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Occurrence and Treatment of PFAS in the Environment and Engineered Systems

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January 19, 2022

Per-and polyfluoroalkyl substances (PFAS)

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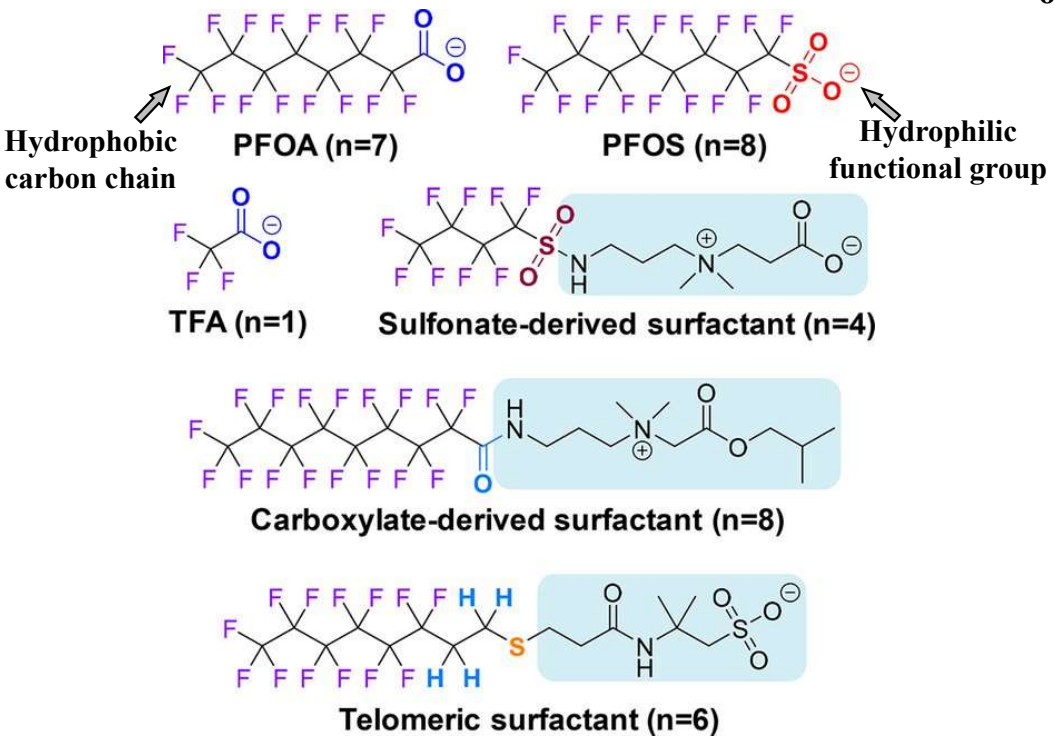
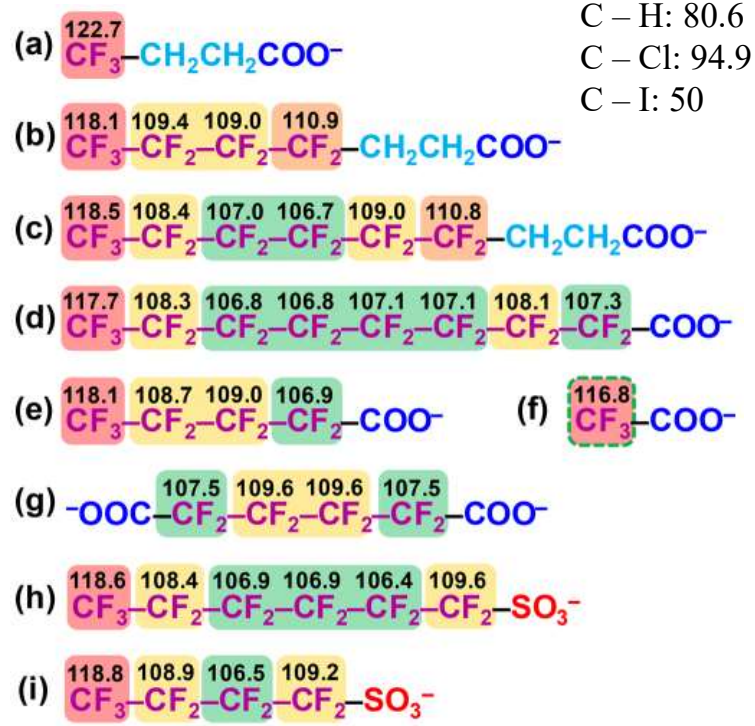
Examples of PFAS structures detected in the environment [1]



Calculated C−F bond dissociation energies (kcal mol^{-1}) of selected PFAS [1]



C – H: 80.6
C – Cl: 94.9
C – I: 50

1. Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Defluorination of per-and polyfluoroalkyl substances (PFASs) with hydrated electrons: structural dependence and implications to PFAS remediation and management. *Environmental science & technology* **2019,** *53*, (7), 3718-3728.

PFAS family tree

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PFAS
C_nF_{2n+1}-R

- **Perfluoroalkyl acids (PFAAs)**
  - **PFCAs ($C_{n-1}F_{2n-1}$-COOH)**
    - PFBA (n=4)
    - PFHxA (n=6)
    - PFOA (n=8)
    - PFDA (n=10)
  - **PFSAs (C_nF_{2n+1}-SO_3H)**
    - PFBS (n=4)
    - PFHxS (n=6)
    - PFOS (n=8)
    - PFDS (n=10)
  - **PFPAs (C_nF_{2n+1}-PO_3H_2)**
    - PFBPA (n=4)
    - PFHxPA (n=6)
    - PFOPA (n=8)
    - PFDPA (n=10)
  - **PFPiAs (C_nF_{2n+1}-PO_2H-C_mF_{2m+1})**
    - C4C4 PFPiA (n,m=4)
    - C6/C6 PFPiA (n,m=6)
    - C8/C8 PFPiA (n,m=8)
    - C6/C8 PFPiA (n=6,m=8)
  - **PFECAs & PFESAs (C_nF_{2n+1}-O-C_mF_{2m+1}-R)**
    - ADONA
    - GenX
    - EEA
    - F-53B
- **PFAA precursors**
  - **PFSF-based substances (C_nF_{2n+1}-SO_2-R)**
    - MeFBSA, MeFOSA, EtFBSA, EtFOSA, MeFBSE, MeFOSE, EtFBSE, EtFOSE, SAmPAP
  - **Fluorotelomer-based substances (C_nF_{2n+1}-C_2H_4-R)**
    - 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 6:2 diPAP, 8:2 diPAP
- **Others**
  - **Fluoropolymers**
    - PTFE
    - PVDF
    - FEP
    - PFA
  - **Perfluoropolyethers (PFPEs)**

PFAS are a class of over **9000** persistent hazardous chemicals

PFAS applications and contamination

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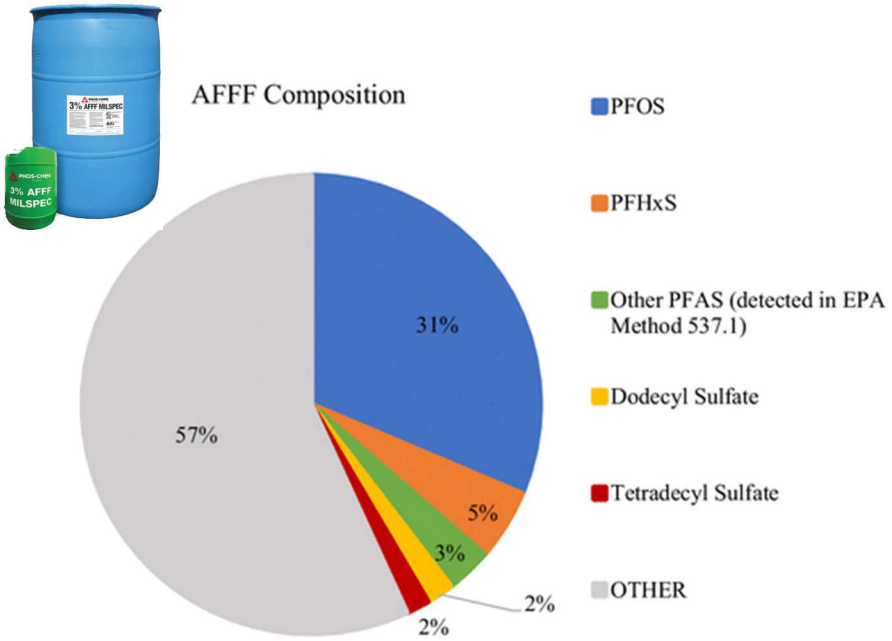
www/earthjustice.org; USEPA



Composition of the legacy 3% aqueous film-forming foam (AFFF) sample [1]

1. Annunziato, K. M.; Doherty, J.; Lee, J.; Clark, J. M.; Liang, W.; Clark, C. W.; Nguyen, M.; Roy, M. A.; Timme-Laragy, A. R., Chemical characterization of a legacy aqueous film-forming foam sample and developmental toxicity in zebrafish (Danio rerio). *Environmental health perspectives* **2020,** *128*, (9), 097006.

PFAS applications and contamination

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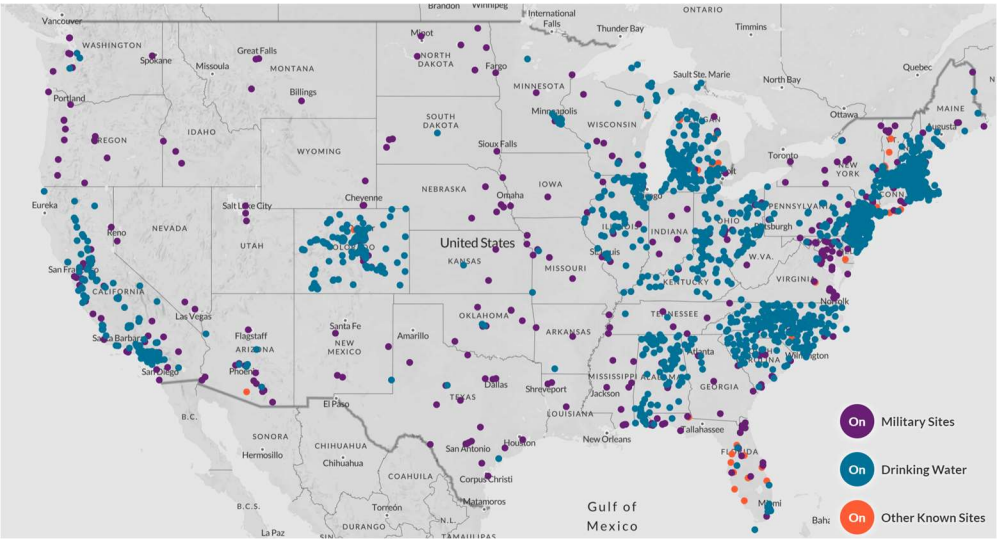
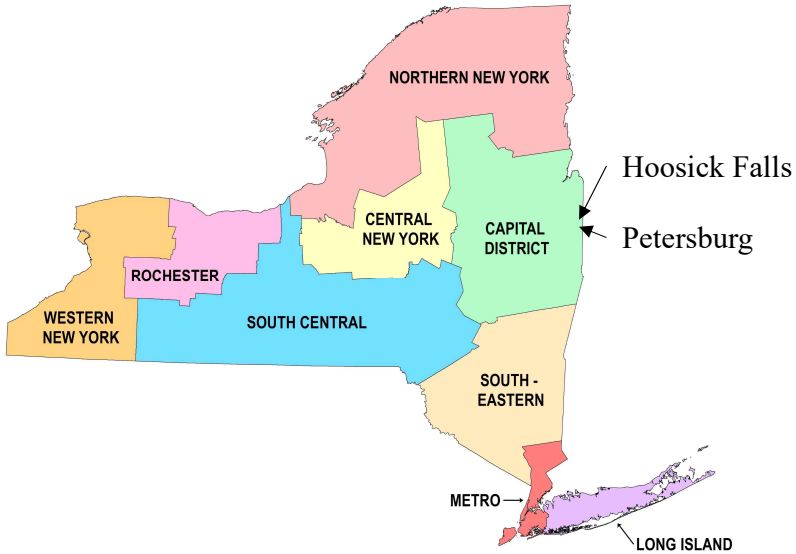


Source: EWG's interactive map

Across the US, hundreds of sites have been contaminated by PFAS and more than 6 million Americans are consuming water containing PFAS higher than EPA advisory level (70 ppt).

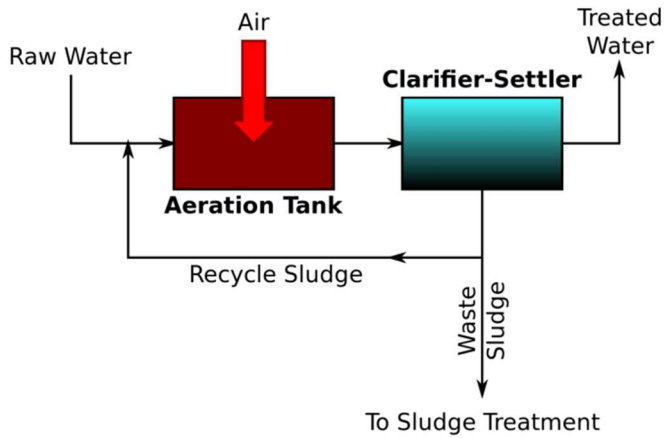


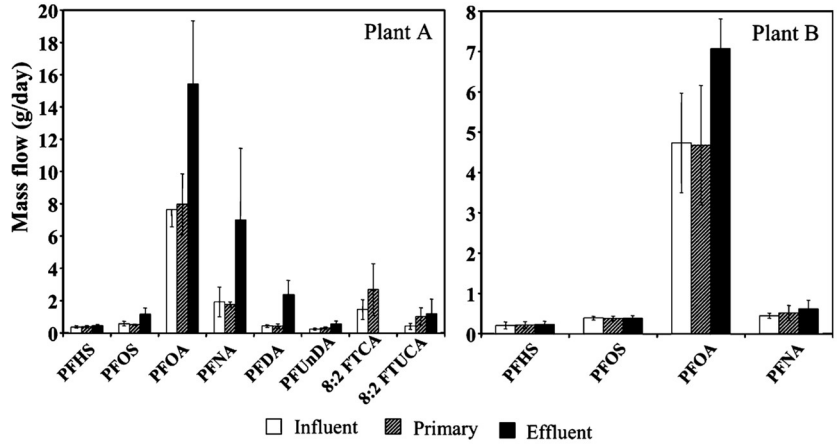
Hoosick Falls [1]: PFOA, Ground water;
Source: Saint-Gobain Performance Plastics facility;
Level: up to 540 ng/L in village supply wells.

Petersburg [2]: PFOA, Ground water & drinking water
Source: Taconic Plastics facility;
Level: up to 152,000 ng/L in wells and 4,200 ng/L in landfill leachate

1. Michaels, R.A. *Environmental Claims Journal*, 2017.
2. *Environmental Remediation Databases Details - Petersburgh Landfill*. New York State Department of Environmental Conservation.

PFAS in sewage sludge



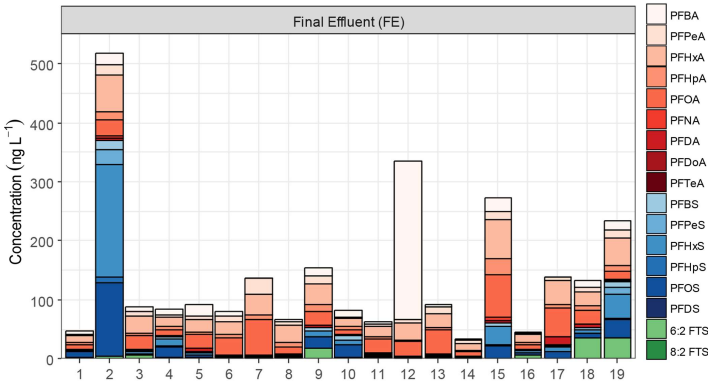


1. Sinclair, E.; Kannan, K., Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants. *Environmental Science & Technology* **2006,** *40*, (5), 1408-1414.

Analyzed PFAS	Concentration	Predominant PFAS	Reference
14 PFAAs (C3-C14)	126 - 809 µg/kg	PFOA: 23.2 - 298 µg/kg	Yan et al., 2012
PFAAs (C4-C8)	Up to 2547 µg/kg	PFOS: 4 - 2440 µg/kg	Alder and van der Voet, 2015
32 PFAS including precursors	5.6 - 963.2 µg/kg	PFOS: 932.9 µg/kg	Semerád et al., 2020
PFAS including precursors	up to 35.7 µg/kg	PAPs: 15 - 20 µg/kg	Eriksson et al., 2017
73 PFAS including precursors	39 - 210 ng F/g	diPAP: 62% of ∑PFAS	Aro et al., 2021
PFAS including precursors	80 - 160 µg/kg	diPAPs, FTSAs, PFPiAs: 95% of ∑PFAS	Loi et al., 2013

PFAS in sewage sludge

Effluent



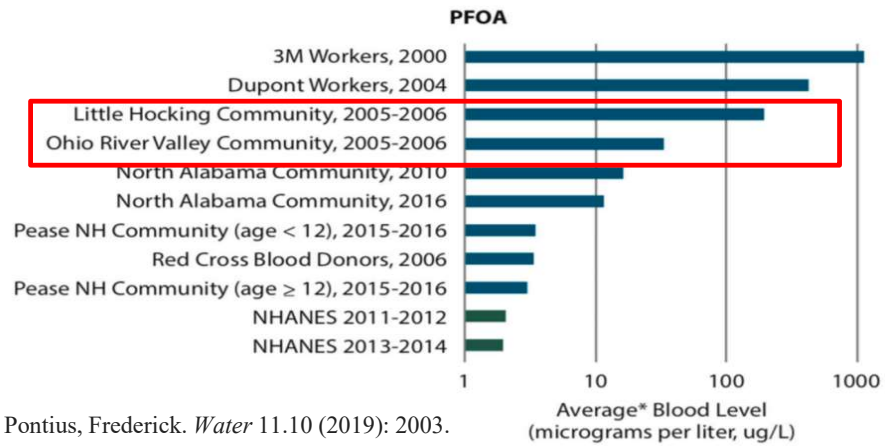
Coggan, et al. *Heliyon* **2019**.

Sewage sludge from Albany (ng/g, dry weight)

PFOA	PFHpA	PFHxA	PFBA	PFOS	PFBS
2.99	0.49	4.21	1.74	7.59	10.29

1. Venkatesan, A. K.; Halden, R. U., National inventory of perfluoroalkyl substances in archived US biosolids from the 2001 EPA National Sewage Sludge Survey. *Journal of hazardous materials* **2013,** *252*, 413-418.

PFAS contamination and regulations



Pontius, Frederick. *Water* 11.10 (2019): 2003.

FOREVER CHEMICALS

New York State has adopted a first-in-the-nation drinking water standard for PFOA & PFOS in 2020:
Maximum Contaminant Level, **10 ppt**.

New Jersey, MCL of PFOA: **14 ppt** and PFOS: **13 ppt**.

Michigan, MCL of PFOA: **8 ppt**; PFOS: **16 ppt**; PFNA: **6 ppt**;

Most of states: EPA health advisory level (**70 ppt** for PFOA and PFOS).

Possible human exposure pathways

PFAS remediation technologies

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Separation/stabilization	Destruction
• Adsorption • Reverse osmosis and nanofiltration • Foam fractionation • Phytoremediation	• Biodegradation • Incineration • Hydrothermal treatment • Photocatalysis • Advanced oxidation or reduction • Ultrasonication • Electrochemical oxidation • Non-thermal plasma

Current work

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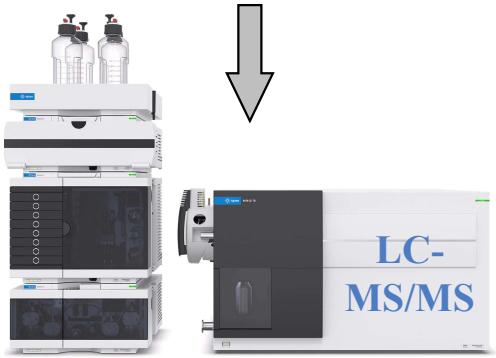
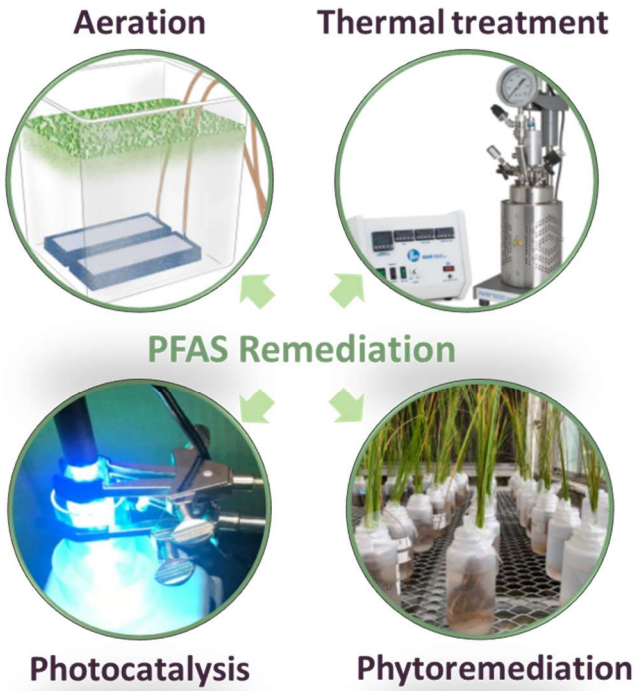
Environmental occurrence



PFAS Analysis

Remediation technologies



Studied PFAS

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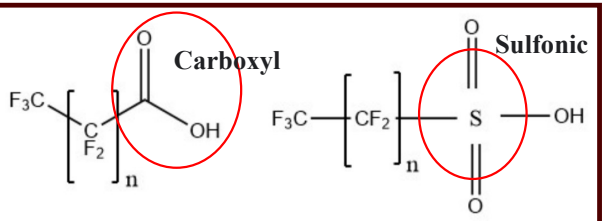
Perfluoroalkyl Acids (PFAAs)



PFCAs

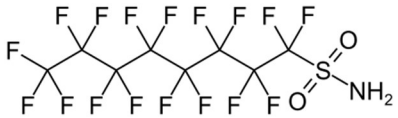
PFBA, PFPeA, PFHxA, PFHpA, PFOA, ...

PFSAs

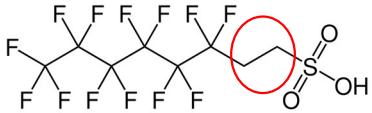
PFBS, PFHxS, PFHpS, PFOS, ...

PFAS intermediates

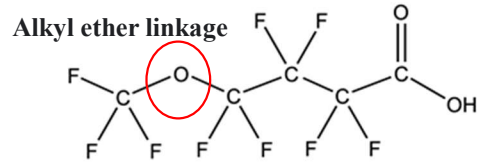
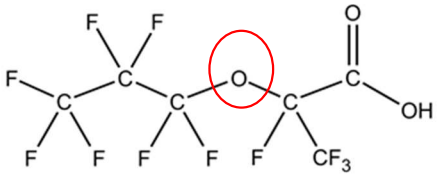
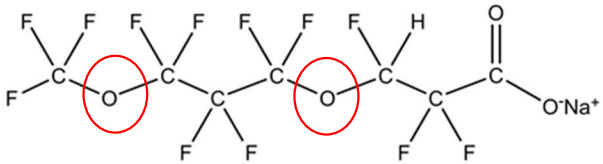
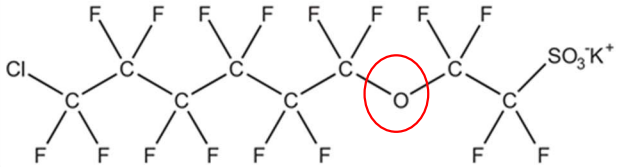
Perfluorooctanesulfonamide (PFOSA)



6:2 fluorotelomer Sulfonate (6:2 FTSA)



Ether-PFAS

Perfluoro(4-methoxybutanoic) acid PFMOBA CAS #: 863090-89-5	
Undecafluoro-2-methyl-3-oxahexanoic acid GenX CAS #: 13252-13-6	
Sodium dodecafluoro-3H-4,8-dioxanonanoate ADONA CAS #: 958445-44-8	
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate F-53B CAS #: 73606-19-6	

Photocatalytic degradation of PFOA

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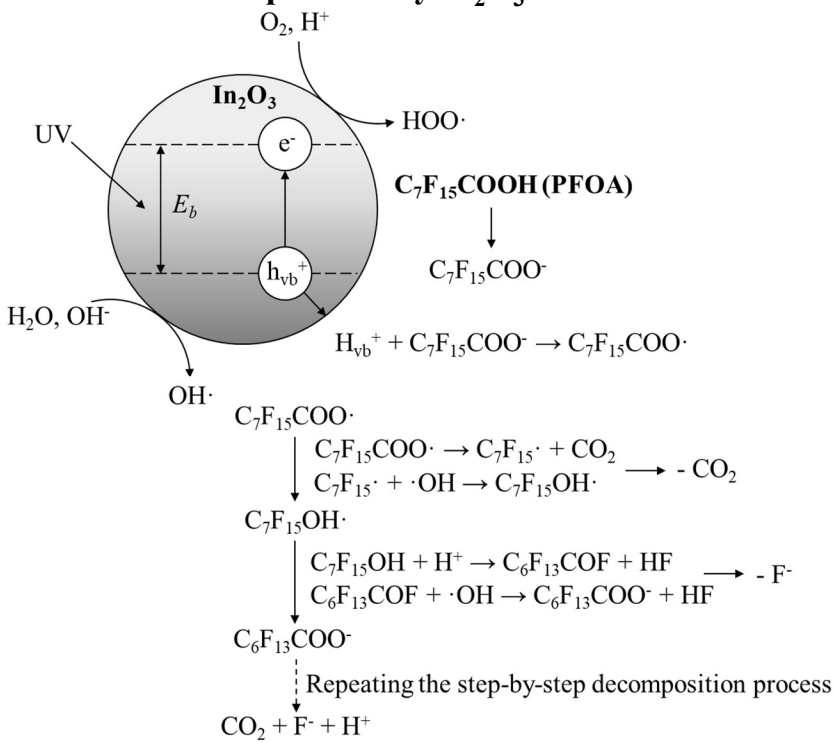
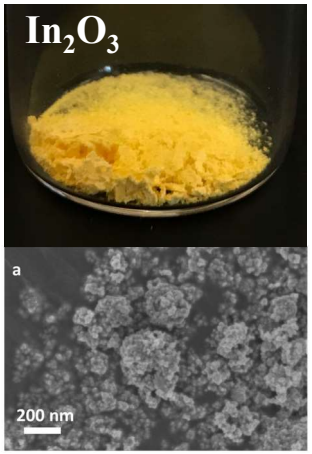
PFOA decomposition by In_2O_3 under UV





Significant factors:

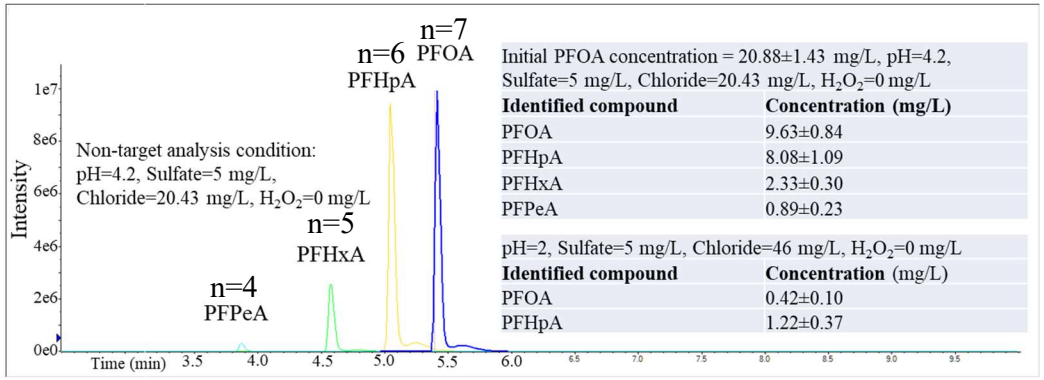
pH (2)

Sulfate (5.00 mg/L)

Chloride (27.31 mg/L)

H_2O_2 (0 mmol/L)

PFOA Decomposition: 97.59%



Initial PFOA concentration = 20.88±1.43 mg/L, pH=4.2, Sulfate=5 mg/L, Chloride=20.43 mg/L, H_2O_2=0 mg/L

Identified compound	Concentration (mg/L)
PFOA	9.63±0.84
PFHpA	8.08±1.09
PFHxA	2.33±0.30
PFPeA	0.89±0.23

pH=2, Sulfate=5 mg/L, Chloride=46 mg/L, H_2O_2=0 mg/L

Identified compound	Concentration (mg/L)
PFOA	0.42±0.10
PFHpA	1.22±0.37

Zhang, W.; Efstathiadis, H.; Li, L.; Liang, Y., Environmental factors affecting degradation of perfluorooctanoic acid (PFOA) by In2O3 nanoparticles. *J. Environ. Sci.* **2020**.

Phytoremediation: selection of plant species

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Native plant species

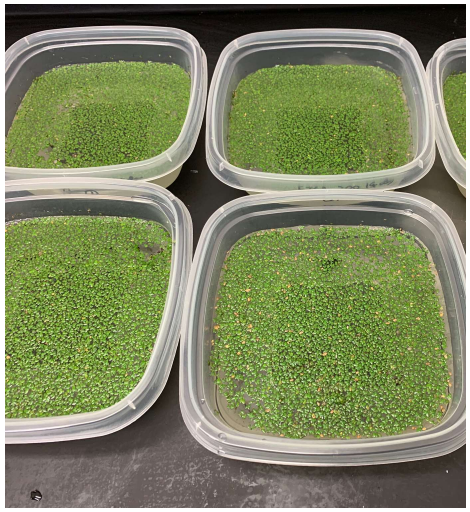
Diversity

High transpiration

Cold resistance

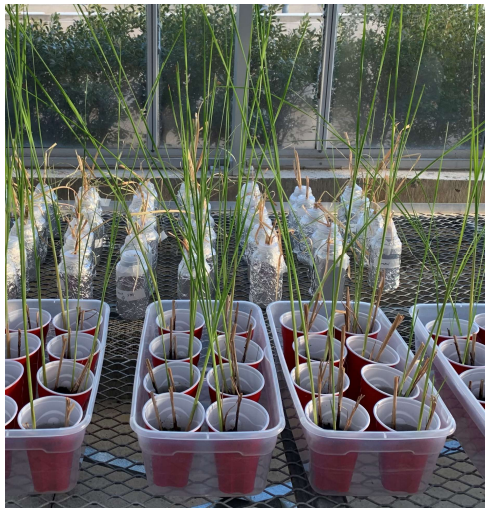
Juncus effusus
Soft rush

Lemna minor
Duckweed



Carex comosa
Longhair sedge

Typha latifolia
Cattail



Phytoremediation – *Juncus effusus*

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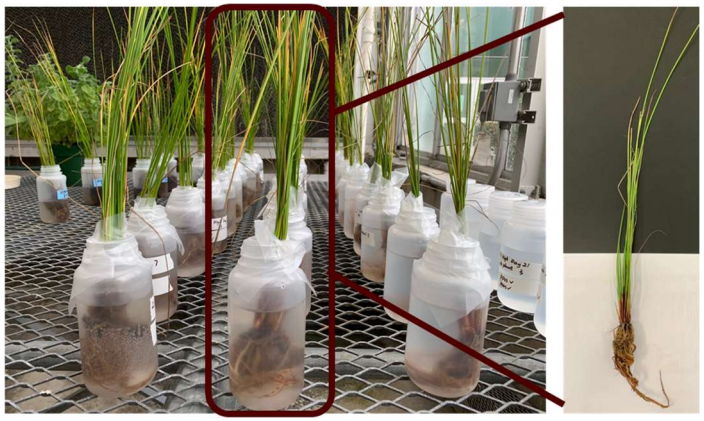
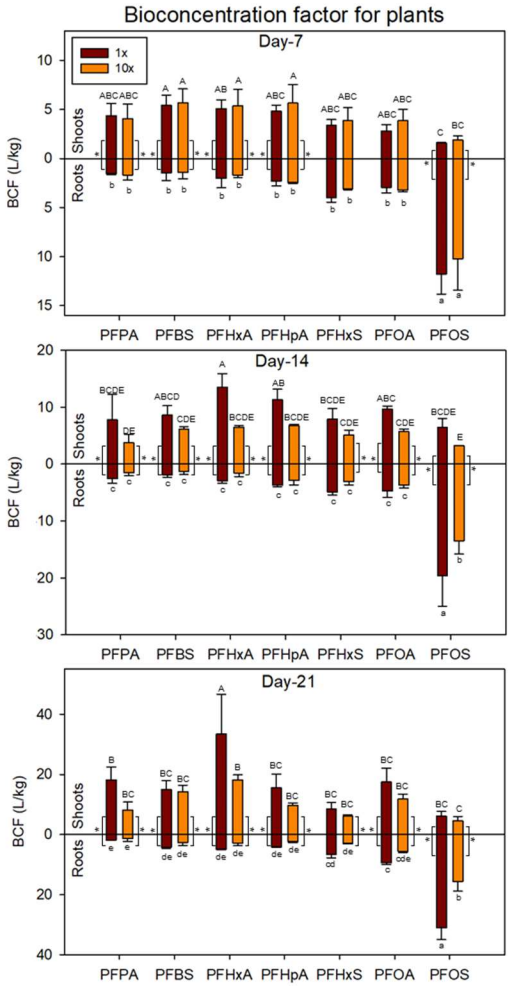
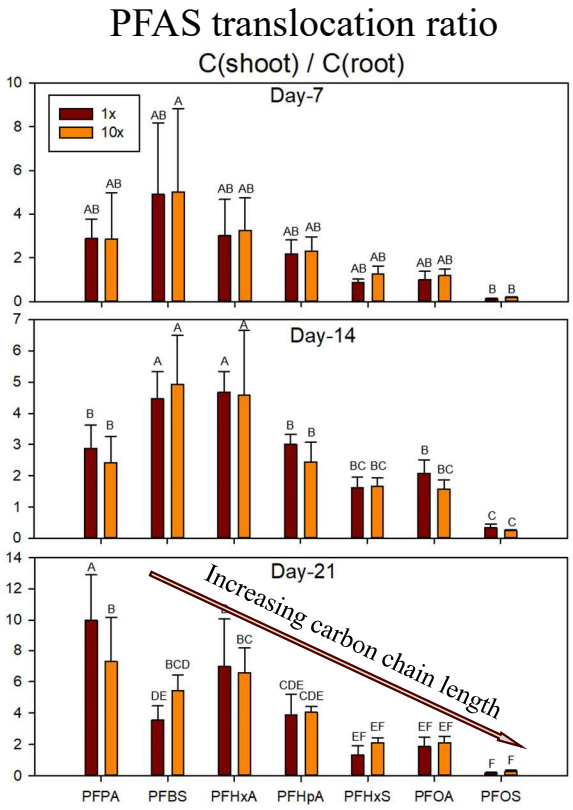


PFPeA-66 µg/L, PFHxA-120 µg/L, PFHpA-75 µg/L, PFOA-250 µg/L
PFBS-110 µg/L, PFHxS-290 µg/L, PFOS-4300 µg/L

- **All studied PFAAs were taken up by plants.**
- **Short chain PFAAs tended to translocate upwards. Long chain PFAAs largely accumulated in the roots.**
- **The removal efficiency of PFAAs achieved 5 – 15 % of spiked PFAAs.**





Zhang, W.; Zhang, D.; Zagorevski, D. V.; Liang, Y., Exposure of Juncus effusus to seven perfluoroalkyl acids: Uptake, accumulation and phytotoxicity. *Chemosphere* **2019,** *233*, 300-308.

PFAA removal by duckweeds

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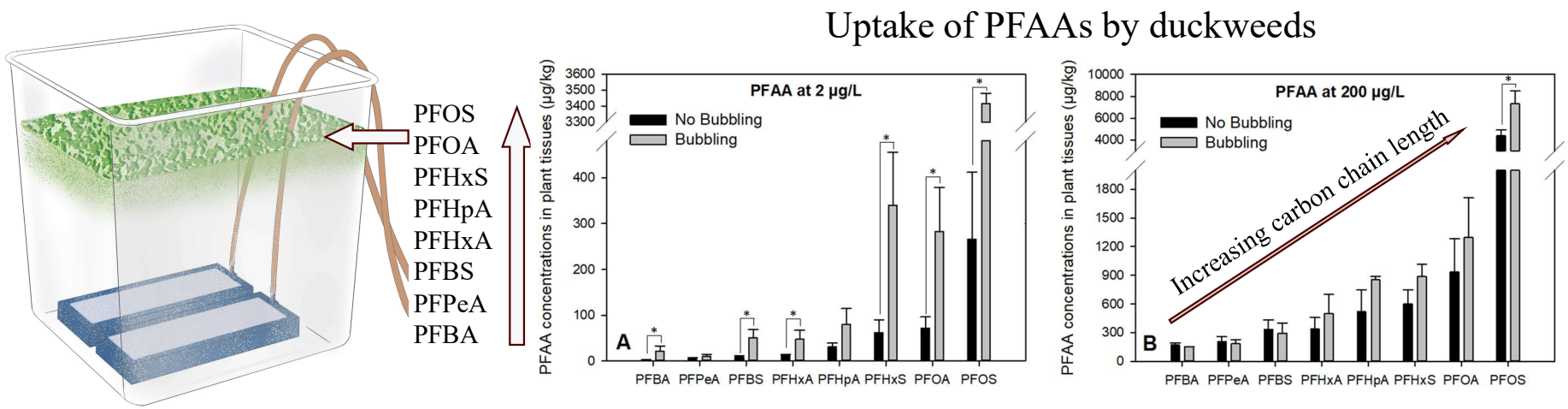
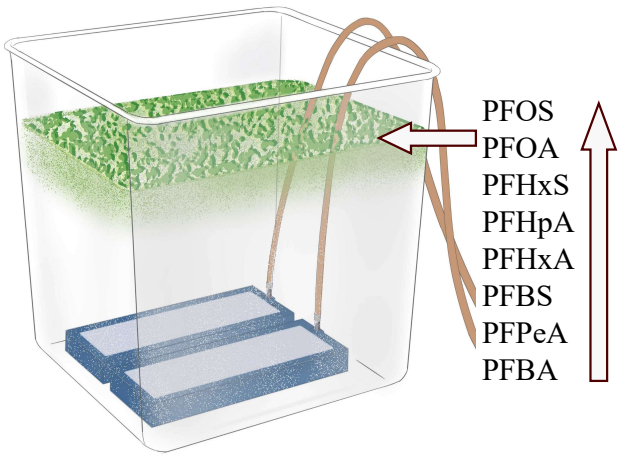


- Without plants, 80% of PFOS and PFOA at 200 ppb were removed by aeration in DI water for 7 h at pH 2.3.
- Without plants, higher ionic strength led to higher removal of long chain PFAS at 2 ppb at all pHs.
- Long chain PFAS tended to be rich in air-water interface, increasing their plant uptake.
- The plant uptake increased with increasing carbon chain length of the selected PFAAs.

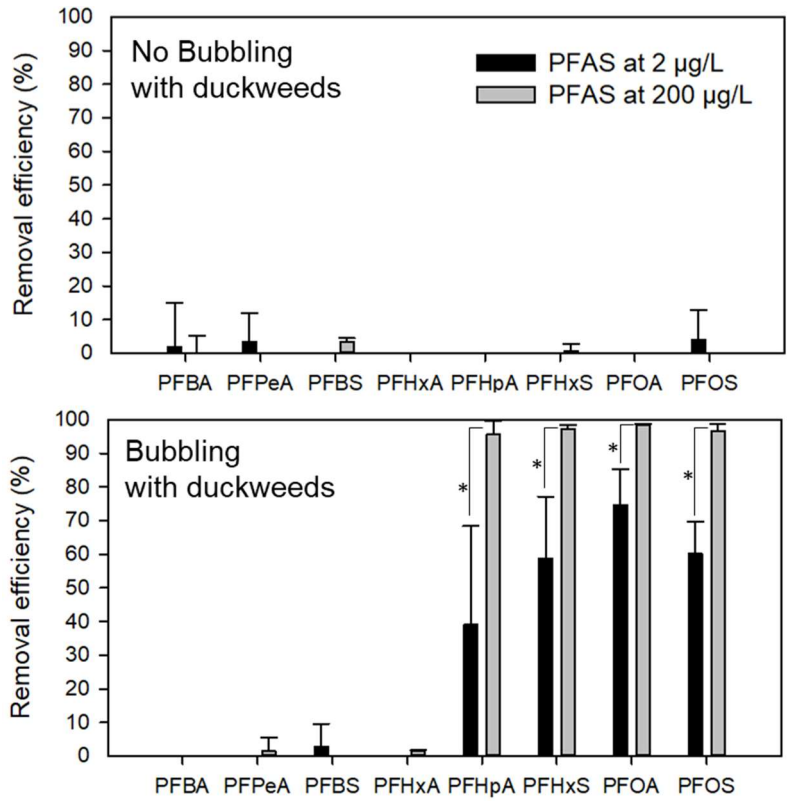
Zhang, W.; Liang, Y., Removal of eight perfluoroalkyl acids from aqueous solutions by aeration and duckweed. *Sci. Total Environ.* **2020**, 138357.

Aeration

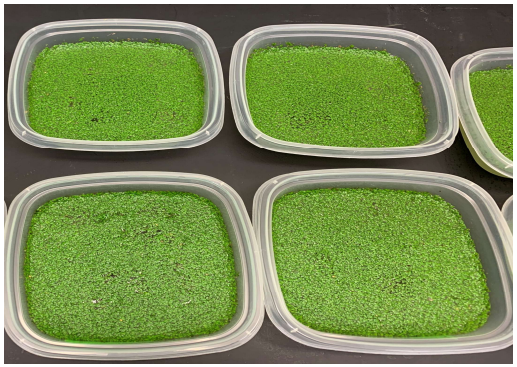


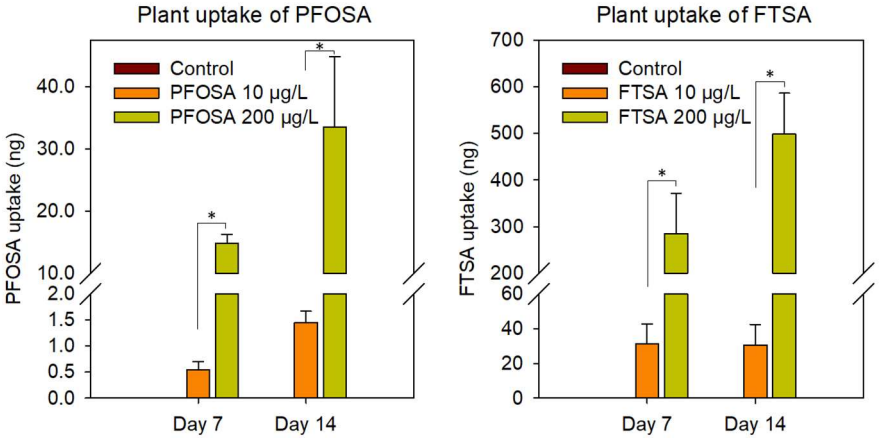
- With duckweed, >95% of long chain PFAS at 200 ppb were removed after 2 weeks.
- Duckweed accumulated 14.4% of spiked PFOS in 2 weeks.

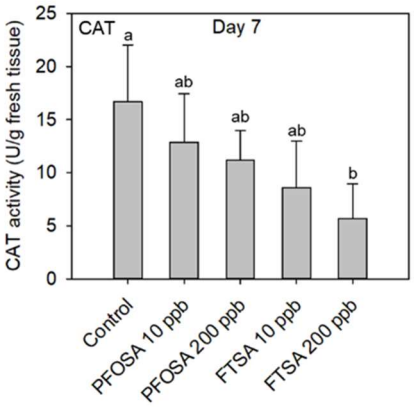
PFAA removal in bulk solution

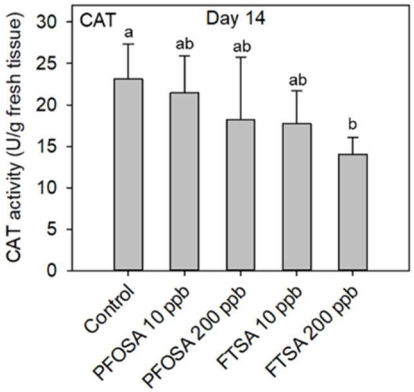


Phytoremediation – plant uptake









- **The selected PFAS intermediates were taken up by duckweeds.**
- **FTSA was more bioavailable to duckweeds.**
- **FTSA decreased the CAT activity and damaged the antioxidative defense system of duckweeds**

Zhang W.*, Liang Y. Interactions between *Lemna minor* and perfluorooctanesulfonamide (PFOSA) and 6:2 fluorotelomer sulfonate (6:2 FTSA). *Chemosphere*. 2021.

Phytoremediation – *Carex comosa*

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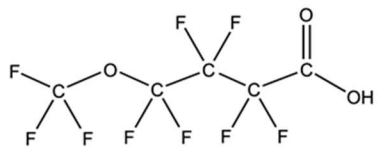
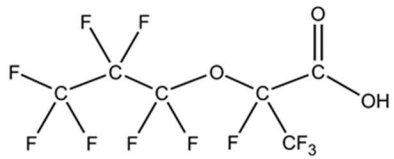
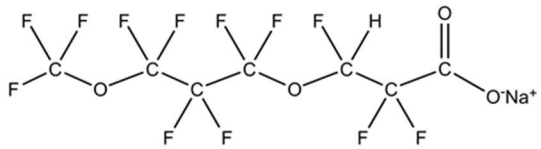
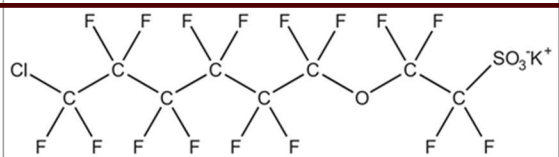
FPOA alternatives

Name, Synonym and CAS#	Structure	Molecular weight	$\log K_{ow}$
Perfluoro(4-methoxybutanoic) acid PFMOBA CAS #: 863090-89-5		280.05	-
Undecafluoro-2-methyl-3-oxahexanoic acid GenX CAS #: 13252-13-6		330.05	4.0 (Hopkins et al., 2018)
Sodium dodecafluoro-3H-4,8-dioxanonanoate ADONA CAS #: 958445-44-8		400.10	4.97 (Gomis et al., 2015)
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate F-53B CAS #: 73606-19-6		570.67	7.03 (Gebbink et al., 2016)

FPOS alternative

Longhair Sedge

Phytoremediation – *Carex comosa*

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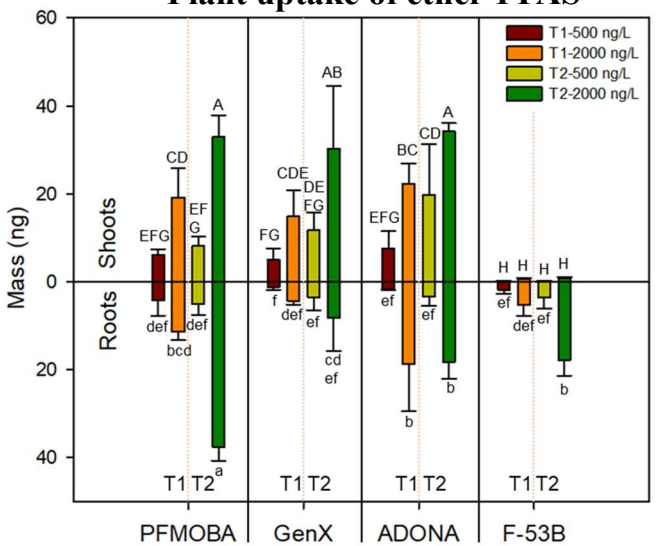
Fractionation of ether-PFAS in soil

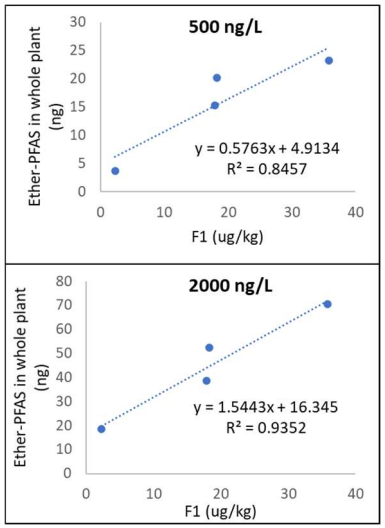
Conc.	Water-soluble F1 (μg/kg)	Base extractable F2 (μg/kg)	Acid extractable F3 (μg/kg)	Non-extractable F4 (μg/kg)
PFMOBA	35.82 ± 3.09	9.01 ± 1.07	0.00 ± 0.00	18.79 ± 11.94
GenX	17.88 ± 7.65	3.71 ± 1.51	0.00 ± 0.00	100.74 ± 6.18
ADONA	18.25 ± 4.12	5.09 ± 0.99	0.00 ± 0.00	110.71 ± 18.85
F-53B	2.26 ± 0.44	64.46 ± 3.89	12.57 ± 1.28	19.88 ± 5.45

Carbon chain length; K_{ow}

Plant uptake of ether-PFAS



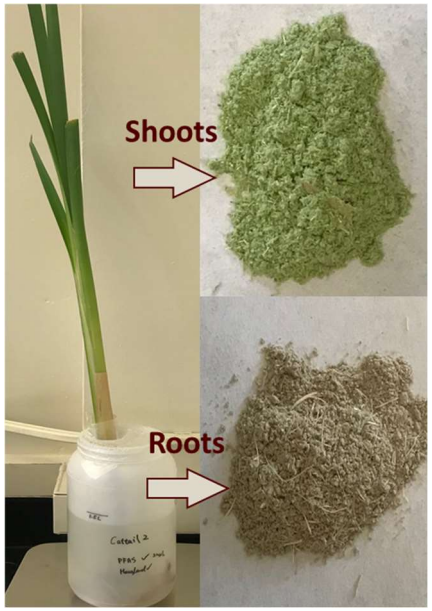
F1 conc. Vs. Plant uptake



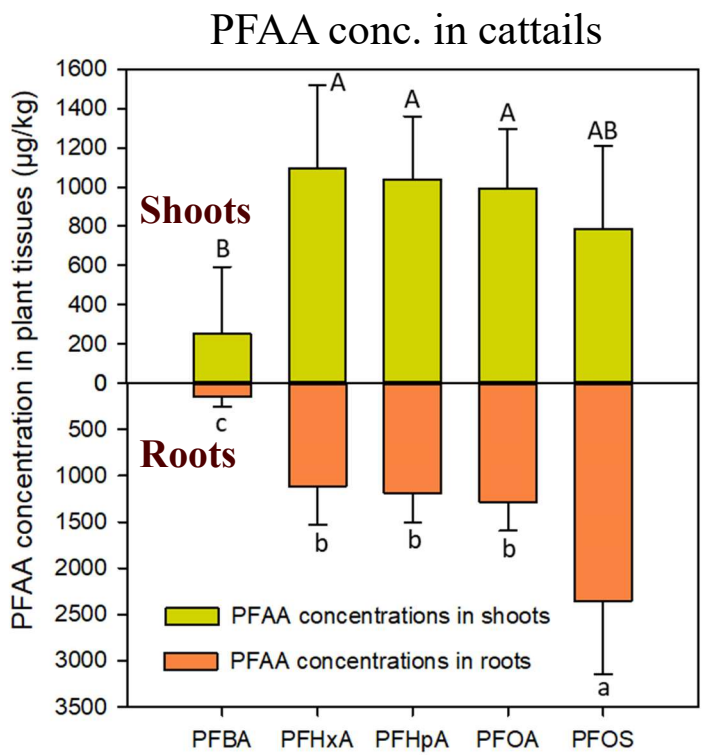
- **Ether-PFAS conc. in water-soluble fraction increased with decreasing carbon chain length and K_{ow}.**
- **Ether-PFAS conc. in water-soluble fraction had a positive linear relationship with plant uptake.**
- **Aging process reduced the bioavailability of ether-PFAS**

Zhang W.*, Cao H., Liang Y. Plant uptake and soil fractionation of five ether-PFAS in plant-soil systems. Science of the Total Environment. 2020. *771*: 144805.

Uptake of PFAS by cattails and research gap



2000 µg/L PFAS



How to handle wet plant biomass containing PFAS?

Hydrothermal liquefaction of PFAA solution

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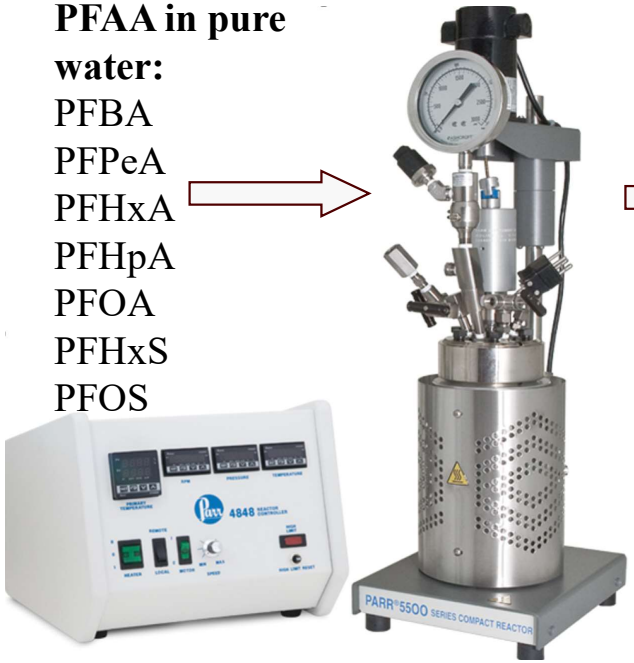
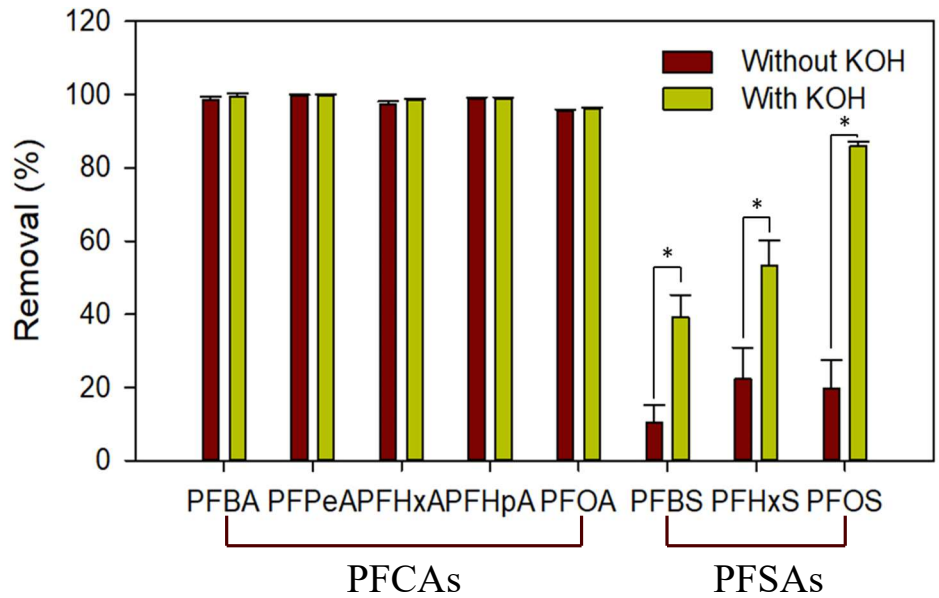
PFAA in pure water:
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFHxS
PFOS



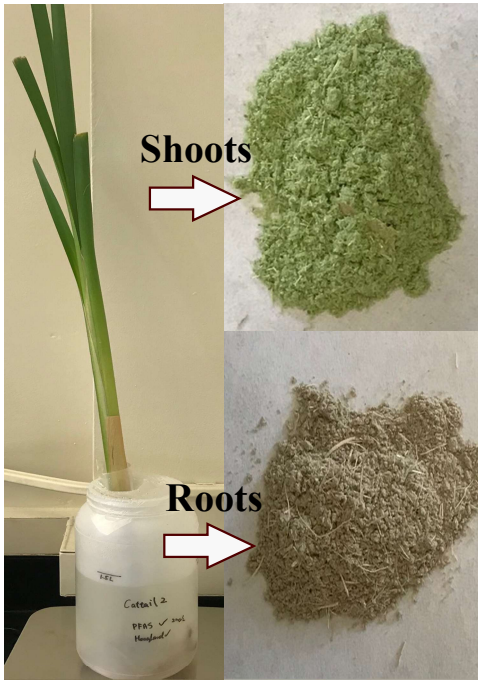
300 ˚C

2 hours



- **Nearly 100% of PFCA degradation.**
- **PFSAs were more resistant to HTL.**
- **KOH improved the degradation of PFSAs.**

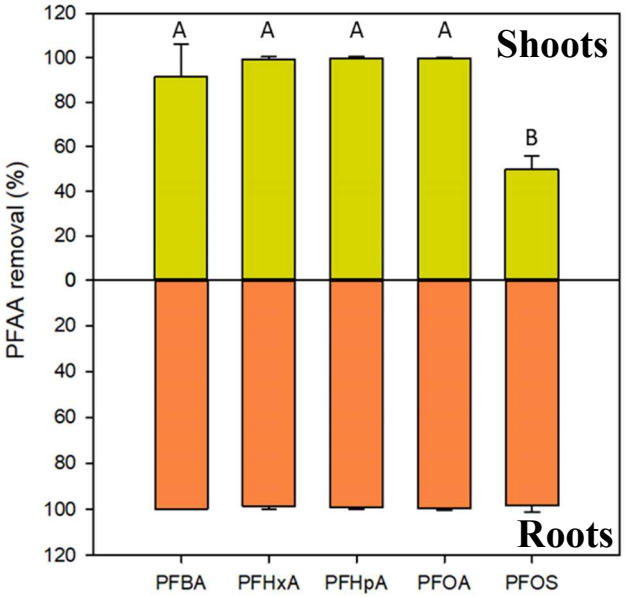
Hydrothermal liquefaction of plant tissues



300 ˚C

2 hours

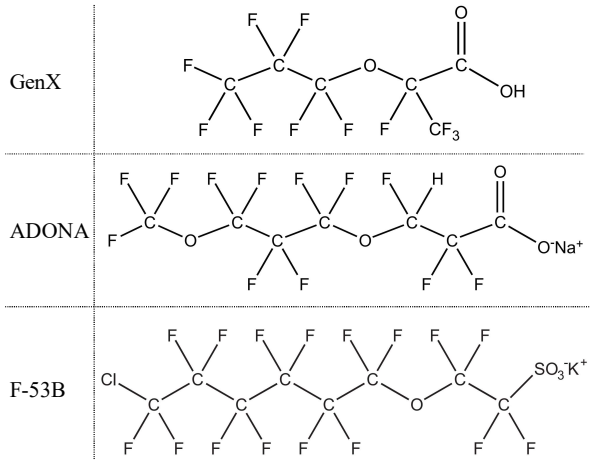
PFAA removal in plant tissues

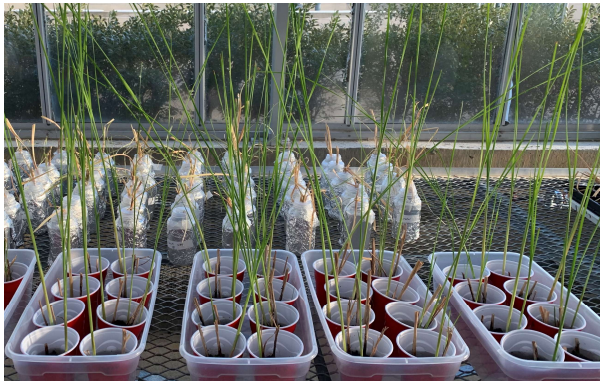


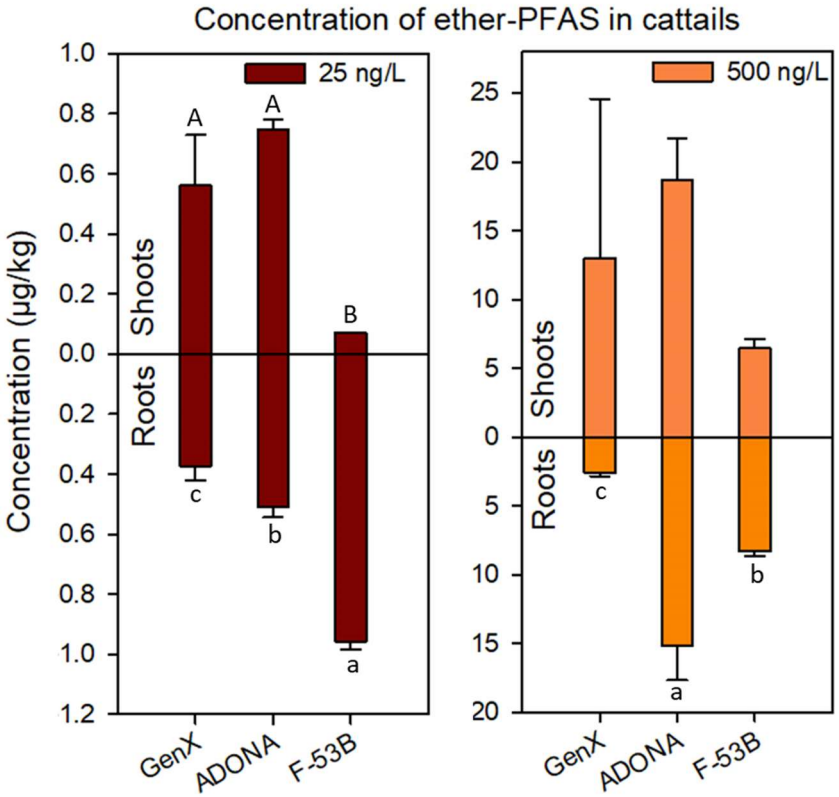
- **Nearly 100% of PFCA degradation.**
- **Plant biomass facilitated PFOS degradation during HTL.**

Zhang, W.; Cao, H.; Mahadevan Subramanya, S.; Savage, P.; Liang, Y., Destruction of Perfluoroalkyl Acids Accumulated in Typha latifolia through Hydrothermal Liquefaction. *ACS Sustain. Chem. Eng.* **2020,** *8*, (25), 9257-9262.

Hydrothermal liquefaction of ether-PFAS





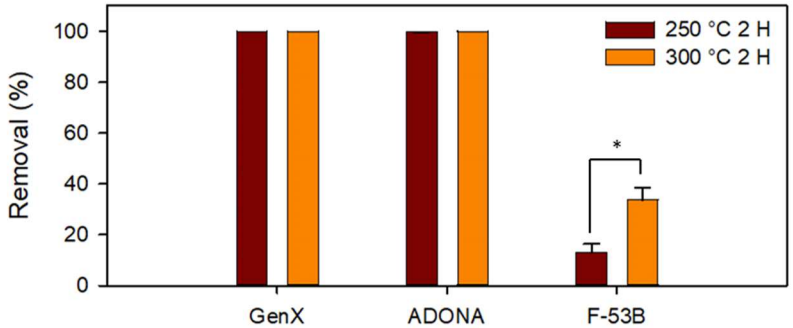


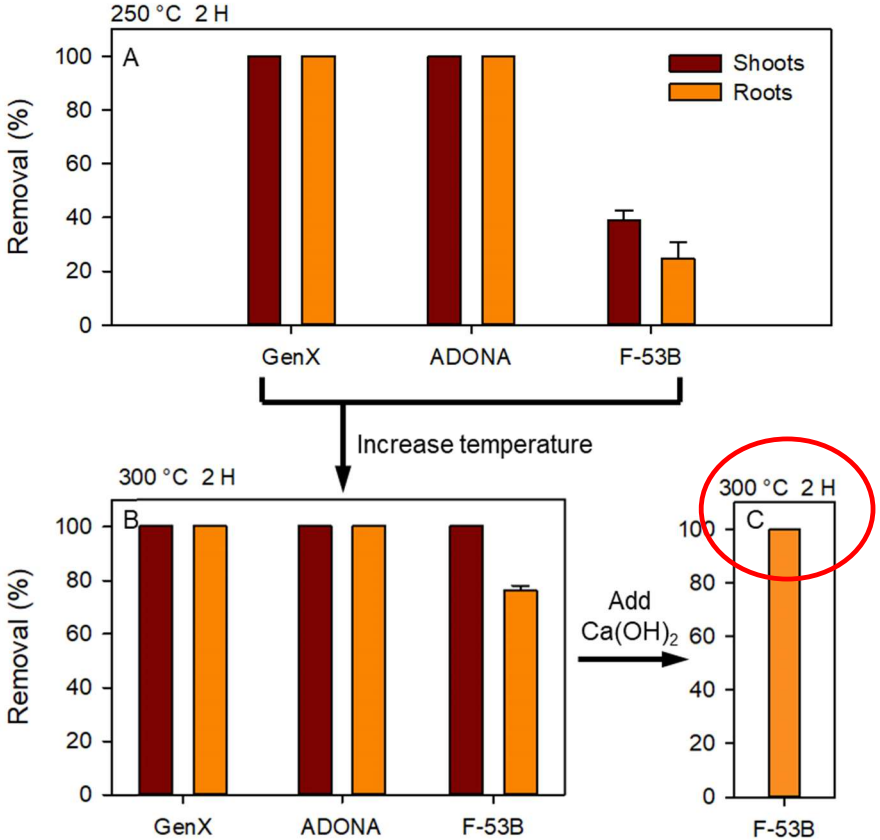
- **F-53B with a long carbon chain and a sulfonic functional group tended to accumulate in roots.**

Hydrothermal liquefaction

With wet plant biomass

Aqueous solution without plant biomass

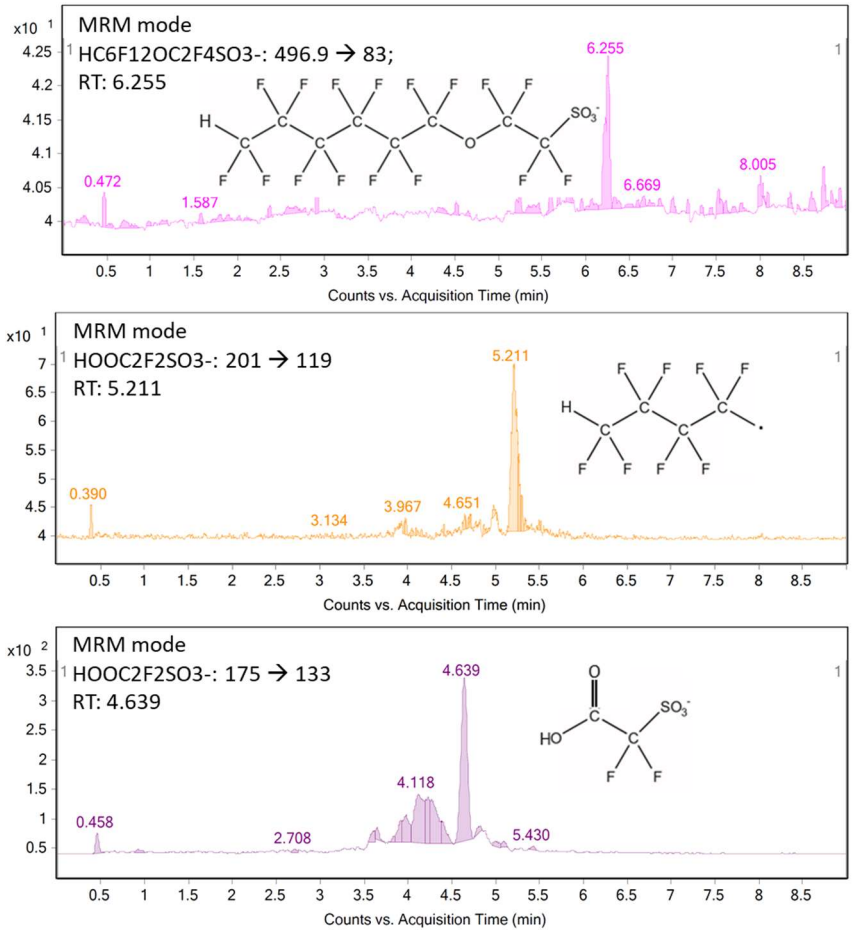


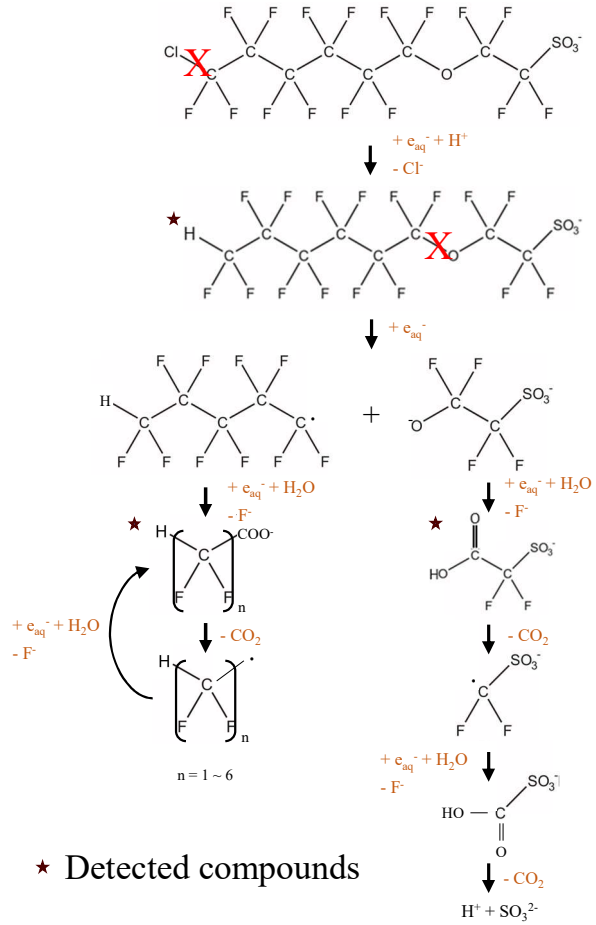


- **GenX and ADONA were totally removed at > 250 °C.**
- **F-53B was more resistant to HTL.**
- **Plant tissues and $Ca(OH)_2$ improved the degradation of F-53B.**

Zhang W.*, Cao H., Liang Y*. Degradation by hydrothermal liquefaction of fluoroalkylether compounds accumulated in cattails (*Typha latifolia*). *Journal of Environmental Chemical Engineering*. 2021. (Major revision)

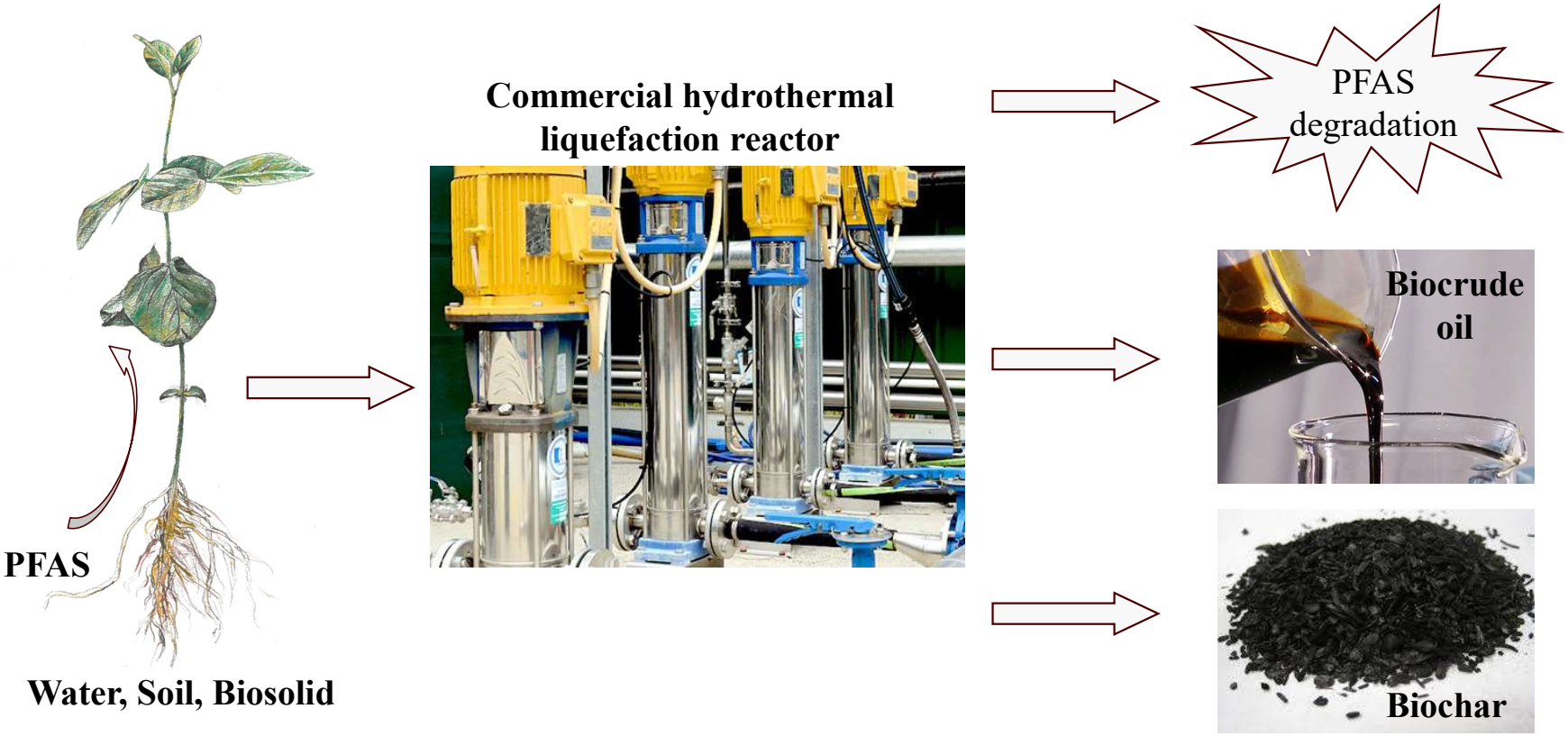
Proposed degradation pathway of F-53B





★ Detected compounds

Proposed treatment train



U.S. Pending Patent: Methods and systems for eliminating environmental contaminants using biomass, US Pat. No.: 63/074,244, Inventor: Yanna Liang, Weilan Zhang

Thermal treatment of sewage sludge

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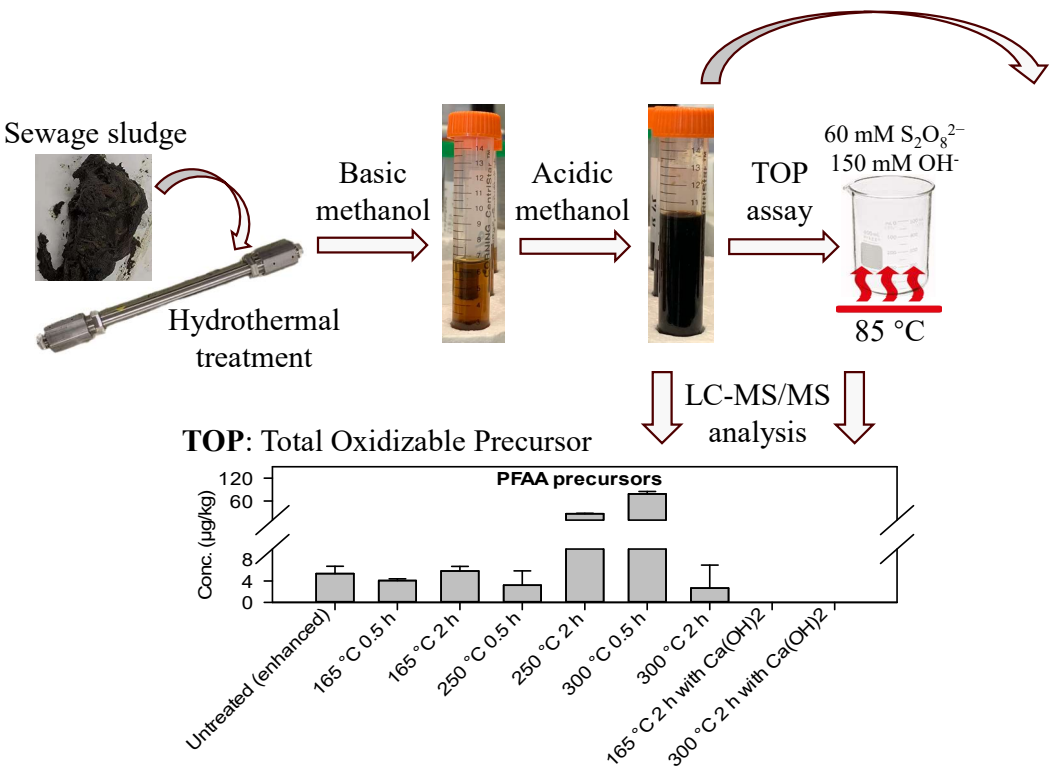
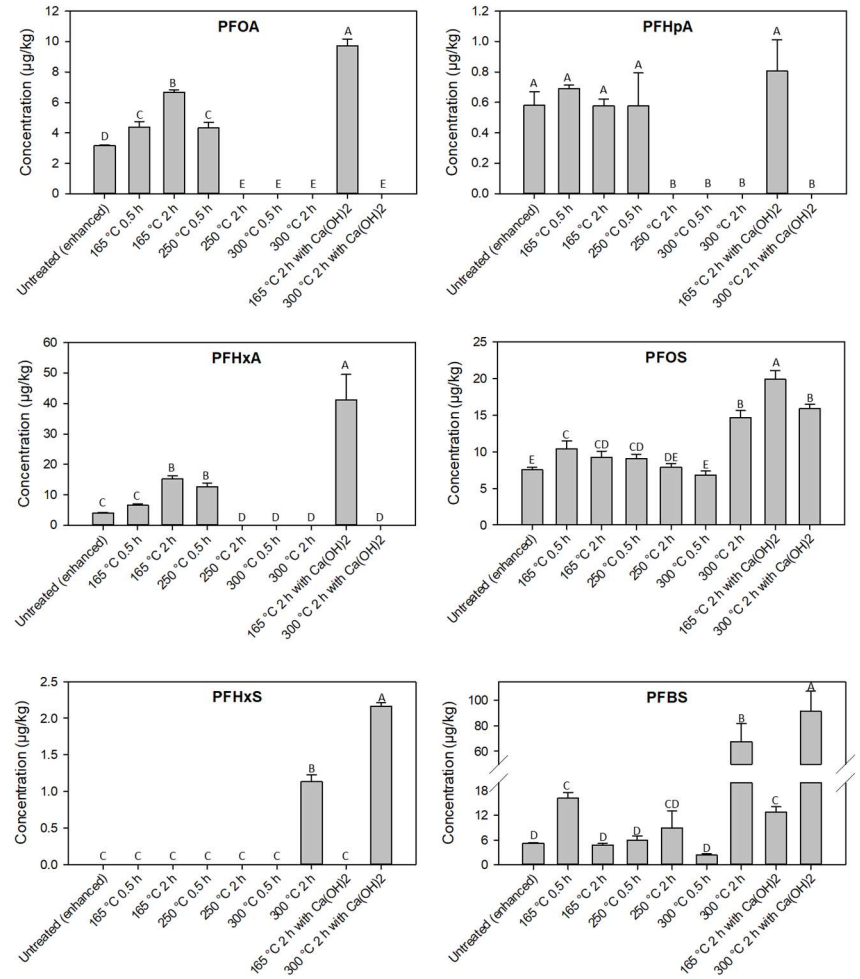




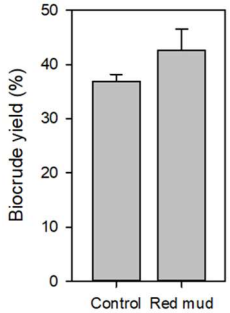
- **Hydrothermal treatment at lower temperature (165 °C, CambiTHP process) could enhance the release of PFAS from sludge.**
- **Hydrothermal treatment at 250 °C for 2 h and 300 °C for 0.5/2 h led to 100% removal of PFCAs.**
- **All tested hydrothermal treatments did not result in removal of PFOS and PFBS.**
- **Treatments with $Ca(OH)_2$ at 165 or 300 °C for 2 h completely removed PFAA precursors.**

Thermal treatment of sewage sludge

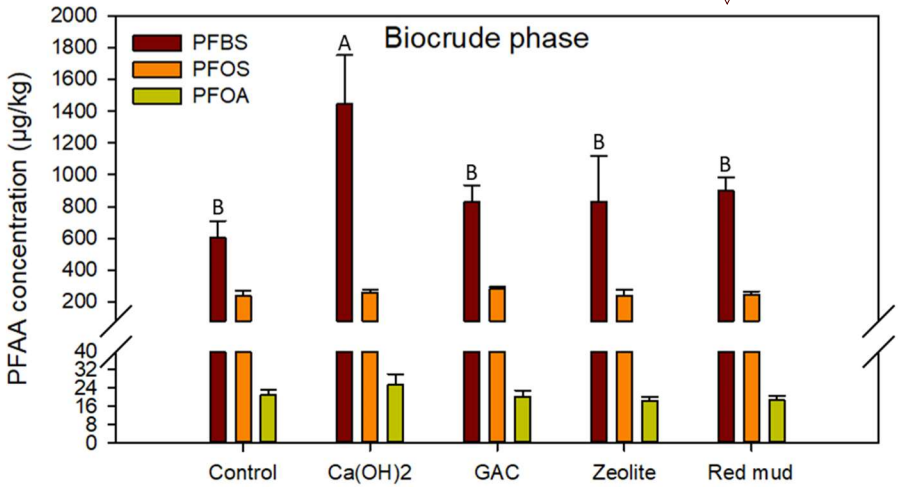
PFBS
PFOS
PFOA
150 µg/kg

300 °C
2 h

Biocrude yield

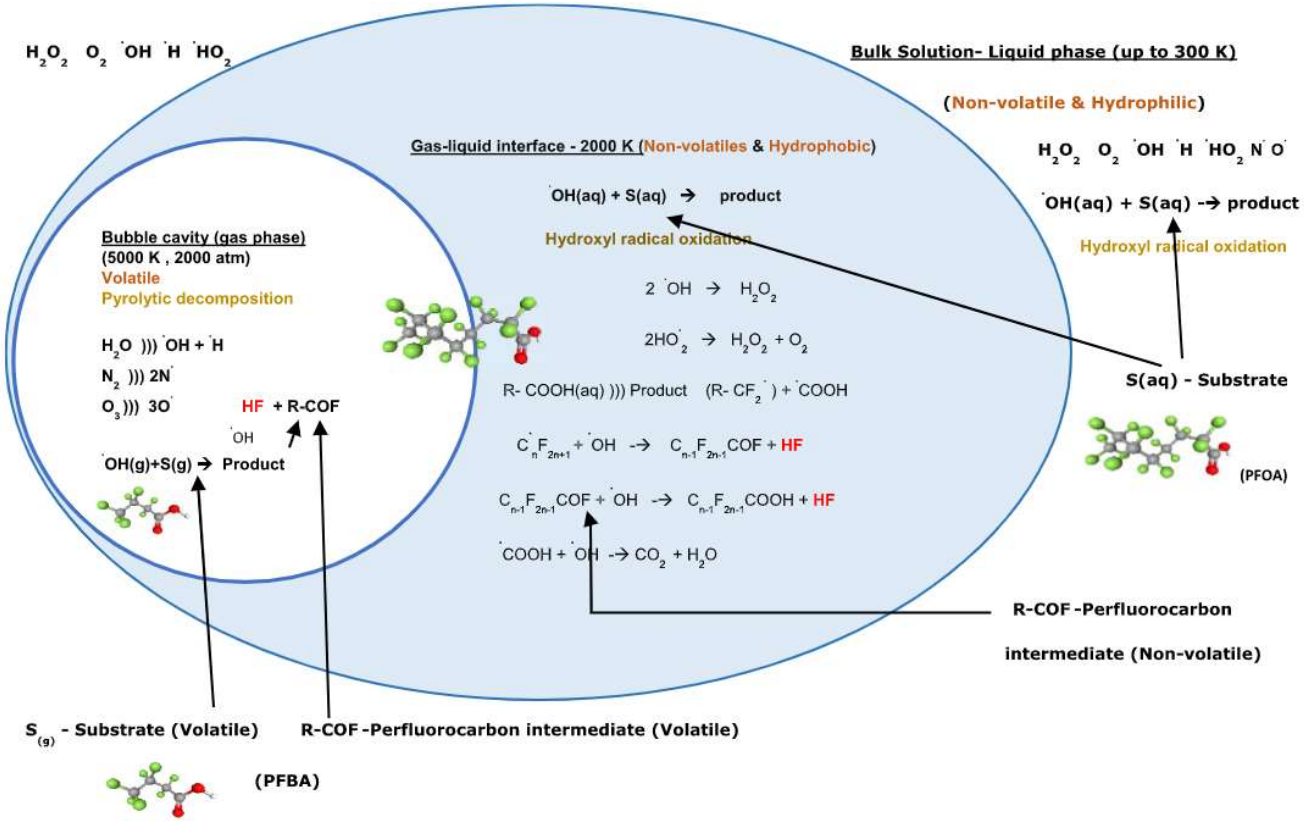


	Carbon conversion efficiency (%)	Energy recovery (%)
Control	65.66 ± 2.42	67.90 ± 2.50
Red mud	76.59 ± 7.58	78.66 ± 8.03



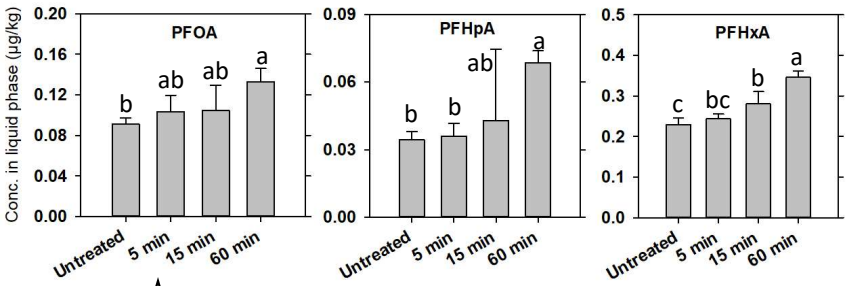
Ultrasonication of sewage sludge

Conceptual model of reactions in three zones of ultrasonic cavitation bubble [1]



1. Wanninayake, D. M., Comparison of currently available PFAS remediation technologies in water: A review. *Journal of Environmental Management* **2021,** *283*, 111977.

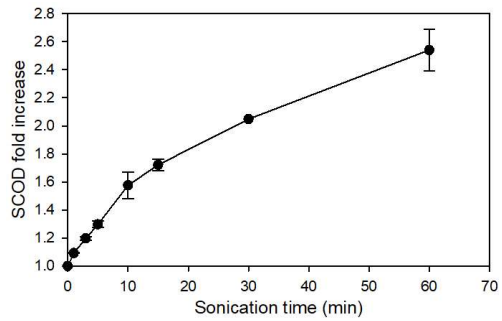
Ultrasonication of sewage sludge



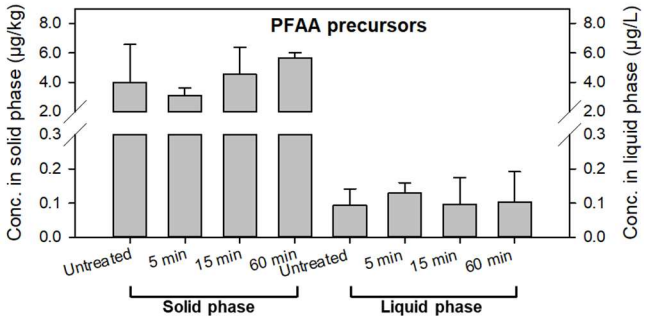
PFAS release

Sludge flocs

SCOD increase



Zhang, W.; Zhang, Q.; Liang, Y., Ineffectiveness of ultrasound at low frequency for treating per-and polyfluoroalkyl substances in sewage sludge. *Chemosphere* **2022,** *286*, 131748.



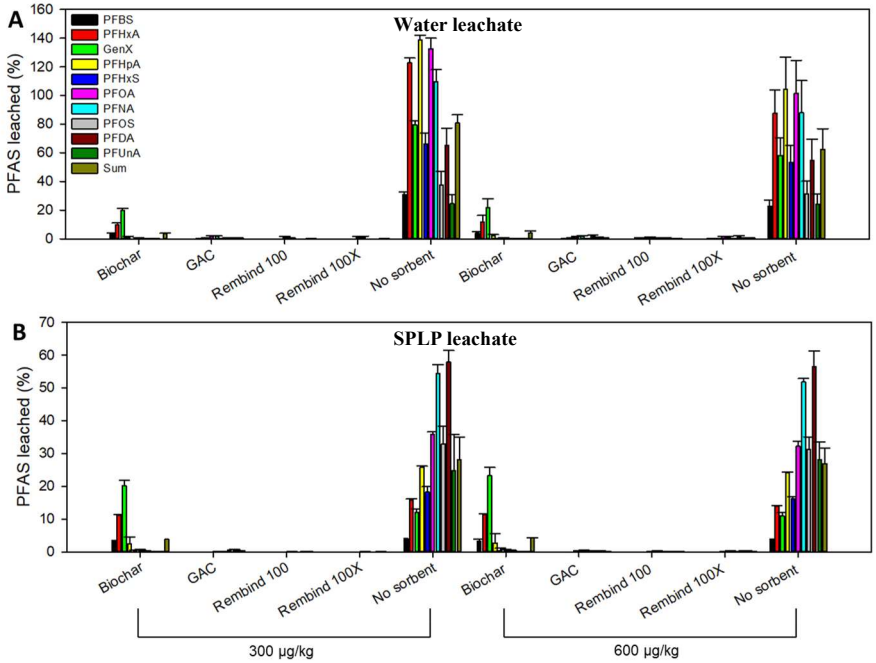
- **Ultrasonication at 20 kHz didn't lead to PFAS removal in the solid phase of sludge.**
- **Concentration of PFAA precursors in the liquid and solid phase of sludge did not change after ultrasonic treatment**
- **Ultrasonication could increase PFOA, PFHpA, PFHxA concentrations in the liquid phase.**
- **Overall, ultrasound at low frequency (20 kHz) was ineffective for PFAS degradation**

PFAS stabilization in soil

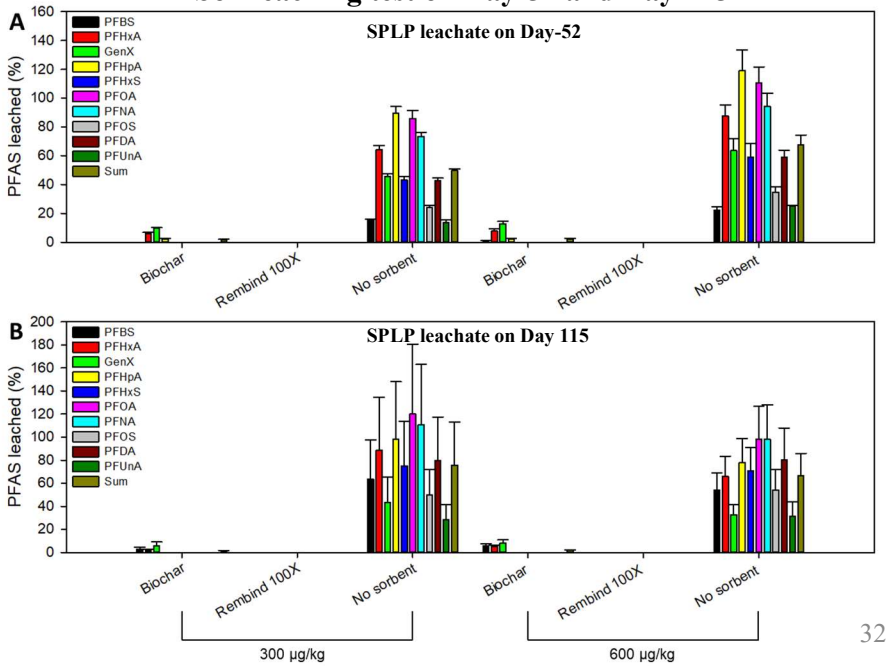
PFBS PFOA
PFHxA PFNA
GenX PFOS
PFHpA PFDA
PFHxS PFUnA

Biochar GAC RemBind 100 RemBind 100X

Soil leaching test on Day-21



Soil leaching test on Day-52 and Day-115



Summary

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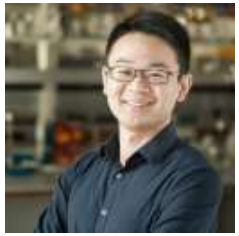
- Photocatalytic degradation using In_2O_3 effectively decomposed PFOA in water.
- PFAS were found to be taken up by studied plants, confirming the feasibility of phytoremediation for PFAS.
- Hydrothermal liquefaction was able to degrade PFAS accumulated in wet plant biomass and transform the biomass to biocrude and biochar.
- PFAS were detected in sewage sludge. Hydrothermal treatment was unlikely to degrade all PFAS in sewage sludge.
- Ultrasound at low frequency (20 kHz) was ineffective for PFAS degradation in sewage sludge.
- Carbon-based sorbents, such as GAC and RemBind® products, reduced the leachable PFAS in soil.

Acknowledgements

Prof. Yanna Liang

Dr. Weilan Zhang



Dr. Tao Jiang

Joseph Yee **Nina Tran**

Thank you!

Questions?

- What are PFAS?
- How can people be exposed to PFAS?
- What are acceptable levels of PFAS in water?
- What is the remediation technology that has been investigated extensively and implemented commercially?
- How does the structure of PFAS affect their plant uptake?