Phytoremediation of PFAS-Impacted Soil & Groundwater

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Abstract

Phytoextraction, also called phytoaccumulation, is the uptake and translocation of contaminants in the soil, or other media, by plant roots into the aboveground portions of the plants. Based on the favorable results of our previous investigation published in the International Journal of Phytoremediation (Huff, et al. 2020) that established the proof of concept, Nutter & Associates, Inc. (NAI), a U.S. Small Business Administration HUBZone-certified company, and Kurt Pennell, Ph.D., P.E. of Brown University are implementing a new phytoremediation investigation to demonstrate the viability of our phytoextraction methodology for PFAS-contaminated sites by conducting an updated grow house investigation using the most effective perfluorooctane sulfonate (PFOS) accumulating plant species identified in our earlier studies and grown in PFOS-impacted soils acquired from up to five DoD facilities employing a statistics-based randomized block design. Successful accumulation during the investigation will be defined by achieving PFOS shoot to soil (or shoot + thatch to soil) concentration ratios that are >1 and which show extrapolated PFOS accumulation rates meeting one-half reduction of the root zone PFOS soil concentrations within a 10-year time horizon. Evidence suggests that this method of phytoremediation can be 50-80% cheaper than other remediation alternatives (EPA National Risk Management Research Laboratory (McCutcheon, S.C. and J.L. Schnoor, 2003)).

Problem Statement

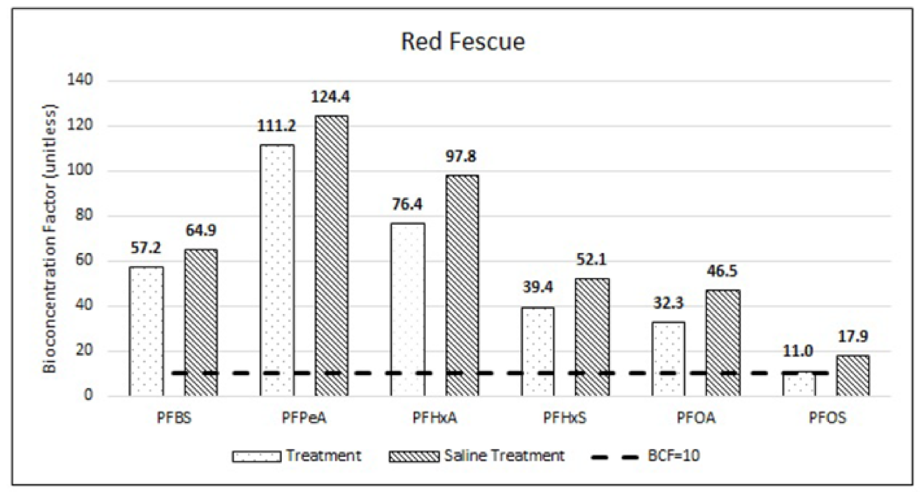
Current leading cleanup approaches for PFAS-impacted soil and sediment consists of expensive and energy consumptive excavation and removal. As the federal hazardous substance designation of PFOS and PFOA became effective on July 8, 2024, there is a pressing need for a viable phytoremediation cleanup methodology to address PFAS-impacted soil and other media.

The Phytoremediation Opportunity

The EPA National Risk Management Research Laboratory has stated that phytoremediation approach can be 50-80% cheaper than other established alternatives. Thus, our phytoextraction methodology and process stands to be more economically viable than other remedial options and it will meet core elements outlined in the ASTM E2893 Standard Guide for Greener Cleanups that include minimizing greenhouse gas emissions, air pollutants, use of materials, generation of waste, disturbance to land and ecosystems, and noise and light disturbance.

Background

Our previous investigation established proof-of-concept for the use of phytoremediation to remediate PFAS-contaminated media via phytoextraction and the results of our investigation were published in the International Journal of Phytoremediation (Huff et al., 2020). Our investigation was sufficient basis for the US Patent Office to grant three Utility Patents for our methodology. A key metric in our study was Bioconcentration Factor (BCF), which is the ratio of contaminant concentration in plant tissue to the contaminant concentration in the soil. A BCF that is > 10 is indicative of strong viability for a plant to be effective in a phytoextraction application. Red fescue (*Festuca rubra*) grass performed best across all PFAS compounds tested in our previous study.



New Investigation

Our initial investigation was based on plants grown in a sand support matrix. Thus, the viability of our phytoextraction technique needs to be vetted to assess whether adequate phytoaccumulation can be achieved with actual PFAS-contaminated soils (e.g., finer textures, mixed mineralogy, greater organic matter, long-term absorption and complexation of PFAS within the soil, and greater biologic activity) found at DoD installations.

An innovation associated with our initial investigation was the use of a saline irrigant containing gypsum and magnesium sulfate dissolved in deionized water. Increases in PFOA and PFOS accumulations were observed in plants grown in soils receiving the saline irrigant; the increases ranged from 44% to 344% greater than contaminated treatments that did not receive salinity amendments (Huff, et al. 2020). Salinity treatments will be further optimized as part of this proposed investigation.

With the initial investigation it was noted that the highest PFOS accumulating plant, *Festuca rubra*, developed a thick (5-10 centimeter) thatch on top of the mineral soil surface (Figures 1-4). This thatch is a combination of dead organic debris, living roots, crowns, and stems of grass (Christians, 2004). As shown in the photographs (Figures 1-4), the *Festuca rubra* thatch was thick enough to be harvested with the grass leaves (shoots), thus accelerating extraction from soil. Analysis of the PFAS concentrations within the thatch was not performed with our initial investigation, but thatch analysis is planned as part of this proposed investigation to determine PFOS extraction rates when shoot and thatch harvesting is combined.

The translocation factor (TF) is a bioaccumulation metric that is defined as the ratio of the shoot concentration (C_{shoot}) to the root concentration (C_{root}) for a particular constituent:

$$TF = C_{shoot}/C_{root}$$

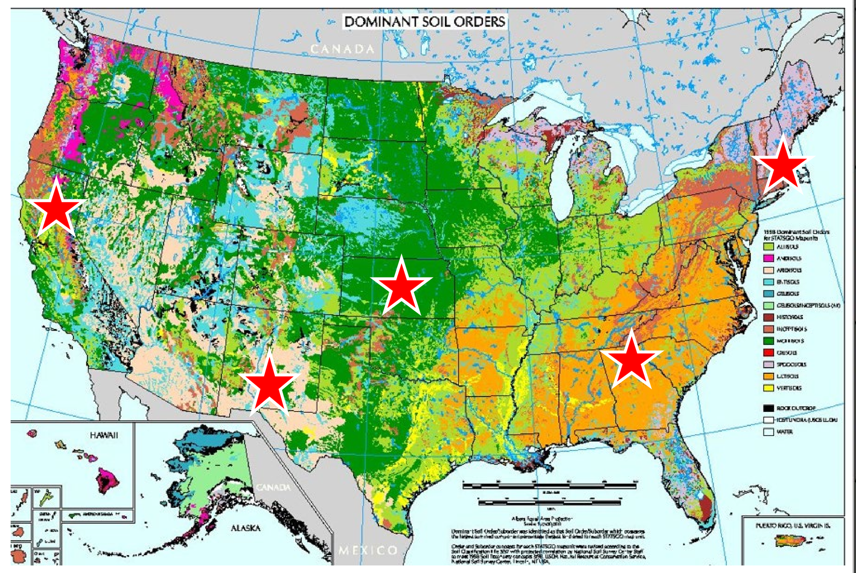
Numerous studies have shown root concentrations typically exceed the shoot concentrations in phytoextraction. Bei Wen et al. (2016) found that the PFOS TF ranged from 0.055 to 0.016 among the seven species they tested. Thus, root PFOS concentrations are generally expected to be substantially larger than the shoot concentrations.

Study Design

1. Conduct a grow house investigation building on previous research (Huff et al., 2020)
2. Use the most effective PFOS-accumulating plant species, *Festuca rubra* (red fescue)
3. Grow plants in PFAS-impacted soils acquired from five DoD facilities: including Dobbins ARB in Marietta, GA and others encompassing multiple soil types (e.g., Ultisols, Mollisols, Aridisols, Andisols, Inceptisols)
    - Dobbins Air Reserve Base, Marietta, Georgia
    - Hanscom Air Force Base, Massachusetts
    - McConnell Air Force Base, Kansas
    - Beale Air Force Base, California
    - Holloman Air Force, New Mexico

4. Investigate based on a statistics-based, randomized block design and include soil amendments shown to improve PFOS accumulation (i.e., salinity amendment, soil oxidation/tilling, fertilizer amendment)

5. Perform lab analysis to determine PFOS uptake levels in shoots and thatch, and evaluate rates of PFOS accumulation in various soil types



★ denotes Air Force base soil sample location.

Expected location and amendment to each soil sample in study.

RF-Dobbins-200
RF-Dobbins-2000
RF-Dobbins-20000
RF-Dobbins-200+S
RF-Dobbins-2000+S
RF-Dobbins-20000+S
RF-Northeast C1
RF-Northeast C1+S
RF-Northeast C2
RF-Northeast C2+S
RF-Midwest C1
RF-Midwest C1+S
RF-Midwest C2
RF-Midwest C2+S
RF-Northwest C1
RF-Northwest C1+S
RF-Northwest C2
RF-Northwest C2+S
RF-Southwest C1
RF-Southwest C1+S
RF-Southwest C2
RF-Southwest C2+S
RF-Control
RF-Control+S

Excessive Thatch. Photo credit: Dr. Kevin Mathias, University of Maryland Extension

Figure 1. *Festuca rubra* after initial transplanting.

Figure 2. *Festuca rubra* at study completion, note the depth and height of the thatch.

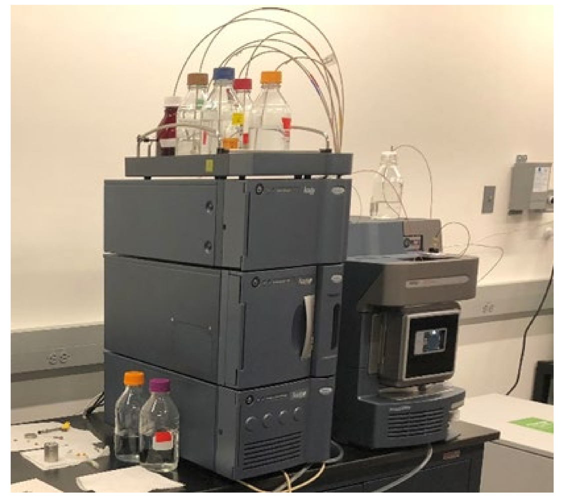
Figure 3. Thatch easily removed from sand support media at the test completion.

Figure 4. Thatch removed at test completion; with no evident sand from the support media.

Progression of red fescue growth from transplant to harvest.

Laboratory Analysis Methodology - Pennell Lab – Brown University School of Engineering

Analysis of plant tissue and soil will be conducted by Kurt Pennell, Ph.D. at Brown University School of Engineering, using state of the art liquid chromatography-mass spectrometry (LC-MS/MS) in accordance with the SERDP and ESTCP memo: Requirements for SERDP and ESTCP Projects Addressing PFAS-related Issues.



Waters uHPLC Xevo TQ-S

Thermo GC QExactive Orbitrap

Thermo LC QExactive HFX Orbitrap

- Targeted analysis of 40 PFAS using Waters uHPLC-MS/MS system (EPA draft method 1633)
- PFAS method verified by an ELAP-certified laboratory (Battelle Memorial, Norwood, MA)
- Non-targeted analysis using high resolution liquid- and gas-chromatograph Thermo Orbitrap mass spectrometers to detect unknown PFAS and/or reaction products
- Metrohm combustion ion chromatography (CIC) for TF and TOF analysis
- Plant tissue PFAS method published (Huff et al., 2020, Inter. J. Phytoremediation)

Objectives

The three primary objectives of the investigation are:

- Goal 1 - achieve and scientifically document adequate phytoaccumulation via phytoextraction by Festuca rubra from natural soils collected from five different regions within the US that have been contaminated from past PFAS releases in a greenhouse setting,
- Goal 2 - confirm and provide greater scientific basis proving specific management techniques (use of a saline irrigant treatment, tillage, synthetic nitrogen fertilizer) will significantly increase the rate of PFAS phytoaccumulation compared to control treatments, and
- Goal 3 - achieve and scientifically document significantly greater PFAS phytoaccumulation through propagating thatch along with stems and leaves (shoots) of Festuca rubra.

References

Bei Wen, Yali Wu, Hongna Zhang, Yu Liu, Xiaoyu Hu, Honglin Huang, Shuzhen Zhang, 2016. The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils. Environmental Pollution 2016, 216, 682-688. https://doi.org/10.1016/j.envpol.2016.06.032

Christians, N. E., 2004. Fundamentals of Turfgrass Management. John Wiley & Sons, Inc., Hoboken, New Jersey.

Huff, D. K., Morris, L. A., Sutter, L., Costanza, J., and Pennell, K. D. 2020. Accumulation of six PFAS compounds by woody and herbaceous plants: potential for phytoextraction. Int. J. Phytoremediation 22, 1538–1550. doi: 10.1080/15226514.2020.1786004

McCutcheon, S. C. and J. L. Schnoor, 2003. Phytoremediation: Transformation and Control of Contaminants. John Wiley & Sons, Inc. Hoboken, NJ.