Geosyntec consultants

UNDERSTANDING PFAS PHYSICAL AND CHEMICAL PROPERTIES TOWARDS AN INFORMED REMEDIAL APPROACH

Presented by:

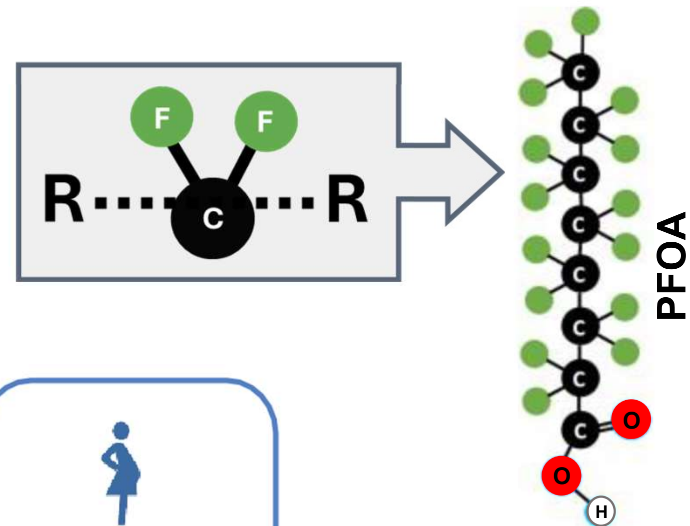
Matthew Bigler

Michael Edgar

Understanding Per- and Poly-fluoroalkyl Substances (PFAS)

- What are PFAS?
  - Group of chemicals (14,735 unique compounds)
  - Fluorine saturated carbons

- What are PFAS health impacts



Cancer Effects
Increased risk of some cancers, including prostate, kidney, and testicular cancers.

Weight Effects
Increased cholesterol levels and/or risk of obesity.

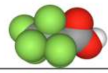
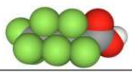
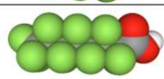
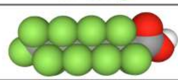
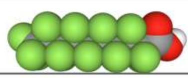
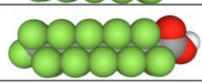
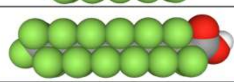
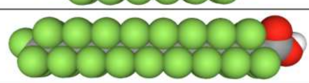
Immune Effects
Reduced ability of the body's immune system to fight infections.

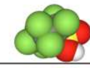
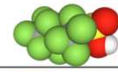
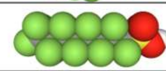
Developmental Effects
Low birth weight, accelerated puberty, bone variations, or behavioral changes.

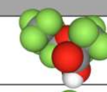
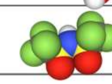
Reproductive Effects
Decreased fertility or increased high blood pressure in pregnant women.

EPA

Current PFAS of concern
(EPA RSLs tables, 2025)

Carboxylates	
PFPrA	
PFBA	
PFHxA	
PFOA	
PFNA	
PFDA	
PFUDA	
PFTeDA	
PFDoDA	
PFODA	(too big for table)

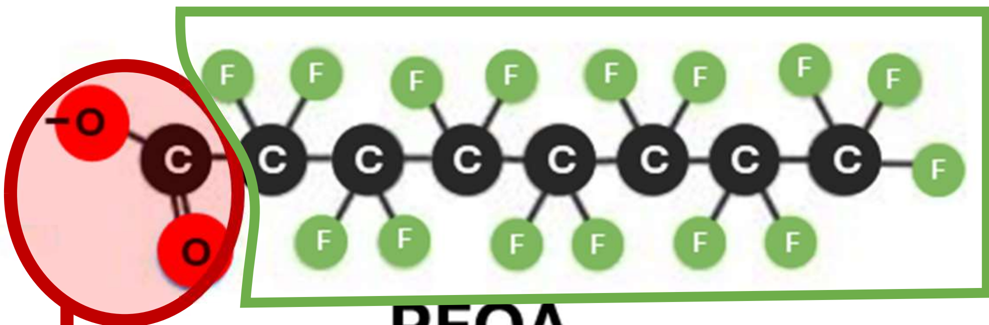
Sulfonates	
PFBS	
PFHxS	
PFOS	

Other	
HFPO-Da	
TFSI	

3D representation of each PFAS

How can we use PFAS chemical characteristics and trends to understand fate, transport, and remedial approaches?

Chemistry of PFAS



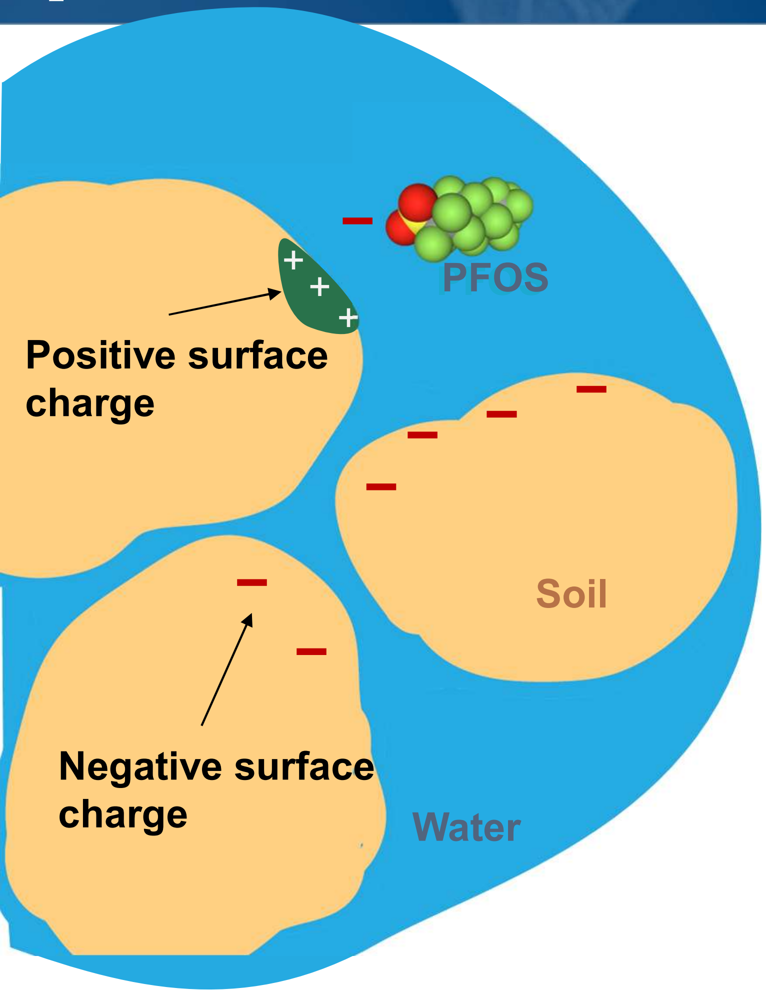
PFOA

Fluorinated Tail
- Hydrophobic
- Magnitude of hydrophobic interactions impacted by chain length

Charged head group
- **All PFAS of concern are negatively charged under standard conditions**
  - CO_2^- for carboxylates (denoted A, e.g. PFOA)
  - SO_3^- for sulfonates (denoted S, e.g. PFOS)
- Controls "head group related" adsorption

PFAS of concern are all **surface active agents** (surfactants). Their characteristics are all governed by:
- Head group interactions
- Tail group interactions

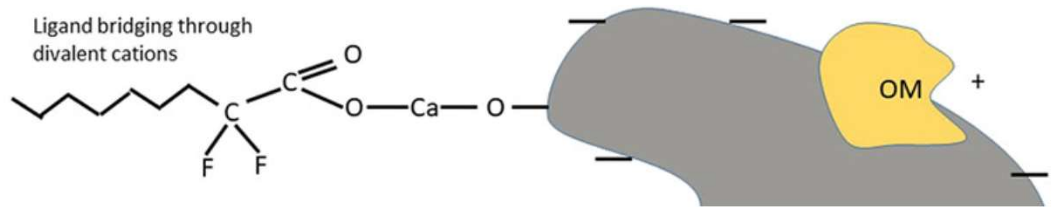
Head Group Driven-Electrostatic interactions



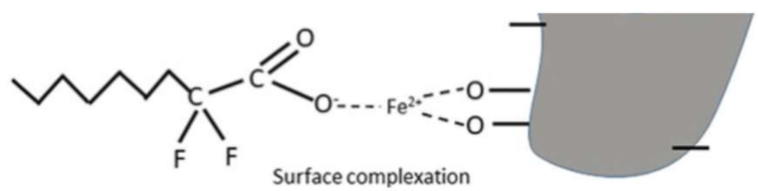
- Charges occur at solid-water interface
  - Charge imbalance at the interface drives accumulation of opposite charge species
  - Same charge species can be repelled
  - Soil is typically negatively charged
- For PFAS of concern positively charged surfaces drive electrostatic retention
  - Short chain PFAS maintain higher charge density

Heap Group Driven – Surface interactions

- Cation bridging
    - Multivalent ions act as a bridge between negatively charged PFAS and negatively charged surface oxygen



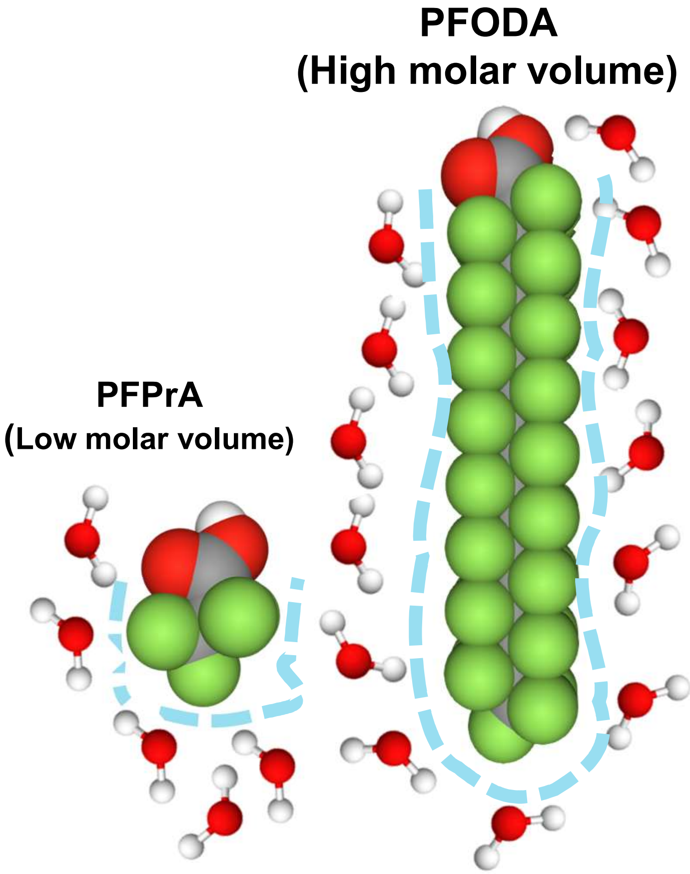
- Surface Complexation
    - PFAS complexation with surface oxygen through multivalent metals



Li, Y., Oliver, D. P., & Kookana, R. S. (2018). A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). The Science of the Total Environment, 628–629, 110–120.

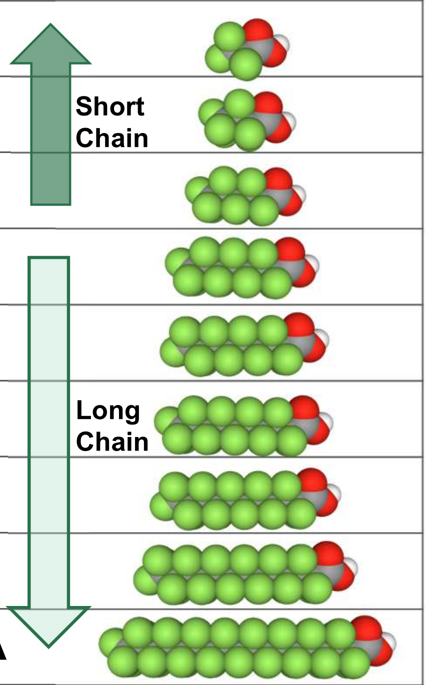
Hydrophobic Interactions

- Hydrophobic forces
  - Minimization of the area of contact between water and non-polar molecules
  - Unfavorable interactions with water drive PFAS to interfaces
  - Significant component of PFAS retention
- Changes in molar volume impact hydrophobic interactions

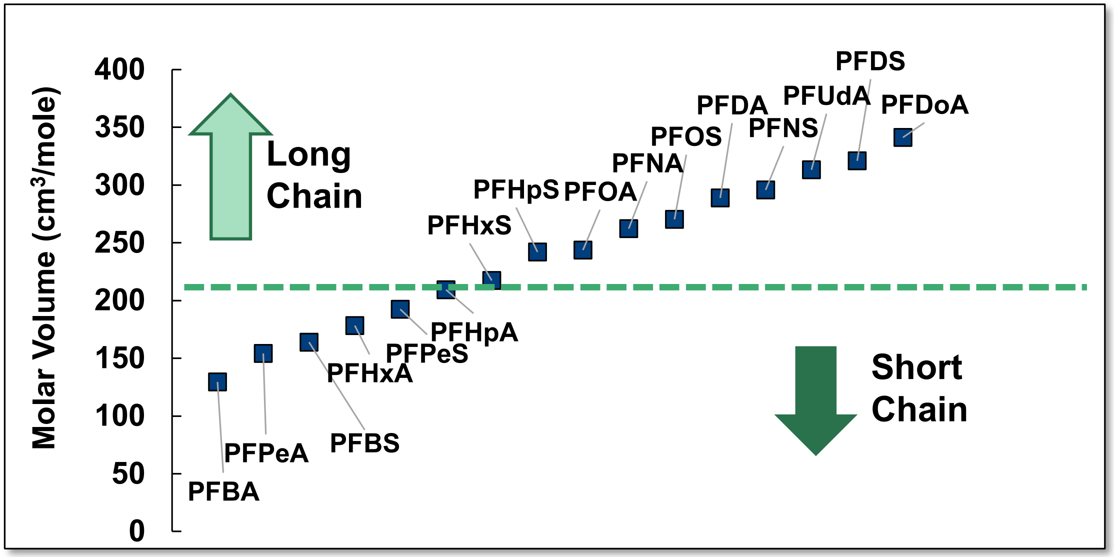


What is molar volume?

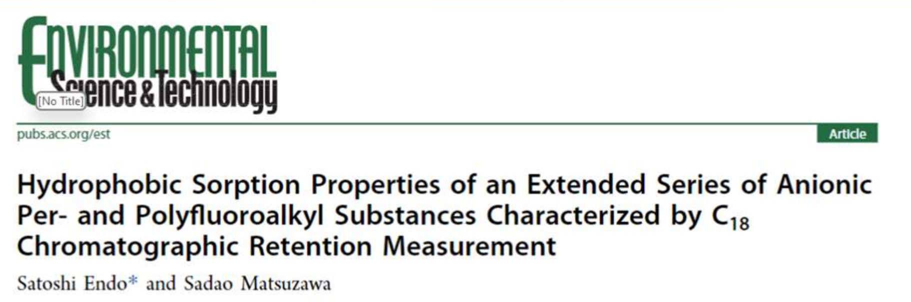
Carboxylates
PFPrA
PFBA
PFHxA
PFOA
PFNA
PFDA
PFUDA
PFTeDA
PFDoDA



- The amount of volume occupied by a compound
- Long chain PFAS have higher molar volumes
- Short chain PFAS have lower molar volumes



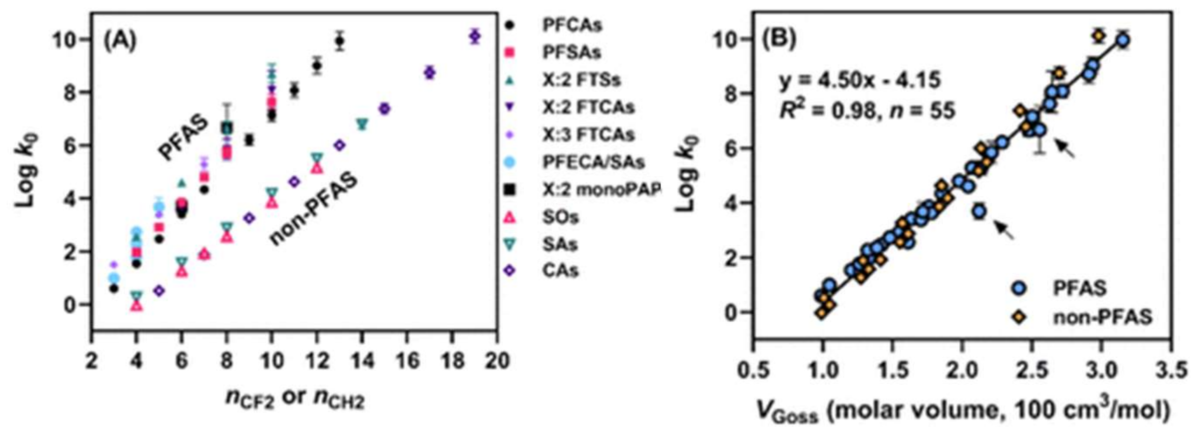
Hydrophobic interactions and molar volume


Environmental Science & Technology
pubs.acs.org/est
Article

Hydrophobic Sorption Properties of an Extended Series of Anionic Per- and Polyfluoroalkyl Substances Characterized by C_{18} Chromatographic Retention Measurement

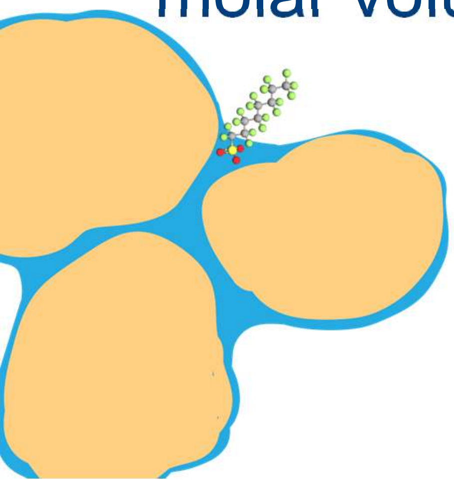
Satoshi Endo* and Sadao Matsuzawa

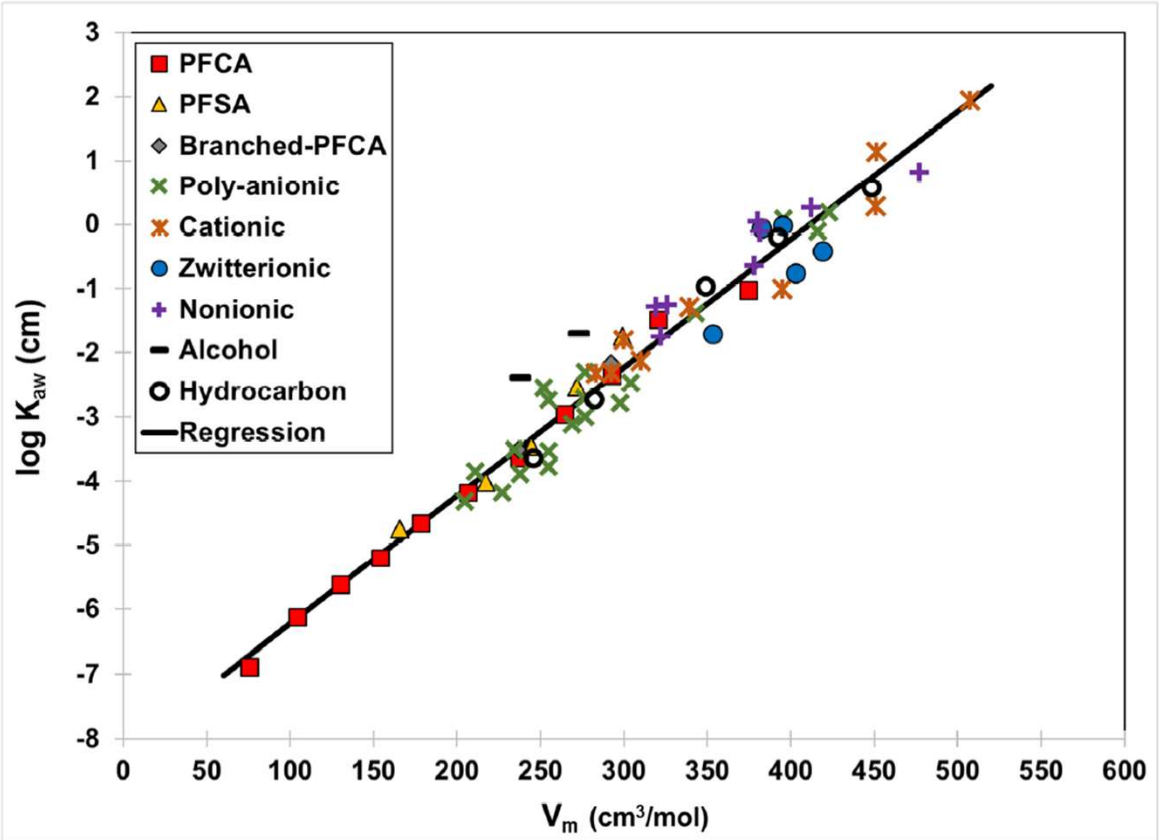
- C_{18} column good analogue for organic carbon
- Log linear relationship with molar volume
- Molar volume often characterized by "number of CF_2"
- No deviations based on "head group"



Magnitude of air-water interfacial adsorption (K_{aw})

- Hydrophobic interactions drive PFAS retention at the air-water interface
- Significant differences in adsorption based on molar volume

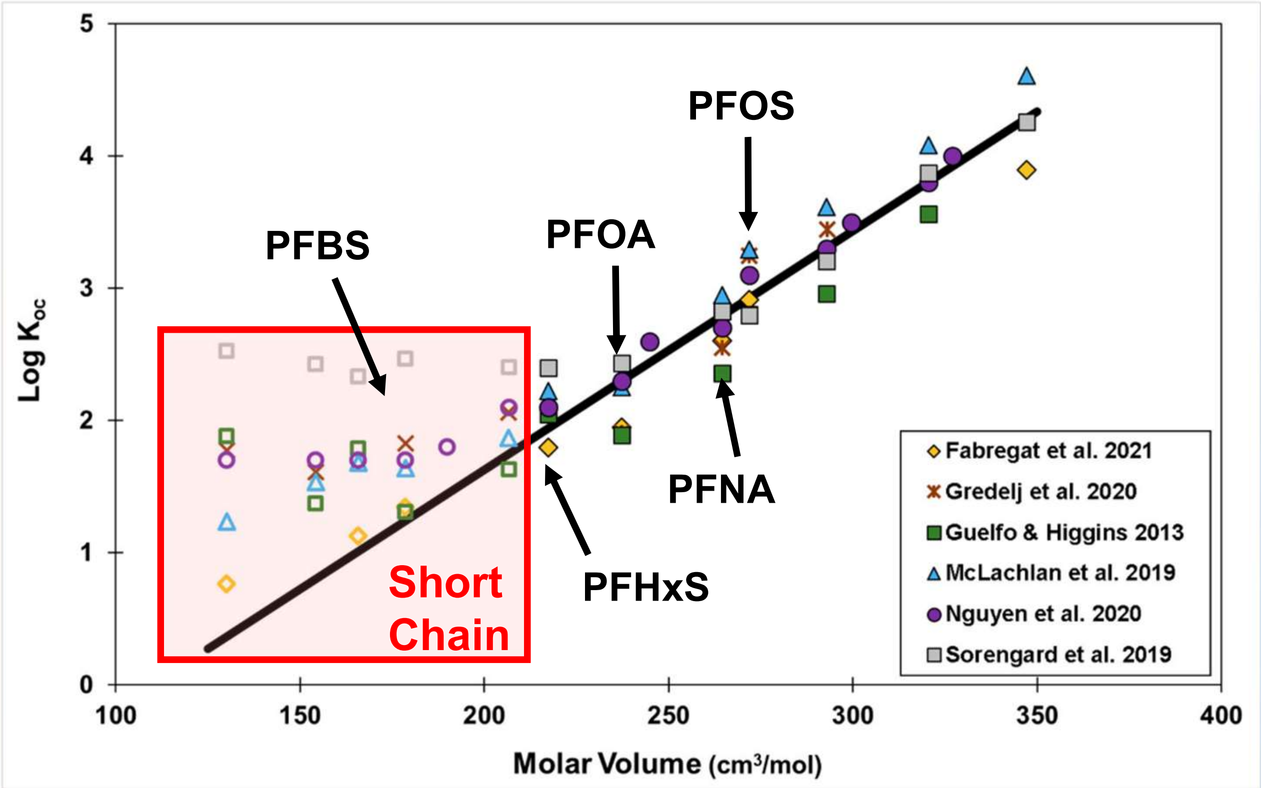




Brusseau, M. L. (2024). A Framework for Developing Tools to Predict PFAS Physical–Chemical Properties and Mass-Partitioning Parameters. *Environments (Basel, Switzerland)*, *11*(8), 164. https://doi.org/10.3390/environments11080164

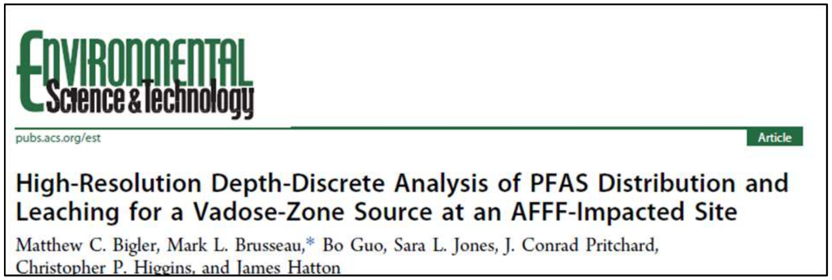
Solid phase adsorption of PFAS

- Log K_{oc} plots of soils
  - Allows for analysis of multiple soils
  - Each soil K_d normalized by its organic content
- Short chain PFAS
  - Largely driven by head group mechanisms
  - Electrostatic interactions
- Long chain PFAS
  - Dominated by hydrophobic interactions
  - No deviation based on head group



Brusseau, & Environmental Science Department, U. of A. (2024). Differential Sorption of Short-Chain versus Long-Chain Anionic Per- and Poly-Fluoroalkyl Substances by Soils. Environments - MDPI.

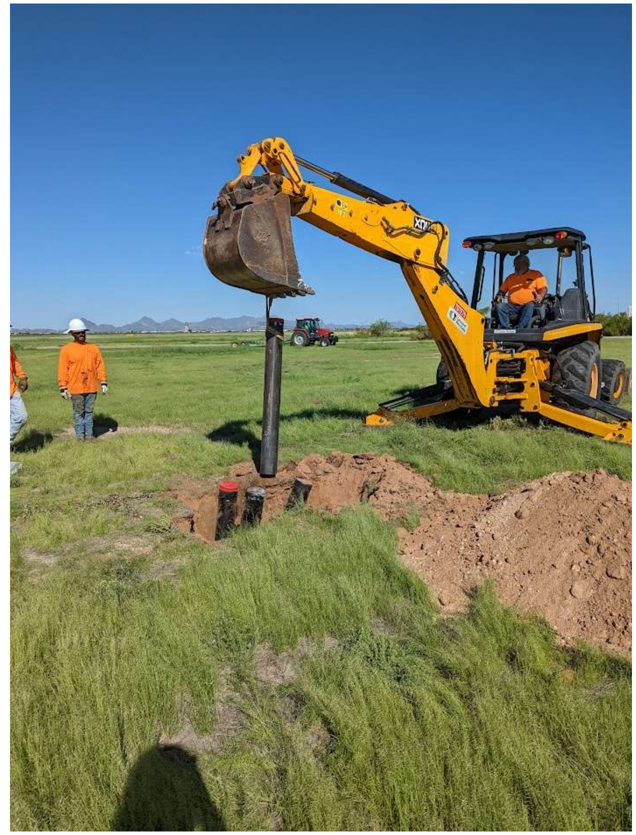
Case Study


Environmental Science & Technology
pubs.acs.org/est
Article

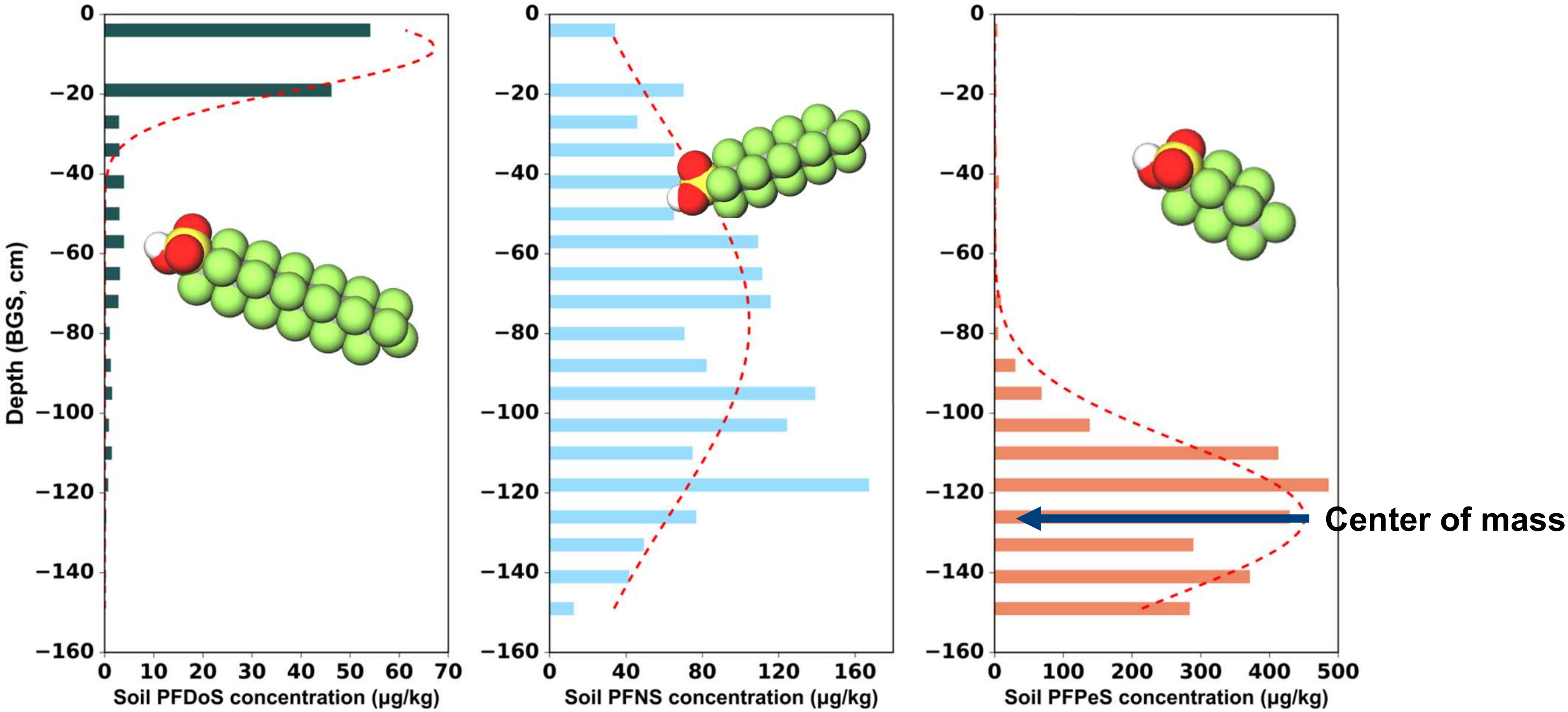
High-Resolution Depth-Discrete Analysis of PFAS Distribution and Leaching for a Vadose-Zone Source at an AFFF-Impacted Site

Matthew C. Bigler, Mark L. Brusseau,* Bo Guo, Sara L. Jones, J. Conrad Pritchard, Christopher P. Higgins, and James Hatton

- AFFF application site
  - Semi-arid environment
  - High evapotranspiration
  - Low infiltration
- 20+ years of PFAS application
  - Unlined fire training area
- 50+ years since first application
- High resolution analysis of PFAS distribution in soil



PFAS distribution in 2-meter high resolution sampling

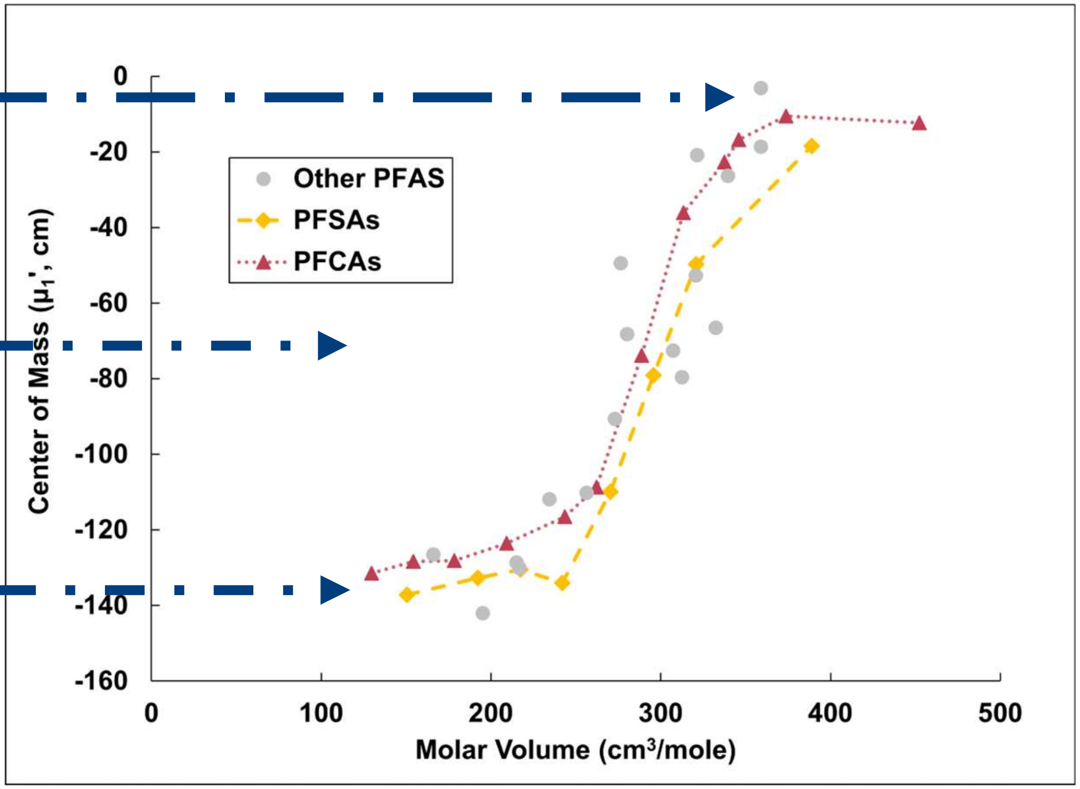


PFAS distribution in 2-meter high resolution sampling

High molar volume PFAS
- little to no leaching in 50 years

Moderate molar volume PFAS
- separated due to differential sorption to:
  - Air-water interface
  - Soil-water interface

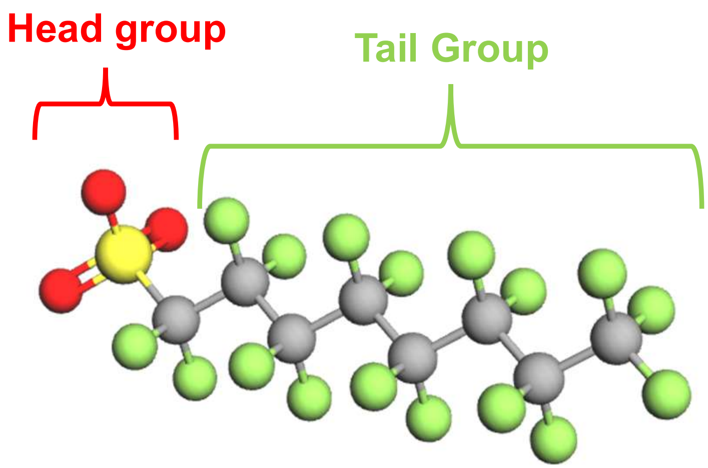
Low molar volume PFAS
- built up in Calcic horizon (caliche)



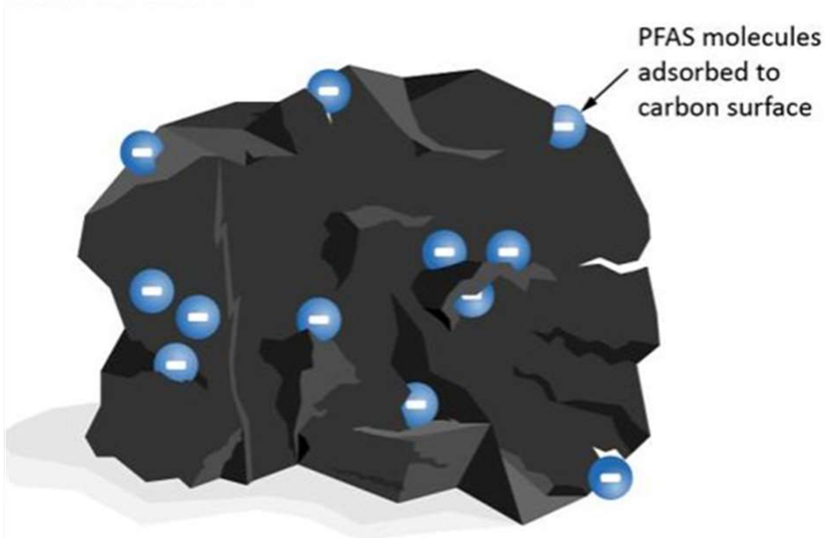
PFAS and treatment technologies

PFAS Treatment Technologies

- Granular Activated Carbon
- Ion Exchange
- Foam Fractionation
- High Pressure Filtration



GAC and PFAS – Removal Mechanism

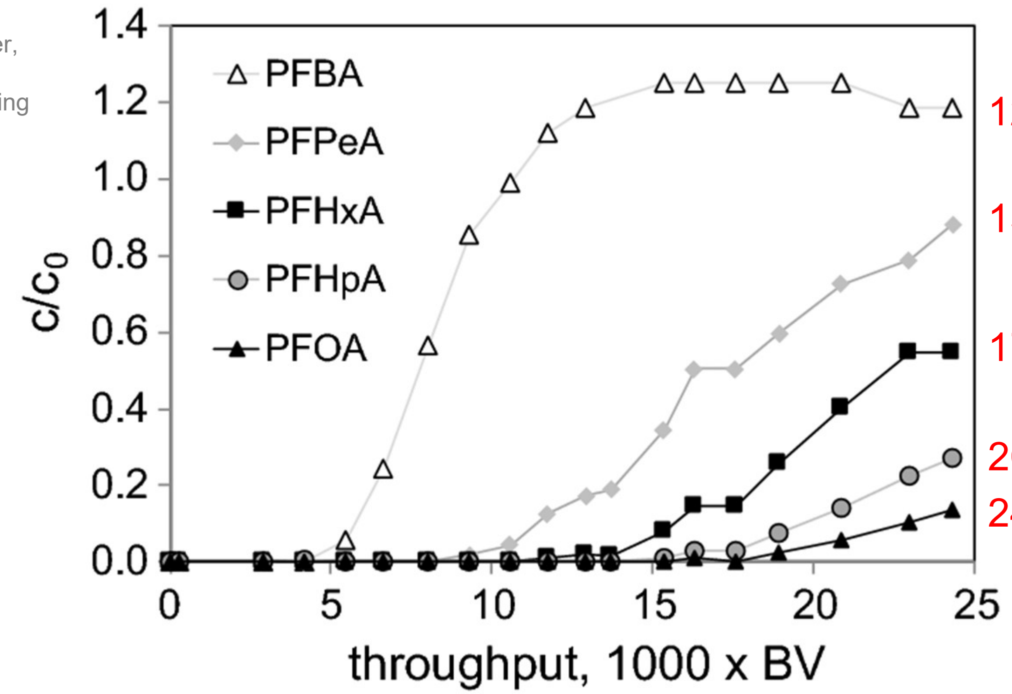


Source: GAO. | GAO-22-105088

Nonpolar, hydrophobic surface of GAC results in adsorption of hydrophobic PFAS

GAC and PFAS – Removal Mechanism

Riegel, Marcel & Haist-Gulde, Brigitte & Sacher, Frank. (2023). Sorptive removal of short-chain perfluoroalkyl substances (PFAS) during drinking water treatment using activated carbon and anion exchanger. Environmental Sciences Europe. 35. 10.1186/s12302-023-00716-5.



129.6 cm^3/mol

154.2 cm^3/mol

178.3 cm^3/mol

209.3 cm^3/mol

243.6 cm^3/mol

More effective at removing long chain PFAS – breakthrough of short-chain PFAS occurs quickly

GAC and PFAS – Interference by DOC

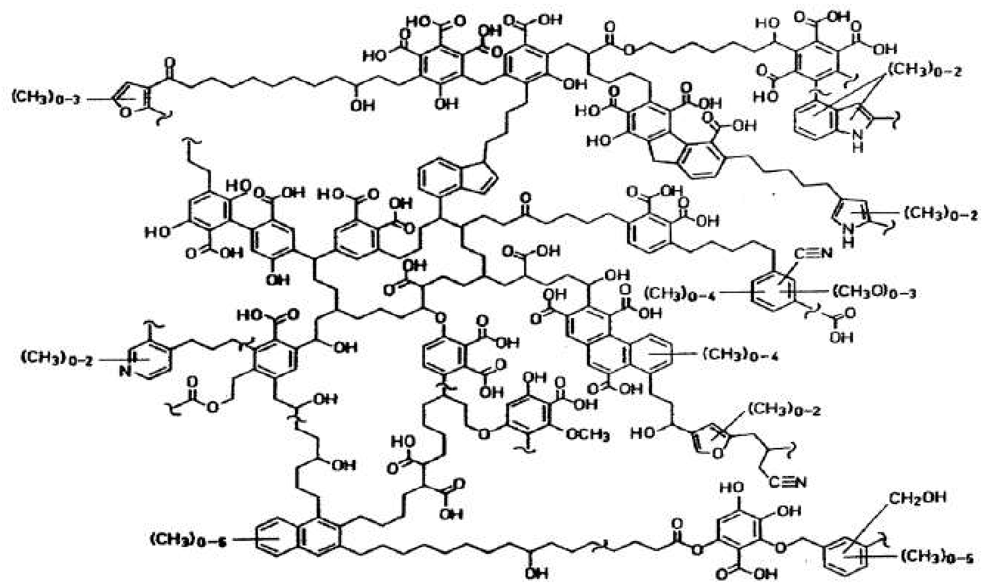


Figure 1

Chemical representation of NOM. Reproduced from Bhatnagar and Sillanpaa, (2017) with permission of the copyright holder, Elsevier

Capacity of GAC is reduced in the presence of DOC

Ion Exchange and PFAS

ELSEVIER

Water Research
Volume 200, 15 July 2021, 117244

Anion exchange resin removal of per- and polyfluoroalkyl substances (PFAS) from impacted water: A critical review

Treavor H. Boyer [a], Yida Fang [b], Anderson Ellis [b], Rebecca Dietz [a], Youn Jeong Choi [b], Charles E. Schaefer [c], Christopher P. Higgins [b], Timothy J. Strathmann [b]

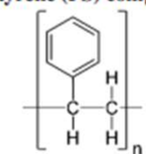
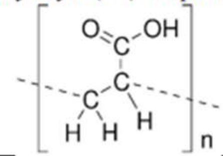
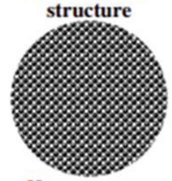
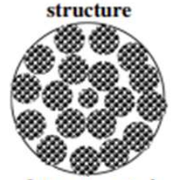
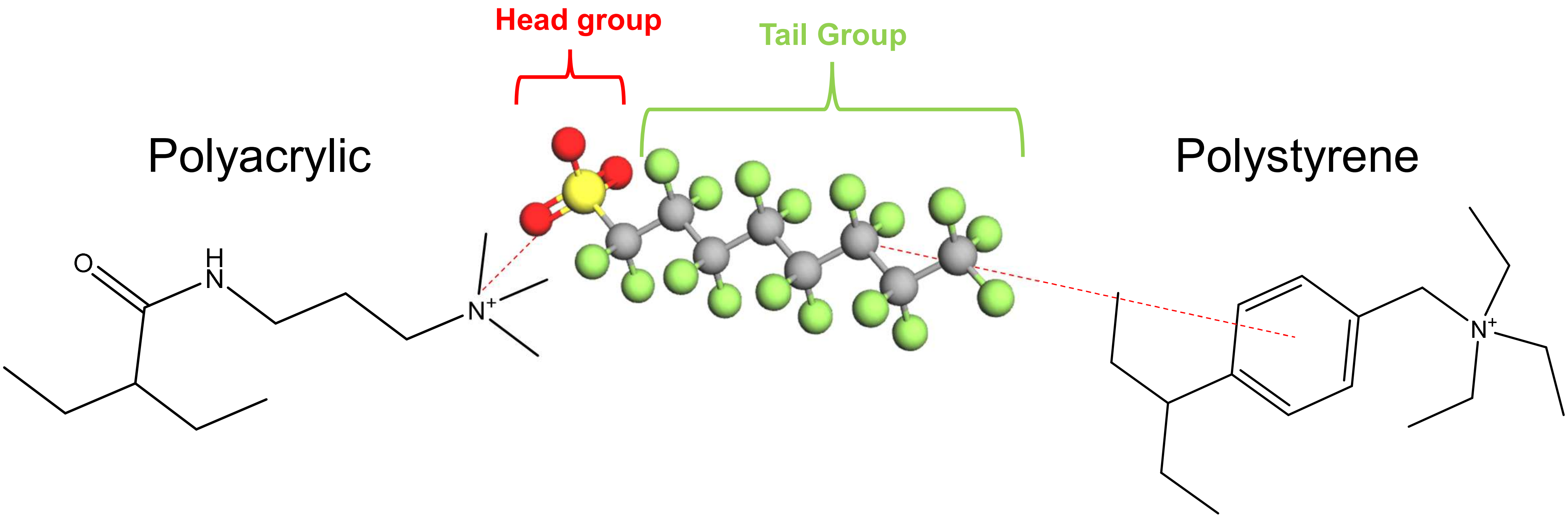
	Polystyrene (PS) composition	Polyacrylic (PA) composition
		
Gel (G) pore structure  Homogeneous solid phase	**Type I, $R{-}N^+(CH_3)_3$** A600 & A600E, PFA400, AS-L K6362, PFA444, Dowex Marathon A, USF A-284, IRA400, USF A-464 **Type I, $R{-}N^+(C_4H_9)_3$** Dowex PSR-2 **Type I bifunctional, $R{-}N^+(C_2H_5)_3/R{-}N^+(C_6H_{13})_3$** A532E **Type II, $R{-}N^+(CH_3)_2C_2H_4OH$** A300, PFA300, IRA410, USF A-244 **Complex amino** PFA694E	**Type I, $R{-}N^+(CH_3)_3$** IRA458 USF A-714 **Type II, $R{-}N^+(CH_3)_2C_2H_4OH$** Not commercially manufactured **Tertiary amine, $R{-}N(CH_3)_2$** IRA67
Macroporous (MP) pore structure  *Interconnected network of macropores*	**Type I, $R{-}N^+(CH_3)_3$** AS-F 500, USF A-674, IRA900 **Type I, $R{-}N^+(C_2H_5)_3$** AS-F 520 A520E **Type I, $R{-}N^+(C_nH_{2n+1})_3$ (n > 2)** AS-F 530 AS-F 555 **Type II, $R{-}N^+(CH_3)_2C_2H_4OH$** IRA910 **Complex amino** A592E **Tertiary amine, $R{-}N(CH_3)_2$** AW-F 100, Macronet MN102, AW-F 111, USF A-399, IRA96	**Type I, $R{-}N^+(CH_3)_3$** A860 IRA958 MIEX **Type II, $R{-}N^+(CH_3)_2C_2H_4OH$** Not commercially manufactured **Tertiary amine, $R{-}N(CH_3)_2$** No resins studied

Figure 1. Classification of strong-base (Type I, Type II, and complex amino) and weak-base (tertiary amine) anion exchange resins investigated for PFAS removal from water.

Ion exchange and PFAS – Resin Backbone

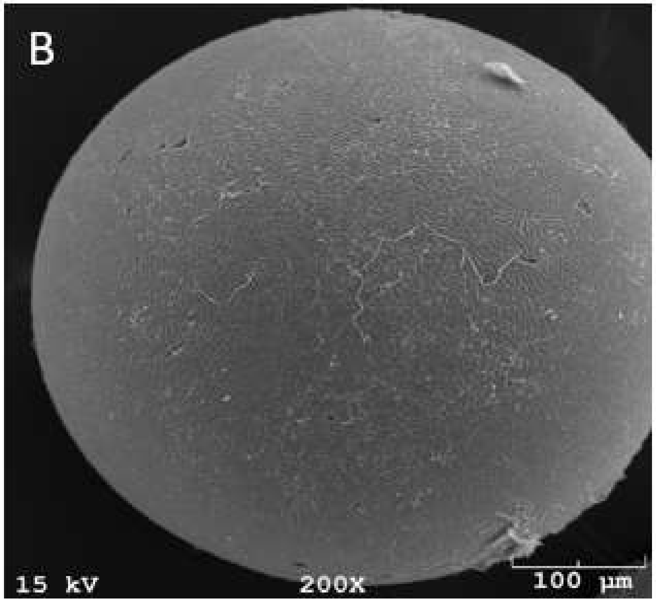


- hydrophilic constituentd
- focus on electrostatic interactions
- Used for short chain removal

- hydrophobic constituents
- focus on π- π interactions
- Used for long chain removal

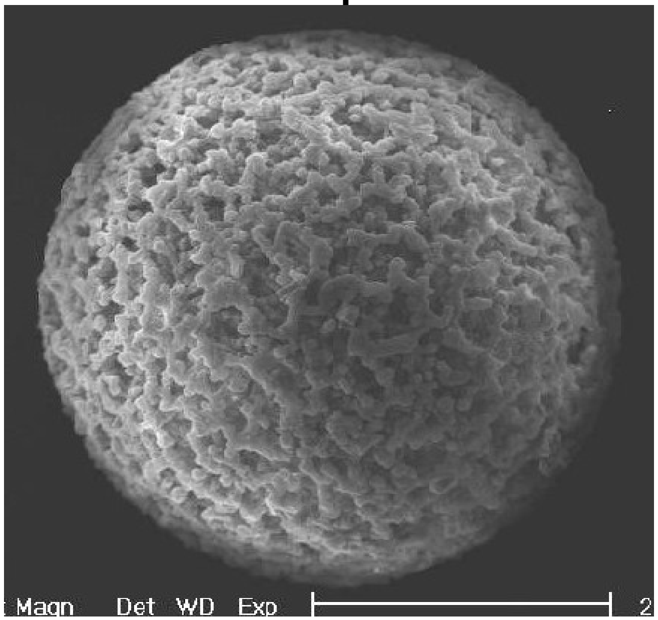
Ion exchange and PFAS – Resin Polymer Matrix

Gel



- Higher capacity
- Size exclusion of large molecules

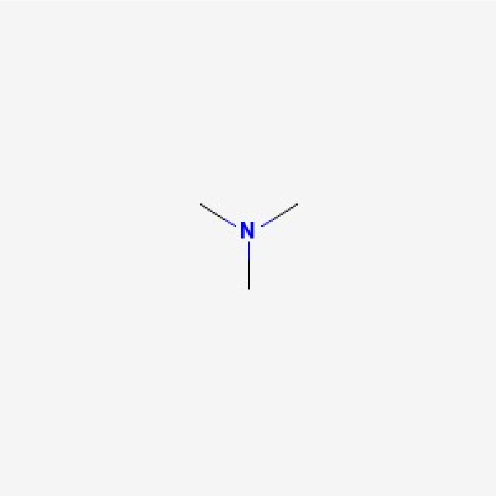
Macroporous



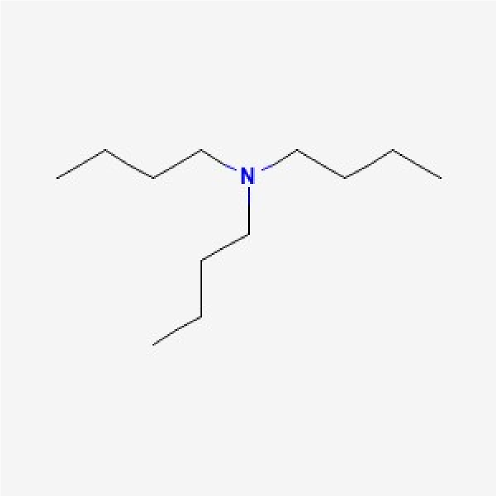
- Resistant to thermal/mechanical shocks

Ion exchange and PFAS – Functional Group Selection

Trimethylamine



Tributylamine

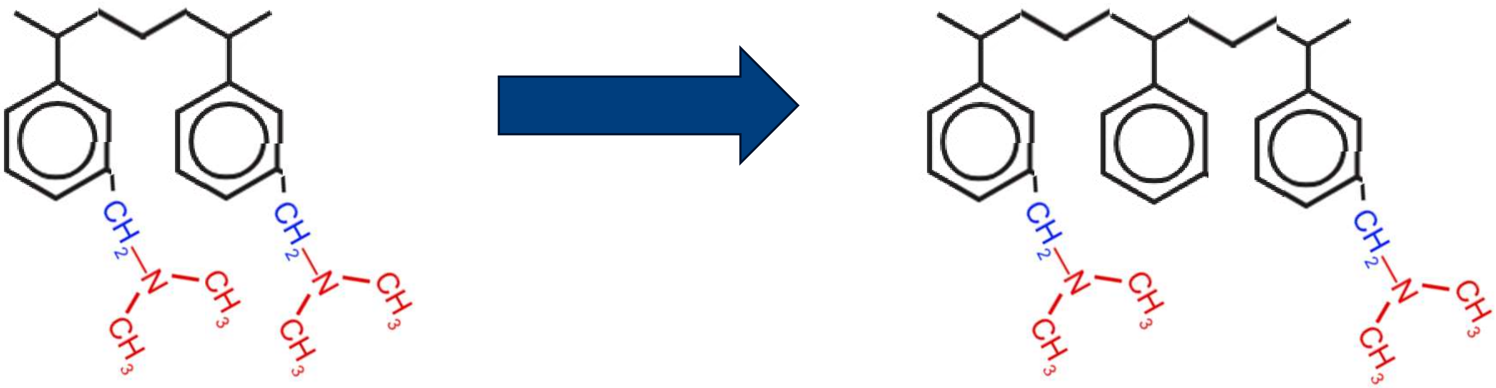


Longer alkylamine chain lengths mean more hydrophobicity, which means more tail group reactivity

Ion exchange and PFAS – PFAS Selective Resins

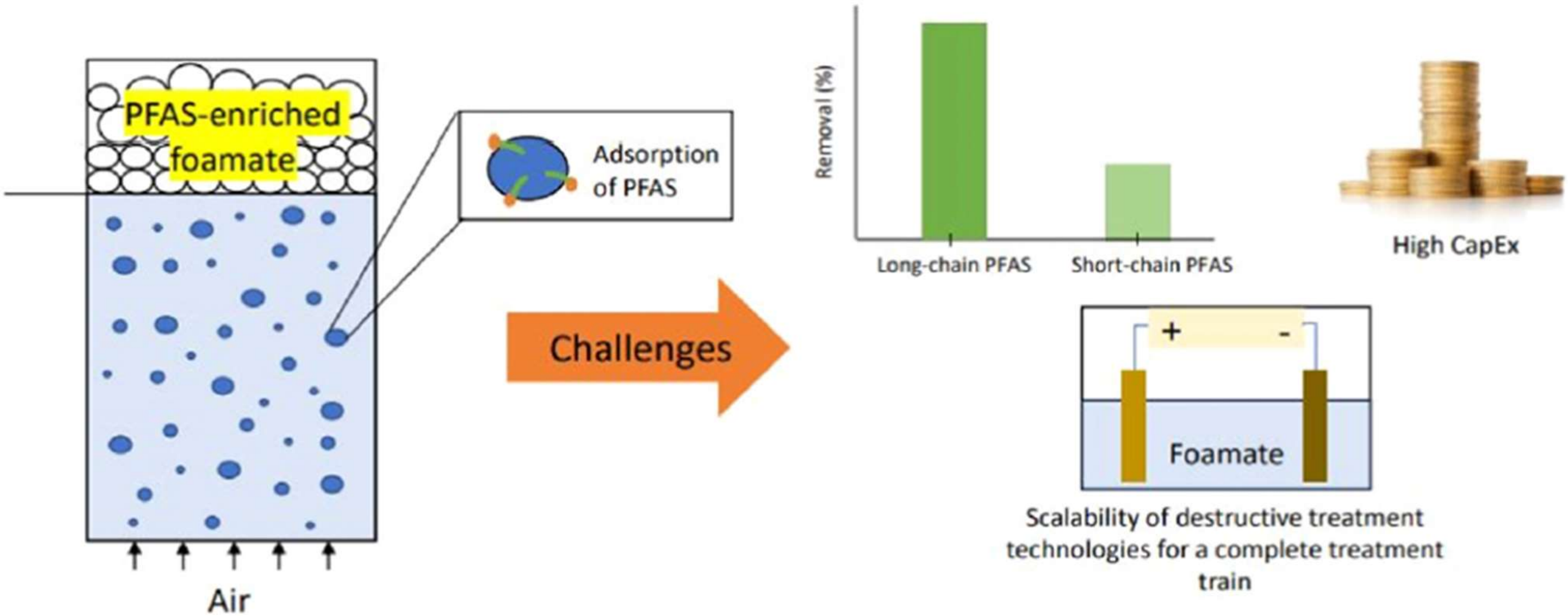
Non-selective resin

Selective Resin



Functional groups are separated to inhibit adsorption of multivalent ions

Foam Fractionation



Angel Chyi En We, Arash Zamyadi, Anthony D. Stickland, Bradley O. Clarke, Stefano Freguia, A review of foam fractionation for the removal of per- and polyfluoroalkyl substances (PFAS) from aqueous matrices,Journal of Hazardous Materials,Volume 465,2024,133182,ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2023.133182.

Foam Fractionation

Advantages

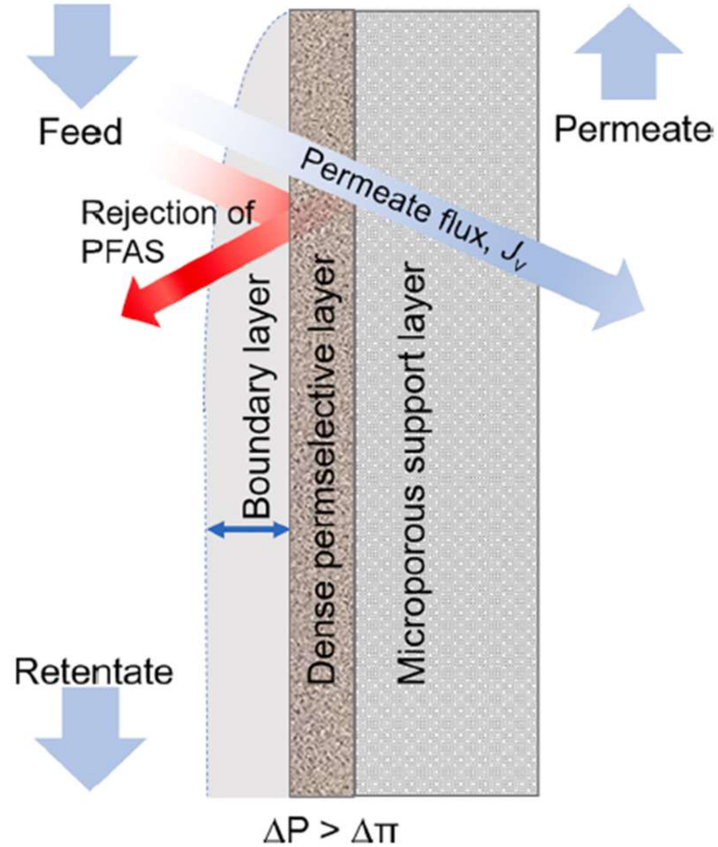
- Foamate has relatively low volume
- Applicable to wide range of water matrices
- Low operational costs

Disadvantages

- High capital costs
- Requires the use of cationic co-surfactants for short-chain PFAS
- Volatile co-contaminants may require additional containment

High Pressure Membrane Treatment

- Nanofiltration (NF) or reverse osmosis (RO)
- PFAS removal based on charge and size exclusion
- 90-99% removal for most PFAS, irrespective of chain length



Tae Lee, Thomas F. Speth, Mallikarjuna N. Nadagouda, High-pressure membrane filtration processes for separation of Per- and polyfluoroalkyl substances (PFAS),Chemical Engineering Journal,Volume 431, Part 2,2022,134023,ISSN 1385-8947,https://doi.org/10.1016/j.cej.2021.134023.

High Pressure Membrane Treatment

- Use is often limited by energy requirements and brine treatment
- Will rarely be more cost effective than both GAC and IX
- More likely to foul in groundwater applications compared to drinking water applications

PFAS Treatment Technologies - Summary

- GAC
  - Great for long-chain removal, short-chain breaks through more quickly
  - DOC will consume GAC capacity
- Ion Exchange
  - Resins can be selective for long- or short-chain PFAS
  - DOC competes with long-chain PFAS removal
  - Inorganic ions compete with short-chain PFAS removal (Nitrate, Perchlorate)
- Foam Fractionation
  - Great for long-chain removal
  - Short-chain removal requires addition of a cationic co-surfactant
  - High capital costs, low operational costs
- Reverse Osmosis
  - High cost, applicable mostly to point-of-use or low volume drinking water streams
  - May be cost effective for specific streams high in DOC, nitrates, or salts

Understanding PFAS towards an informed remedial approach

- Understanding PFAS retentions mechanisms
  - Head group interactions
  - Hydrophobic interactions
- These mechanisms often control fate, transport, and remedial approach
- We use our understanding of PFAS characteristics to tailor our treatment and reduce costs