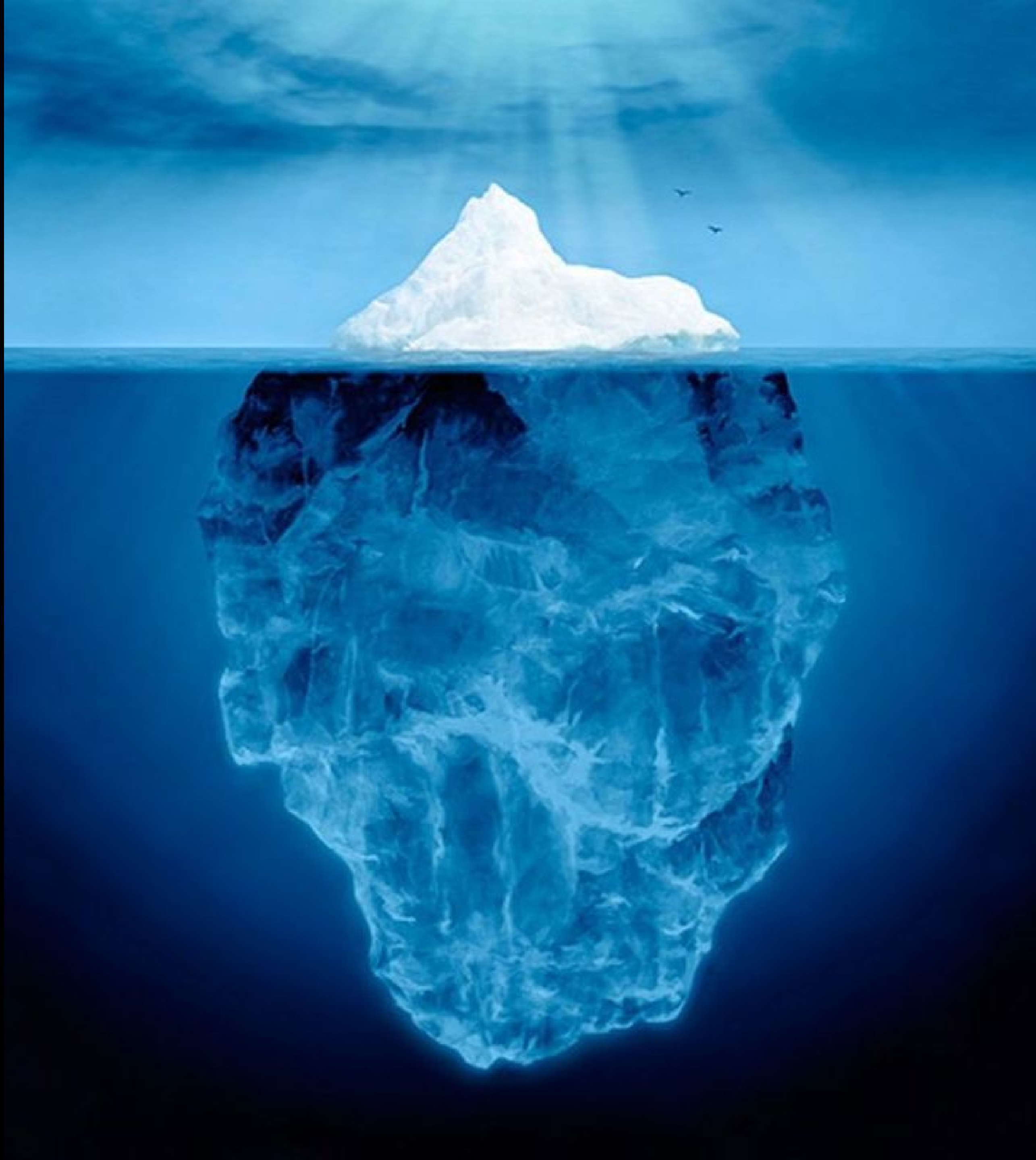
What do we know about PFAS?



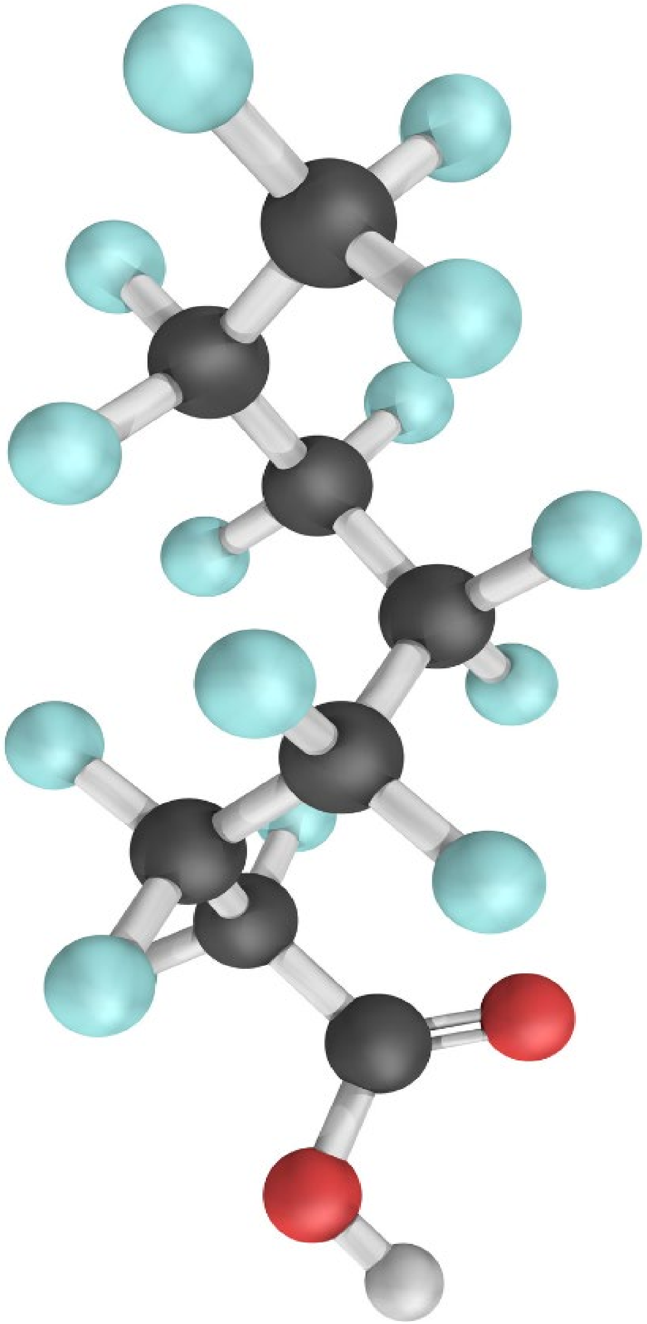
→ **Zhiyong Xia, Ph.D.**

National PFAS Technical Leader
GHD Inc., Bowie, MD

Oct. 26, 2023

Agenda

- PFAS structure and properties
- Regulations
- Mobility
- Testing
- Treatment technologies
- Summary



Where PFAS are found?

- AFFF, C6 for fire-fighting

- Clothing and carpets
- Outdoor textiles and sporting equipment

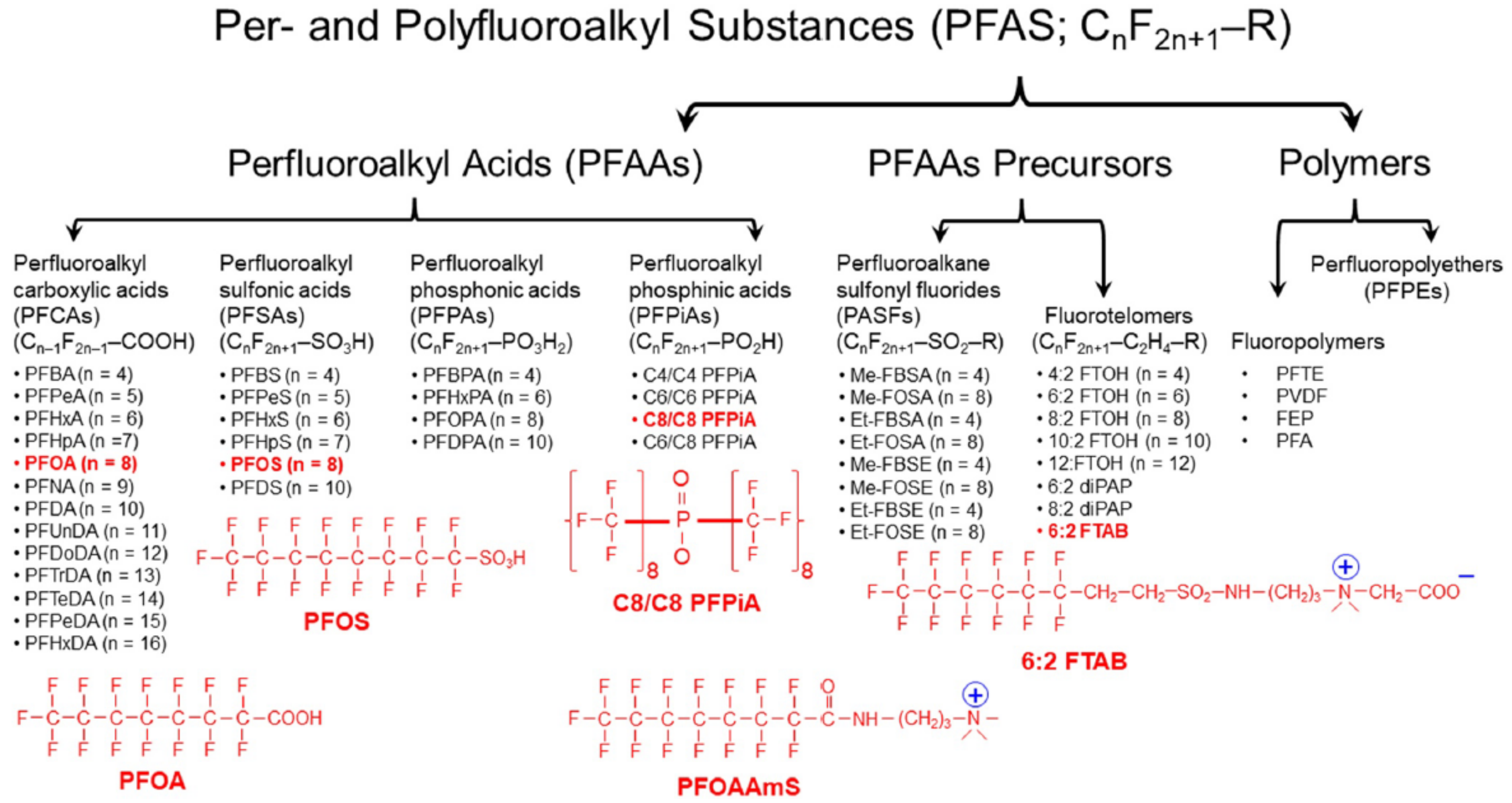
- Cleaning agents and fabric softeners
- Polishes and waxes, latex paints
- Ski and snowboarding waxes

- Pesticides and herbicides
- Hydraulic fluids
- Windshield wipers

- Non-stick cookware
- Polymer films
- Some bottled water
- Dental floss
- Food packaging

PFAS: per-, polyfluoroalkyl substances

> 12,000 identified



Per- and Polyfluoroalkyl Substances (PFAS; C_nF_{2n+1}–R)

Perfluoroalkyl Acids (PFAAs)

Perfluoroalkyl carboxylic acids (PFCAs) ($C_{n-1}F_{2n-1}$–COOH)
- PFBA (n = 4)
- PFPeA (n = 5)
- PFHxA (n = 6)
- PFHpA (n =7)
- **PFOA (n = 8)**
- PFNA (n = 9)
- PFDA (n = 10)
- PFUnDA (n = 11)
- PFDoDA (n = 12)
- PFTrDA (n = 13)
- PFTeDA (n = 14)
- PFPeDA (n = 15)
- PFHxDA (n = 16)

Perfluoroalkyl sulfonic acids (PFSAs) (C_nF_{2n+1}–SO_3H)
- PFBS (n = 4)
- PFPeS (n = 5)
- PFHxS (n = 6)
- PFHpS (n = 7)
- **PFOS (n = 8)**
- PFDS (n = 10)

Perfluoroalkyl phosphonic acids (PFPAs) (C_nF_{2n+1}–PO_3H_2)
- PFBPA (n = 4)
- PFHxPA (n = 6)
- PFOPA (n = 8)
- PFDPA (n = 10)

Perfluoroalkyl phosphinic acids (PFPiAs) (C_nF_{2n+1}–PO_2H)
- C4/C4 PFPiA
- C6/C6 PFPiA
- **C8/C8 PFPiA**
- C6/C8 PFPiA

PFAAs Precursors

Perfluoroalkane sulfonyl fluorides (PASFs) (C_nF_{2n+1}–SO_2–R)
- Me-FBSA (n = 4)
- Me-FOSA (n = 8)
- Et-FBSA (n = 4)
- Et-FOSA (n = 8)
- Me-FBSE (n = 4)
- Me-FOSE (n = 8)
- Et-FBSE (n = 4)
- Et-FOSE (n = 8)

Fluorotelomers (C_nF_{2n+1}–C_2H_4–R)
- 4:2 FTOH (n = 4)
- 6:2 FTOH (n = 6)
- 8:2 FTOH (n = 8)
- 10:2 FTOH (n = 10)
- 12:FTOH (n = 12)
- 6:2 diPAP
- 8:2 diPAP
- **6:2 FTAB**

Polymers

Fluoropolymers
- PFTE
- PVDF
- FEP
- PFA

Perfluoropolyethers (PFPEs)

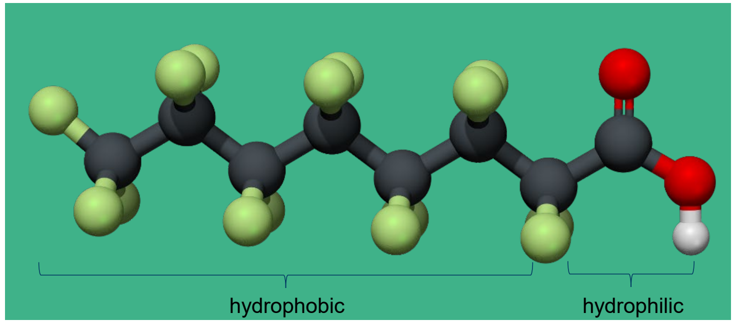
Figure 1. Per- and polyfluoroalkyl substances (PFASs) family tree including perfluoroalkyl acids (PFAAs), PFAA precursors (e.g., perfluoroalkane sulfonyl fluorides and fluorotelomers), and polymers (e.g., fluoropolymers and perfluoropolyethers). PFAAs include perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonic acids, perfluoroalkyl phosphonic acids (PFPAs), perfluoroalkyl phosphinic acids, perfluoroalkyl ether carboxylic acids , and perfluoroether sulfonic acids. Molecular structures of typical PFAS compounds (in red) including anionic PFOA and perfluorooctanesulfonic acid, C8/C8 PFPiA, cationic perfluoroctaneamido ammonium iodide, and zwitterionic 6:2 fluorotelomer sulfonamide alkylbetaine are highlighted.

Reviews of Geophysics 2022, 60, e2021RG000765. https://doi.org/10.1029/2021RG000765

PFAS have unique properties

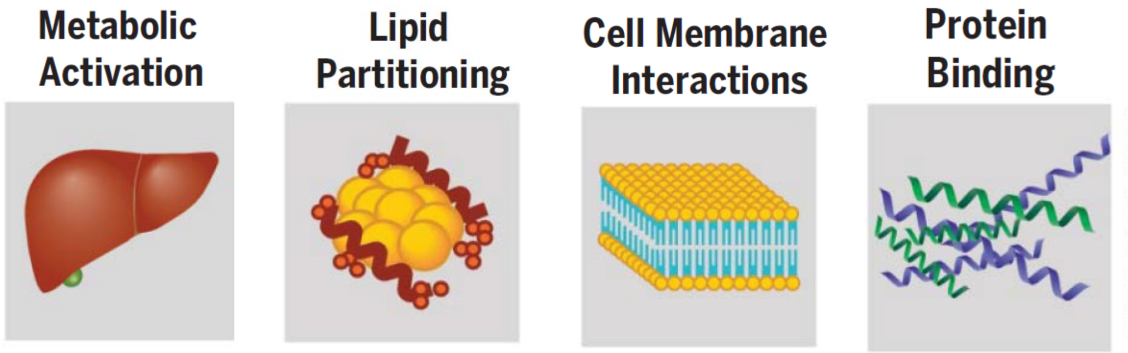
‘Smart’ Chemicals

- Extremely stable, and change as they go
- The soil water partition coefficient increases with the molecular weight
- There is a range of size, functionality, structure
  - Terminal compounds:
    - Low vapor pressure, soluble in water not a candidate for long range transport
  - Precursors compounds:
    - Volatile and can travel long distance in the atmosphere
    - Textile coatings, paper packaging, AFFF
- Conventional technology does not treat PFAS well



Why PFAS are particularly concerning?

- Ubiquitous, used since 1940s
- Hard to live without it: household items, industrial products
- Found in air, rain, soil, water, plants, even in artic wildlife
- Move with water, air and soil
- Recalcitrant: tough C-F bond, 485 kJ/mol
- Bioaccumulate (long chain >short chain) and cause health issues



Metabolic Activation

Exposure to precursor compounds result in the formation of terminal acids and sulfonates

Lipid Partitioning

PFAS can transit lipid bilayers and accumulate in tissues

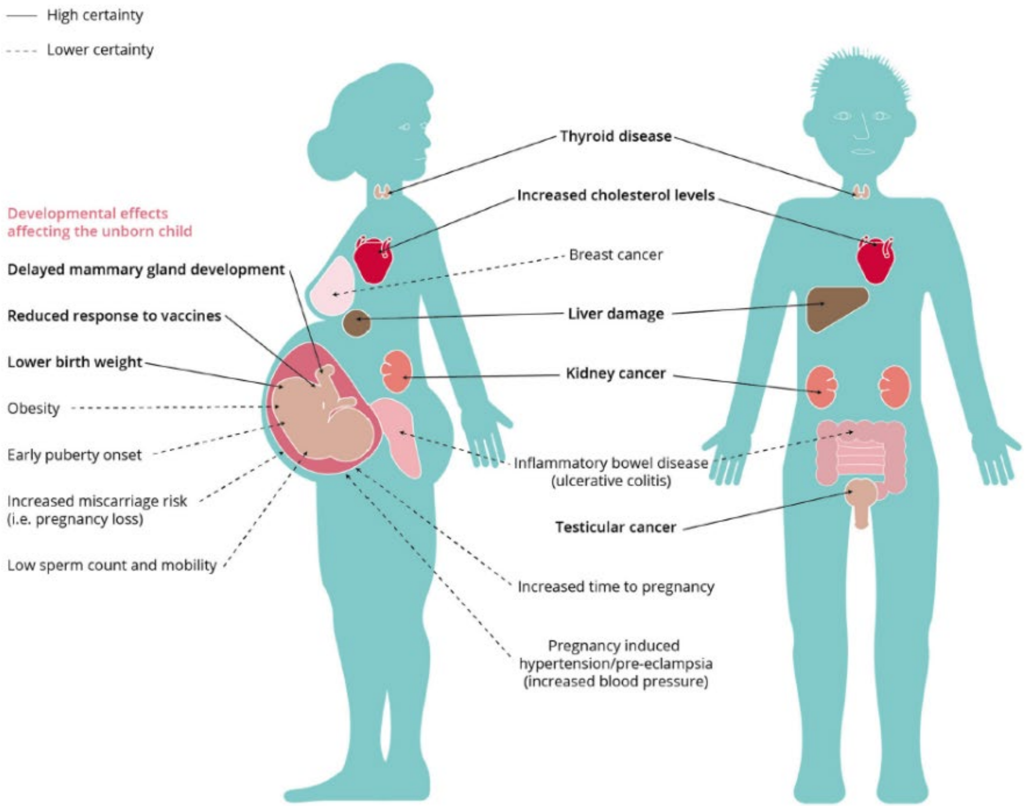
Cell Membrane Interactions

PFAS alter cell membrane potential and integrity changing cytosolic pH

Protein Binding

Protein binding of PFAS help describe bioaccumulation models and hepatotoxicity

Science 375, 512 (2022)



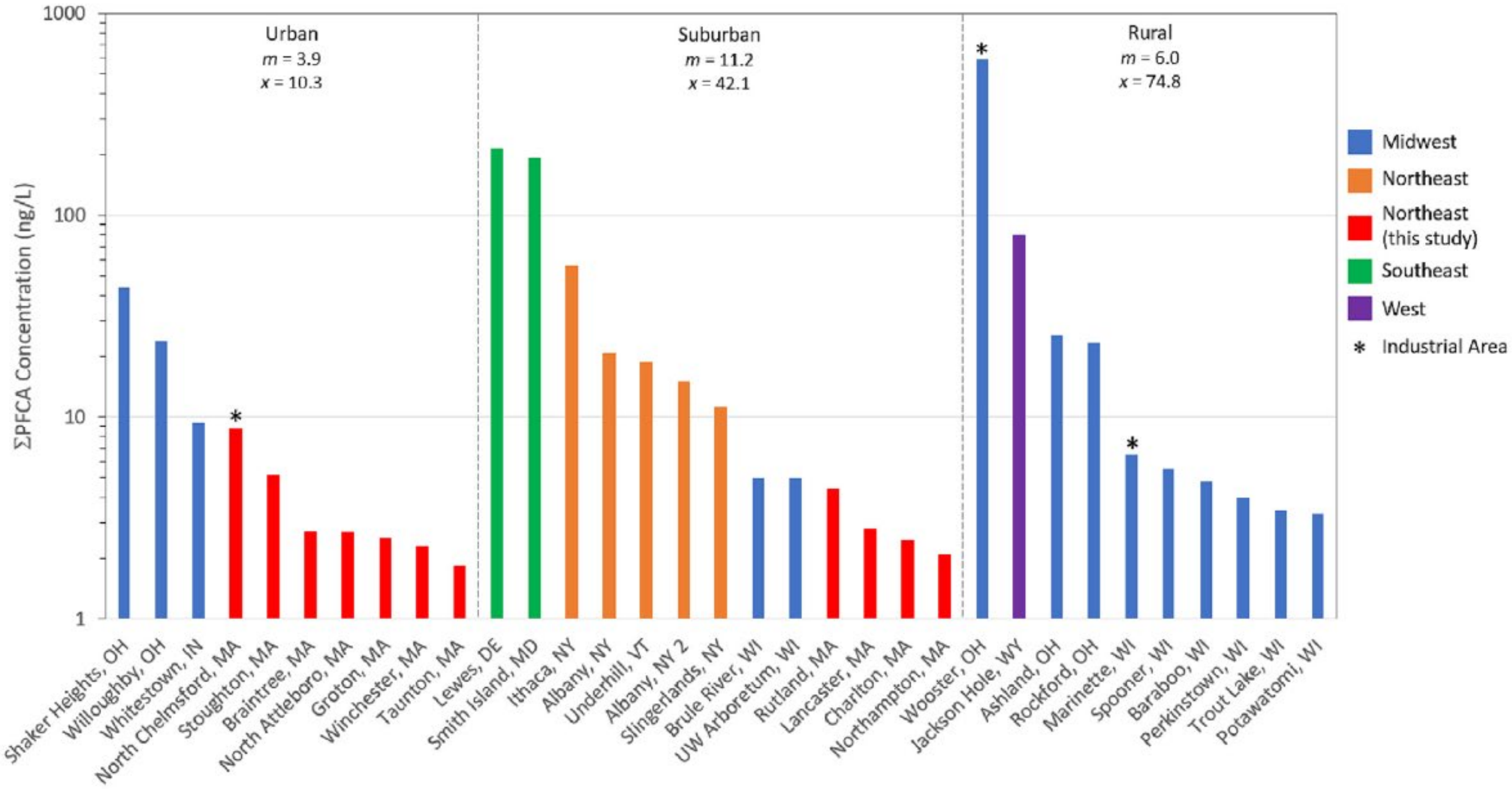
S. E. Fenton, et al. "Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research"

Environ. Toxicol. Chem. 2021, 40, 606–630

PFAS are in the background

North America Precipitation

PFAS= ∑(PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA)



Science of the Total Environment 890 (2023) 164051

PFAS can be made with two major technologies

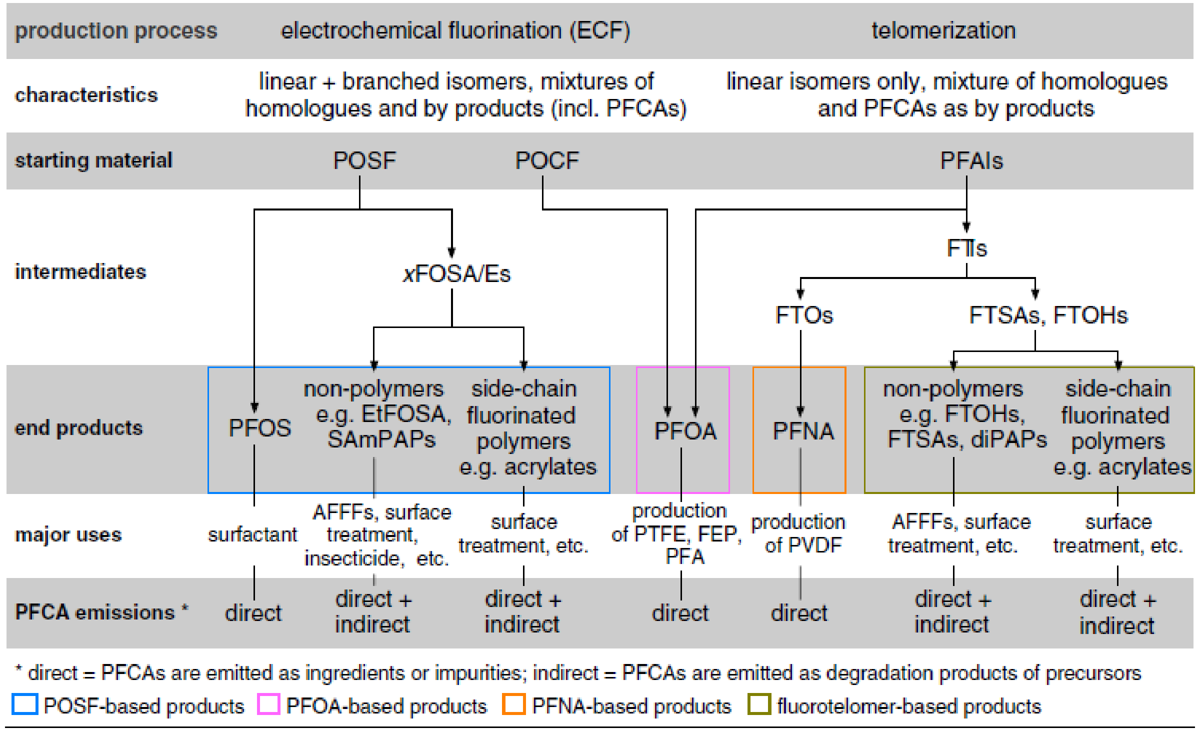
Electrochemical fluorination (ECF)

- 3M first used ECF in late 1940s
- By late 1990s, 3M was making PFAS mainly using ECF.
- Generate **linear and branched isomers**
- Also chain can be **both even and odd length**

Telomerization

- Dupont introduced this in 1942
- Commercial use 1970s and increased significantly in 2000s.
- **Linear isomers**
- **Even chains** as the building bocks are tetrafluoroethylene and ethylene

Octane sulfonyl fluoride electrolysis in anhydrous HF, leading to the replacement of all the H atoms by F atoms



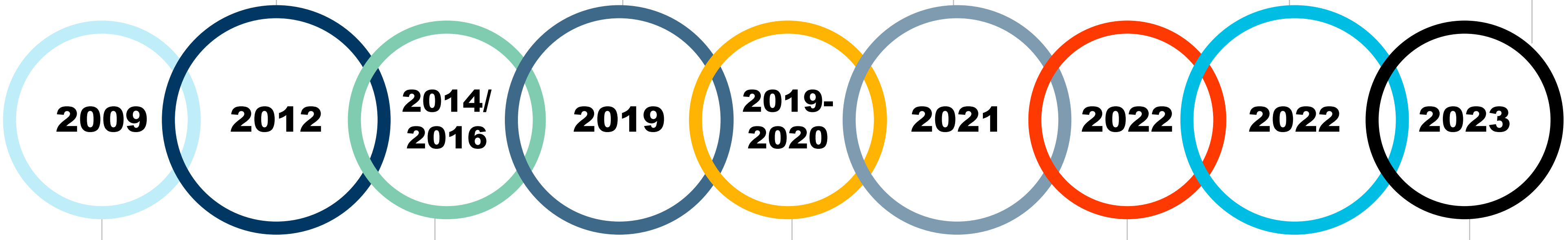
* direct = PFCAs are emitted as ingredients or impurities; indirect = PFCAs are emitted as degradation products of precursors

🟦 POSF-based products 🟪 PFOA-based products 🟧 PFNA-based products 🟩 fluorotelomer-based products

Environment International 70 (2014) 62–75

pentafluoroethyl iodide (PFEI) is reacted with tetrafluoroethylene $CF_2=CF_2$ to yield a mixture of perfluoroalkyl iodides and can react with $CH_2=CH_2$ forming a telomer

PFAS regulations are evolving



2009

US EPA Provisional DW Health Advisory:

PFOA: 400 ppt

PFOS: 200 ppt

2012

UCMR 3 Published

PFAS Minimum RL:
10,000 – 90,000 ppt

2014/ 2016

US EPA Final DW Health Advisory:

PFOA: 70 ppt

PFOS: 70 ppt

2019

States begin banning PFAS containing products

2019-2020

Various US States Develop DW Standards for PFAS

5 – 20 ppt

2021

UCMR 5 Published

PFAS Minimum RL:

2,000 – 8,000 ppt

2022

Interim DW Health Advisory:

- PFOA: 0.004 ppt
- PFOS: 0.02 ppt
- GenX: 10 ppt
- PFBS: 2000 ppt

2022

US EPA Proposes CERCLA 'hazardous substance' PFAS Rule

2023

US EPA finalized TSCA (any) PFAS rule 10/11/23: no minimums and article importers requirement

US EPA DRAFT MCLs:

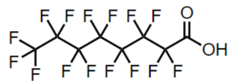
- PFOA: 4 ppt
- PFOS: 4 ppt
- HI = 1 for PFNA, PFHxS, PFBS, GenX

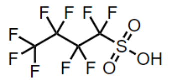
New MCL was proposed on March 2023

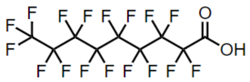
-National Primary Drinking Water Regulation (NPDWR)

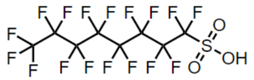
EPA's Proposed Action for the PFAS NPDWR

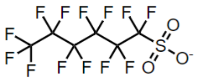
	Compound	Proposed MCLG	Proposed MCL (enforceable levels)
	PFOA	**0 ppt***	**4.0 ppt***
	PFOS	**0 ppt***	**4.0 ppt***
developmental	**PFNA**	**1.0 (unitless) Hazard Index**	**1.0 (unitless) Hazard Index**
thyroid	**PFHxS**		
thyroid	**PFBS**		
liver	**HFPO-DA (commonly referred to as GenX Chemicals)**		

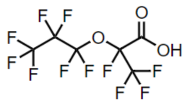

perfluorooctanoic acid (PFOA)

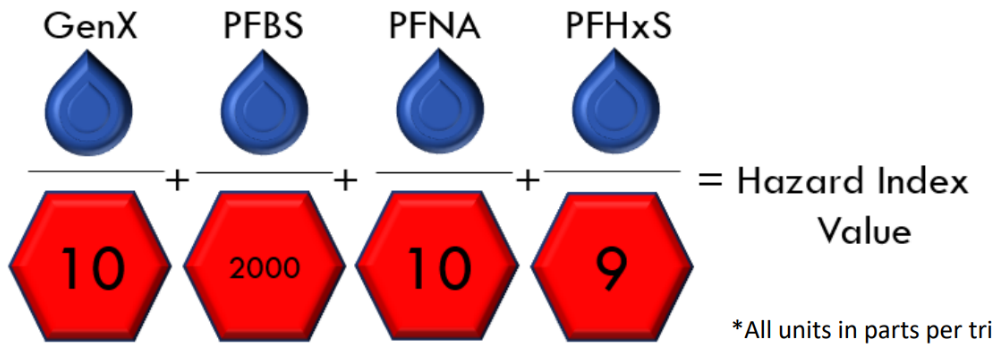

perfluorobutane sulfonic acid (PFBS)


perfluorononanoic acid (PFNA)


perfluorooctanesulfonic acid (PFOS)


perfluorohexane sulfonate (PFHxS)


hexafluoropropylene oxide dimer acid

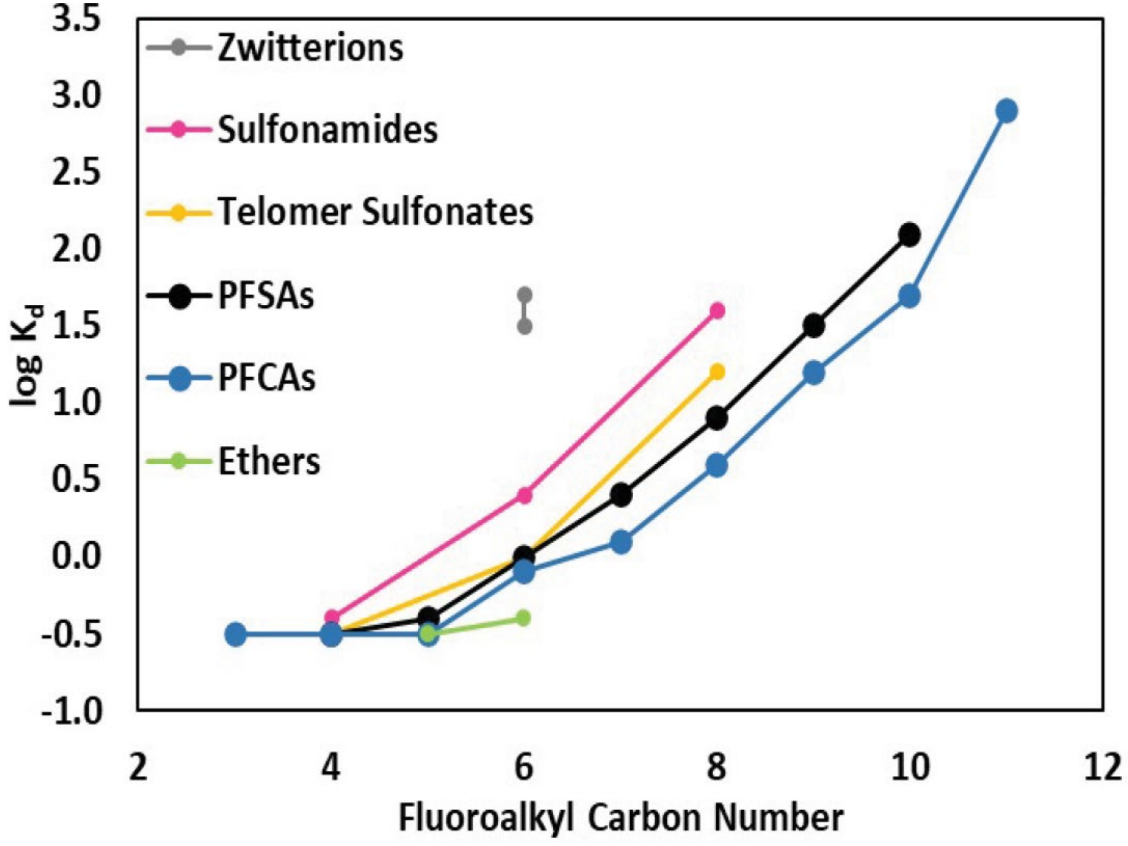


*All units in parts per trillion (ppt)

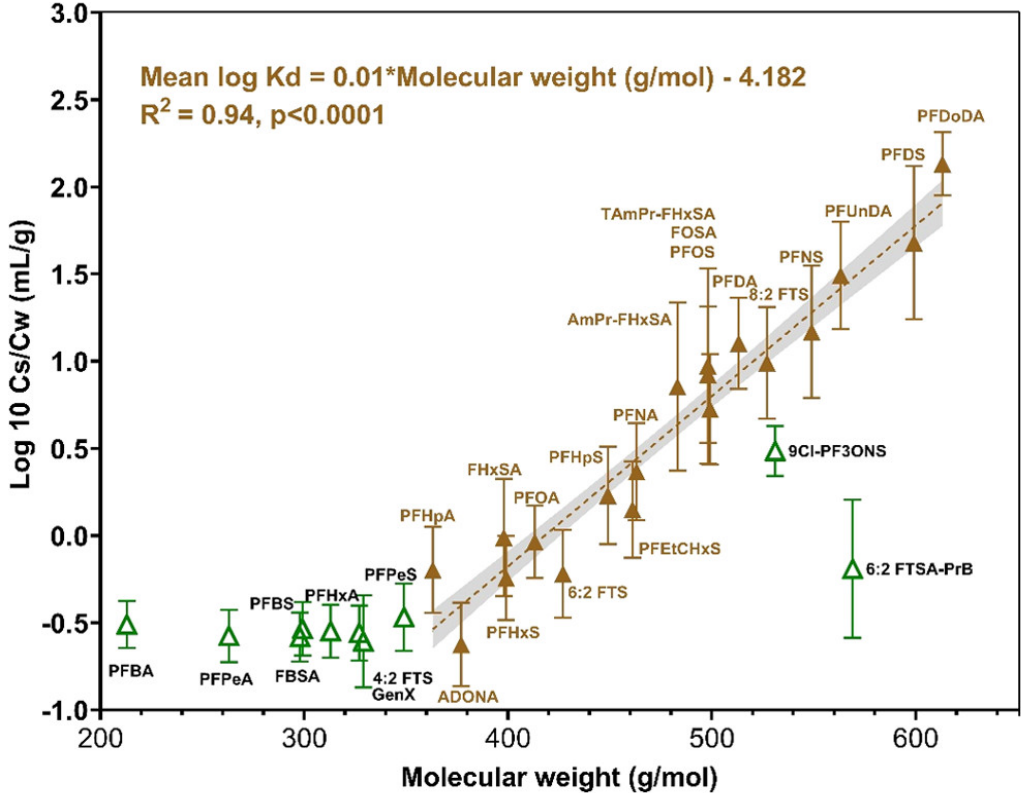
Source: Proposed PFAS National Primary Drinking Water Regulation, March 29, 2023, United States EPA, Office of Water

https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

Mobility decreases with chain length (>C5)



Science 2022, 375, eabg9065



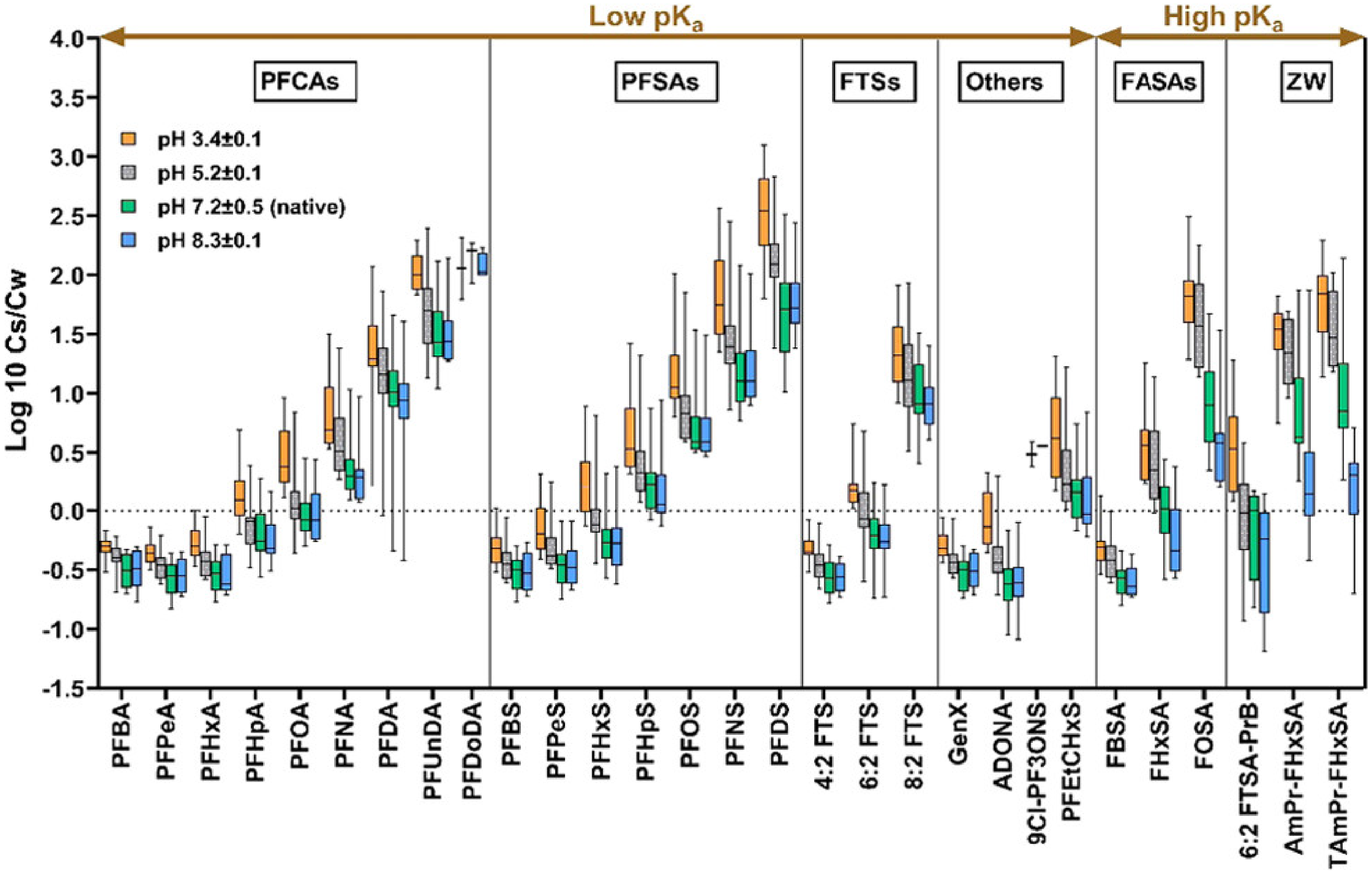
Environ. Sci. Technol. 2020, 54, 15883−15892

pH affects mobility

pKa ≤ 2

pKa > 2)

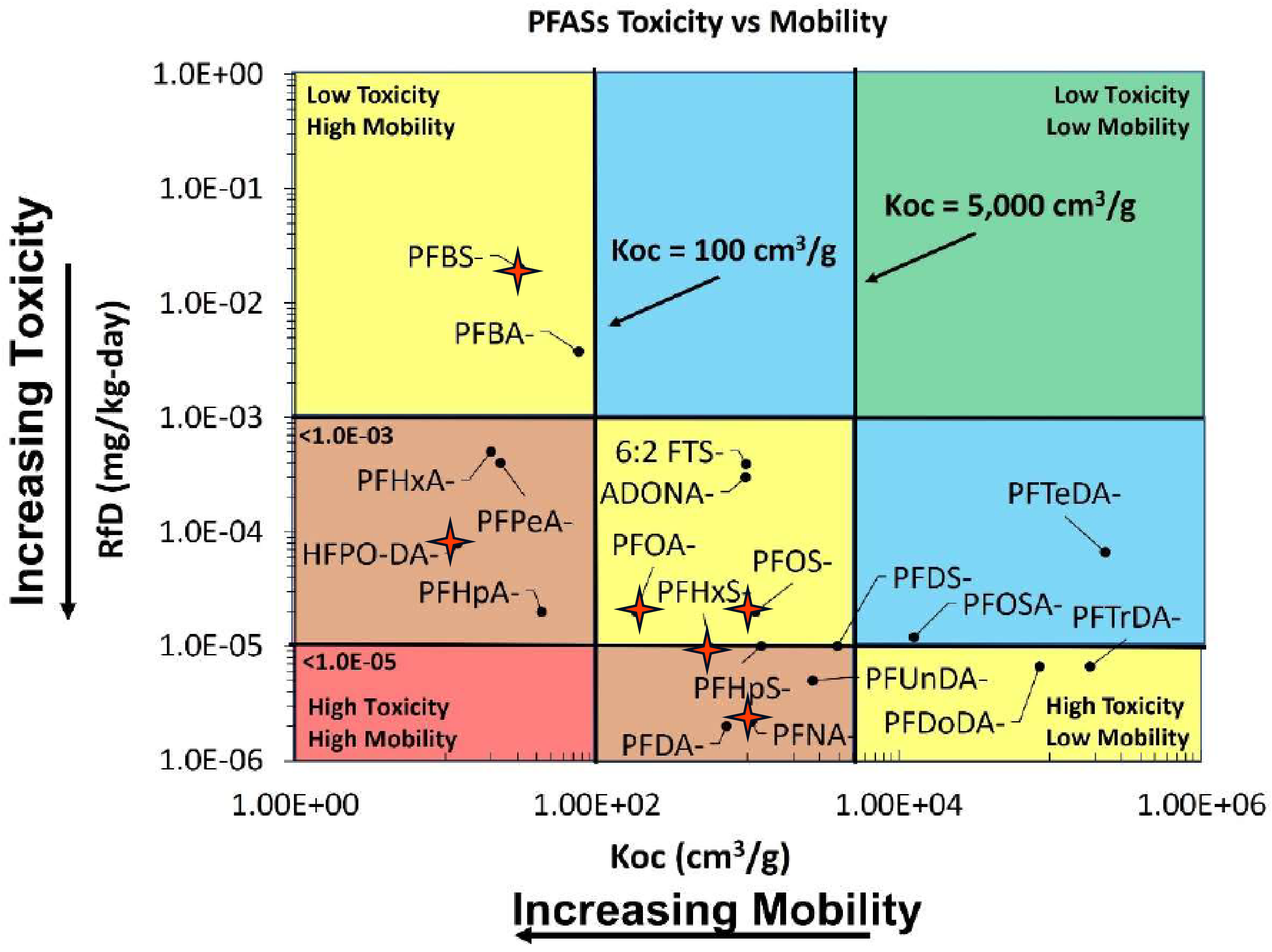
Increasing Mobility



Environ. Sci. Technol. 2020, 54, 15883−15892

- High pH → low Kd (basic condition increases PFAS mobility)
- High pKa PFAS have greater pH dependence

Mobility and toxicity vary with structure



R. Brewer, HIDOH April 2023

PFAS targeted analysis

No.	Name	Name	CASRN	EPA 533 (25 PFAS)	EPA 537.1 (18 PFAS)	Draft EPA 1633 (40 PFAS)
	Perfluoroalkyl carboxylic acids (PFCA)					
1	Perfluorobutanoic acid	PFBA	375-22-4	X		X
2	Perfluoropentanoic acid	PFPeA	2706-90-3	X		X
3	Perfluorohexanoic acid	PFHxA	307-24-4	X	X	X
4	Perfluoroheptanoic acid	PFHpA	375-85-9	X	X	X
5	Perfluorooctanoic acid	PFOA	335-67-1	X	X	X
6	Perfluorononanoic acid	PFNA	375-95-1	X	X	X
7	Perfluorodecanoic acid	PFDA	335-76-2	X	X	X
8	Perfluoroundecanoic acid	PFUnA	2058-94-8	X	X	X
9	Perfluorododecanoic acid	PFDoA	307-55-1	X	X	X
10	Perfluorotridecanoic acid	PFTrDA	72629-94-8		X	X
11	Perfluorotetradecanoic acid	PFTeDA	376-06-7		X	X
	Perfluoroalkyl sulfonic acids (PFSA)					
1	Perfluoropropane sulfonic acid	PFPrS	423-41-6			
2	Perfluorobutane sulfonic acid	PFBS	375-73-5	X	X	X
3	Perfluoropentane sulfonic acid	PFPeS	2706-91-4	X		X
4	Perfluorohexane sulfonate	PFHxS	355-46-4	X	X	X
5	Perfluoroheptane sulfonate	PFHpS	375-92-8	X		X
6	Perfluorooctane sulfonic acid	PFOS	1763-23-1	X	X	X
7	Perfluorononane sulfonic acid	PFNS	68259-12-1			X
8	Perfluorodecane sulfonic acid	PFDS	335-77-3			X
9	Perfluorododecanesulfonic acid	PFDoS	79780-39-5			X
	Perfluoroalkane sulfonamides					
1	Perfluorooctane sulfonamide	FOSA	754-91-6			X
2	N-Methylperfluorooctane sulfonamide	MeFOSA	31506-32-8			X
3	N-Ethylperfluorooctane sulfonamide	EtFOSA	4151-50-2			X
	Perfluorooctane sulfonamide ethanols					
1	N-Methylperfluorooctane sulfonamidoethanol	MeFOSE	24448-09-7			X
2	N-Ethylperfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2			X
	Perfluorooctane sulfonamidoacetic acids					
1	N-Ethylperfluorooctanesulfonamido acetic acid	N-EtFOSAA	2991-50-6		X	X
2	N-Methylperfluorooctanesulfonamido acetic acid	N-MeFOSAA	2355-31-9		X	X
	Fluorotelomer sulfonic acids					
1	1H,1H,2H,2H-Perfluorohexanesulfonic acid	4:2 FTSA	757124-72-4	X		X
2	1H,1H,2H,2H-Perfluorooctanesulfonic acid	6:2 FTSA	27619-97-2	X		X
3	1H,1H,2H,2H-Perfluorodecanesulfonic acid	8:2 FTSA	39108-34-4	X		X
	Per- and Polyfluoroether carboxylic acids					
1	Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	X	X	X
2	4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	X	X	X
3	Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	X		X
4	Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	X		X
5	Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	X		X
	Ether sulfonic acids					
1	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	X	X	X
2	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	X	X	X
3	Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7	X		X
	Fluorotelomer carboxylic acids					
1	3-Perfluoropropyl propanoic acid	3:3 FTCA	356-02-5			X
2	2H,2H,3H,3H-Perfluorooctanoic acid	5:3 FTCA	914637-49-3			X
3	3-Perfluoroheptyl propanoic acid	7:3 FTCA	812-70-4			X

Total Oxidizable Precursor (TOP) assay has limitations

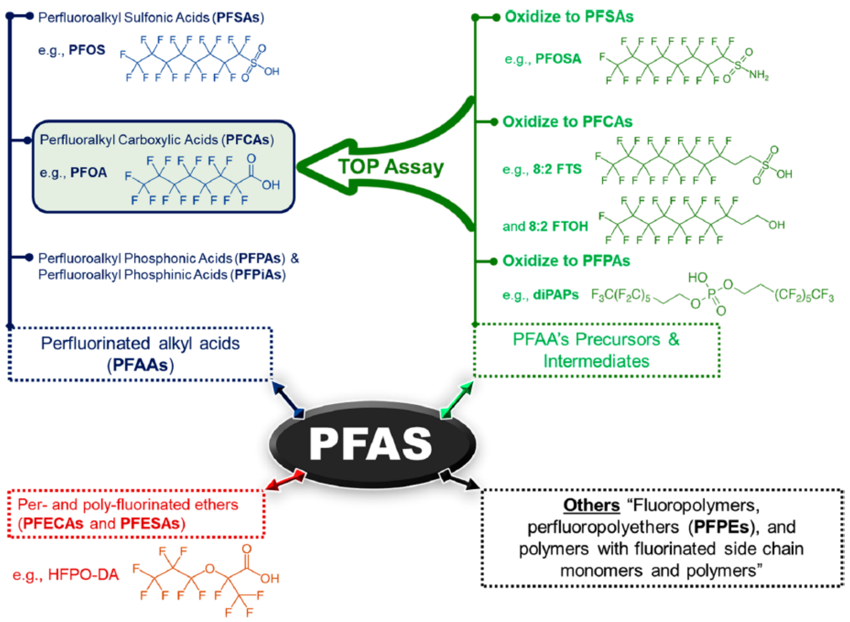
Heat (85°C) and alkaline (pH>13) activated free radical (•OH from persulfate) reaction for converting precursors into terminal products

Sample

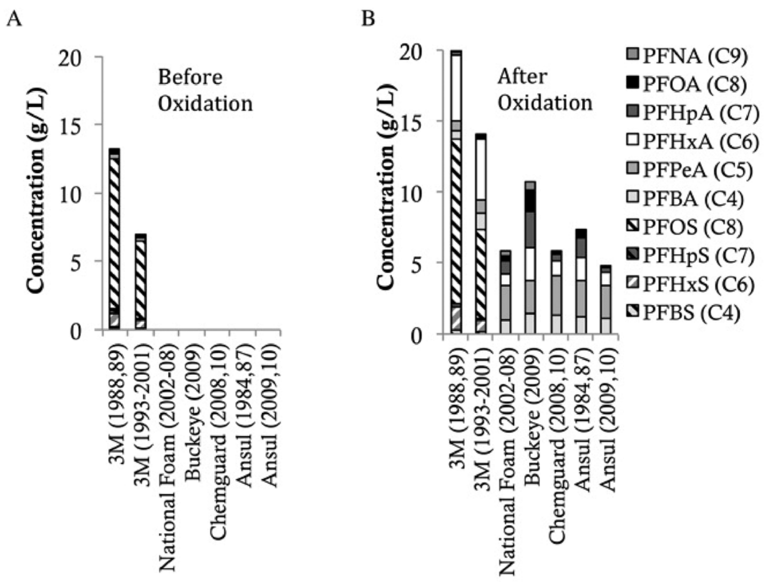
Sample1:
Raw
Targeted analysis
$$\sum_{raw} PFAS$$

Sample 2:
TOP oxidation
Targeted analysis
$$\sum_{TOP} PFAS$$

$$[Precursors] = \sum_{raw} PFAS - \sum_{TOP} PFAS$$



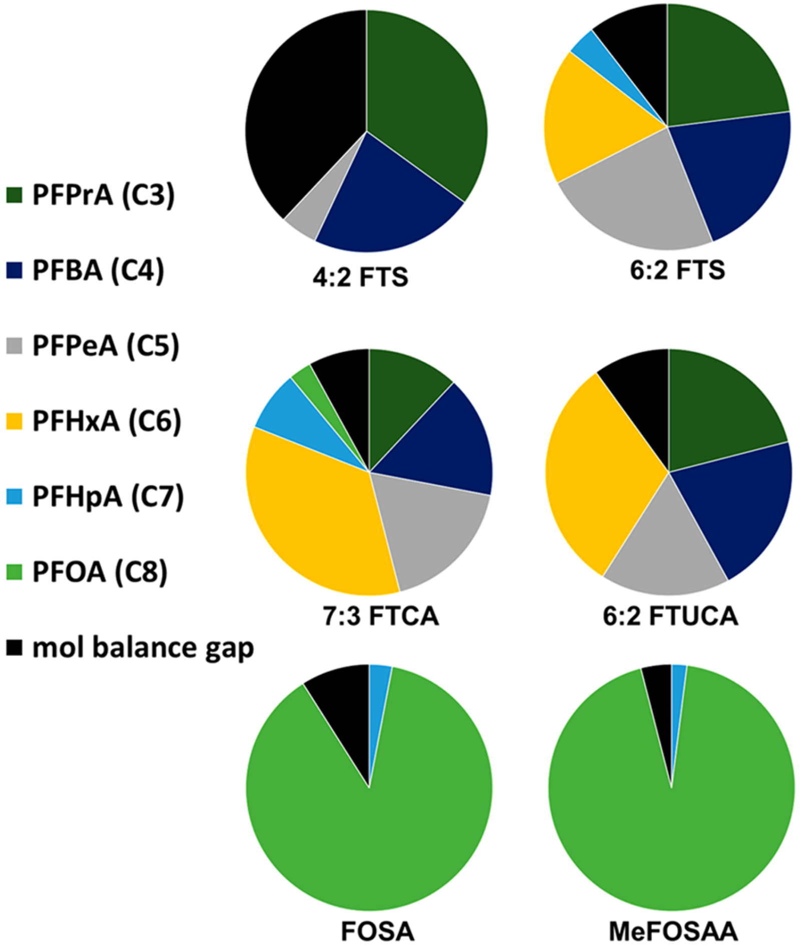
Environ. Sci. Technol. Lett. **2023, 10, 292−301**



Environ. Sci. Technol. **2013, 47, 8187−8195**

TOP can underestimate precursor levels

Ultra short trifluoroacetic acid (TFA) and short perfluoropropionic acid (PFPrA) are not normally measured

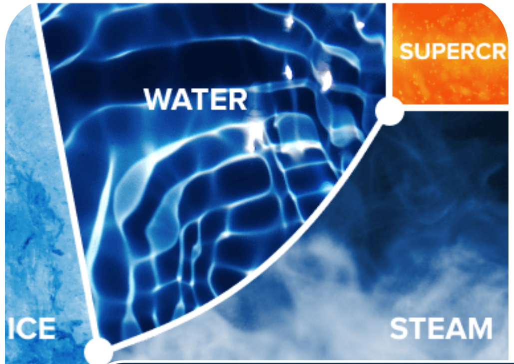


Environ. Sci. Technol. Lett. 2023, 10, 292−301

Current holistic PFAS treatment strategies

Separation
- GAC
- AIX
- FluoroSorb
- Dexsorb

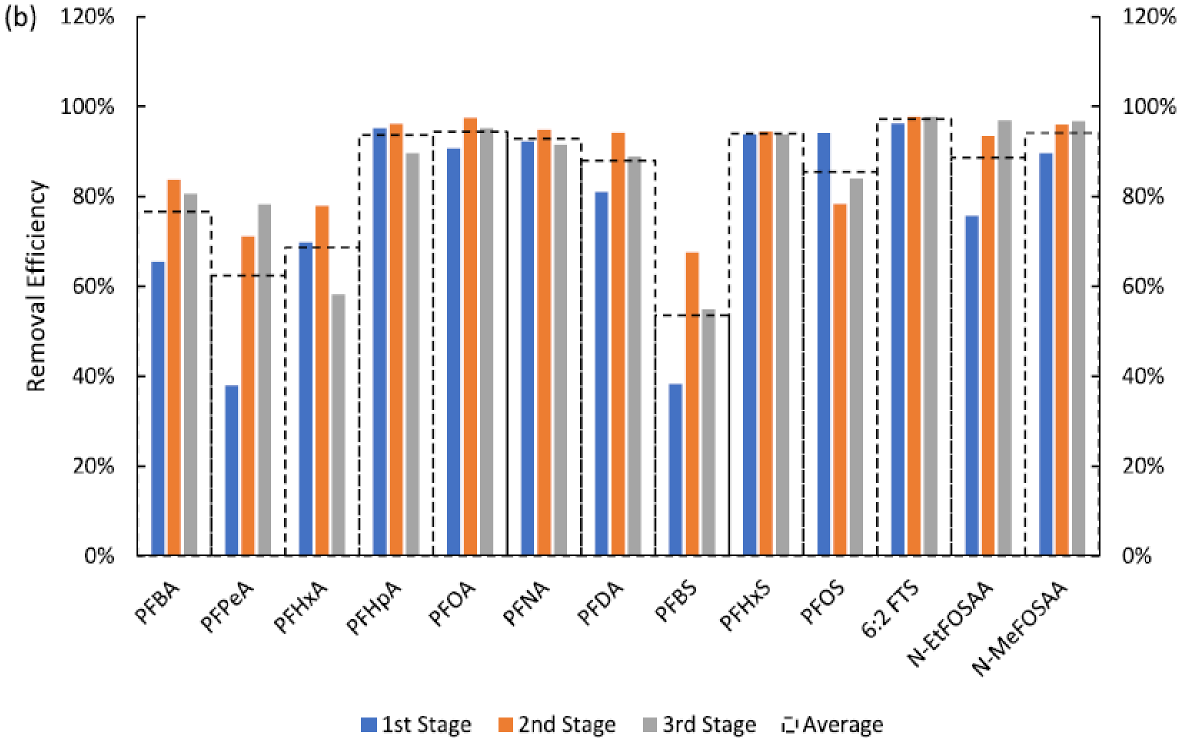
Concentration
- RO
- NF
- Foam fractionation
- Regeneration



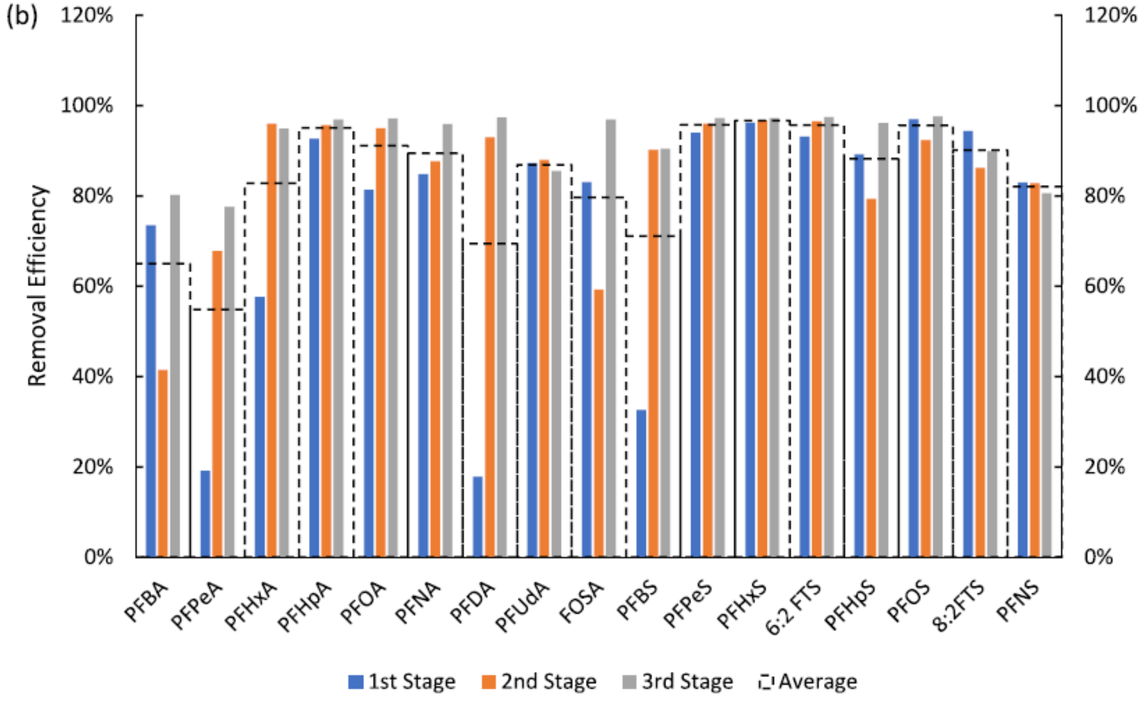
Destruction
- SCWO
- HALT
- EO
- Thermal

Foam fractionation is not effective in removing short chain species

Leachate



AFFF impacted ground water



Chemosphere 311 (2023) 137004

Can we improve membrane performance?

-Molecular dynamics simulations guided ligand design

Adsorption of PFAS onto the CH chain is entropy driven

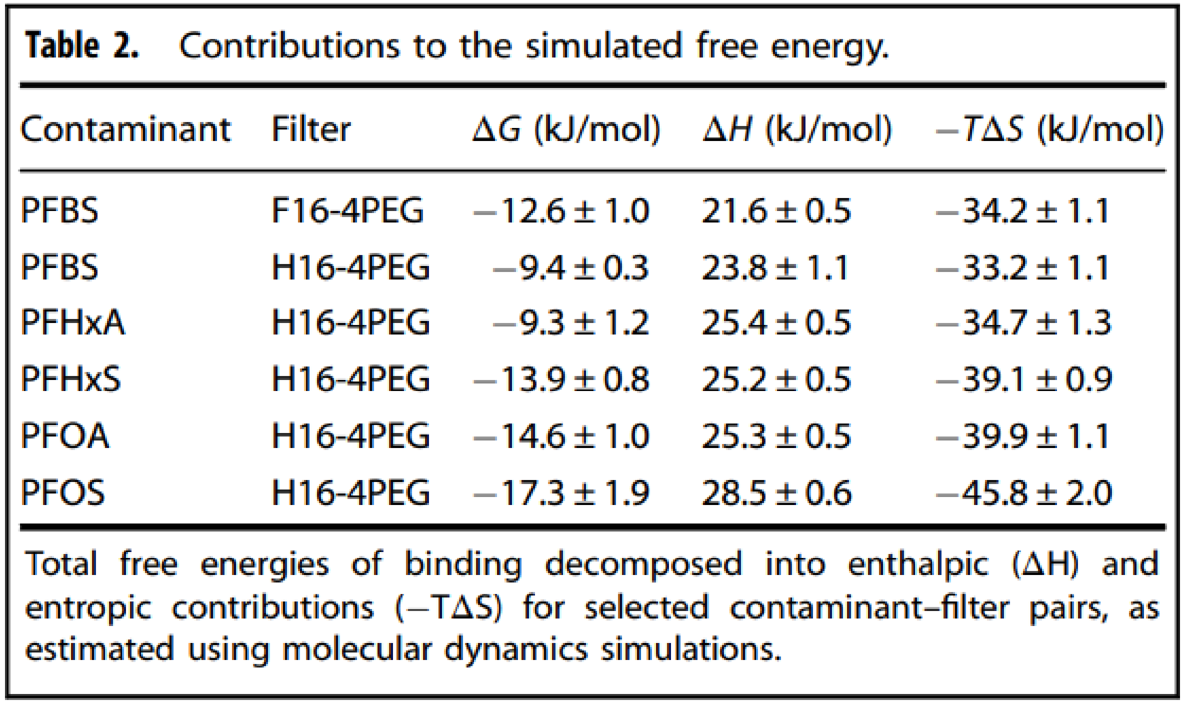
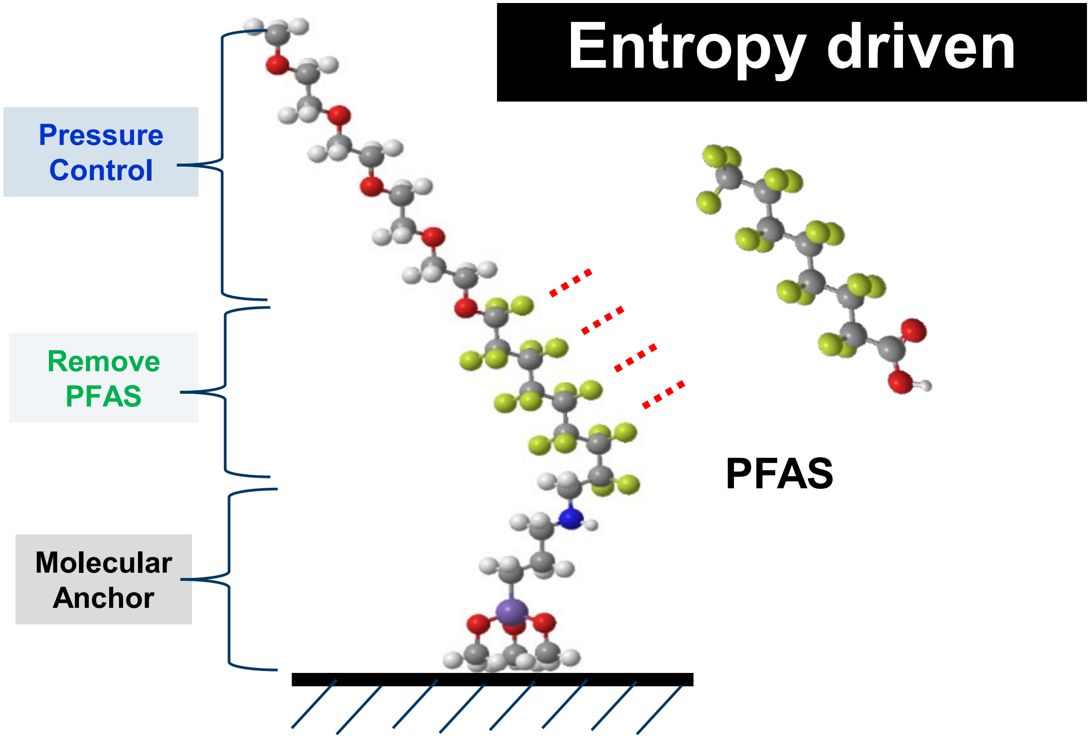


Table 2. Contributions to the simulated free energy.

Contaminant	Filter	ΔG (kJ/mol)	ΔH (kJ/mol)	$-T\Delta S$ (kJ/mol)
PFBS	F16-4PEG	-12.6 ± 1.0	21.6 ± 0.5	-34.2 ± 1.1
PFBS	H16-4PEG	-9.4 ± 0.3	23.8 ± 1.1	-33.2 ± 1.1
PFHxA	H16-4PEG	-9.3 ± 1.2	25.4 ± 0.5	-34.7 ± 1.3
PFHxS	H16-4PEG	-13.9 ± 0.8	25.2 ± 0.5	-39.1 ± 0.9
PFOA	H16-4PEG	-14.6 ± 1.0	25.3 ± 0.5	-39.9 ± 1.1
PFOS	H16-4PEG	-17.3 ± 1.9	28.5 ± 0.6	-45.8 ± 2.0

Total free energies of binding decomposed into enthalpic (ΔH) and entropic contributions ($-T\Delta S$) for selected contaminant–filter pairs, as estimated using molecular dynamics simulations.

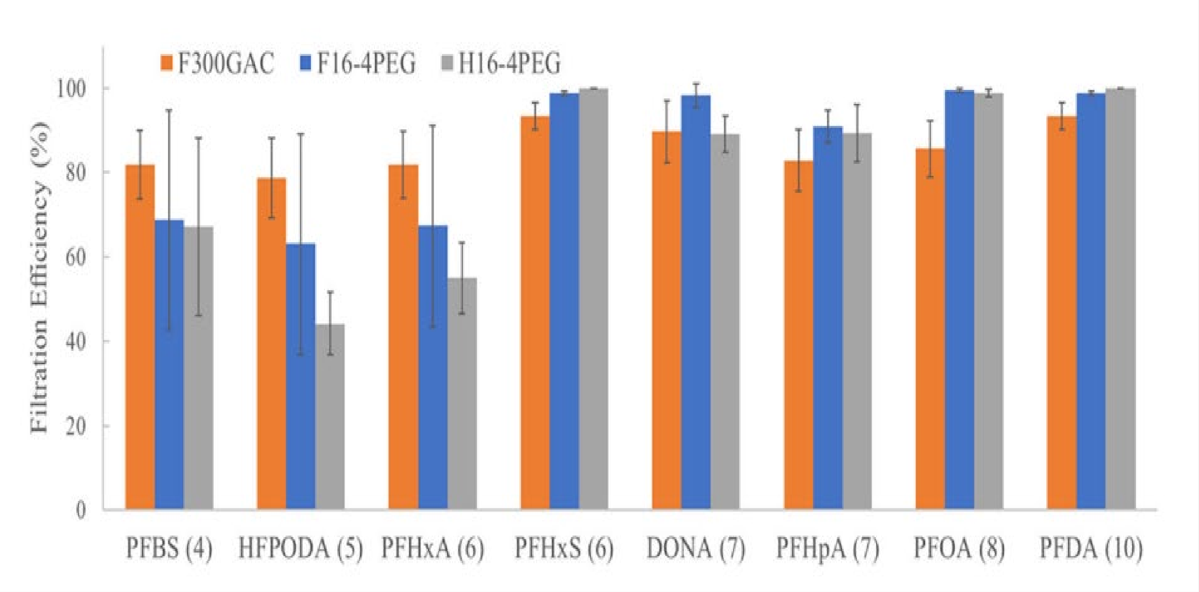
‘H16 ligand’



J. K. Johnson, K. M. Salerno, D. R. Schlesinger, N. Q. Le , J. S. Ko and Z. Xia “Removing forever chemicals via amphiphilic functionalized membranes”
Nature npj Clean Water 2022 (5)55.

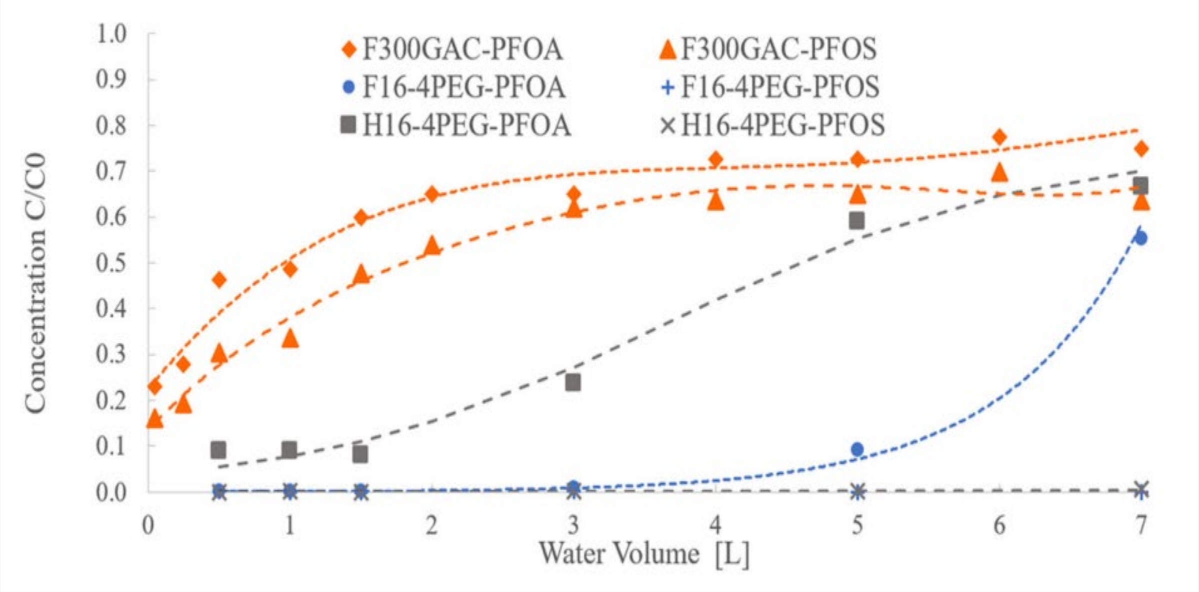
Novel ligands show promising performance

Capture efficiency



Numbers in parenthesis are number of carbons

Breakthrough curves



J. K. Johnson, K. M. Salerno, D. R. Schlesinger, N. Q. Le , J. S. Ko and Z. Xia "Removing forever chemicals via amphiphilic functionalized membranes" ***Nature npj Clean Water 2022 (5)55****.*

Breaking CF bonds via destruction technologies

SCWO

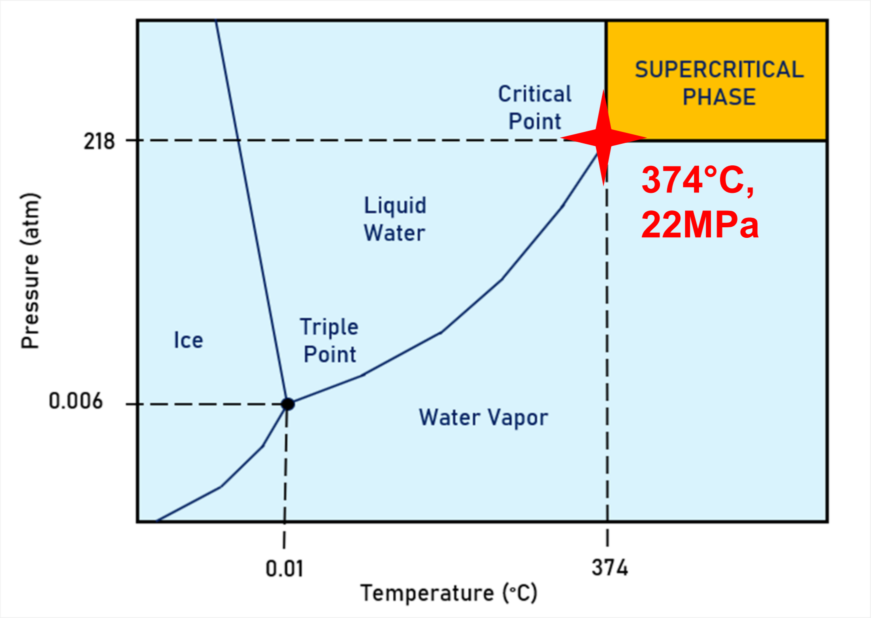
Super Critical Water Oxidation (SCWO) in the presence of air to generate radicals for breaking C-F bonds (600°C, 24MPa, air)

HALT

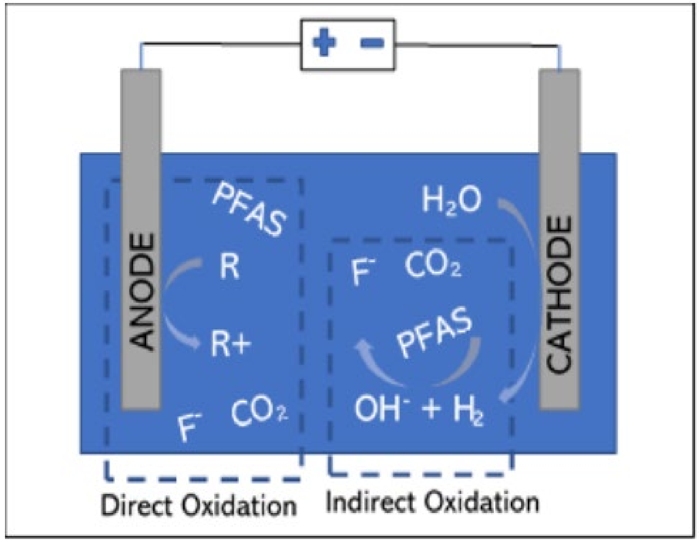
Hydrothermal alkaline treatment (HALT) using sub-critical water under high pH to generate radicals for breaking C-F bonds (350°C, 25MPa, 10min, pH>14)

EO

Electrochemical oxidation (EO) to generate free radicals to oxidize PFAS. Novel stable electrodes are needed



EPA/600/R-22/257



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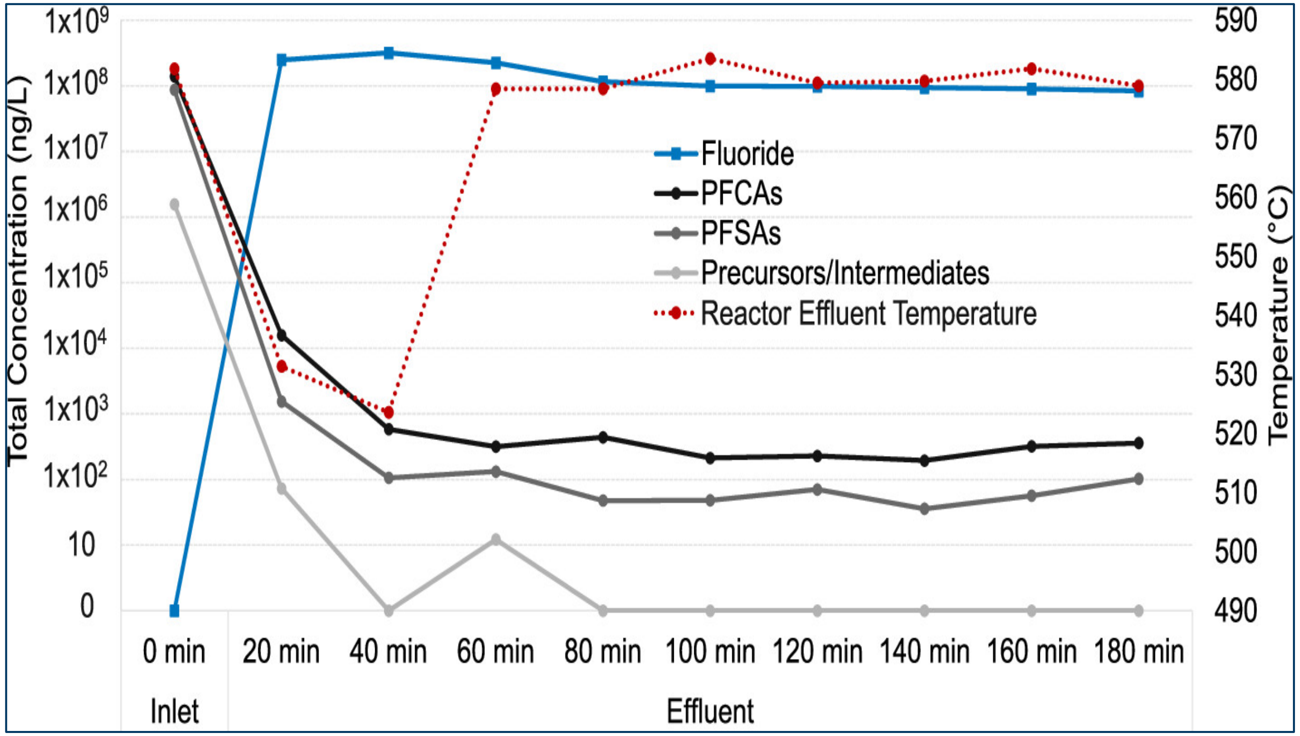
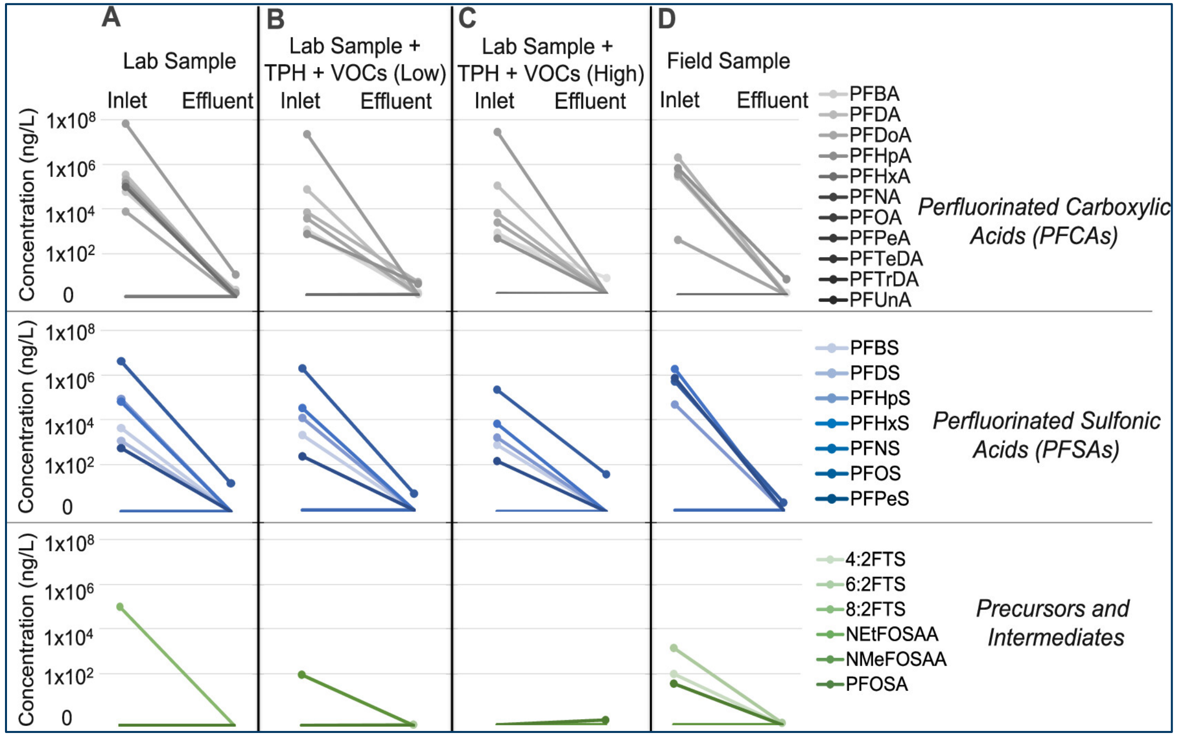
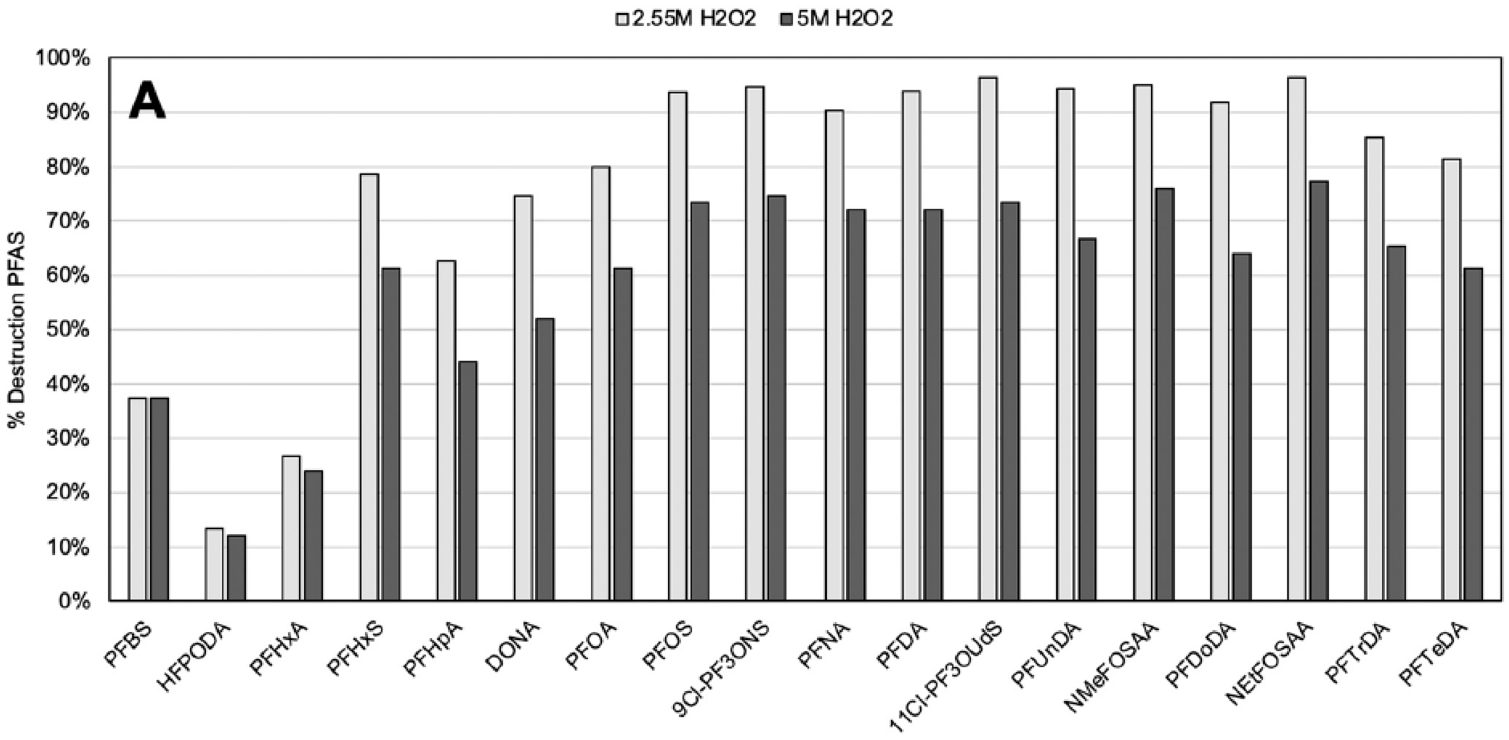
Super Critical Water Oxidation (SCWO)



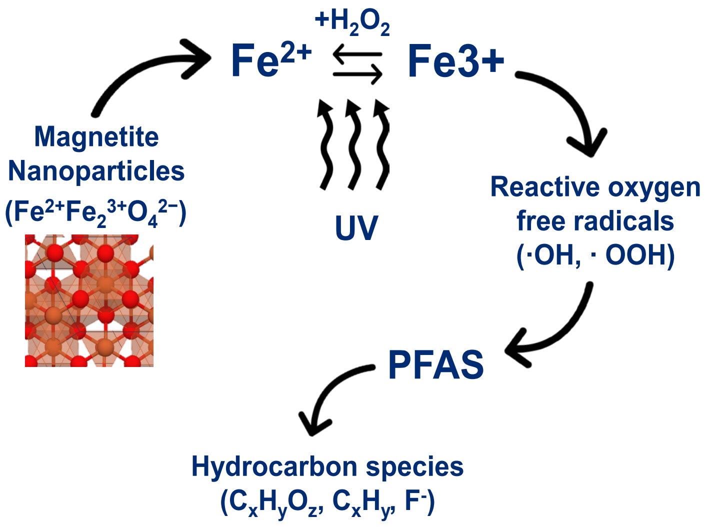


ACS EST Water 2023, 3, 8, 2053-2062

Nano-Fenton chemistry shows promise



Ecofriendly Fenton Chemistry



$+H_2O_2$

$Fe^{2+} \leftrightarrows Fe3+$

UV

Magnetite Nanoparticles ($Fe^{2+}Fe_2^{3+}O_4^{2-}$)

Reactive oxygen free radicals (·OH, · OOH)

PFAS

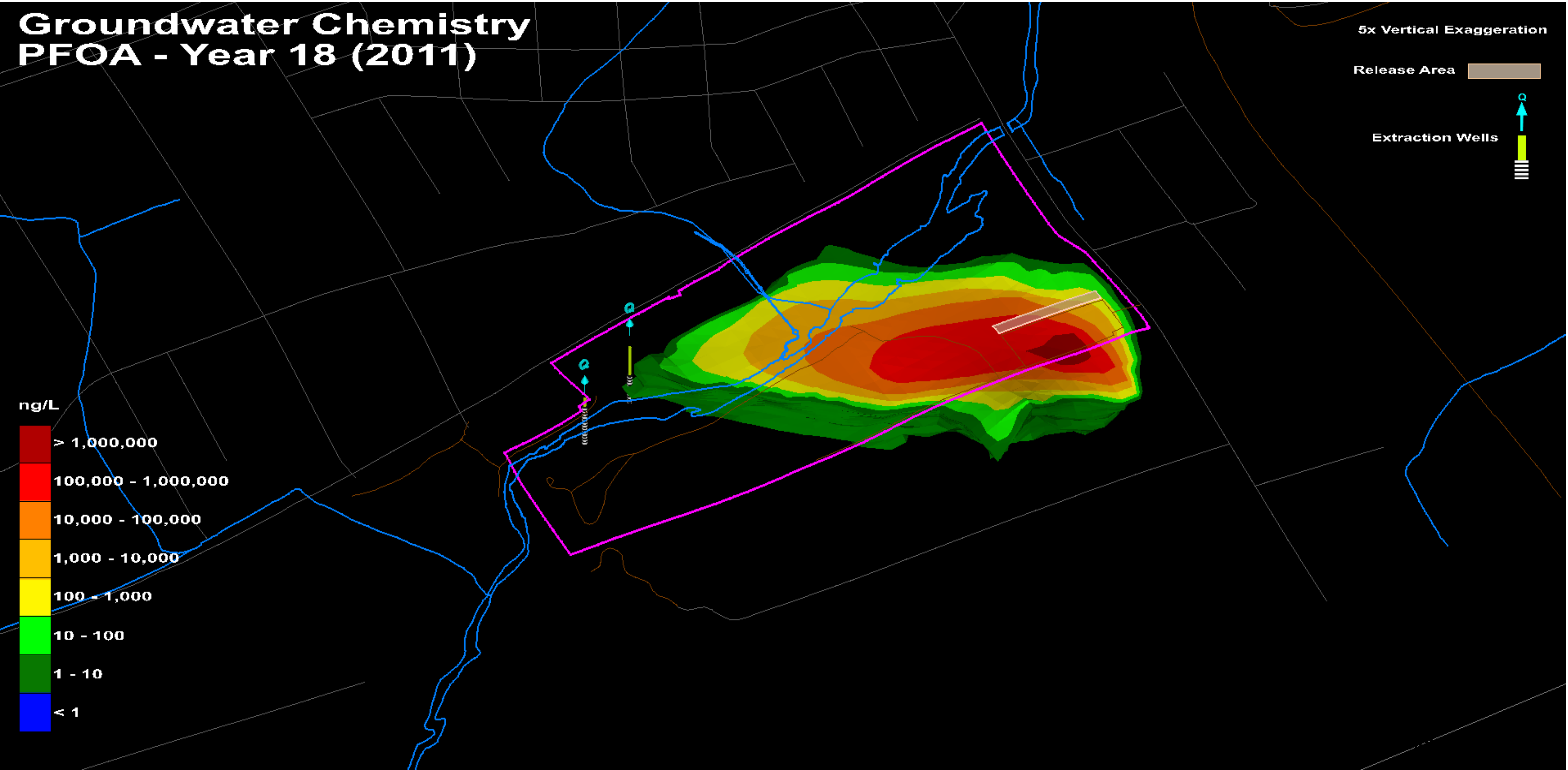
Hydrocarbon species ($C_xH_yO_z$, C_xH_y, F^-)

Ecofriendly technology that achieved >90% PFAS destruction efficiency

D. R. Schlesinger, C. McDermott, N. Q. Le, J. S. Ko, J. K. Johnson, P. A. Demirev and Z. Xia “Destruction of per/poly-fluorinated alkyl substances by magnetite nanoparticle-catalyzed UV-Fenton reaction”

Environ. Sci.: Water Res. Technol., 2022, 8, 2732–2743.

Modeling can be leveraged to simulated PFOA motion



Summary

- PFAS can be treated by either capturing techniques or destruction techniques. PFAS capture is still the dominant treatment technology with destruction technologies emerging.
- With the development of analytical means, more precursors are identified in the environment. The fate, transport and transformation of these precursors can further complicate the treatment of PFAS and should be further evaluated.
- When assessing PFAS issues, background noise should also be considered (even in remote locations).

Questions?

Contact

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