Effectiveness of Soil Sorbent Modifications and Soybeans on N-EtFOSAA Transformation

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Abstract

PFAS is an organic chemical with high environmental mobility that has demonstrated an increase in levels within NYS streams and surrounding soils. This chemical, commonly produced as a result of plastic manufacturing and firefighting foams, is aqueous, furthering the difficulty of removal of such a cancerous material. The use of plants to potentially absorb PFAS, as well as other chemicals, has been a developed concept for a while. However, dealing with specific species of plants and different effects that humans can apply to a polluted site have not been researched in as much depth. The use of phytoremediation has its limits, what ways can man assist in benefiting treatment of a site, while still using the efficiency brought by plants.

This project studied the effects of powdered activated carbon, a natural clay, and a modification of both these sorbents, on soil and the uptake of PFAS in soybean plants. After collecting samples of soybean plants grown in their respective spiked sorbent, they underwent analysis to determine how much PFAS had been absorbed by the soybeans. This involved extraction of PFAS and chemicals from the leaves and shoots of all soybean plants and soil.

The outcomes of this research present a new and more cost and time efficient way to remediate the spread of PFAS. These sorbents also appear less harmful to plants growing in polluted areas, presenting a novel remediation tactic that is more gentle but still as effective, compared to other remediation techniques involving the use of harmful chemicals.

Introduction

Chemical contamination due to human interactions with the environment has posed a severe threat to all life since the 1940s. Heavy metal contamination and Bisphenol A produced from the manufacturing of plastics have been among the most common pollutants caused by human interactions with the environment. Removal techniques of these chemicals include soil washing, electrolytic recovery, filtration, and even just relocation of mass amounts of soil. All the techniques present controversial issues however, whether economically, or simply the methods cause more harm than good to the surrounding environment in the long term.

A new environmental contaminant, comparable to BPA's, has surfaced. Per- and polyfluoroalkyl substances (PFAS) are recent contaminants that have been known to cause cancers and reproductive harm to animals and humans alike. Through production of plastics and fire-fighting foams, PFAS have infiltrated water supplies and surrounding soils, making its way into the environment. Because of its high solubility in water, remediation of PFAS has proved challenging, as its environmental mobility is immoderate. Like processes developed for heavy metals, cleanup of PFAS has resorted to removal of chucks of contaminated soil, or possible sorbents being used to limit mobility of the pollutant any further. An economical and time efficient technique to manage this pollutant is necessary to adequately control the spread of this dangerous compound.

Phytoremediation, the use of plants to control and rectify polluted sites, has been a common concept since the early 1990s. Most notably applied at Chernobyl through the use of sunflowers to uptake radionuclides, phytoremediation has been shown to remove heavy metals and similar compounds on a mass scale. Remediation information on PFAS, which are soluble in water, is limited. This system takes advantage of plants' distinctive root systems, and ability to move water and nutrients throughout its entirety. The movement and degradation techniques present in plants make uptake of any pollutants extremely efficient with this process. For any phytoremediation to be effective, however, the species of plant chosen must be specific to the chemicals being removed. Soybeans (*Glycine max*) are ideal for PFAS, along with mustard plants, due to their longer roots and short germination cycles.

One issue that arises however, is that when PFAS reacts under certain abiotic or biotic conditions, it can transform into different harmful variations such as PFOS and PFOSA. Because of this, stabilizing PFAS in the environment prior to transformation is a priority. One technique being examined is altering soils with known sorbents to stabilize PFAS. Natural sorbents such as clay and carbon are well known for their stabilizing qualities in oils and heavy metals, making them applicable to doing something similar with PFAS. Iron oxide hydroxide (FeO(OH)) is another chemical compound known for its removal abilities of phosphorus from various lakes and aquariums. Modifying carbon and clay further with the addition of iron oxide hydroxide could enhance the soil's ability to stabilize PFAS and increase chances of remediation.

Methods and Materials

Soil and Plant Preparation

Four sorbents: powdered activated carbon (PAC), iron oxide hydroxide modified PAC (Lee et al. 2017), montmorillonite clay, and a modified montmorillonite clay (MClay) (Zhou et al., 2010, and Zhou et al., 2008) were added to a base soil gathered from a local farm in Albany, NY. Soil was hand sifted and ground using a mortar and pestle. Soil pH was 7.38 +- 0.41, and organic matter components was only 4.82 +- 0.12%. The soil was air dried and 170g of the dried and sifted soil were placed into a total of 21, 18-ounce plastic cups. Each of 15 plastics cups were spiked with 300 nanograms/kg of PFAS precursor N-ethy perfluorooctane sulfonamido acetic acid (N-EtFOSAA), while 3 additional cups were left unspiked. The last 3 cups were spiked, but additionally autoclaved at 121° C for 45 minutes to track the effect of pre-existing soil bacterium. In 3 of the filled plastic cups, PAC, a known sorbent for many pollutants in soils, was added to the spiked soil. Montmorillonite clay, a known natural stabilizing sorbent, was added to another 3 already-filled cups. MClay was dedicated to 3 of the remaining 9 cups, while MPAC sorbent and a control group were divided evenly into the last of the plastic cups.

Soybean seedlings that had been germinating in sand for one week prior, were transplanted into each of these 18 cups. An additional set of cups was also created, mimicking the set-up of the 18 initial cups, without any soybean sprouts to measure the effect of soybean germinations in N-EtFOSAA, the PFAS precursor that had been spiked in all the soils. After germination continued for 35 days in the new cups, plant tissue and roots were harvested. The dirt was rinsed off, and plant tissue was freeze dried at –37° C for 48 hours. Plant roots, shoots, and remaining soil from each cup was air dried in a fume hood for 15 consecutive days and initial weight measurements were taken to observe any possible changes due to plant uptake.

Extraction and PFAS Analysis

A water leaching test was conducted to measure the effectiveness of modified and regular soil on stabilizing PFAS and managing PFAS environmental mobility. 1 gram of the PFAS spiked soil was mixed with 10ng of 13C2-PFHxA surrogate. This mixture was then added to a tub with 20 mL of water (at a pH of 7) and shaken for 24 hours. After 24 hours, the sample was centrifuged at 4500 rpm for 20 minutes. The water and any other potential pollutants that had been mixed in were then collected through hand pipetting for solid phase extraction (SPE) using HyperSep C18.

A methanol extraction was also administered, to measure PFAS and other transformations after their reactions to the soil and sorbents. The process for preparing samples for analysis through LC/MS followed processes developed from Houtz et al., 2013. 1 gram of harvested shoots from each of the 18 different samples, was combined with 10 nanograms of the same 13C2-PFHxA surrogate in a 50 mL test tube that contained 5 mL of methanolic ammonium hydroxide. The mixture was hand shaken briefly, then vortexed for 20 seconds. All test tubes underwent sonication at 35° C for 30 minutes, then machine shaken at 150 rpm for 2 hours. Samples were centrifuged at 4500 rpm for an additional 20 minutes. After centrifuging, a layer of supernatant remained in each sample. This layer was carefully pipetted off into a 15 mL tube. To ensure complete removal of all pollutants this process was repeated two more times. After complete collection, roughly 7-8 mL of supernatant remained, which was evaporated with nitrogen. To reconstitute, 1.5 mL of methanol was added (Houtz. et al., 2013) prior to SPE, which ensured dissolution of all excess chemicals that could disrupt analysis of PFAS. After the supernatant was reconstituted, SPE ENVI-carbon cartridges were initially rinsed with methanol as an extra precaution for absorption and were run through the SPE-ENVI cartridges to filter out all organic material. This separated the sample away from excess organic material and impurities to make processing through LC/MS easier. This methanol extraction process was conducted for roots of soybean samples. For the sorbent soil samples, the process was identical without the hand pipetting of supernatant, which was unnecessary, as sludge remained at the bottom. The supernatant was simply hand poured into their respective 50 mL tubes continuing with the methanol extraction process. Both the leaching and methanol extraction process were applied to all spiked soil samples and their respective soybean harvested roots and shoots, including the control soil cups without spiked N-EtFOSAA or soybean sprouts.

Results and Discussion

Extracts from SPE cartridges were run through LC/MS with the 1290 Infinity II LLC and 6470 Triple Quad Mass Spectrometer to determine final N-EtFOSAA and other transformation results and the effect of each individual sorbent. Initial dry biomass of soybeans transplanted into the spiked soil was considerably lower compared to the biomass of seedlings grown in control soil without PFAS.

Figure 1: Image of germinating soybean sprouts in soil cups in greenhouse under natural lighting.

Transformation Analysis

The sorbent MClay however, had the lowest biomass measured, and soybean plants were almost all killed off. For soybean roots, uptake of N-EtFOSAA and transformations of PFOS and PFOSA were contained well. PAC and MPAC consistently decreased significant amounts of N-EtFOSAA, as well as PFOSA and PFOS, two transformations of the spike.

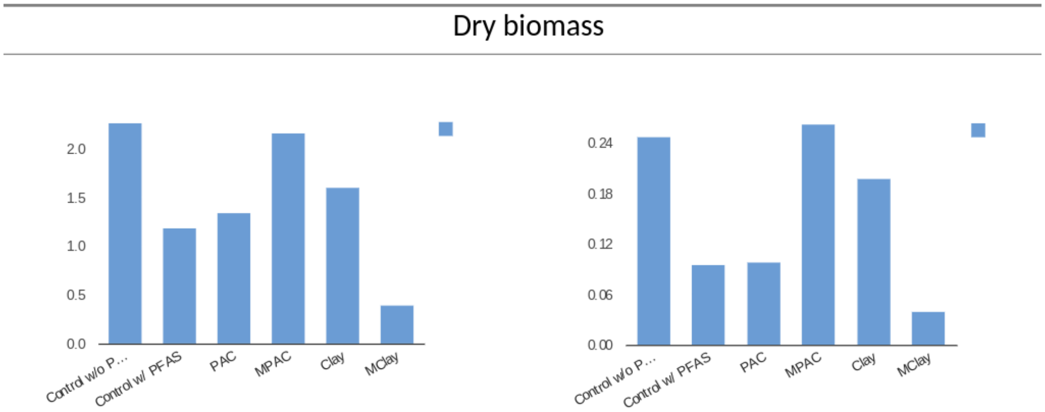

Figure 2: Fluctuations of total initial dry biomass prior to analysis and extraction.

Note: MClay is statistically lower compared to every other sample.

The autoclaved control soil and the regular control soil, both without plant cultivation, experienced transformation of N-EtFOSAA to three different products, N-EtFOSA, PFOSA, and PFOS. However, of these three products, water leachability test came back significant only for PFOSA and PFOS. Since both the autoclaved control group, and the regular, no-seedling control group both had three N-EtFOSAA transformation products that weren't drastically different, it's possible to rule that bacterium in soils does not play a role in transformation of PFAS, concluding that autoclaving samples is not necessary in the future.

Methanol results showed the same PFAS transformations, however with plant cultivation. For N-EtFOSAA and its transformations, PAC was the most effective in decreasing methanol extraction availability. MPAC was successful in decreasing extraction for only N-EtFOSAA and PFOS, but not PFOSA. MClay only was successful in decreasing PFOSA products. The extraction effectiveness of both PAC and MPAC are comparable, however extraction levels of products on MPAC are noticeably higher, making PAC the better candidate in limiting N-EtFOSAA extraction through methanol.

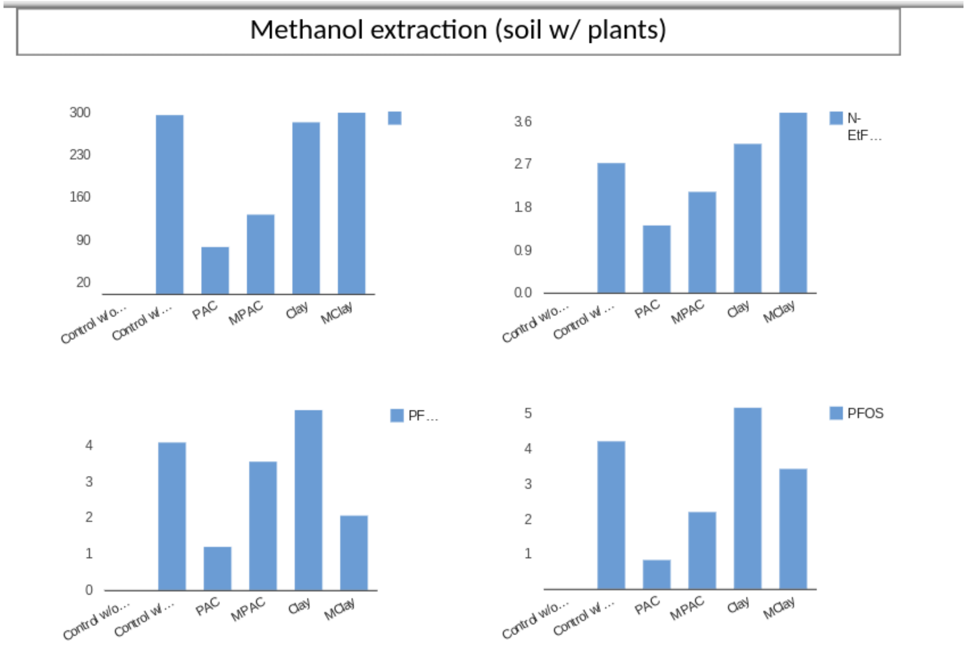

Figure 3: Displays results from Methanol Extraction analysis. A: Control group (top left), B: N-EtFOSAA (top right), C: PFOSA (bottom left), D: PFOS (bottom right). The graphs display the effectiveness of PAC and MPAC in providing limited methanol extraction.

In the results with soils without plants, transformations of N-EtFOSAA remained similar to soils with plants, suggesting that the spiked soil interaction with soybeans is not the sole cause of these product transformations. Instead, this strongly suggests the interaction between soil and PFAS itself could be the leading cause. In addition to not causing transformations of PFAS, plant growth, coupled with each individual sorbent/soil combination, also showed to be beneficial in restricting water leachability and methanol extraction, supporting the fact that plant growth can help restrict biomobility of PFAS in the environment.

Discussion

The use of soybean seedlings, coupled with effective sorbents and their modification demonstrated effectiveness in preventing PFAS transformation. This is applicable to the many cases of PFAS pollution near streams or bodies of water that deal with runoff constantly. The positive effects of MPAC and PAC combined with soybean plants have on water leachability of the spiked soils show promising effects in containing a polluted area that is under constant exposure to the movement of water. The negative effects of MClay however, strengthen the need for balance when using plants as mediators of pollutants. The extreme natural nutrients in montmorillonite clay paired with the iron oxide hydroxide modification provides an overwhelming abundance of nutrients for soybeans, interfering with the uptake and processing of N-EtFOSAA. Understanding the effects that soil alone has on PFAS also assists in making alterations to soils for possible remediation tasks. Soil alone, without any microorganisms or bacteria, has shown the ability to produce transformations of PFAS, meaning that more efficient ways to control the transformations must be developed, as plants and modified sorbents, even the most effective ones such as PAC or MPAC, can only do so much.

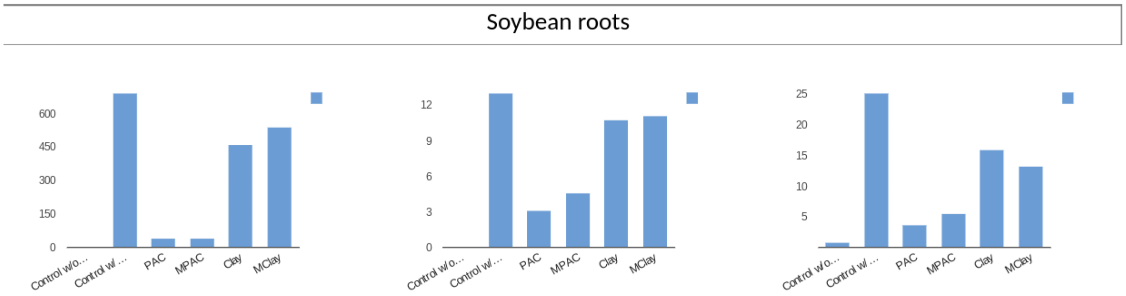

Figure 4: Levels (from left to right) of A: partial N-EtFOSAA transformation, B: PFOSA, and C: PFOS of each sorbent modification. PAC and MPAC uptake were significantly reduced at the roots.

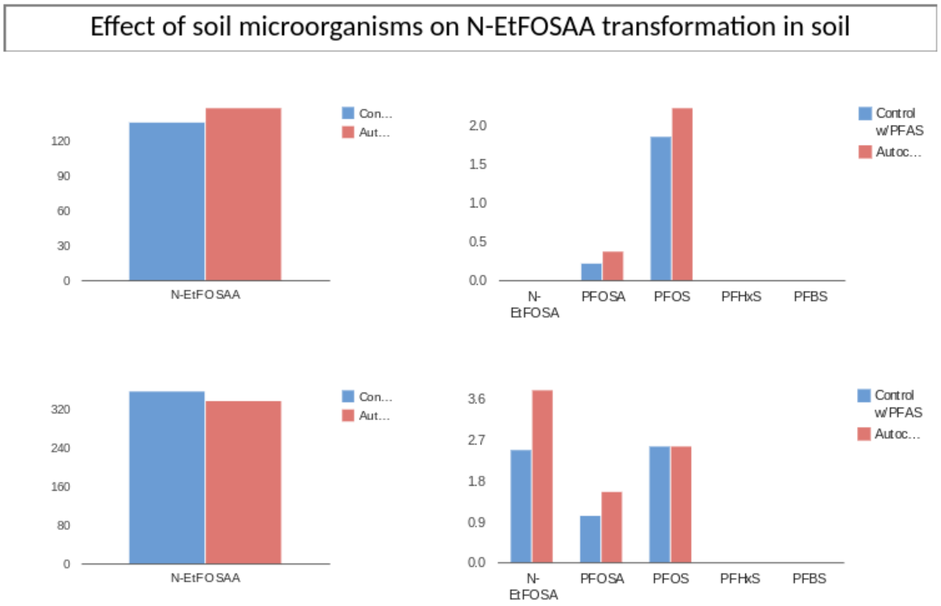

Figure 5: Transformations of N-EtFOSAA and the comparable similarities between the control group, and the autoclave group. Considering the lack of substantial differentiation, interaction with microorganisms in soil does not impact PFAS transformation.

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