors, while negatively charged and/or hydrophilic sorbents, such as the unmodified clay, should be avoided in the stabilization process. These results could provide valuable information for developing effective amendments for stabilizing PFAS in sludge or biosolids. Future research should evaluate the long-term effect of the stabilization approach using actual sludge from wastewater treatment facilities.

1. Introduction

The wide applications and persistence of per- and polyfluoroalkyl substances (PFAS) have led to their ubiquity in various environmental matrices, such as household dust (Paul et al., 2009), water (Morales-McDevitt et al., 2021; Shoeib et al., 2004; Shoeib et al., 2005), and soil (Boulanger et al., 2005; Kubwabo et al., 2005; Weiss et al., 2021). Besides numerous reports on toxicity of PFAS (Gaballah et al., 2020; Hall et al., 2022; Tang et al., 2023), they also exhibit ecological risks, notably impacting microbial community structures and the abundance of functional genes related to the nitrogen cycle in soil-microbe-plant systems (Jiang et al., 2021, 2022). One of the major sources of PFAS contamination is biosolids or treated sewage sludge that has been used as fertilizer or soil amendment for land applications in agriculture. Sewage sludge has been considered a sink for PFAS (Bai and Son, 2021; Higgins et al., 2005), since the conventional processes used at the wastewater treatment plants (WWTPs) for treating wastewater are not able to properly remove PFAS from the water, and PFAS could accumulate in the resulting sludge by adsorption during the processing.

In recent years, the detection of PFAS in sludge and biosolids has been reported globally (Johnson, 2022; Munoz et al., 2022; Semerad et al., 2020). Most of the studies focused on a small subset of perfluoroalkyl acids (PFAAs), such as pefluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). PFAAs are recognized as end products from the degradation of precursors and are stable in the environment. Most recent studies have revealed, however, that PFAAs only contribute to a small percentage of total organic fluorine (TOF) (Nikiforov, 2021; Thompson et al., 2023). For instance, it was reported that sewage sludge tested in the US contained significant loads of non-measured PFAS beyond the 28 targeted ones (Winchell et al., 2021). A recent survey on biosolids from seven WWTPs in the US revealed they contained PFAS with concentrations ranging from 323 ± 14.1 to 1100 ± 43.8 μg/kg dry weight, and over 75% of the PFAS fluorine mass was attributed to precursors (Schaefer et al., 2022). In sediment samples from Lake Erie that historically received biosolids inputs, the ratio between concentrations of perfluorooctane sulfonamide (PFOSA) to $\sum_{22}$PFAS was up to 1616 (Chu and Letcher, 2017). In a survey of 11 WWTPs in the US, two PFOS precursors, namely N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) and N-methyl-perfluorooctane sulfonamido acetic acid (N-MeFOSAA), reached up to 335 and 126 μg/kg, respectively, in the anaerobically digested sludge (Higgins et al., 2005). Therefore, treating PFAA precursors in sewage sludge is an important step in mitigating the adverse impacts of PFAS on humans and environmental health. Otherwise, these precursors, although not regulated currently, may pose as a reservoir for PFAAs that have been regulated tightly and force removal of PFAAs to be a cumbersome task.

Although several methods, such as advanced oxidation processes (AOPs) (Barisci and Suri, 2021), have been examined to remove or destroy PFAA precursors in aqueous solutions, only a limited number of technologies has been developed to mitigate the dispersion of precursors in sludge (Garg et al., 2023). Additionally, certain drawbacks existed in these limited strategies, such as low effectiveness and high energy consumption (Kumar et al., 2023). For example, the Cambi thermal hydrolysis process (CambiTHP) was studied to destruct PFAS in sewage sludge (Zhang and Liang, 2021). Treatments at 250 °C for 2 h or 300 °C for 0.5 h, however, significantly increased the concentrations of PFAA precursors. With the addition of $Ca(OH)_2$ and at 165 or 300 °C for 2 h, the precursors completely disappeared, but the extractable PFAAs were significantly elevated. This could be due to the increased conversion of PFAA precursors into perfluoroalkyl carboxylic acids (PFCAs) under alkaline conditions.

Alternatively, as a non-destructive technique, stabilization has been demonstrated to be effective in immobilizing PFAS in sludge to prevent them from leaching into the surrounding environment (Zhang et al., 2022). A previous study (Zhang et al., 2022) applying different sorbents for PFAS stabilization in sludge showed that granular activated carbon (GAC) and RemBind sorbents at a dose of 1 or 2 wt% led to significantly lower leachable PFAAs and undecafluoro-2-methyl-3-oxahexanoic acid (GenX). Moreover, the effectiveness of stabilizing a PFAA precursor, N-EtFOSAA, in soil has been proven (Zhang et al., 2023). In soil amended with powdered activated carbon (PAC), the water leachable and methanol extractable N-EtFOSAA and its transformation products were significantly reduced (Zhang et al., 2023). To our best knowledge, however, there have been no published studies examining this technique regarding PFAA precursors in sewage sludge or biosolids, which are more heterogeneous and have completely distinct compositions compared to soil.

Recently, a green clay-based sorbent was synthesized by modifying montmorillonite with cetyltrimethylammonium chloride (CTAC). The resulting modified clay manifested much higher PFAS (including PFAA precursors) adsorption performance than commercial sorbents (e.g., GAC and PAC) in aqueous solutions (Jiang et al., 2023). To expand the application of modified clay and evaluate its efficacy in stabilizing PFAA precursors in sludge, two representative precursors were selected and tested in this study, namely N-EtFOSAA and 6:2 fluorotelomer sulfonic acid (6:2 FTSA). Both precursors have been widely detected in the actual sewage sludge (Higgins et al., 2005; Ruan et al., 2015). Given the facts that PFAS are ubiquitous in sludge from WWTPs, and thousands of PFAS structures could be present in highly complex sludge, PFAS-free sludge was generated using a sequencing batch reactor (SBR) in the lab. Through this study, it is expected that the mechanisms underlying the stabilization of the precursors by the chosen sorbents will be elucidated. Insights gained from this study may help guide the development of novel and improved sorbents for minimizing or eliminating leaching of PFAS in sewage sludge or biosolids to nearby environment.

2. Materials and methods

2.1. SBR setup and operation

To generate PFAS-free sludge, the SBR system was set up in a lab-scale reactor with a working volume of 15 L simulating real wastewater treatment processes. The rectangular reactor was made of acrylic plastic plexiglass and equipped with aeration and mixing systems, which was operated at room temperature. The sludge inoculum was obtained from a local municipal WWTP in the greater Capital Region of Albany, New York, US, the basic characteristics of which can be found in the published report (Zhang et al., 2022). Before inoculation, the inoculum was centrifuged, dewatered, and diluted 100 times to minimize introducing PFAS to the SBR. Then a 14-d sludge acclimation process was performed, during which around 10% of the sludge was discharged each day. The acclimation process aimed to gradually introduce the sludge to the new environment, facilitating the adaptation of microorganisms present in the sludge and optimizing their performance. The SBR was operated in a sequencing batch mode with a cycle time of 24 h, comprising four stages: filling, reaction, settling, and decant. The generated sludge was analyzed for pH, total solids (TS), total volatile solids (TVS), ash content, sludge volume index (SVI), total organic carbon (TOC), and total nitrogen (TN). The details of influent artificial wastewater, SBR operation, and characterization of the sludge can be found in Text S1.

2.2. *Preparation of clay sorbents*

The detailed synthesis for the unmodified and modified clays used in this study has been previously described (Jiang et al., 2023). Briefly, a two-step process was employed, starting with the addition of montmorillonite K10 (Alfa Aesar, Haverhill, MA, USA) to a Na_2CO_3 solution and stirring for 3 h. A few drops of concentrated hydrochloric acid were then added for neutralization, followed by rinsing with deionized (DI) water until no Cl^- was detectable and drying overnight to generate the unmodified clay. The obtained solids were then mixed with a CTAC solution for modification at a CTAC/CEC (cation exchange capacity) ratio of 0.85 and stirred at 80 °C for 2 h, followed by rinsing with DI water and drying overnight to produce the modified clay sorbent.

2.3. *Stabilization experiments*

The stabilization experiments were performed in 50-mL polypropylene centrifuge tubes with caps closed tightly. To evaluate the effectiveness of modified clay in stabilizing PFAA precursors, experiments were conducted using lab-generated PFAS-free sludge spiked with N-EtFOSAA (SynQuest Laboratories, Alachua, FL, USA) at 375 μg/kg or 6:2 FTSA (SynQuest Laboratories, Alachua, FL, USA) at 460 μg/kg (Higgins et al., 2005; Schaefer et al., 2022; Zhang et al., 2022). Additionally, the stabilization performance of another two sorbents, namely unmodified clay and PAC (Calgon Carbon, Pittsburgh, PA, USA), was also comparatively examined. The dose of each sorbent in sludge for stabilization was 1% (wet weight based). To determine any changes in the sorbents' stabilization effectiveness over time, the subsamples were collected from each group on Days 5, 18, and 47 after sorbent addition. All treatments with a selected sorbent and controls without a sorbent were established with three replicates, and all setups were stored at 4 °C. More experimental details were described in Text S2.

2.4. *Sequential leaching and analysis of PFAS*

The collected wet sludge subsamples (ca. 6 g with 0.3 g dry weight for each) from the triplicates in each group were subjected to sequential leaching of PFAS by pure water, acidic water (pH 4.2) following the US EPA SW-846 Test Method 1312, Synthetic Precipitation Leaching Procedure (SPLP), and basic methanol with 0.1 M NH_4OH. Leaching by water and acidic water simulates typical precipitation and acid rain, respectively, while leaching by basic methanol is assumed to extract all residual PFAS. The leaching procedure and sample treatment have been described in detail in Text S3 and the published report (Zhang et al., 2022).

PFAS analysis was performed to measure the concentrations of the two studied precursors (i.e., N-EtFOSAA and 6:2 FTSA) and their possible degradation products, as well as frequently detected PFAS in sewage sludge from WWTPs, i.e., perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, and GenX (Semerad et al., 2020; Yang et al., 2022; Zhang et al., 2023). To ensure accuracy in PFAS analysis, ^{13}C-PFOA and ^{13}C-PFOS were added at 10 μg/L as internal standards to all samples prior to analysis. PFAS were measured by a 1290 Infinity II UPLC coupled with a 6470 Triple Quad Mass Spectrometer manufactured by Agilent Technologies (Santa Clara, CA, USA). The Student's *t*-test, which is a statistical hypothesis test commonly used to determine if there is a significant difference between the means of two groups (Mishra et al., 2019), was performed to assess the significance of differences between two data sets. A p-value <0.05 was considered statistically significant. The details of PFAS quantification, instrumental parameters, and quality control were provided in Text S4, Tables S1 and S2, and prior publications (Jiang et al., 2023; Zhang and Liang, 2020, 2021).

3. Results and discussion

3.1. *Characteristics of the SBR sludge*

The activated sludge produced by the SBR system had characteristics that were comparable to the actual sewage sludge from WWTPs. The pH of the generated sludge was 7.2 ± 0.6 and the SVI was 85 mL/g, which fell within the typical ranges of actual sludge (Martins et al., 2003; Painter and Loveless, 1983). The TS content of the mixed liquor in the reactor was 0.32 ± 0.015% and the TVS ranged from 62% to 65% of the TS, with the ash content being 35–38%, indicating the presence of a significant amount of biodegradable organic matter in the sludge. The TOC of the dewatered sludge was 195 ± 16 g/kg dry weight and the TN content was 18.2 ± 3.1 g/kg dry weight, which were similar to those of real sludge from WWTPs (Tao et al., 2011). Overall, the close similarity between the SBR sludge and those from WWTPs indicated that by using the artificial sludge, this study can provide valuable information and guidelines for handling real PFAS-containing sewage sludge. The SBR system is proven to be useful in producing sludge without PFAS. After three months of stable operation, targeted analysis revealed absence of N-EtFOSAA, 6:2 FTSA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFBS, PFHxS, PFOS, and GenX.

3.2. *Mass balance and degradation of precursors*

The mass balance (mol%), which refers to the recovery of the total leached precursors and their quantifiable transformation products from the sludge samples compared with the initial molar mass of spiked precursors, was displayed in Fig. 1. The data showed all spiked PFAA precursors were extracted by the sequential leaching process, with recoveries falling within the accepted range of 70–130% (Guideline, 1997). Within this range, the recoveries higher or lower than 100% were mainly due to matrix effects given the complex nature of sludge. Specifically, the recovery of spiked N-EtFOSAA was found to be between 81.6% and 129.1%, while that of spiked 6:2 FTSA was between 73.9% and 113.9%. The statistical analysis also showed no significant difference between the masses of spiked and total leached precursors ($p > 0.05$) for all groups. A previous study showed that a significant amount of non-extractable residues (NER) of PFAS was formed in PFAS-spiked sandy loam soil amended with PAC after 60 days (Zhang et al., 2022, 2023). In the present study, however, the close to 100% of recovery of the initially spiked precursors indicated that NER was not formed, at least during the experimental duration of 47 days. This could be due to the differences between soil and sludge with respect to physicochemical properties (Epstein et al., 1976; Kranz et al., 2020; Stamatiadis et al., 1999). For example, different soils comprise various amounts of sand, silt, clay, humic materials and minerals, all of which are absent in the artificial sludge used in this study. The lab-made sludge, although in close resemblance to real sewage sludge, mainly consisted of microbial cells. The real sludge, however, does contain organic matter and minerals in the raw wastewater being treated. Thus, it is unknown at this point whether NER will be formed between PFAS in real sludge and a given sorbent. Further studies with longer durations and a broader investigation of various environmental factors are needed to obtain a

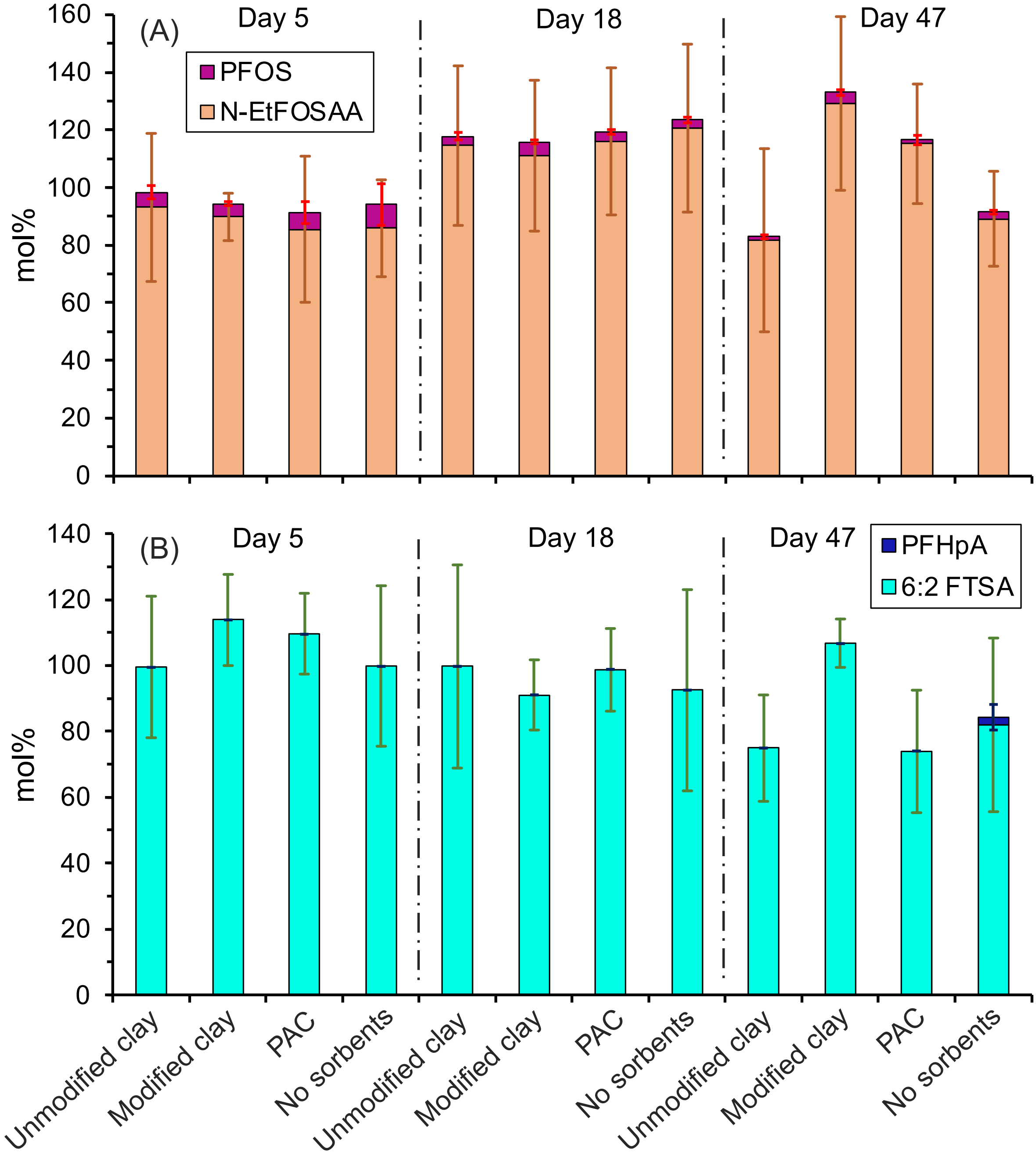


Fig. 1. Mass balance (mol%) of spiked and total leached N-EtFOSAA (A) and 6:2 FTSA (B) and total leached degradation products at the three different times (i.e., Days 5, 18, and 47) during stabilization using unmodified clay, modified clay, PAC, and without sorbents. Error bar indicates standard deviation of the mean for triplicate experiments.

more comprehensive understanding of the fate and transformation of PFAS precursors, including their potential formation of NER.

Both N-EtFOSAA and 6:2 FTSA can undergo degradation, with PFAAs as the final products. N-EtFOSAA was found to be degraded to PFOS in previous studies (Avendaño and Liu, 2015; Zhang et al., 2023), while 6:2 FTSA can be degraded to several PFCAs, including PFHxA and PFHpA (Urtiaga et al., 2018; Yang et al., 2022). This study confirmed that N-EtFOSAA underwent degradation, with a percentage ranging from 1.54 ± 0.76% to 8.77 ± 7.17% degrading to PFOS. Since there was no significant change in the percentage of PFOS over time, it showed that the majority of the degradation process of N-EtFOSAA took place in the initial phase. As time progressed, the rate of degradation became much slower, and the percentage of PFOS present in the sludge remained relatively stable. This might be due to the declining bioavailability of N-EtFOSAA resulting from processes such as adsorption to sludge particles and organic matter, or sequestration in microorganisms. Additionally, keeping all treatment and control groups at 4 °C certainly reduced microbial activities, which may also slow the precursor biodegradation. In contrast, the degradation of 6:2 FTSA was limited under the tested conditions (4 °C), with 2.59 ± 3.79% degrading to PFHpA only in the sludge without sorbents on Day 47, and no other PFCA degradation products were detected. Based on these findings, given the fact that the degradation products only represented a small proportion of the total precursor mass, they were not considered in further data analysis as discussed in the following.

3.3. Stabilization of N-EtFOSAA by the sorbents

The percentage of precursor in each leachate (i.e., water, SPLP, and methanol), with a total of 100%, was analyzed to investigate the leaching behavior of the precursors by different solvents. The results, as depicted in Fig. 2, showed that basic methanol leached most of the spiked N-EtFOSAA from the sludge samples, ranging from 83.5 ± 4.8% to 99.2 ± 4.6%, regardless of the presence or absence of a sorbent. The findings are in line with the US EPA's recommendation of basic methanol as the default solvent for extracting PFAS in biosolids, as stated in the EPA Draft Method 1633. Specifically, the absence of a sorbent resulted in 5.2 ± 0.5%, 4.0 ± 0.7%, and 90.8 ± 10.8% of leached N-EtFOSAA in water, SPLP, and methanol leachates, respectively, on Day 5. The precursor percentage in water leachate increased to 6.3 ± 0.2% on Day 18 and to 9.4 ± 0.8% on Day 47, while the percentage in methanol leachate decreased over time, indicating the possibility of remobilization of N-EtFOSAA after its adsorption onto the sludge.

Among the three sorbents applied, the modified clay was found to be the most effective in stabilizing N-EtFOSAA. The precursor percentage in the water leachate decreased from 1.4 ± 0.07% on Day 5 to 1.1 ± 0.03% ($p < 0.01$) on Day 18 and to 0.8 ± 0.03% ($p < 0.001$) on Day 47 (Fig. 2). These percentages were significantly lower ($p < 0.001$) than those in the control group on the same time points. The precursor percentage in methanol leachate for the modified clay increased over time from 98.6 ± 5.9% on Day 5–99.2 ± 4.6% on Day 47, with no leaching from SPLP. The findings suggested that the stabilization of N-EtFOSAA was increasingly enhanced over time without remobilization occurring, indicating that the modified clay could have excellent long-term

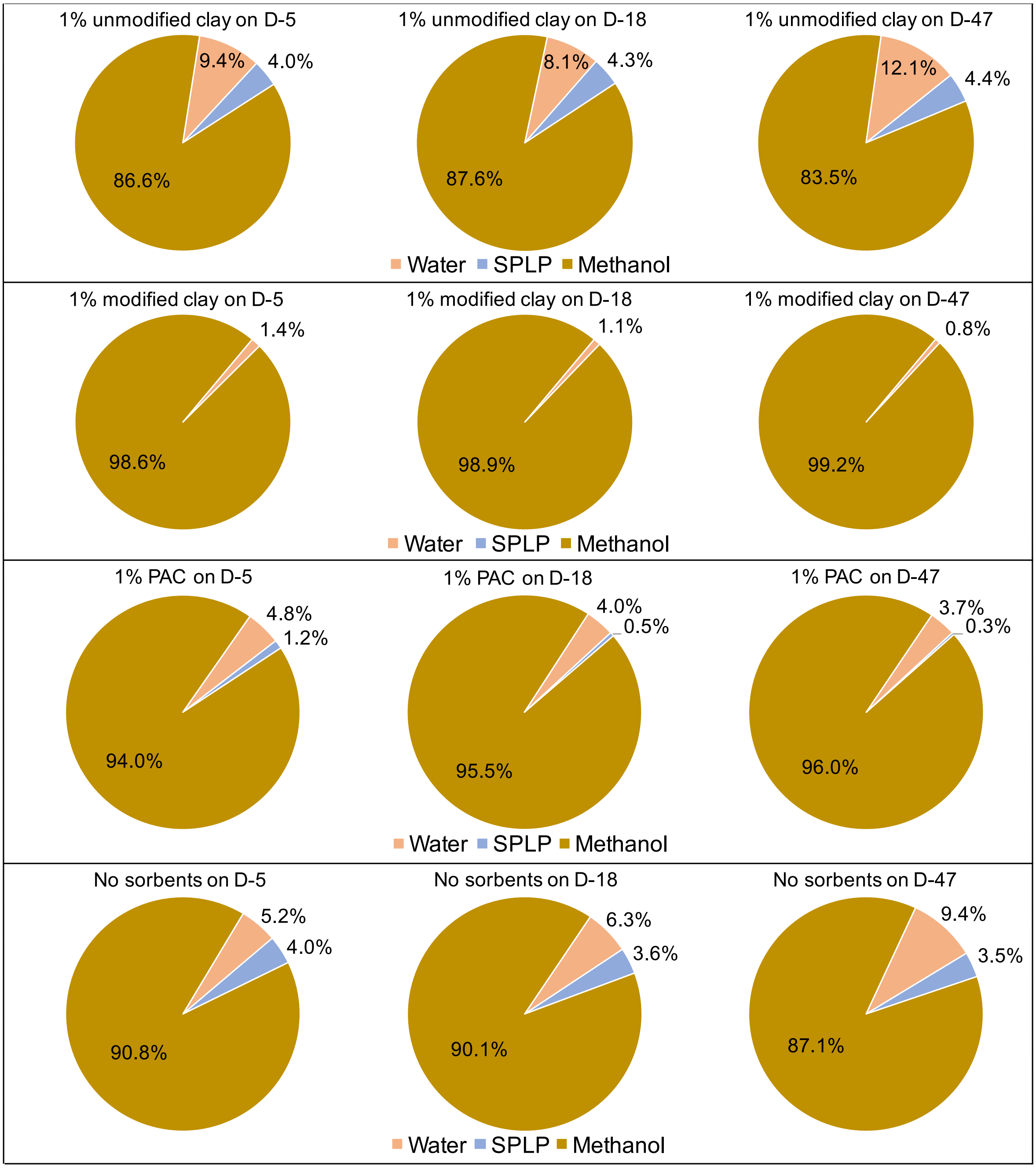


Fig. 2. The percentage of leached N-EtFOSAA by water, SPLP, and basic methanol at three different time points (i.e., Days 5, 18, and 47) during stabilization using unmodified clay, modified clay, PAC, and without sorbents. The data represents the mean values of triplicate experiments.

stabilization performance. PAC also showed a stabilizing effect on N-EtFOSAA over time, although its performance was less effective than that of the modified clay. The use of PAC resulted in a decrease in the N-EtFOSAA percentage in water leachate from 4.8 ± 0.2% on Day 5 to 3.7 ± 0.3% ($p < 0.01$) on Day 47, while the percentage in SPLP leachate decreased from 1.2 ± 0.2% on Day 5 to 0.3 ± 0.1% ($p < 0.01$) on Day 47, and the percentage in methanol leachate increased over time. In contrast, unmodified clay exhibited poor stabilization performance for N-EtFOSAA, with the total precursor percentages in water and SPLP leachates being higher than those from the control sludge without a sorbent, indicating the treatment by unmodified clay may promote the leaching of N-EtFOSAA from the sludge. Additionally, the increasing precursor percentage in water over time demonstrated possible remobilization of N-EtFOSAA in the sludge amended with unmodified clay.

3.4. Stabilization of 6:2 FTSA by the sorbents

As presented in Fig. 3, the results showed that water was capable of leaching the majority of spiked 6:2 FTSA from the sludge in the absence of a sorbent, ranging from 64.3 ± 10.4% on Day 5–74.5 ± 11.8% on Day 47. This suggested that 6:2 FTSA had a low tendency to be adsorbed by the sludge, making it easy to be leached by water only. The increasing 6:2 FTSA percentage in water over the course of the treatment indicated potential remobilization after its adsorption onto the sludge. Similar to N-EtFOSAA, 6:2 FTSA was poorly stabilized by the unmodified clay. The higher total precursor percentages in water and SPLP leachates compared to the control (Fig. 3) showcased a negative effect of the unmodified clay toward 6:2 FTSA stabilization.

The modified clay and PAC, however, had a significantly positive

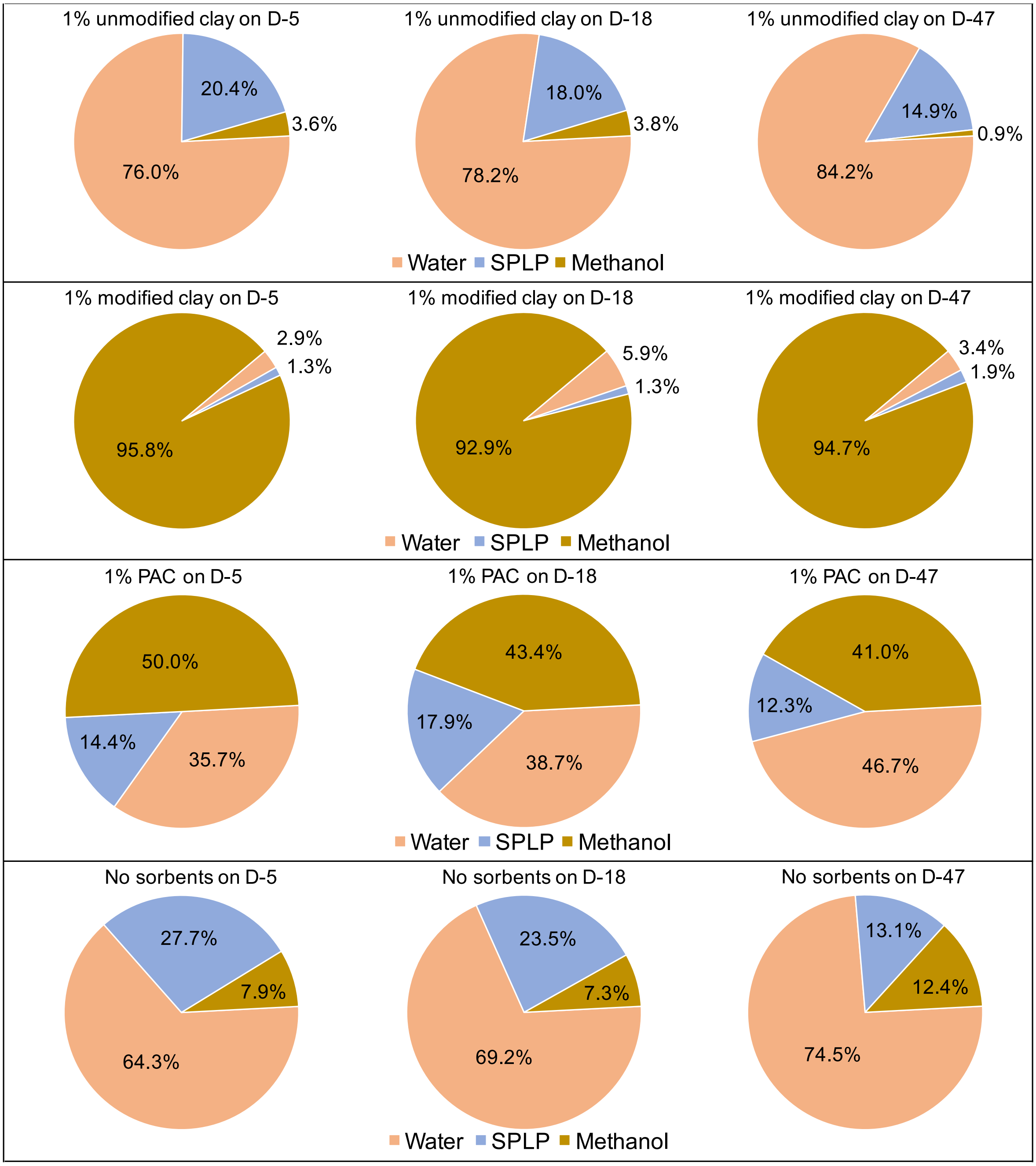


Fig. 3. The percentage of leached 6:2 FTSA by water, SPLP, and basic methanol at three different time points (i.e., Days 5, 18, and 47) during stabilization using unmodified clay, modified clay, PAC, and without sorbents. The data represents the mean values of triplicate experiments.

impact on the stabilization of 6:2 FTSA. The modified clay demonstrated the highest efficacy in stabilizing 6:2 FTSA, as evidenced by the lowest precursor percentages in water and SPLP leachates. Specifically, the percentages in water and SPLP leachates were 2.9 ± 1.5% and 1.3 ± 0.2%, respectively, on Day 5, which were dramatically lower than those from the control sludge without sorbents, i.e., 64.3 ± 10.4% ($p < 0.001$) and 27.7 ± 1.0% ($p < 0.0001$), respectively. The treatment by modified clay resulted in a slight increase in 6:2 FTSA percentage in water leachate from Days 5–47. Although the increase was insignificant, the long-term effect of the modified clay on stabilizing this precursor warrants further investigations. Compared to the modified clay, the stabilization effect of PAC was less. The use of PAC led to 35.7 ± 2.3% and 14.4 ± 1.7% of 6:2 FTSA in water and SPLP leachate, respectively, on Day 5. However, the markedly elevated precursor percentage in water leachate over time suggested that significant remobilization could occur with PAC used in a long term.

3.5. *Comparison of stabilization behaviors of the two precursors*

N-EtFOSAA and 6:2 FTSA are two types of PFAA precursors with different physicochemical properties. Both N-EtFOSAA and 6:2 FTSA have an eight-carbon chain, but the former has all carbon atoms in the carbon chain perfluorinated, while only six carbon atoms are perfluorinated for the latter. Additionally, 6:2 FTSA possesses a sulfonate functional group, whereas N-EtFOSAA has a more complex functional group (Zhang et al., 2023). Furthermore, N-EtFOSAA has a higher solid-water partition coefficient than 6:2 FTSA ($\log K_{OC} = 3.23 \pm 0.18$ versus 2.1 ± 0.5 L/kg, respectively) (Higgins and Luthy, 2006; Nguyen et al., 2020), indicating N-EtFOSAA is more hydrophobic than 6:2 FTSA. The physicochemical characteristics of PFAS can significantly influence their interactions with sludge and sorbents. For instance, the disparity in hydrophobicity may partially account for the higher adsorption tendency of N-EtFOSAA compared to 6:2 FTSA in the sludge without sorbents. N-EtFOSAA, being more hydrophobic, is likely to have a stronger attraction to the hydrophobic organic components present in the sludge. While the partition coefficient provides valuable information on the relative affinity of precursors for sludge, it is worth noting that other processes may also affect their behavior in complex environmental systems, such as sorption/desorption kinetics, transport processes, and interactions with natural organic matter (NOM). Further investigations are warranted to fully understand the behavior and fate of N-EtFOSAA and 6:2 FTSA in sludge.

Furthermore, the physicochemical properties of N-EtFOSAA and 6:2 FTSA may explain why their stabilization was negatively affected by the unmodified clay. The adsorption of PFAS onto clay surfaces is believed to be primarily controlled by electrostatic interactions and hydrophobic interactions (Jiang et al., 2023; Sarkar et al., 2012). Previous studies have demonstrated that the unmodified clay has a negatively charged surface and a hydrophilic nature (Hong, 2016; Jiang et al., 2023). The negative impact of the unmodified clay on stabilization might be due to the electrostatic repulsion between the negatively charged clay surface and precursor molecules without any hydrophobic interactions. The modified clay, in contrast, has been engineered to contain quaternary ammonium cations (QAC) that provided a positively charged and hydrophobic surface (Jiang et al., 2023). This positive charge could attract the negatively charged functional groups of N-EtFOSAA and 6:2 FTSA through electrostatic interactions, which was followed by hydrophobic interactions between the hydrophobic precursor carbon chains and the QAC alkyl chains. These findings could help guide the development of more effective sorbents for stabilizing PFAS in sludge or biosolids.

3.6. *Limitations and implications*

In light of the close similarity between the sludge generated from the SBR system in the lab and those from WWTPs, findings from this study could be translated to practical scenarios. However, confirmation of results from this study needs to be conducted using actual sludge. In addition, designed as a study to prove the concept, this work had a narrow focus on two precursor compounds, three sorption materials, and a relatively short experimental duration. It is possible that other degradation products were formed from the two precursors and were not quantified by the targeted analysis. Thus, non-targeted high resolution MS analysis may be needed to fully understand biodegradation of the two precursors in sludge. Although the intermediate degradation products of precursors were not considered in the evaluation of stabilization effectiveness, their exploration merits further investigation in future studies. With respect to the experimental duration, 47 days were long enough to assess the short-term stabilization performance of sorbents (Zhang et al., 2022). Similar timeframe has been used in other studies to evaluate PFAS uptake by plant (ca. 97% reduction; 40 and 80 days) (Zhang and Liang, 2022) and earthworms (>95% reduction; 28 days) (Jarjour et al., 2022). To fully evaluate the effectiveness of the stabilization approach, long-term observation and monitoring of field studies where sorbent amended sludge is land applied are needed. Furthermore, besides PFAS stabilization, the potential impact of the amendments, including the modified clay, on availability and dynamics of nutrients and organic matter in sludge or biosolids should be carefully investigated.

A preliminary analysis revealed the basic cost of the modified clay is approximately $0.75/kg. This only considered the reagents consumed in the synthesis process, and did not include cost of electricity for heating. High energy consumption was not perceived since the synthesis process was performed at 80 °C, much lower than that required for AC production (>400–800 °C). For comparison, the selling price of AC ranges from $1.5 to $14.6 per kg (Inyang and Dickenson, 2015; Volchek et al., 2018). Considering the high stabilization capacity of the modified clay, it is expected to be more cost-effective than the AC-based sorbents.

The success of this stabilization method would offer a sustainable solution for WWTPs facing challenges in disposing of PFAS-containing sludge and biosolids. This technology could be integrated into WWTPs or sludge processing facilities to help mitigate the release of PFAS into the environment. The rates of stabilization observed in this study may help in determining the appropriate dosage of sorbents required for efficient and long-lasting stabilization of PFAS. Additional engineering of the modified clay and other sorbents may be required to achieve complete stabilization of all PFAS in sludge and prevent long-term leaching into surrounding water environment. The development of such sorbents should consider the characteristics of both sorbents and PFAS, as well as the interactions between them. Further research is also needed to assess the possible influence of evapotranspiration on the fate and transport of PFAS in stabilized sludge upon applying to soils. Only until all these limitations are addressed in a comprehensive manner, can this stabilization approach be tested in the field.

4. Conclusions

This study investigated the efficacy of sorbents, including modified clay, unmodified clay, and PAC, in stabilizing two precursors of PFAAs, N-EtFOSAA and 6:2 FTSA, in artificial sewage sludge. The results indicated that the sequential leaching process extracted all precursors spiked into the PFAS-free sludge produced by the lab-scale SBR. It was observed that N-EtFOSAA was resistant to leaching from the sludge by water and acidic water. At the same time, 6:2 FTSA exhibited a lower affinity to sludge in the absence of sorbents, which can be attributed to the differences in their hydrophobicity. The modified clay was the most effective sorbent in stabilizing both precursors, mainly because of its positively charged and hydrophobic surface, demonstrating excellent stabilization performance without remobilization. PAC also showed a stabilizing effect on both precursors, although its performance was inferior to that of the modified clay. The unmodified clay exhibited the lowest stabilization performance for both precursors and even promoted their leaching, possibly due to the electrostatic repulsion between this material and the precursor molecules.

CRediT authorship contribution statement

Tao Jiang: Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Validation, Writing – original draft, Writing – review & editing. **Md. Nahid Pervez:** Data curation, Writing – review & editing. **Monica M. Quianes:** Data curation. **Weilan Zhang:** Methodology. **Vincenzo Naddeo:** Writing – review & editing. **Yanna Liang:** Conceptualization, Methodology, Formal analysis, Validation, Writing – review & editing, Resources.

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.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge financial supports from University at Albany, State University of New York, and the US National Science Foundation (award number CBET 2225596).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.140081.

References

Avendaño, S.M., Liu, J., 2015. Production of PFOS from aerobic soil biotransformation of two perfluoroalkyl sulfonamide derivatives. Chemosphere 119, 1084–1090.

Bai, X., Son, Y., 2021. Perfluoroalkyl substances (PFAS) in surface water and sediments from two urban watersheds in Nevada, USA. Sci. Total Environ. 751, 141622.

Barisci, S., Suri, R., 2021. Removal of polyfluorinated telomer alcohol by Advanced Oxidation Processes (AOPs) in different water matrices and evaluation of degradation mechanisms. J. Water Proc. Eng. 39, 101745.

Boulanger, B., Vargo, J.D., Schnoor, J.L., Hornbuckle, K.C., 2005. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. Environ. Sci. Technol. 39 (15), 5524–5530. https://doi.org/10.1021/es050213u.

Chu, S., Letcher, R.J., 2017. Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America. Sci. Total Environ. 607–608, 262–270. https://doi.org/10.1016/j.scitotenv.2017.06.252.

Epstein, E., Taylor, J., Chaney, R., 1976. Effects of Sewage Sludge and Sludge Compost Applied to Soil on Some Soil Physical and Chemical Properties. Wiley Online Library.

Gaballah, S., Swank, A., Sobus, J.R., Howey, X.M., Schmid, J., Catron, T., McCord, J., Hines, E., Strynar, M., Tal, T., 2020. Evaluation of developmental toxicity, developmental neurotoxicity, and tissue dose in zebrafish exposed to GenX and other PFAS. Environ. Health Perspect. 128 (4), 047005.

Garg, A., Shetti, N.P., Basu, S., Nadagouda, M.N., Aminabhavi, T.M., 2023. Treatment technologies for removal of per-and polyfluoroalkyl substances (PFAS) in biosolids. Chem. Eng. J. 453, 139964.

Guideline, I., 1997. Q2B validation of analytical procedures: methodology. Fed. Regist. 62.

Hall, S.M., Zhang, S., Hoffman, K., Miranda, M.L., Stapleton, H.M., 2022. Concentrations of per-and polyfluoroalkyl substances (PFAS) in human placental tissues and associations with birth outcomes. Chemosphere 295, 133873.

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environ. Sci. Technol. 39 (11), 3946–3956.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40 (23), 7251–7256.

Hong, J.S., 2016. Aggregation of hydrophilic/hydrophobic montmorillonites at oil-water interface. Appl. Clay Sci. 119, 257–265. https://doi.org/10.1016/j.clay.2015.10.025.

Inyang, M., Dickenson, E., 2015. The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: a review. Chemosphere 134, 232–240. https://doi.org/10.1016/j.chemosphere.2015.03.072.

Jarjour, J., Yan, B., Munoz, G., Desrosiers, M., Sauvé, S., Liu, J., 2022. Reduced bioaccumulation of fluorotelomer sulfonates and perfluoroalkyl acids in earthworms (Eisenia fetida) from soils amended with modified clays. J. Hazard Mater. 423, 126999.

Jiang, T., Geisler, M., Zhang, W., Liang, Y., 2021. Fluoroalkylether compounds affect microbial community structures and abundance of nitrogen cycle-related genes in soil-microbe-plant systems. Ecotoxicol. Environ. Saf. 228, 113033.

Jiang, T., Zhang, W., Ilango, A.K., Feldblyum, J.I., Wei, Z., Efstathiadis, H., Yigit, M.V., Liang, Y., 2023. Surfactant-modified clay for adsorption of mixtures of per-and polyfluoroalkyl substances (PFAS) in aqueous solutions. ACS Applied Engineering Materials 1 (1), 394–407.

Jiang, T., Zhang, W., Liang, Y., 2022. Uptake of individual and mixed per-and polyfluoroalkyl substances (PFAS) by soybean and their effects on functional genes related to nitrification, denitrification, and nitrogen fixation. Sci. Total Environ. 838, 156640.

Johnson, G.R., 2022. PFAS in soil and groundwater following historical land application of biosolids. Water Res. 211 https://doi.org/10.1016/j.watres.2021.118035.

Kranz, C.N., McLaughlin, R.A., Johnson, A., Miller, G., Heitman, J.L., 2020. The effects of compost incorporation on soil physical properties in urban soils - a concise review. J. Environ. Manag. 261 https://doi.org/10.1016/j.jenvman.2020.110209.

Kubwabo, C., Stewart, B., Zhu, J.P., Marro, L., 2005. Occurrence of perfluorosulfonates and other perfluorochemicals in dust from selected homes in the city of Ottawa, Canada. J. Environ. Monit. 7 (11), 1074–1078. https://doi.org/10.1039/b507731c.

Kumar, R., Dada, T.K., Whelan, A., Cannon, P., Sheehan, M., Reeves, L., Antunes, E., 2023. Microbial and thermal treatment techniques for degradation of PFAS in biosolids: a focus on degradation mechanisms and pathways. J. Hazard Mater. 452, 131212.

Martins, A.M.P., Heijnen, J.J., van Loosdrecht, M.C.M., 2003. Effect of feeding pattern and storage on the sludge settleability under aerobic conditions. Water Res. 37 (11), 2555–2570. https://doi.org/10.1016/s0043-1354(03)00070-8.

Mishra, P., Singh, U., Pandey, C.M., Pandey, G., 2019. Application of student's t-test, analysis of variance, and covariance. Ann. Card Anaesth. 22 (4), 407–411. https://doi.org/10.4103/aca.ACA_94_19.

Morales-McDevitt, M.E., Becanova, J., Blum, A., Bruton, T.A., Vojta, S., Woodward, M., Lohmann, R., 2021. The air that we breathe: neutral and volatile PFAS in indoor air. Environ. Sci. Technol. Lett. 8 (10), 897–902.

Munoz, G., Michaud, A.M., Liu, M., Duy, S.V., Montenach, D., Resseguier, C., Watteau, F., Sappin-Didier, V., Feder, F., Morvan, T., Houot, S., Desrosiers, M., Liu, J.X., Sauve, S., 2022. Target and nontarget screening of PFAS in biosolids, Composts,and other organic waste products for land application in France. Environ. Sci. Technol. 56 (10), 6056–6068. https://doi.org/10.1021/acs.est.1c03697.

Nguyen, T.M.H., Bräunig, J., Thompson, K., Thompson, J., Kabiri, S., Navarro, D.A., Kookana, R.S., Grimison, C., Barnes, C.M., Higgins, C.P., 2020. Influences of chemical properties, soil properties, and solution pH on soil–water partitioning coefficients of per-and polyfluoroalkyl substances (PFASs). Environ. Sci. Technol. 54 (24), 15883–15892.

Nikiforov, V.A., 2021. Hydrolysis of FTOH precursors, a simple method to account for some of the unknown. Chemosphere 276. https://doi.org/10.1016/j.chemosphere.2021.130044.

Painter, H.A., Loveless, J.E., 1983. Effect of temperature and PH value on the growth-rate constants of nitrifying bacteria in the activated-sludge process. Water Res. 17 (3), 237–248. https://doi.org/10.1016/0043-1354(83)90176-8.

Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 43 (2), 386–392. https://doi.org/10.1021/es802216n.

Ruan, T., Lin, Y., Wang, T., Liu, R., Jiang, G., 2015. Identification of novel polyfluorinated ether sulfonates as PFOS alternatives in municipal sewage sludge in China. Environ. Sci. Technol. 49 (11), 6519–6527.

Sarkar, B., Xi, Y.F., Megharaj, M., Krishnamurti, G.S.R., Bowman, M., Rose, H., Naidu, R., 2012. Bioreactive organoclay: a new technology for environmental remediation. Crit. Rev. Environ. Sci. Technol. 42 (5), 435–488. https://doi.org/10.1080/10643389.2010.518524.

Schaefer, C.E., Hooper, J., Modiri-Gharehveran, M., Drennan, D.M., Beecher, N., Lee, L., 2022. Release of poly-and perfluoroalkyl substances from finished biosolids in soil mesocosms. Water Res. 217, 118405.

Semerad, J., Hatasova, N., Grasserova, A., Cerna, T., Filipova, A., Hanc, A., Innemanova, P., Pivokonsky, M., Cajthaml, T., 2020. Screening for 32 per- and polyfluoroalkyl substances (PFAS) including GenX in sludges from 43 WWTPs located in the Czech Republic - evaluation of potential accumulation in vegetables after application of biosolids. Chemosphere 261. https://doi.org/10.1016/j.chemosphere.2020.128018.

Shoeib, M., Harner, T., Ikonomou, M., Kannan, K., 2004. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl Ethers. Environ. Sci. Technol. 38 (5), 1313–1320. https://doi.org/10.1021/es0305555.

Shoeib, M., Harner, T., Wilford, B.H., Jones, K.C., Zhu, J., 2005. Perfluorinated sulfonamides in indoor and outdoor air and indoor dust: occurrence, partitioning, and human Exposure. Environ. Sci. Technol. 39 (17), 6599–6606. https://doi.org/10.1021/es048340y.

Stamatiadis, S., Doran, J.W., Kettler, T., 1999. Field and laboratory evaluation of soil quality changes resulting from injection of liquid sewage sludge. Appl. Soil Ecol. 12 (3), 263–272.

Tang, L., Qiu, W., Zhang, S., Wang, J., Yang, X., Xu, B., Magnuson, J.T., Xu, E.G., Wu, M., Zheng, C., 2023. Poly-and perfluoroalkyl substances induce immunotoxicity via the TLR pathway in zebrafish: links to carbon chain length. Environ. Sci. Technol. 57 (15), 6139–6149.

Tao, J.J., Wu, S.L., Sun, L.B., Tan, X.B., Yu, S.M., Zhang, Z.B., 2011. Composition of waste sludge from municipal wastewater treatment plant. In: 2011 International Conference on Fuzzy Systems and Neural Computing, vol. Ii. Fsnc 2011, pp. 575–578.

Thompson, J.T., Robey, N.M., Tolaymat, T.M., Bowden, J.A., Solo-Gabriele, H.M., Townsend, T.G., 2023. Underestimation of per-and polyfluoroalkyl substances in biosolids: precursor transformation during conventional treatment. Environ. Sci. Technol. 57 (9), 3825–3832.

Urtiaga, A., Soriano, A., Carrillo-Abad, J., 2018. BDD anodic treatment of 6:2 fluorotelomer sulfonate (6:2 FTSA). Evaluation of operating variables and by-product formation. Chemosphere 201, 571–577. https://doi.org/10.1016/j.chemosphere.2018.03.027.

Volchek, K., Yao, Y., Brown, C.E., 2018. Remediation of PFAS contaminated soil. In: Kempisty, D.M., Xing, Y., Racz, L. (Eds.), Perfluoroalkyl Substances in the Environment: Theory, Practice, and Innovation. CRC Press, Taylor & Francis Group, Boca Raton, FL, USA, p. 391.

Weiss, J.M., Jones, B., Koekkoek, J., Bignert, A., Lamoree, M.H., 2021. Per-and polyfluoroalkyl substances (PFASs) in Swedish household dust and exposure of pet cats. Environ. Sci. Pollut. Res. 28 (29), 39001–39013.

Winchell, L.J., Ross, J.J., Wells, M.J., Fonoll, X., Norton Jr., J.W., Bell, K.Y., 2021. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: a state of the science review. Water Environ. Res. 93 (6), 826–843.

Yang, S.H., Shan, L.B., Chu, K.H., 2022. Fate and transformation of 6:2 fluorotelomer sulfonic acid affected by plant, nutrient, bioaugmentation, and soil microbiome interactions. Environ. Sci. Technol. 56 (15), 10721–10731. https://doi.org/10.1021/acs.est.2c01867.

Zhang, W., Jiang, T., Liang, Y., 2022. Stabilization of per-and polyfluoroalkyl substances (PFAS) in sewage sludge using different sorbents. Journal of Hazardous Materials Advances 6, 100089.

Zhang, W., Liang, Y., 2020. Removal of eight perfluoroalkyl acids from aqueous solutions by aeration and duckweed. Sci. Total Environ. 724, 138357 https://doi.org/10.1016/j.scitotenv.2020.138357.

Zhang, W., Liang, Y., 2021. Effects of hydrothermal treatments on destruction of per-and polyfluoroalkyl substances in sewage sludge. Environ. Pollut. 285, 117276.

Zhang, W., Liang, Y., 2022. Changing bioavailability of per-and polyfluoroalkyl substances (PFAS) to plant in biosolids amended soil through stabilization or mobilization. Environ. Pollut. 308, 119724.

Zhang, W., Wellington, T.E., Liang, Y., 2023. Effect of two sorbents on the distribution and transformation of N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) in soil-soybean systems. Environ. Pollut. 318, 120941.