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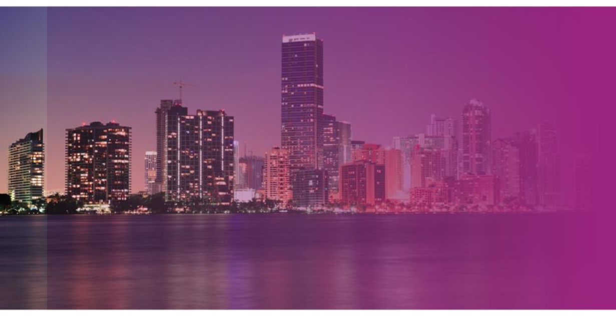

Current Research on Phytoremediation of PFASs

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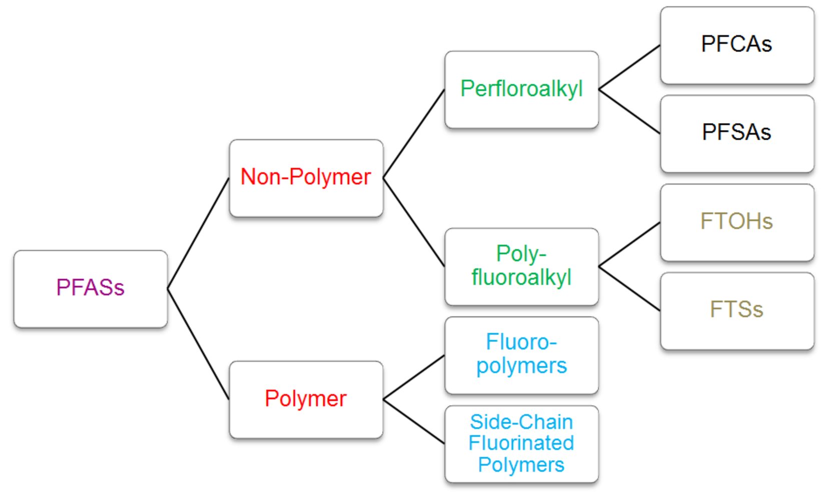
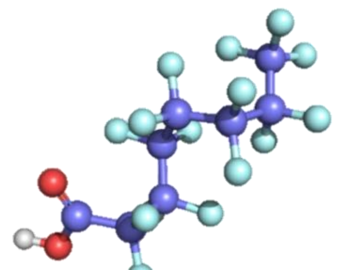
Background and Objectives

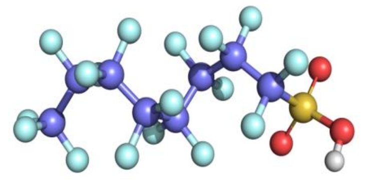
Poly- and Perfluoroalkyl Substances (PFASs) are a ubiquitous and environmentally persistent and varied group of problematic synthetic chemicals, broadly grouped as polymers and non-polymers. At least 42 families and subfamilies and 268 compounds are recognized. Perfluoroalkyl Acids (PFAAs) composed of Perfluoroalkane Sulfonic Acids (PFSAs) and Perfluoroalkyl Carboxylic Acids (PFCAs), have been subjected to much regulatory scrutiny, with majority of the studies conducted on PFOA and PFOS.



Remedial treatment options are limited due to the inherently stable carbon-fluorine bond. Identified scalable treatment options include granular activated carbon and possibly other sorbent media scrubbing. Other experimental and biological treatment approaches have been implemented in bench- and pilot-scale, including enzyme-catalyzed oxidative humification reactions (ECOHRs).



PFOA



PFOS

However, plant-assisted remediation (phytoremediation) of PFAS is poorly understood, with the majority of established research geared toward the evaluation of uptake and translocation of PFASs from soil or groundwater into agricultural targets such as food crops. There is also an enormous toxicological lexicon on PFASs uptake into plants, organisms and people, but few papers have been published on phytoremediation of PFASs. Our objective was to explore current research and single out potential phytoremediation mechanisms capable of degrading PFASs.

Approach and Activities

In 2016 through early 2017, AECOM funded an innovation proposal for evaluating the feasibility of plant-assisted remediation (phytoremediation) of PFASs. The work progressed in four stages, with the culmination of a White Paper *Plant-Assisted Remediation of PFASs* (May 2017), which identified relevant research, but considered the varied and sometimes unusual physio-chemical nature of PFASs in context with the principles which govern contaminant uptake and degradation in plants. Early on we discovered that precedent research on plant uptake of unrelated non-ionic organic chemicals such as various pesticides and polychlorinated compounds served as a practical proxy for looking at phytoremediation of PFASs.

1. • Literature Search
2. • Prepare Citation Index
   • Identify Applicable Existing Research
3. • Develop White Paper
4. • Identify Research Needs

To our knowledge, this is the first comprehensive assessment on the feasibility of phytoremediation of PFASs. We acknowledge that portions of the research are speculative. Our intention was to convey plausible mechanisms for field-scale phytoremediation.

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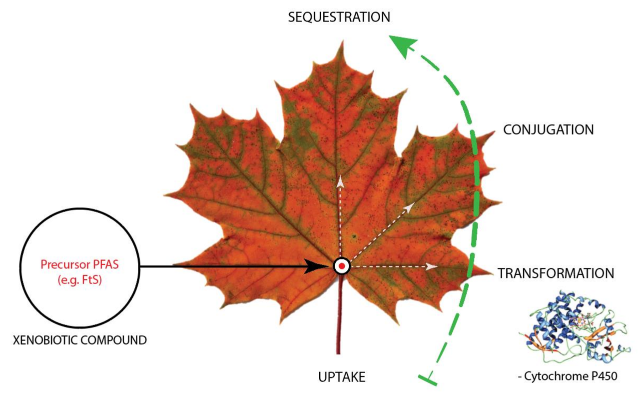
Plausible Phytoremediation Mechanisms

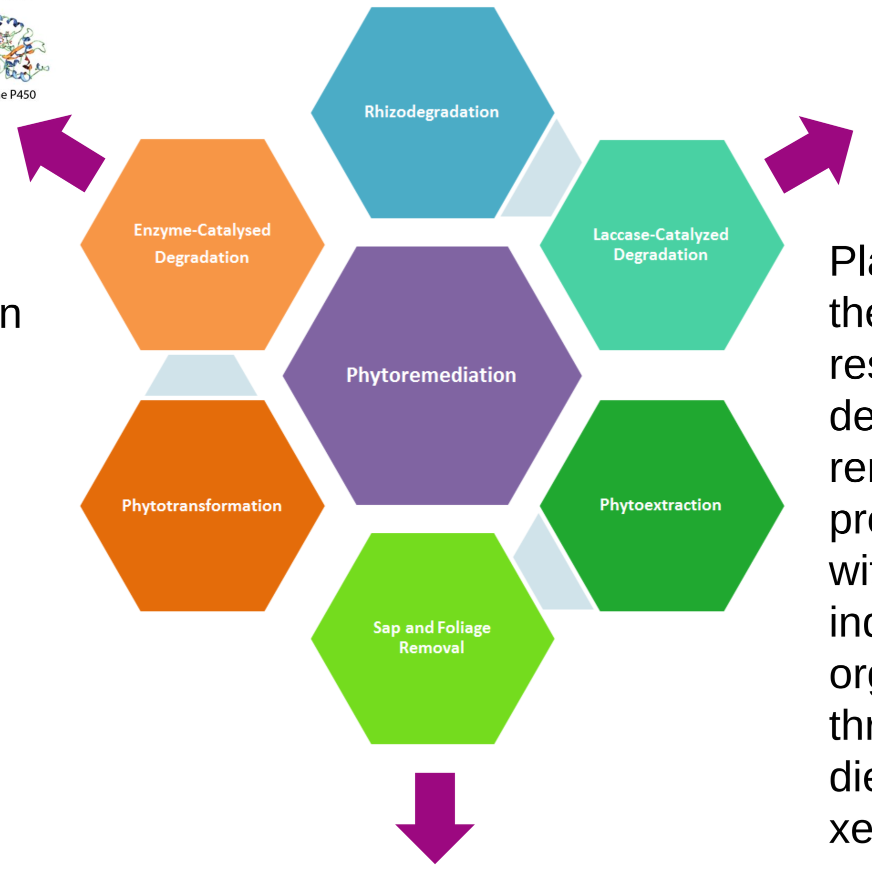
Plausible phytoremediation processes include rhizodegradation, phytoextraction, and phytotransformation. Phytovolatilization and phytophotolysis are not practical due to the non-volatile nature and ultraviolet resistance of most PFASs. In two of the processes we are suggesting that cytochrome enzymes, including P450, monooxygenase, peroxidase, and peroxygenase, and fungal- and bacteria-derived laccase may play a role in transformation of some PFASs (e.g. protonated forms, FTSs, or forms identified in aerobic degradation pathways).



Conceptual *in Planta* Transformation Mechanisms

Uptake and transport occurs primarily through translocation stream via xylem flow. Transformation of amenable PFAS salts, alcohols or precursor compounds is potentially facilitated by Cytochrome P450 or other plant-based enzymes.

Applicable Phytoremediation Processes For Remediation of PFASs

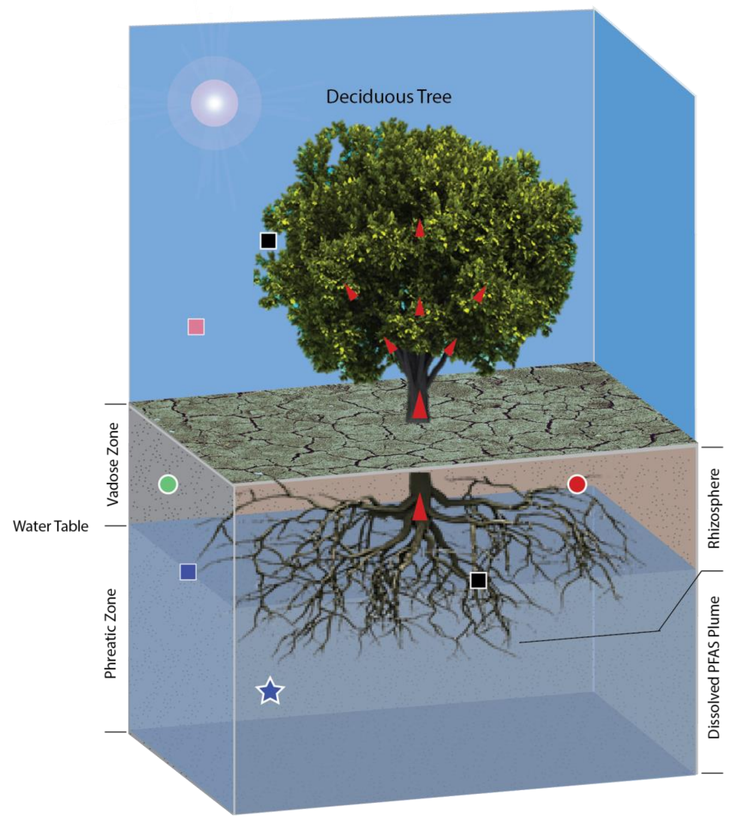


Laccase Production in Mycorrhizae

Plant-assisted bioremediation is the process by which organisms residing in the root zone alter or degrade chemicals. This is a soil remediation approach. The process is usually co-metabolic, with carbon being provided to indigenous soil-dwelling organisms and mycorrhizae, through plant exudation and root die-back, in the presence of xenobiotic chemicals. The process occurs aerobically and is facilitated as an enzyme-catalyzed (oxidative) degradation.

Factors Potentially Governing Uptake of PFASs

PFASs vary in behavior due to differences in chain length, chemical formulations, bonds, and presence of ionic and non-ionic receptors that govern the solubility and proclivity to stay in solution or bind to soil or mineral substrates. These are physio-chemical properties of PFAS compounds that influence uptake into plants. This is a complex model not dominated by singular processes, but rather suggests several processes working both concurrently and in stages.



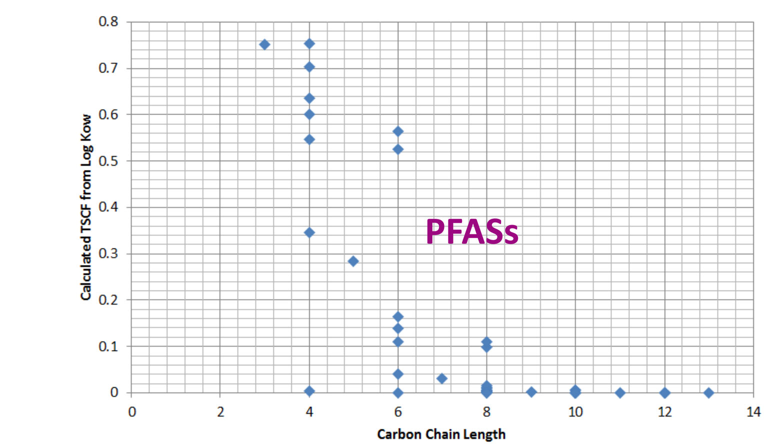
- Chemical Uptake
- Tree Type, Health, Transpiration Rate
- Ambient Weather Conditions
- Soil Sorption. K_{oc}, Microbiology
- Soil pH, Mineralogy, Sorption Substrates
- Solubility of PFASs, Log K_{ow}, pKa, pH
- Hydrogeology and Geochemistry

Findings

- Over 1,300 PFASs-related citations were reviewed. Less than 20 papers were found pertaining to uptake of PFASs into plants. Three papers were identified on tree uptake. Through late 2016, a single paper (a graduate thesis) has been documented on Phytoremediation of PFASs (Gobelius, 2016).
- Calculated Transpiration Stream Concentration Factors (TSCF) from octanol-water partitioning coefficients (log K_{ow}) for most PFASs suggest very low theoretical mass transfer. Some of the more promising compounds, with relatively low Log K_{ow} are presented in the table below.
- A mass uptake for PFOS was calculated to be **0.015 mg per square meter per year**, assuming log K_{ow} (0.001), concentration (0.1 mg/L), transpiration (500 L per m^2 per year), and fractional water use (0.3). Calculated mass uptake for PFBA is higher at **11.27 mg per square meter per year**.
- Carbon chain length (6 or less) is probably a more reliable screening metric for phytoextraction than Log K_{ow}, as our highest calculated TSCF values were for the shorter chain PFASs, as shown in graph below.
- In plants, potential transformation pathways are poorly understood and catalysts are likely limited to enzymes. Some PFASs such as PFCAs and non-protonated forms are probably entirely resistant to transformation.
- Accumulated and non-transformable PFASs present in foliage may be re-introduced into the environment after leaf abscission or foliage dye-back.
- Rhizodegradation, phytoextraction, and phytotransformation are the most promising phytoremediation approaches.

	Substance	Acronym	Molecular Formula	log Kow	Calculated TSCF from log Kow
PFCAs	Perfluorobutanoic Acid	PFBA	C_3F_7COOH	2.82	0.751
	Perfluoropentanoic Acid	PFPeA	C_4F_9COOH	3.43	0.547
	Perfluorohexanoic Acid	PFHxA	$C_5F_{11}COOH$	4.06	0.284
PFSAs	Perfluorobutane Sulfonic acid	PFBS	$C_4F_9SO_3H$	3.9	0.346
PFPAs	Perfluorobutyl Phosphonic Acid	PFBPA	$C_4F_9SOO_2H_2$	2.19	0.753
	Perfluorohexyl Phosphonic Acid	PFHxPA	$C_6F_{13}COO_2H_2$	3.48	0.525
FTSs	1H, 1H, 2H, 2H-Perfluorohexanesulfonic Acid	H4-PFHxS (4:2 FTS)	$C_4F_9CH_2CH_2SO_3H$	3.21	0.635
FTOHs	Perfluorethylethanol 4:2	4:2 FTOH	$C_4F_9CH_2CH_2OH$	3.3	0.600
PAPs	4:2 Fluortelomerphosphatemonoester	4:2 monoPAP	$C_4F_9CH_2CH_2OP(O)(OH)_2$	1.99	0.703
	6:2 Fluortelomerphosphatemonoester	6:2 monoPAP	$C_6F_{13}CH_2CH_2OP(O)(OH)_3$	3.39	0.564

TSCF = Transpiration Sctream Concentration Factor



Is Phytoremediation of PFASs Feasible?

In terms of meeting USEPA drinking water health advisory levels of 70 parts per trillion (ppt or ng/L) for PFOA and PFOS, phytoremediation of the stringently patrolled compounds PFOA and PFOS is probably not achievable in terms of meeting a cleanup goal. However, there are factors favorable for plant-assisted remediation of <u>some</u> of these compounds, including:

- Shallow nature of contaminant emplacement, particularly at AFFF fire-treatment source areas,
- High water solubility for some of the compounds,
- Log Kow values allowing for transport via xylem stream,
- Chemicals potentially transformable under aerobic conditions, and
- Chemicals amenable to enzyme-mediated catalysis.

Prospective plants for consideration include those with deep and vigorous root systems and ideally, capable of transpiring lots of water (>1000 l/m^2/year). Ideally, spreading root systems, with high biomass, are more effective at water uptake than deep tap root systems. Plants and trees favorable for rhizodegradation include grasses and genera with mycorrhizal fungal associations. Trees of the genus *Persea* (avocado) are intriguing from a phytotransformation perspective due to the high production and occurrence of Cytochrome P450 monooxygenase present in both fruit and tree tissues.