PFAS Transport in Source Zones

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SRP Risk-e Learning Webinar: Tools for PFAS Site Characterization

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Contaminant Transport Group
University of Arizona

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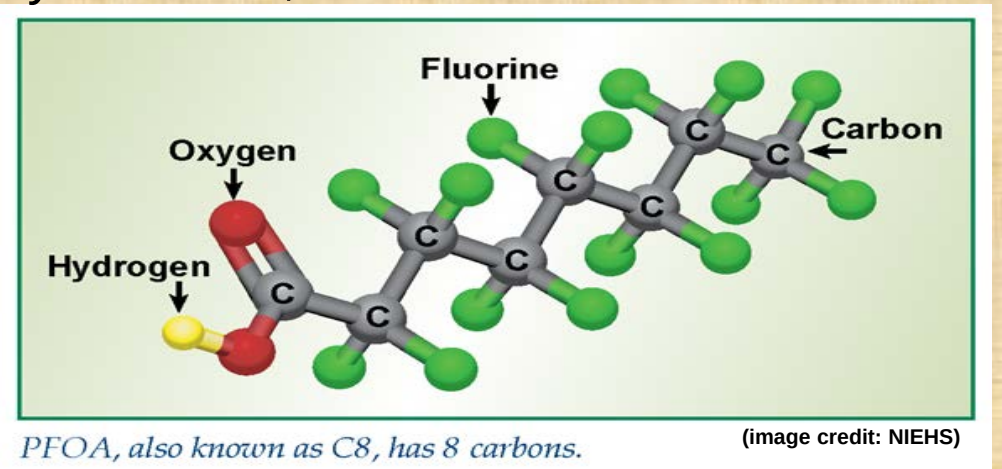
PFAS = Per- and polyfluoroalkyl substances

*By definition, PFAS contain fluorine atoms



PFAS Definition: Molecule contains at least one fully fluorinated methyl [–CF_3] or methylene [–CF_2–] carbon atom (OECD, 2021)

There are >14,000 different PFAS
(EPA CompTox Chemicals Dashboard, 2022)

>>> PFAS have several special attributes that make them unique contaminants

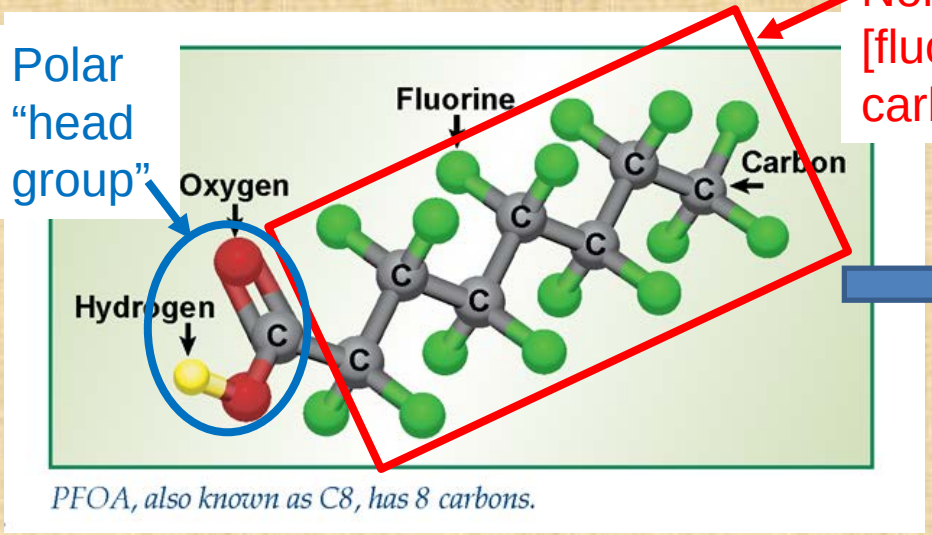
PFAS Properties

Many PFAS are **amphiphilic** (contain both nonpolar & polar regions)

***behave as surfactants

Polar "head group"

Nonpolar "tail" [fluorinated carbon chain]



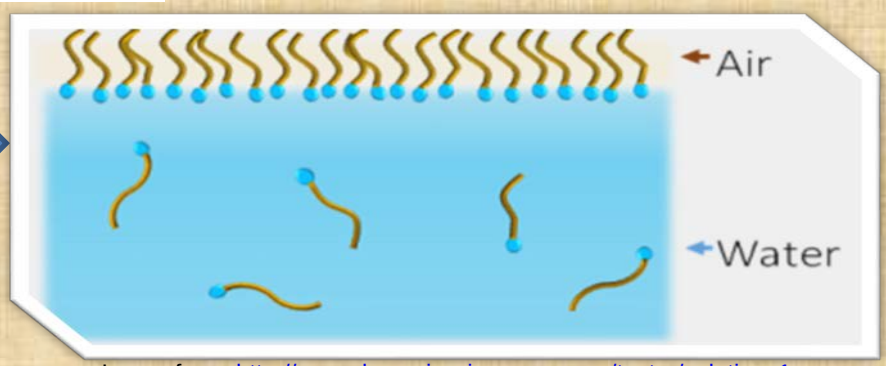


Image from: http://www.dynamicscience.com.au/tester/solutions1/chemistry/foodchemistry/emulsions.htm

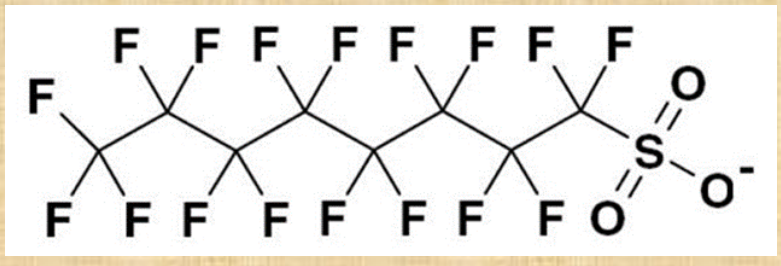
PFAS chains are both hydrophobic and oleophobic

*Provides water and oil repellency

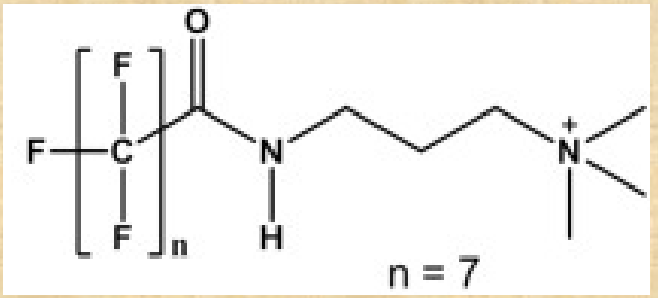
PFAS Structures

- PFAS have different types of **surfactant headgroups**

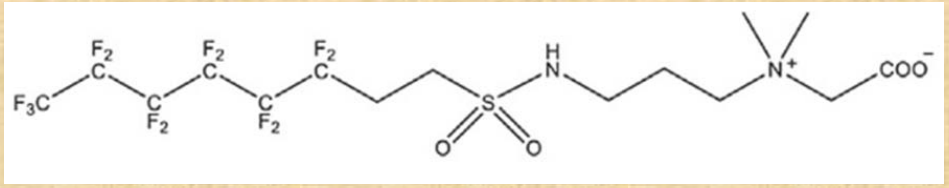
Anionic



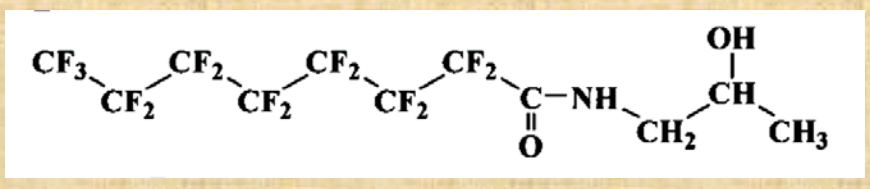
Cationic



Zwitterionic



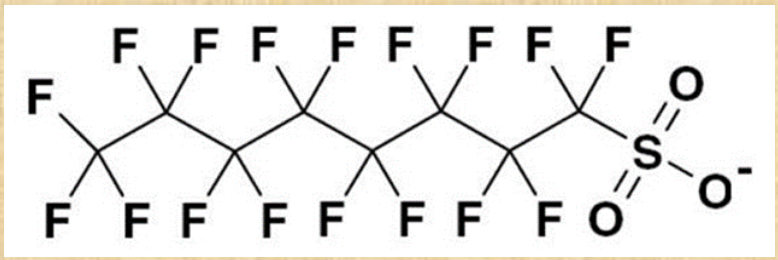
Nonionic



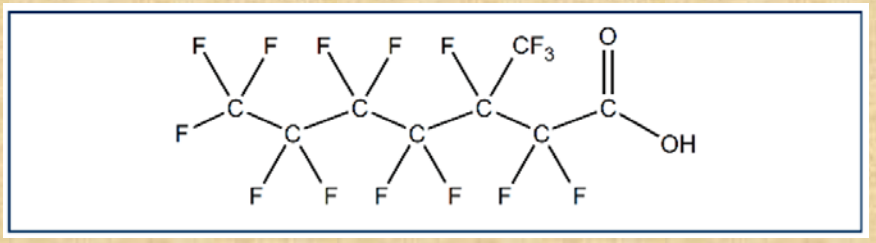
PFAS Structures

- PFAS have different **tail structures**
  - Per vs Poly
  - Straight-chained vs branched

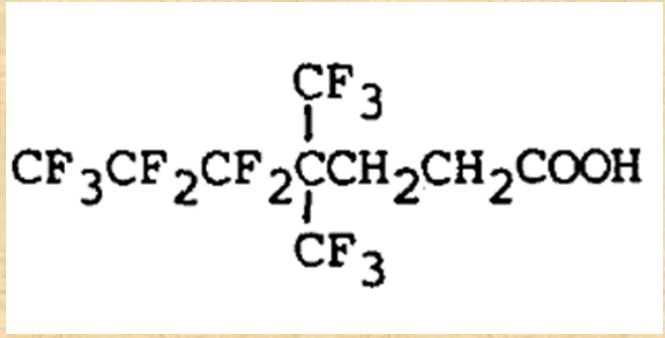
Straight-chained **Perfluoroalkyls**

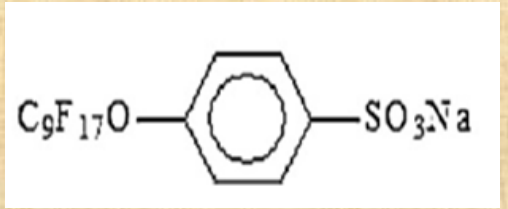


Branched



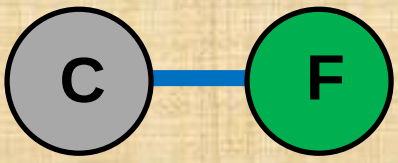
Polyfluoroalkyls





Many PFAS are Persistent

- Carbon-fluorine bonds are very strong



→ **difficult to break down**

- Therefore they remain in the environment for a very long time

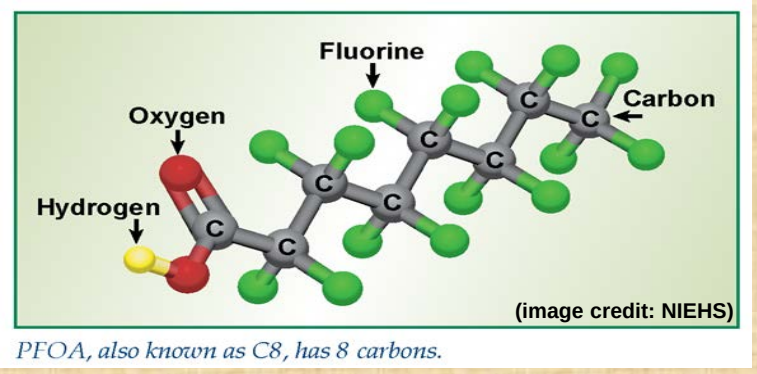
- Critical Note: some PFAS are degradable = "**precursors**"

  >>> contaminant source for persistent PFAS

PFAS Compounds

>> These unique properties make PFAS useful for many applications

>>However, they cause characterizing and modeling PFAS transport and fate to be complex



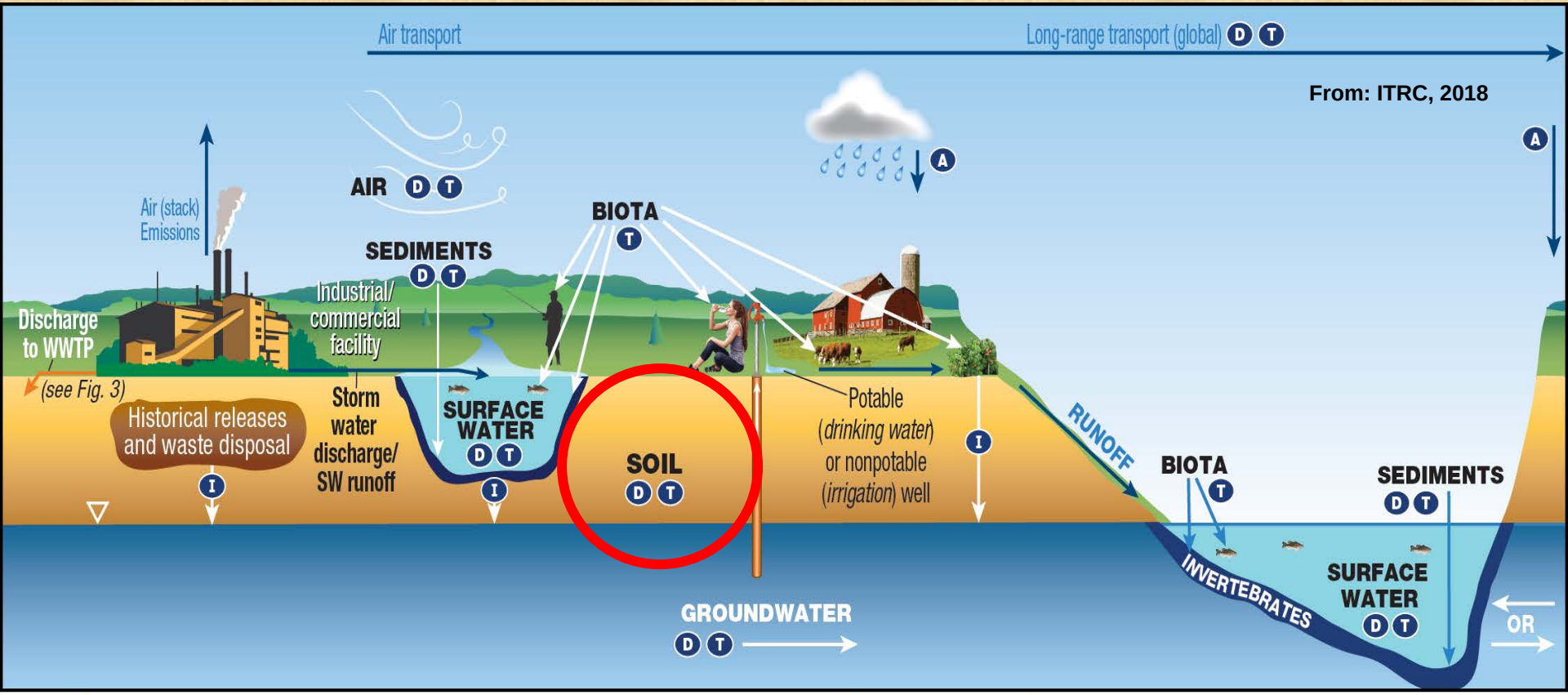
PFOA, also known as C8, has 8 carbons.

To characterize and model PFAS transport and fate, we need to understand their unique properties

PFAS Transport & Fate in the Environment

>>> Release to:

- -atmosphere
- -surface water
- -soil
- -groundwater



PFAS migration in the vadose zone is a function of several factors:

- Source type
  - e.g., AFFF sites vs biosolids-application sites
  - types of PFAS and relevant concentration ranges
- Site conditions
  - Soil properties (sorptive constituents, air-water interfacial area)
  - Physical and geochemical heterogeneity
  - Water saturation magnitude and distribution
  - Potential precursor presence and transformation
  - Presence of other contaminants
- Precipitation/Evapotranspiration/Infiltration
- **Retention processes**

Surfactant Behavior of PFAS

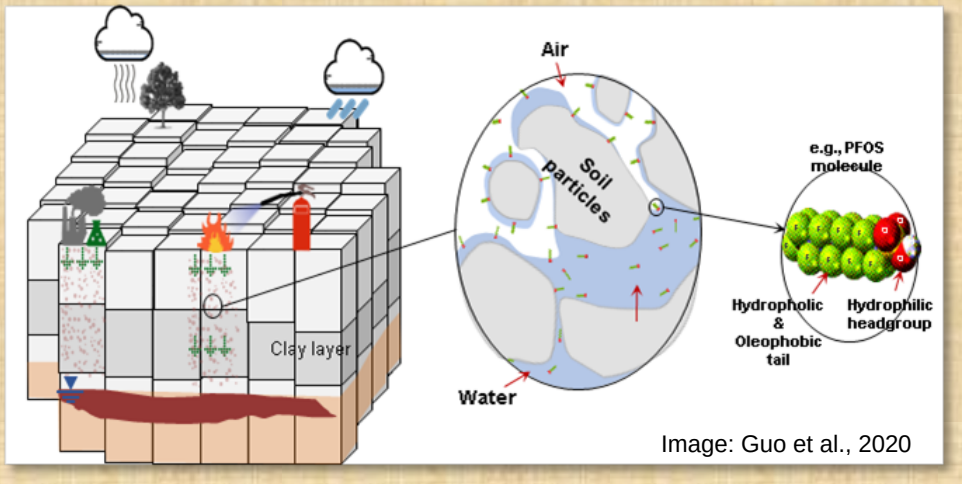


Image: Guo et al., 2020

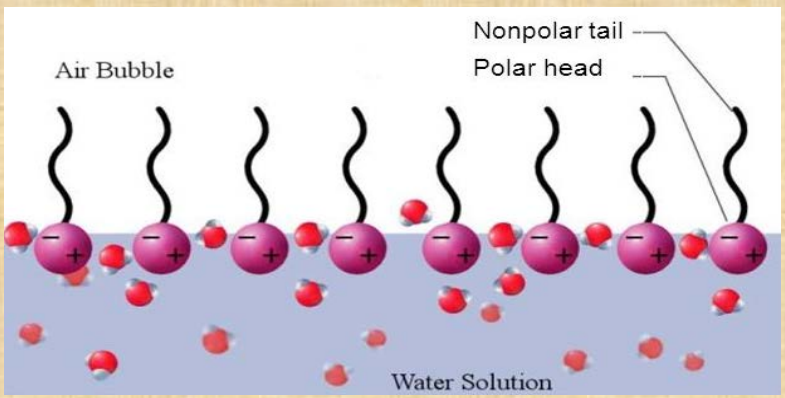
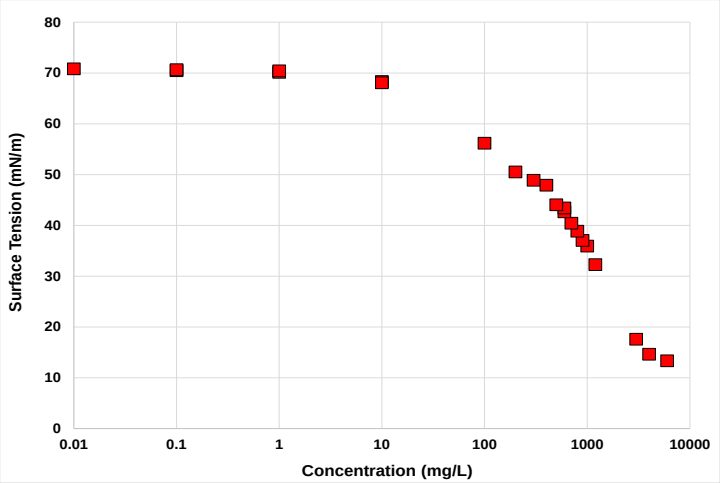


Image: https://en.wikipedia.org/wiki/Langmuir%E2%80%93Blodgett_film

- Adsorption at the air-water interface
- Ramifications:
  - Potential to cause surfactant-induced flow
  - Increased retention and retardation for transport

Surfactant-Induced Flow

Adsorption of PFAS at air-water interface reduces surface tension (σ)



>>> Unsaturated Porous Media

Changes in surface tension impact capillary pressure: $h = \frac{\sigma}{\sigma_0} h_0$

This causes water flow

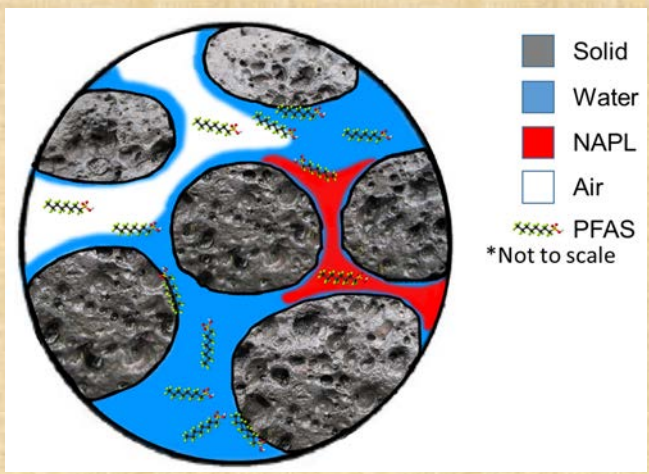
- **Surfactant-induced flow leads to:**
  - Transient flow
  - Impacts to solute transport
  - Changes in local water saturation
  - Changes in the magnitude of air-water interfacial area
  - Impact on the magnitude of retention by air-water interfacial adsorption

>>> Complex, interconnected flow and transport behavior

Fluid-Fluid Interfacial Retention

- Transport in source zones is influenced by additional retention processes: >>>> ***this adds complexity***
  - **Adsorption at air-water interfaces in vadose zones**
  - **Adsorption at NAPL-water interfaces in NAPL source zones**

    [NAPL = chlorinated solvents, fuels]



From: Brusseau, 2018

Comprehensive Retention Model for PFAS

Phase	*Source Zone*[a]	*Plume*[b]
Aqueous[c]		
Sorbed by solid phase		
Vapor		
Adsorbed at air-water interface		
Adsorbed at air-NAPL interface		
Adsorbed at NAPL-water interface		
Absorbed by NAPL		

Relevant for vast majority of PFAS at essentially all sites

Relevant for many critical PFAS of concern at many sites

Relevant for select PFAS at some sites

Not relevant

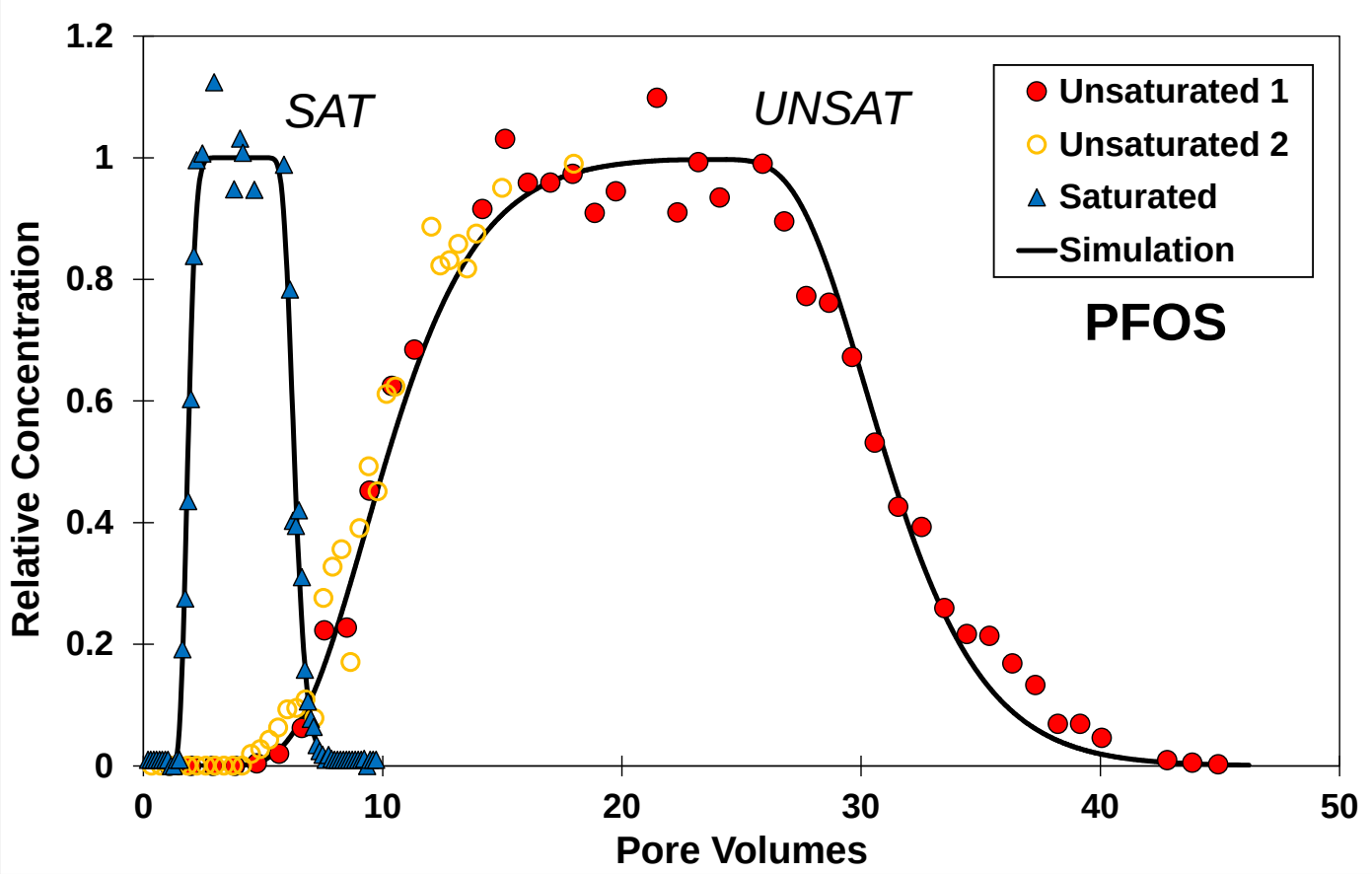
From: Brusseau et al., 2019b

PFAS Transport Experiments

- PFAS transport: **unsaturated** conditions

****Greater retardation for transport in unsaturated conditions; a result of adsorption at the air-water interface**

From: Brusseau et al. 2019, 2021



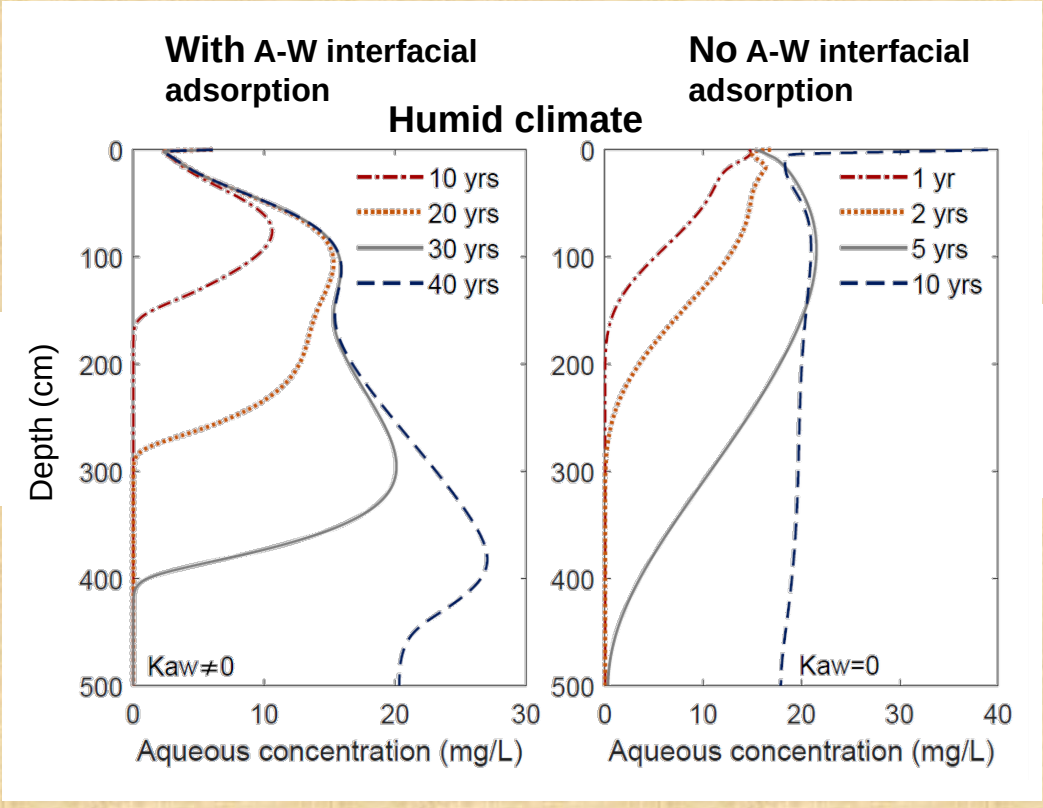
Example Simulation: PFAS Migration at a Fire Training Area

- Temporal evolution of vertical profiles of PFOS (Vinton soil)

Air-water interfacial adsorption significantly increases retention and decreases migration rate in the vadose zone

>>> Increases time to reach groundwater

Leaching front arrives in 35 years



Leaching front arrives in 5 years

From: Guo, Zeng, and Brusseau, 2020

Retention of PFAS

- Retardation Factor for aqueous-phase transport of PFAS influenced by solid-phase adsorption and air-water interfacial adsorption:

$$R = 1 + K_d \rho_b/\theta_w + \boxed{K_{aw} A_{aw}/\theta_w}$$

Magnitude of AWIA

K_d = solid-phase adsorption coefficient

K_{aw} = air-water interfacial adsorption coefficient

A_{aw} = air-water interfacial area

ρ_b = bulk density of porous medium

θ_w = volumetric water content

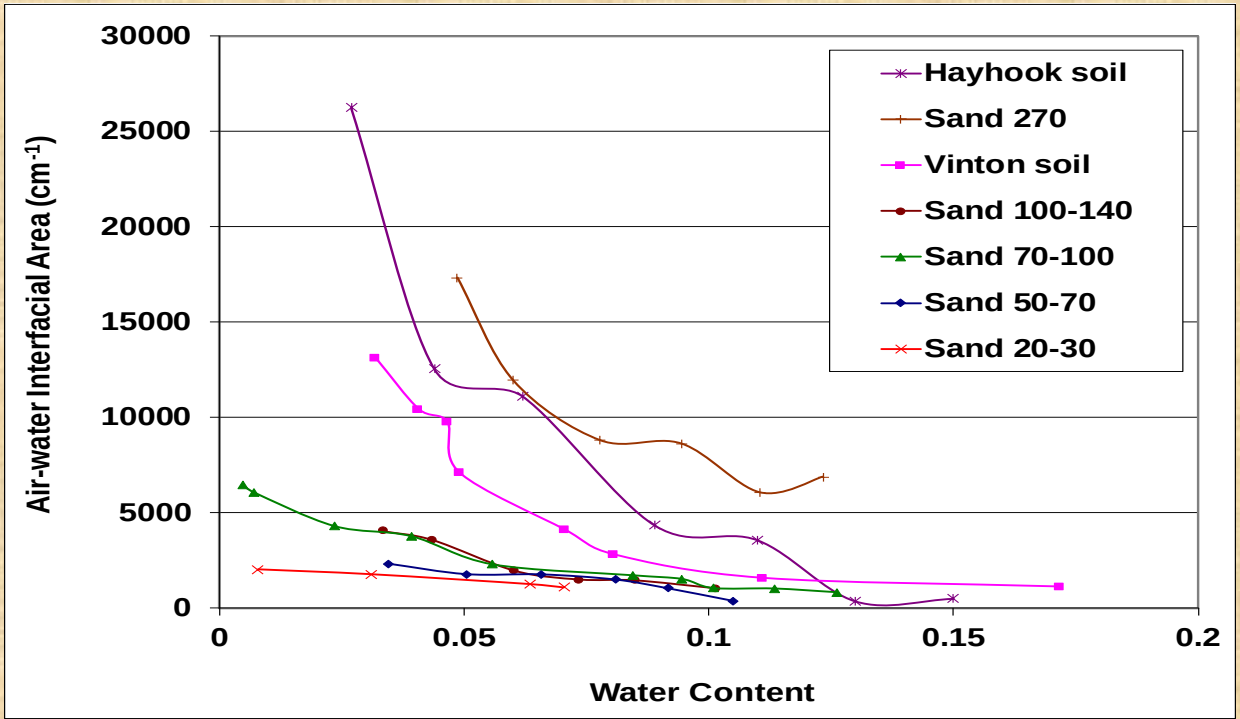
Air-Water Interfacial Area

Air-water interfacial area (A_{aw}) is a function of:

- Soil properties- Interfacial area is larger for media with smaller grains and larger solid-surface areas

- Water saturation- Interfacial area increases as wetting-fluid content decreases

Air-water interfacial areas measured for unsaturated media

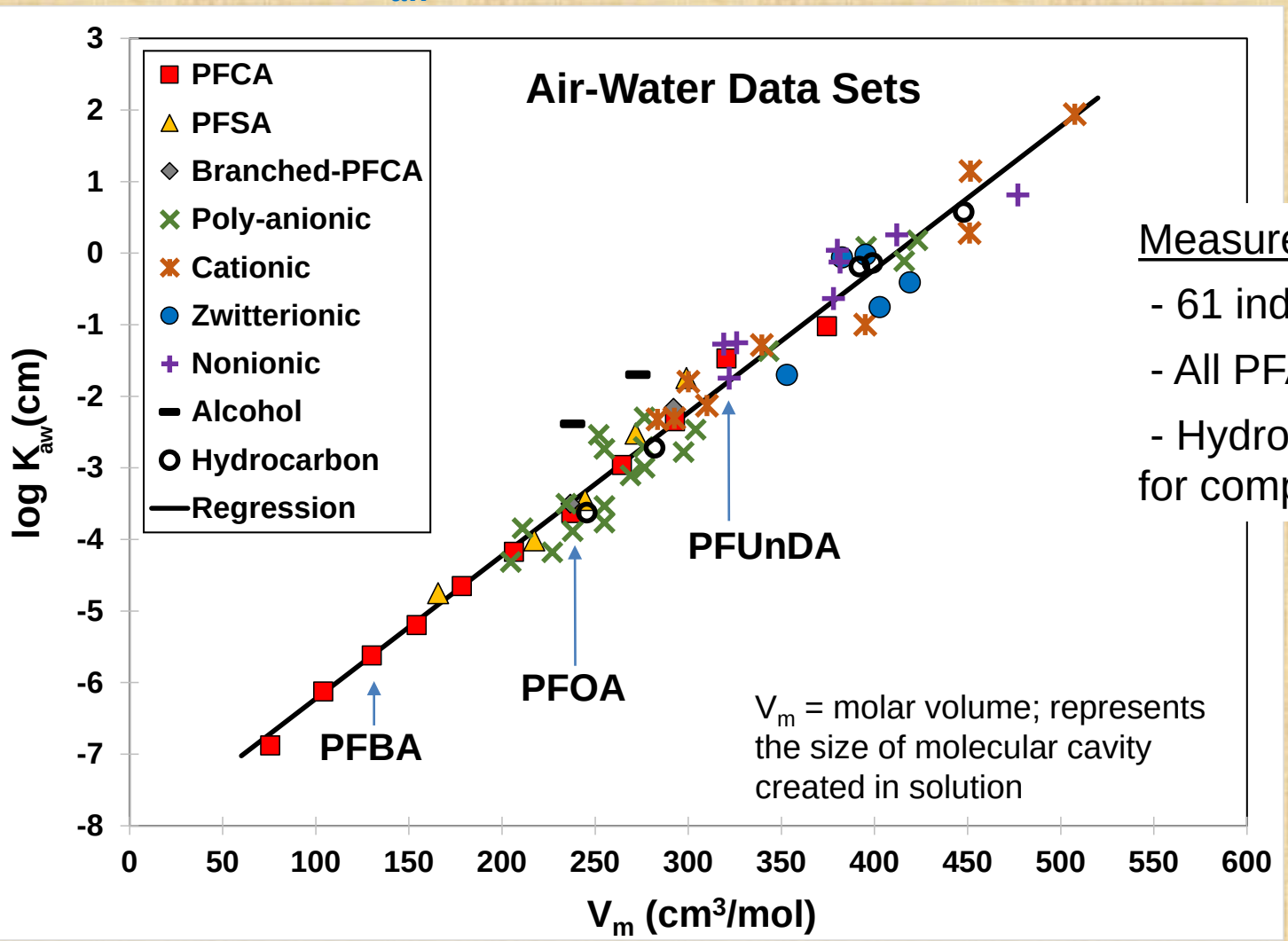


From: Peng and Brusseau, 2005. The impact of soil texture on air-water interfacial areas in unsaturated sandy porous media. Water Resources Research, 41, 1-8.

K_{aw} for PFAS

Quantitative-Structure – Property Relationship Analysis

- K_{aw} is larger for larger PFAS



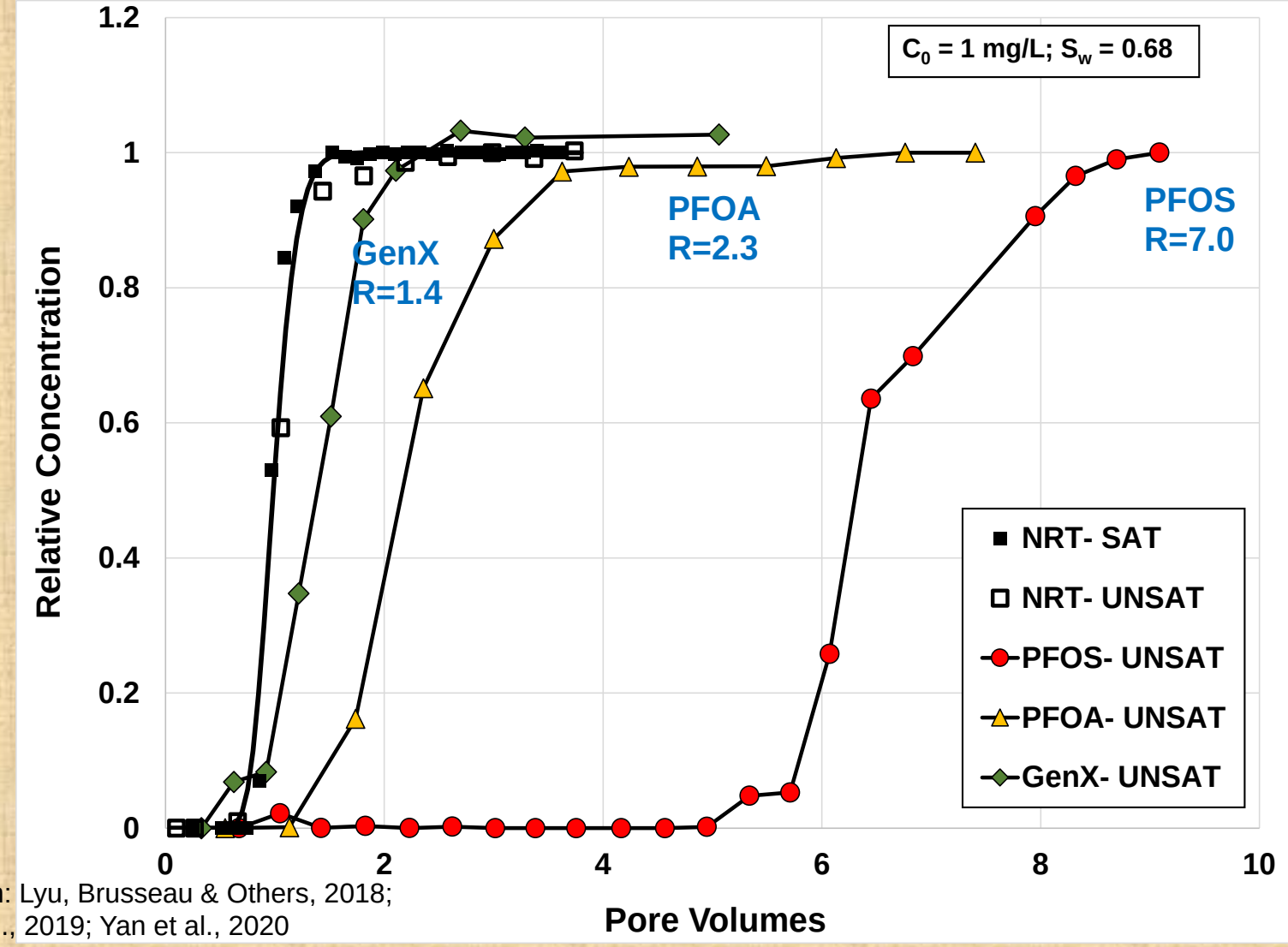
Measured data include:

- 61 individual PFAS
- All PFAS structure types
- Hydrocarbon surfactants for comparison

From: Brusseau, 2019b; Brusseau & Van Glubt, 2021

R and PFAS Molecular Structure

- **Retardation is larger for longer-chain PFAS**



Compiled from: Lyu, Brusseau & Others, 2018; Brusseau et al., 2019; Yan et al., 2020

Solid-phase Sorption

- Sorption of PFAS by soil, sediment, and aquifer material (geomedia) is complex
- Function of PFAS molecular structure and the geochemical properties of the geomedia

Geomedia are geochemically heterogeneous

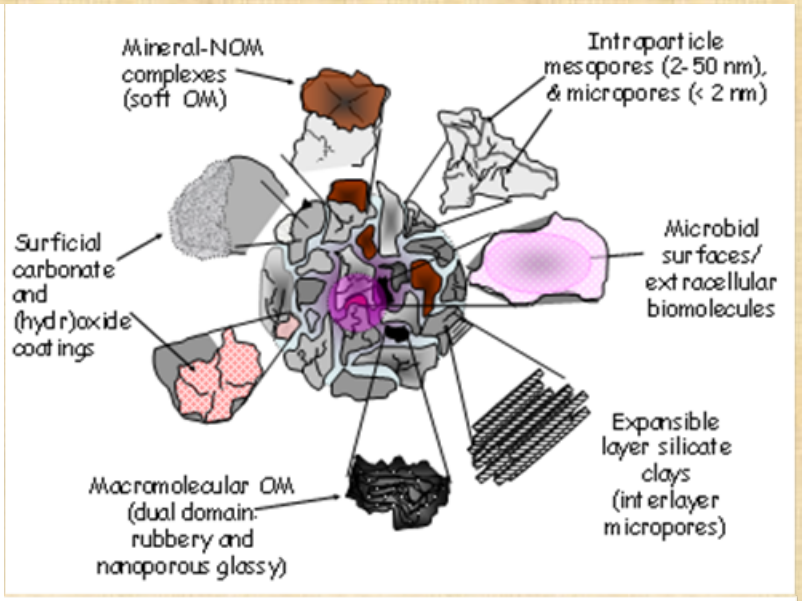
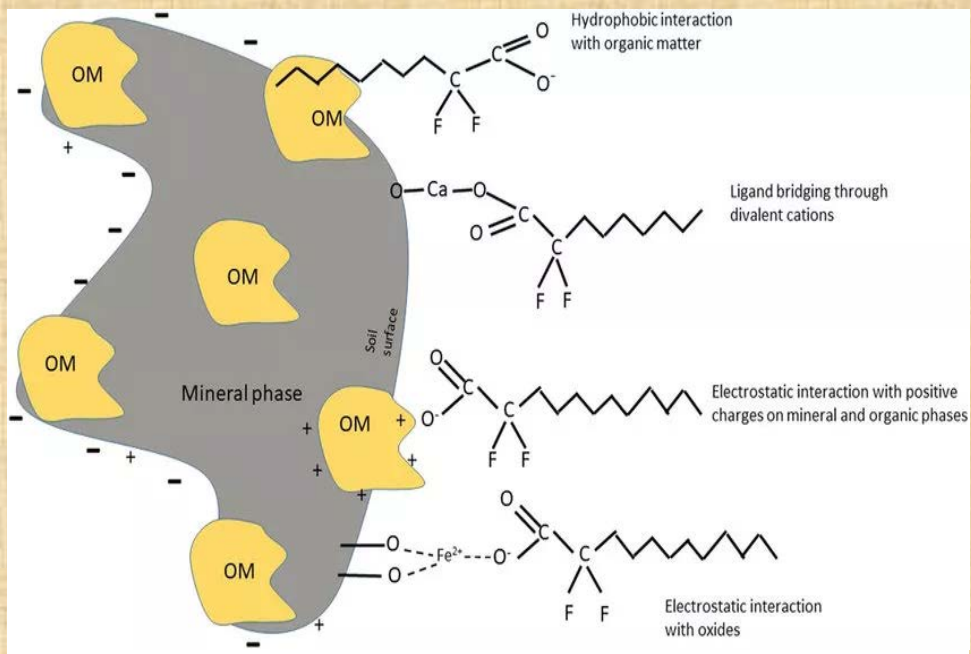


Figure A. Biogeochemically-reactive solid-water interfaces present in natural and waste-impacted geomedia (from Chorover and Brusseau, 2008)

Multiple Sorption Mechanisms

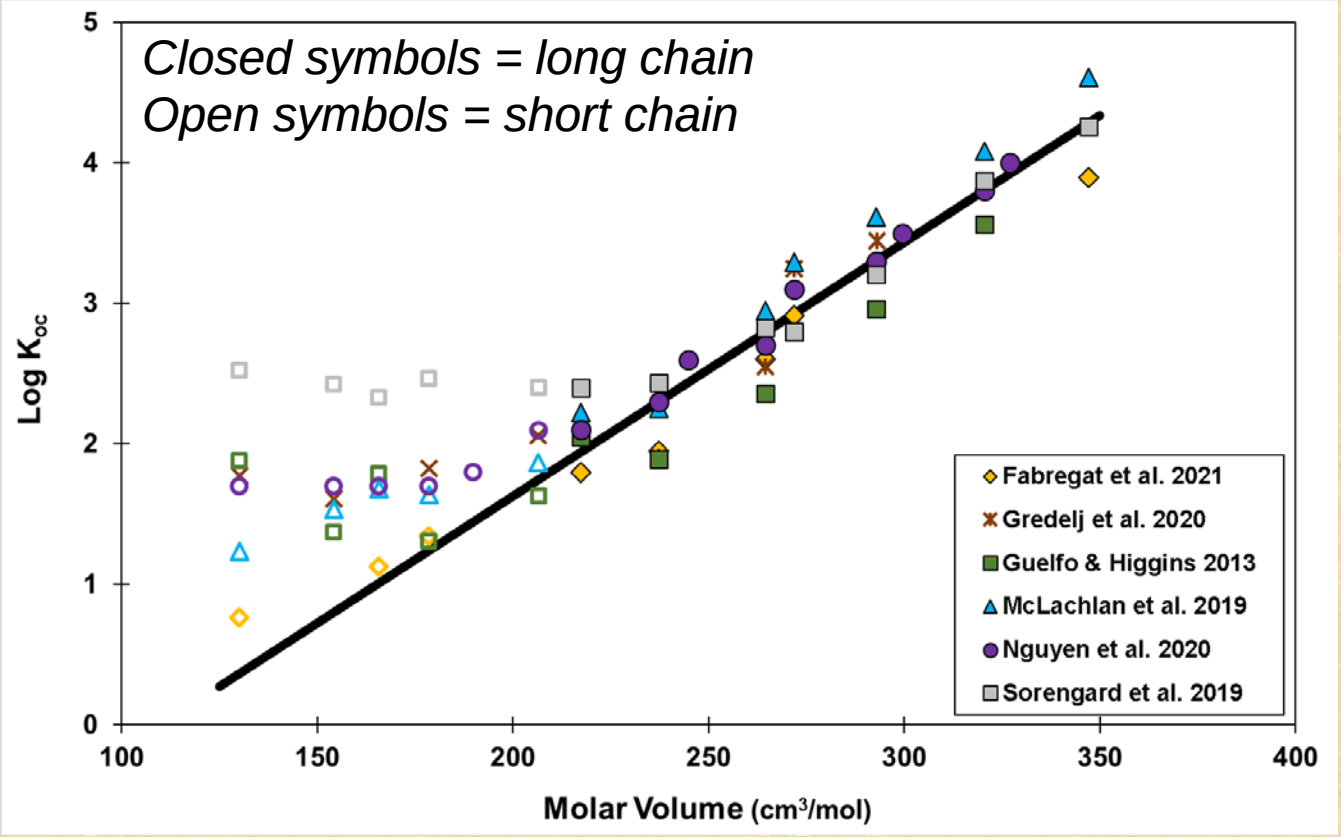


From: Li, Y., Oliver, D.P., Kookana, R.S., 2018. Sci. Total Environ. 628/629, 110-120.

Solid-phase Sorption

- Meta-analysis of short-chain vs long-chain anionic PFAS sorption

Short-chain PFAS exhibit greater sorption than predicted from long-chain behavior

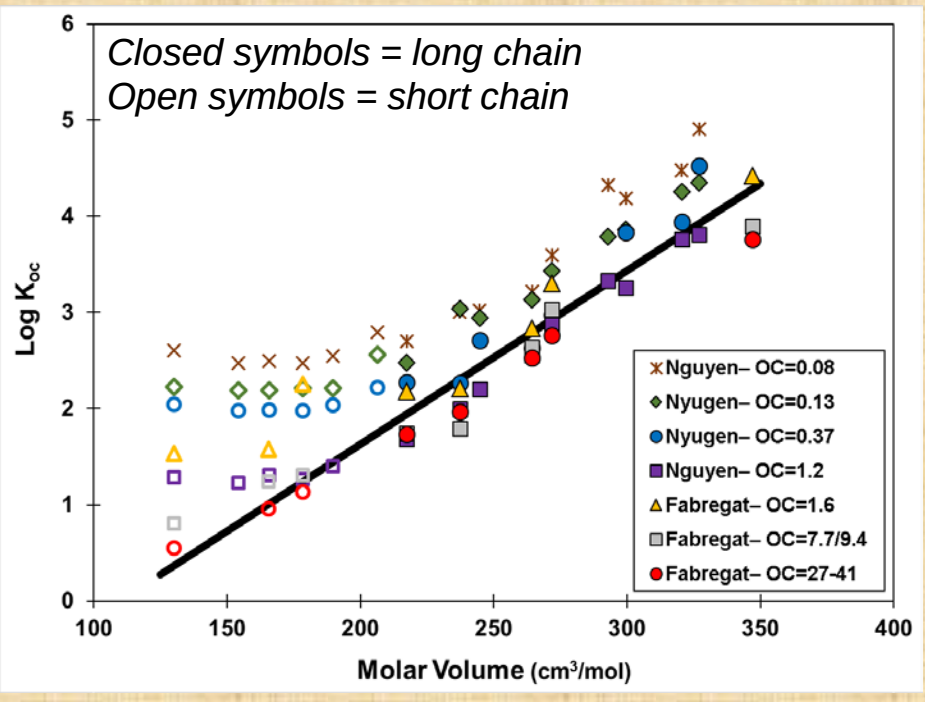


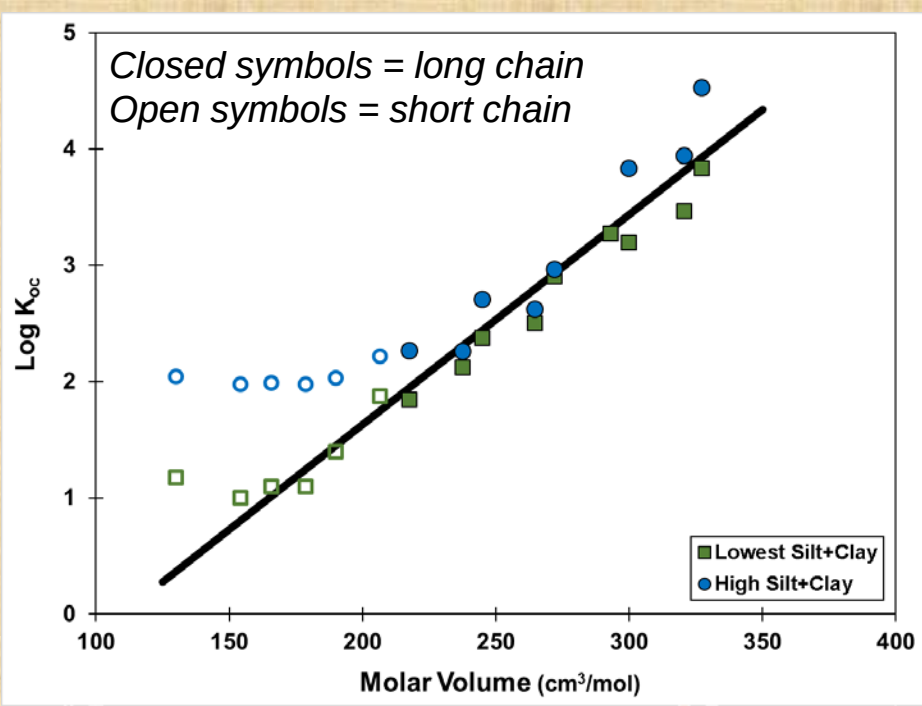
From: Brusseau, 2023c

Solid-phase Sorption

- Meta-analysis of short-chain vs long-chain anionic PFAS sorption

Short-chain PFAS sorption strongly influenced by organic-carbon content & silt + clay content

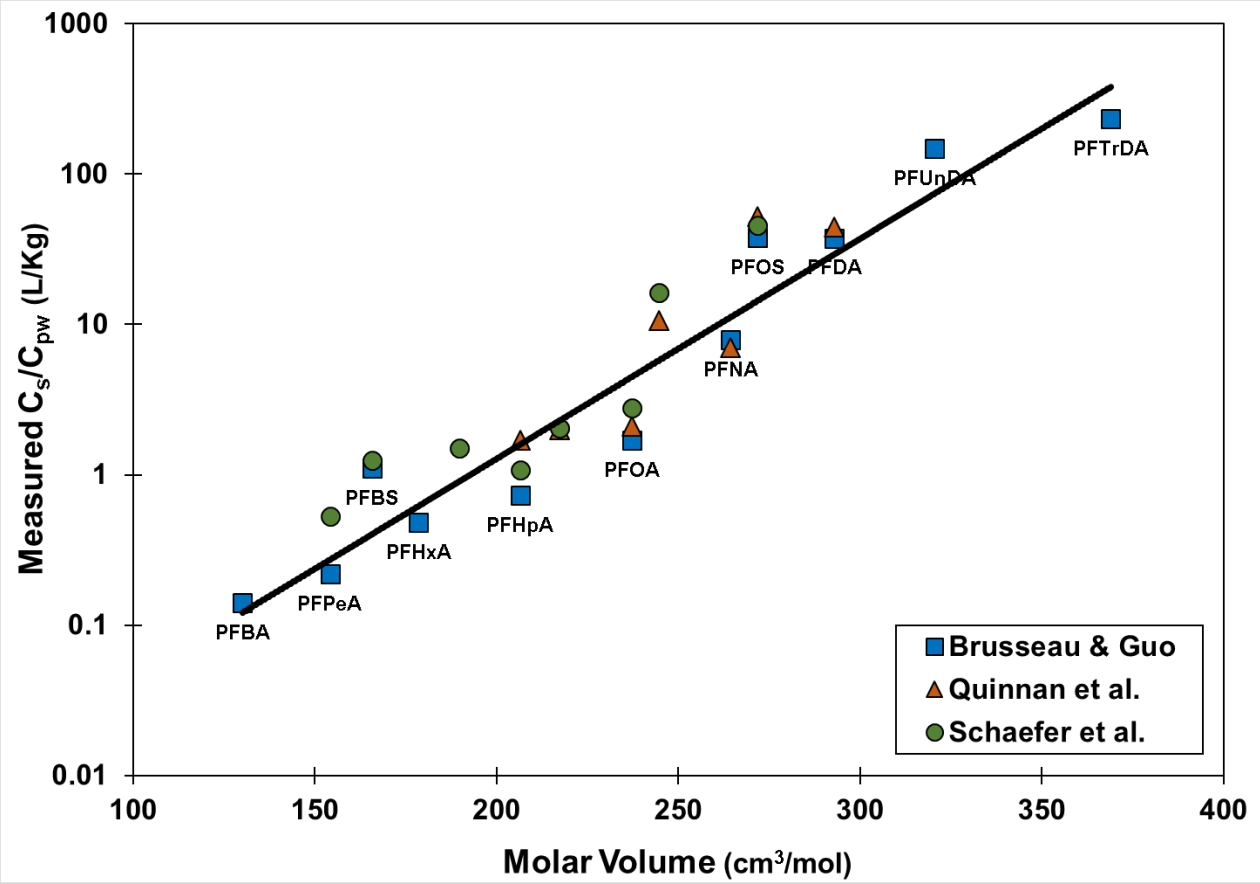




From: Brusseau, 2023c

Field Study of PFAS in the Vadose Zone

Soil vs Porewater concentrations



C_s = Soil Concentration

C_{pw} = Porewater Conc

$$\frac{C_s}{C_{pw}} = \frac{\theta_w}{\rho_b} R_d$$

$$R_d = \left(1 + K_d \frac{\rho_b}{\theta_w} + K_{aw} \frac{a_{aw}}{\theta_w}\right)$$

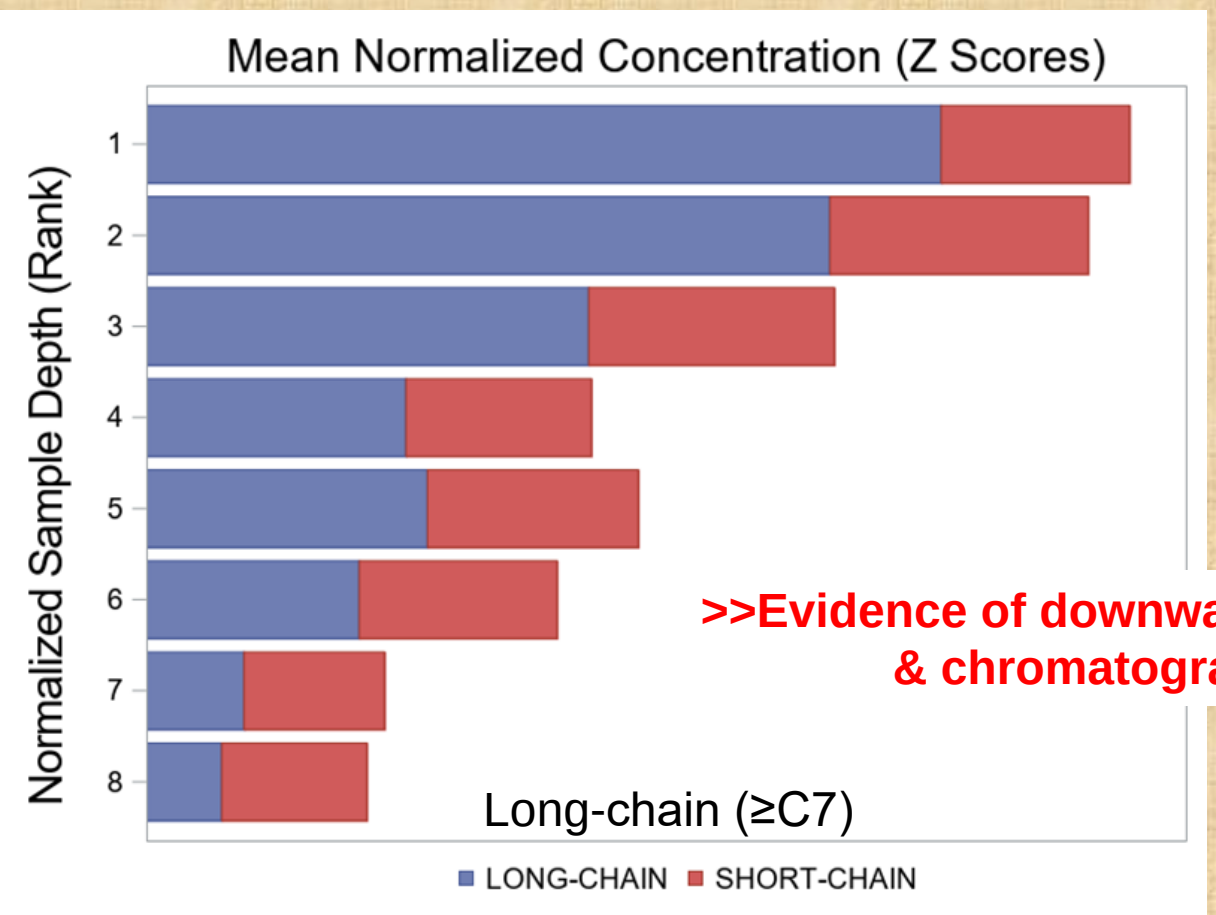
>>Evidence that PFAS distributes between soil and porewater as anticipated for these three systems

From: Brusseau, 2023d

Field Study of PFAS in the Vadose Zone

Vadose-zone concentration distributions

Depth distribution of **total PFAS** in soil as a function of chain length



- The data represent 124 boreholes across 30 AFFF sites for which at least 8 depth-discrete samples were collected for each borehole.

- Depth interval spans from ground surface to top of saturated zone (gw).

>>Evidence of downward migration & chromatographic separation

From: Brusseau, Anderson, & Guo, 2020

Other Factors

- Physical heterogeneity & preferential flow
  - May reduce retention and led to enhanced transport
- Colloids
  - Potential facilitated transport
- PFAS mixtures
  - Impact of co-solute interaction on retention
- Co-contaminants
  - Impact on PFAS retention
- Precursors and non-characterized PFAS
  - Potential impacts

Summary

- Retention and leaching in the vadose zone is complex- influenced by multiple processes
- Adsorption at the air-water interface can be significant
- On-going research to determine relevance of processes and how to parameterize models for different conditions

>>> We have developed an initial understanding of the relevant transport processes; the critical issue now is to translate this knowledge into practice

Thank You

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