PFAS Passive Sampling

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STEEP

Sources, Transport, Exposure & Effects of PFASs

UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

THE UNIVERSITY OF RHODE ISLAND GRADUATE SCHOOL OF OCEANOGRAPHY

Lohmann Lab at URI

- Rainer Lohmann
- Jarod Snook, Melissa Woodward
- Christine Gardiner, Matt Dunn

Collaborators

US EPA in Narragansett RI (Brian Clark)

Brown University (Robert Hurt and Zachary Saleeba)

Larry Barber (USGS)

NIH National Institute of Environmental Health Sciences *Superfund Research Program*

HARVARD T.H. CHAN SCHOOL OF PUBLIC HEALTH

SILENT SPRING INSTITUTE Researching the Environment and Women's Health

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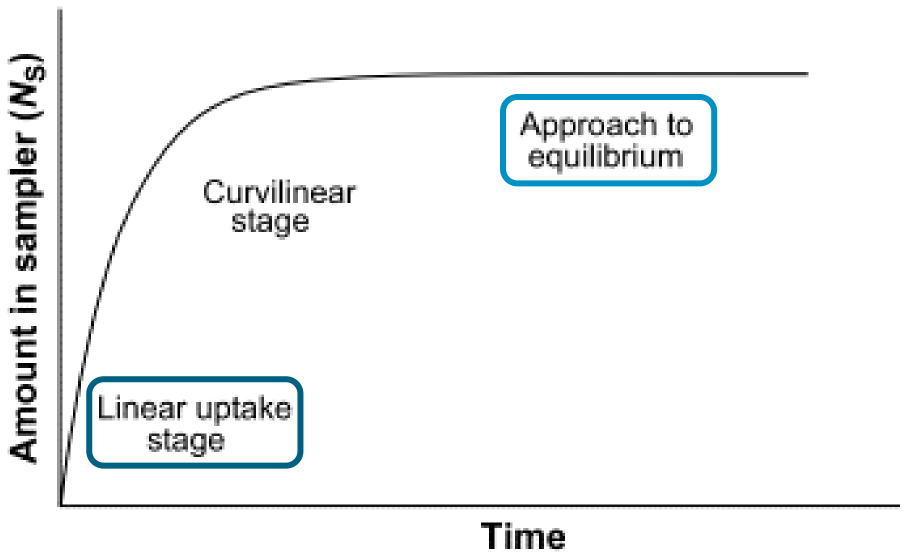
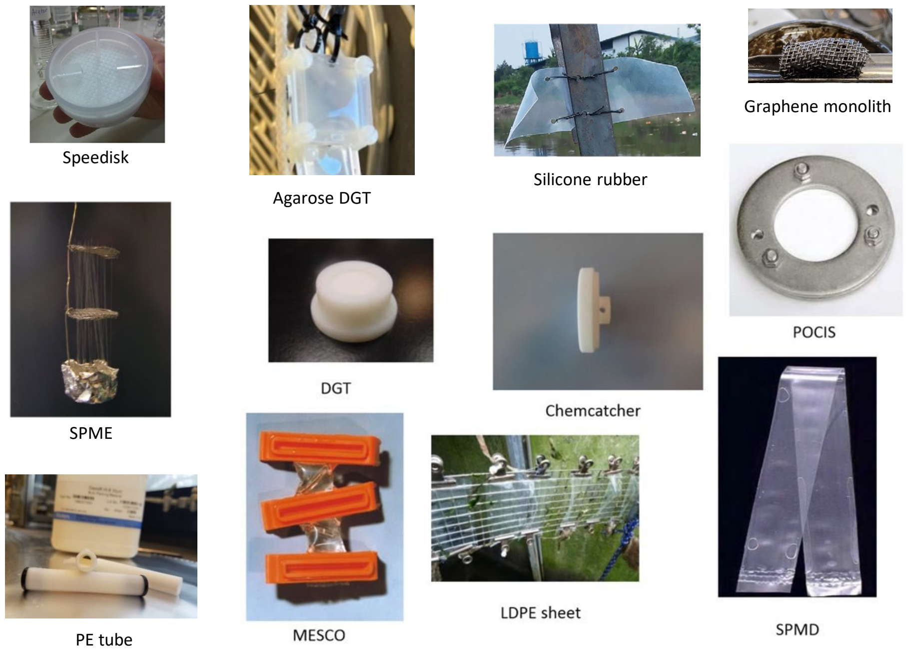
Passive samplers

- measure **activity of pollutants** (dissolved, bioavailable, gas phase)
- uptake by **diffusion** of analyte (from the sampled media to a receiving phase in the PS)





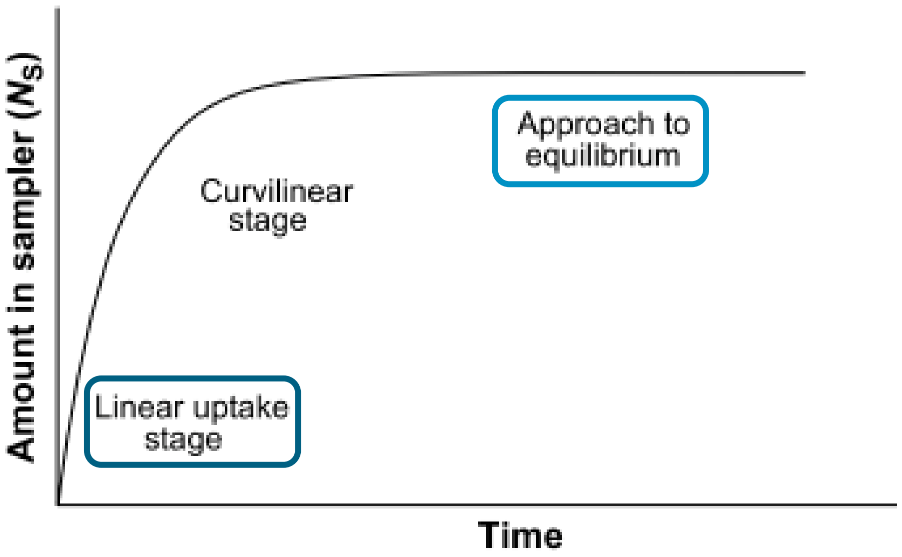
Advantages

- non-mechanical; easy to deploy and require no maintenance
- independent on a power or other energy supply
- can be deployed in **a range of environments** (sites with limited security, remote, with little/no infrastructure)
- used for short (days) or long-term (months) monitoring
- **effectively pre-concentrate pollutants** compare to spot sampling

Deriving dissolved/gaseous concentrations from passive sampling

- general equation

$$N_S = C_W K_{SW} m_S \left[1 - \exp\left(-\frac{R_S\, t}{K_{SW} m_S}\right)\right]$$



for short time = kinetic passive sampler

$$N_S = C_W\, R_S\, t \qquad C_W = \frac{N_S}{R_S\, t}$$

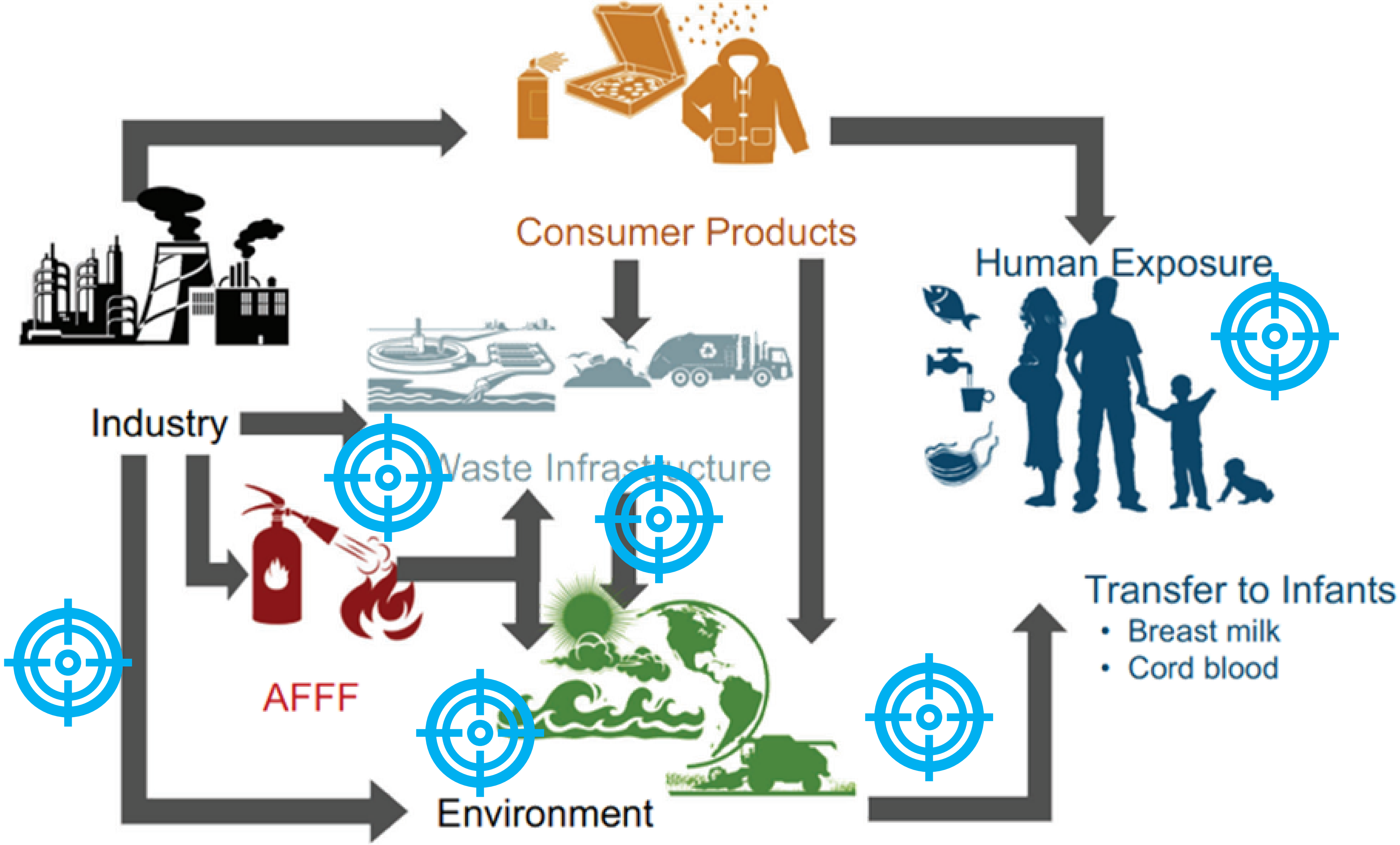
- sampling rate (R_S)
- length of the deployment (t)

for long time = equilibrium passive sampler

$$N_S = C_W\, K_{SW}\, m_S \qquad C_W = \frac{N_S}{K_{SW}\, m_S}$$

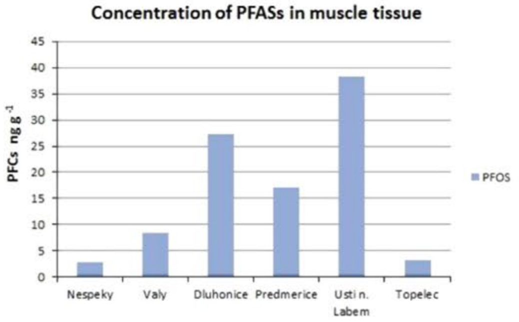
- sampler/water partitioning (K_{SW})
- mass of sampler (m_S)

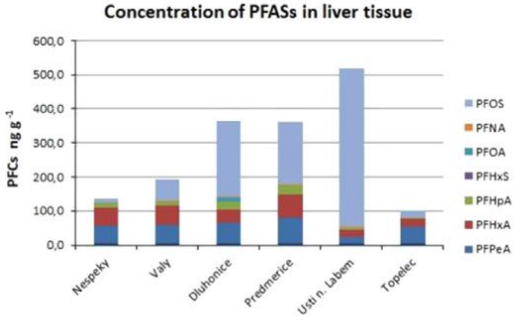
Passive sampler applications

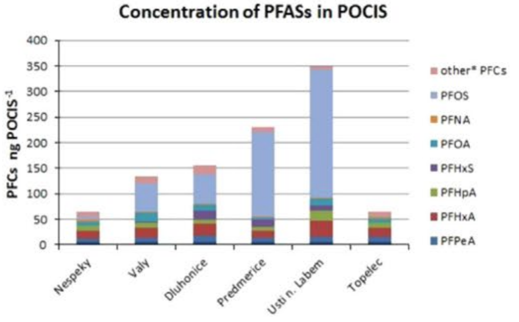


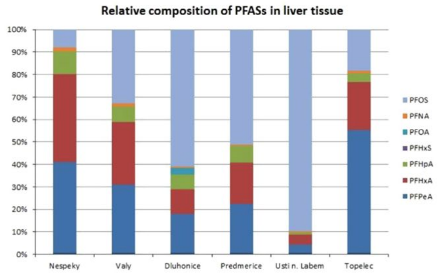
Sunderland, E. et al. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects. *Journal of Exposure Science & Environmental Epidemiology*, *29*(2), 131–147 (**2019**)

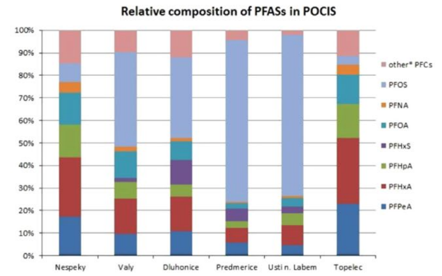
Why passives might be useful

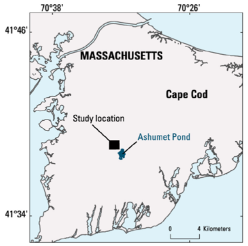


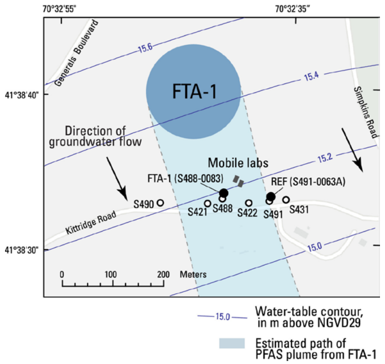


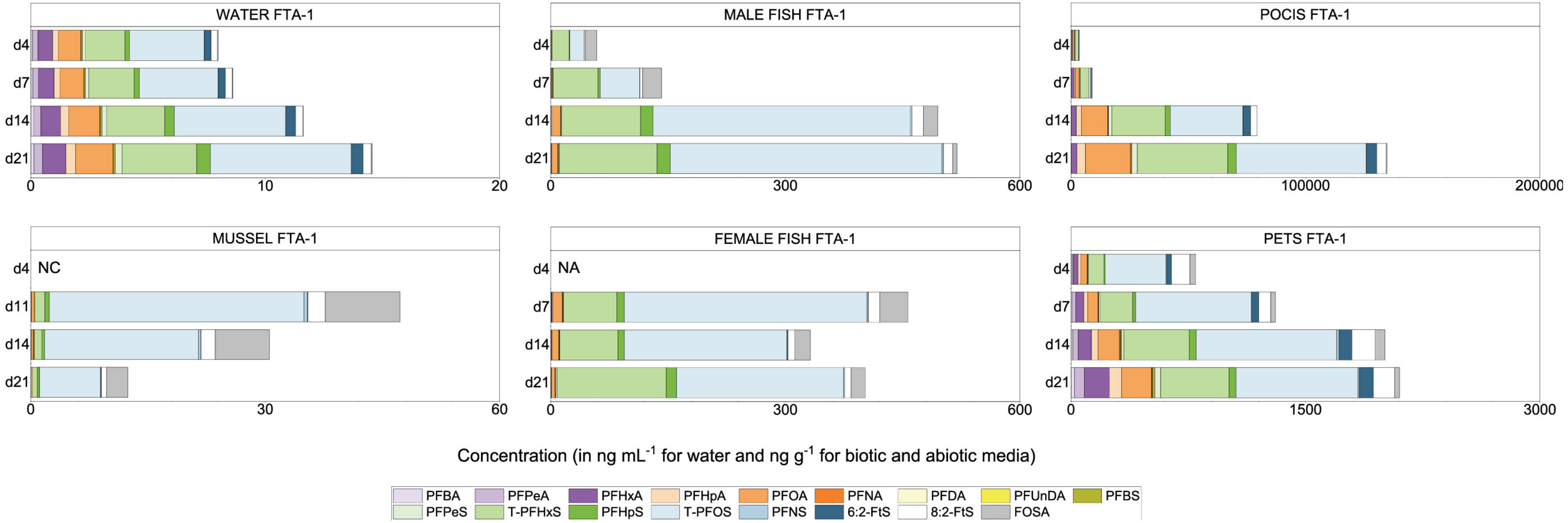












Cerveny, D. *et al.* Perfluoroalkyl substances in aquatic environment-comparison of fish and passive sampling approaches. *Environmental Research* 144, 92–98 (**2016**)
Barber, L. B. et al. Uptake of Per- and Polyfluoroalkyl Substances by Fish, Mussel, and Passive Samplers in Mobile-Laboratory Exposures Using Groundwater from a Contamination Plume at a Historical Fire Training Area, Cape Cod, Massachusetts. *Environ. Sci. Technol. 57*, 5544–5557 (**2023**).

When passives might be essential

Monitoring Programs:

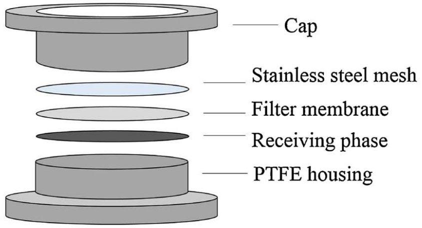
- Global and Local
- Persistent Organic Pollutants (POPs)
- Long-Range Transport
- Air

International Treaties:

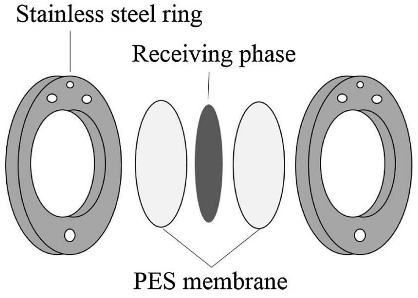
- Implementation
- Stockholm Convention on POPs
- Air (exclusively until 2009)
- **Water (PFAS)**

Passive samplers for dissolved PFAS

Chemcatcher



POCIS



DGT

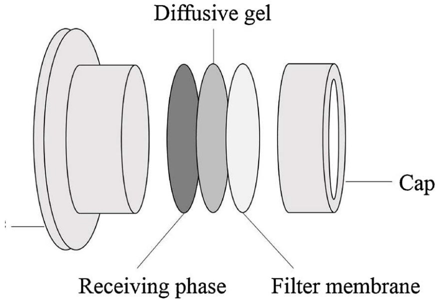


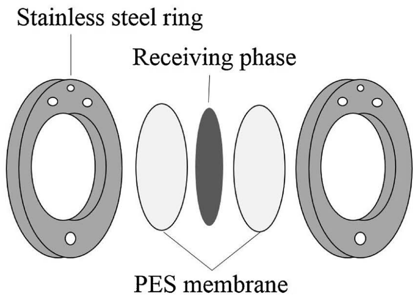
Table 1
The comparison of components of the three samplers.

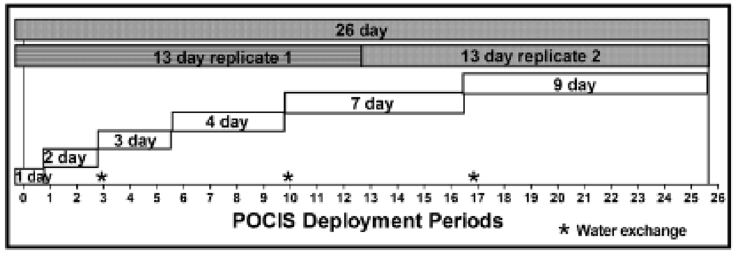
	Limiting diffusion membrane	Diffusion gel	Receiving phase
Chemcatcher	PES PS PC LDPE	/	SDB-RPS SDB-XC C_{18} disk
POCIS	PES Nylon	/	Sorbents of pesticide-POCIS[a] Oasis HLB sorbent
DGT	PES PTFE	Polyacrylamide gel Agarose gel Nylon	XAD 18 XAD 1 MIP TiO_2 Activated charcoal Oasis HLB sorbent Oasis MAX sorbent

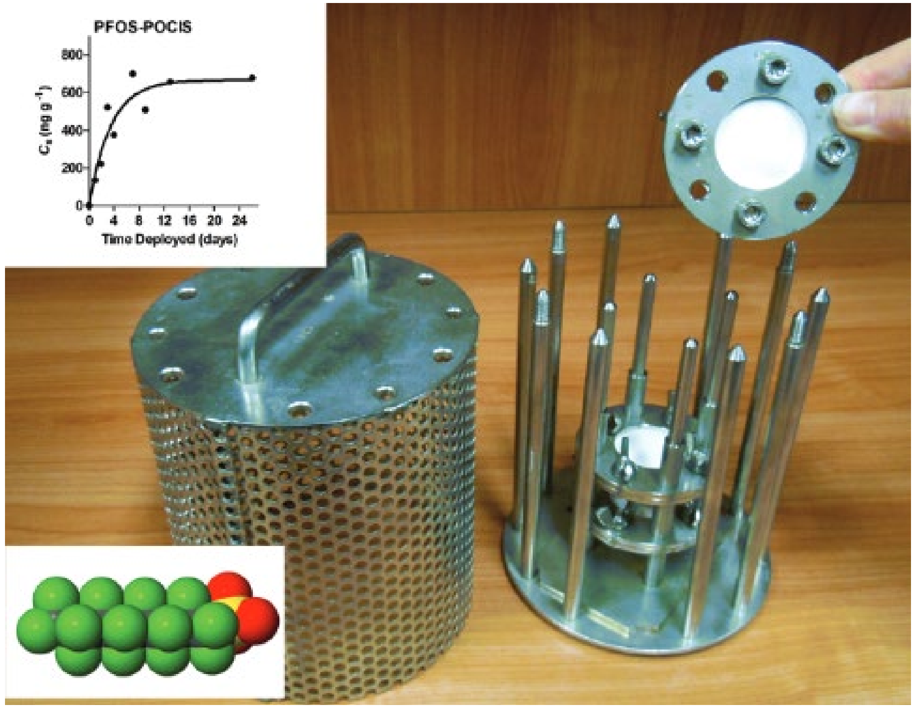
[a] Triphasic sorbent admixture of Isolute ENV + polystyrene divinylbenzene and Ambersorb 1500 or 572 carbon dispersed on S-X3 Biobeads.

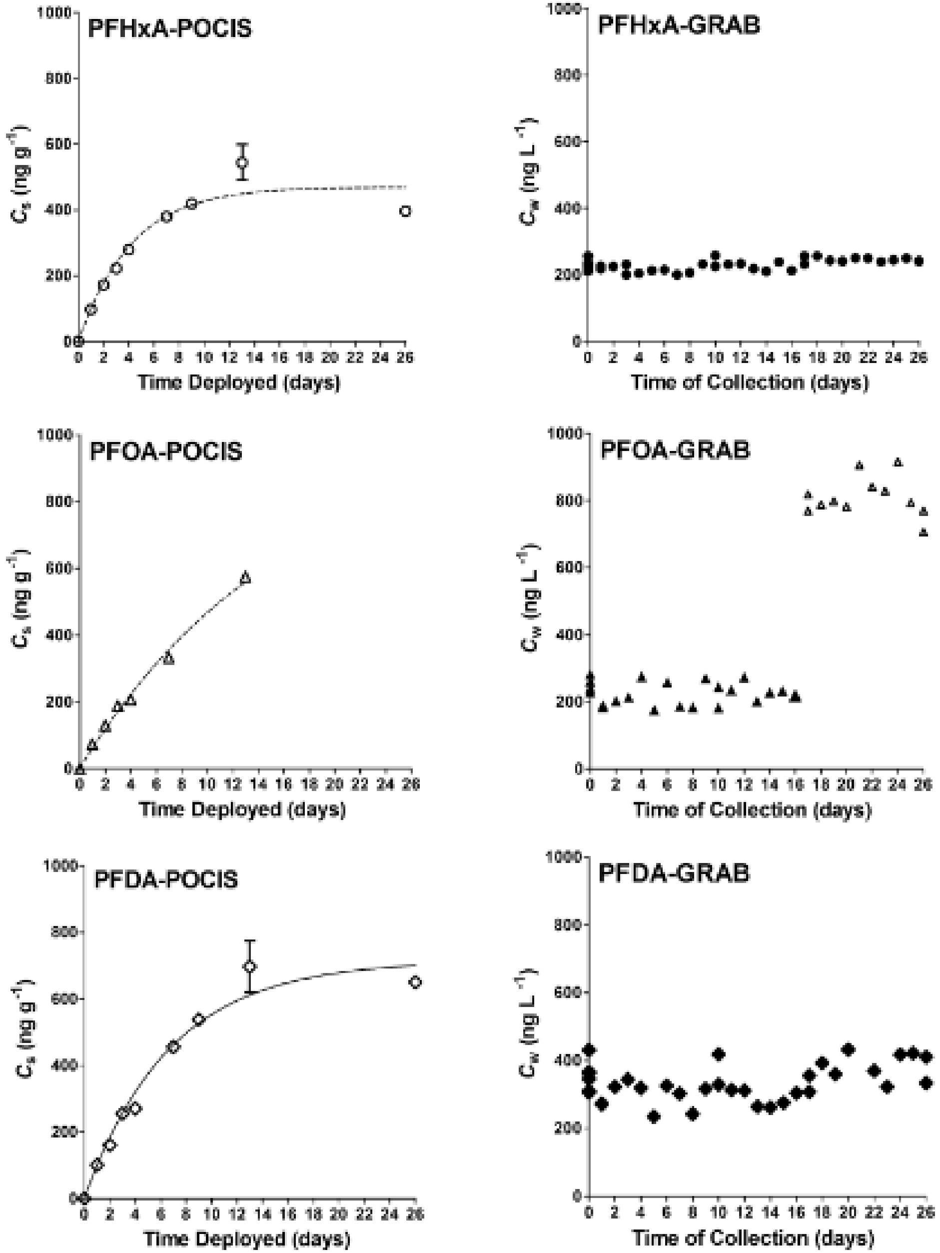
Gong, X., et al, Passive sampling for monitoring polar organic pollutants in water by three typical samplers. *Trends in Environmental Analytical Chemistry* 17, 23–33 (**2018**).

1st trial of POCIS for PFAS

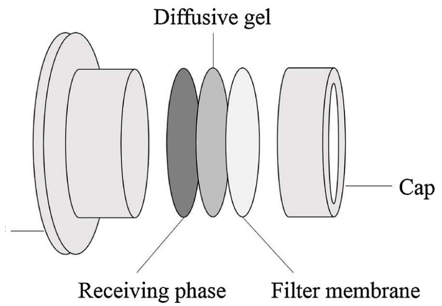




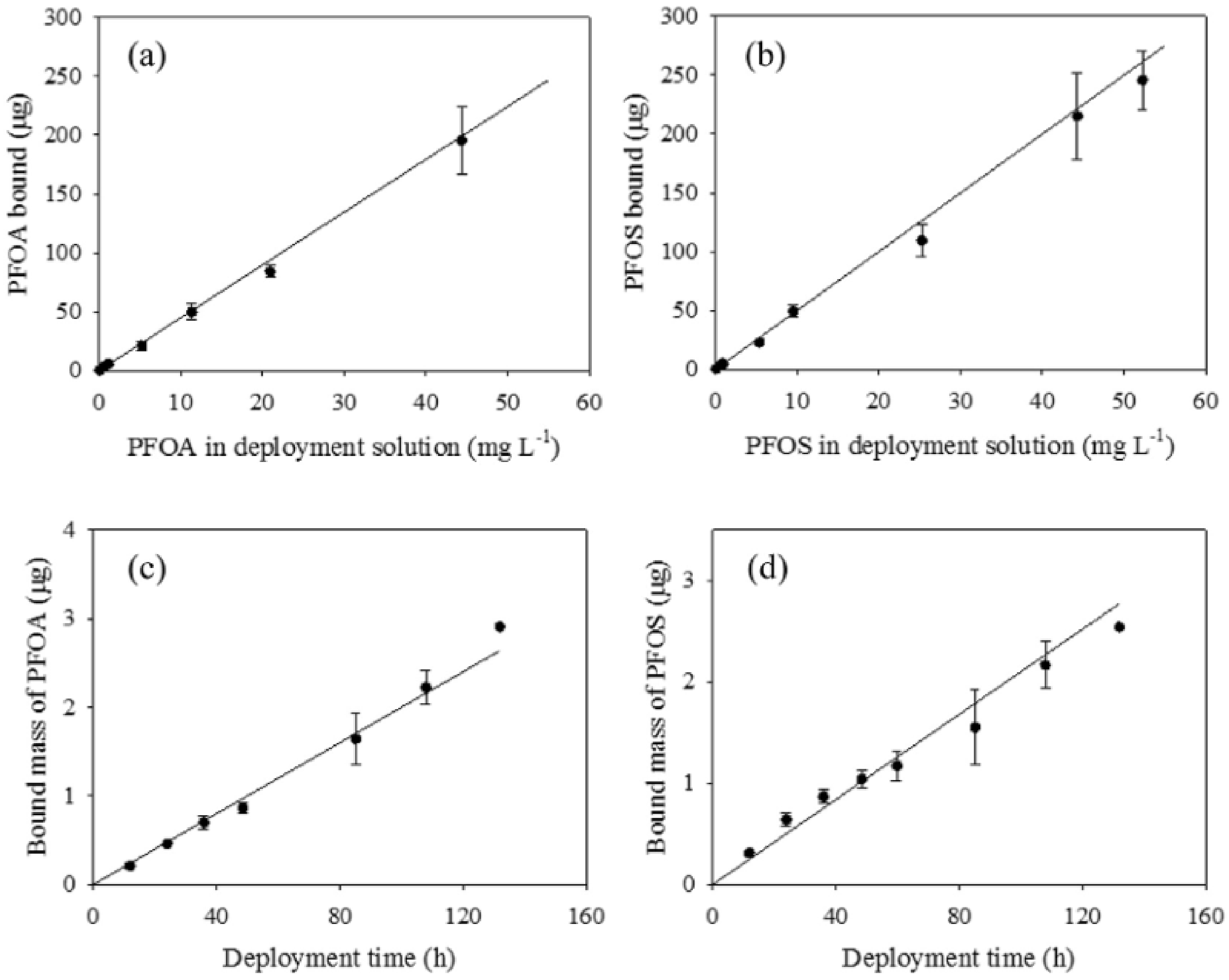




A new approach for PFAS - DGT

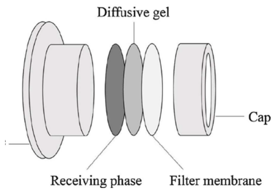


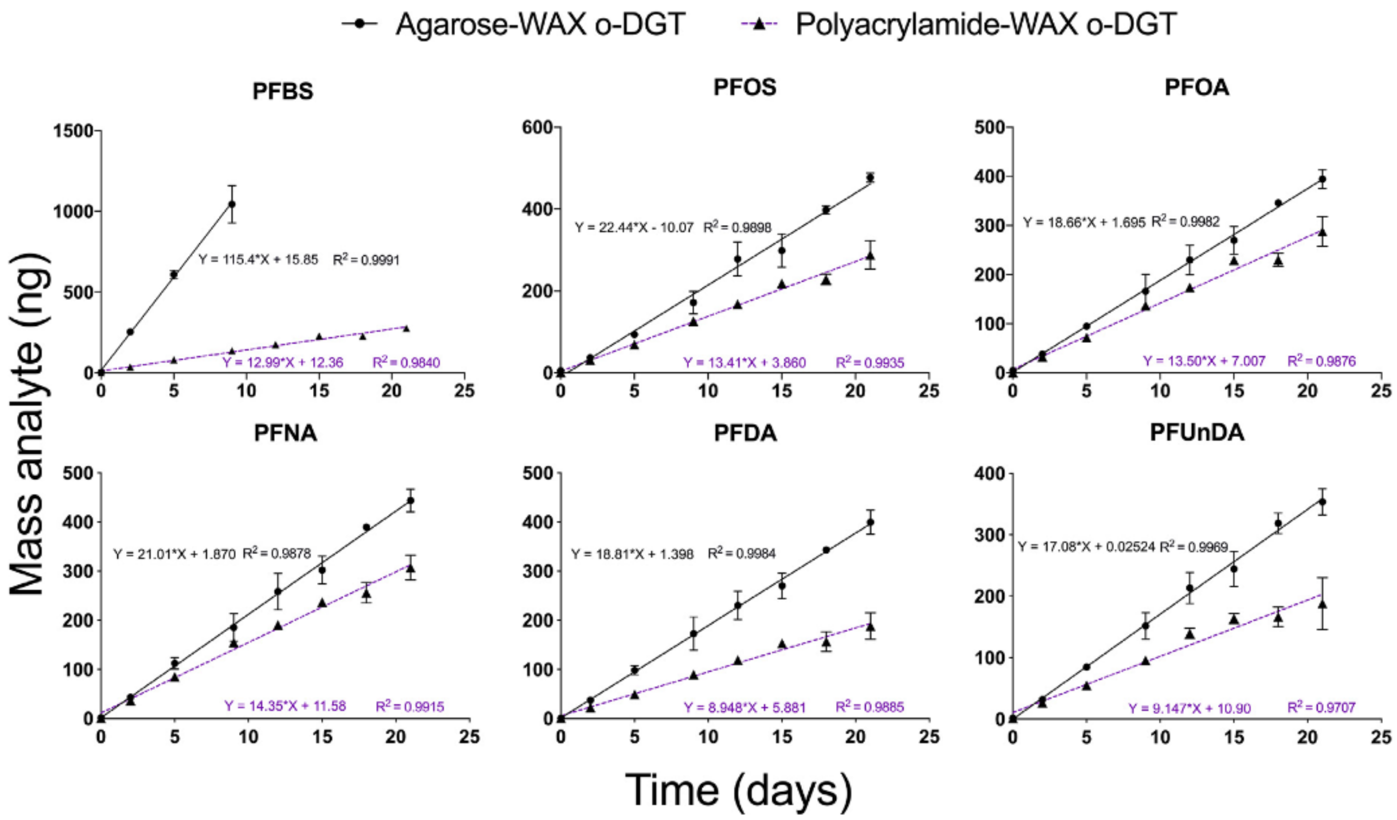
$$C_{DGT} = M \times \Delta g / (D \times A \times t)$$

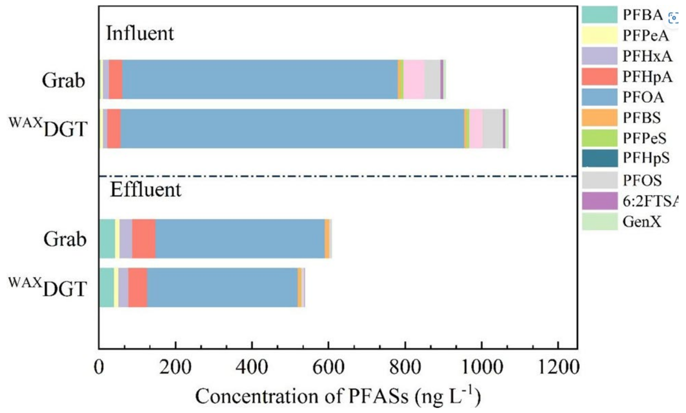


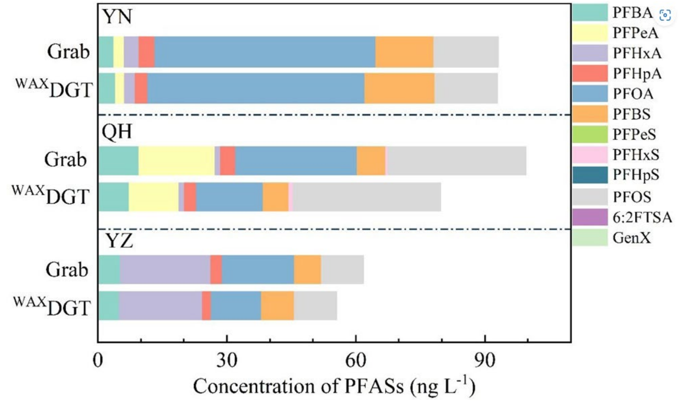
M…	measured mass on binding gel (ng)
t…	time (s)
A…	DGT sampling area (cm^2)
Δg…	Gel thickness of the diffusion layer (cm)
D…	PFAS diffusion coefficient ($cm^2\ s^{-1}$)
t…	temperature

DGT calibrations and field trails



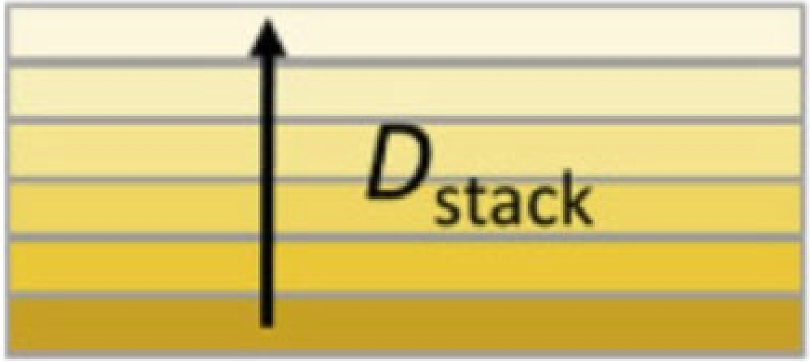


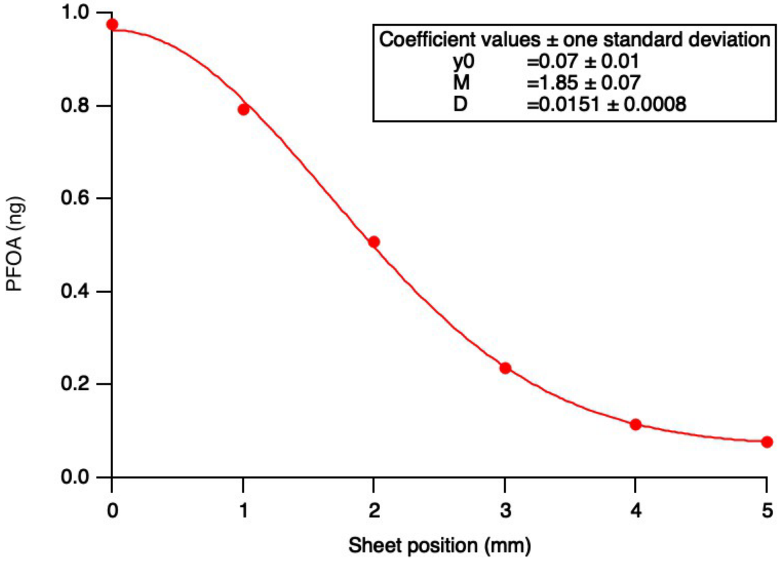


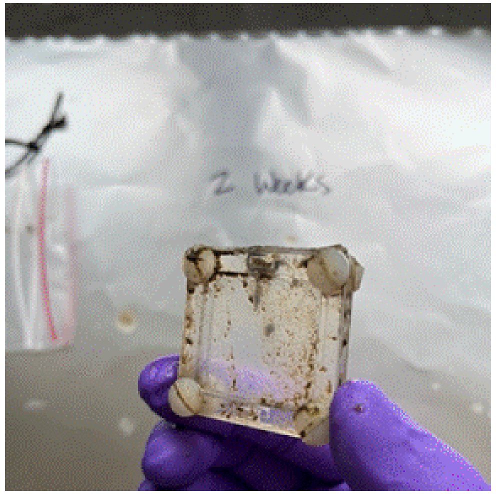


Guan, D.-X. et al. In situ measurement of perfluoroalkyl substances in aquatic systems using diffusive gradients in thin-films technique. *Water Research* **144**, 162–171 (2018).
Fang, Z. et al. Development and Applications of Novel DGT Passive Samplers for Measuring 12 Per- and Polyfluoroalkyl Substances in Natural Waters and Wastewaters. *Environmental Science & Technology* (**2021**)

A novel DGT prototype



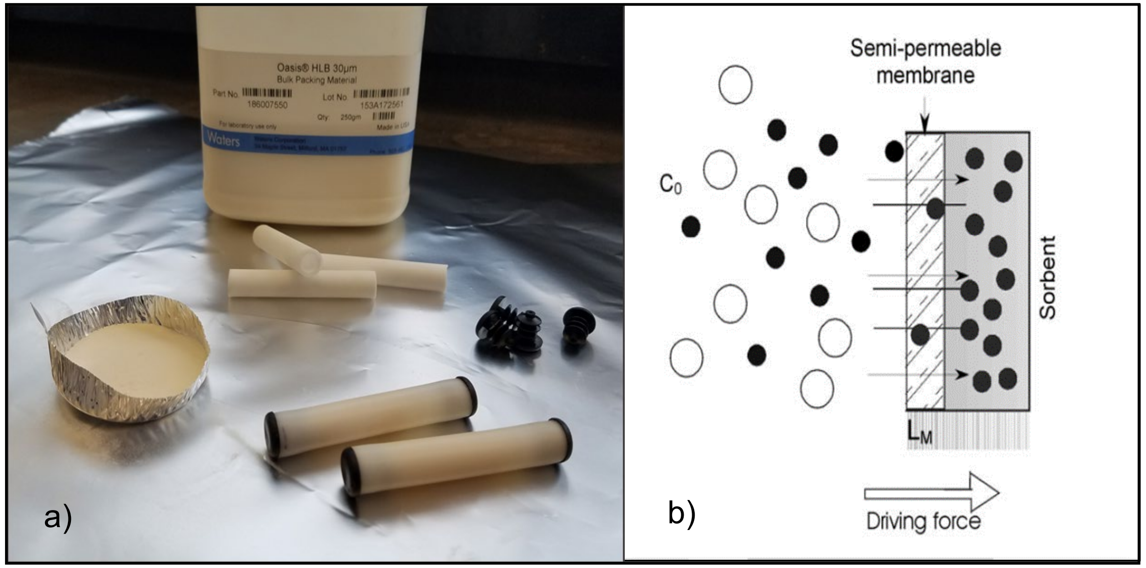


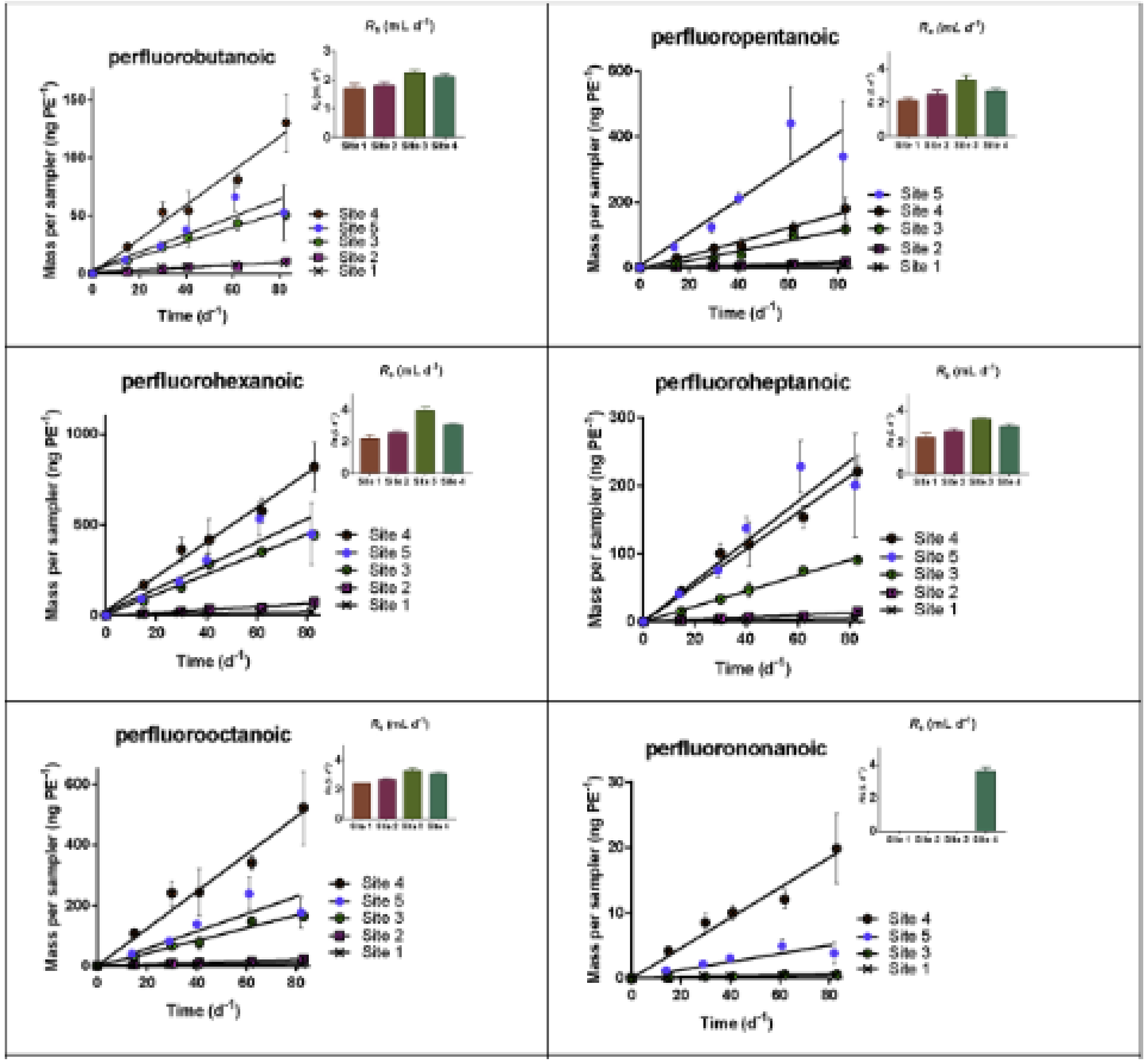


Snook et al. (unpublished)

PE-tube sampler for PFAS in GW

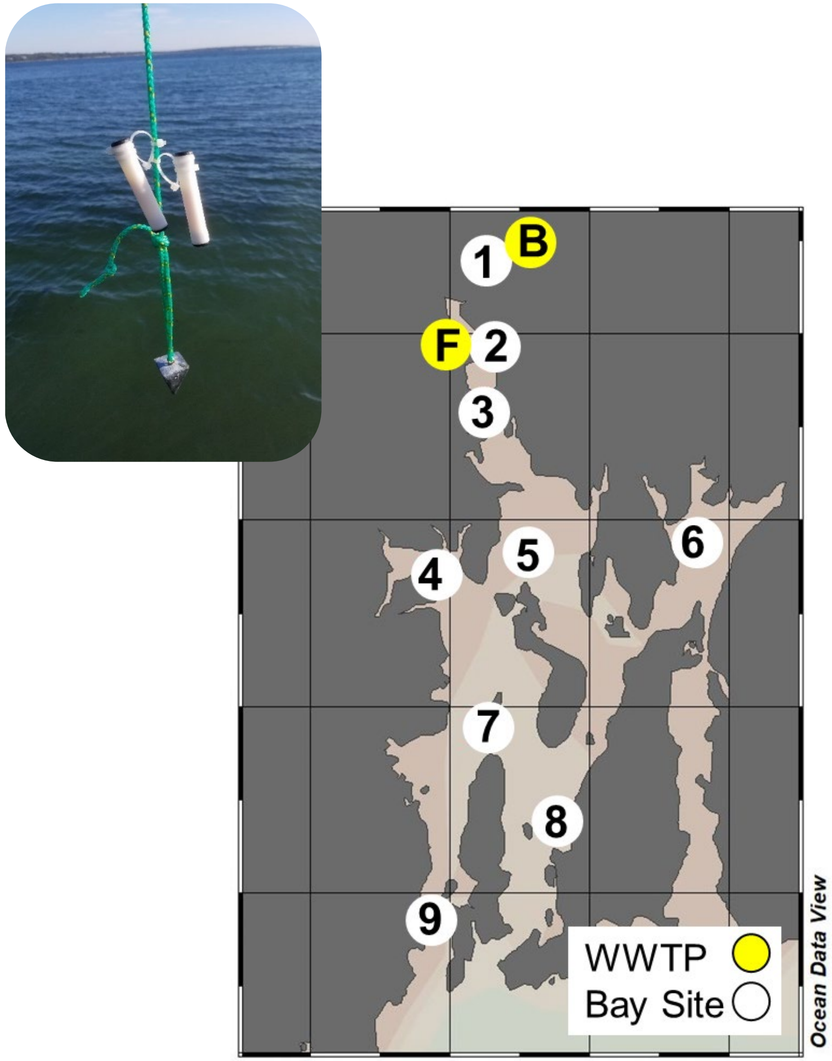
- microporous PE membrane
- powdered sorbent

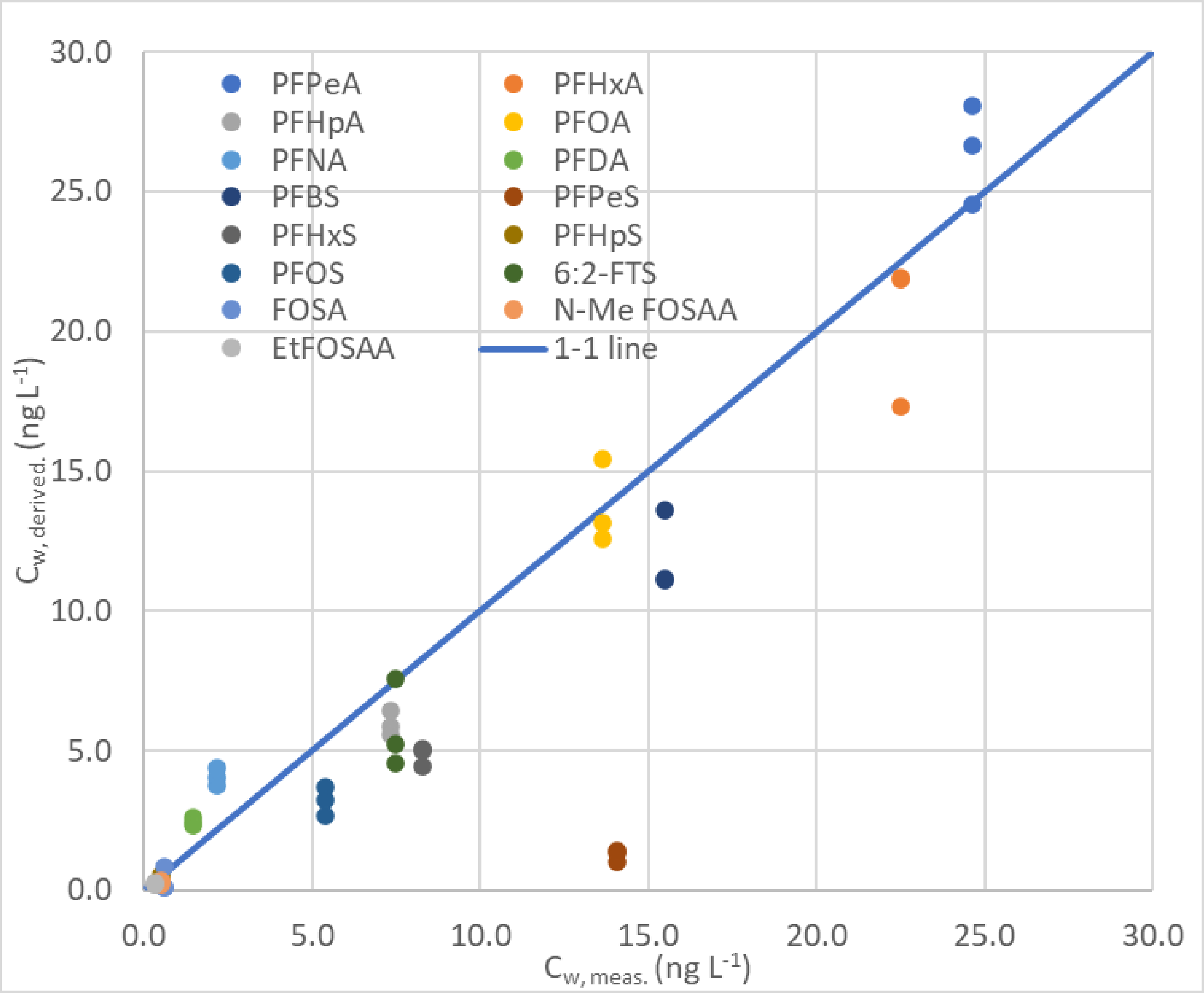




Kaserzon, S. L. et al. Calibration and validation of a novel passive sampling device for the time integrative monitoring of per- and polyfluoroalkyl substances (PFASs) and precursors in contaminated groundwater. *Journal of Hazardous Materials* 366, 423–431 (**2019**).

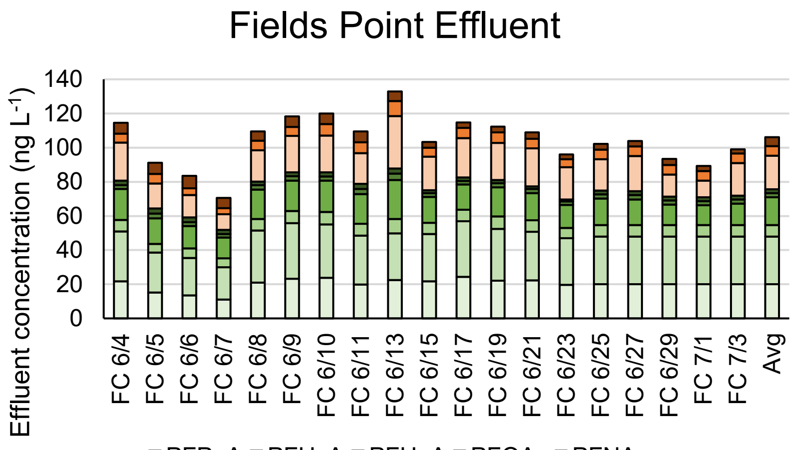
PE-tube sampler for PFAS in surface and ocean water

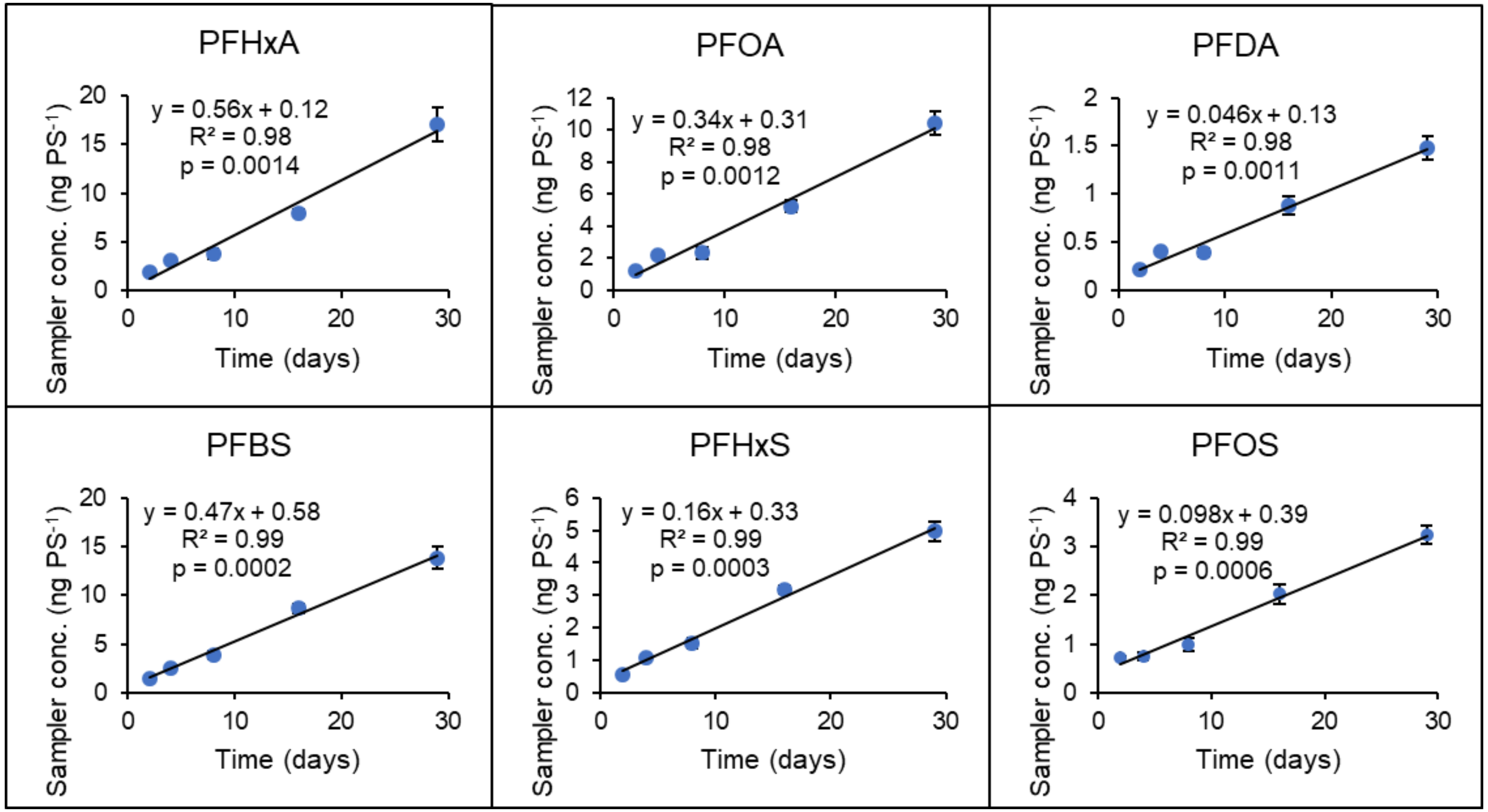




Gardiner, C. et al. Field Validation of a Novel Passive Sampler for Dissolved PFAS in Surface Waters. *Environmental Toxicology and Chemistry* **(2022)**

PE-tube sampler for PFAS in surface and ocean water

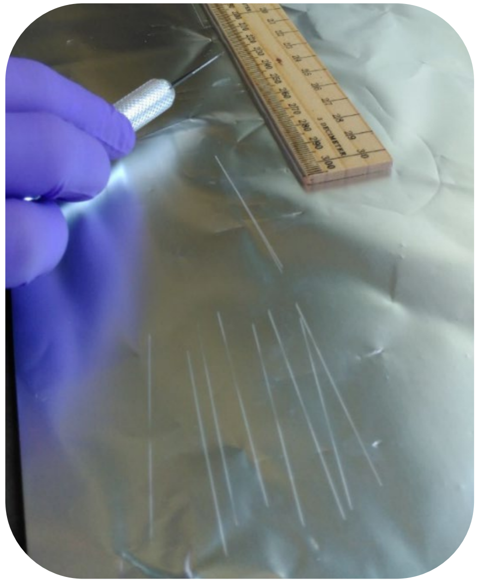




Laboratory Validation of Novel Passive Samplers for PFAS

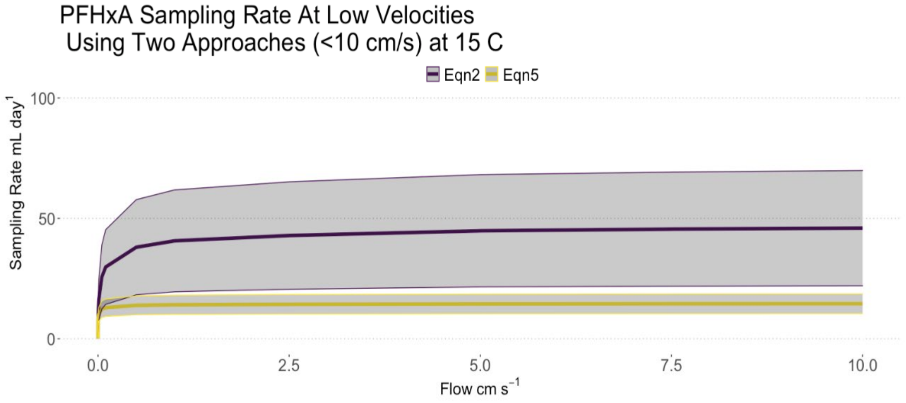
Microporous
PE-tube

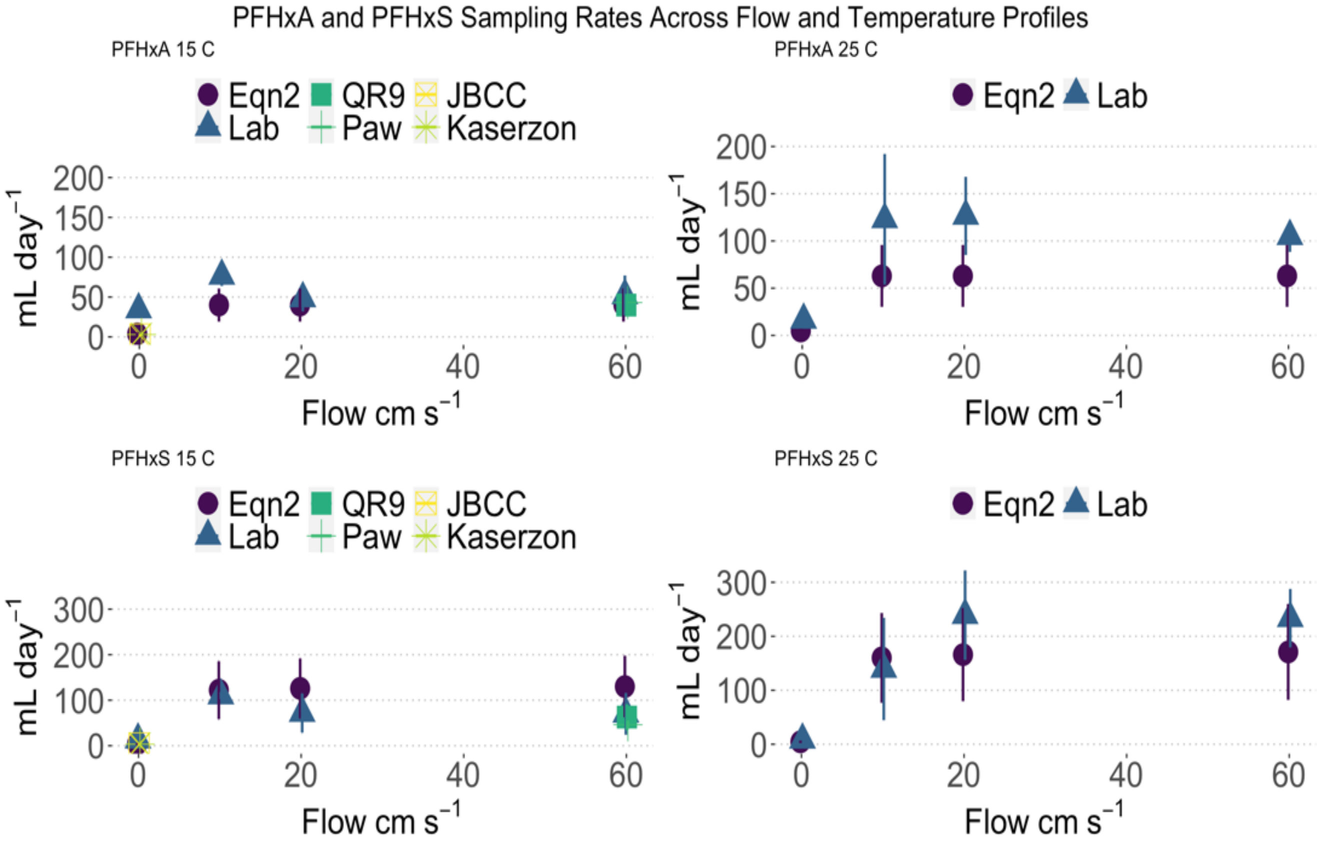
Solid Phase Micro Extraction
SPME fibers



Nanomaterial
Graphene hydrogel

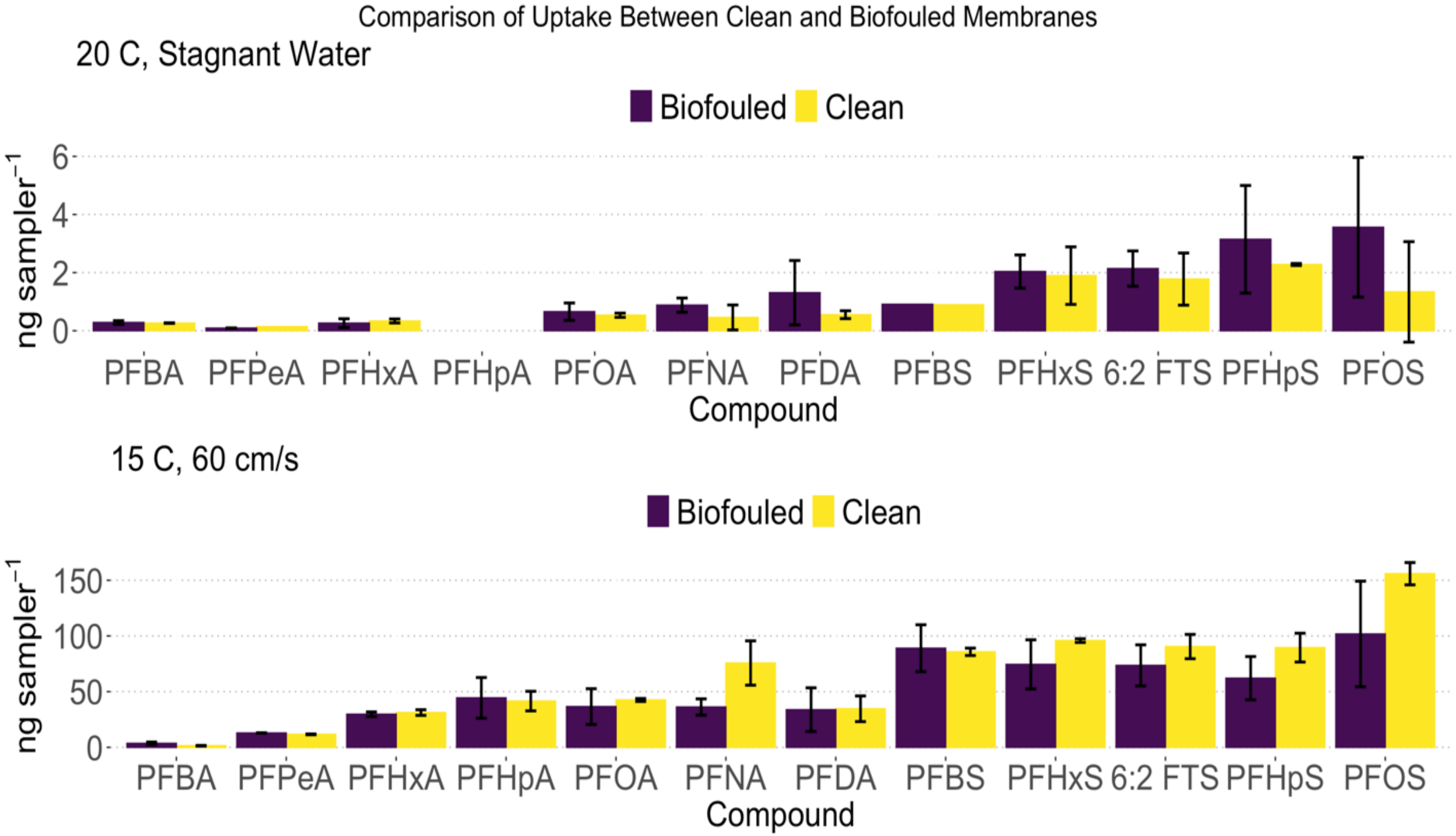
PE-tube sampler – flow and temperature





Dunn, M., Becanova, J., Snook, J., Ruyle, B. & Lohmann, R. Calibration of Perfluorinated Alkyl Acid Uptake Rates by a Tube Passive Sampler in Water. *ACS EST Water* 3, 332–341 (**2023**)

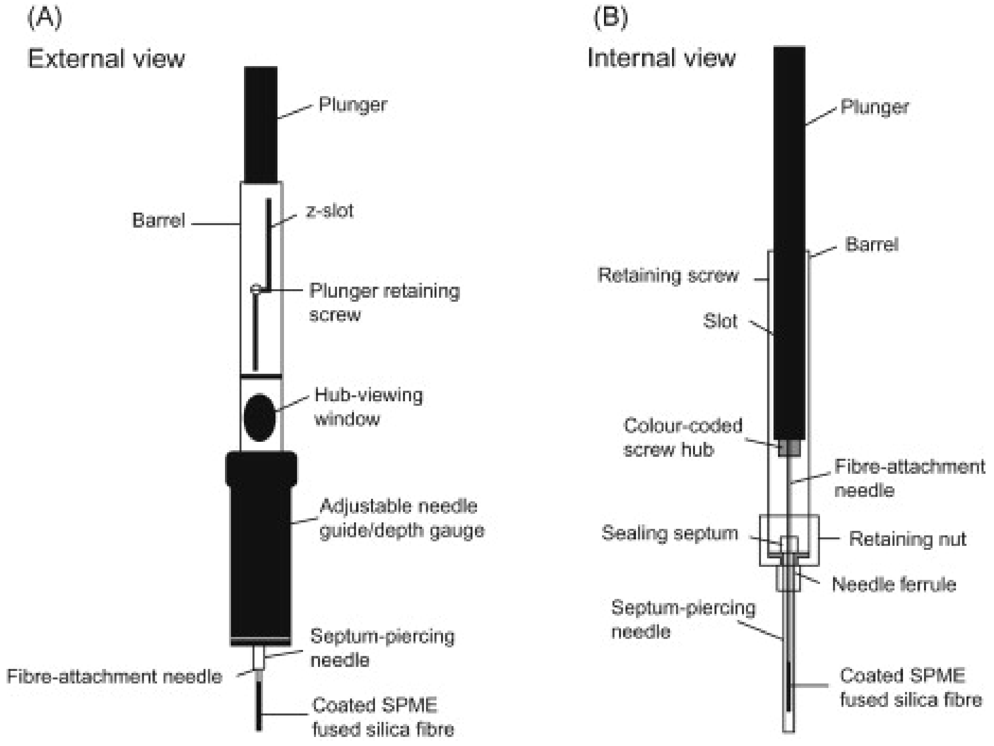
PE-tube sampler – biofouling



Dunn, M., Becanova, J., Snook, J., Ruyle, B. & Lohmann, R. Calibration of Perfluorinated Alkyl Acid Uptake Rates by a Tube Passive Sampler in Water. *ACS EST Water* 3, 332–341 (**2023**)

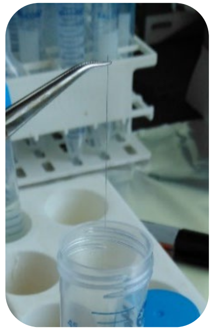
SPME fiber

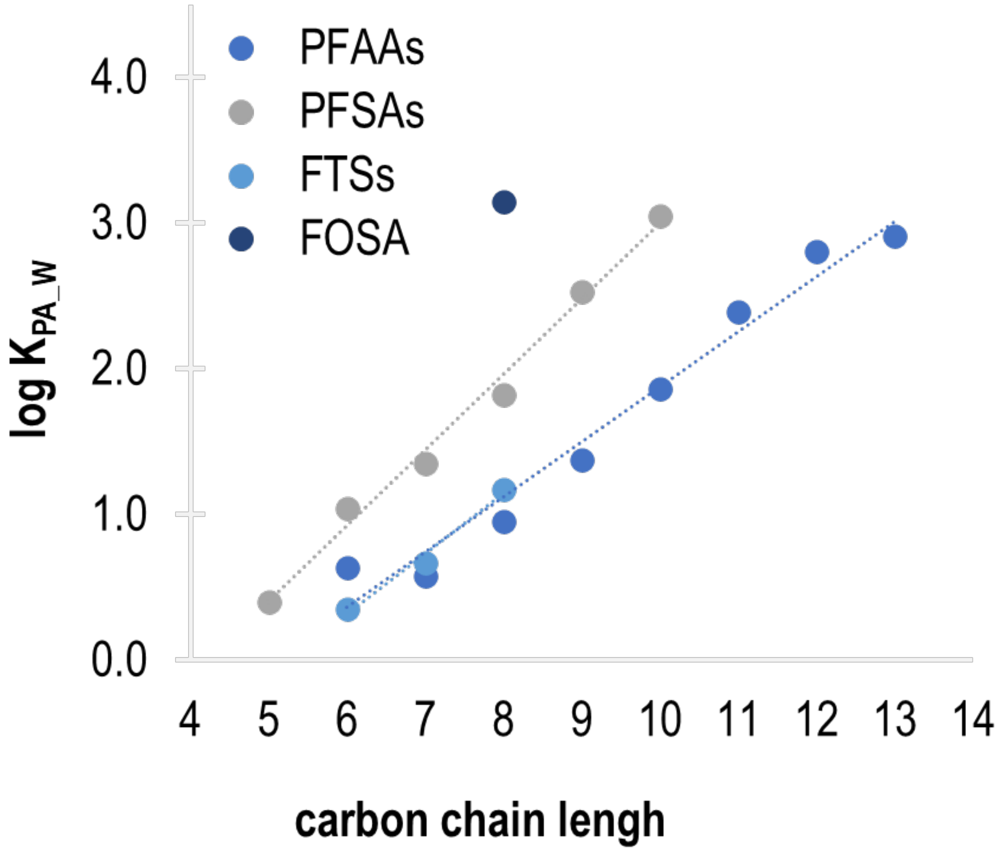
- developed in ‘90s for **rapid sampling and sample preparation** (in the laboratory and onsite)
- originally used for a direct transfer of the non-polar analytes into a gas chromatograph
- commercially available fibers - silica core coated with various polymers in a metal needle



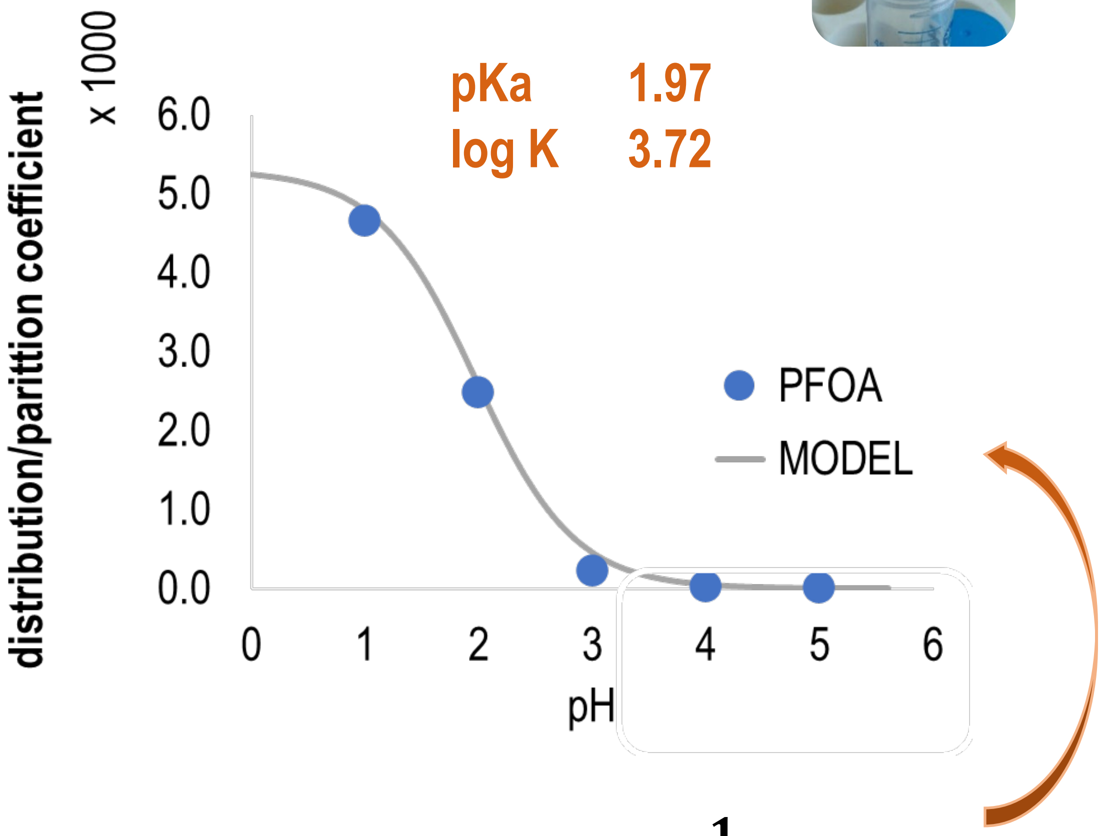
- optic fibers coated with esterified acrylic copolymer = **polyacrylate** (9 - 50 μm)
- sorption of neutral molecules (forms) with non-specific van der Waals

PFAS characteristics using SPME





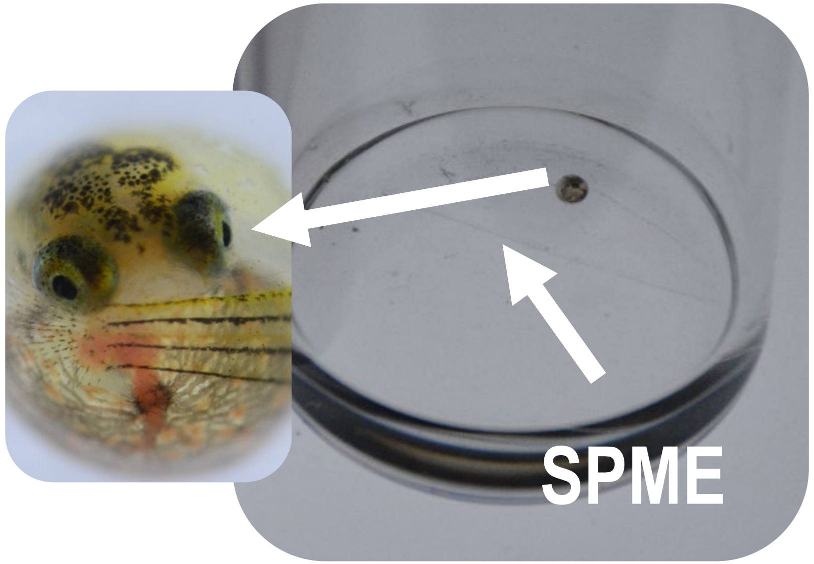
TENDENCY TO SORB ON FIBER
= hydrophobicity

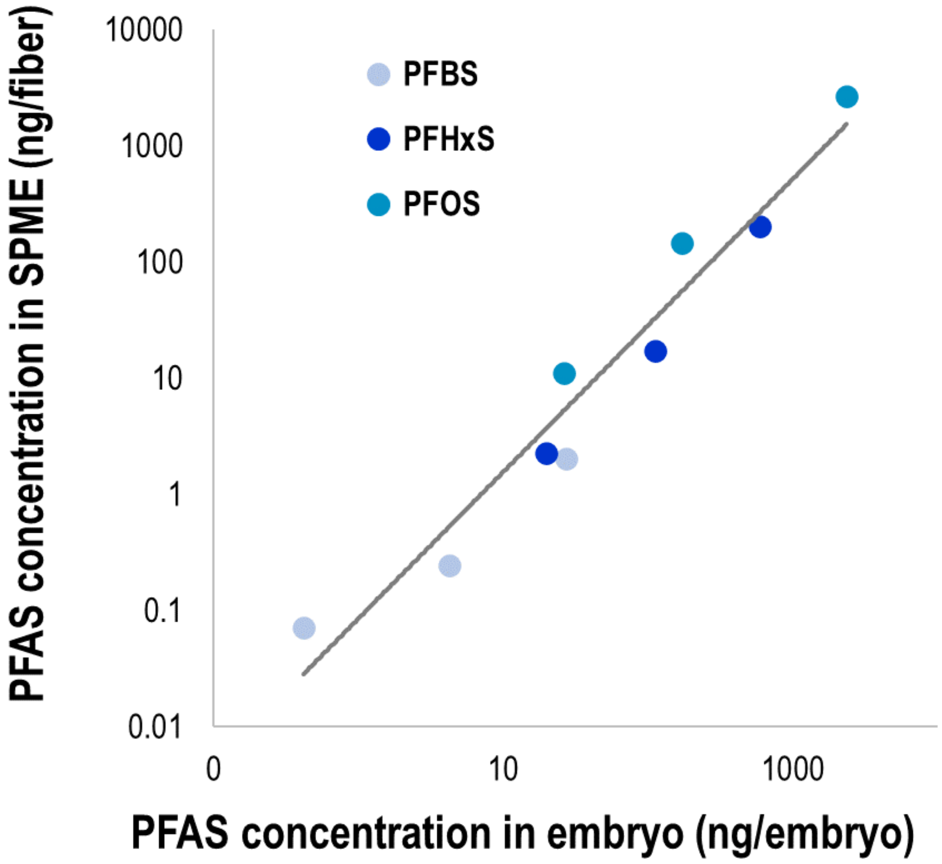


$$\log D = \log K + \log \left(\frac{1}{1+10^{(pH-pKa)}}\right)$$

SPME – A biomimetic sampler

- fiber co-exposed with embryos (*Fundulus heteroclitus*) to C4, C6 and C8 PFSA (6 days)
- after exposure - the embryos and fibers were separated, wash in water and archived by **ultra low freezing**

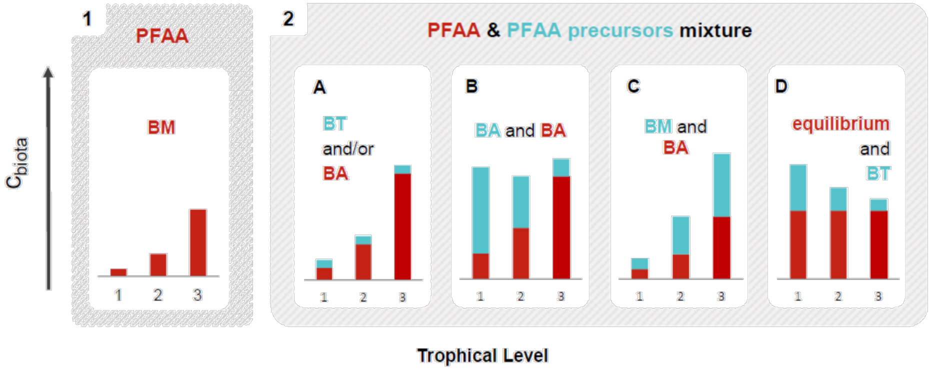


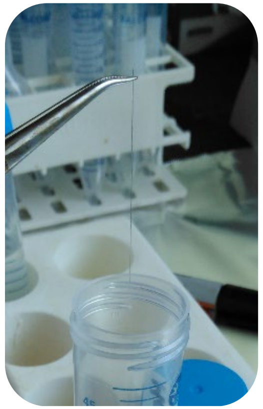


SPME fiber application

- a proxy tool for bioaccumulation of PFAS in biota (freshwater and marine environment)

Biotransformation (BT) and observed biomagnification (BM) and bioaccumulation (BA) of PFAA across trophic levels





From the Bottom Up: Deciphering Bioaccumulation and Biomagnification of PFAS in Plankton

Rainer Lohmann | University of Rhode Island

ER22-3139

Objective | Approach | Benefits

Objective

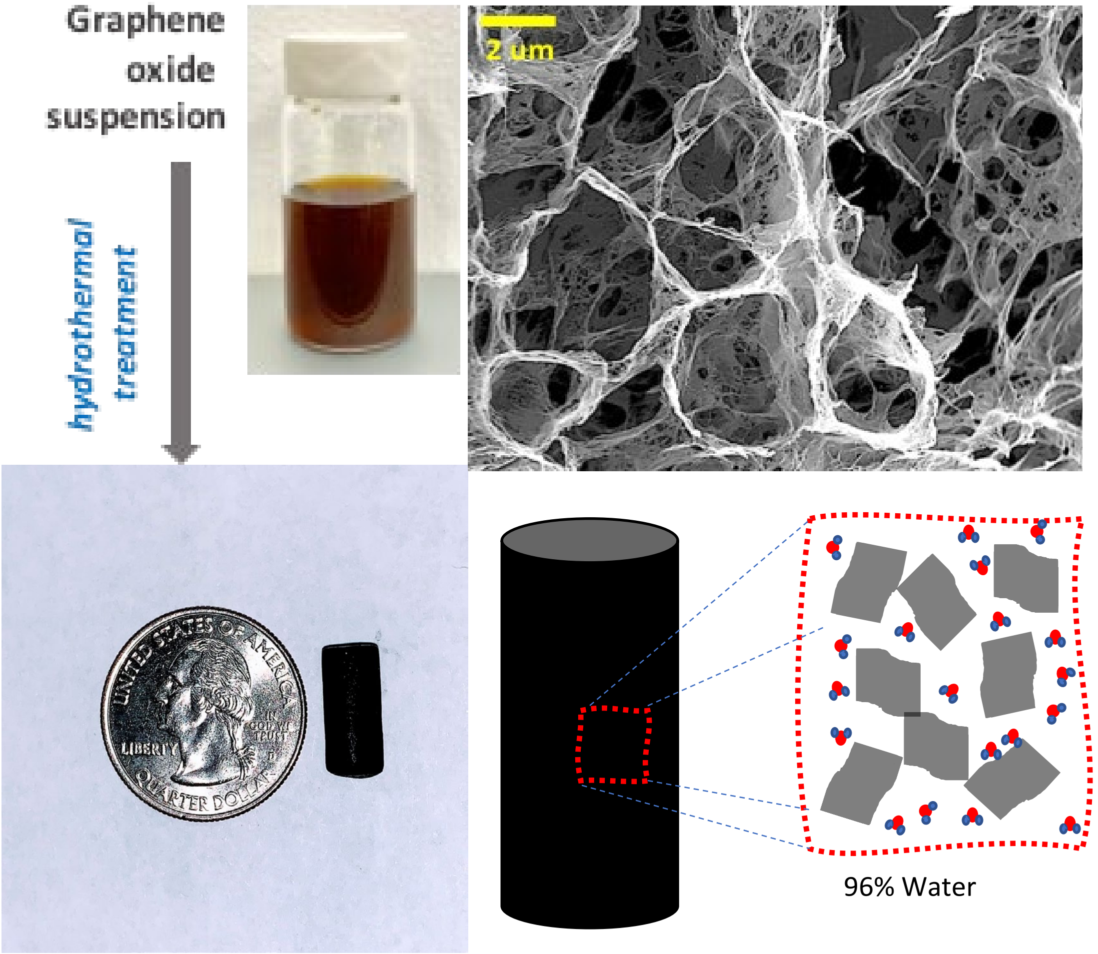
The major objective of this project is the evaluation of the bioaccumulation, biotransformation and biomagnification of per- and polyfluoroalkyl substances (PFAS) in plankton at the base of the marine food web. Specifically, the project team will derive the uptake, transformation, and bioaccumulation of PFAS in marine phytoplankton (trophic level 1), zooplankton (trophic level 2), and fish, with a focus on understanding the uptake of PFAS at the base of marine food webs. This project is based on the notion that a proper understanding of PFAS behavior at the base of the food web is needed before food web modelling should be undertaken.

Graphene hydrogel monolith

- 10 ml of homogeneous graphene oxide aqueous dispersion (2 mg/mL)
- heating in autoclave (180ºC for 10 hours)
- cooling 2 hours in aqueous solutions

GO mass	12 mg
water content	96%
hydrogel volume	425 mm^3
hydrogel stability	> 1 month*

* in artificial sea water

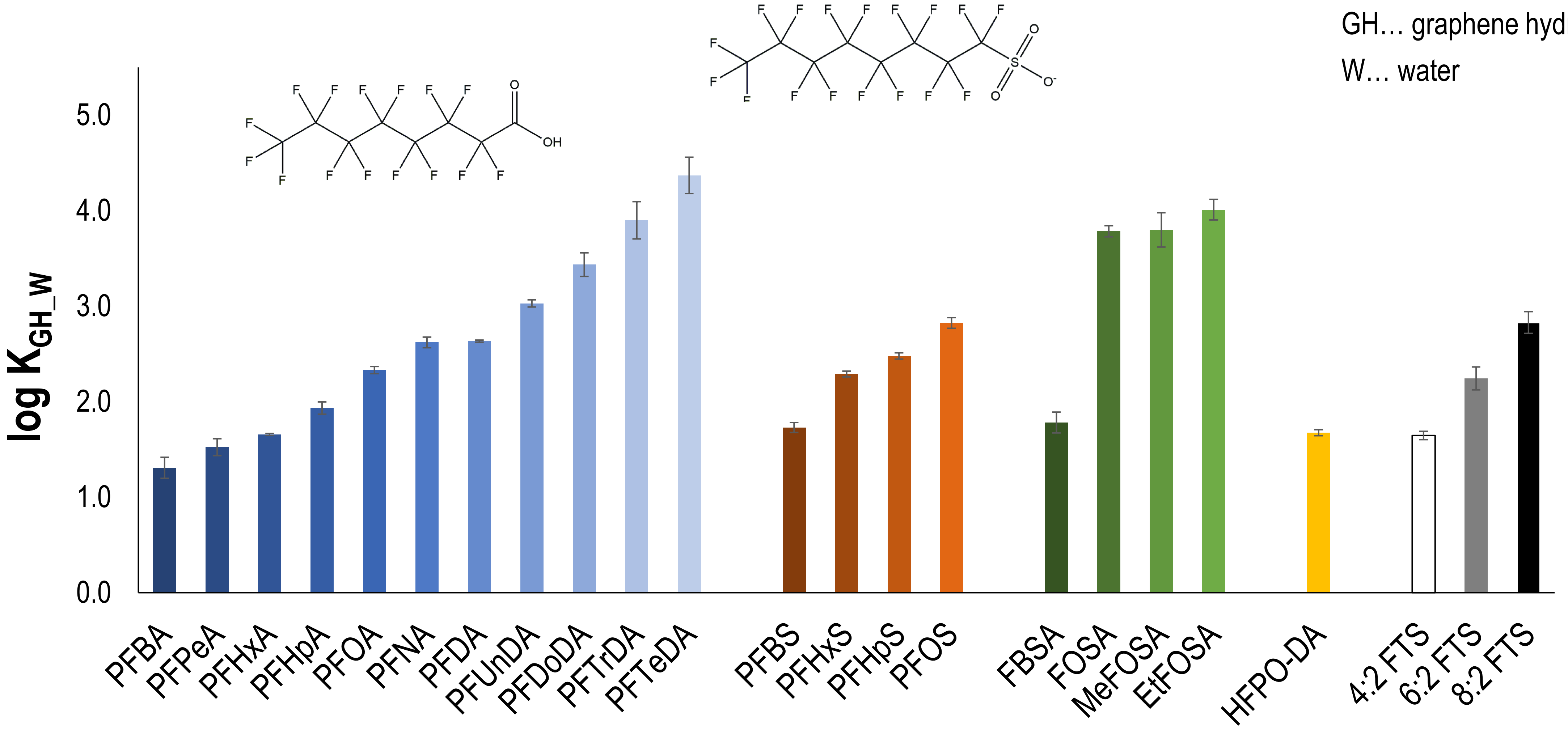


Graphene monolith hydrogel

$$K_{GH\_W} = \frac{c_{GH}}{c_W}$$

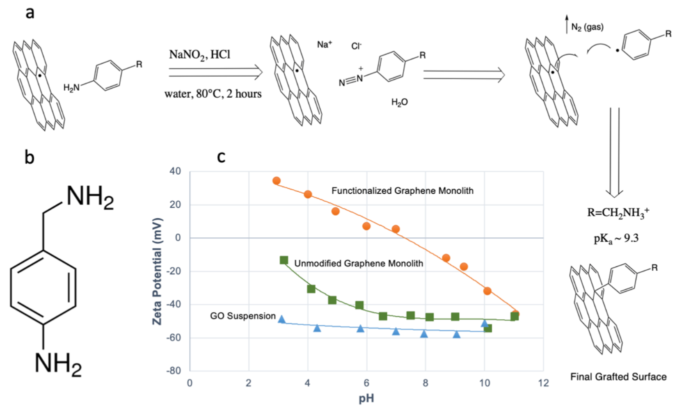
GH… graphene hydrogel

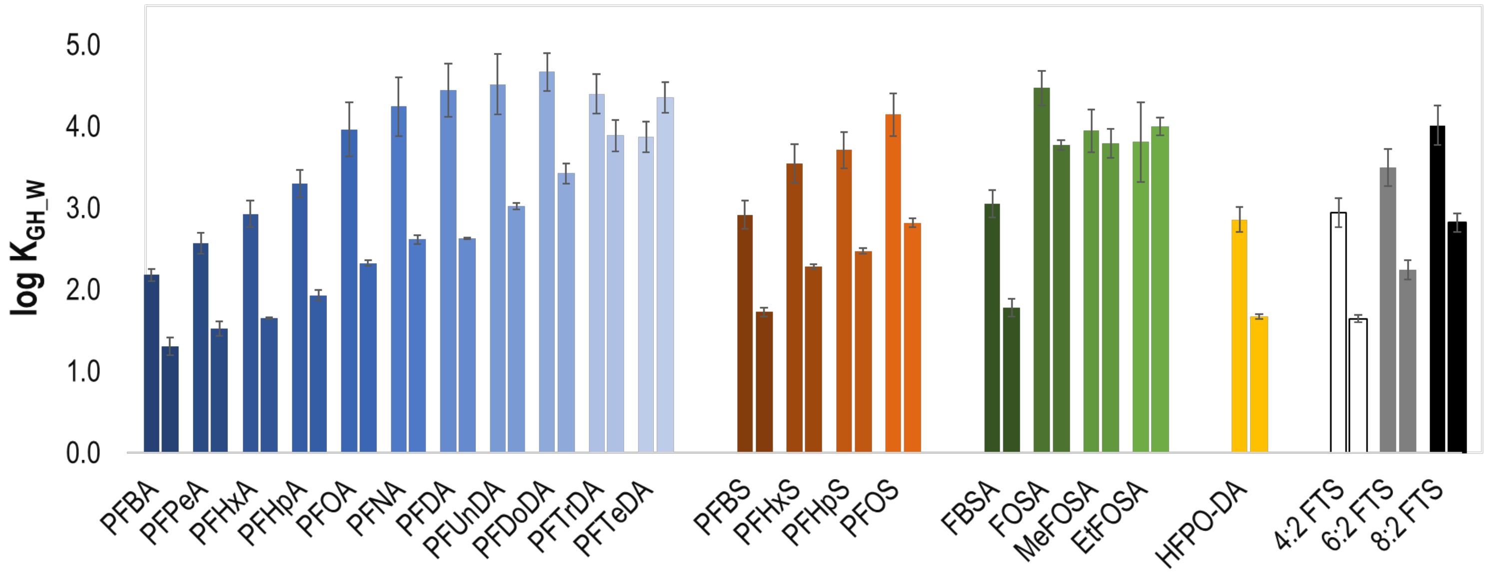
W… water

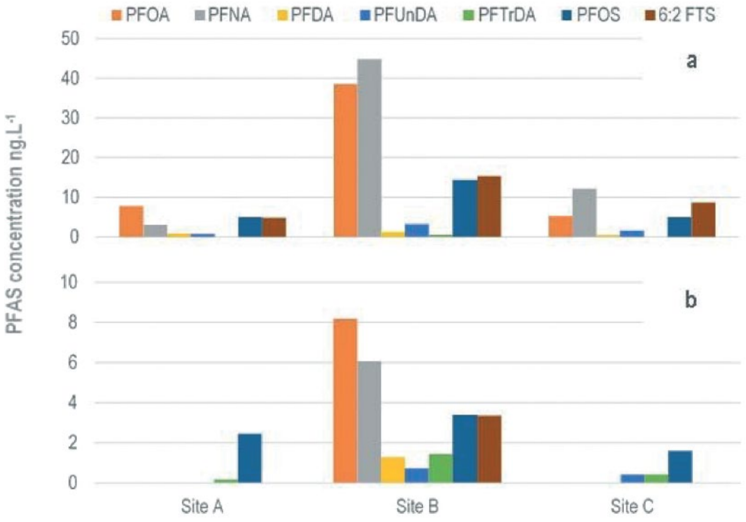


Advanced materials for PFAS passive sampler

- modified/functionalized graphene oxide with 4-Aminobenzylamine (4-ABA) → positively charged GO







PFAS profiles

- PFAS water concentration (ng L^{-1}) at 3 localities (site A, site B and site C) in Delaware River (New Jersey, USA).
- The concentrations were derived from a) analysis of water grabs or b) analysis of graphene monoliths samplers.

Becanova, J. et al. A graphene-based hydrogel monolith with tailored surface chemistry for PFAS passive sampling. *Environmental Science: Nano* 8, 2894–2907 (**2021**).

Modified graphene hydrogel application

Bioavailability, Bioaccumulation, and Toxicity of PFAS in Benthic Biota Exposed to Impacted Marine Sediments

Carrie McDonough | The Research Foundation for The SUNY Stony Brook University

ER22-3263

Objective | Approach | Benefits

Objective

The overarching objective of this project is to describe key factors influencing per- and polyfluoroalkyl substance (PFAS) uptake, bioaccumulation, and toxicity for key coastal benthic biota with distinct ecological traits, function, and physiology. The specific objectives are to:

1. Measure changes in PFAS bioavailability, uptake, and bioaccumulation associated with key variables (sediment characteristics; PFAS molecular structure; PFAS mixture complexity) for aqueous film-forming foam (AFFF)-associated PFAS in major groups of benthic organisms (worm; clam; fish; crab).
2. Evaluate the importance of diet as a PFAS exposure route for benthic consumers.
3. Determine the relative potency of individual PFAS and PFAS mixtures with respect to survival and development for benthic species in the larval stage.

Conclusions

Passive samplers can be useful tools for PFAS activity and transfer

- Sediment as localized hotspots
- Several options for dissolved PFASs
- Porewater samplers to be developed

Sedimentary bioaccumulation

- Biomimetic samplers not yet operationalized

Lack of field or laboratory studies

- Several efforts in the works (mostly in lab phase)
- Some first field deployments

STEEP

Sources, Transport, Exposure & Effects of PFASs

UNIVERSITY OF RHODE ISLAND SUPERFUND RESEARCH PROGRAM

THE UNIVERSITY OF RHODE ISLAND GRADUATE SCHOOL OF OCEANOGRAPHY

Lohmann Lab at URI

- Rainer Lohmann
- Jarod Snook, Melissa Woodward
- Christine Gardiner, Matt Dunn

NIH National Institute of Environmental Health Sciences *Superfund Research Program*

HARVARD T.H. CHAN SCHOOL OF PUBLIC HEALTH

SILENT SPRING INSTITUTE Researching the Environment and Women's Health

Collaborators

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