Revisiting Sludge Pretreatment: Can Thermal Hydrolysis and Ultrasonication Destruct PFAS?

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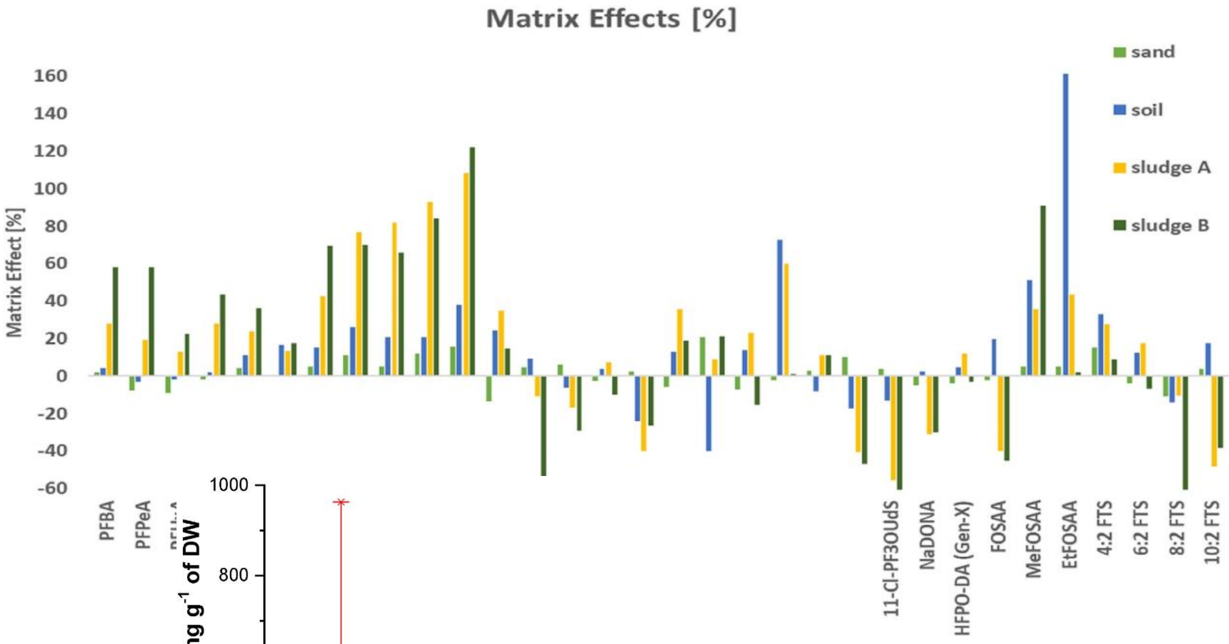
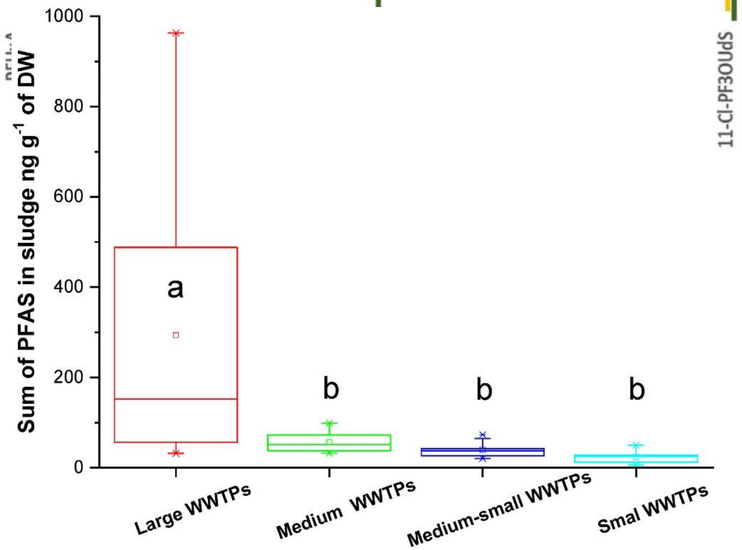
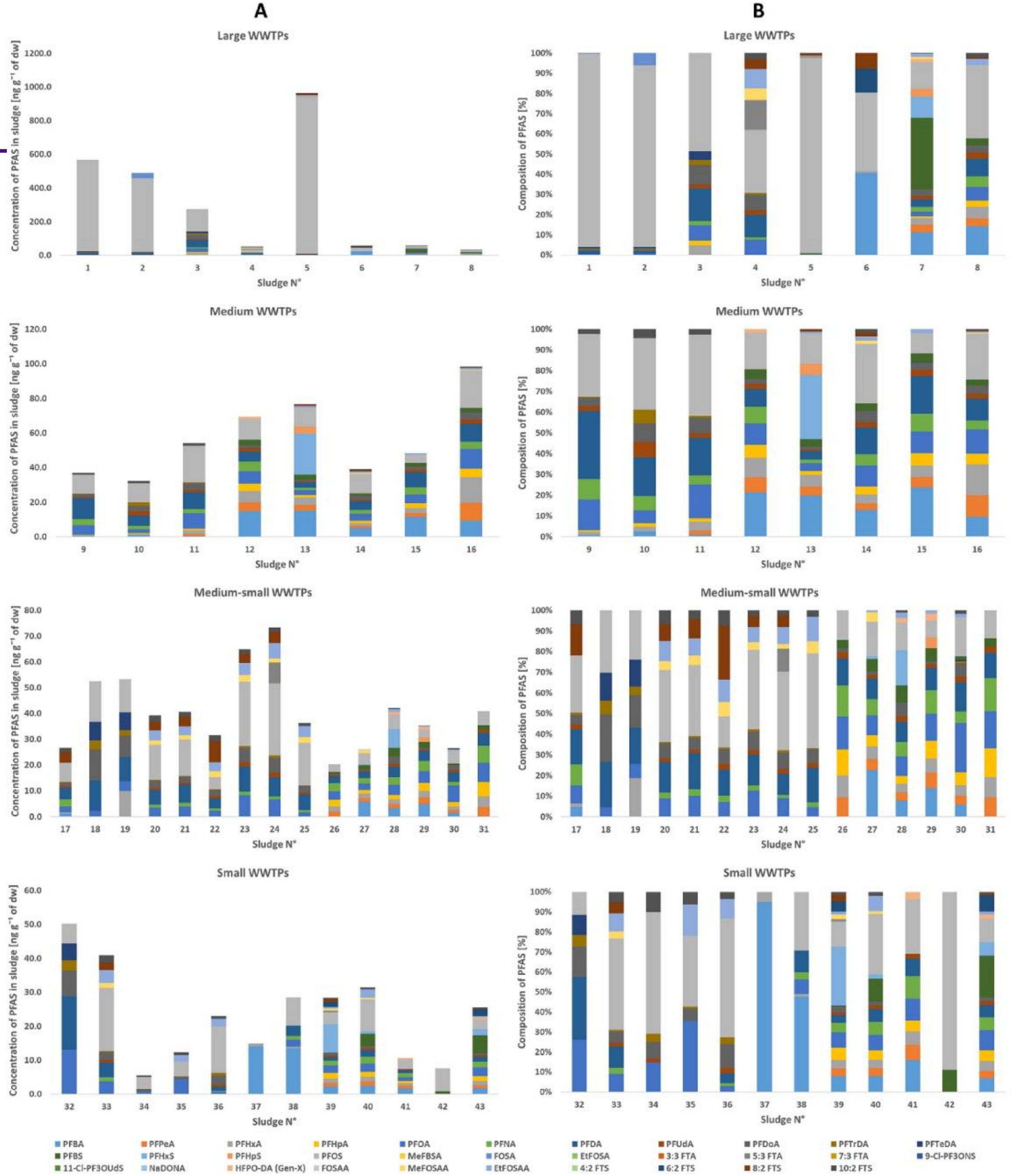
PFAS in sludges in Czech Republic

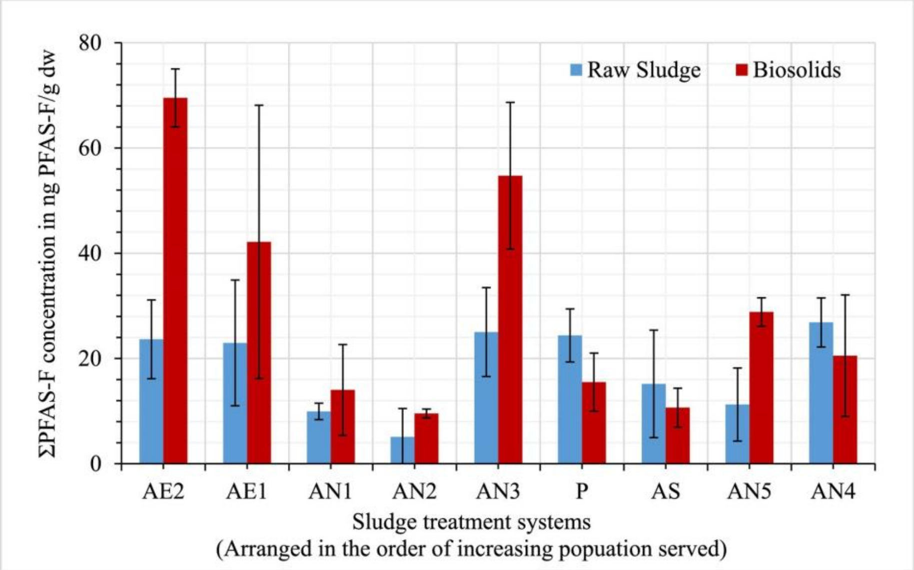


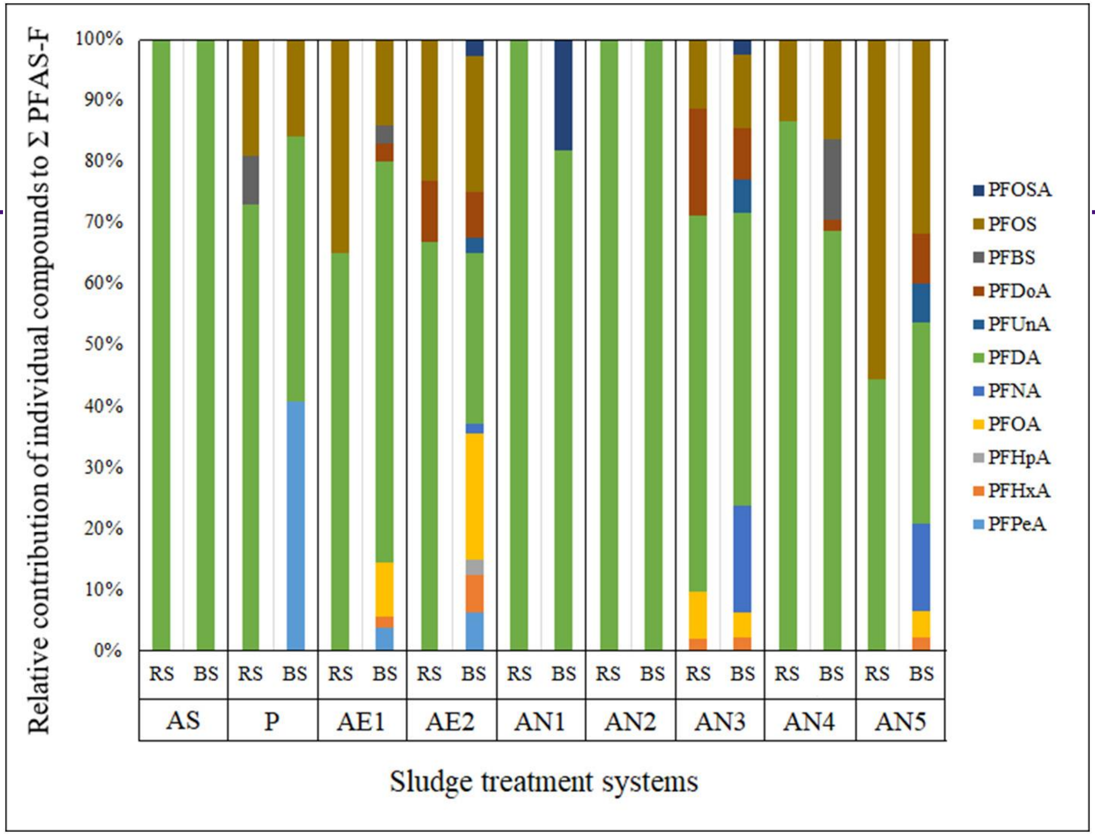


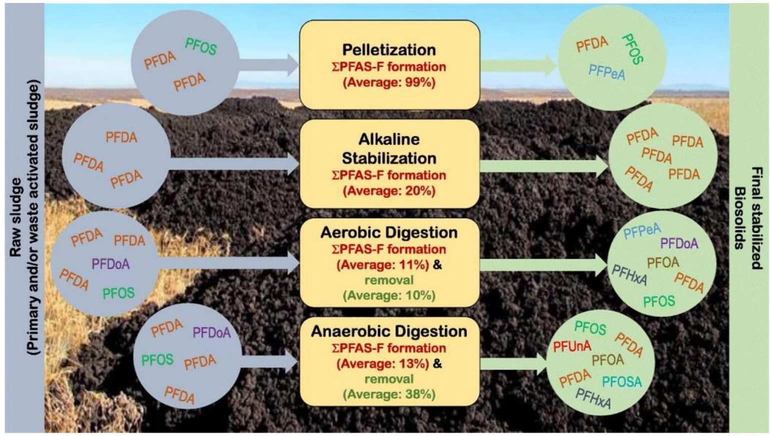


Semerád, Jaroslav, et al. "Screening for 32 per-and polyfluoroalkyl substances (PFAS) including GenX in sludges from 43 WWTPs located in the Czech Republic-Evaluation of potential accumulation in vegetables after application of biosolids." Chemosphere 261 (2020): 128018.

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 NY biosolids and compost

PFAS	Conc. before composting (µg/Kg)	Conc. after composting (µg/Kg)	Conc. in biosolids leachate (ng/L)	Conc. in compost leachate (ng/L)
Perfluorobutanoic acid (PFBA)	ND-84.0	ND-83	ND-56.6	31.0-1240
Perfluoropentanoic acid (PFPeA)	ND-36.8	1.82-31.8	1.8-22.7	68.1-527
Perfluorohexanoic acid (PFHxA)	2.08-121	0.25-11.1	4.51-34.3	280-2500
Perfluoroheptanoic acid (PFHpA)	ND-13.7	0.25-11.1	1.16-3.69	27.4-137
Perfluorooctanoic acid (PFOA)	1.28-116	3.04-53.3	6.12-34.0	104-376
Perfluorononanoic acid (PFNA)	1.29-26.6	1.42-18.5	0.97-62.2	ND-77.9
Perfluorodecanoic acid (PFDA)	2.84-71.8	4.81-47.5	0.45-9.13	ND-21.1
Perfluoroundecanoic acid (PFUnA)	ND-16.2	0.96-9.38	ND-1.85	ND-0.88
Perfluorododecanoic acid (PFDoA)	2.36-26.2	1.27-10.2	ND-1.71	ND-0.58
Perfluorotridecanoic Acid (PFTriA)	ND-6.15	ND-3.96	ND-16.8	ND-0.67
Perfluorotetradecanoic acid (PFTeA)	1.19-9.22	0.36-3.73	ND-1.08	ND-0.9
Perfluorobutanesulfonic acid (PFBS)	ND-239	1.19-48.9	ND-16.3	40.6-1100
Perfluorohexanesulfonic acid (PFHxS)	ND-6.02	0.76-6.86	ND-3.79	ND-74.0
Perfluoroheptanesulfonic Acid (PFHpS)	ND-3.83	ND-9.08	ND-0.87	ND-2.14
Perfluorooctanesulfonic acid (PFOS)	9.64-94.7	13.9-42.7	2.25-19.8	ND-105
Perfluorodecanesulfonic acid (PFDS)	ND-6.7	0.3-4.78	ND-4.35	ND

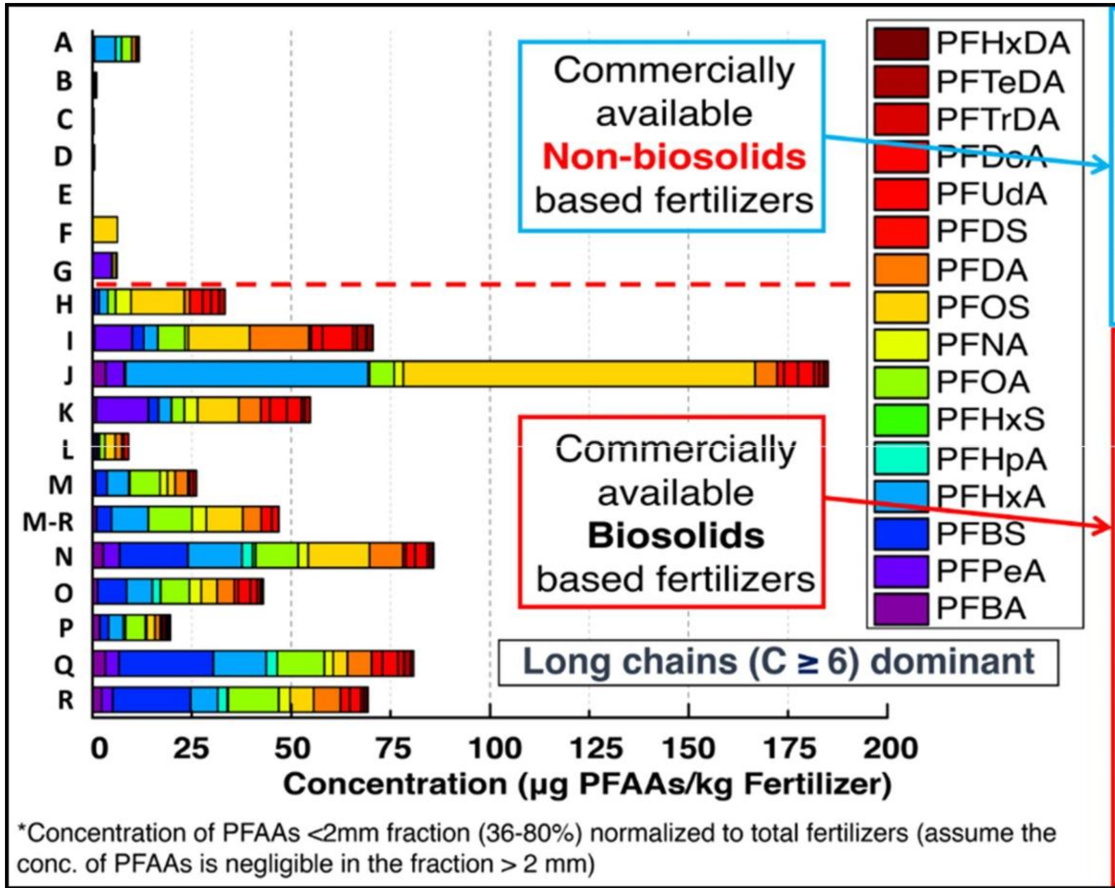
Summary of Biosolids-Amended Soil Sampling Data Maine, 2019

29 fields, 1 sample each

ng/g (ppb)

	Mean	Maximum	Minimum	Screening
PFOA	3.06	12.90	1.05	2.5
PFOS	8.76	20.90	2.13	5.2

PFAAs in biosolids based fertilizers



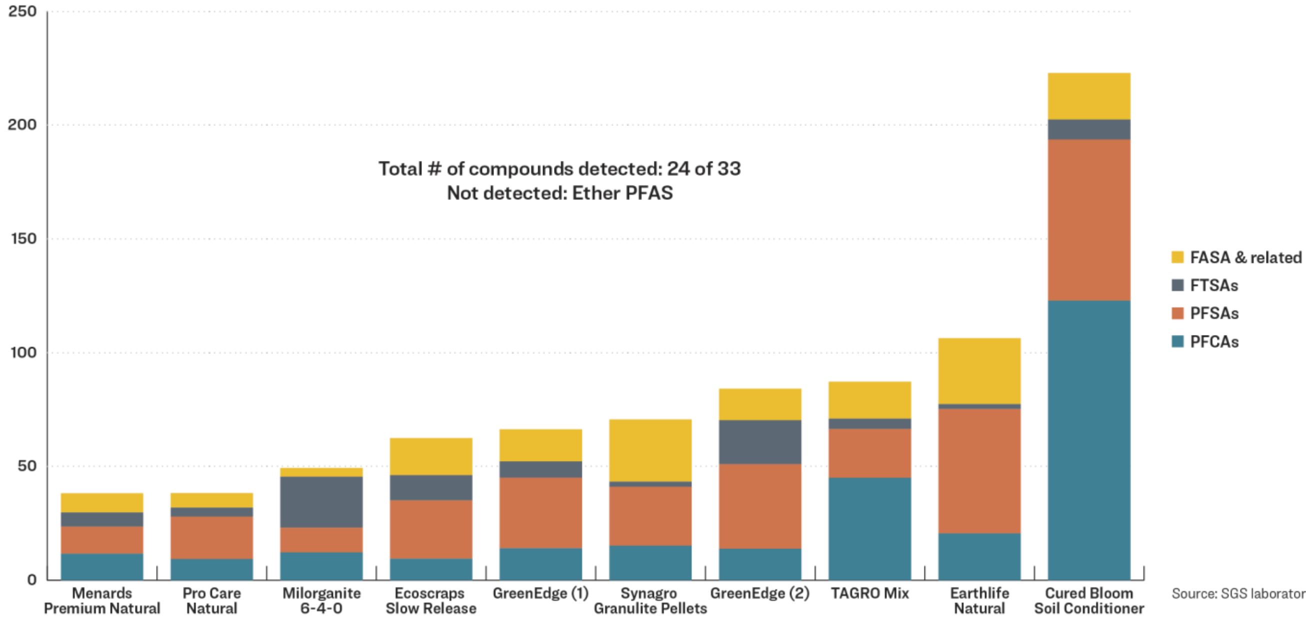
Fertilizer	Description
A	Food and yard compost
B	Compost with untreated wood products
C	Manure compost
D	Manure and peat compost
E	Mushroom compost
F	Mushroom compost
G	Peat/compost based growing mix
H	Heat-dried granular biosolids
I	Heat-dried granular biosolids
J	Heat-dried granular biosolids
K	Heat-dried 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.

Nine fertilizers from eight states and DC

Product Name	Where Purchased	Biosolids Source	Percent Biosolids
Pro Care Natural Fertilizer	Lowes	Georgia—multiple locations	85.5 - 91.5
EcoScraps Slow Release Fertilizer	The Home Depot	Unknown—company based in Nevada	100
Milorganite 6-4-0 Fertilizer	The Home Depot	Milwaukee, WI—Metropolitan Sewerage District	100
Cured Bloom Soil Conditioner	W.S. Jenks & Sons Washington, DC	Washington, DC Water—Blue Plains Advanced Wastewater Treatment Plant	100
Menards Premium Natural Fertilizer	Menards	Unknown—company based in Wisconsin	100
GreenEdge Slow Release Fertilizer	The Home Depot	Jacksonville, FL—JEA sewer collection system	100
Earthlife Natural Fertilizer	York Woods Tree & Products, Eliot, ME	Quincy, MA—New England Fertilizer Company (NEFCO)	100
Synagro Granulite Fertilizer Pellets	Sacramento, CA Pelletizer	Elk Grove, CA— Sacramento Regional Wastewater Treatment Plant	100
TAGRO Mix	Ace Hardware	Tacoma, WA—Central Wastewater Treatment Plant	50

Perfluoroalkyl sulfonates (PFSAs)	Perfluoroalkyl carboxylates (PFCAs)	PFAS ethers	Perfluoroalkane sulfonamides (FASAs & Related)	Fluorotelomer sulfonic acids (FTSAs)
PFBS	PFBA	HPO-DA (GenX)	PFOSA	4:2 FTS
PFPeS	PFPeA	ADONA	N-MeFOSA	6:2 FTS
PFHxS	PFHxA	9Cl-PF3ONS*	N-EtFOSA	8:2 FTS
PFHpS	PFHpA	11Cl-PF3OUdS*	MeFOSAA	
PFOS	PFOA	*components of F-53B	EtFOSAA	
PFNS	PFNA		N-MeFOSE	
PFDS	PFDA		N-EtFOSE	
PFDoS	PFUnA		**Red** = detected in at least one product (multiple products in most cases).	
	PFDoA		**Black** = not detected	
	PFTrDA			
	PFTeDA			



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

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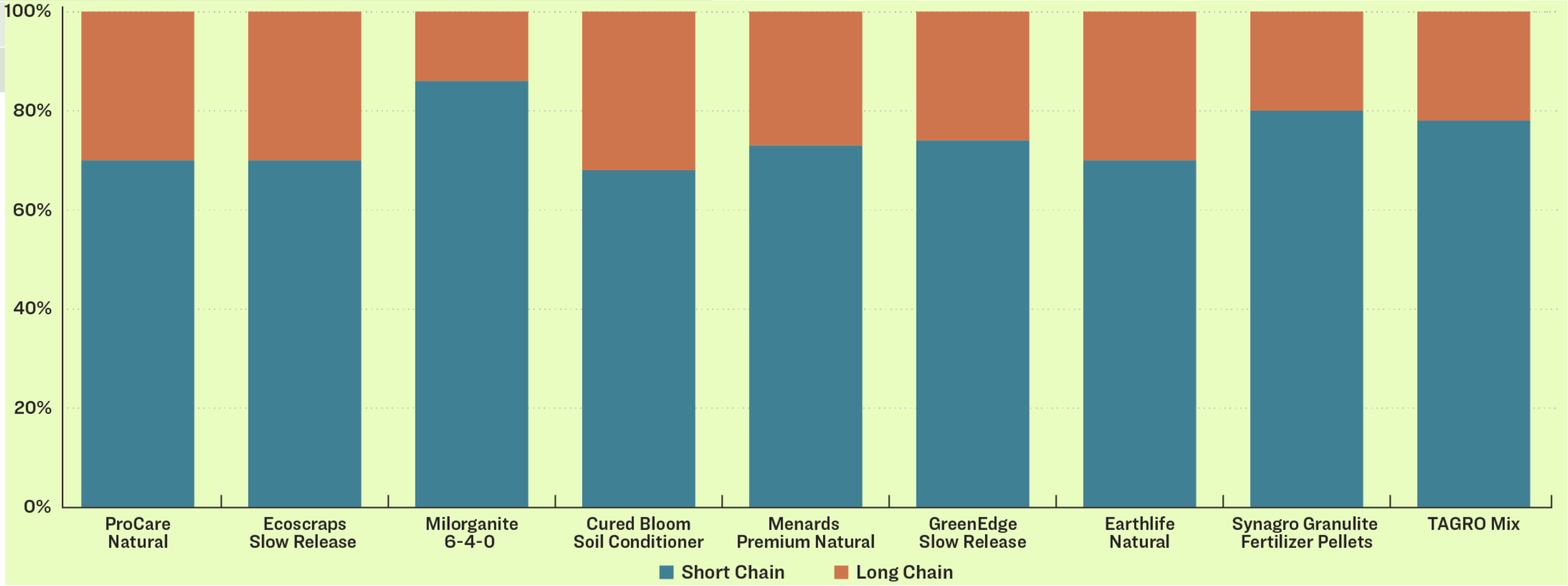
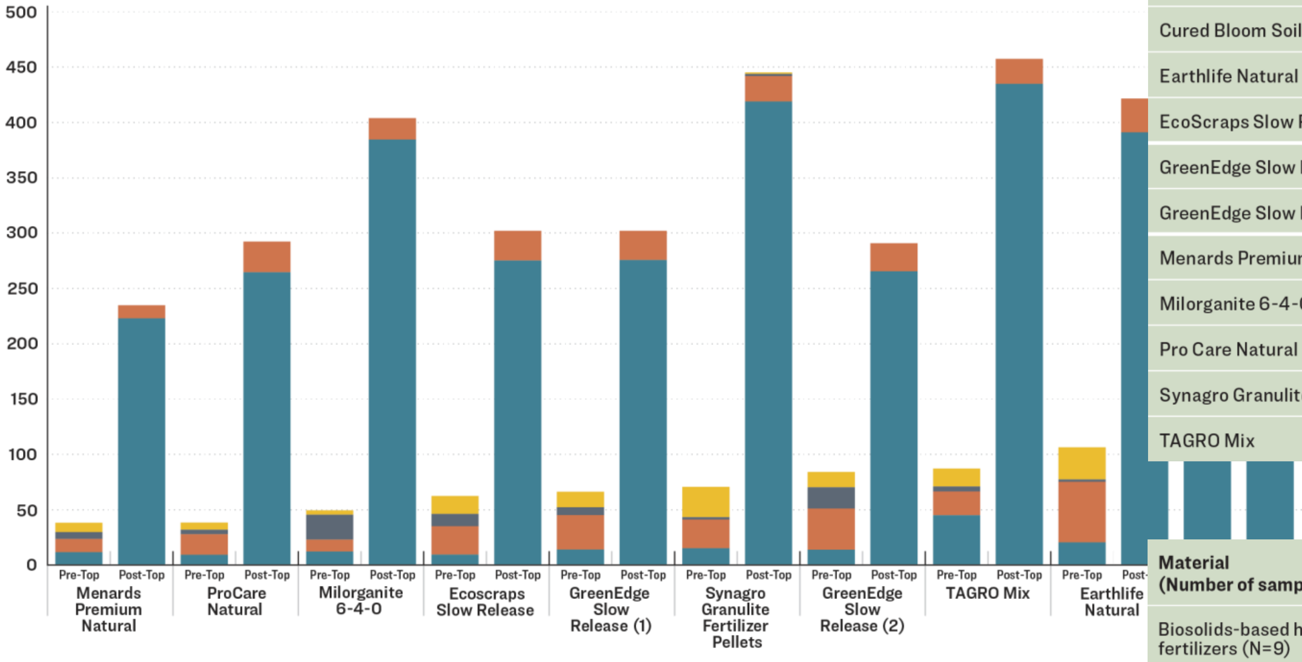
PFAS in fertilizers derived from sludge (ppb)

Product Name	PFOA	PFOS
Cured BLOOM	23.8	22.1
Earthlife Natural Fertilizer	2.75	17.3
Ecoscraps Slow Release Fertilizer	1.2	16.9
GreenEdge Slow Release Fertilizer	1.39	13.5
GreenEdge Slow Release Fertilizer	1.66	12.9
Menards Premium Natural Fertilizer	1.01	9.05
Milorganite 6-4-0 Fertilizer	0.67	8.66
Pro Care All Natural Fertilizer	0.94	14.9
Synagro Granulite Fertilizer Pellets		
TAGRO Mix		



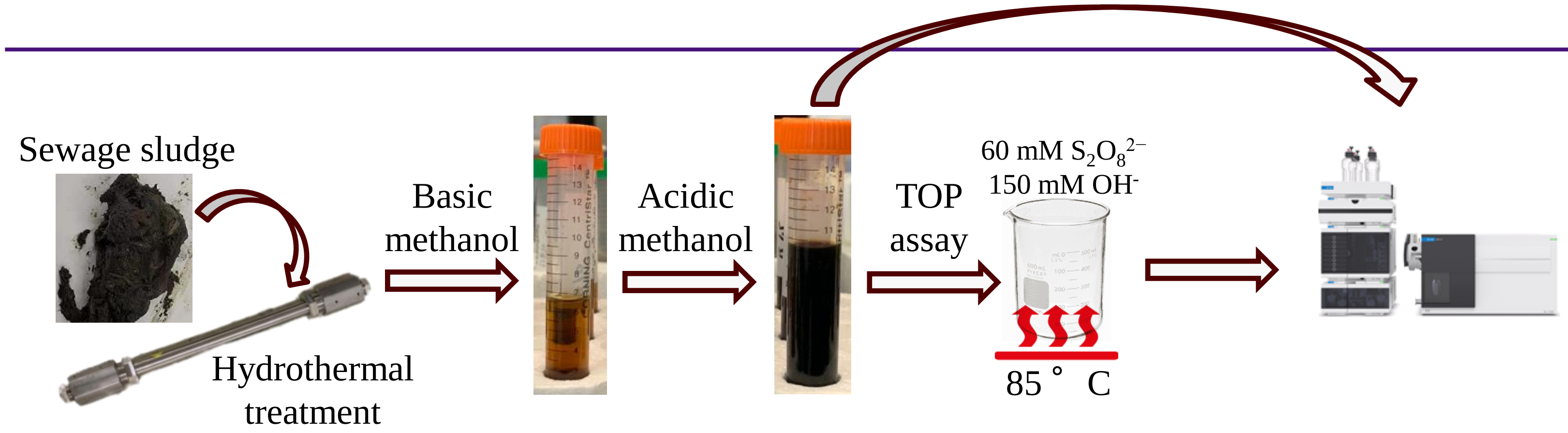
TOP and TOF assays



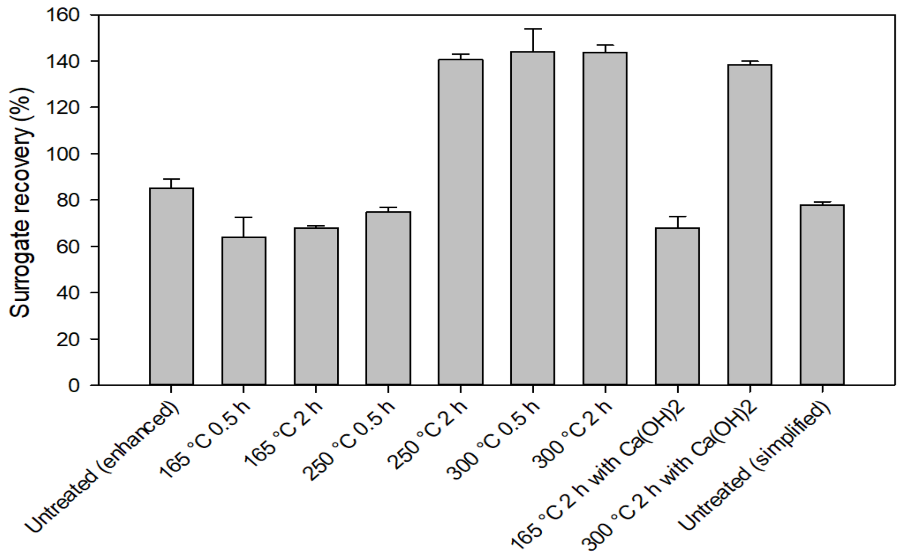
Product	Fluoride (ppb)	Total Fluorine (ppb)	Sum of known PFAS (ppb)
Cured Bloom Soil Conditioner	<500	131,000	223
Earthlife Natural	500	184,000	106
EcoScraps Slow Release	<500	179,000	62
GreenEdge Slow Release (1)	900	321,000	84
GreenEdge Slow Release (2)	1000	319,000	66
Menards Premium Natural	<500	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

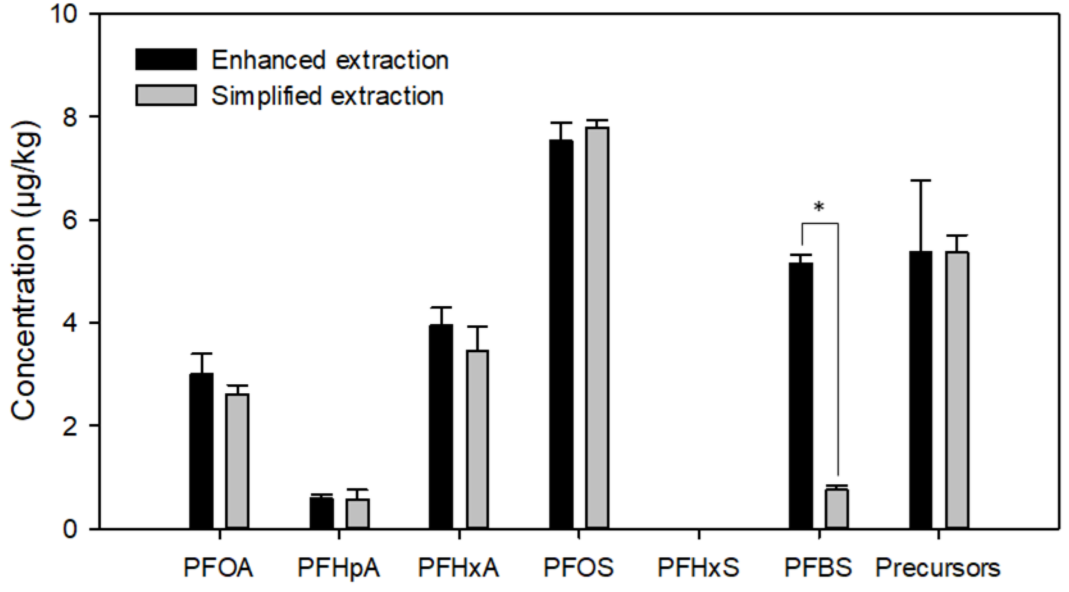
Can thermal hydrolysis destruct PFAS in sludge?



Surrogate recoveries

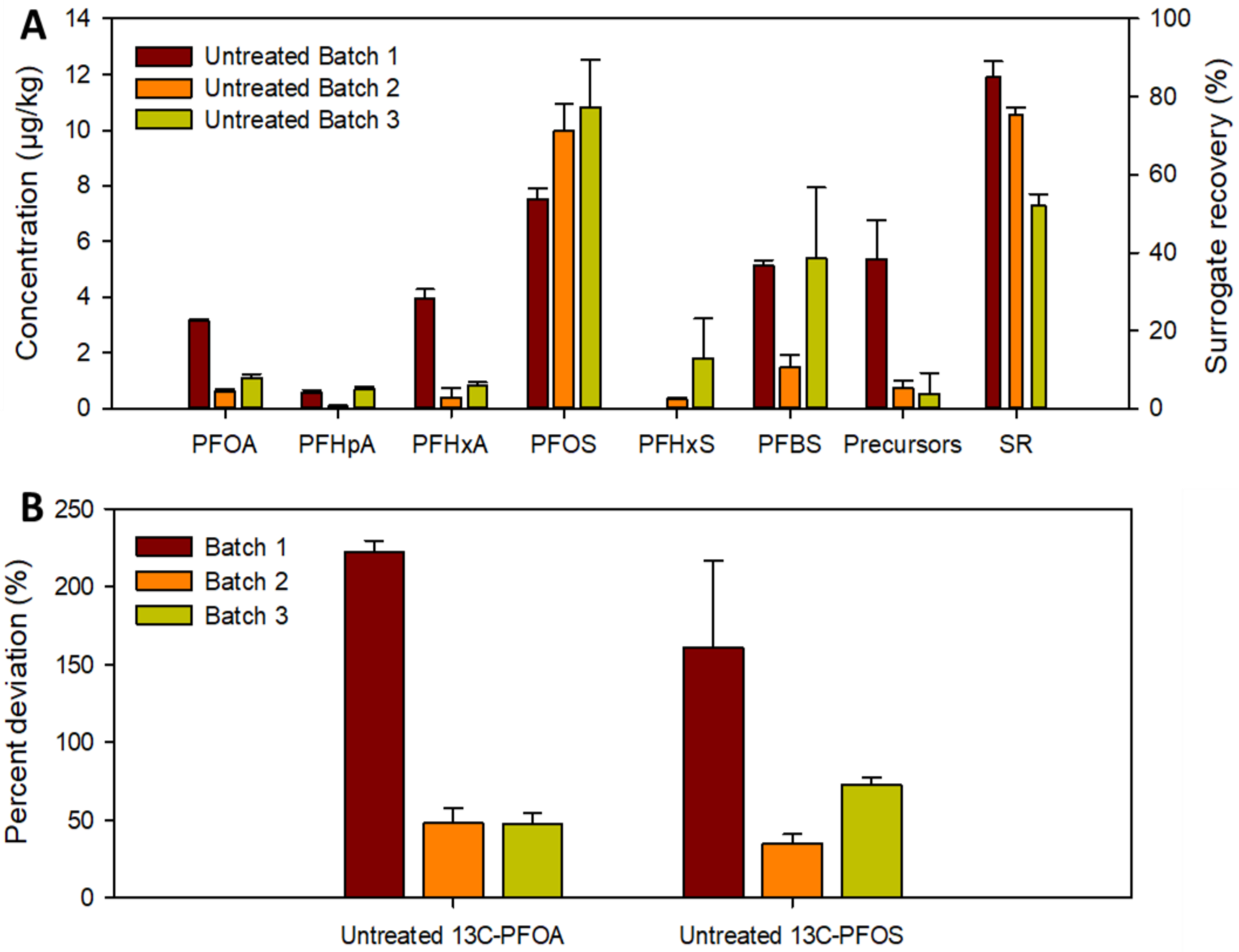


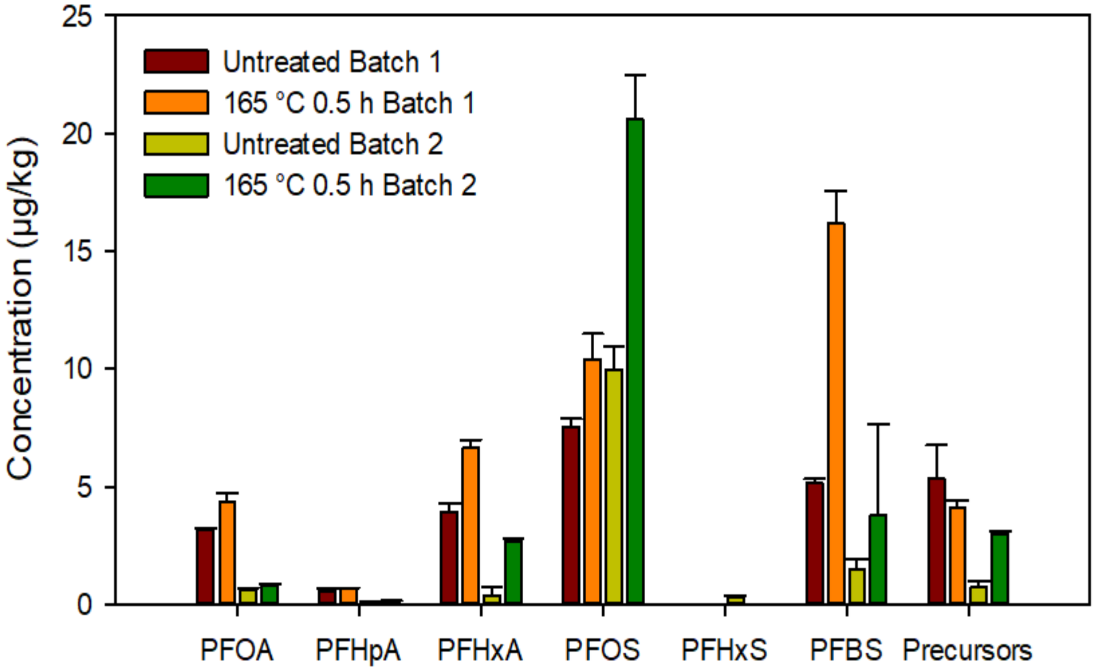
PFAS extraction comparison



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

Batch effect





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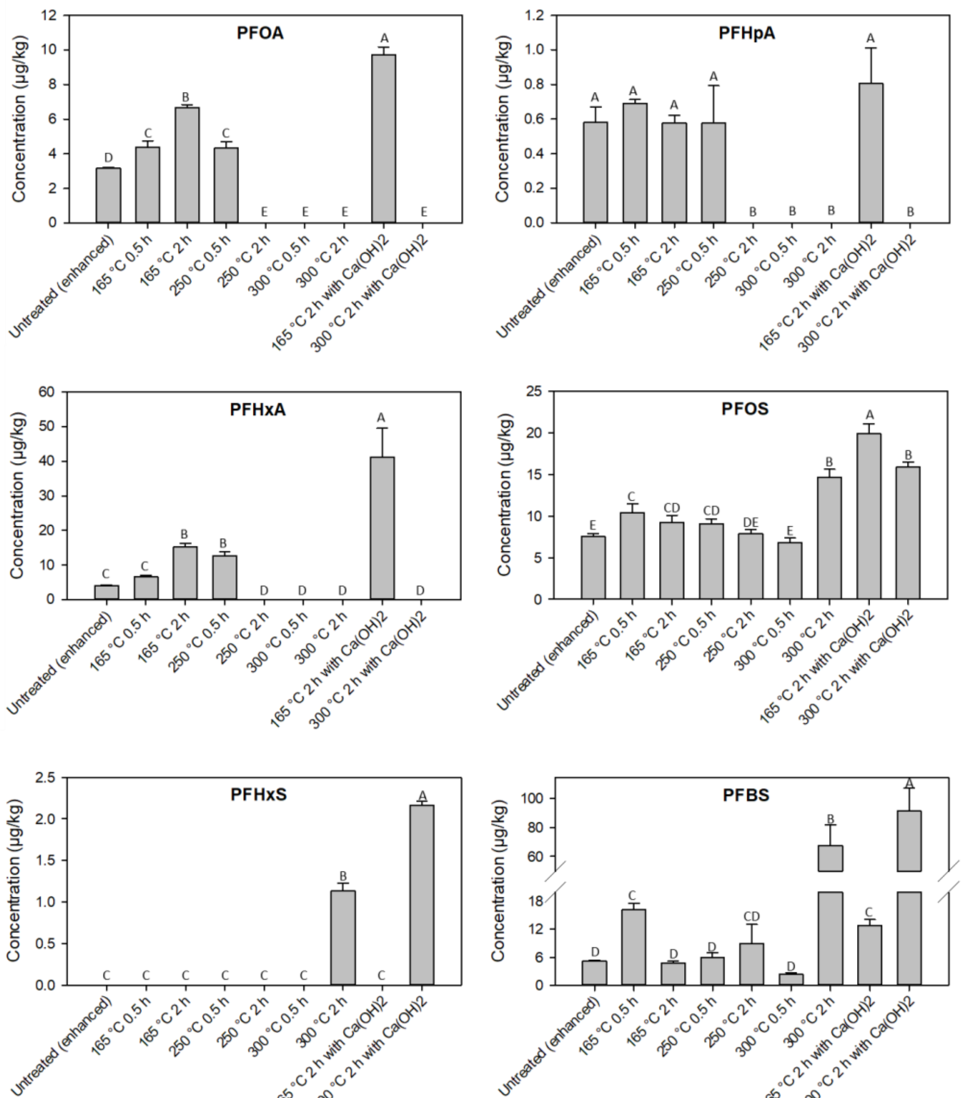
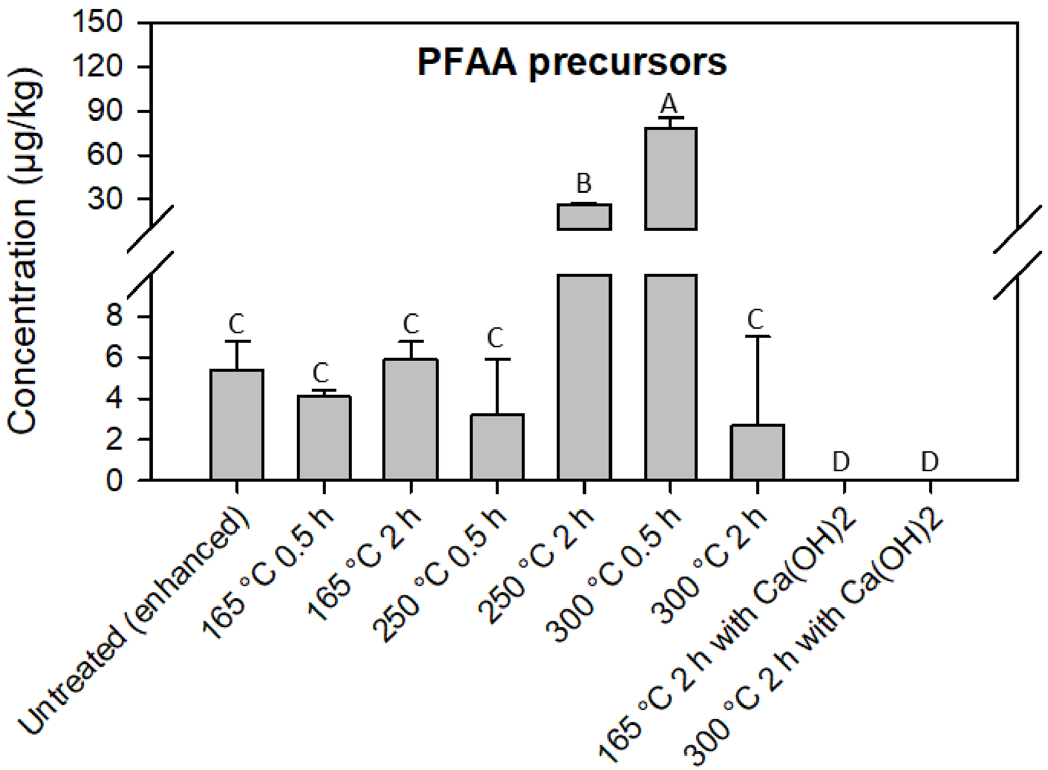
PFAS change due to treatment





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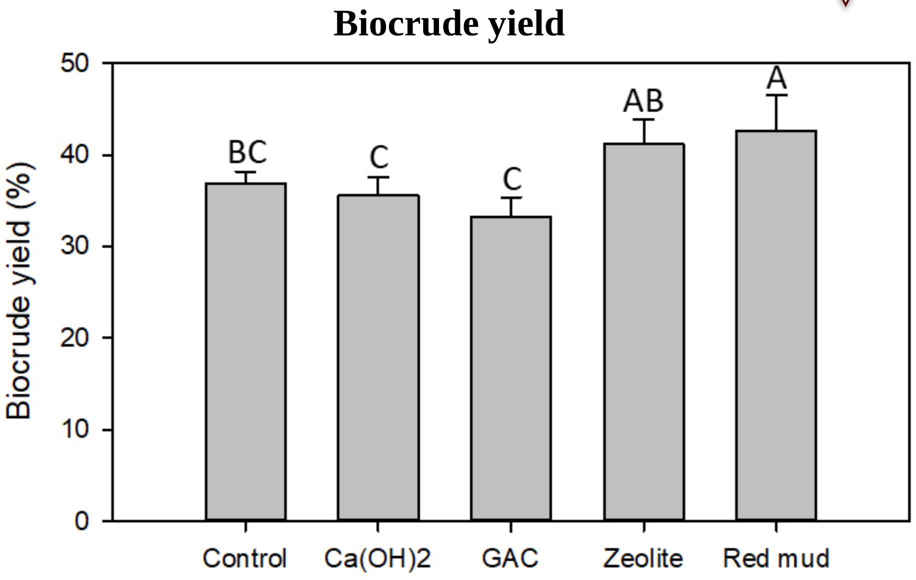
Hydrothermal liquefaction of PFAS in sludge

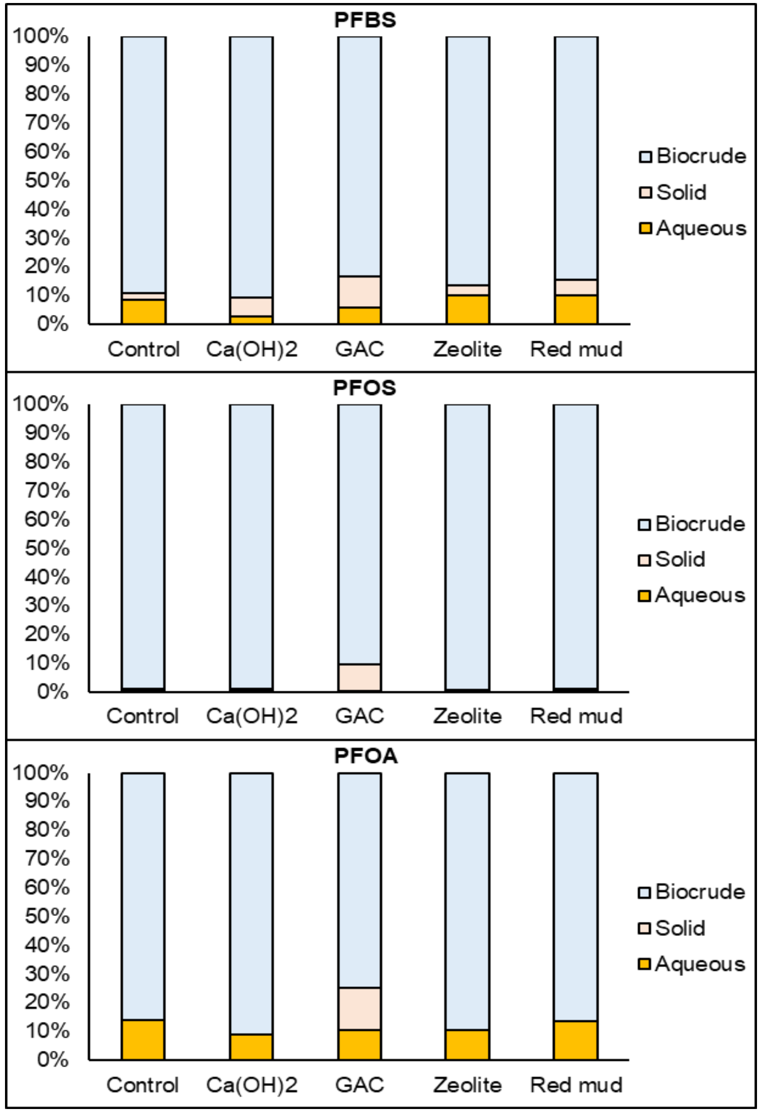
PFBS
PFOS
PFOA
150 µg/kg

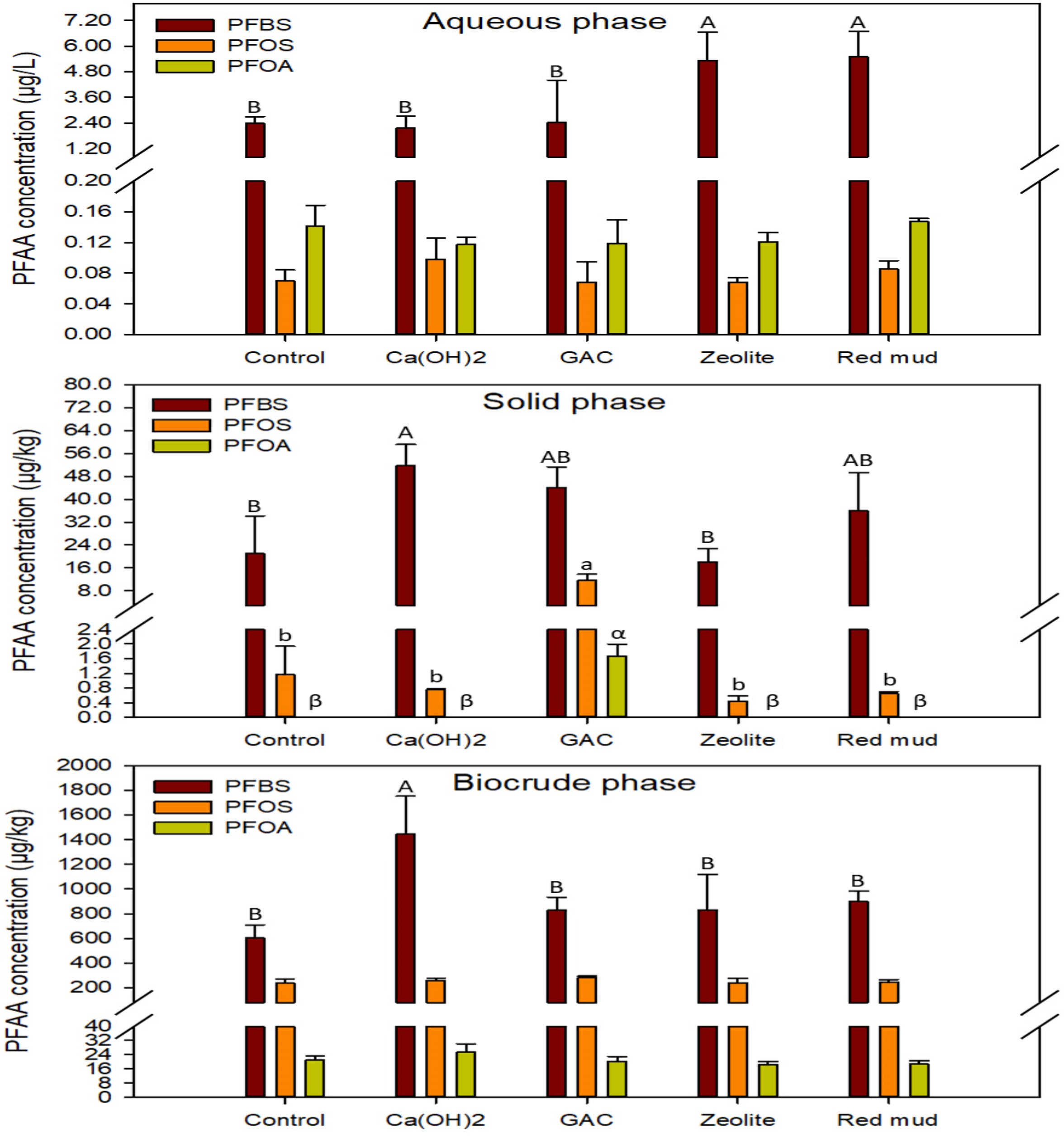
300 °C
2 h



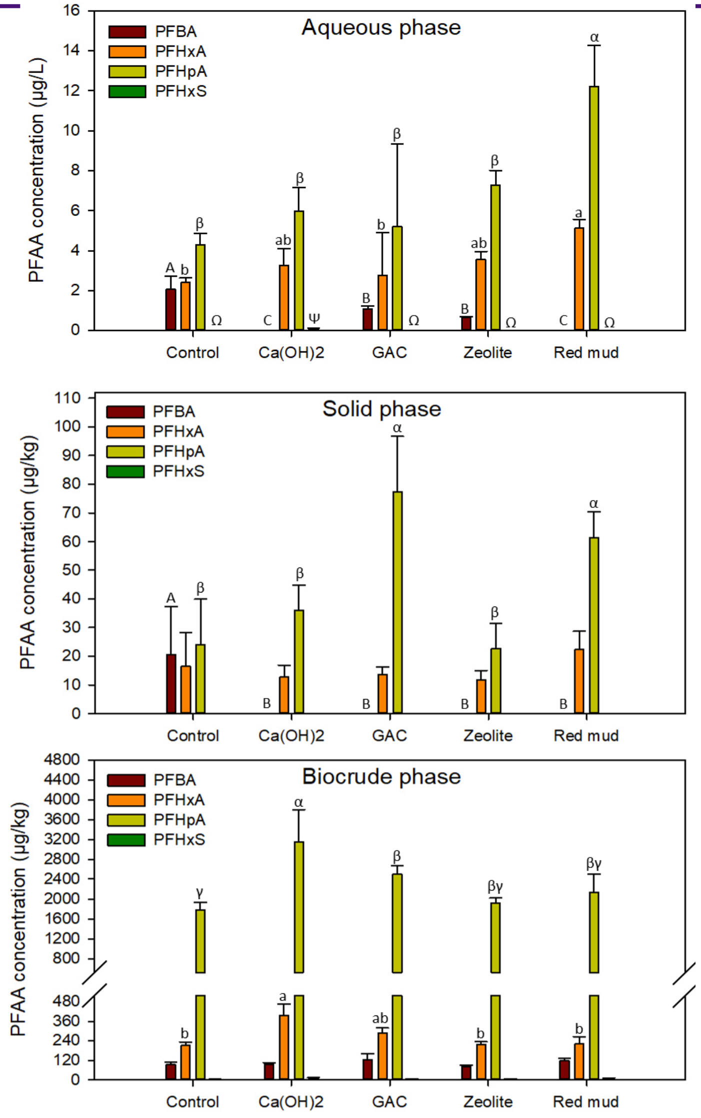
Zhang, W.L., **Liang. Y-N.** 2021. Hydrothermal liquefaction of sewage sludge – effect of four reagents on relevant parameters related to biocrude and PFAS. Journal of Environmental Chemical Engineering. 10 (1), 107092.

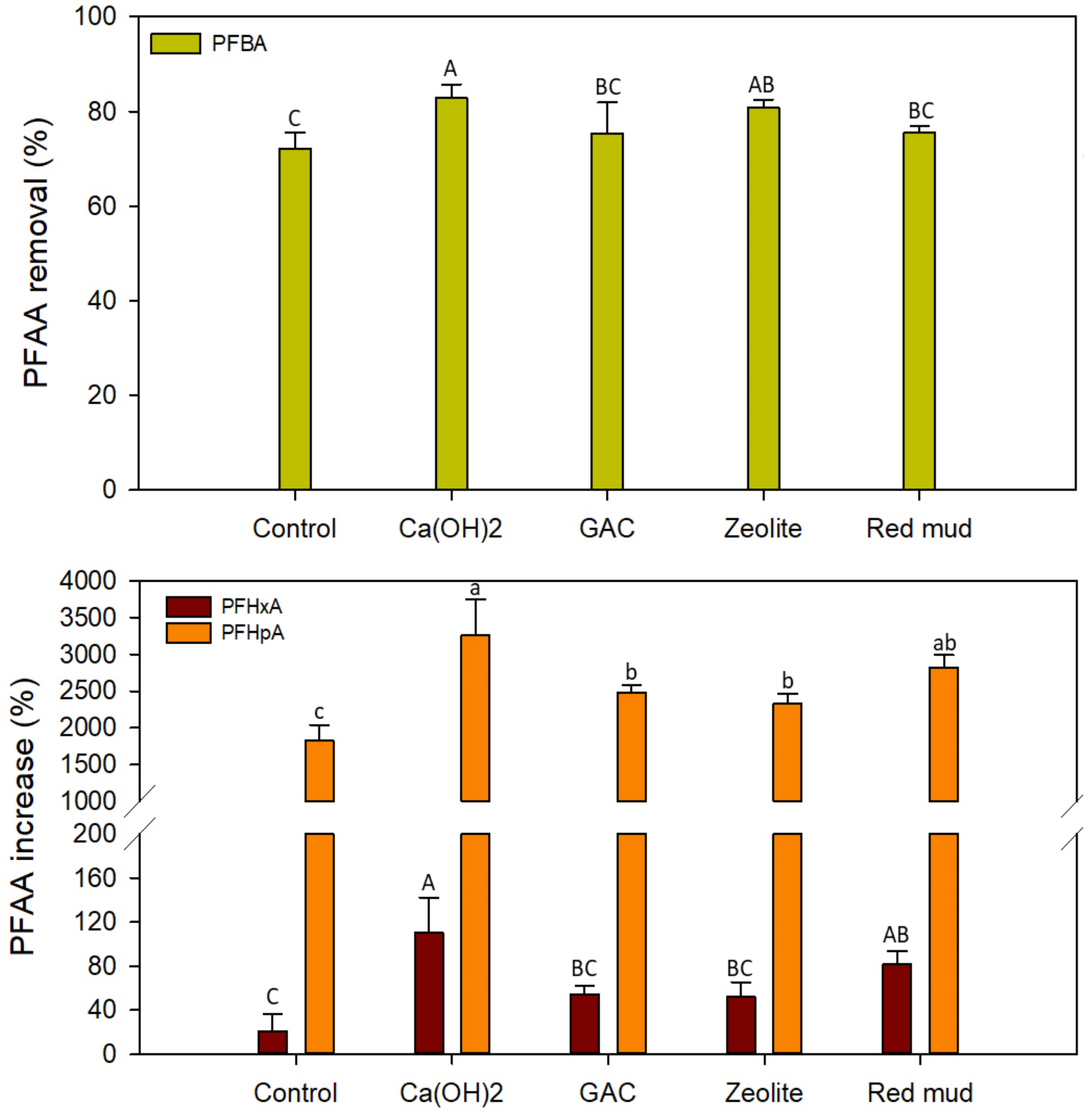
PFAS distribution after HTL



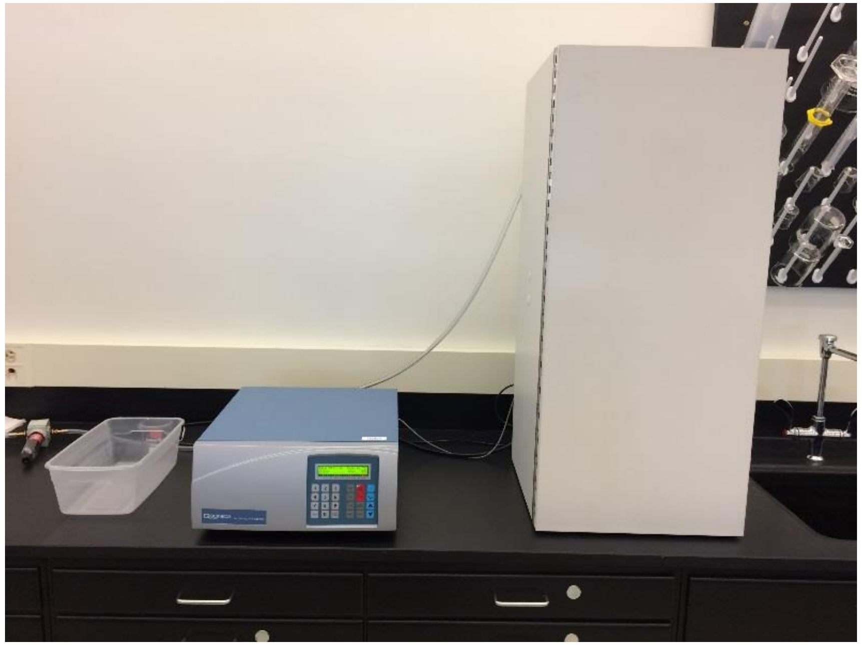


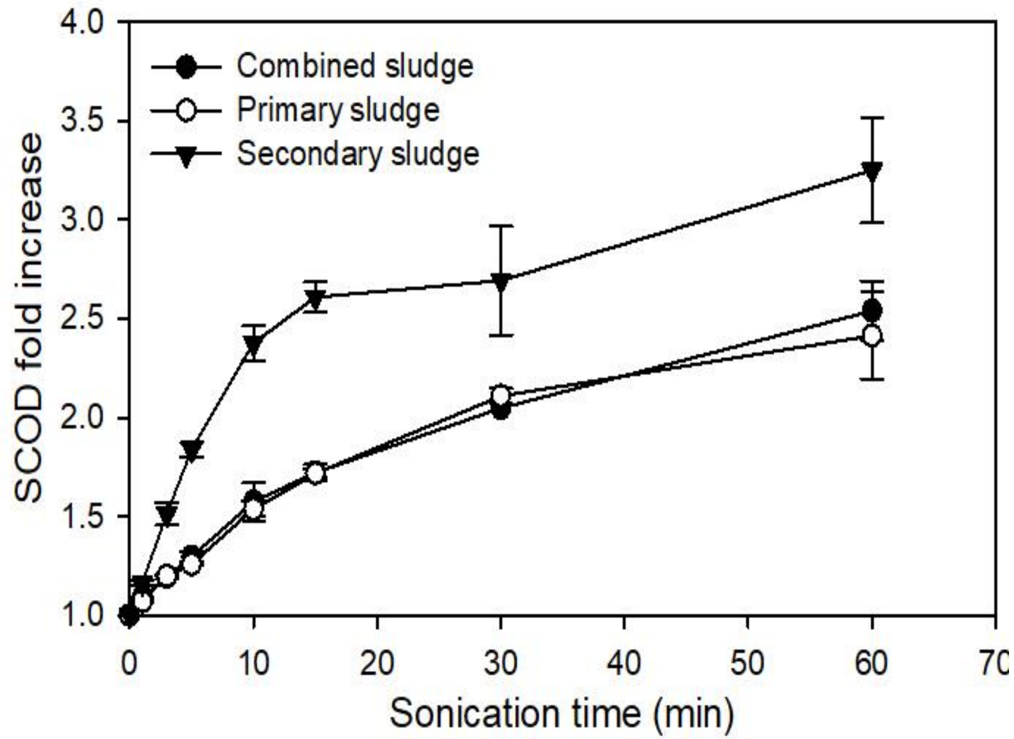
Other non-spiked PFAS





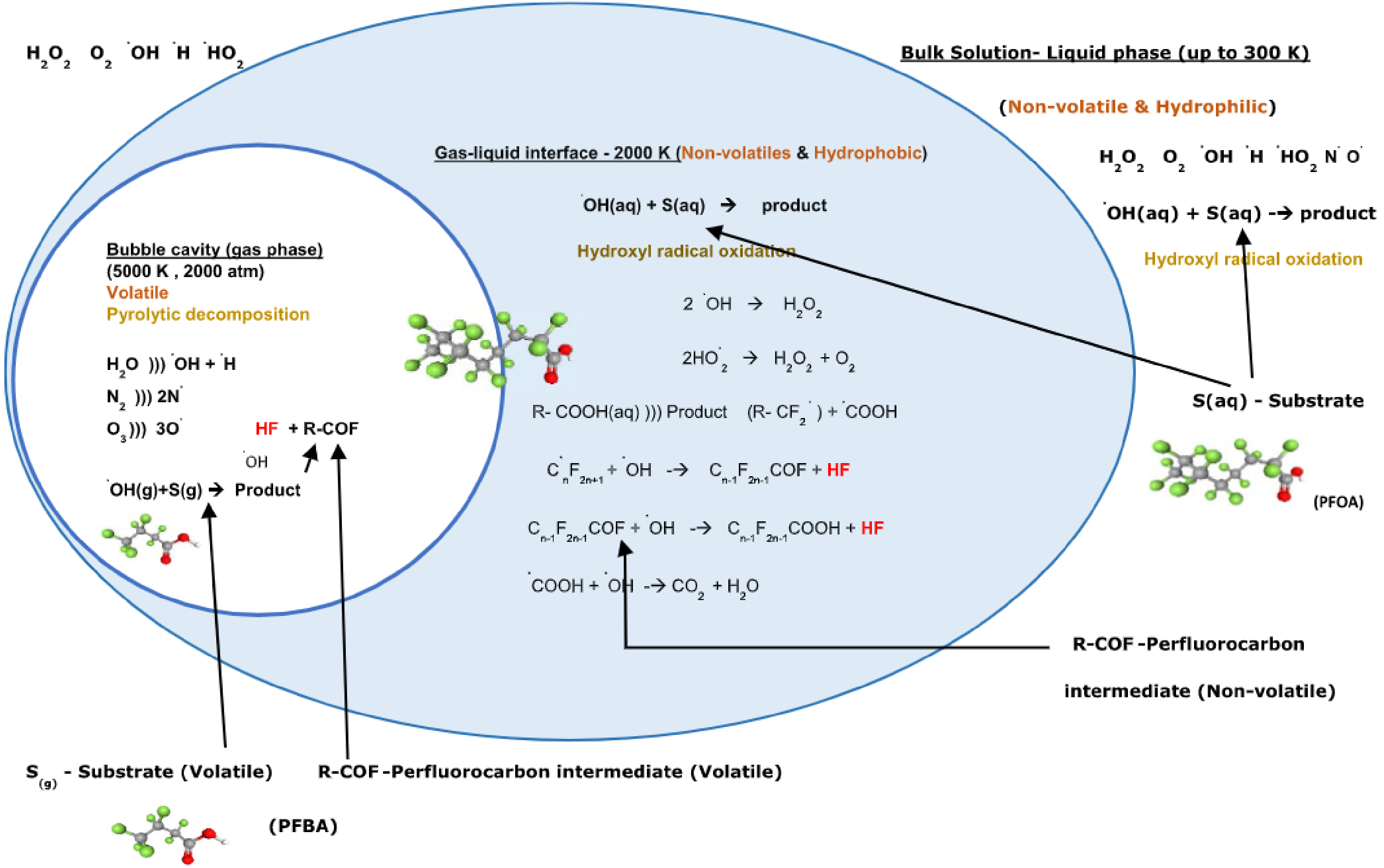
Sonication for enhancing sludge digestibility





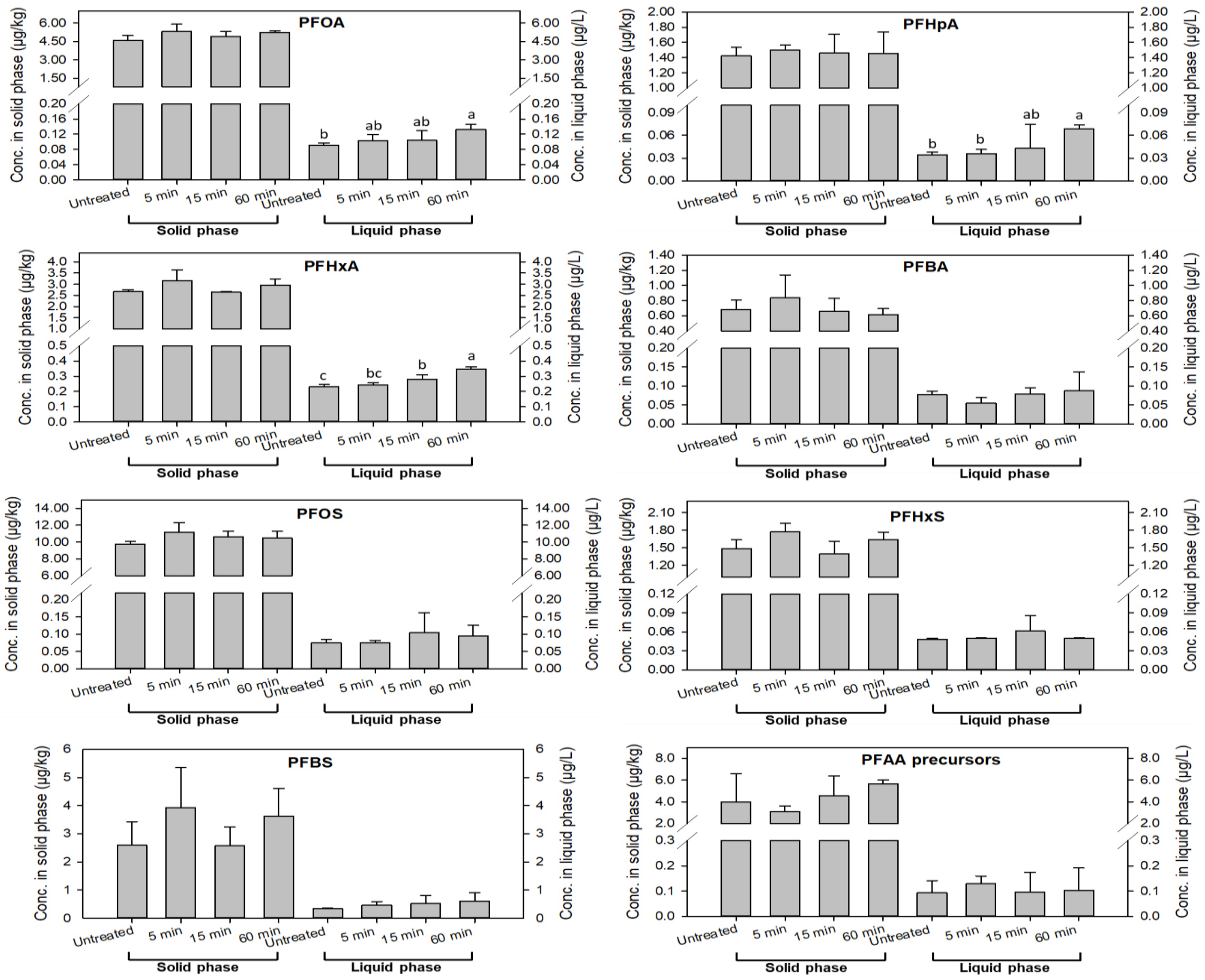
Ultrasonication for PFAS destruction

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.

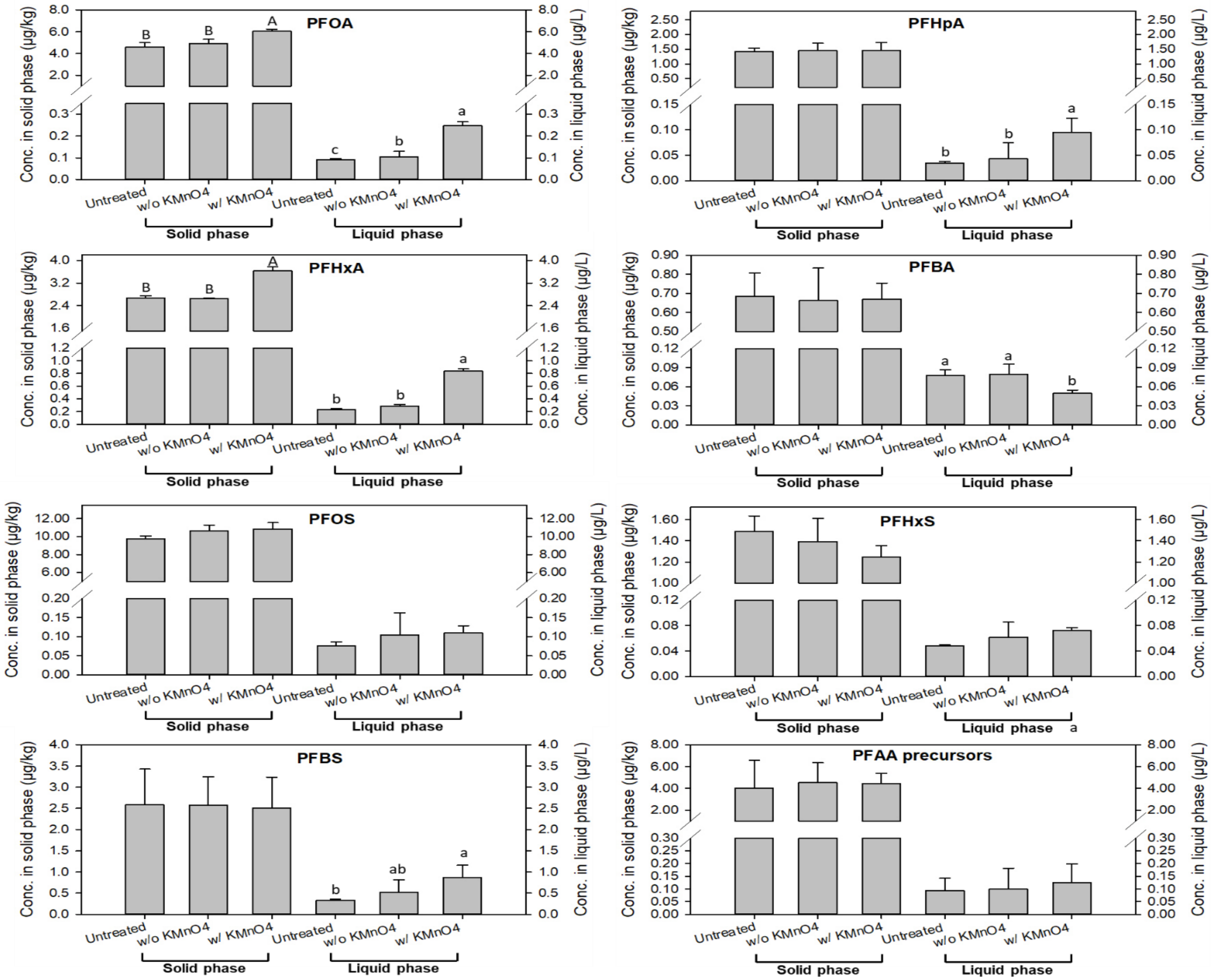
Sonication: time effect on PFAAs and precursors



- 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.

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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Take home message

- More unknowns than what are known.
- Characterization of PFAS precursors.
- Change, transformation of precursors during treatment.
- Innovative sludge treatment/handling needed.

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