

Per- and polyfluoroalkyl substances (PFAS): Passive samplers & nontargeted/bulk analysis

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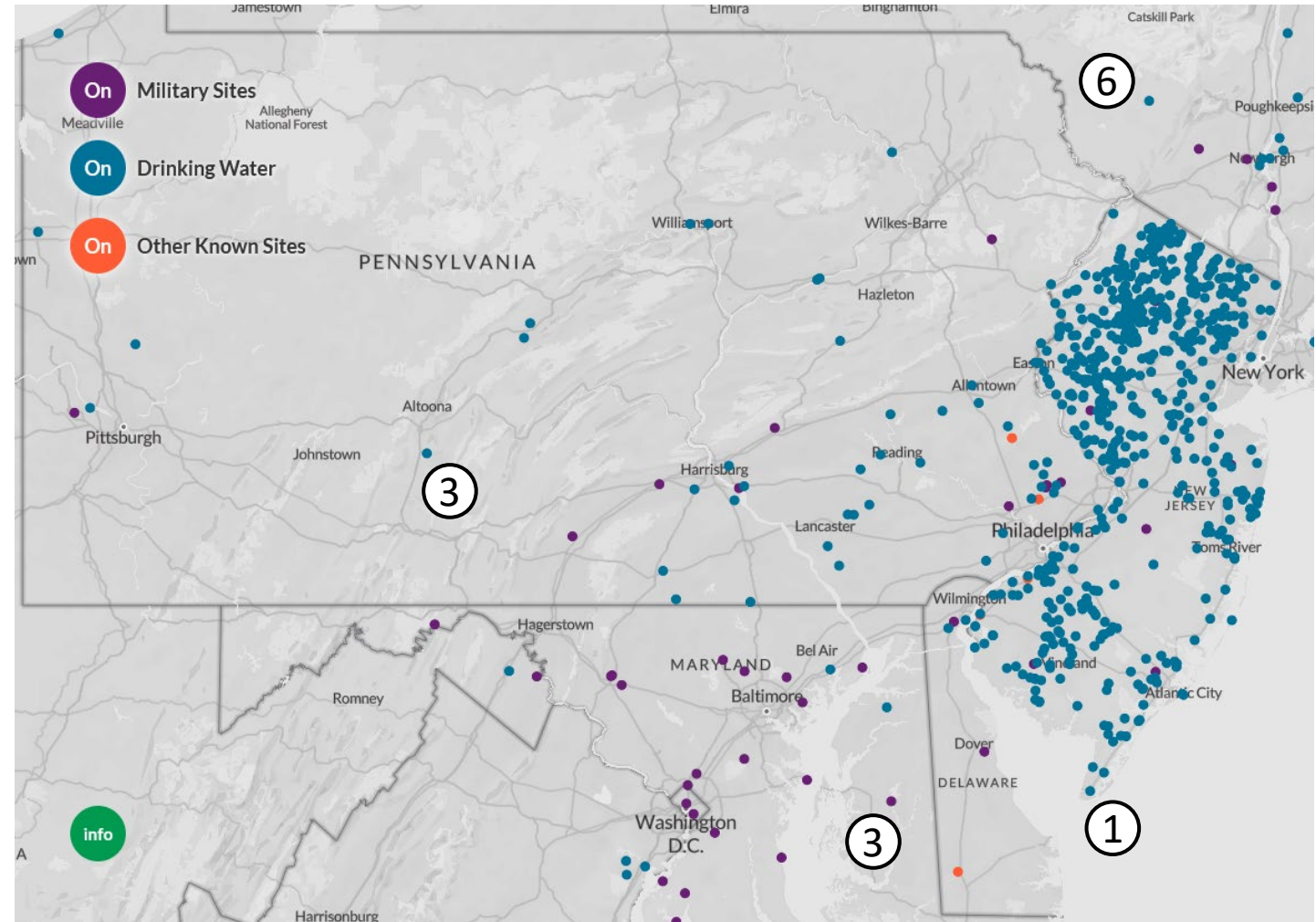
We need more options for PFAS sampling and quantitation to fill existing gaps in temporal and spatial resolution at sites of concern

The availability of PFAS datasets are still quite limited for most locations.

Contract labs are asking for \$537 per sample for EPA 1633 analysis, meaning that the costs of triplicate analysis are over \$1600 USD.

Targeted methods measure ~40 (of over 12,000) PFAS. [EPA CompTox]

Site personnel, partners, and regulators need *additional* options for collecting PFAS data.



https://www.ewg.org/interactive-maps/pfas_contamination/

Part 1: Passive samplers [targeted]

Passive samplers are commonly deployed to collect information about time-averaged or -integrated contaminant concentrations

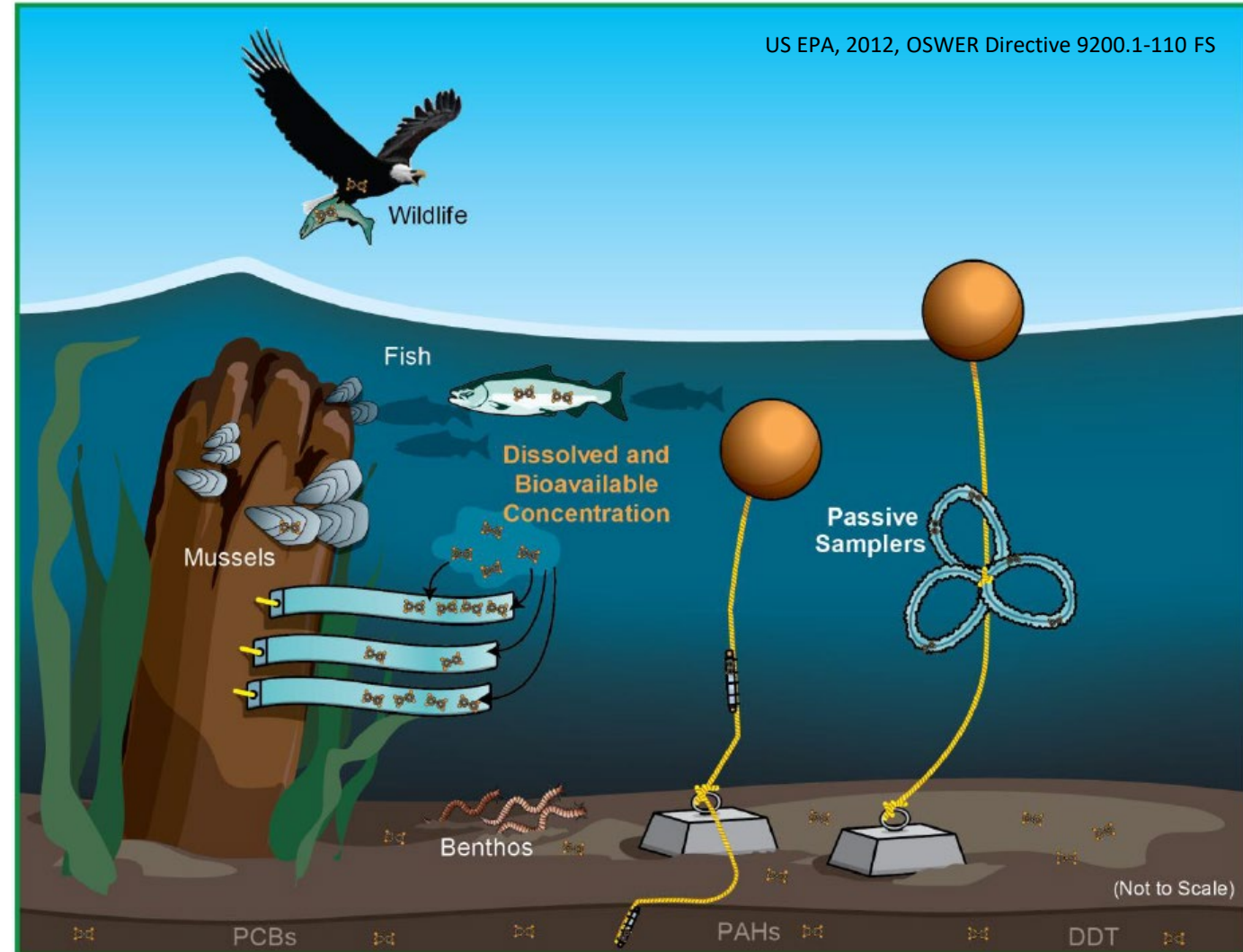
The passive sampling concept relies on known equilibrium or kinetic relationships between the sampler and contaminant, enabling back calculation of time-averaged or -integrated contaminant concentrations in the dissolved phase.

For **equilibrium** samplers:

$$K_d = \frac{q_s}{C_w}$$

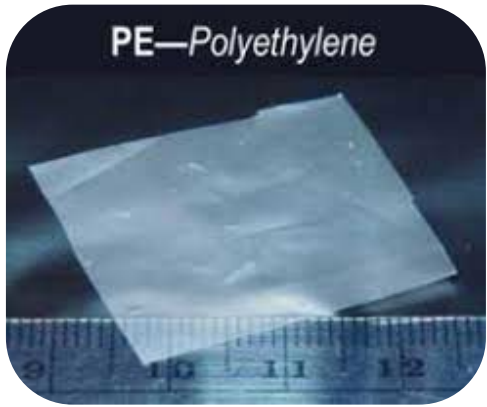
For **kinetic** samplers:

$$R_s = \frac{q_s M_s}{C_w t}$$



Conventional passive sampling approaches are targeted at hydrophobic (nonpolar) or hydrophilic (polar) compounds

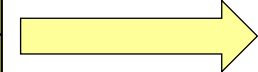
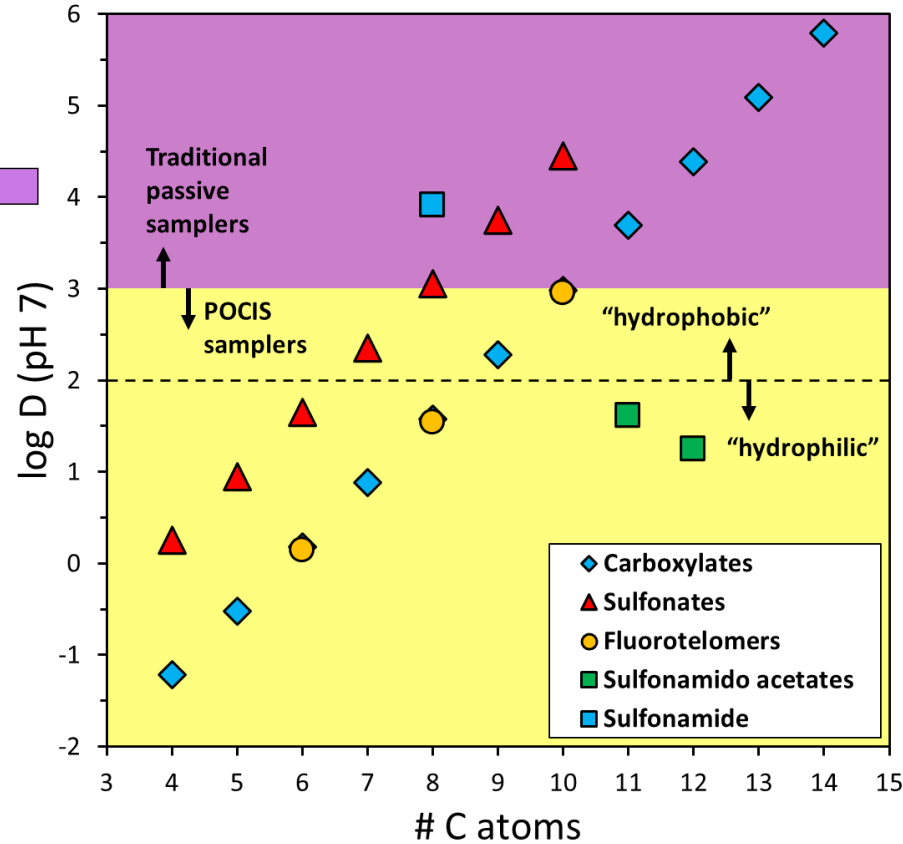
The variable physicochemical properties of PFAS mandate new approaches.



Short-chain PFAS



Long-chain PFAS



Short-chain PFAS



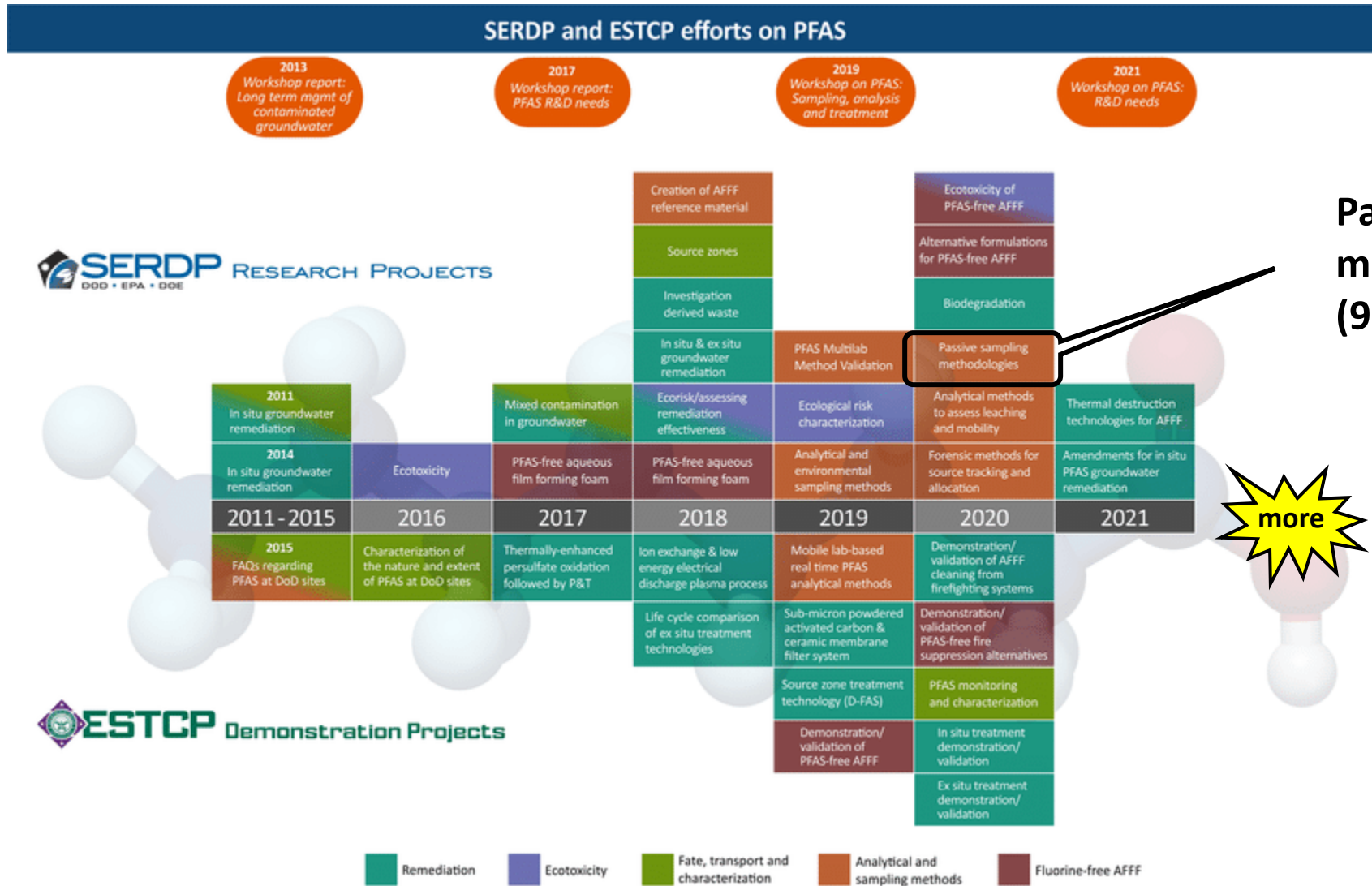
Long-chain PFAS



<https://encrypted-tbn0.gstatic.com/images?q=tbn:ANd9GcSNl80wnr9ir8-dd63FGuKLuo8sD5Gh1ddEXCD2dNileZnqexYfpO0hDm8JUkNb6DVzSw&usqp=CAU>

https://www.est-lab.com/img/pocis_oncarrier_250.jpg

Strategic Environmental Research and Development Program (SERDP, DoD) has been driving a lot of PFAS research efforts



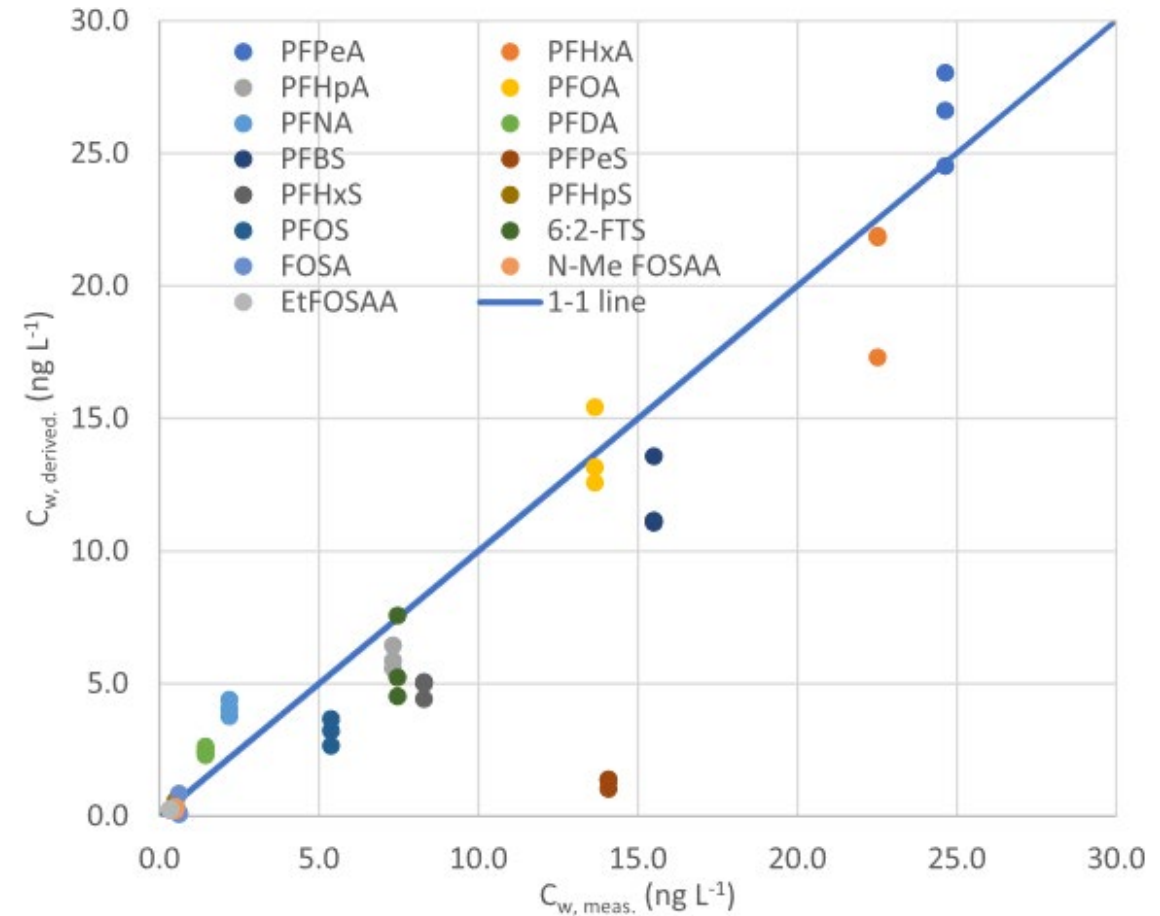
Passive sampling projects funded by SERDP – you can find more information on the project pages

- ER20-1211: Passive Samplers for Per- and Polyfluoroalkyl Substances with Innovative Sorbents (Mei Sun, University of North Carolina at Charlotte)
- ER20-1098: Development of a Novel PFAS Passive Sampler with Efficient Sorbent Media and Robust Membrane Barrier (Yin Wang, University of Wisconsin, Milwaukee)
- ER20-1073: Ion-Exchange Membranes as Passive Samplers for Chemically-Diverse PFAS (Lee Blaney, University of Maryland, Baltimore County)
- ER20-1293: Development and Field-Testing of Advanced Passive Samplers for PFAS (Rainer Lohmann, University of Rhode Island)
- ER20-1156: Development of Passive Sampling Methodologies for Per- and Polyfluoroalkyl Substances (Sarit Kaserzon, The University of Queensland)
- ER20-1363: Development of a Diffusive Gradients in Thin-Films Passive Sampling Methodology for Per- and Polyfluoroalkyl Substances in Water (Julian Fairey, University of Arkansas)
- ER20-1127: Osorb Media Use in PFAS Samplers (Craig Divine, Arcadis)
- ER20-1336: Development of Novel Functionalized Polymeric Thin Films for Equilibrium Passive Sampling of PFAS Compounds in Surface and Groundwater (Upal Ghosh, University of Maryland, Baltimore County)
- ER21-5104: Demonstration of a High Resolution Passive Profiler (HRPP) for Characterizing the Distribution of PFAS in Groundwater (Andrew Jackson, Texas Tech University)

Projects are ongoing, but preliminary results are promising – polyethylene tube samplers (Lohmann) showed good performance in surface waters



Microporous polyethylene tubes filled with HLB media.
Caveat: different calibrations for each water source (*i.e.*, R_s values).

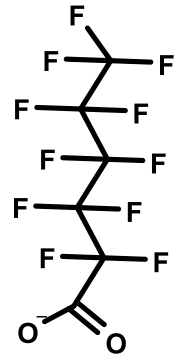
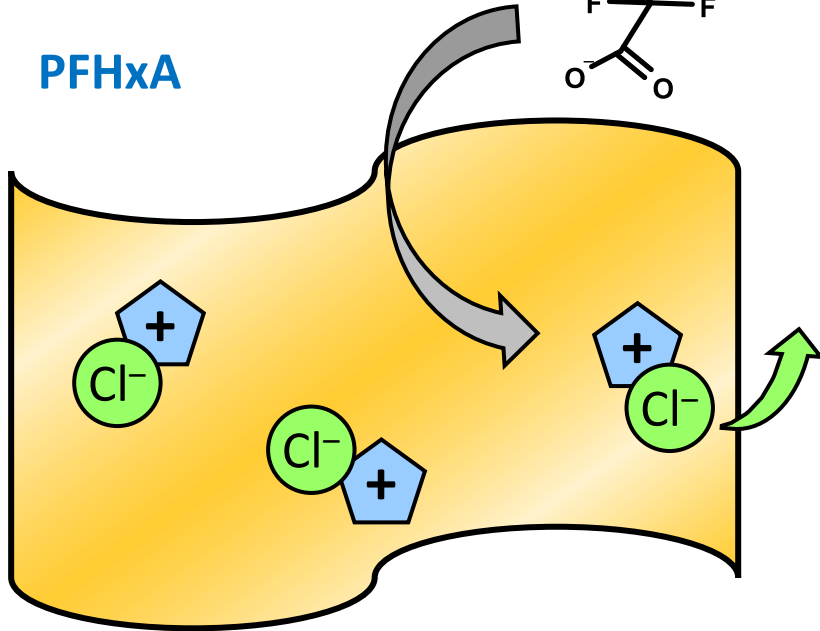


[Gardiner *et al.*, 2022, *Environ. Toxicol. Chem.*]

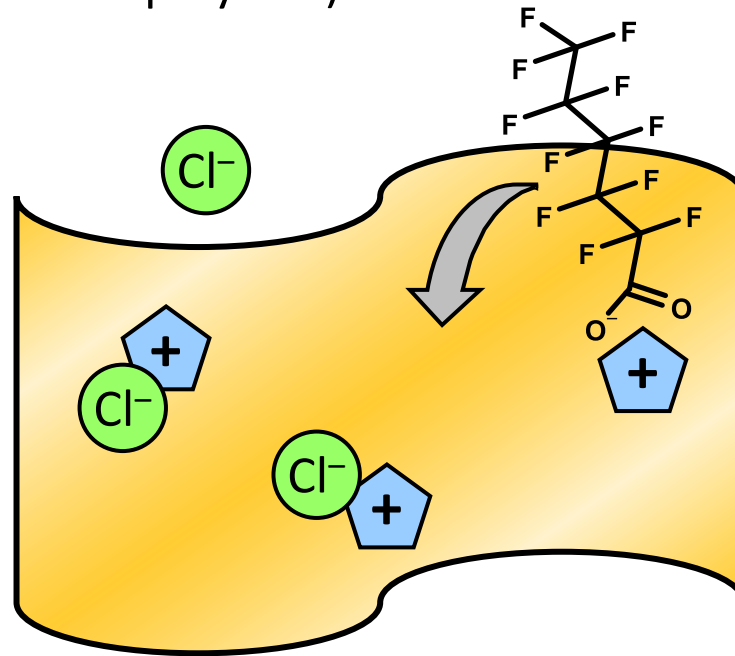
PFAS uptake by some samplers is initiated by ion-exchange reactions at $-N^+R_3$ sites and enhanced by hydrophobic interactions at the tail group

Step 1: Ion-exchange reaction (PFAS head group reacts with fixed-charge of IEM)

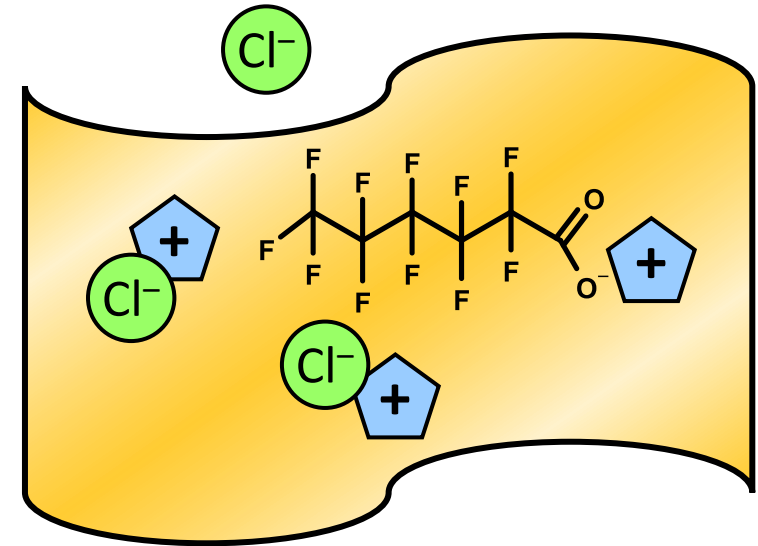
PFHxA



Step 2: Hydrophobic-hydrophobic interactions (PFAS tail folds down and interacts with polymer)



Increased selectivity with chain-length comes (partly) from the interactions with hydrophobic tail and (partly) from greater electron-withdrawing effects



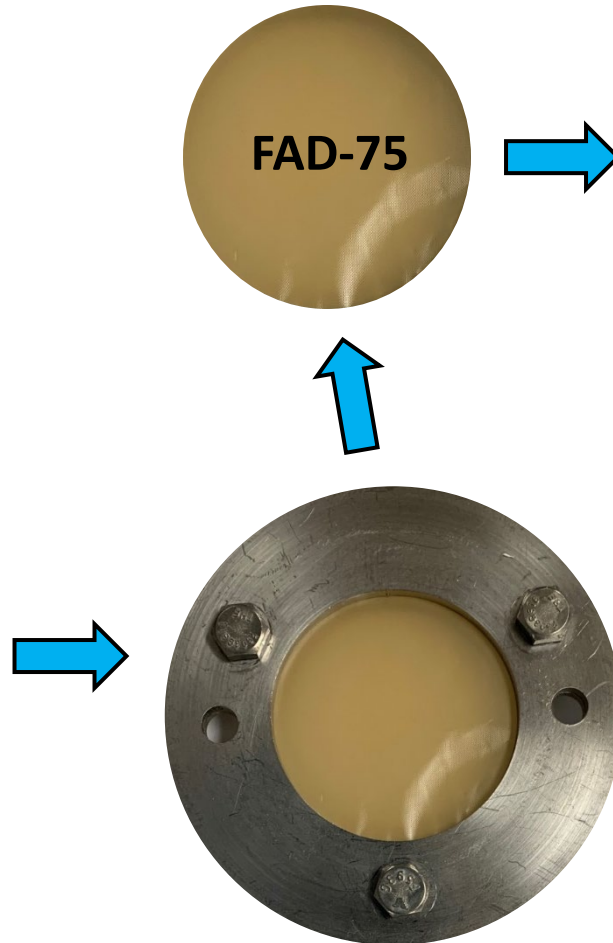
[ER20-1073, Blaney & He]

Importantly, our membrane can be effectively dissolved in methanol, which ensures 100%* recovery for back-calculation of $[PFAS]_{aq}$

1. Deploy samplers



2. Retrieve samplers and membranes



3. Add membranes to methanol with 0.2 M NH_4Ac



4. Membrane dissolves, releasing PFAS and Cl

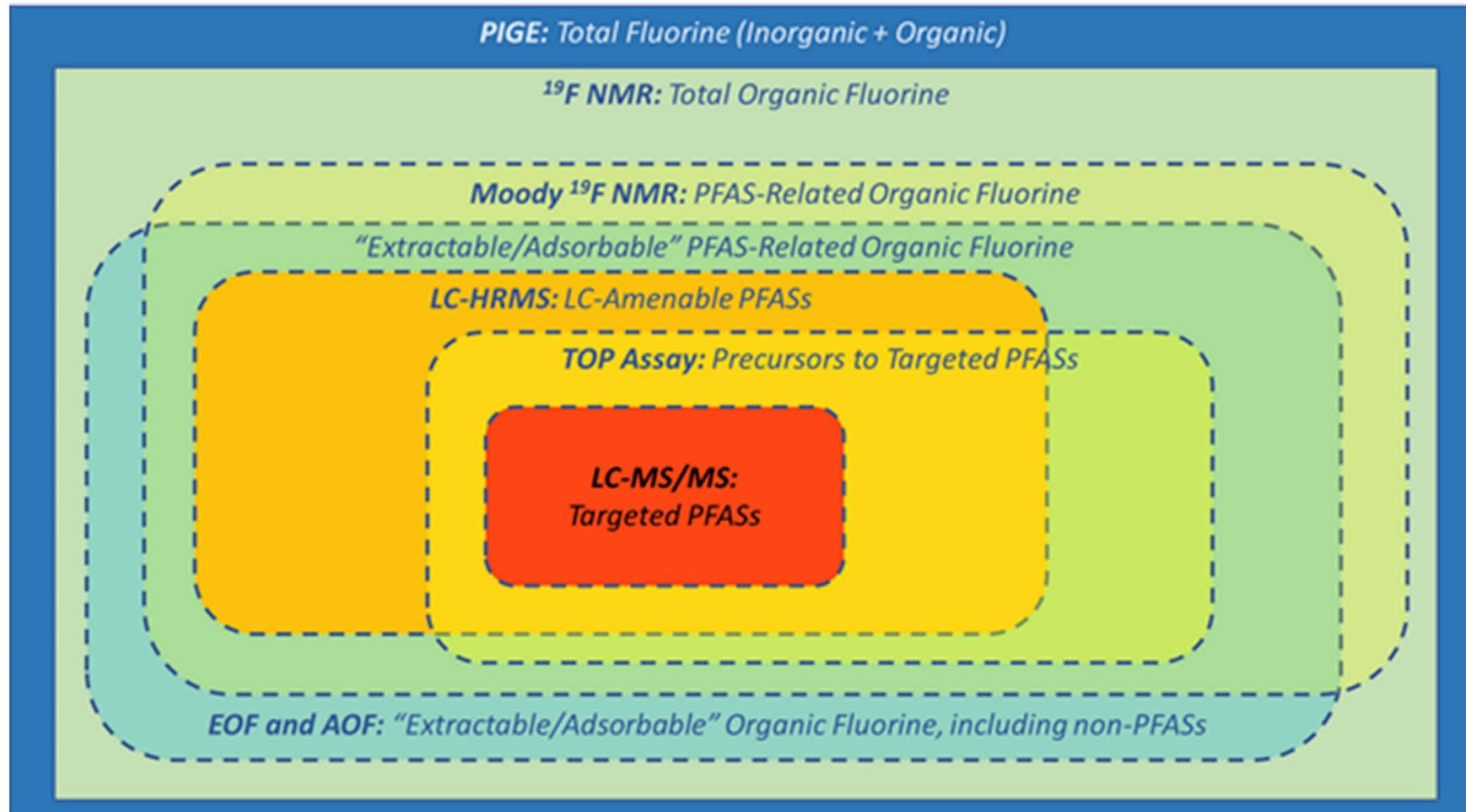


5. Use selectivity factor to back-calculate the aqueous-phase PFAS concentrations

[ER20-1073, Blaney & He]

Part 2: Nontargeted (and bulk) PFAS analysis

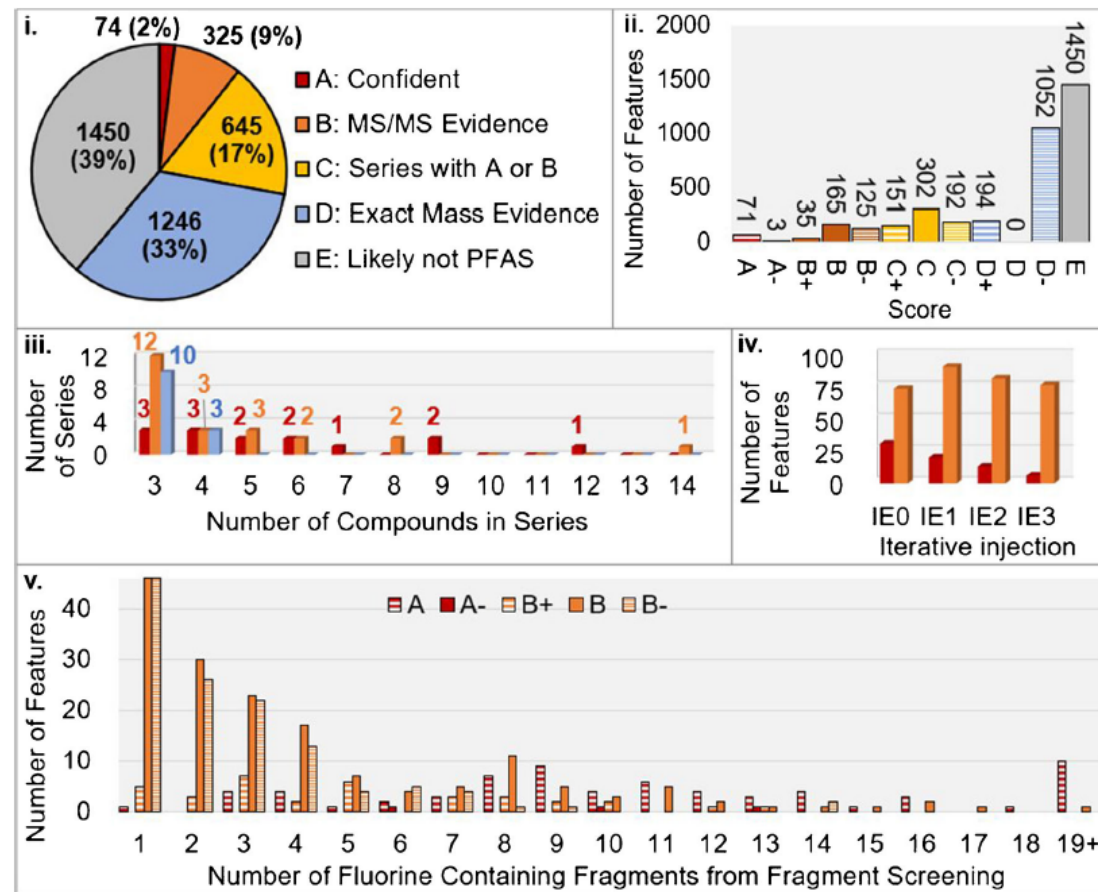
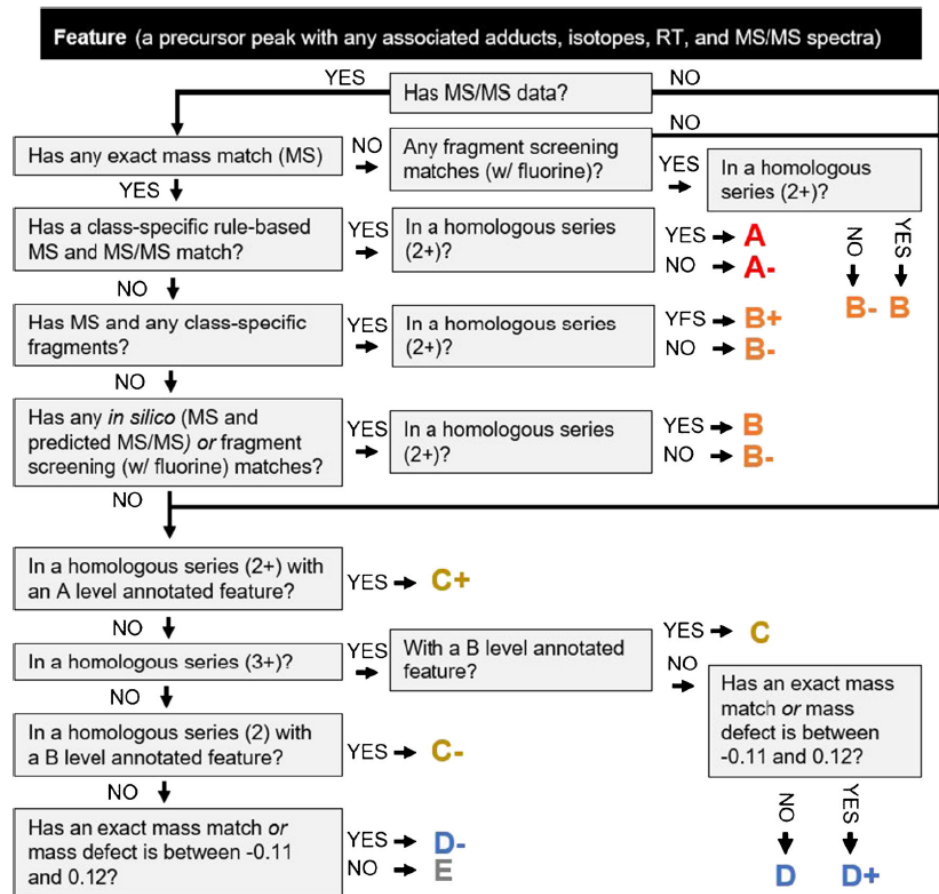
What fluorine is being measured?



[McDonough *et al.*, 2019, *Curr. Opin. Environ. Sci. Health*]

High-resolution mass spectrometry – determine chemical formula of unknown PFAS, but care must be taken in extending results to structures

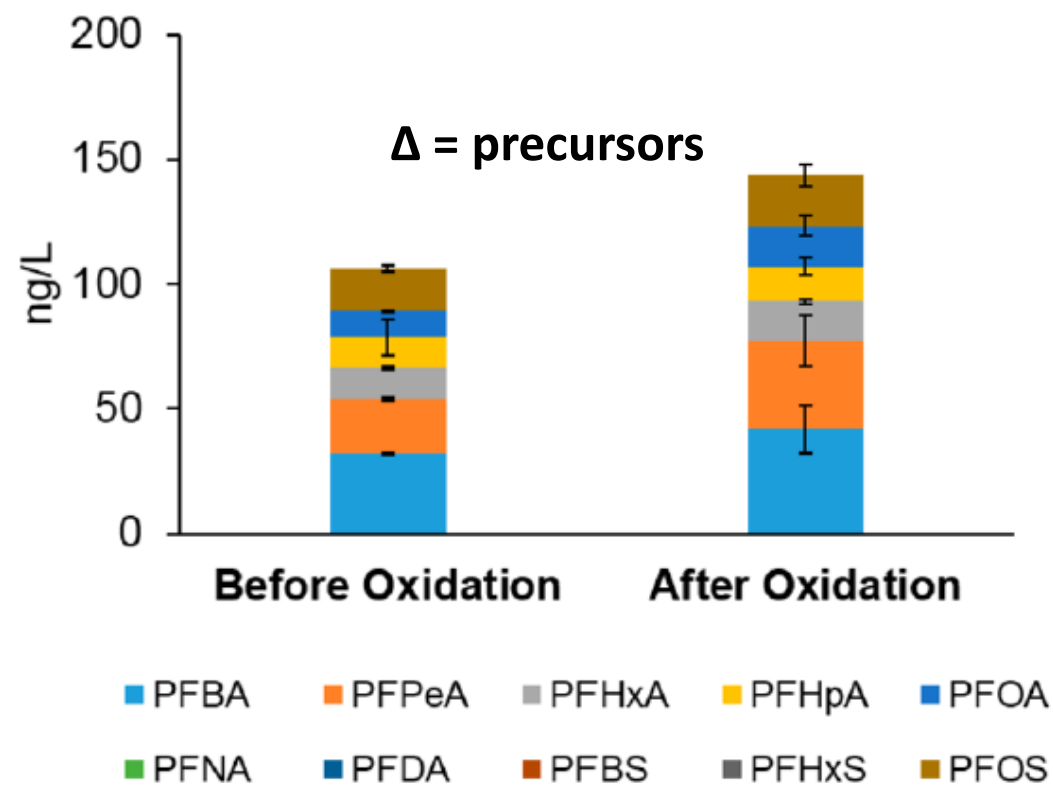
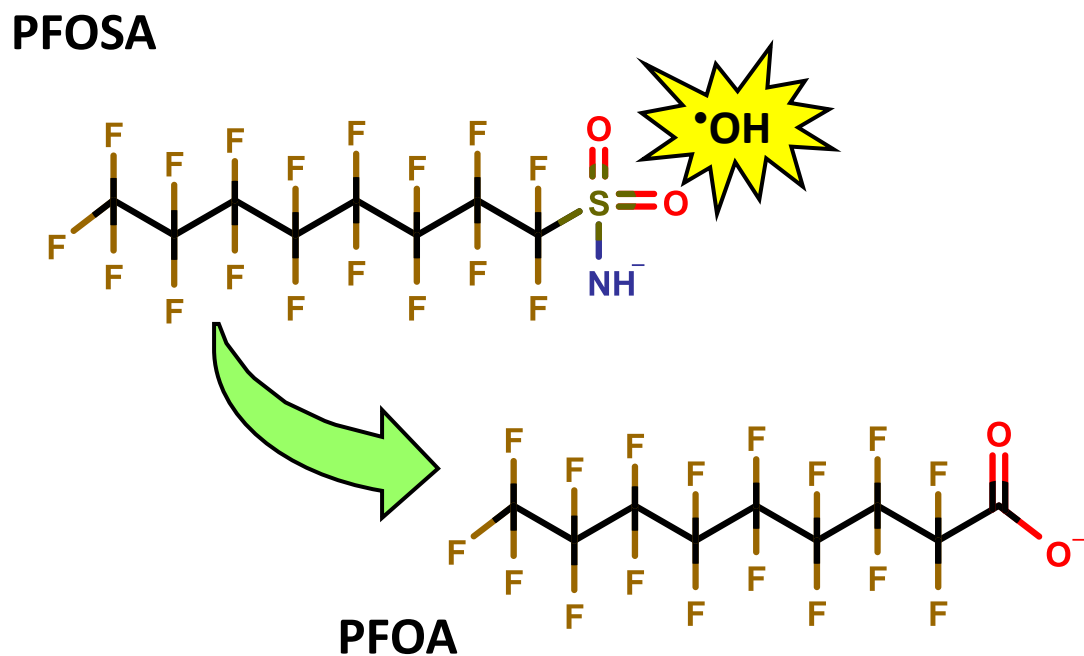
I don't expect that this tool will be important for the regulatory community *per se*, but could identify new targeted PFAS.



[Koelmel *et al.*, 2022, *Anal. Bioanal. Chem.*]

Total oxidizable precursors (TOP) assay – bulk analysis of precursors that would eventually transform into targeted/regulated PFAS

The TOP assay generates a high concentration of hydroxyl radicals ($\cdot\text{OH}$), which degrade the nonfluorinated head groups of PFAS and generate terminal perfluorinated compounds.



Well developed for clean* water samples, application to more complex samples requires careful protocols and optimization.

[Zhang *et al.*, 2019, *ES&T Lett.*]

Combustion ion chromatography for adsorbable/extractable organic fluorine – this tool is being increasingly used

Careful optimization is required, recoveries can vary by substrate and operating conditions.

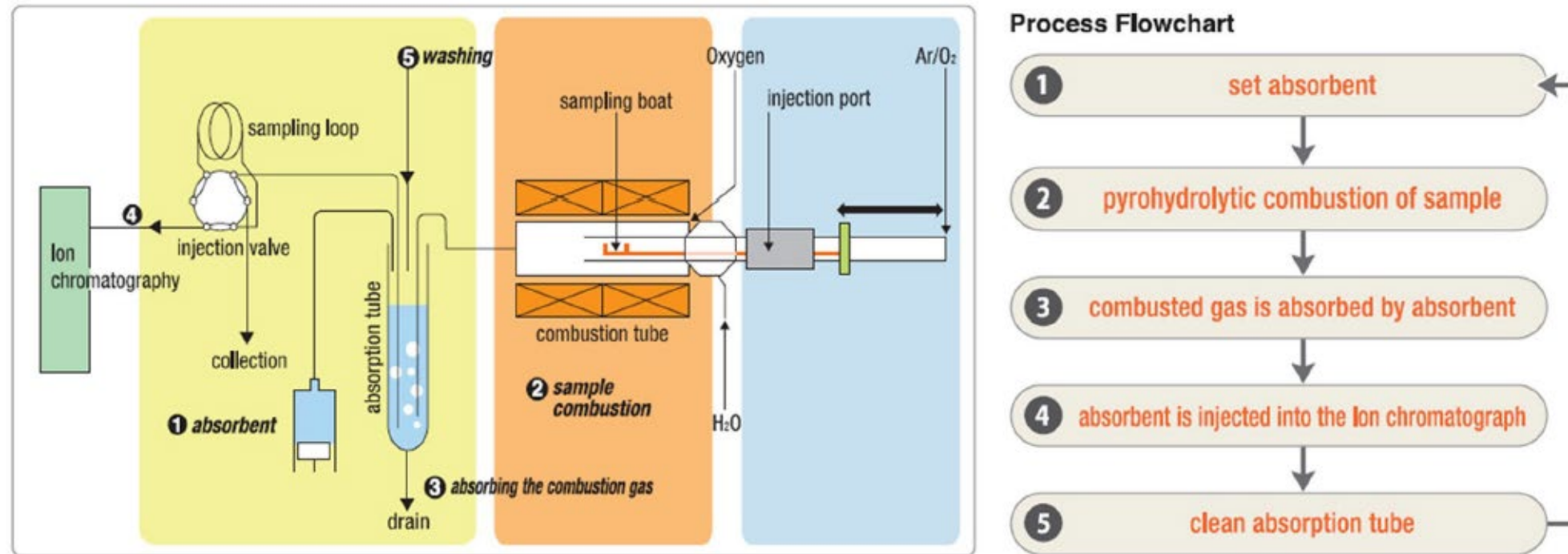
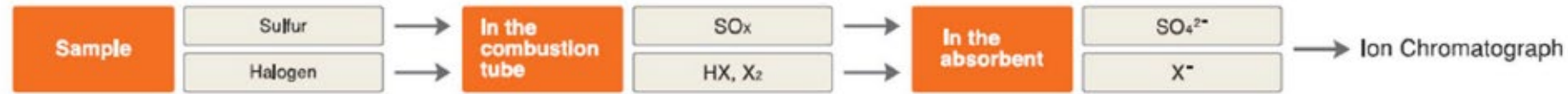
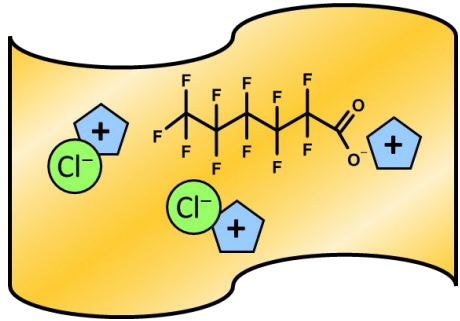


Figure 1. Diagram of a CIC system for the determination of adsorbable organic halogens²³

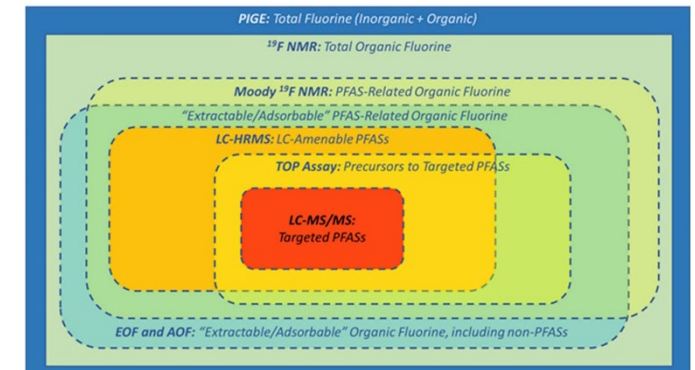
[Thermo Fisher]

Conclusions



Passive samplers. Diverse types of passive samplers are being developed and preliminary results are promising, but there is a need to work towards universal calibration. Samplers with high selectivity for ultrashort- and short-chain PFAS will be most valuable.

Nontargeted analysis. A number of new tools are available for bulk or nontargeted PFAS analysis, some of these are more academic/exploratory in nature (but will inform future regulated PFAS), whereas others are broadly suitable for application with appropriate QA/QC.



Thanks for your attention

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