Stabilization of PFAS in Soil and Sewage Sludge and Innovative Sorbents Designed for this Purpose

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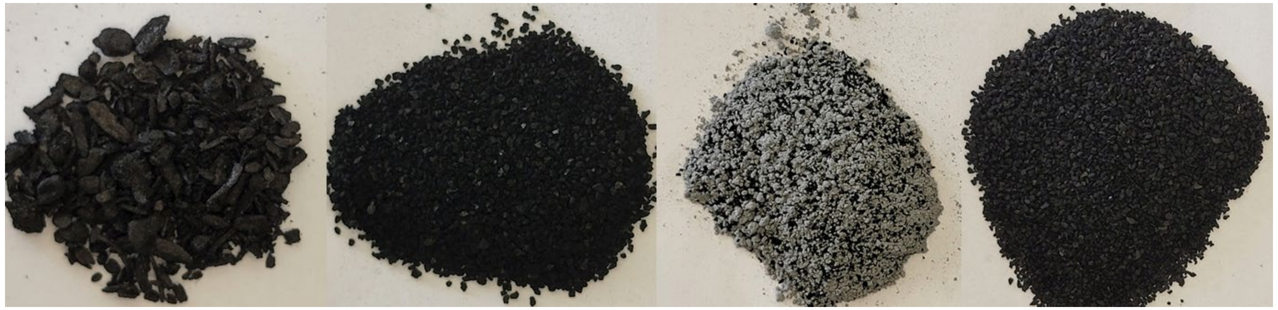
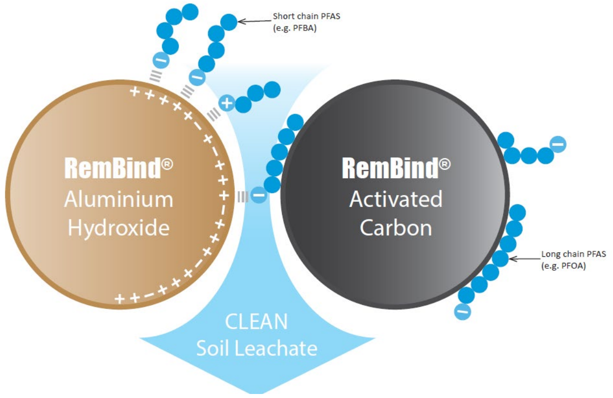
PFAS stabilization in soil

Biochar GAC RemBind 100 RemBind 100X





Soil amendment, 2%

PFCAs (C6-C11)	PFSAs (C4-C8)
PFHxA	PFBS
PFHpA	PFHxS
PFOA	PFOS
PFNA	**Alternative**
PFDA	GenX
PFUnA	

- 300 µg/kg
- 600 µg/kg

Leaching test →

Water → EPA SPLP → Methanol

Zhang, W.; Liang, Y., Performance of different sorbents toward stabilizing per-and polyfluoroalkyl substances (PFAS) in soil. *Environmental Advances* **2022,** *8*, 100217.

PFAS leaching by water and SPLP

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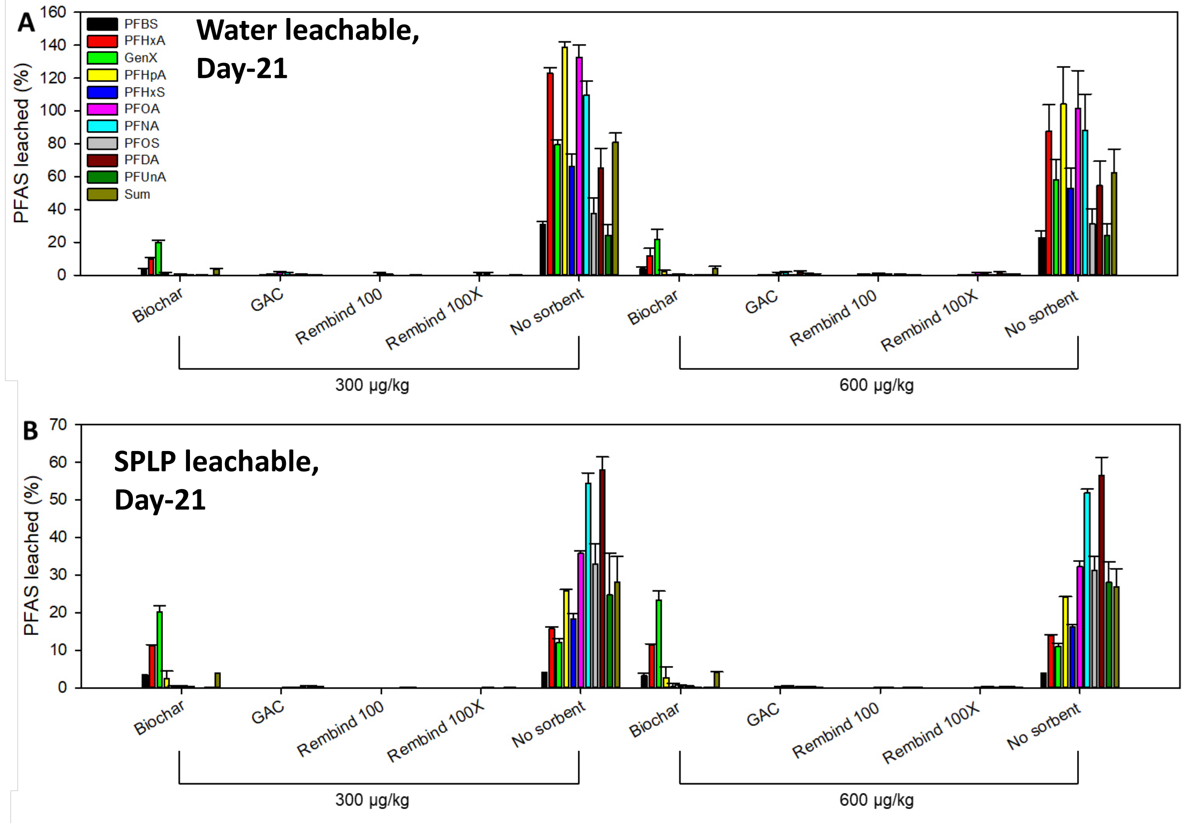
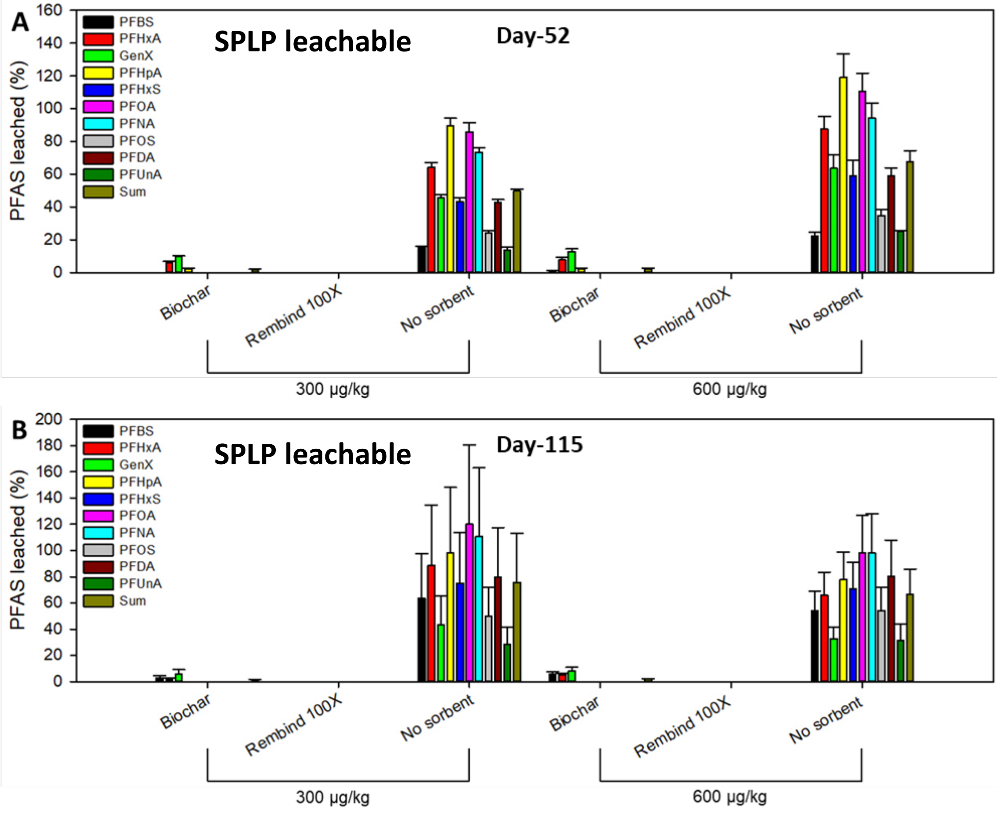
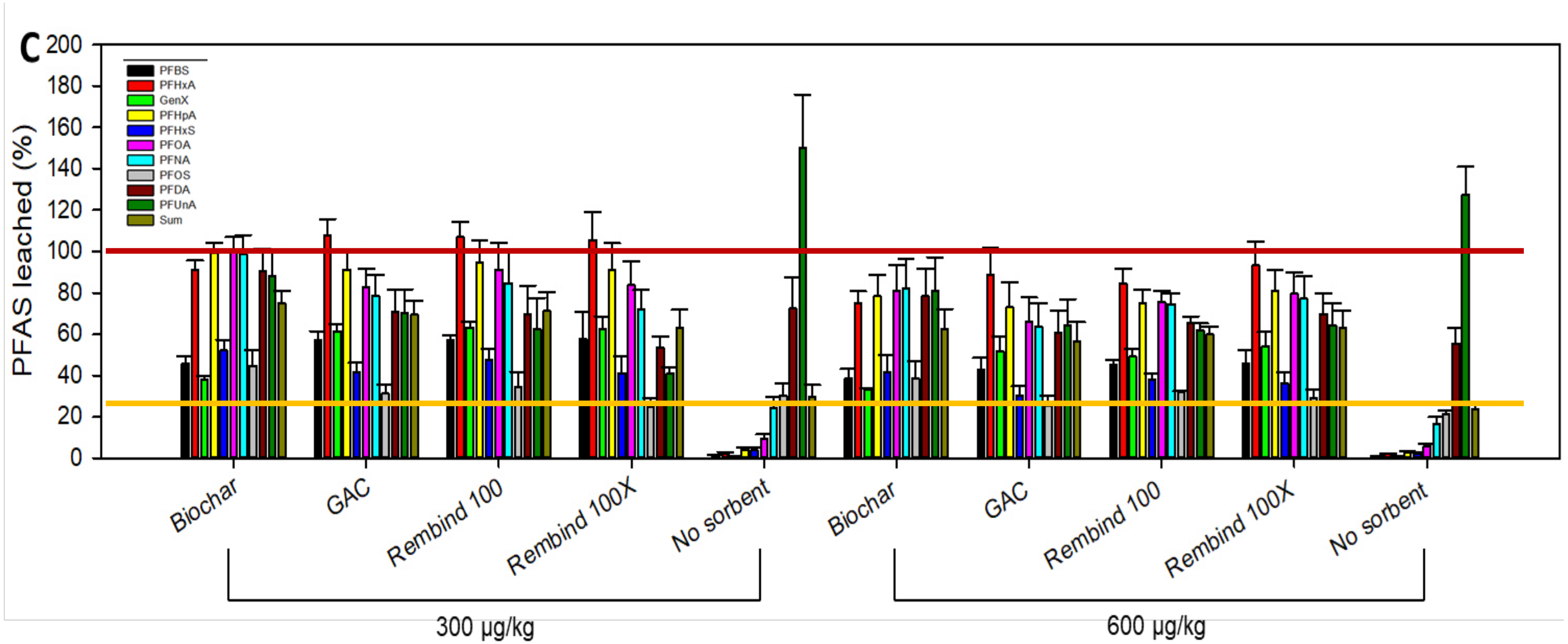




- GAC and RemBind® products reduced the water and SPLP leachable PFAS by 99%.
- Biochar stabilized long chain PFAS but had limited sorption for short chain PFAS.
- Increasing treatment time improved the sorption of short-chain PFAS to biochar.
- Aging of the sorbents in soil did not cause any release of the stabilized PFAS.

PFAS leaching by basic methanol



With GAC, Rembind:

- Leachable PFCAs: PFHxA > PFHpA > PFOA > PFNA > PFDA > PFUnA
- Leachable PFSAs: GenX ≈ PFBS > PFHxS > PFOS
- In total, around 60% of PFAS are extractable by basic methanol after 21 days.

Is this good enough?

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The definition of bound residue

Bound pesticide residues in the soil are unextractable and chemically unidentifiable pesticide residues remaining in the fulvic acids, humic acids and humin fractions after exhaustive sequential extraction with nonpolar organic and polar solvents. Environmental Task Group, American Institute of Biological Sciences, 1975

Remediation endpoint for stabilization is that the contaminants form irreversibly bound residues with soil and the bound residues need to survive harsh extraction by any type of organic solvent, such as toluene and hexane. Lath et al., Environmental Chemistry 2018, 15, (8), 472-480.

Stabilization of PFAS in Sewage Sludge

Truth:

- Sewage sludge contains numerous PFAS.
- Around 50% of sludge is land applied after certain stabilization process.

Questions:

- Can the process of preparing sludge to biosolids remove or degrade PFAS?
- What PFAS are in biosolids?
- What needs to be done to enable biosolids to be land-applied continuously?

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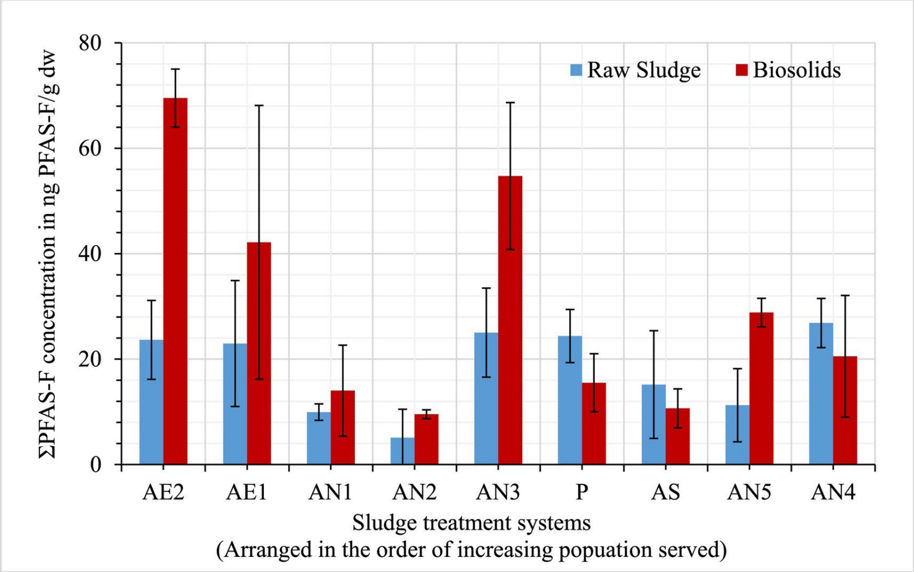
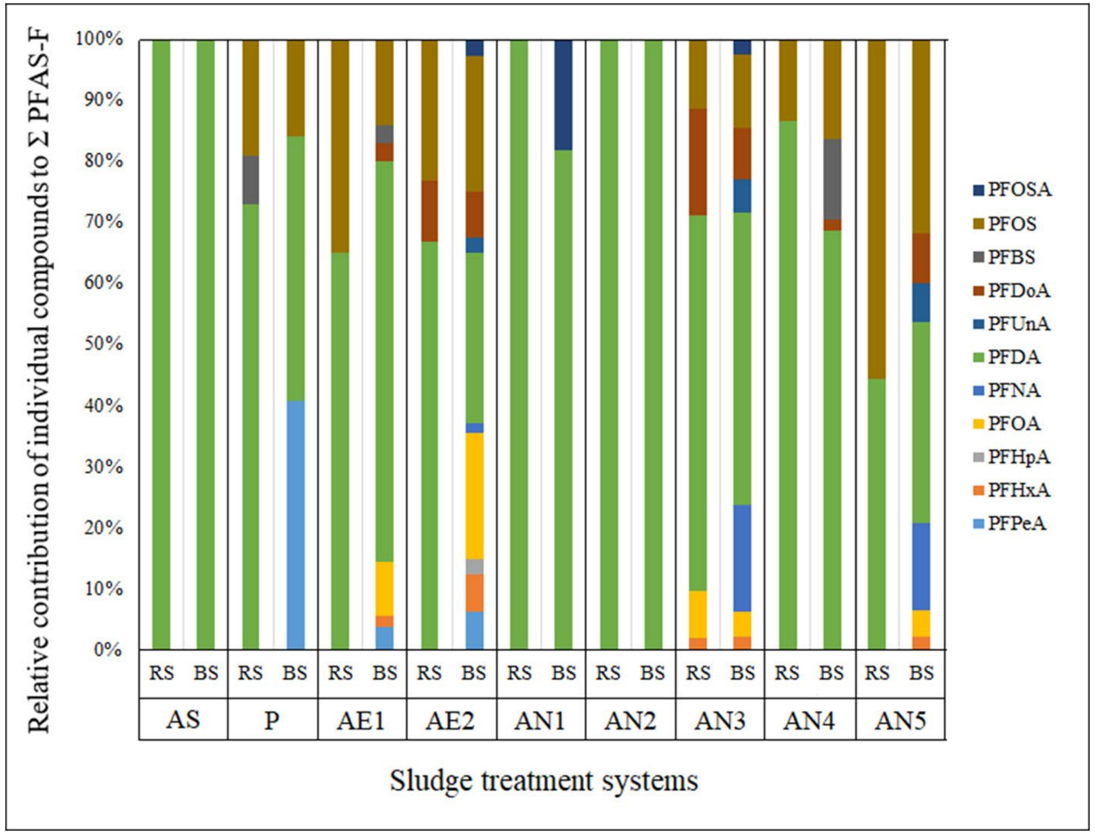
PFAS in sludge vs. biosolids

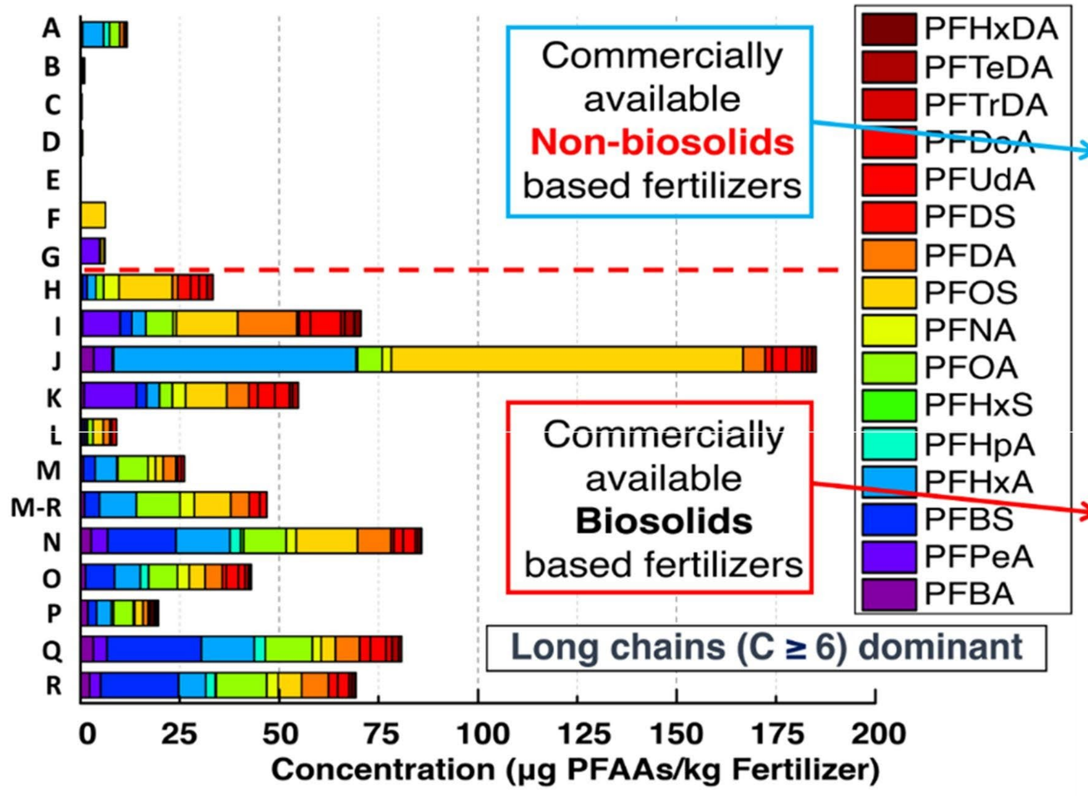




pelletization (P), alkaline stabilization (AS), aerobic (AE1, AE2) or anaerobic (AN1 to AN5)

Lakshminarasimman, Narasimman, et al. "Removal and formation of perfluoroalkyl substances in Canadian sludge treatment systems–A mass balance approach." Science of The Total Environment 754 (2021): 142431.

PFAAs in biosolids based fertilizers

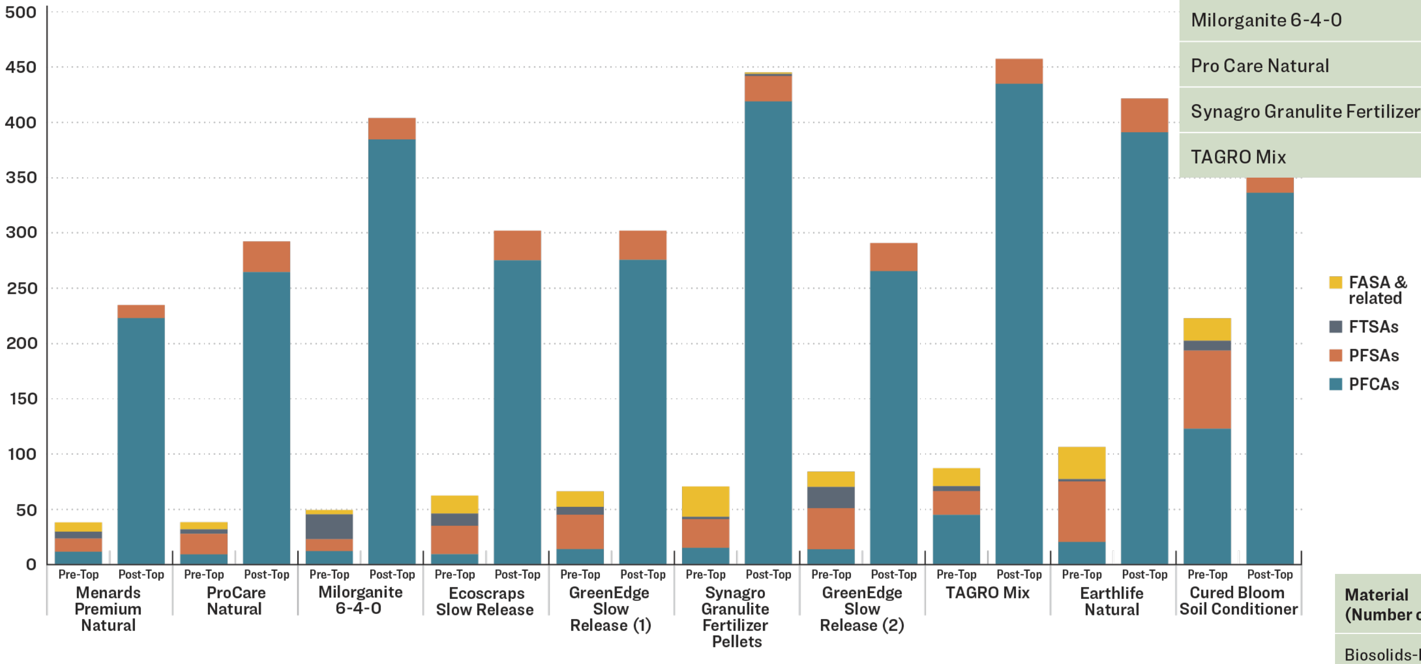


*Concentration of PFAAs <2mm fraction (36-80%) normalized to total fertilizers (assume the conc. of PFAAs is negligible in the fraction > 2 mm)

Fertilizer	Description
A	Food and yard compost
B	Compost with untreated wood products
C	Manure compost
D	Manure and peat compost
E	Mushroom compost
F	Mushroom compost
G	Peat/compost based growing mix
H	Heat-dried granular biosolids
I	Heat-dried granular biosolids
J	Heat-dried granular biosolids
K	Heat-dried granular biosolids
L	Heat-dried granular biosolids
M	Biosolids blended with maple sawdust and aged bark
M-R	Biosolids Cake (before blending)
N	Composted biosolids with woodchips
O	Composted biosolids with woodchips
P	Composted biosolids with municipal solid waste
Q	Composted biosolids with residential yard trimmings
R	Composted biosolids with plant materials

Bolan, Nanthi, et al. "Distribution, behaviour, bioavailability and remediation of poly-and per-fluoroalkyl substances (PFAS) in solid biowastes and biowaste-treated soil." Environment International 155 (2021): 106600.

TOP and TOF assays

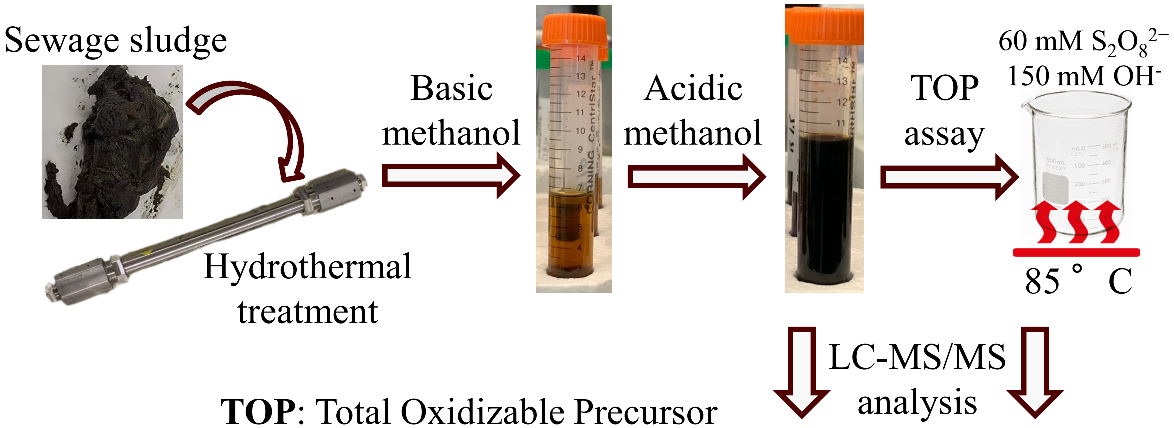


Product	Fluoride (ppb)	Total Fluorine (ppb)	Sum of known PFAS (ppb)
Cured Bloom Soil Conditioner	<500	131,000	223
Earthlife Natural	500	184,000	106
EcoScraps Slow Release	<500	179,000	62
GreenEdge Slow Release (1)	900	321,000	84
GreenEdge Slow Release (2)	1000	319,000	66
Menards Premium Natural	<500	215,000	38
Milorganite 6-4-0	<500	180,000	49
Pro Care Natural	<500	206,000	38
Synagro Granulite Fertilizer Pellets	600	61,000	71
TAGRO Mix	<1.0	13,000	83

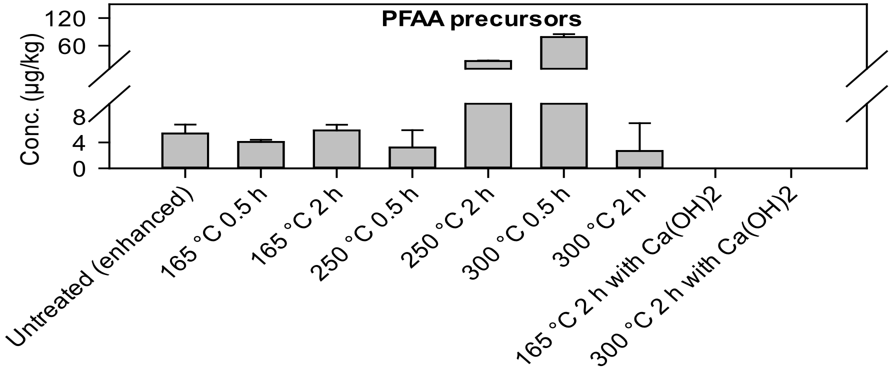
Material (Number of samples)	PFAS measured by LC/MS/MS	PFAS measured after oxidation with TOP Assay	Total fluorine	Reference
Biosolids-based home fertilizers (N=9)	38–233	234 to 445	13,000–321,000	This study
Swedish sewage sludges (N=4)	95–170	Not measured	600–2,700 ppb (extractable organic F)	Eriksson 2015
Biosolids-based home fertilizers (N=11)	9–199	50–320	Not measured	Lazcano 2020
Compost made from yard and food wastes (N=1)	~22	62	Not measured	Lazcano 2020
Non-biosolids commercial compost (N=6)	0.1–1.1	Not measured	Not measured	Lazcano 2020
Commercial compost not made from biosolids (N=7)	29–76	~30–110	Not measured	Choi 2019
Compost with no food containers and home compost (N=3)	2.4–7.6	<10	Not measured	Choi 2019

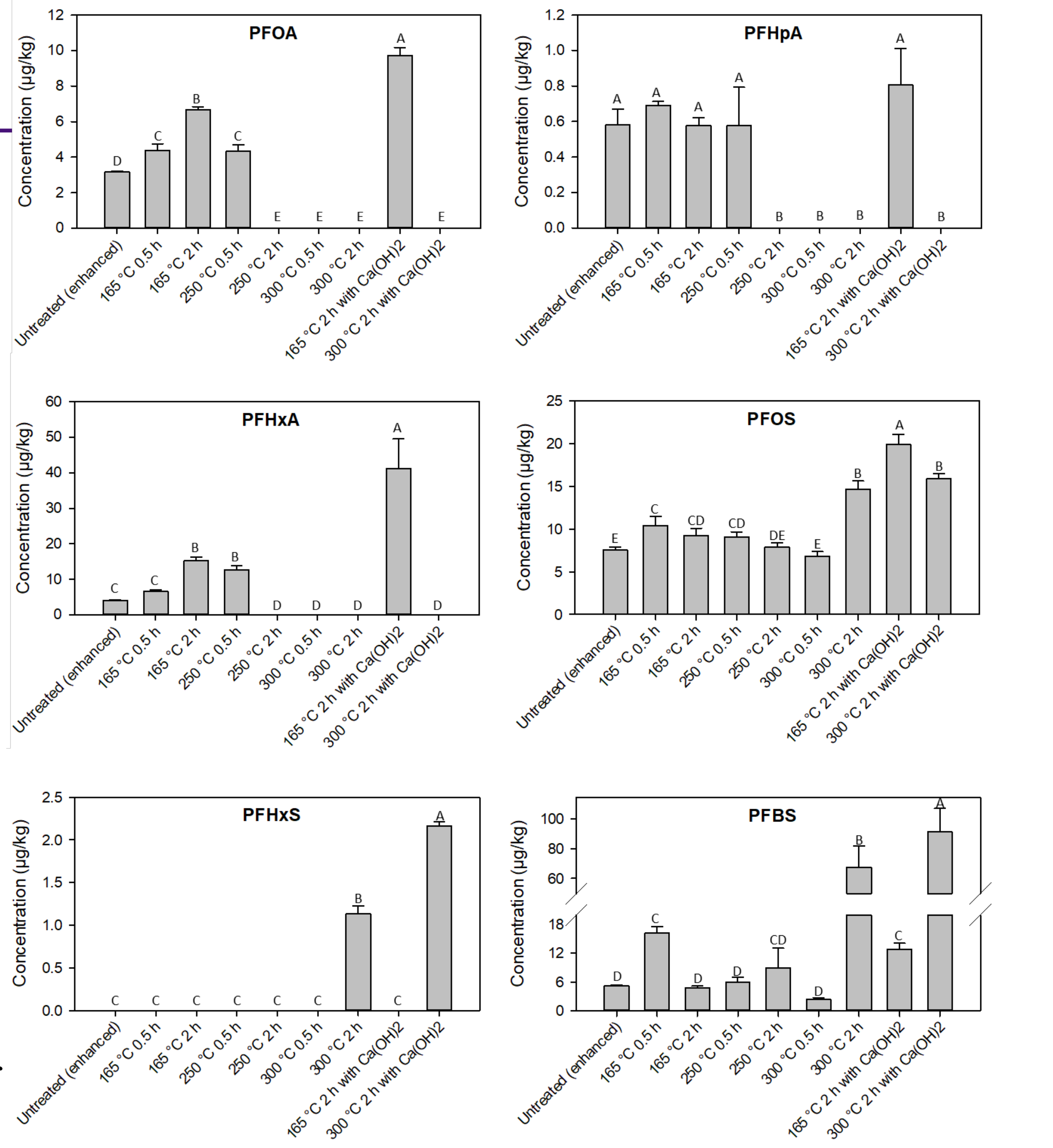
https://www.sierraclub.org/sludge-garden-toxic-pfas-home-fertilizers-made-sewage-sludge#:~:text=Persistent%20chemicals%20like%20PFAS%20are,chemicals%20back%20into%20the%20environment.

Thermal treatment of sewage sludge



TOP: Total Oxidizable Precursor

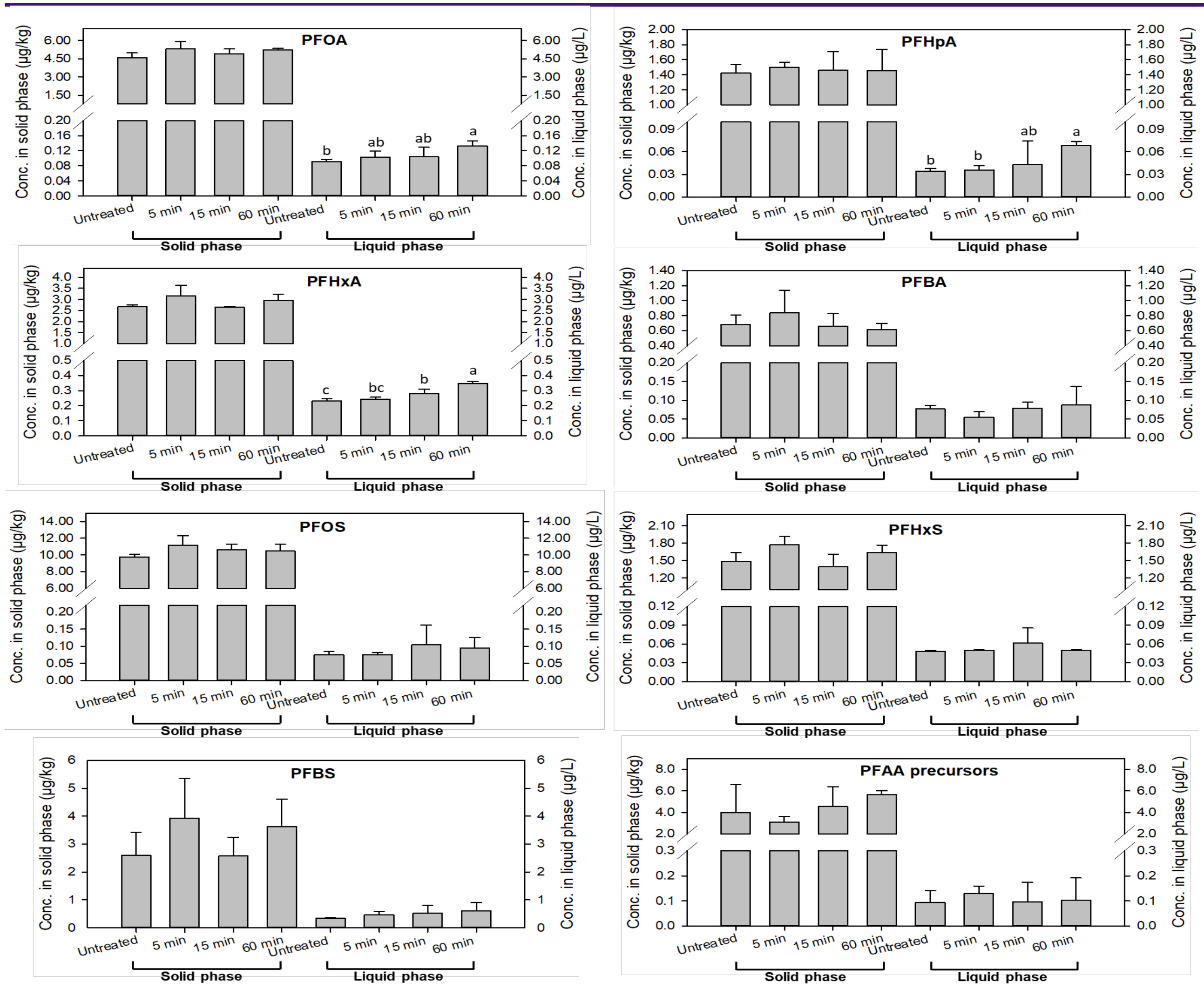


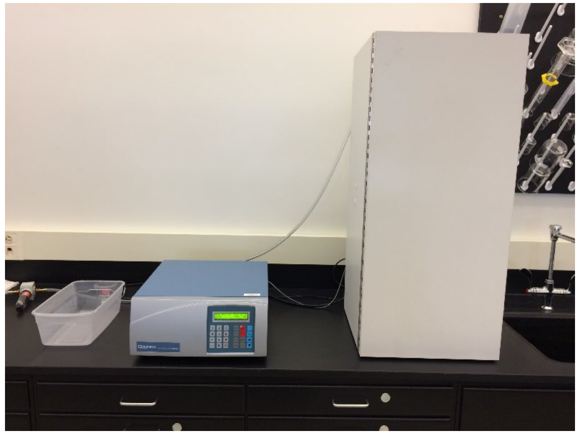


- **Hydrothermal treatment at lower temperature (165 ° C, CambiTHP process) could enhance the release of PFAS from sludge.**
- **Hydrothermal treatment at 250 ° C for 2 h and 300 ° C for 0.5/2 h led to 100% removal of PFCAs.**
- **All tested hydrothermal treatments did not result in removal of PFOS and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

Zhang, W.L., **Liang. Y-N.** 2021. Effects of Hydrothermal Treatments on PFAS in sewage sludge. Environmental Pollution. 285, 117276.

Sonication: time effect on PFAAs and precursors





- Increasing time increased conc. of PFOA, PFHpA and PFHxA in the liquid phase.
- Overall, ultrasound at low frequency (20 kHz) is ineffective for PFAS degradation.

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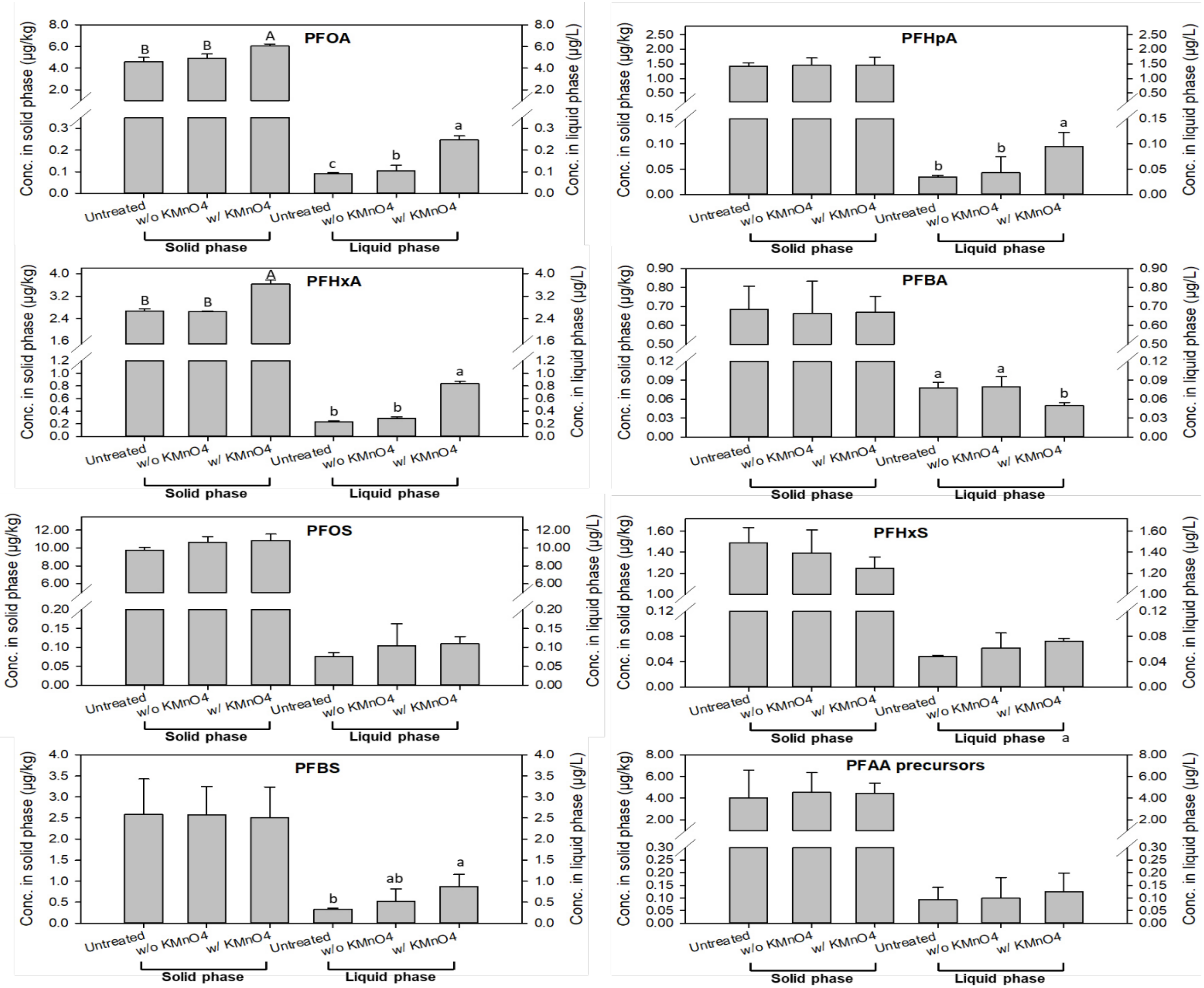
Zhang, W.; Zhang, Q.; Liang, Y., Ineffectiveness of ultrasound at low frequency for treating per-and polyfluoroalkyl substances in sewage sludge. *Chemosphere* **2022,** *286*, 131748.

Effect of permanganate



The presence of KMnO4 increased the concentration of PFOA, PFHpA, PFHxA and PFBS in the liquid phase and PFOA and PFHxA in the solid phase.

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PFAS stabilization in sewage sludge

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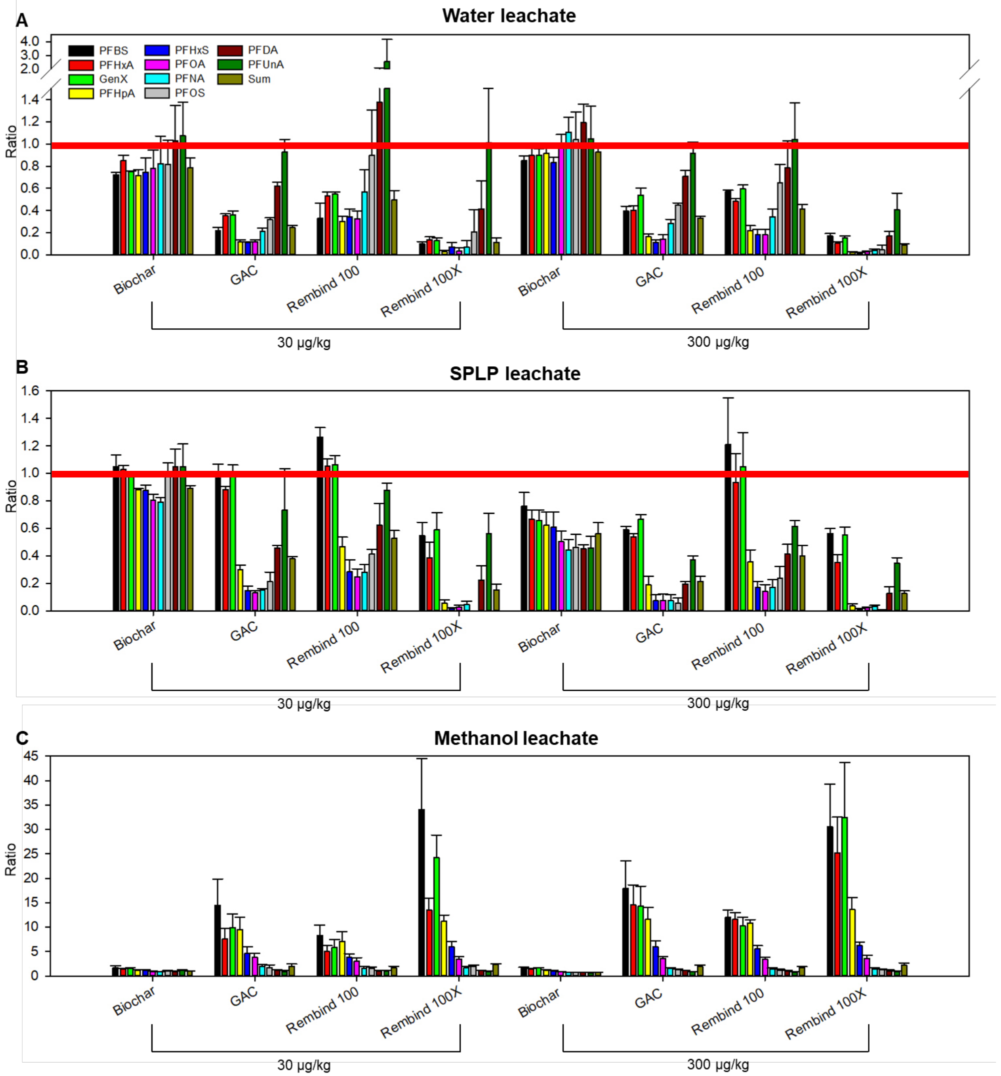
Water

EPA SPLP

Methanol

PFCAs (C6-C11)	PFSAs (C4-C8)
PFHxA	PFBS
PFHpA	PFHxS
PFOA	PFOS
PFNA	**Alternative**
PFDA	GenX
PFUnA	

- 30 µg/kg
- 300 µg/kg



- RemBind 100X had the best performance regarding stabilizing PFAS in sewage sludge.
- Biochar showed a limited effect on decreasing leaching of PFAS in sewage sludge.

Zhang, W.; Jiang, T.; Liang, Y., Stabilization of per-and polyfluoroalkyl substances (PFAS) in sewage sludge using different sorbents. *Journal of Hazardous Materials Advances* **2022**, 100089.

PFAS stabilization in sewage sludge

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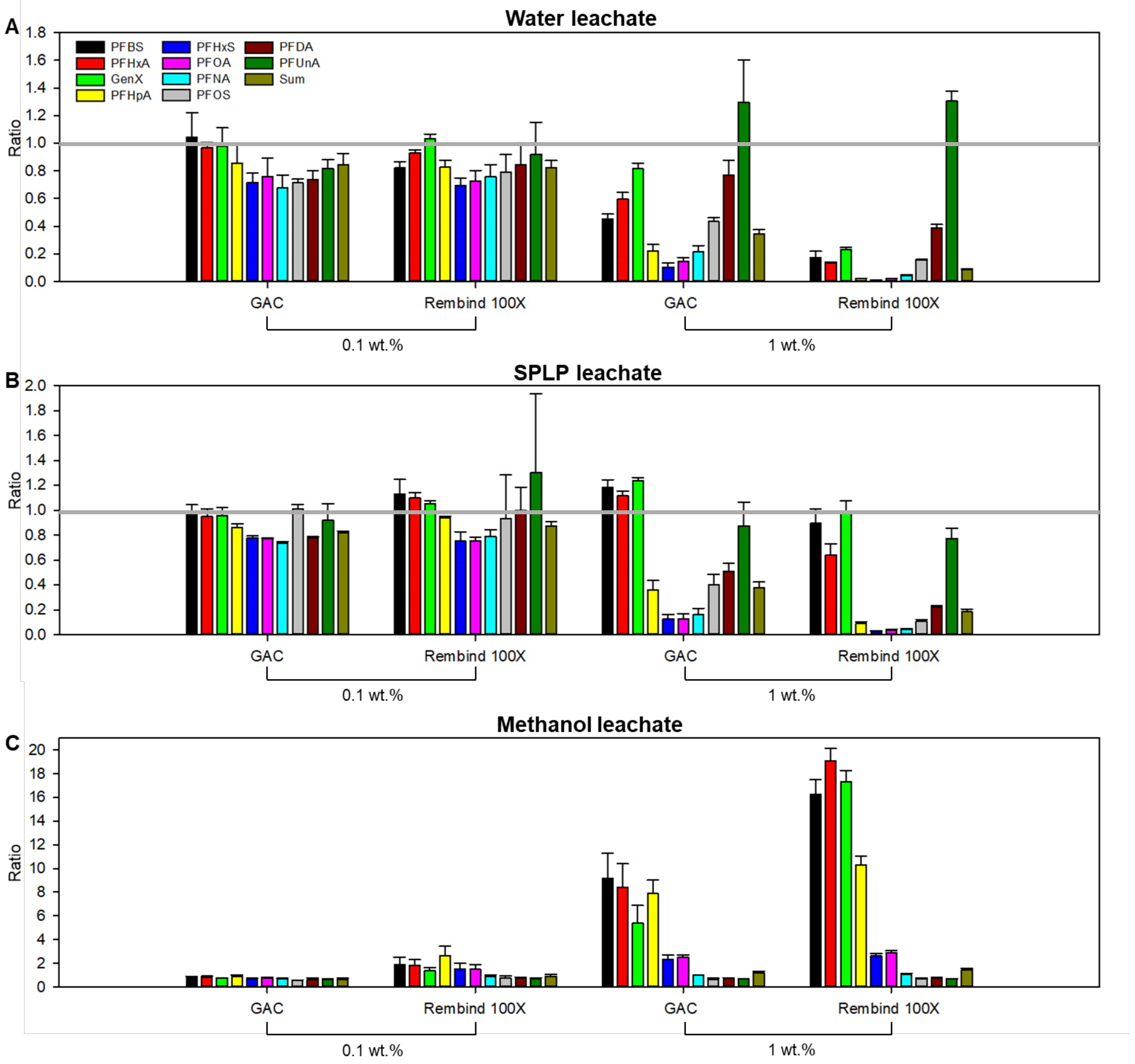
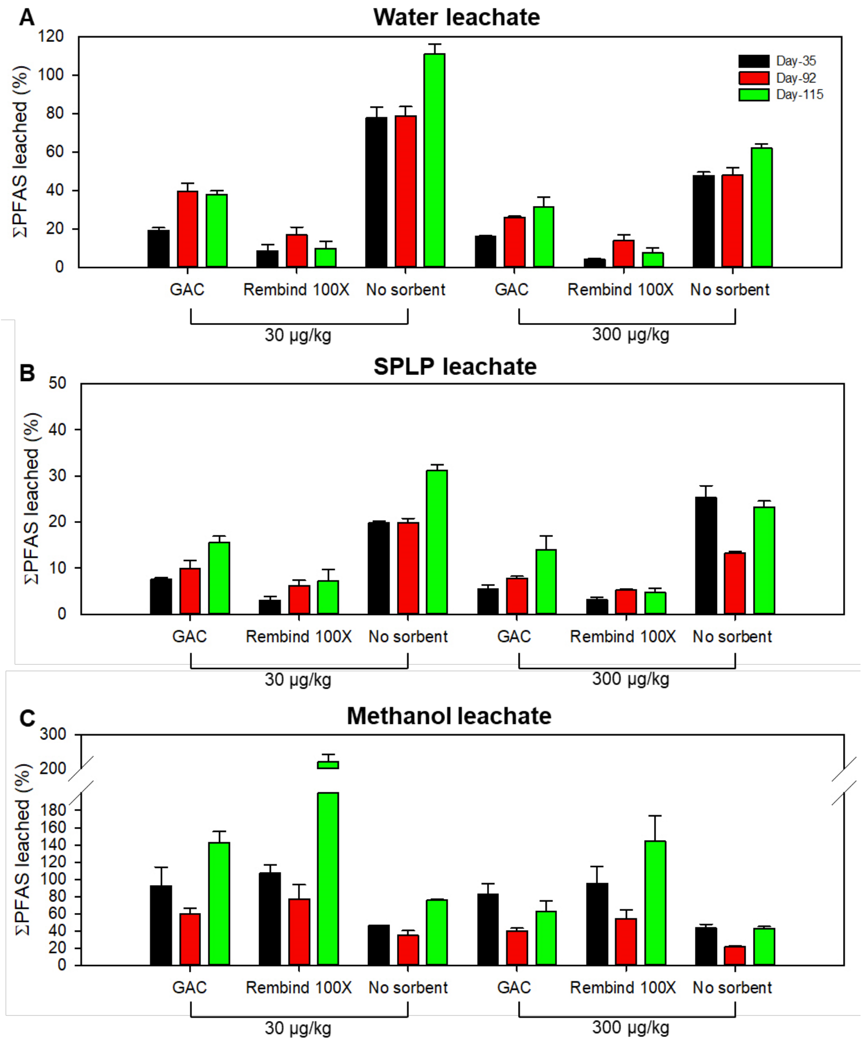
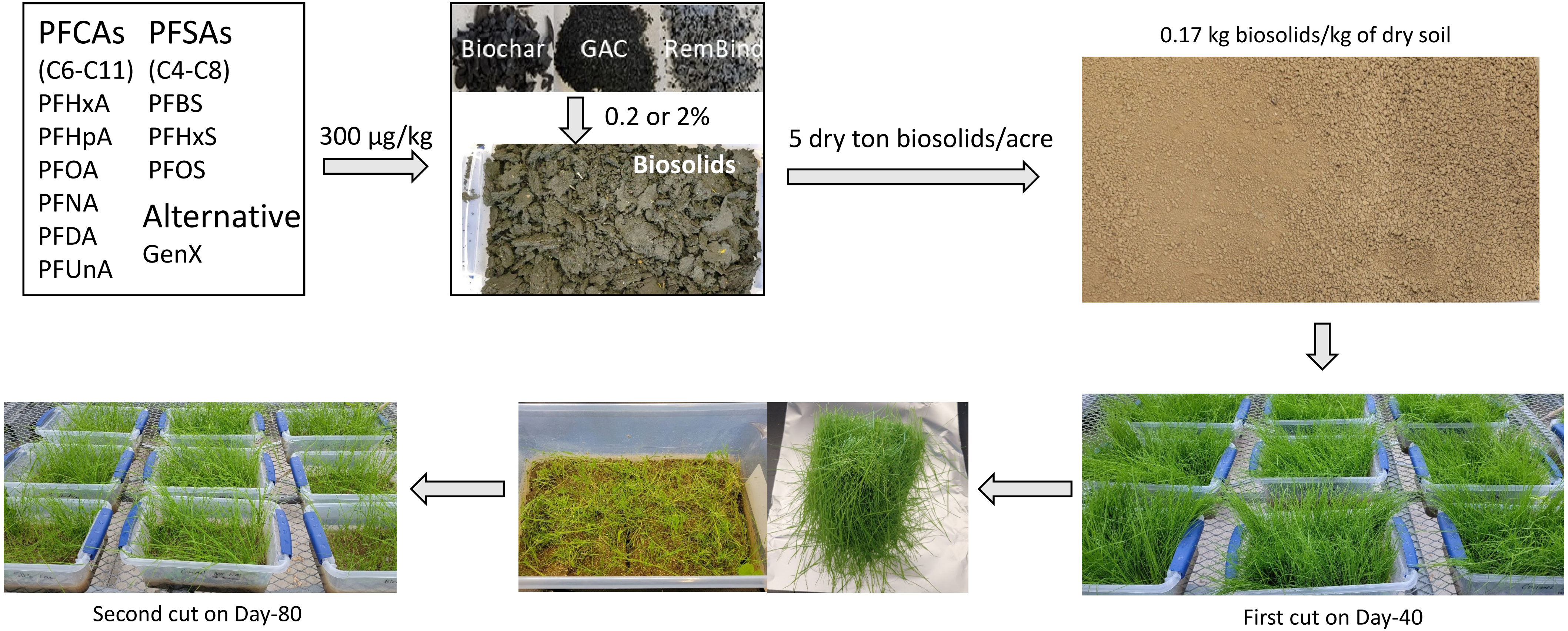


- A higher dose of sorbents led to lower leachable ∑PFAS by water and SPLP.



- The aging process led to remobilization of stabilized PFAS in sludge.

Bioavailability of PFAS in sludge



Zhang, W.; Liang, Y., Changing bioavailability of per- and polyfluoroalkyl substances (PFAS) in biosolids amended soil through stabilization or mobilization. *Environmental Pollution* 2022, 308, 119724.

PFAS in grass shoots

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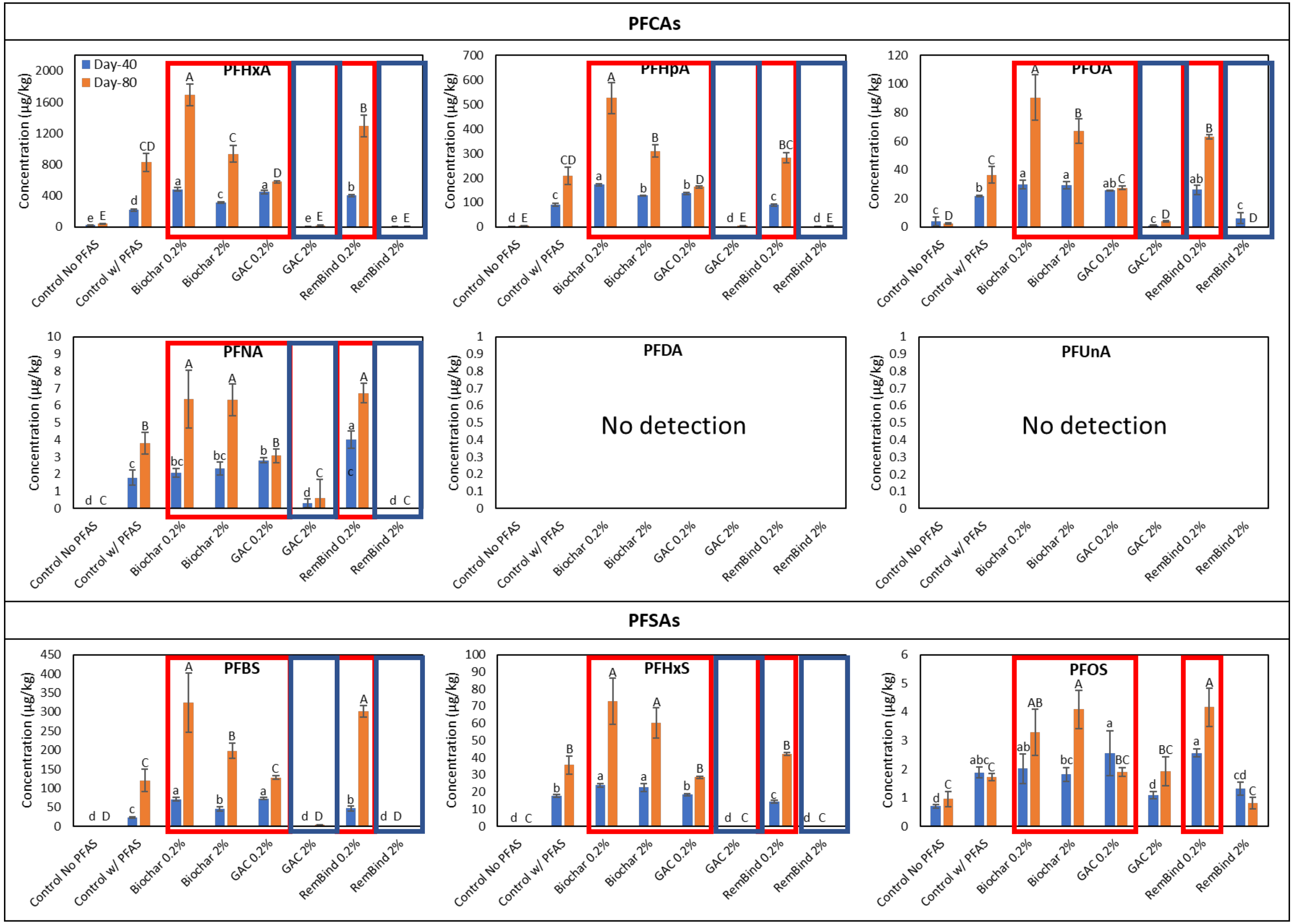

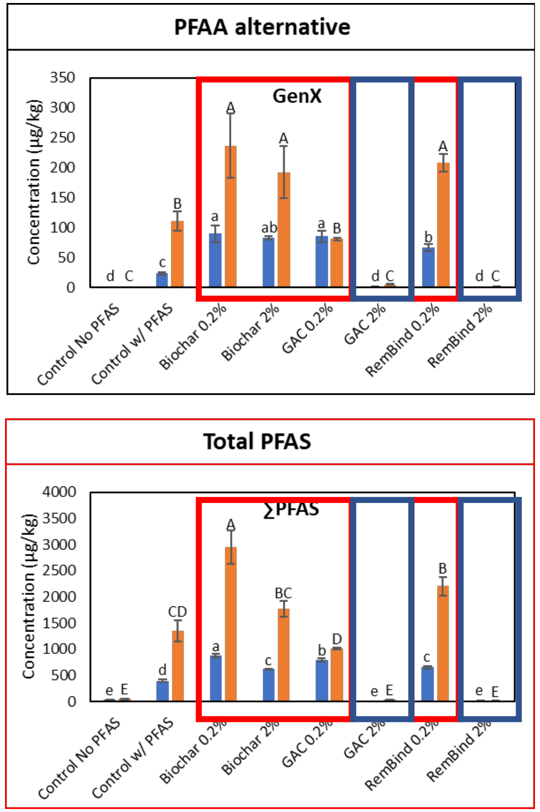

- Stabilization with GAC or RemBind at 2% reduced PFAS bioavailability in biosolids.
- Biochar at 0.2 – 2%, GAC and RemBind at 0.2% promoted the uptake of PFAS by timothy-grass.
- Mowing and regrowth of timothy-grass promoted its uptake of PFAS.

SPLP leachable PFAS in sludge

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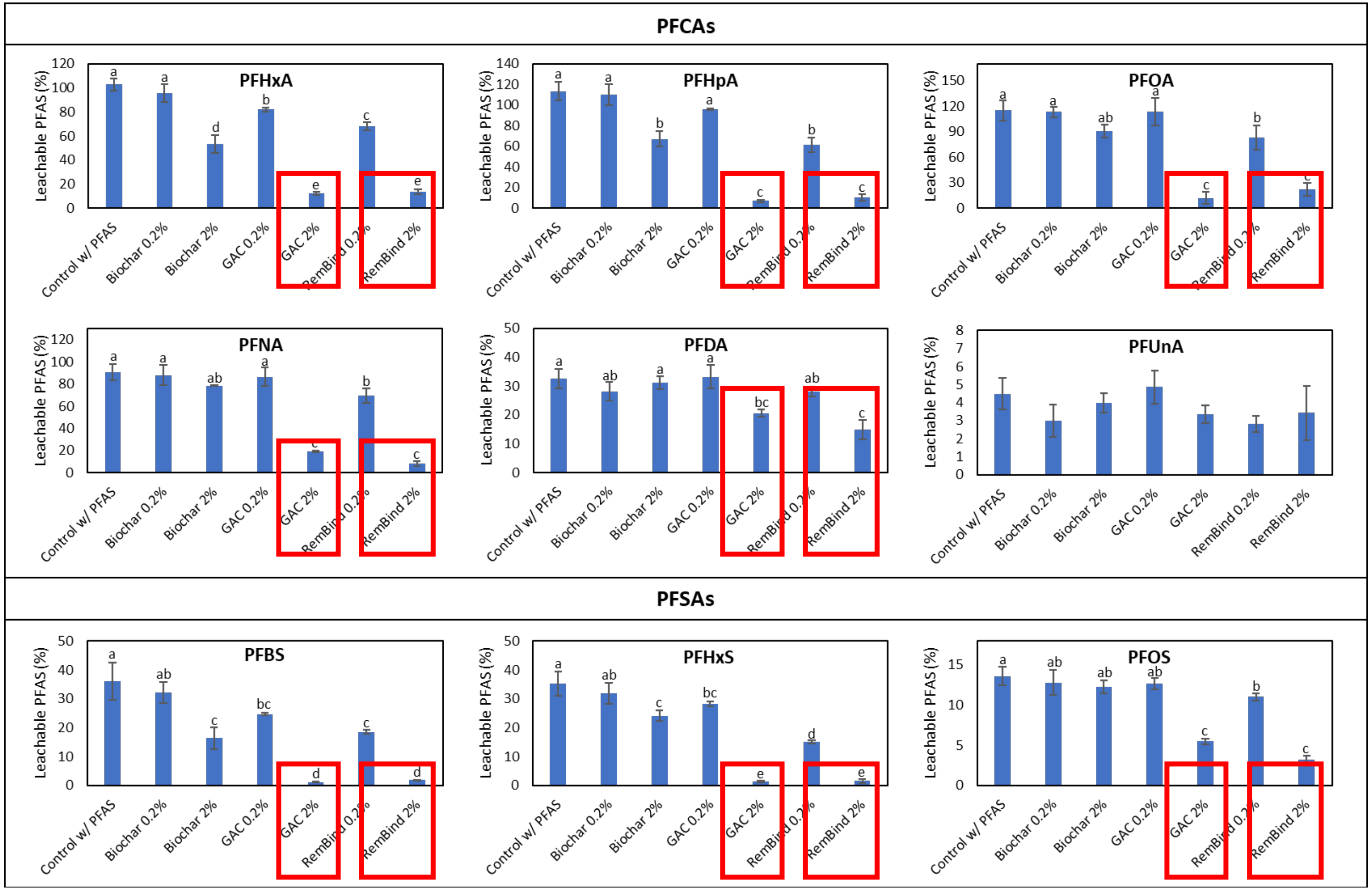
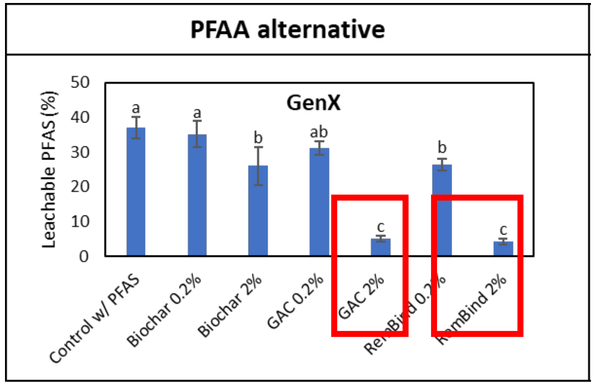
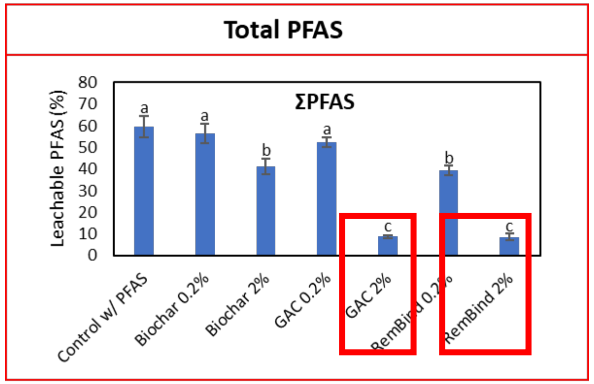


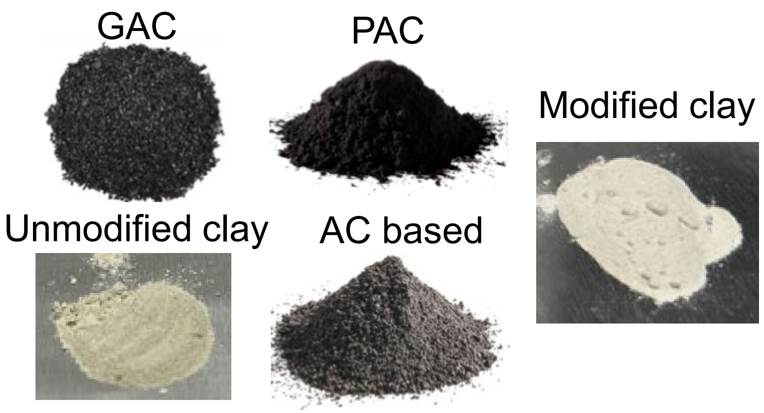


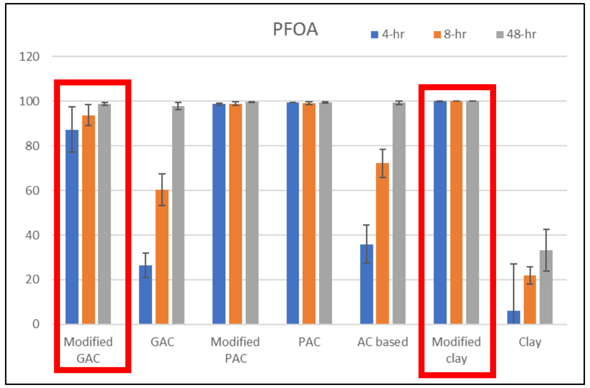


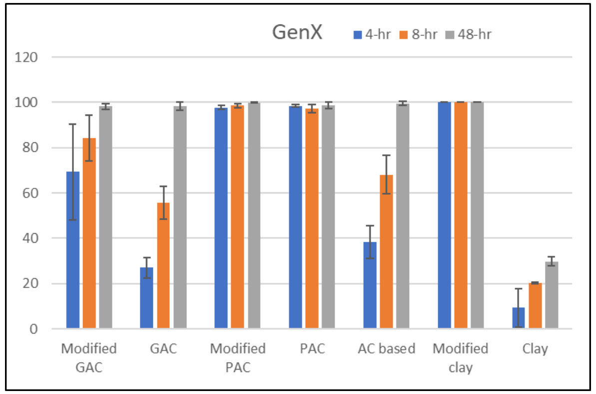
- Stabilization with GAC or RemBind at 2% significantly reduce SPLP leachable PFAS in biosolids-amended soil

Innovative Green and Low-cost Sorbents for Stabilizing All Types of PFAS

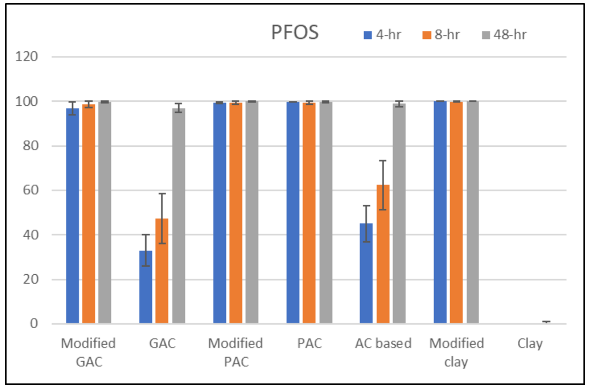
Adsorption Tests – Comparison with Other Sorbents

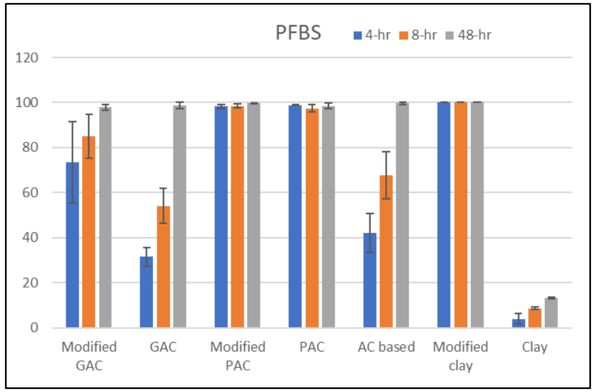






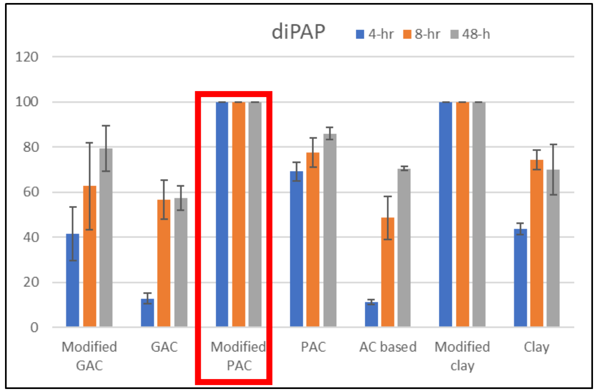
PFCAs, GenX

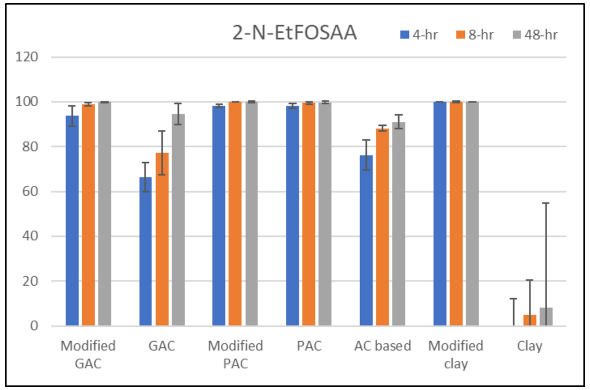


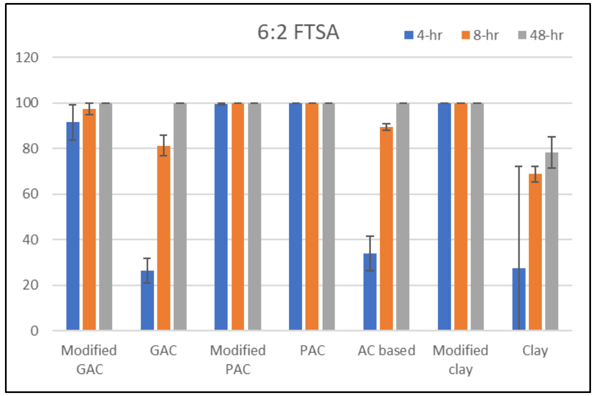


PFSAs

- PFAS initial concentration: 10 ppb
- Sorbent dosage: 100 mg/L water



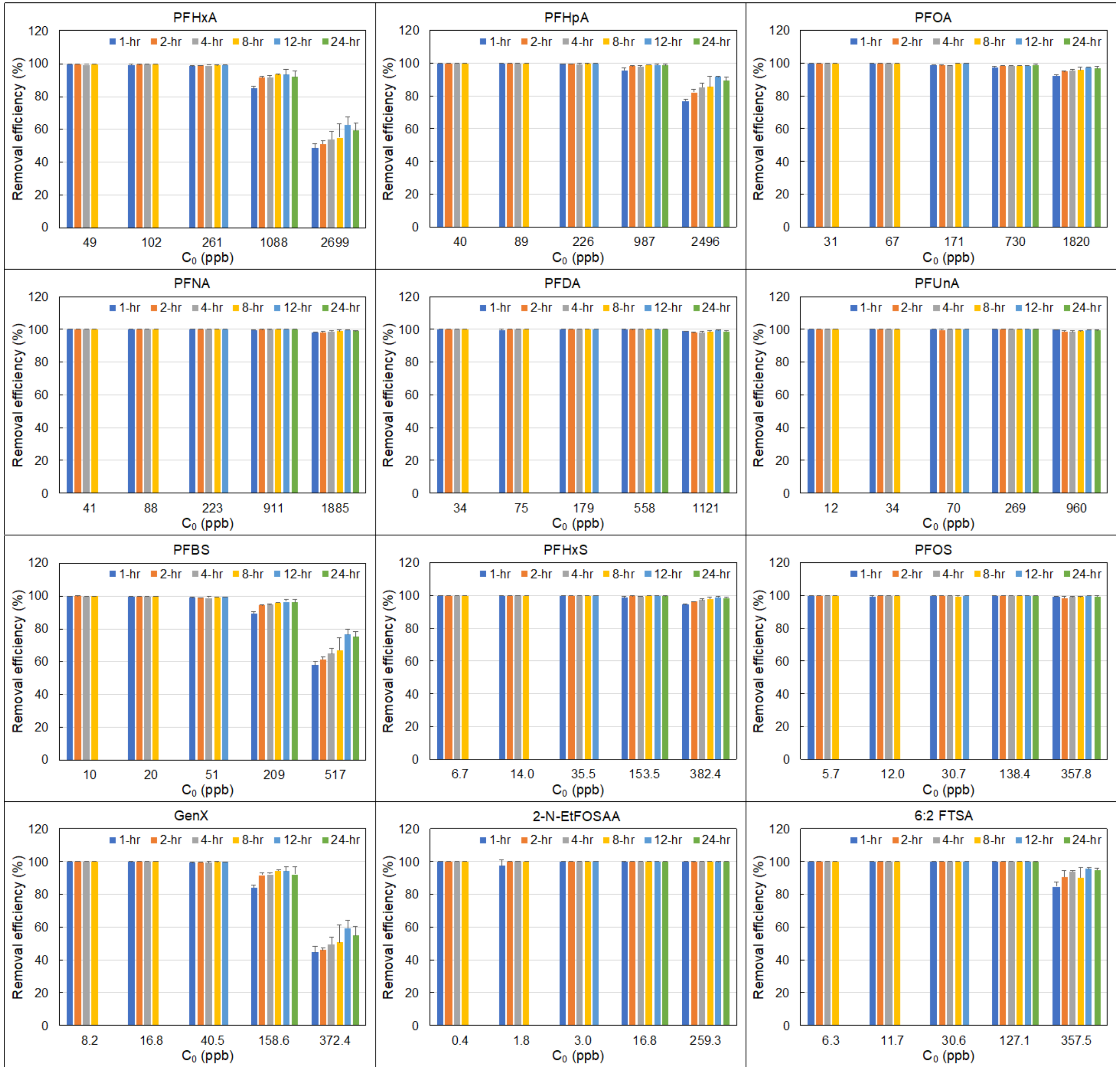




Precursors

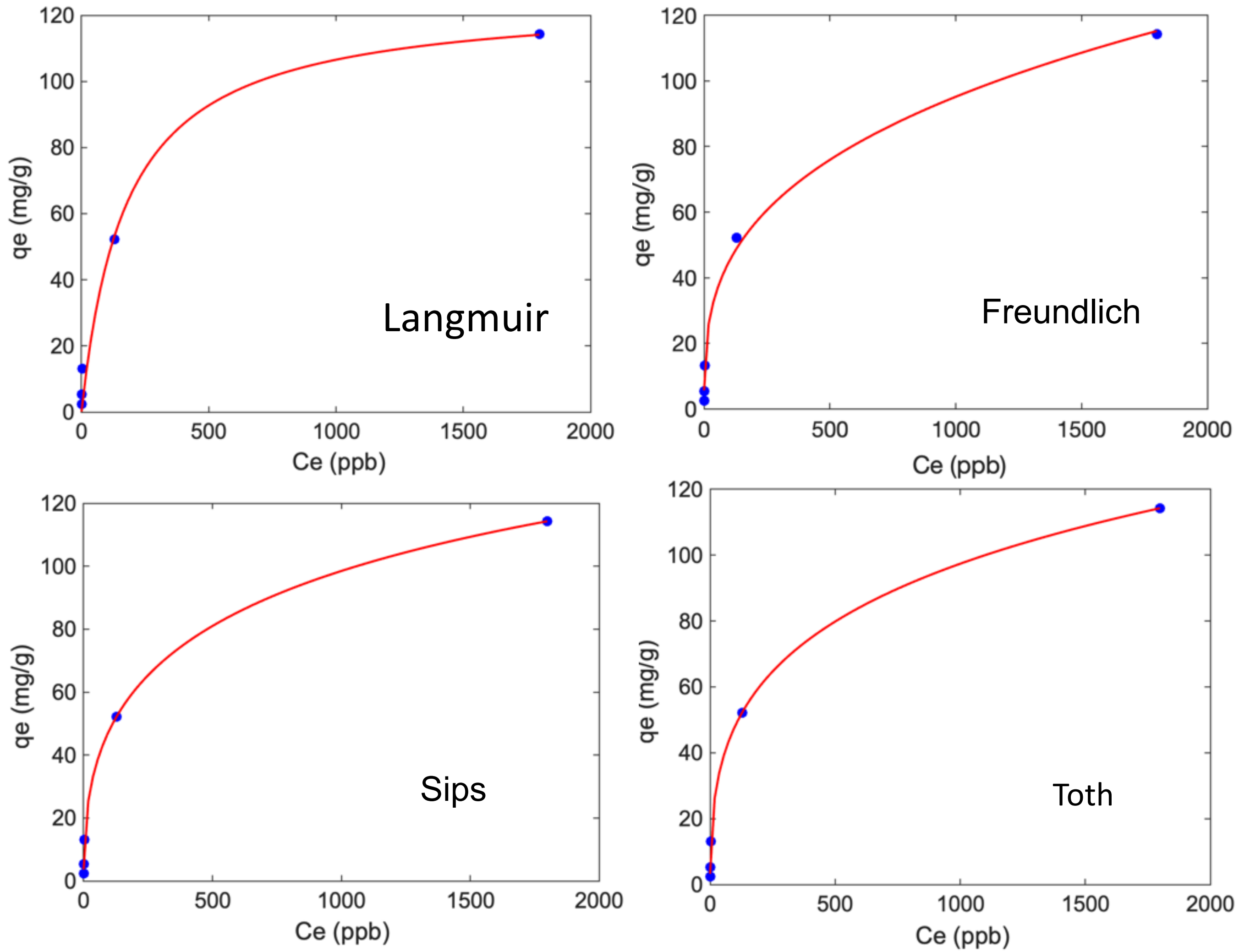
Adsorption Tests – Kinetics for modified clay

- Sorbent dosage: 100 mg/L water
- PFAS mixture in pure water



Adsorption Tests – Isotherms

$\sum$PFAS C_e (ppb)	$\sum$PFAS q_e tested (mg/g)	$\sum$PFAS q_e calculated (mg/g)			
		Langmuir	Freundlich	Sips	Toth
0.17	2.45	0.12	5.63	3.64	3.25
0.44	5.29	0.31	7.65	5.44	5.20
3.06	13.18	2.15	14.44	12.35	12.71
128.79	52.17	53.06	48.82	52.32	52.31
1798.93	114.30	114.11	115.25	114.27	114.27
	R^2	0.9939	0.9975	0.9998	0.9999



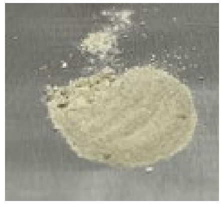
- Maximum adsorbed PFAS in tests: 114 mg/g sorbent
- Modeled adsorption capacity (Sips): 255 mg/g sorbent

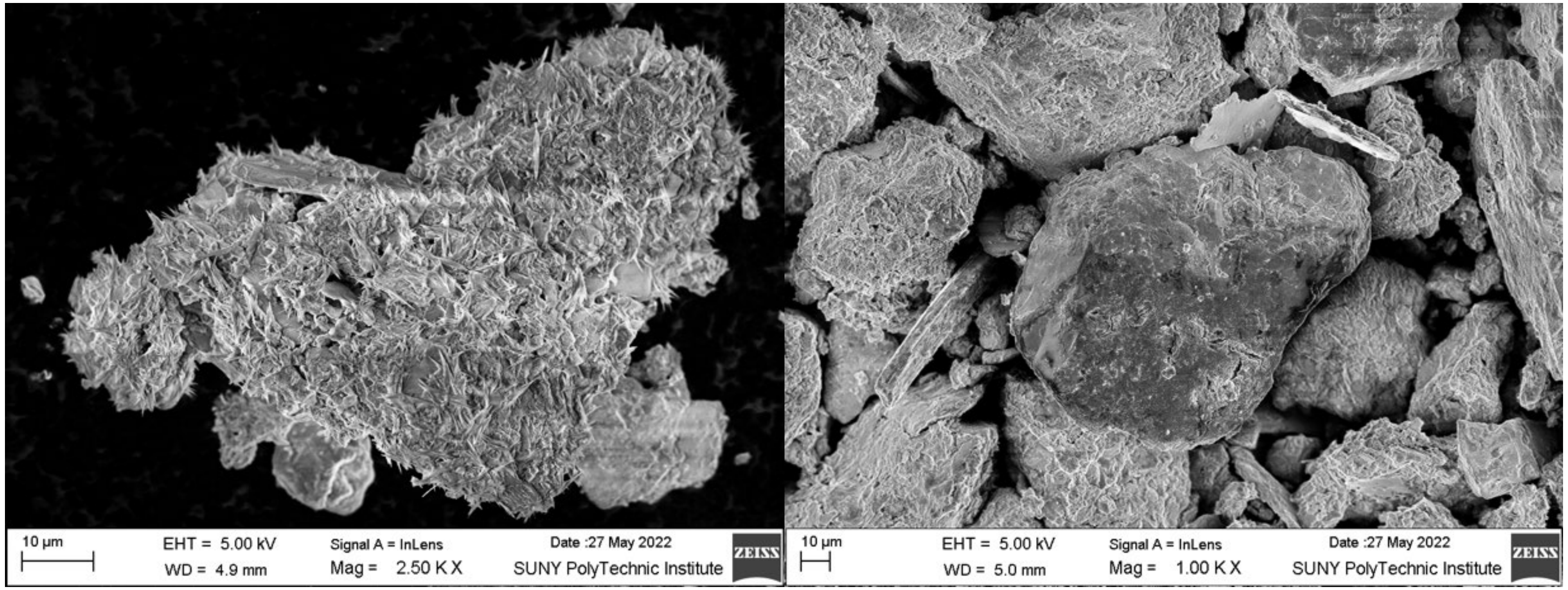
Sorption capacity comparison

Sorbent	Dosage (mg/L)	PFAS	C_0 (ppm)	Capacity (mg/g)	Refs.
Commercial GAC Filtrasorb 400	200	PFOA	0.5	2.52	Zhi and Liu, 2015
		PFOS	0.5	2.59	
Commercial PAC BPL	200	PFOA	0.5	2.49	Zhi and Liu, 2015
		PFOS	0.5	2.48	
MatCARE	10,000	PFOS	200	45	Das, et al., 2013
Clay-based #1	50	PFOA	5	120[a]	Wang, et al., 2021
	50	PFOS	5	290[a]	
Clay-based #2	-	PFOS	500	456[a]	Zhou, et al., 2010
Note: a: modeled value					

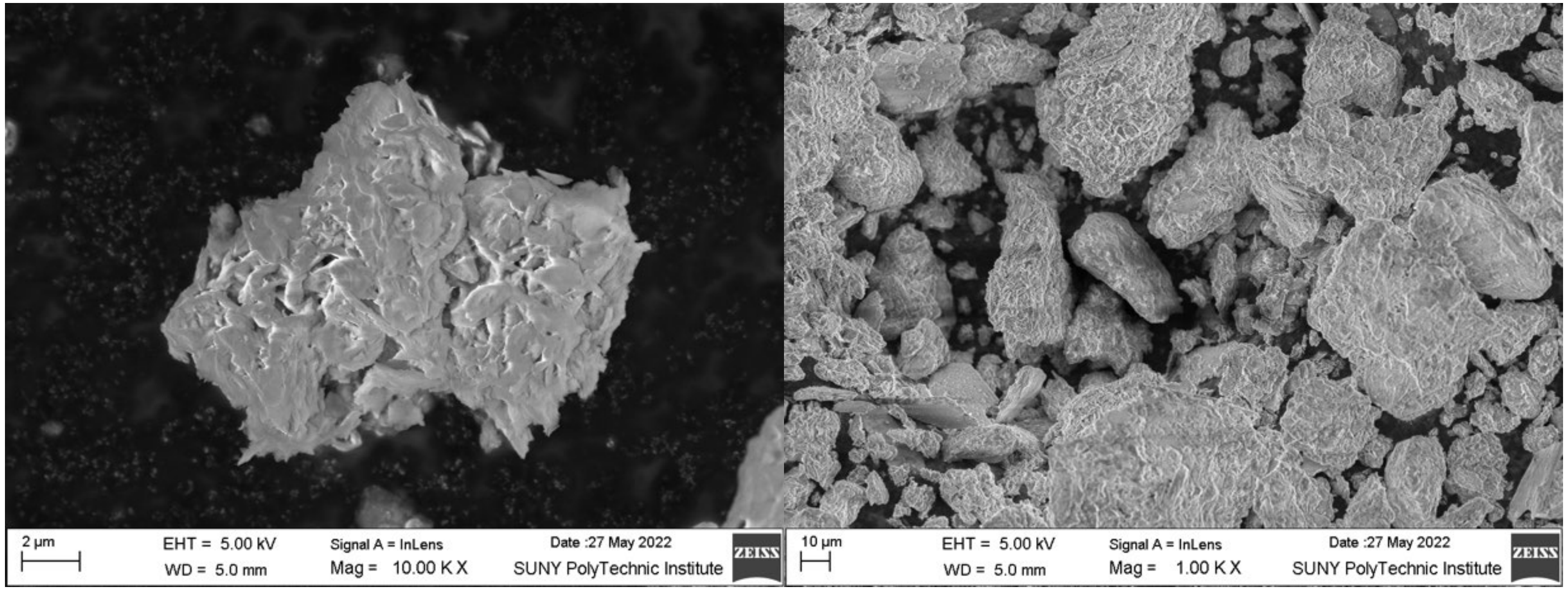
Morphology by Scanning Electron Microscopy (SEM)

Unmodified clay





Modified clay

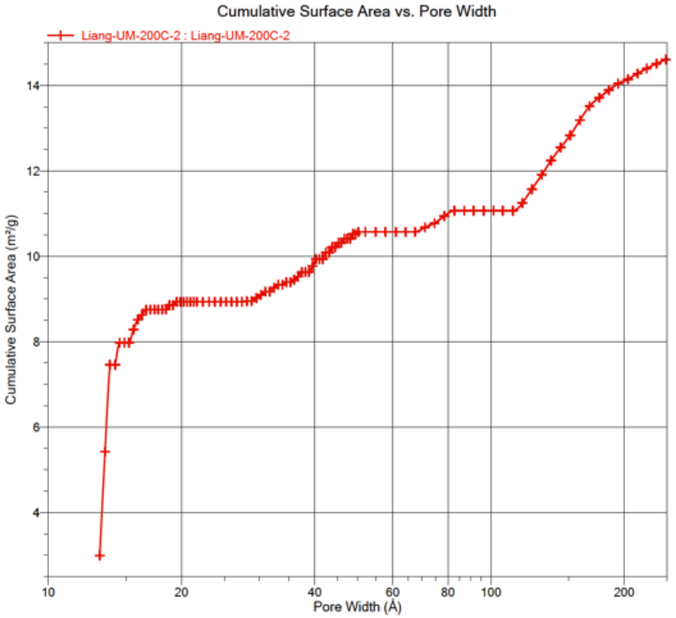


- Smoother surface and smaller particle size after modification
- Porous and layered structure

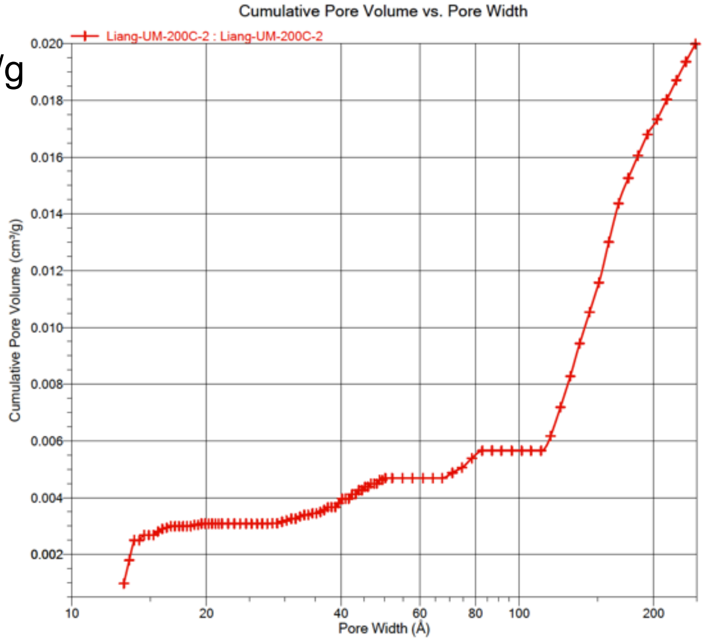
Surface Area

Pore Volume

Unmodified clay



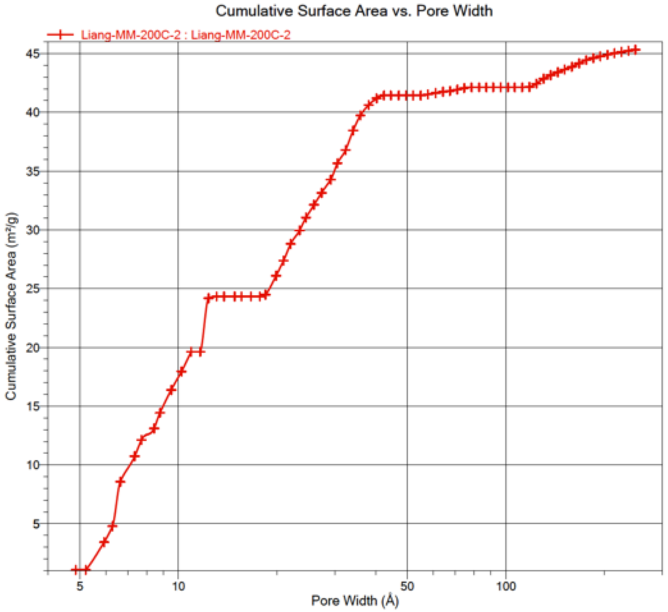
14.61 m^2/g



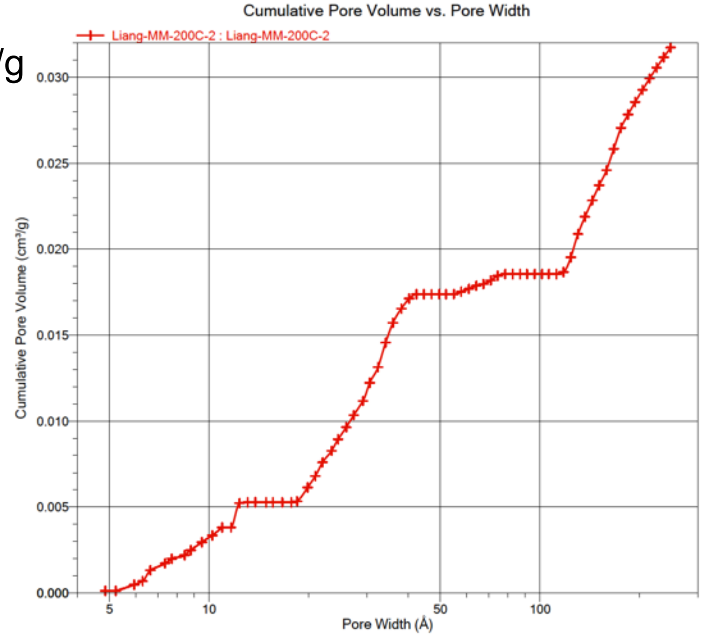
0.02 cm^3/g

Quantity of Adsorbed N_2 = 0.636 mmol/g

Modified clay



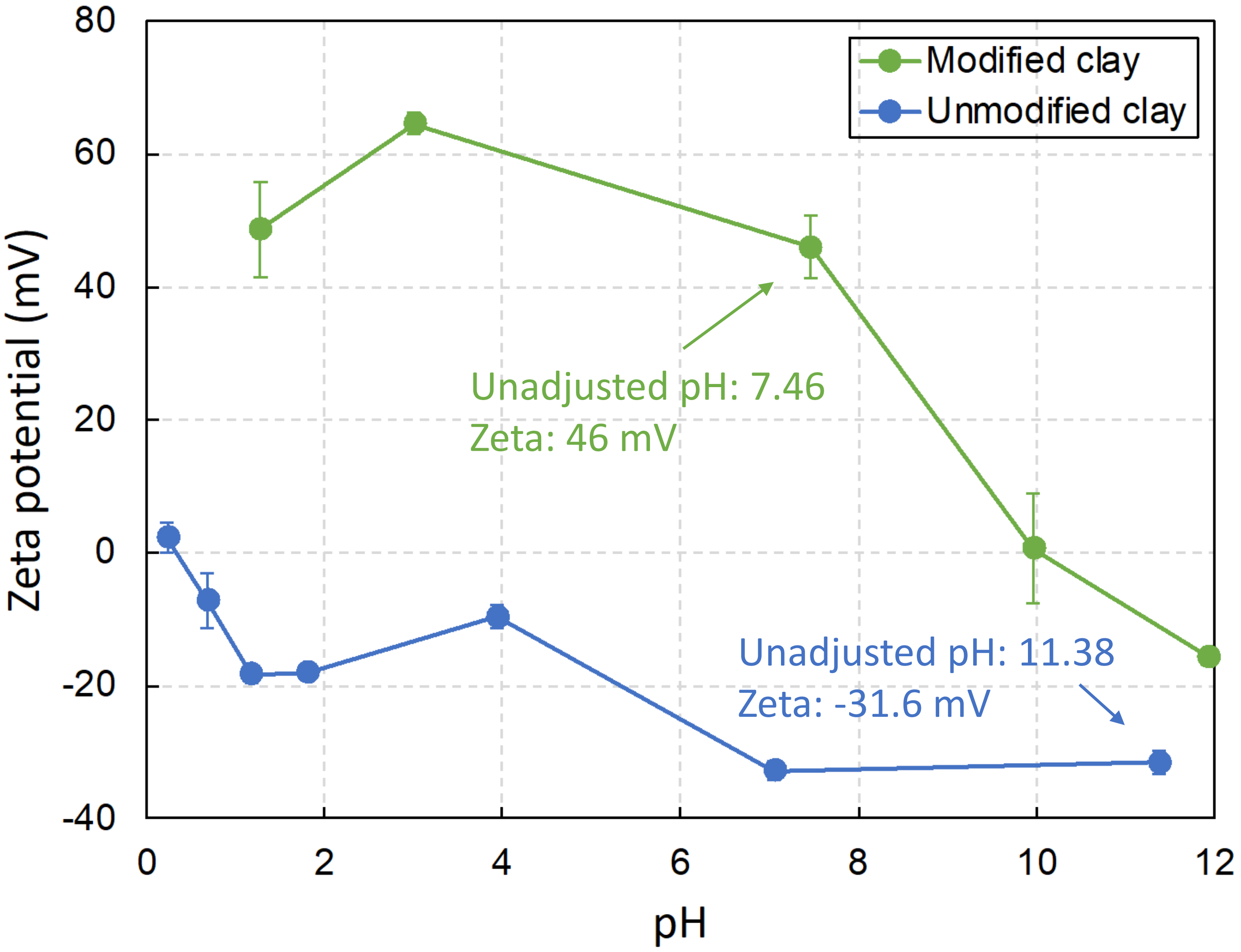
45.34 m^2/g



0.032 cm^3/g

Quantity of Adsorbed N_2 = 0.918 mmol/g

Zeta Potential



- Positive Zeta indicates positively charged particles
- PFAS negatively charged at environmentally relevant pH
- More positively charged sorbents tend to have better PFAS adsorption performance

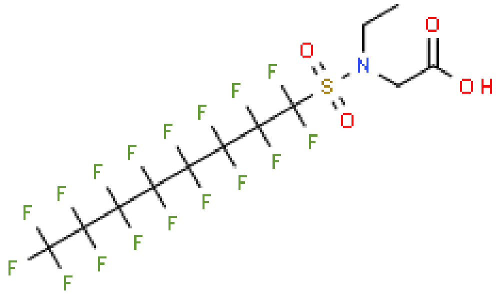
Uniqueness and Cost analysis

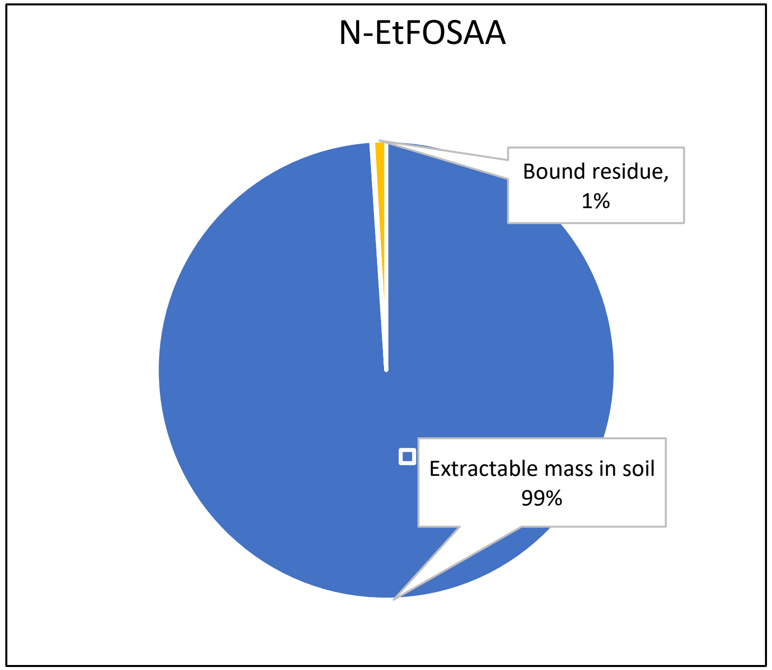
Uniqueness:

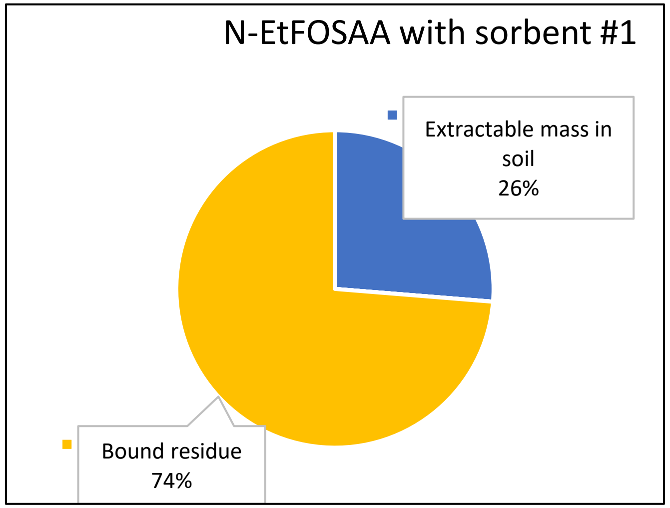
- Superior adsorption performance
- Much less costly
- Much shorter contact time
- Significantly lower greenhouse emissions
- Cleaner technology

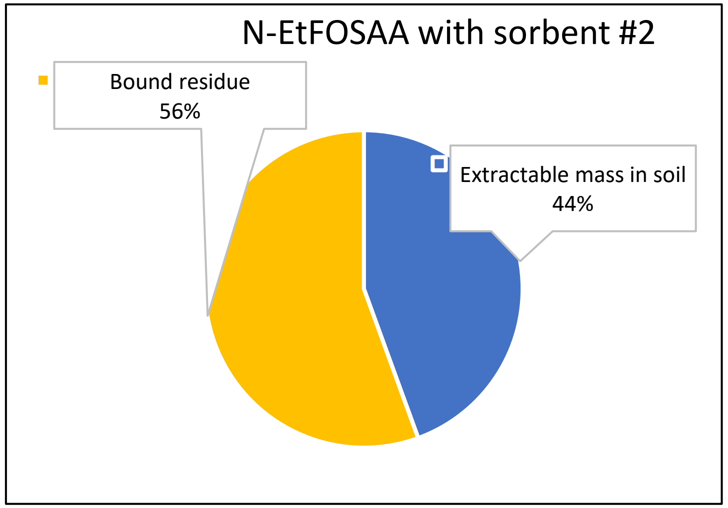
Sorbent	Market price (/ton)
Activated biochar	$246
Synthetic AC	$1,500
Filtrasorb 400 GAC	$5,770
Hydraffin CC8x30 GAC	$14,600
MatCARE (clay-based)	$26,000
Amberlite IRA 400 resin	$88,000
Amberlite XAD4 resin	$218,000
Modified clay	$750 (estimated)

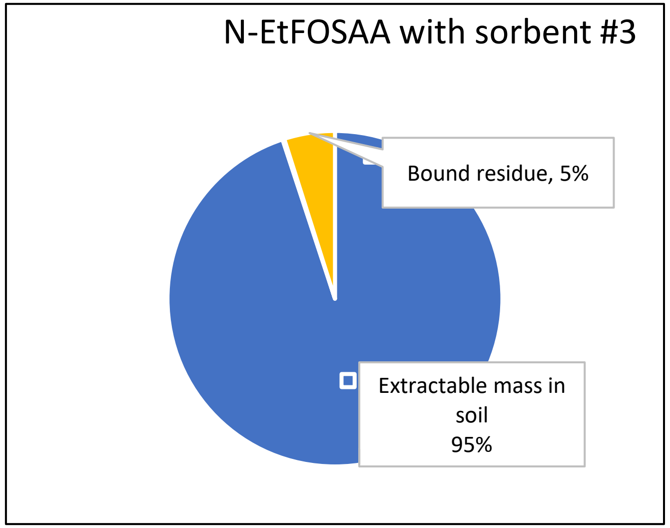
True bound residue of N-Ethylperfluorooctane sulfonamidoacetic acid (N-EtFOSAA) in soil with or without a sorbent

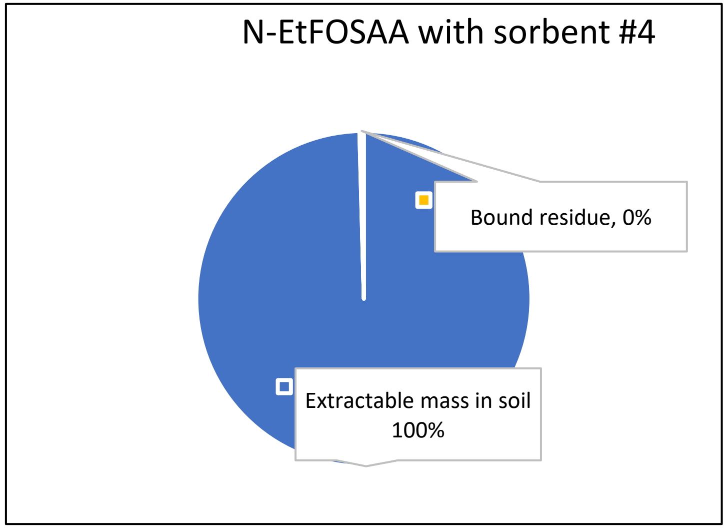




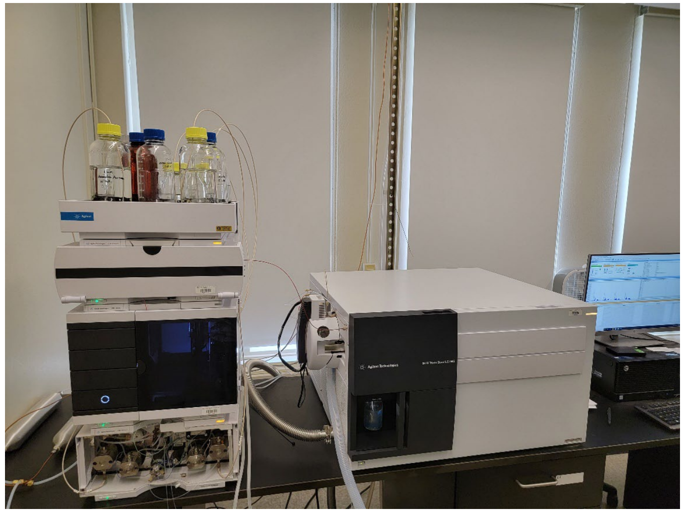


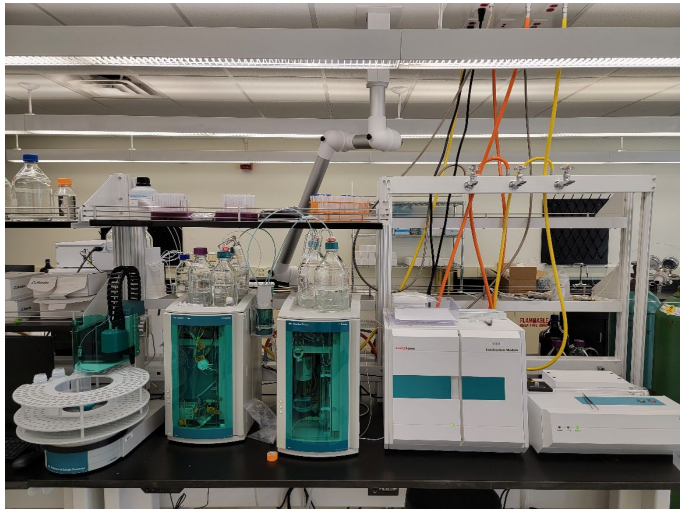






Capability for conducting PFAS research





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