



Effect of two sorbents on the distribution and transformation of N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) in soil-soybean systems[☆]

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ABSTRACT

The broad application of perfluoroalkyl acid (PFAA) precursors has led to their occurrence in soil, resulting in potential uptake and bioaccumulation in plants. In this study, we investigated the effect of powdered activated carbon (PAC) and montmorillonite on the distribution and transformation of a perfluorooctanesulfonic acid (PFOS) precursor, N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA), in soil-plant systems. The results showed that N-EtFOSAA at 300 µg/kg was taken up by soybean roots and shoots together with its transformation products (i.e., perfluorooctane sulfonamide (PFOSA), PFOS), while decreasing the biomass of shoots and roots by 47.63% and 61.16%, respectively. PAC amendment significantly reduced the water leachable and methanol extractable N-EtFOSAA and its transformation products in soil. In the presence of soybean and after 60 days, 73.5% of the initially spiked N-EtFOSAA became non-extractable bound residues. Compared to the spiked controls, the PAC addition also decreased the total plant uptake of N-EtFOSAA by 94.96%. In contrast, montmorillonite showed limited stabilization performance for N-EtFOSAA and its transformation products and was ineffective to lower their bioavailability. Overall, the combination of PAC and soybean was found to be effective in immobilizing N-EtFOSAA in soil.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been widely used in coating materials, fast food packaging, paints, stain resistant products, and aqueous film-forming foams (AFFFs) since the 1950s (Prevedouros et al., 2006; Wang et al., 2014; Wang et al., 2013). This class of man-made chemicals are water/oil repellent and resistant to degradation due to the unique fluorinated structure and the high strength of C–F bonds (Al Amin et al., 2021; Dadashi Firouzjaei et al., 2021). Because of their persistent nature, PFAS have been detected in various environmental matrices, including but are not limited to water (Kurwadkar et al., 2021; Xu et al., 2021), soil (Ahmed et al., 2020; Houtz et al., 2013), and biosolids (Bolan et al., 2021; Lenka et al., 2021; Pepper et al., 2021). Previous reports have demonstrated that PFAS in the contaminated environment can be taken up by plants and animals (Death et al., 2021; Lesmeister et al., 2021; Lilienthal et al., 2017). The potential health risks associated with PFAS bioaccumulation and biomagnification have raised serious concerns among all stakeholders of

our society and demand effective approaches for removing PFAS from the environment.

Perfluoroalkyl acids (PFAAs) are commonly recognized as stable end products of PFAS degradation (Lu et al., 2020; Verma et al., 2021). Thus, regulatory actions globally have focused on PFAAs only. For example, 19 states in the U.S. have established the maximum contaminant levels (MCLs) for PFAAs as of March 2022, including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorodecanoic acid (PFDA). In June of 2022, the U.S. EPA announced new health advisories for GenX (10 ng/L) and perfluorobutanesulfonic acid (PFBS, 2000 ng/L) in drinking water and released interim updated health advisories for PFOA (0.004 ng/L) and PFOS (0.02 ng/L).

Responding to regulatory requirement, numerous PFAS remediation technologies have been targeting only PFAAs. Although the need to remove PFAAs from contaminated environments is urgent and strong, ignoring the source of PFAAs will lead to PFAS remediation forever as

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precursors of PFAAs can be degraded to PFAAs by biotic and abiotic processes.

(Houtz et al., 2013; Houtz and Sedlak, 2012; Schaefer et al., 2018). Detection of PFAA precursors in environmental and biological samples has been widely reported (Houtz et al., 2013; Langberg et al., 2020; Zhang et al., 2021b). While some precursors can be degraded easily, others can persist in the environment for a long period of time (Al Amin et al., 2021; Zhang et al., 2021b). Besides their resistance to degradation, the chemical structures of countless precursors remain to be elucidated (Houtz et al., 2016). This leads to difficulties in designing methods and approaches for removing or destroying these precursor compounds in the environment.

As an important PFOS precursor, N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) has been used in various consumer products, like carpets, insecticides, and packaging paper (Ye et al., 2015). The broad application of N-EtFOSAA has led to its occurrence in the environment (Barola et al., 2020; Nguyen et al., 2016) and human blood (Ahrens et al., 2010; Gebbink et al., 2015; Yeung et al., 2013). This precursor is also detected in sewer systems, biosolids, and biosolids amended soil worldwide. For example, N-EtFOSAA was found in the influent (5.1 ± 0.8 ng/L) and effluent (3.6 ± 0.2 ng/L) of a wastewater treatment plant in Iowa City, IA (Boulanger et al., 2005). Moodie et al. (2021) investigated the PFAS levels in Australian biosolids and showed that the concentration of N-EtFOSAA was around 50 $\mu\text{g/kg}$. The concentration of N-EtFOSAA in the biosolids-amended soil collected from Chicago, IL was reported to be in the range of 42–72 $\mu\text{g/kg}$ (Sepulvado et al., 2011). N-EtFOSAA in soil could be bioaccumulated in plants, hence entering the food chain and causing health issues to animals and humans. For instance, Wen et al. (2018) found that N-EtFOSAA was taken up by crops, such as alfalfa, lettuce, maize, mung bean, radish, ryegrass, and soybean from biosolids-amended soil. During the plant uptake process, transformation of N-EtFOSAA occurred in the soil-plant system. N-ethyl perfluorooctane sulfonamide (N-EtFOSA), perfluorooctane sulfonamide (PFOSA), perfluorooctane sulfonamide acetate (FOSAA), and PFOS were detected as the transformation products.

A broad range of technologies are currently available for the remediation of PFAS contaminated soil (Bolan et al., 2021). While destructive technologies may degrade PFAS precursors in soil to different extents, the degradation is oftentimes not complete and leads to formation of degradation intermediates that may persist in the environment (Cui et al., 2020; Zhang et al., 2022). Non-destructive technologies, on the other hand, recognize the presence of PFAS in soil, but seek to prevent their migration horizontally and vertically to surrounding environments (Barth et al., 2021; Bolan et al., 2021).

Among non-destructive technologies, in recent years, stabilization by adding a sorbent to enhance PFAS fixation in the original environment has gained momentum. In soil, hydrophobic interactions, electrostatic interactions, covalent bonding, and hydrogen bonding could occur between PFAS and soil components, such as soil organic matter (SOM) and minerals (Alves et al., 2020; Xiao et al., 2011; Zhao et al., 2014). To promote these interactions toward the goal of stabilization, a wide range of sorbents, such as biochar, activated carbon (AC), AC based materials, clay minerals, and different mixtures of carbon and minerals, have been tested (Askeland et al., 2020; Hale et al., 2017; Hearon et al., 2022; Kabiri and McLaughlin, 2021; Lath et al., 2018; Silvani et al., 2019; Sorengard et al., 2019; Sörensöngård et al., 2019). Among these sorbents, RemBind, an AC-based material, when combined with Portland cement, demonstrated >99% decrease in total PFAS leachability from soil as assessed by EPA Method 1315 (McDonough et al., 2021). Our previous research also revealed that granular activated carbon (GAC) and RemBind products were able to decrease water leachable PFAS in soil by >99% (Zhang and Liang, 2022). The remaining PFAS in soil, however, were extractable by basic methanol to different degrees depending on the functional groups and carbon-fluoride chain lengths. Thus, RemBind, probably one of the best sorbents on the market for stabilization, does not lead to formation of bound residues that can resist and

survive harsh extractions by organic solvents (Northcott and Jones, 2000).

Given RemBind's inability to form strong and irreversibly bound structures with soil and the fact that stabilization of PFAS precursors in soil is an uncharted territory, in this study, we sought to investigate the transformation and distribution of N-EtFOSAA in soil-plant systems with or without a sorbent. Powdered activated carbon (PAC) was chosen as a representative of carbon-based materials. Recently, clay-based materials showed promising performance in immobilizing PFAS (Hearon et al., 2022; Wang et al., 2021). Thus, montmorillonite clay was also selected as a clay-based material in this study for stabilizing N-EtFOSAA in soil-plant systems. Soybean was used as the model plant considering its importance in agriculture. The high protein (~40%) and oil (~20%) content make it the fourth most important grain crop worldwide, after wheat, maize, and rice (Grassini et al., 2021). Concentrations of N-EtFOSAA and its transformation products in soil and soybean tissues were determined to gain insights of this precursor's fate and distribution in the tested soil-plant systems.

2. Materials and methods

1. Soil preparation and plant cultivation

The information of chemicals and reagents used in this study was shown in Table S1. The particle size of PAC (REMPAC, Calgon Carbon, Pittsburgh, PA) and montmorillonite K10 clay (Alfa Aesar, Haverhill, MA, USA) was 10.21 ± 2.56 μm and 53.29 ± 27.35 μm , respectively. The iodine number (ASTM D4607) of the PAC was 400–650. The specific surface area of montmorillonite was 220–270 m^2/g . The sandy loam soil used for this study was collected from a farm in Albany County, NY. The physicochemical properties of the soil were detailed in the Supplementary data file. Before use, the soil was air-dried, sieved through 2 mm, and mixed with vermiculite in a 1:1 vol ratio for improving soil aeration and water retention. Afterwards, the prepared soil (170 g) was allocated to 18 oz plastic cups. To investigate the effect of soil microorganisms on the transformation of N-EtFOSAA, three cups of soil were sterilized by autoclaving at 121 °C for 45 min. These were noted as autoclaved controls. The stock solution of N-EtFOSAA was then added to the prepared soil and autoclaved controls, reaching the target concentration of 300 $\mu\text{g/kg}$. To further homogenize N-EtFOSAA with soil, water was added to each cup until the soil was saturated. Six cups filled with the prepared soil but without N-EtFOSAA spiking were also prepared and referred to as non-spiked controls. To test the effect of light irradiation on the transformation of N-EtFOSAA, three cups filled with the prepared soil with N-EtFOSAA spiking were wrapped with aluminum foil for preventing any light exposure. These were termed as light controls. After 10 days of aging under a fume hood, one of the two sorbents (i.e., PAC, montmorillonite) at a dose of 1% (dry wt. based) was added to the prepared soil spiked with N-EtFOSAA and homogenized with the soil using a glass rod. No sorbents were added to the non-spiked controls, autoclaved controls, and light controls. A set of spiked controls but without any sorbents was prepared as well. Each treatment had 3 replicates. The detailed experimental design was shown in Table S2.

Glycine max (L.) Merr. (soybean) seeds were obtained from Johnny's Selected Seeds (Winslow, ME, USA). The soybean seeds were first germinated in moist sand (40–100 mesh). After a week, young seedlings with similar sizes were individually transplanted into the prepared cups and cultivated in a greenhouse with daily watering. To determine the effect of soybean on N-EtFOSAA transformation in soil, an identical set of treatments with a sorbent but without soybean planting was also prepared. On Day-35 after transplanting, all plants were pulled out of the soil and separated into roots and shoots. The plant tissues after water rinsing, were freeze-dried at -37 °C for 48 h and the dry weight of soybean was recorded. Soybean roots, shoots, and the soil after air drying in a fume hood for 15 days were subject to PFAS extraction and quantification.

2. PFAS extraction, leaching, and analysis

N-EtFOSAA and its transformation products in the freeze-dried shoots and roots and air-dried soil were extracted according to a previously developed procedure, which was detailed in SI (Zhang et al., 2021a; Zhang et al., 2020; Zhang et al., 2019).

Leaching tests for soil were conducted following Australian Standard leaching procedure, AS4439. Briefly, 1 g of representative soil sample in each cup was spiked with 10 ng of $^{13}\text{C}_2$ -PFHxA as a surrogate for assessing the extraction efficiency and transferred to a 50-mL polypropylene (PP) centrifuge tube containing 20 mL of deionized water at pH = 7. The mixture was shaken on an end over end mixer overnight at room temperature. After centrifuging at 4500 rpm for 20 min, the supernatant of the mixture was collected and subject to solid phase extraction (SPE) using HyperSep C18 cartridges (Thermo Scientific, Waltham, MA, USA).

Methanol extractable PFAS in soil were extracted followed by the method developed by Houtz et al. (2013). In short, 1 g soil sample in each cup was spiked with 10 ng of $^{13}\text{C}_2$ -PFHxA and transferred into a 50-mL PP tube containing 5 mL of methanolic ammonium hydroxide (0.1%). The mixture was then vortexed for 20 s, sonicated for 30 min at 35 °C, and shaken at 150 rpm for 2 h. After centrifugation at 4500 rpm for 20 min, the supernatant was transferred to a new PP tube. The residual was further extracted twice with the same methanolic ammonium hydroxide. The methanol extracts from 3 rounds of extraction were combined and subject to SPE using an ENVI-Carb cartridges (Thermo Scientific, Waltham, MA, USA). Afterwards, alkaline hydrolysis was carried out on the methanol extracted soil samples to release the hydrolysable portion of non-extractable residues (NER) according to the method published by Zhu et al. (2021). Briefly, the pre-extracted soil was transferred to a 20-mL glass tube containing 1.25 g of potassium hydroxide, 1 mL ultrapure water, and 10 mL methanol. The closed tubes were sonicated for 15 min, heated at 105 °C for 24 h, and sonicated again for 15 min. Then, 8 mL of acetonitrile/water (60/40) solution was added to each glass tube. The mixture was acidified to a pH value of 4–5, sonicated for 15 min, shaken at 150 rpm for 24 h, and sonicated again for 15 min. After centrifugation, the supernatant was collected, dried over anhydrous sodium sulfate, evaporated under N_2 gas, reconstituted in 6 mL of methanol, and subject to SPE using the ENVI-Carb cartridges. A set of blanks with clean sand instead of soil samples was prepared and underwent the same alkaline hydrolysis process to check the background PFAS in the hydrolysable fraction.

Besides the soil treated with a sorbent, three non-spiked controls, three autoclaved controls, and three replicates of N-EtFOSAA spiked soil without a sorbent or without soybean cultivation were also subject to PFAS leaching and extraction to determine the background PFAS in

clean soil, and the effect from: soil microorganisms and light irradiation on N-EtFOSAA transformation, sorbent and soybean. N-EtFOSAA and the transformation products in the extracts were then quantified using a 1290 Infinity II LC system coupled with a 6470 Triple Quad Mass Spectrometer (LC-MS/MS, Agilent Technologies, Santa Clara, CA, USA). The operational parameters for LC-MS/MS, detection limits of studied PFAS, and PFAS recovery efficiencies in plant tissues and soil were listed in Table S3.

3. Results and discussion

1. Plant growth and uptake of N-EtFOSAA

The exposure of soybean plants to N-EtFOSAA for 35 days resulted in significantly lower dry weight of plant shoots and roots compared to that of control plants without N-EtFOSAA exposure (Fig. 1), indicating the toxicity of this PFAA precursor to soybean at 300 $\mu\text{g}/\text{kg}$. Adding PAC or montmorillonite to soil at 1% did not mitigate this toxic effect. So far, there are limited data on the interactions between N-EtFOSAA and plants. Only one paper specifically studied the uptake of N-EtFOSAA by plants including alfalfa, Italian ryegrass, lettuce, maize, mung bean, radish, and soybean (Wen et al., 2018). At an exposure concentration of $151 \pm 12 \mu\text{g}/\text{kg}$ in biosolids-amended soil, no toxic effect of N-EtFOSAA was observed for all studied plant species. In Wen's study (Wen et al., 2018), the soil amended by biosolids had a SOM content of 3.35%, which is similar to the SOM content of 4.82% for the soil used in our study. Thus, the difference in the observed toxicity could be due to concentration of N-EtFOSAA or other components of the soil rather than the SOM and the phytotoxicity of this compound may be site specific. Future research is warranted to establish the dose-response relationship for this precursor.

Consistent with the previous study (Wen et al., 2018), N-EtFOSAA was able to be taken up by soybean roots grown in soil without sorbent amendment. In our study, its concentration in the roots was $690.68 \pm 139.06 \mu\text{g}/\text{kg}$ (Fig. 2). The upward translocation of this long chain PFAA precursor, however, was limited. The concentration of N-EtFOSAA in the soybean shoots grown in soil without sorbent amendment was only $1.84 \pm 0.79 \mu\text{g}/\text{kg}$, leading to a translocation factor ($C_{\text{shoot}}/C_{\text{root}}$) of 0.0028 ± 0.0016 . We previously reported that the translocation factor of PFOS at an exposure concentration of 100 $\mu\text{g}/\text{kg}$ to soybean plants was 0.057 ± 0.003 (Jiang et al., 2022), which is significantly higher than that of its precursor, N-EtFOSAA. N-EtFOSAA and PFOS share the same C–F backbone. But the former has higher molecular weight due to the presence of the ethyl amino acetate head in addition to the structure of PFOS. Higgins and Luthy (2006) determined the partitioning behavior of these two compounds in natural sediments and reported that the

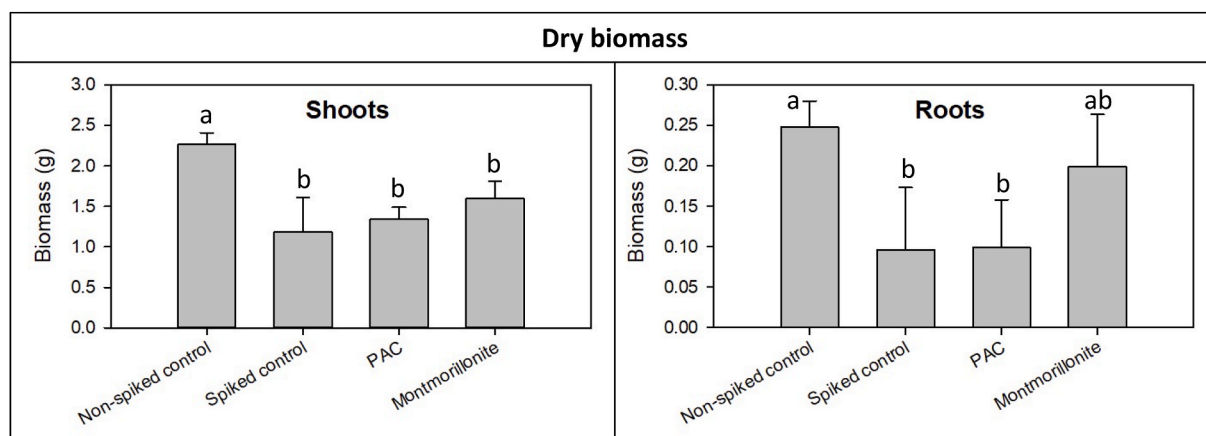


Fig. 1. Dry biomass of soybean shoots and roots. Error bars represent standard deviations ($n = 3$). Different letters in lower case represent significant differences among the treatments ($p < 0.05$).

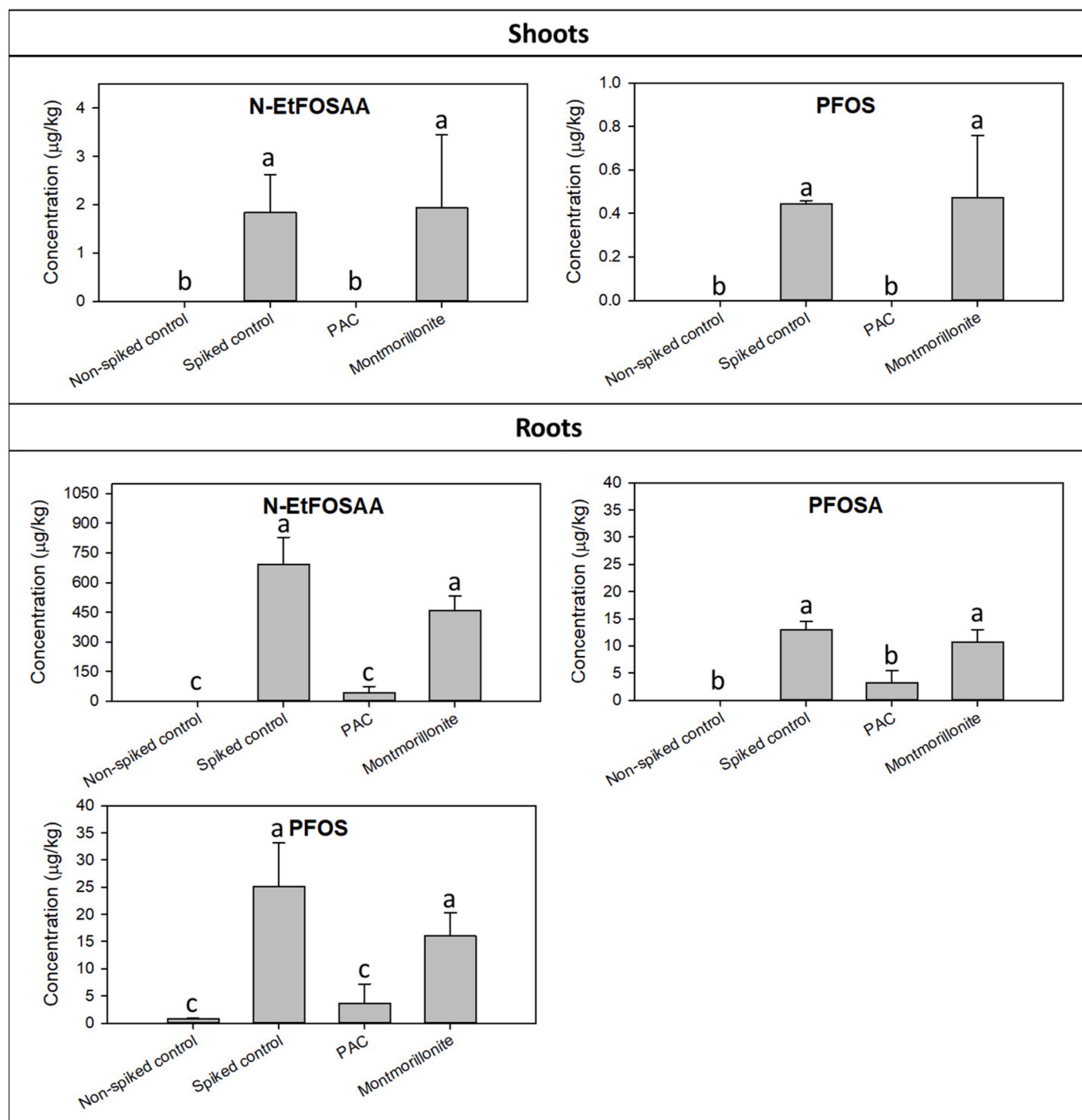


Fig. 2. Concentrations of N-EtFOSAA and its transformation products in soybean shoots and roots. Error bars represent standard deviations ($n = 3$). Different letters in lower case represent significant differences among the treatments ($p < 0.05$).

partition coefficient ($\log K_{oc}$) of N-EtFOSAA and PFOS was 3.23 ± 0.18 L/kg and 2.57 ± 0.13 L/kg, respectively, indicating that N-EtFOSAA is more hydrophobic than PFOS. Thus, the upward translocation was found to be negatively correlated to the hydrophobicity of PFAS when the carbon chain length was the same.

PAC amendment to soil significantly reduced the N-EtFOSAA concentration in soybean roots and shoots and decreased the total plant uptake of N-EtFOSAA by 94.96% compared to those without PAC (Fig. 2). This is in line with numerous studies reporting the effectiveness of PAC for PFAS removal in water through adsorption (Pauletto and Badosz, 2022; Son and An, 2022; Son et al., 2020). Hydrophobic

interactions, electrostatic interactions, and formation of hydrogen bonds between PFAS and AC surface were found to be involved in the adsorption process. Among them, hydrophobic interactions were usually reported to be the dominant adsorption mechanism (Pauletto and Badosz, 2022). Although there was no specific data describing the adsorption behavior of N-EtFOSAA on PAC, our study indicated that this sorbent remarkably decreased the bioavailability of N-EtFOSAA to soybean. In contrast, the effect of montmorillonite on plant uptake of N-EtFOSAA was insignificant. This could be due to the limited adsorption of N-EtFOSAA on pristine montmorillonite surface, which is hydrophilic (Tian et al., 2022) and negatively charged (zeta potential \approx

−35 mV) with a surface charge density of $-6.03 \pm 1.5 \text{ mC/m}^{-2}$ at pH ≈ 7 (Delgado et al., 1986; Guo and Yu, 2017). The electrostatic repulsion between the negatively charged clay surface and anionic N-EtFOSAA molecules may significantly reduce the adsorption performance of montmorillonite.

In agreement with the finding reported by Wen et al. (2018), two transformation products of N-EtFOSAA (i.e., PFOSA, PFOS) were detected in soybean. No perfluoroalkane sulfonates (PFSA)s with a carbon chain shorter than PFOS were found in the plant tissues. Transformation of N-EtFOSAA was reported in sludge and soil through a proposed pathway: N-EtFOSAA \rightarrow N-EtFOSA \rightarrow PFOSA \rightarrow PFOS (Avendaño and Liu, 2015; Rhoads et al., 2008). PFOS is extremely stable, and no previous studies showed its degradation to shorter chain PFSA)s in soil-plant systems (Wen et al., 2018). Therefore, PFOS was most likely the terminal transformation product in this study.

The concentration of PFOSA and PFOS in soybean roots grown in soil without sorbent amendment was $25.15 \pm 7.95 \text{ } \mu\text{g/kg}$ and $13.00 \pm 1.54 \text{ } \mu\text{g/kg}$, respectively. With PAC, the concentrations of PFOSA and PFOS in soybean roots decreased by 75.73% and 85.58%, respectively compared to the unamended controls, while montmorillonite was ineffective in reducing the plant uptake of these transformation products. In soybean shoots derived from those without a sorbent, PFOS was $0.44 \pm 0.02 \text{ } \mu\text{g/kg}$. With PAC amendment, PFOS was non-detectable in the shoots. PFOSA, however, was not detected in the shoots in all treatments and controls. N-EtFOSAA, PFOSA, and PFOS have the same hydrophobic carbon chain, while the complexity of their functional head group decreases progressively. As mentioned above, N-EtFOSAA has higher partition coefficient ($\log K_{oc} = 3.23 \pm 0.18 \text{ L/kg}$) than PFOS ($\log K_{oc} = 2.57 \pm 0.13 \text{ L/kg}$) in natural sediments (Higgins and Luthy, 2006). Ahrens et al. (2011) investigated the partition coefficients of PFAS detected in the sediments collected from Japan and reported that the $\log K_{oc}$ value of PFOSA ($4.1 \pm 0.35 \text{ L/kg}$) was slightly higher than that of PFOS ($3.7 \pm 0.56 \text{ L/kg}$). Thus, the hydrophobicity of N-EtFOSAA and PFOSA is speculated to be similar and higher than that of PFOS. Reasonably, the translocation factors of these compounds correlated negatively with their hydrophobicity. Considering the low concentration of PFOSA and PFOS in soybean roots, the absence of PFOSA and low level of PFOS in soybean shoots were expected.

2. Fractionation and transformation of N-EtFOSAA in soil

Once spiked to soil, PFAS could associate themselves with different soil components. Fig. 3 showed the percent recovery of water leachable, methanol extractable, and hydrolysable N-EtFOSAA in soil with or without a sorbent. The water leachable PFAS is considered as the most mobile fraction in soil and bioavailable to plants, thus posing the highest risk to the environment (Zhang et al., 2021a; Zhang and Liang, 2022). Compared to the unamended soil, PAC significantly decreased the water

leachable N-EtFOSAA in soil with soybean by 96.53%, while montmorillonite had no effect in this regard. This was in agreement with the observation that PAC significantly lowered the concentration of N-EtFOSAA in soybean (Fig. 2). In spiked control soil and soil amended with montmorillonite, cultivation of soybean plants remarkably decreased the water leachable N-EtFOSAA. For example, when combining the detected N-EtFOSAA in plant tissues and water leachable fraction in soil with plant cultivation, the total mass of N-EtFOSAA was still significantly lower than that in the spiked control soil without plant cultivation (Fig. S1), implying that immobilization of N-EtFOSAA in soil by soybean took place. Previous research has shown that plants could reduce the mobility and transport of pollutants in soil by uptake and/or immobilization (Pulford and Watson, 2003). The immobilization could be contributed by binding between contaminants and organic matter released by plant roots (Bolan et al., 2021; Bolan et al., 2011). (Kaplan et al., 2016).

In the water leachable fraction, PFOSA and PFOS were found in the soil spiked with N-EtFOSAA but were not detectable in the non-spiked controls, confirming the transformation of N-EtFOSAA to these two compounds in soil. The exact concentrations of N-EtFOSAA and these transformation products were shown in Fig. 4. PAC amendment significantly decreased the water leachability of PFOSA and PFOS, which correlated positively with low concentrations of these two in soybean compared to the unamended controls (Fig. 2). In contrast, montmorillonite increased the water leachable PFOSA and PFOS in soil without soybean. With plant cultivation, the effect of montmorillonite on N-EtFOSAA transformation to PFOSA and PFOS was insignificant (Fig. 4 and S1). This could be due to immobilization of N-EtFOSAA and its degradation products by soybean roots as explained above.

Basic methanol extraction has been considered as an exhaustive method for extracting PFAS from a given sample. It is why methanolic ammonium hydroxide is used in EPA Draft Method 1633 for extracting PFAS from soil and other solid samples. As shown in Fig. 3, PAC significantly reduced the percent recovery of N-EtFOSAA in this fraction, especially with plant cultivation in soil. The reduction of methanol extractable N-EtFOSAA in soil with plant cultivation by montmorillonite, however, was insignificant. Besides PFOSA and PFOS, another transformation product, N-EtFOSA, was detected in the methanol extractable (Fig. 4). This compound was not found in the water leachable fraction or plant tissues, implying its low water solubility and less bioavailability compared to other degradation products. PAC was also effective in decreasing the methanol extractable PFOSA and PFOS in soil with soybean (Fig. S1). Without soybean, the decrease of methanol extractable PFOSA and PFOS by PAC was negligible. Apparently, plant cultivation improved the stabilization performance of PAC for N-EtFOSAA transformation products. Like in the water leachable fraction, montmorillonite increased the concentration of PFOSA and PFOS in the methanol extractable fraction (Fig. 4).

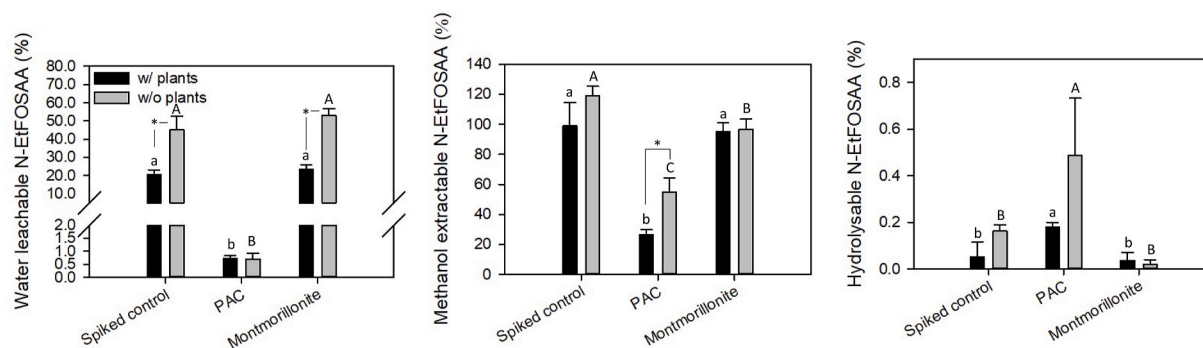


Fig. 3. Percent recovery of water leachable, methanol extractable, and hydrolysable N-EtFOSAA in soil spiked with 300 $\mu\text{g/kg}$ of N-EtFOSAA. Error bars represent standard deviations ($n = 3$). Different letters in lower and upper cases represent significant differences among the treatments ($p < 0.05$). Asterisks indicate significant differences between PFAS concentration in soil with or without plant cultivation (Student's t -test, $p < 0.05$).

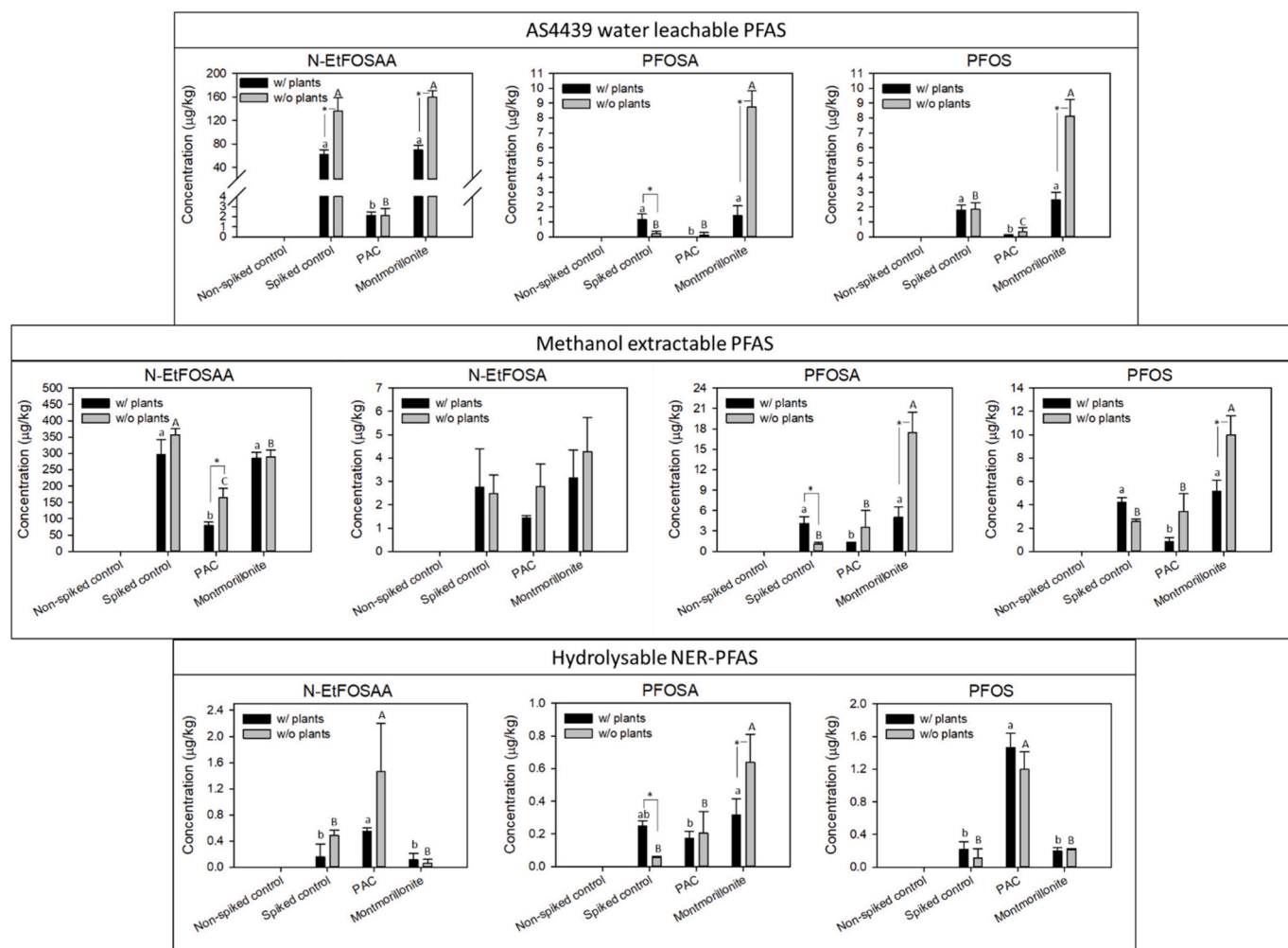


Fig. 4. Concentrations of water leachable, methanol extractable, and hydrolysable N-EtFOSAA and its transformation products in soil with or without plant cultivation. Error bars represent standard deviations ($n = 3$). Different letters in lower and upper cases represent significant differences among the treatments ($p < 0.05$). Asterisks indicate significant differences between PFAS concentration in soil with or without plant cultivation (Student's t-test, $p < 0.05$).

PFAS that cannot be extracted by basic methanol is considered as non-extractable residues (NER, also known as bound residues). Since these NER are not extractable by conventional solvent, they are non-detectable by common analytical protocols but are still possible to remobilize with changes of environmental conditions (Lesmeister et al., 2021). In order to comprehensively understand the fate of N-EtFOSAA and its transformation products in the soil-plant systems, alkaline hydrolysis of the NER was performed to hydrolyze the covalent bonding between sulfonate head groups of PFAS and hydroxyl groups of SOM/-sorbents (Zhu et al., 2021). As shown in Figs. 3 and 4, N-EtFOSAA, PFOSA, and PFOS in the hydrolysable fraction had significantly lower concentrations than their counterparts in the water leachable and methanol extractable fractions. Relatively, more N-EtFOSAA and PFOS were released from soil with PAC than those from soil without sorbent amendment, implying that N-EtFOSAA and PFOS could be bound to PAC and form (sulfonic) ester bonds during the stabilization process.

Based on results discussed above, the transformation of N-EtFOSAA to N-EtFOSA, PFOSA, and PFOS occurred in the studied soil-plant systems, which was similar to what was proposed in the previous publications (N-EtFOSAA \rightarrow N-EtFOSA \rightarrow PFOSA \rightarrow PFOS) (Avendaño and Liu, 2015; Rhoads et al., 2008). To help us gain insights of the mechanisms responsible for N-EtFOSAA degradation, we tested the effect of soil microorganisms and light exposure on N-EtFOSAA transformation by comparing the transformation products in the spiked controls, autoclaved controls, and light controls after 60 days of aging. It was

found that N-EtFOSAA underwent a comparable transformation process in the original soil, the sterilized soil, and the soil in dark (Fig. 5). Thus, it is reasonable to hypothesize that abiotic reactions played a key role in degrading N-EtFOSAA in soil. This hypothesis was also supported by the observation that higher concentrations of PFOSA and PFOS were detected in the soil amended with montmorillonite than those in the unamended controls (Fig. 4). Liu et al. (2021) found that the perfluoroalkyl sulfonamide-based precursors such as perfluorooctane sulfonamido betaine (PFOSB) and 3-dimethyl amino perfluorooctanesulfonamide (PFOSAm) had high microbial stability, and their transformation to PFASs in soil was dominantly through abiotic oxidation and reduction processes. Regarding N-EtFOSAA, Wen et al. (2018) found that plant cultivation promoted the transformation of this precursor to N-EtFOSA and PFOS in biosolids amended soil and proposed that the enhanced transformation was due to the stimulation of soil microbial growth by root exudates. In our study, the steam sterilization process (121 °C for 45 min) may not be strong enough to inactivate all soil microorganisms. Thus, the effect of microbial activities on the fate of N-EtFOSAA in soil cannot be entirely ruled out. It is worth noting that other transformation products of N-EtFOSAA such as perfluorooctane sulfonamide acetate (FOSAA) may also exist in the soil-plant systems (Wen et al., 2018). Further investigation is needed to deepen our understanding of the fate of N-EtFOSAA in the environment.

3. Distribution of N-EtFOSAA in the soil-plant systems

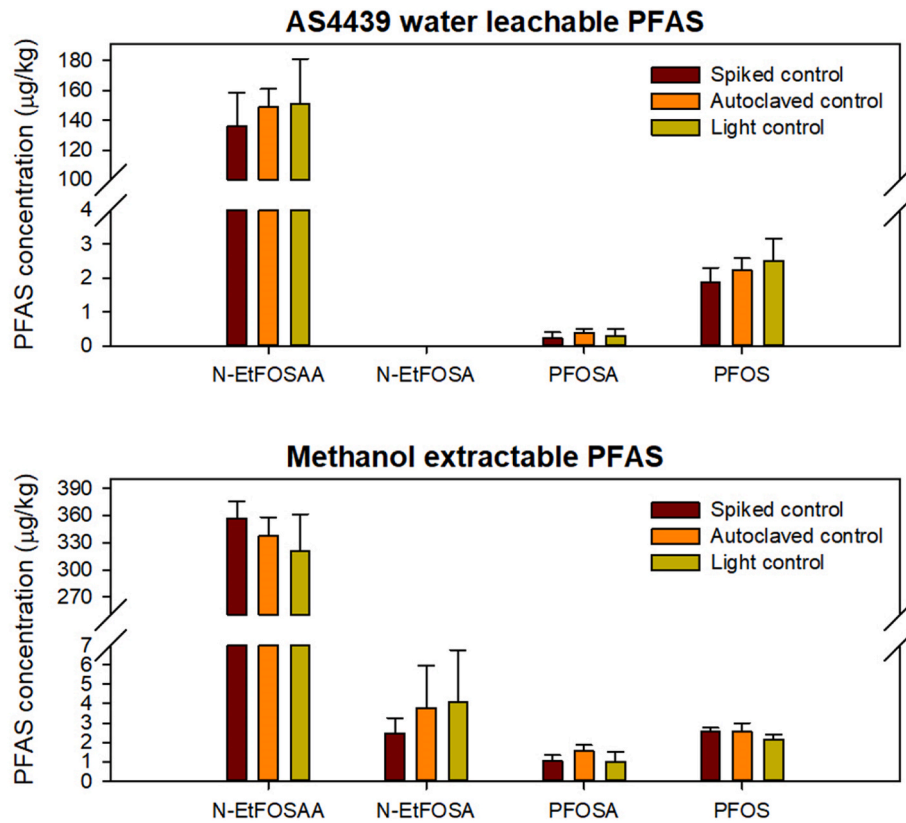


Fig. 5. Concentrations of N-EtFOSAA and its transformation products in N-EtFOSAA spiked soil (spiked controls), autoclaved soil with N-EtFOSAA spiking (autoclaved controls), and N-EtFOSAA spiked soil without light exposure (light controls). Error bars represent standard deviations ($n = 3$).

Fig. 6 showed the mass distribution of N-EtFOSAA in different soil-plant systems. Without sorbent amendment, 98.96% of spiked N-EtFOSAA was methanol extractable. The high recovery of the spiked N-EtFOSAA by using methanolic ammonium hydroxide demonstrated the effectiveness of this solvent for N-EtFOSAA extraction in soil. For these spiked controls, 0.12% of N-EtFOSAA was taken up by plants, and less than 1% stayed in the NER fraction. With PAC amendment, a large amount of methanol extractable N-EtFOSAA became non-extractable. The percentage of NER dramatically increased from 0.84% in the spiked controls to 73.53%. Meanwhile, the percentage of N-EtFOSAA in plant tissues decreased from 0.12% to 0.01%, indicating a remarkable reduction of N-EtFOSAA bioavailability. With montmorillonite, the NER was 4.86% of the total spiked, indicating its limited capability in binding N-EtFOSAA to form NER. Unexpectedly, this clay mineral increased the plant uptake of N-EtFOSAA from 0.12% in the spiked controls to 0.18%.

Hydrolysis using KOH released <0.2% of NER for all treatments and controls, indicating a small contribution of ester bonds in the NER. The hydrolysable portion of the NER is recognized as moderately bound. The remaining NER deemed as permanently bound, could be attributed by ether and carbon-carbon bonds formed between N-EtFOSAA and SOM/sorbent. Cleaving these bonds requires degradation of the NER using BBr_3 and RuO_4 as detailed in the paper published by Zhu et al. (2021). Thus, the PAC used in this study led to the formation of irreversibly bound residues at 73.5% of the initially spiked. For montmorillonite, it was 4.9% and significantly higher than the 0.8% observed in the un-amended controls.

Our results demonstrated that a suitable sorbent is needed in order to maximize formation of permanently bound NER. Without a sorbent, although PFOS was found to form irreversibly bound NER in a silty clay top soil in 120 days, this fraction of the NER was completely remobilized

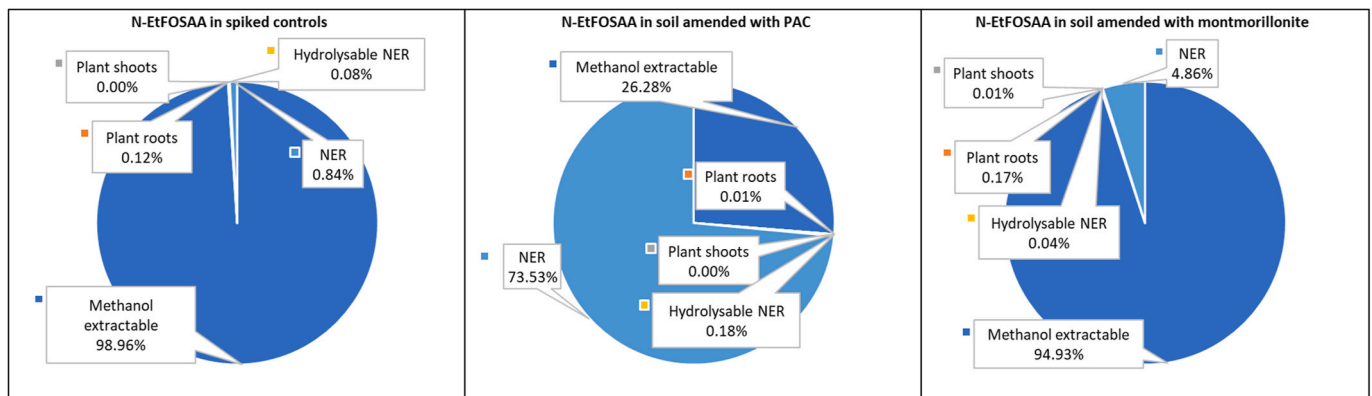


Fig. 6. Percentage distribution of N-EtFOSAA in the soil-plant systems with or without sorbent amendment.

after 180 days, leaving a small percentage of NER being moderately bound (Zhu et al., 2021). In our study, the results derived from PAC are highly encouraging. However, given the duration of 60 days, it is not exactly clear at this stage whether the true bound residues will remain intact after longer periods of time. Therefore, future research is warranted to investigate the stability and the structure of the bound residues. Additionally, other sorbents may be tested for promoting formation of NER. The correlation between SOM and bound residue formation needs to be understood as well.

4. Conclusion

In this study, the effect of PAC and montmorillonite on the distribution, transformation and bioavailability of N-EtFOSAA in soil-plant systems was investigated. The results indicated that N-EtFOSAA was bioavailable to soybean plants and can be taken up by the roots and shoots. Transformation of N-EtFOSAA in soil was observed, and the transformation products (i.e., PFOSA, PFOS) were also detected in soybean tissues. PAC amendment significantly reduced the water leachable and methanol extractable N-EtFOSAA and its transformation products (i.e., PFOSA, PFOS) in soil and led to formation of non-extractable bound residues, resulting in remarkably lower uptake of these compounds by soybean plants. In contrast, montmorillonite showed limited stabilization performance for N-EtFOSAA and its degradation products and was ineffective to decrease their bioavailability. Overall, this study revealed that PAC is beneficial for promoting the formation of NER between N-EtFOSAA and soil. Cultivation of soybean further led to enhanced stabilization of PFAS when compared to those without soybean. Results from this study proved the concept that it may be feasible to stabilize PFAS in soil-plant systems when a suitable sorbent is used.

Credit author statement

Weilan Zhang: Methodology, Investigation, Validation, Formal analysis, Writing – original draft, Tamia E. Wellington: Investigation, Validation, Yanna Liang: Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.120941>.

References

- Ahmed, M., Johir, M., McLaughlin, R., Nguyen, L.N., Xu, B., Nghiem, L.D., 2020. Per- and polyfluoroalkyl substances in soil and sediments: occurrence, fate, remediation and future outlook. *Sci. Total Environ.* 748, 141251.
- Ahrens, L., Taniyasu, S., Yeung, L.W., Yamashita, N., Lam, P.K., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere* 79, 266–272.

- Ahrens, L., Yeung, L.W., Taniyasu, S., Lam, P.K., Yamashita, N., 2011. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. *Chemosphere* 85, 731–737.
- Al Amin, M., Luo, Y., Nolan, A., Robinson, F., Niu, J., Warner, S., Liu, Y., Dharmarajan, R., Mallavarapu, M., Naidu, R., 2021. Total oxidisable precursor assay towards selective detection of PFAS in AFFF. *J. Clean. Prod.* 328, 129568.
- Alves, A.V., Tsianou, M., Alexandridis, P., 2020. Fluorinated surfactant adsorption on mineral surfaces: implications for PFAS fate and transport in the environment. *Surfaces* 3, 516–566.
- Askeland, M., Clarke, B.O., Cheema, S.A., Mendez, A., Gasco, G., Paz-Ferreiro, J., 2020. Biochar sorption of PFOS, PFOA, PFHxS and PFHxA in two soils with contrasting texture. *Chemosphere* 249, 126072.
- Avendaño, S.M., Liu, J., 2015. Production of PFOS from aerobic soil biotransformation of two perfluoroalkyl sulfonamide derivatives. *Chemosphere* 119, 1084–1090.
- Barola, C., Moretti, S., Giusepponi, D., Paoletti, F., Saluti, G., Cruciani, G., Brambilla, G., Galarini, R., 2020. A liquid chromatography-high resolution mass spectrometry method for the determination of thirty-three per- and polyfluoroalkyl substances in animal liver. *J. Chromatogr. A* 1628, 461442.
- Barth, E., McKernan, J., Bless, D., Dasu, K., 2021. Investigation of an immobilization process for PFAS contaminated soils. *J. Environ. Manag.* 296, 113069.
- Bolan, N., Sarkar, B., Yan, Y., Li, Q., Wijesekara, H., Kannan, K., Tsang, D.C., Schauerte, M., Bosch, J., Noll, H., 2021. Remediation of poly- and perfluoroalkyl substances (PFAS) contaminated soils—To mobilize or to immobilize or to degrade? *J. Hazard Mater.* 401, 123892.
- Bolan, N.S., Park, J.H., Robinson, B., Naidu, R., Huh, K.Y., 2011. Phytostabilization: a green approach to contaminant containment. *Adv. Agron.* 112, 145–204.
- 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, 5524–5530.
- Cui, J., Gao, P., Deng, Y., 2020. Destruction of per- and polyfluoroalkyl substances (PFAS) with advanced reduction processes (ARPs): a critical review. *Environ. Sci. Technol.* 54, 3752–3766.
- Dadashi Firouzjaei, M., Zolghadr, E., Ahmadi, S., Taghvaei, N., Akbari Afkhami, F., Nejati, S., Elliott, M.A., 2021. Chemistry, abundance, detection and treatment of per- and polyfluoroalkyl substances in water: a review. *Environ. Chem. Lett.* 1–19.
- Death, C., Bell, C., Champness, D., Milne, C., Reichman, S., Hagen, T., 2021. Per- and polyfluoroalkyl substances (PFAS) in livestock and game species: a review. *Sci. Total Environ.* 774, 144795.
- Delgado, A., Gonzalez-Caballero, F., Bruque, J., 1986. On the zeta potential and surface charge density of montmorillonite in aqueous electrolyte solutions. *J. Colloid Interface Sci.* 113, 203–211.
- Gebbink, W.A., Glynn, A., Berger, U., 2015. Temporal changes (1997–2012) of perfluoroalkyl acids and selected precursors (including isomers) in Swedish human serum. *Environ. Pollut.* 199, 166–173.
- Grassini, P., La Menza, N.C., Edreira, J.I.R., Monzón, J.P., Tenorio, F.A., Specht, J.E., 2021. Soybean, Crop Physiology Case Histories for Major Crops. Elsevier, pp. 282–319.
- Guo, Y., Yu, X., 2017. Characterizing the surface charge of clay minerals with Atomic Force Microscope (AFM). *AIMS Materials Science* 4, 582–593.
- Hale, S.E., Arp, H.P.H., Slinde, G.A., Wade, E.J., Bjørseth, K., Breedveld, G.D., Straith, B. F., Moe, K.G., Jartun, M., Høisæter, Å., 2017. Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility. *Chemosphere* 171, 9–18.
- Hearon, S.E., Orr, A.A., Moyer, H., Wang, M., Tamamis, P., Phillips, T.D., 2022. Montmorillonite clay-based sorbents decrease the bioavailability of per- and polyfluoroalkyl substances (PFAS) from soil and their translocation to plants. *Environ. Res.* 205, 112433.
- Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 40, 7251–7256.
- Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* 47, 8187–8195.
- Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environ. Sci. Technol.* 46, 9342–9349.
- Houtz, E.F., Sutton, R., Park, J.-S., Sedlak, M., 2016. Poly- and perfluoroalkyl substances in wastewater: significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Res.* 95, 142–149.
- 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.
- Kabiri, S., McLaughlin, M.J., 2021. Durability of sorption of per- and polyfluorinated alkyl substances in soils immobilized using common adsorbents: 2. Effects of repeated leaching, temperature extremes, ionic strength and competing ions. *Sci. Total Environ.* 766, 144718.
- Kaplan, D.I., Xu, C., Huang, S., Lin, Y., Tolic, N., Roscioli-Johnson, K.M., Santschi, P.H., Jaffe, P.R., 2016. Unique organic matter and microbial properties in the rhizosphere of a wetland soil. *Environ. Sci. Technol.* 50, 4169–4177.
- Kurwadkar, S., Dane, J., Kanel, S.R., Nadagouda, M.N., Cawdrey, R.W., Ambade, B., Struckhoff, G.C., Wilkin, R., 2021. Per- and Polyfluoroalkyl Substances in Water and Wastewater: A Critical Review of Their Global Occurrence and Distribution. *Science of the Total Environment*, 151003.
- Langberg, H.A., Breedveld, G.D., Slinde, G.A., Grønning, H.M., Høisæter, Å., Jartun, M., Rundberget, T., Jensen, B.M., Hale, S.E., 2020. Fluorinated precursor compounds in sediments as a source of perfluorinated alkyl acids (PFAS) to biota. *Environ. Sci. Technol.* 54, 13077–13089.

- Lath, S., Navarro, D.A., Losic, D., Kumar, A., McLaughlin, M.J., 2018. Sorptive remediation of perfluorooctanoic acid (PFOA) using mixed mineral and graphene/carbon-based materials. *Environ. Chem.* 15, 472–480.
- Lenka, S.P., Kah, M., Padhye, L.P., 2021. A review of the occurrence, transformation, and removal of poly-and perfluoroalkyl substances (PFAS) in wastewater treatment plants. *Water Res.* 199, 117187.
- Lesmeister, L., Lange, F.T., Breuer, J., Biegel-Engler, A., Giese, E., Scheurer, M., 2021. Extending the knowledge about PFAS bioaccumulation factors for agricultural plants—A review. *Sci. Total Environ.* 766, 142640.
- Lilienthal, H., Dieter, H.H., Hölzer, J., Wilhelm, M., 2017. Recent experimental results of effects of perfluoroalkyl substances in laboratory animals—Relation to current regulations and guidance values. *Int. J. Hyg Environ. Health* 220, 766–775.
- Liu, M., Munoz, G., Vo Duy, S., Sauvé, S., Liu, J., 2021. Stability of nitrogen-containing polyfluoroalkyl substances in aerobic soils. *Environ. Sci. Technol.* 55, 4698–4708.
- Lu, D., Sha, S., Luo, J., Huang, Z., Jackie, X.Z., 2020. Treatment train approaches for the remediation of per-and polyfluoroalkyl substances (PFAS): a critical review. *J. Hazard Mater.* 386, 121963.
- McDonough, J.T., Anderson, R.H., Lang, J.R., Liles, D., Matteson, K., Olechiw, T., 2021. Field-scale demonstration of PFAS leachability following in situ soil stabilization. *ACS Omega*.
- Moodie, D., Coggan, T., Berry, K., Kolobaric, A., Fernandes, M., Lee, E., Reichman, S., Nuggeoda, D., Clarke, B.O., 2021. Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids. *Chemosphere* 270, 129143.
- Nguyen, T.V., Reinhard, M., Chen, H., Gin, K.Y.-H., 2016. Fate and transport of perfluoro- and polyfluoroalkyl substances including perfluorooctane sulfonamides in a managed urban water body. *Environ. Sci. Pollut. Control Ser.* 23, 10382–10392.
- Northcott, G.L., Jones, K.C., 2000. Experimental approaches and analytical techniques for determining organic compound bound residues in soil and sediment. *Environ. Pollut.* 108, 19–43.
- Pauletto, P.S., Bandoz, T.J., 2022. Activated carbon versus metal-organic frameworks: a review of their PFAS adsorption performance. *J. Hazard Mater.* 425, 127810.
- Pepper, I.L., Brusseu, M.L., Prevatt, F.J., Escobar, B.A., 2021. Incidence of Pfas in soil following long-term application of class B biosolids. *Sci. Total Environ.* 793, 148449.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* 40, 32–44.
- Pulford, I., Watson, C., 2003. Phytoremediation of heavy metal-contaminated land by trees—a review. *Environ. Int.* 29, 529–540.
- Rhoads, K.R., Janssen, E.M.-L., Luthy, R.G., Criddle, C.S., 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. *Environ. Sci. Technol.* 42, 2873–2878.
- Schaefer, C.E., Choyke, S., Ferguson, P.L., Andaya, C., Burant, A., Maizel, A., Strathmann, T.J., Higgins, C.P., 2018. Electrochemical transformations of perfluoroalkyl acid (PFAA) precursors and PFAAs in groundwater impacted with aqueous film forming foams. *Environ. Sci. Technol.* 52, 10689–10697.
- Sepulvado, J.G., Blaine, A.C., Hundal, L.S., Higgins, C.P., 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environ. Sci. Technol.* 45, 8106–8112.
- Silvani, L., Cornelissen, G., Botnen Smebye, A., Zhang, Y., Okkenhaug, G., Zimmerman, A.R., Thune, G., Sævarsson, H., Hale, S.E., 2019. Can biochar and designer biochar be used to remediate per- and polyfluorinated alkyl substances (PFAS) and lead and antimony contaminated soils? *Sci. Total Environ.* 694, 133693.
- Son, H., An, B., 2022. Investigation of adsorption kinetics for per- and poly-fluoroalkyl substances (PFAS) adsorption onto powder activated carbon (PAC) in the competing systems. *Water, air. & Soil Pollution* 233, 1–17.
- Son, H., Kim, T., Yoom, H.-S., Zhao, D., An, B., 2020. The adsorption selectivity of short and long per-and polyfluoroalkyl substances (PFASs) from surface water using powder-activated carbon. *Water* 12, 3287.
- Sorengard, M., Kleja, D.B., Ahrens, L., 2019. Stabilization of per-and polyfluoroalkyl substances (PFASs) with colloidal activated carbon (PlumeStop®) as a function of soil clay and organic matter content. *J. Environ. Manag.* 249, 109345.
- Söregård, M., Kleja, D.B., Ahrens, L., 2019. Stabilization and solidification remediation of soil contaminated with poly- and perfluoroalkyl substances (PFASs). *J. Hazard Mater.* 367, 639–646.
- Tian, M., Meng, X., Liu, Q., Li, W., You, X., Liu, C., Fortner, J.D., 2022. Hydrophilic montmorillonite in tailoring the structure and selectivity of polyamide membrane. *J. Membr. Sci.* 120674.
- Verma, S., Varma, R.S., Nadagouda, M.N., 2021. Remediation and mineralization processes for per-and polyfluoroalkyl substances (PFAS) in water: a review. *Sci. Total Environ.* 794, 148987.
- Wang, M., Orr, A.A., Jakubowski, J.M., Bird, K.E., Casey, C.M., Hearon, S.E., Tamamis, P., Phillips, T.D., 2021. Enhanced adsorption of per-and polyfluoroalkyl substances (PFAS) by edible, nutrient-amended montmorillonite clays. *Water Res.* 188, 116534.
- Wang, Z., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbühler, K., 2014. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ. Int.* 70, 62–75.
- Wang, Z., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environ. Int.* 60, 242–248.
- Wen, B., Pan, Y., Shi, X., Zhang, H., Hu, X., Huang, H., Lv, J., Zhang, S., 2018. Behavior of N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) in biosolids amended soil-plant microcosms of seven plant species: accumulation and degradation. *Sci. Total Environ.* 642, 366–373.
- Xiao, F., Zhang, X., Penn, L., Gulliver, J.S., Simcik, M.F., 2011. Effects of monovalent cations on the competitive adsorption of perfluoroalkyl acids by kaolinite: experimental studies and modeling. *Environ. Sci. Technol.* 45, 10028–10035.
- Xu, B., Liu, S., Zhou, J.L., Zheng, C., Weifeng, J., Chen, B., Zhang, T., Qiu, W., 2021. PFAS and their substitutes in groundwater: occurrence, transformation and remediation. *J. Hazard Mater.* 412, 125159.
- Ye, F., Zushi, Y., Masunaga, S., 2015. Survey of perfluoroalkyl acids (PFAAs) and their precursors present in Japanese consumer products. *Chemosphere* 127, 262–268.
- Yeung, L.W., Robinson, S.J., Koschorreck, J., Mabury, S.A., 2013. Part II. A temporal study of PFOS and its precursors in human plasma from two German cities in 1982–2009. *Environ. Sci. Technol.* 47, 3875–3882.
- Zhang, J., Gao, L., Bergmann, D., Bulatovic, T., Surapaneni, A., Gray, S., 2022. Review of Influence of Critical Operation Conditions on By-Product/intermediate Formation during Thermal Destruction of PFAS in Solid/biosolids. *Science of the Total environment*, 158796.
- Zhang, W., Cao, H., Liang, Y., 2021a. Plant uptake and soil fractionation of five ether-PFAS in plant-soil systems. *Sci. Total Environ.* 771, 144805.
- Zhang, W., Cao, H., Mahadevan Subramanya, S., Savage, P., Liang, Y., 2020. Destruction of perfluoroalkyl acids accumulated in *Typha latifolia* through hydrothermal liquefaction. *ACS Sustain. Chem. Eng.*
- Zhang, W., Liang, Y., 2022. Performance of different sorbents toward stabilizing per-and polyfluoroalkyl substances (PFAS) in soil. *Environmental Advances* 8, 100217.
- Zhang, W., Pang, S., Lin, Z., Mishra, S., Bhatt, P., Chen, S., 2021b. Biotransformation of perfluoroalkyl acid precursors from various environmental systems: advances and perspectives. *Environ. Pollut.* 272, 115908.
- Zhang, W., Zhang, D., Zagorevski, D.V., Liang, Y., 2019. Exposure of *Juncus effusus* to seven perfluoroalkyl acids: uptake, accumulation and phytotoxicity. *Chemosphere*.
- Zhao, L., Bian, J., Zhang, Y., Zhu, L., Liu, Z., 2014. Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. *Chemosphere* 114, 51–58.
- Zhu, X., Song, X., Schwarzbauer, J., 2021. First insights into the formation and long-term dynamic behaviors of nonextractable perfluorooctanesulfonate and its alternative 6:2 chlorinated polyfluorinated ether sulfonate residues in a silty clay soil. *Sci. Total Environ.* 761, 143230.