Equilibrium-based Passive Sampling for PFAS: PFASsive™

Brent G. Pautler, Ph.D.

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Passive Sampling

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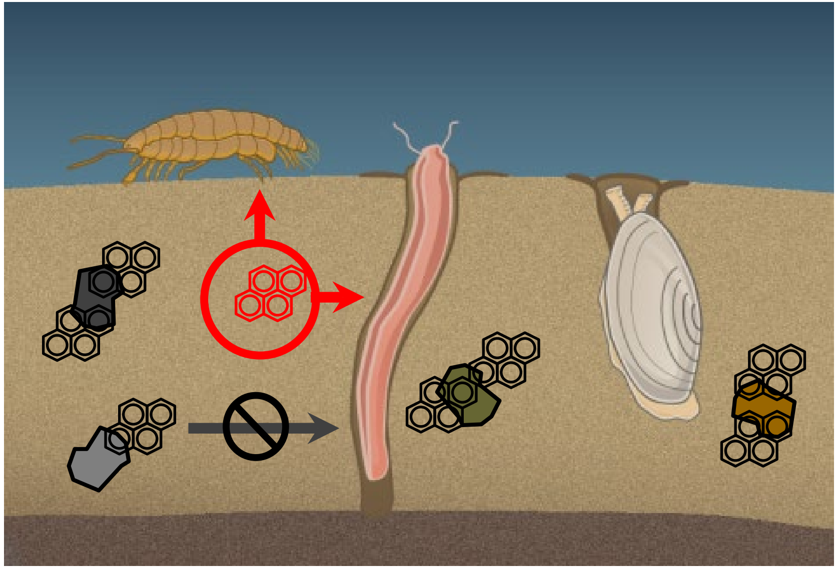
C_{free}: Core Concepts



- Only a small fraction of chemicals in sediment (or water, or soil) are **freely-dissolved** and available to organisms
  - Most **bound** to sediment solids (organic matter, clay, etc.)
- Passive sampling allows us to measure the concentration of freely-dissolved chemicals (C_{free})

The Passive Sampling Advantage

- **Freely dissolved** concentration (C_{free}) measurement as opposed to total mass
- **Advantages:**
  - Correlated to actual toxicity, mobility and bioaccumulation for environmental receptors
  - Risk assessment – compared directly to water quality criteria and aquatic organism protection
- **Practical applications**
  - Site Characterization
  - Remediation Design
  - Long Term Monitoring

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What about PFAS C_{free}?

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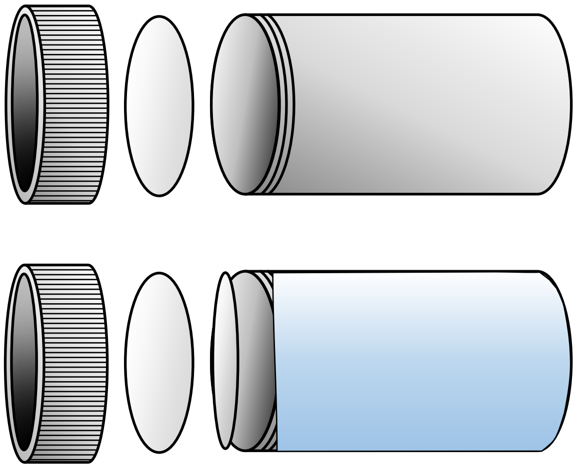
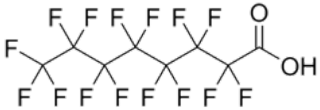
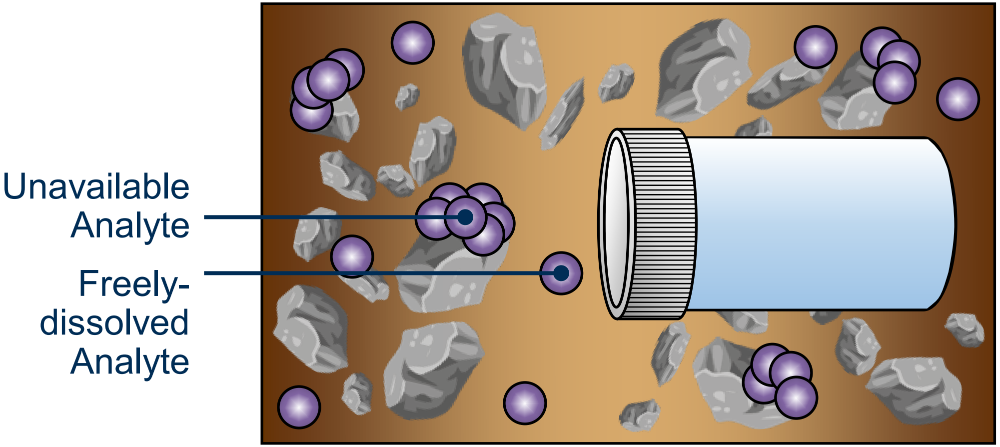
PFASsive™ – Dialysis Sampler

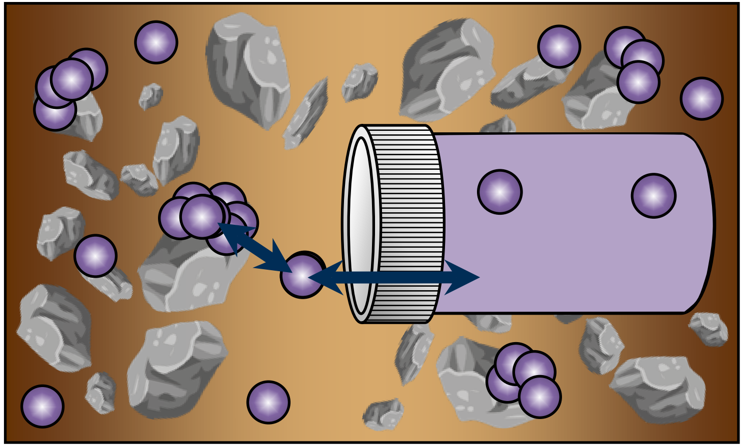


- Small container capped with semi-permeable membrane
- Can also have protective outer cap (with open permeations)
- Filled with ultrapure water

PFASsive™ – Dialysis Sampler

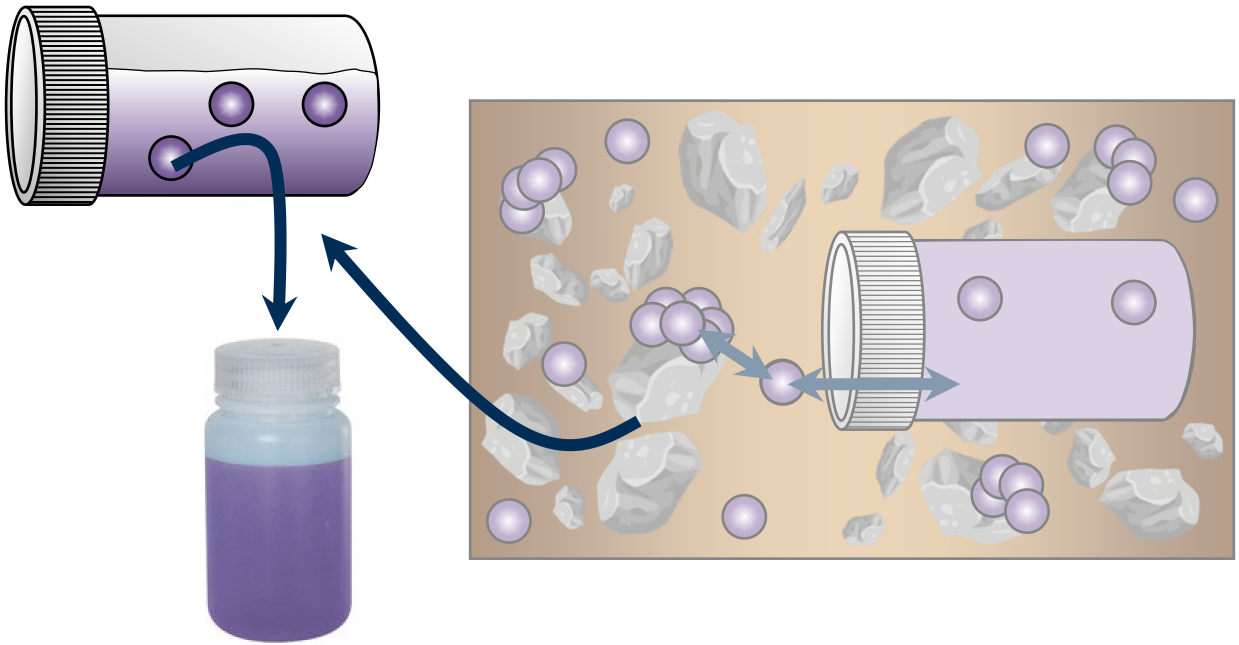






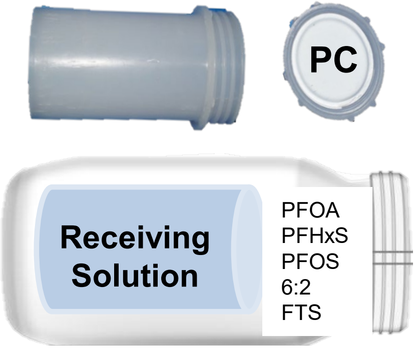
- Sampler inserted into sediment matrix
- Solution in sampler equilibrates with freely-dissolved species in sediment (days-weeks)

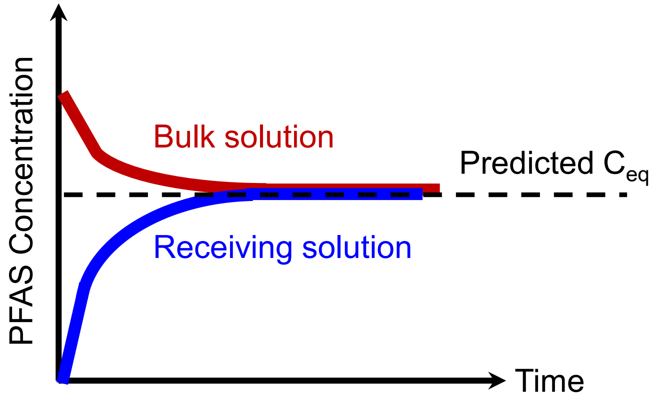
PFASsive™ – Dialysis Sampler

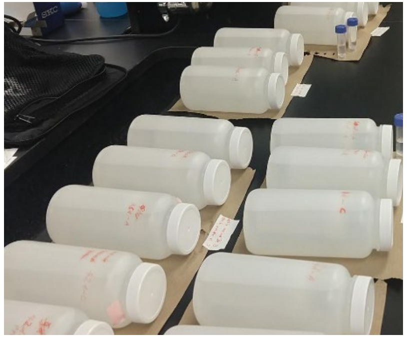


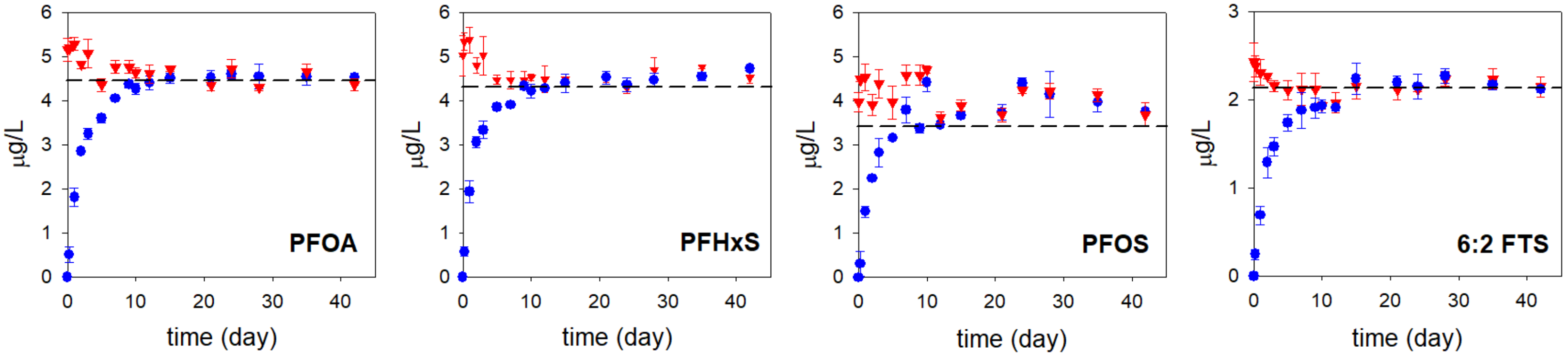
- Sampler removed from sediment, solution transferred and preserved, measured for target analytes using standard methods for water (e.g., EPA 1633)
- Results in ng/L

Suitable Materials?

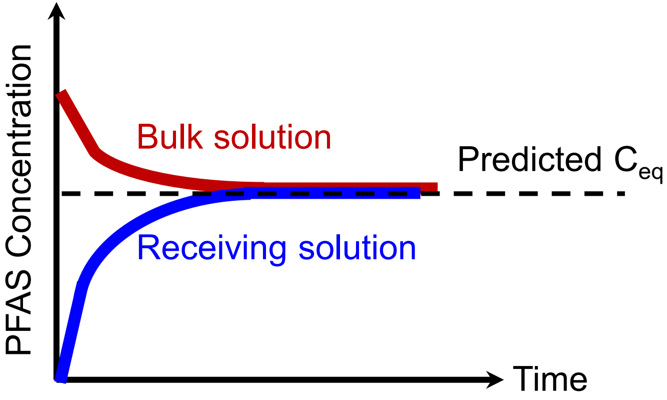


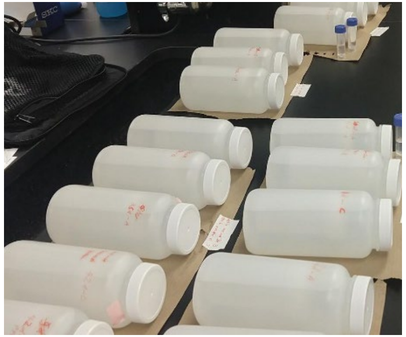




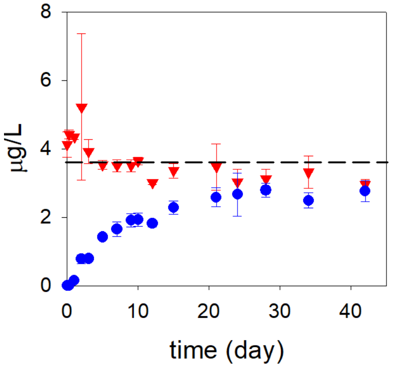


Suitable Materials?





PFASsive™



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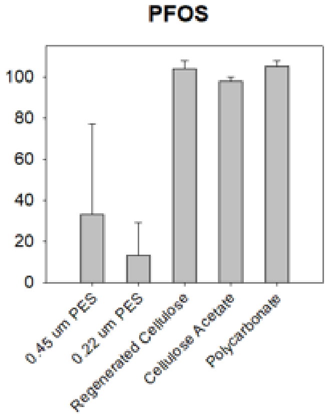
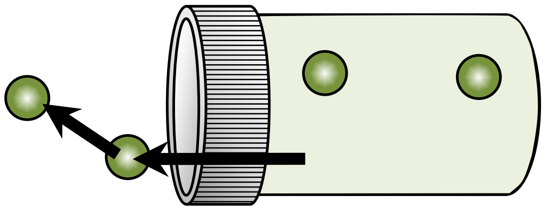
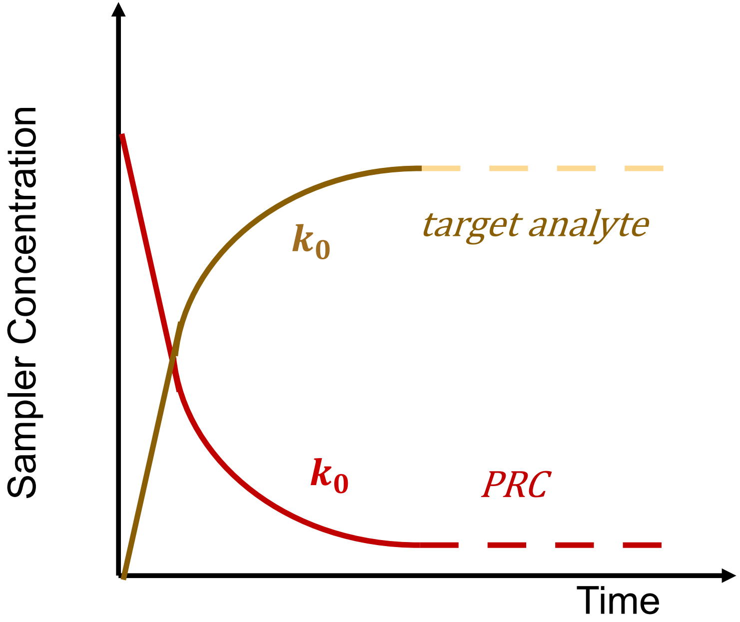


How do I know I am at equilibrium?

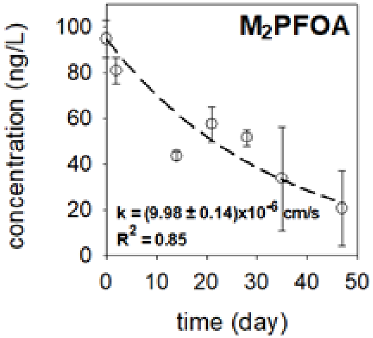
Use a reverse tracer (Performance Reference Compound)

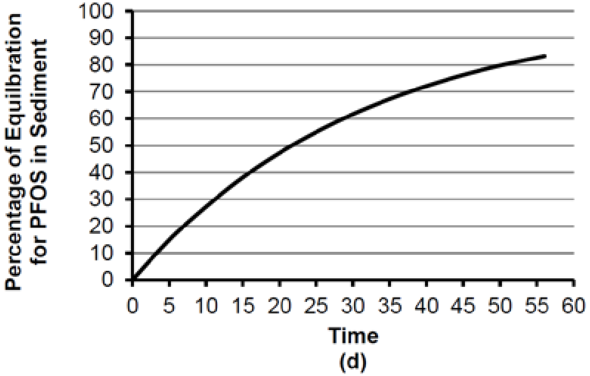


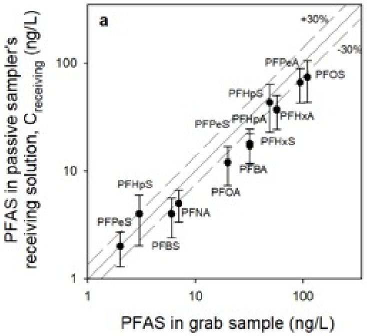
$$k_{0,analyte} = k_{0,PRC} \times \frac{D_{analyte}}{D_{PRC}}$$

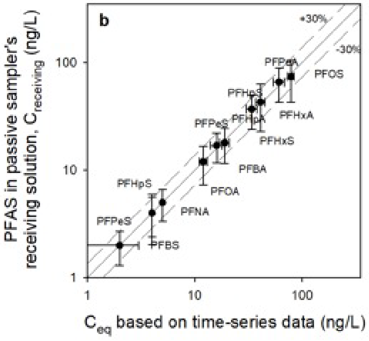


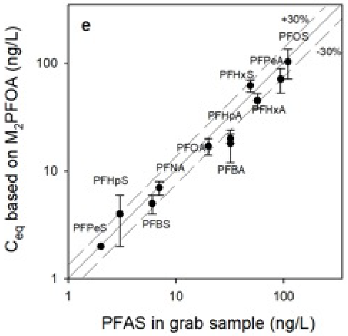
PFASsive™ – Field Data Highlights

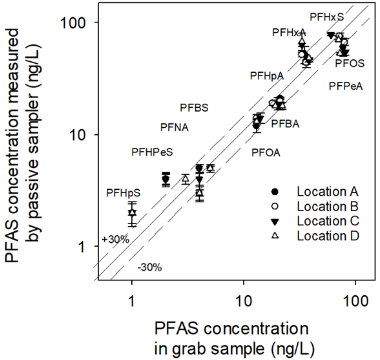












Medon et al. Environmental Science: Processes & Impacts, 2023 , 25(5) 980-995.

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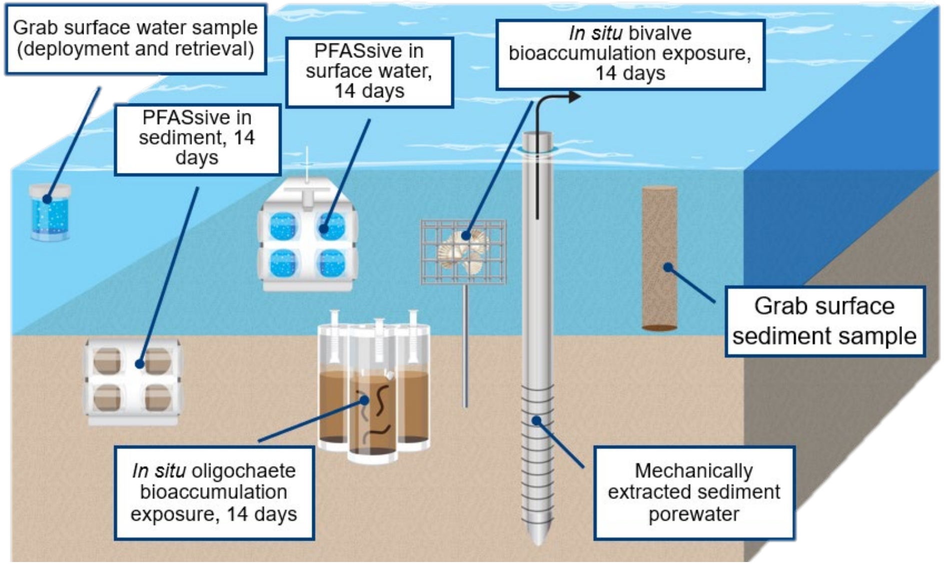
PFASsive™: Solution for PFAS Monitoring!

PFASsive™ | ESTCP



PFASsive™: ESTCP ER23-7741

ESTCP

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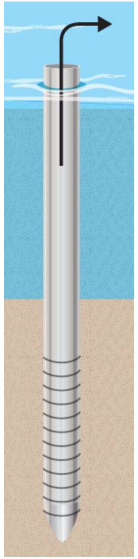
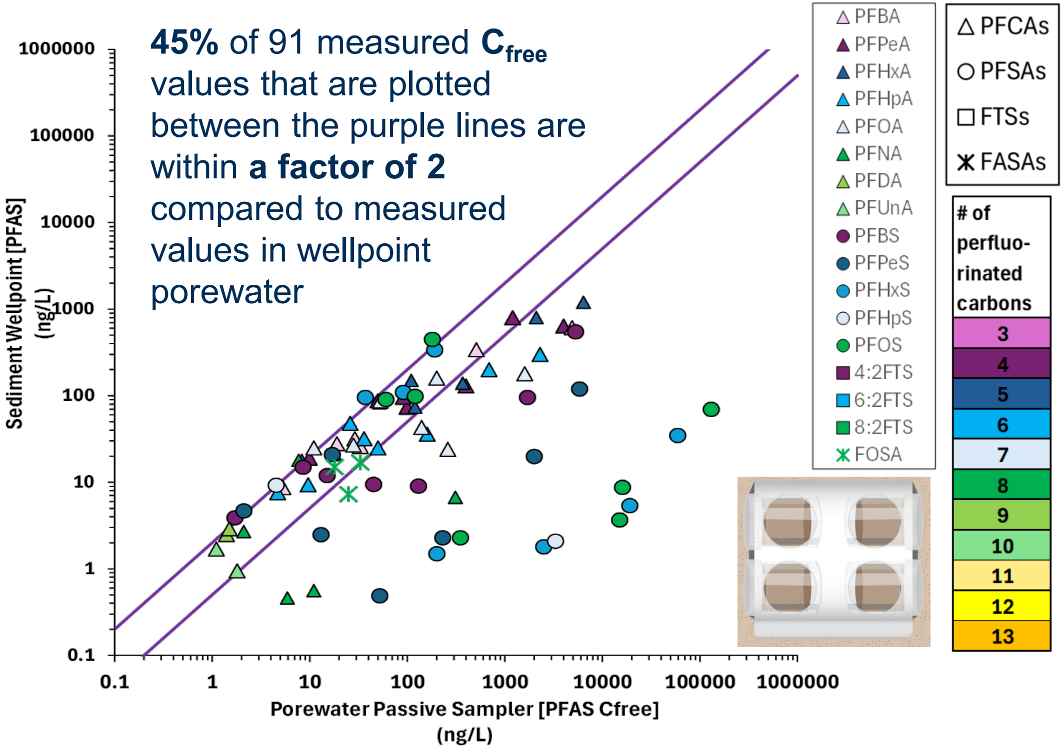
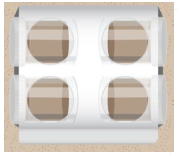


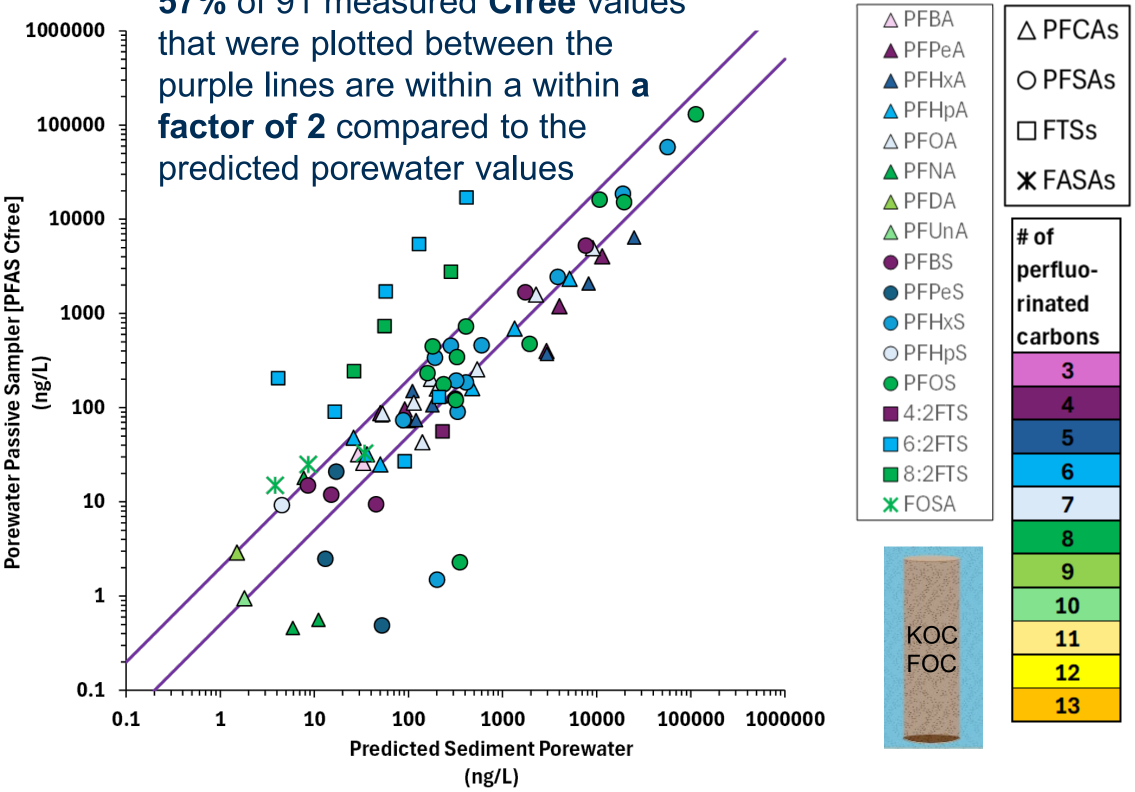


Passive Samplers in Sediment and Mechanically Extracted Sediment Porewater (Wellpoints)

PFASsive™: ESTCP ER23-7741



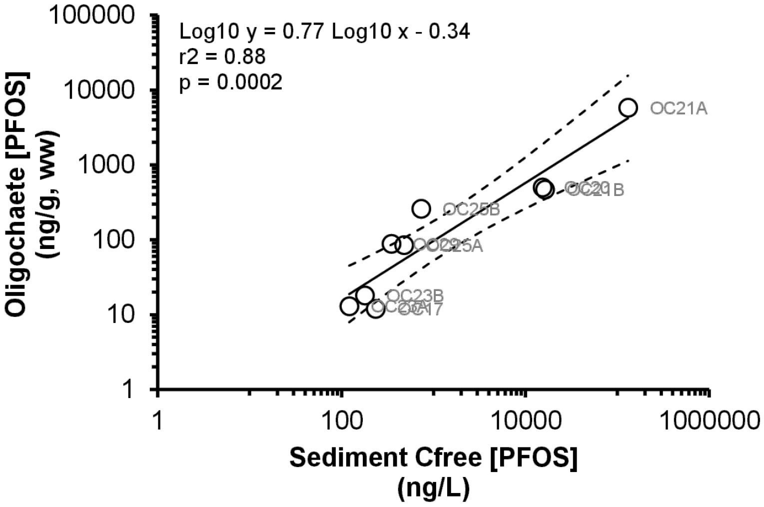
57% of 91 measured **Cfree** values that were plotted between the purple lines are within a within **a factor of 2** compared to the predicted porewater values

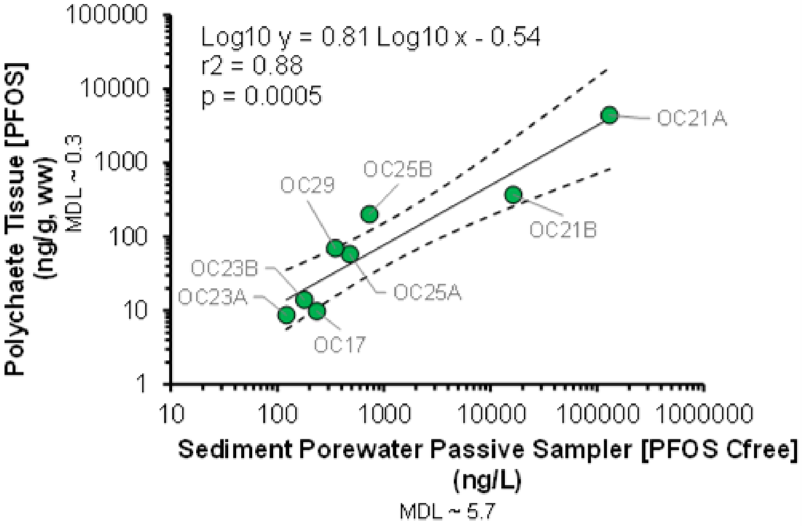


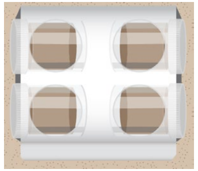
Better Correlation of PFASsive™ with calculated PW PFAS

Predicted PW = [Measured Sediment PFAS] ÷ ([Measured Sediment OC] × Literature-derived PFAS KOC)

PFASsive™: ESTCP ER23-7741







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But I want it all!

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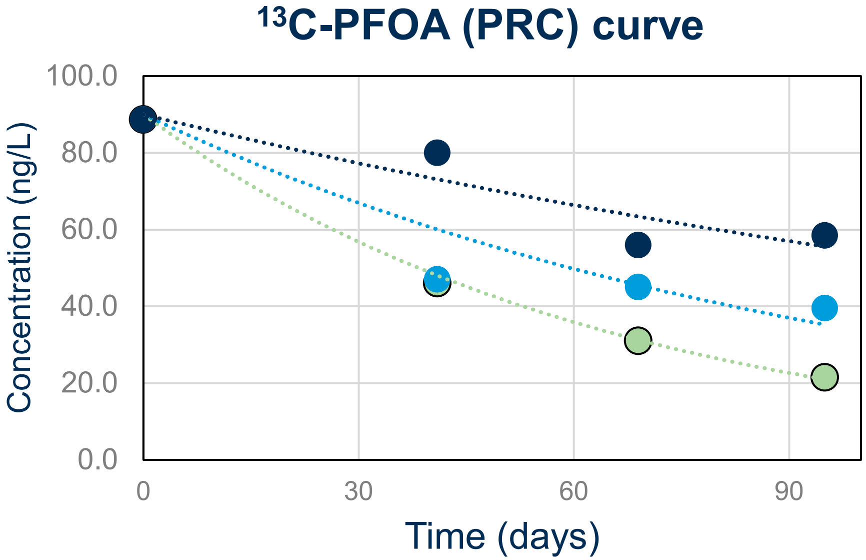
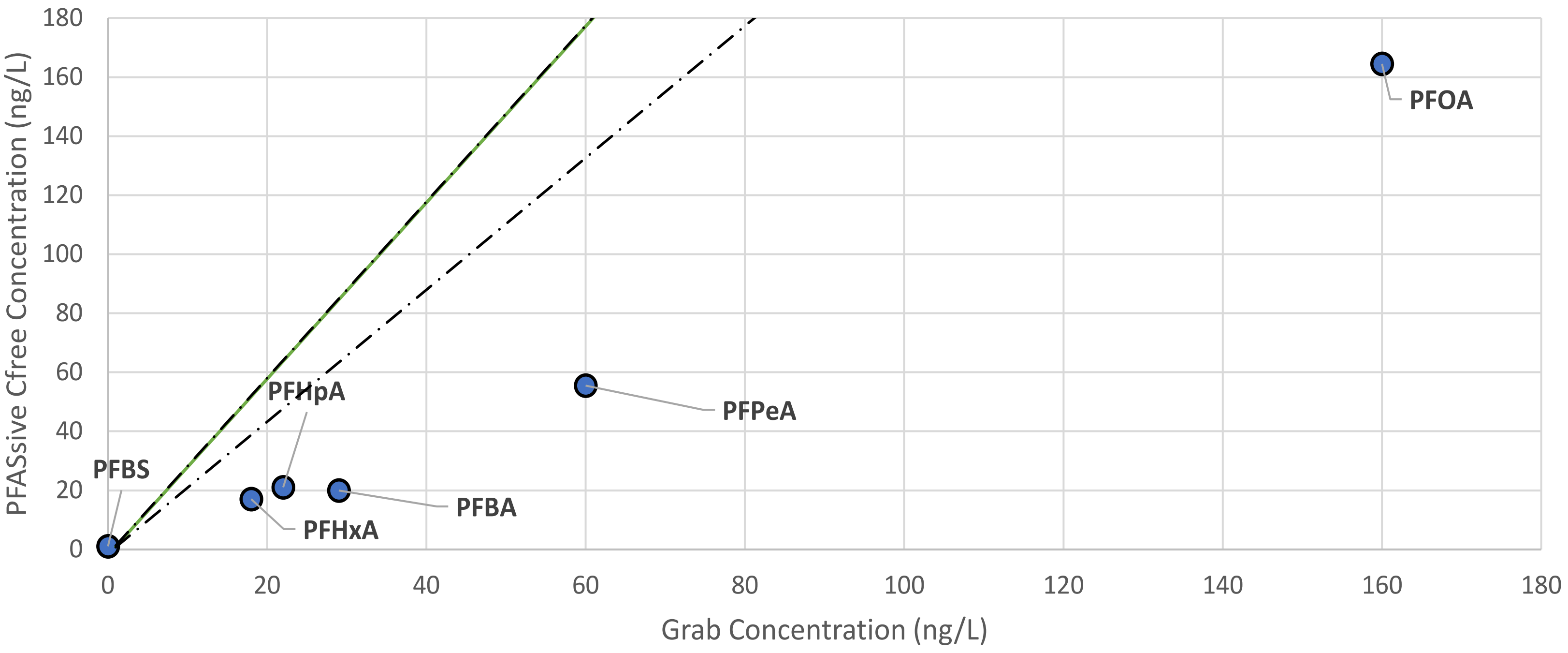
PFASsive™: Groundwater Validation

PFASsive™

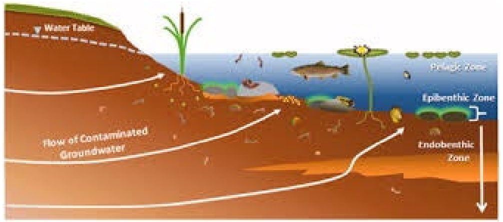


PFASsive™: Groundwater Validation

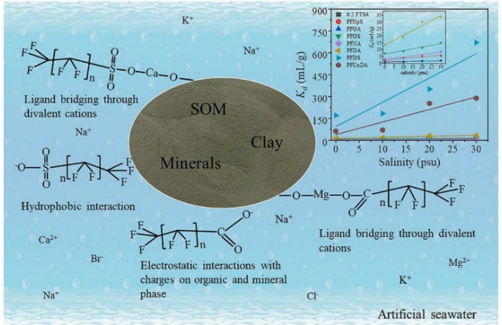


I want it All

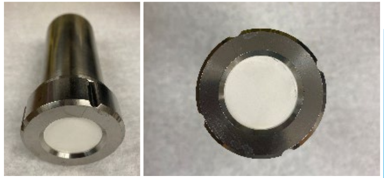
Marine Environments, Groundwater and mixed contaminants?

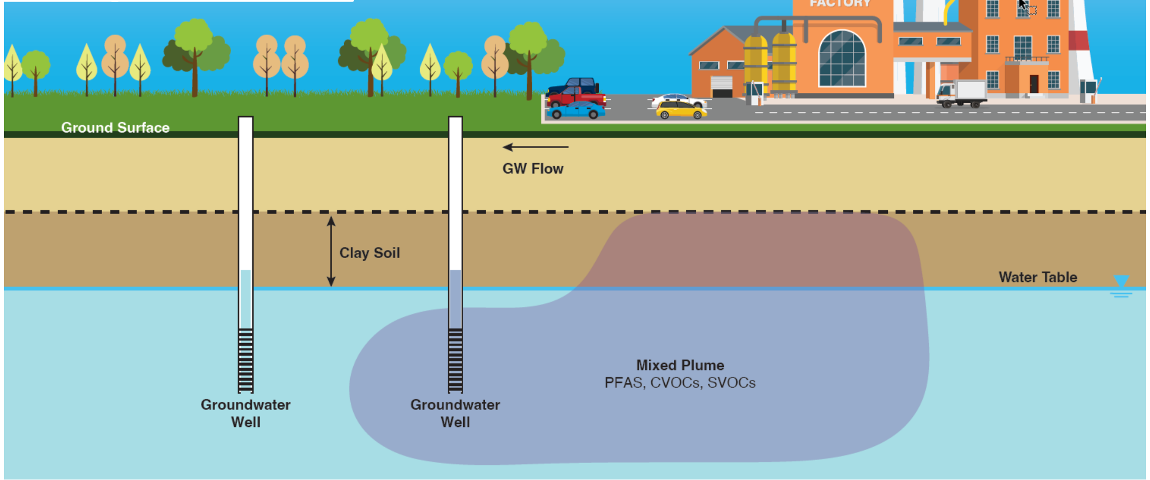


Roy et al., (2019) *Can. Water Resour. J.* 44: 205-211



Yin et al., (2022) *Environ. Pollut.* 300: 118957

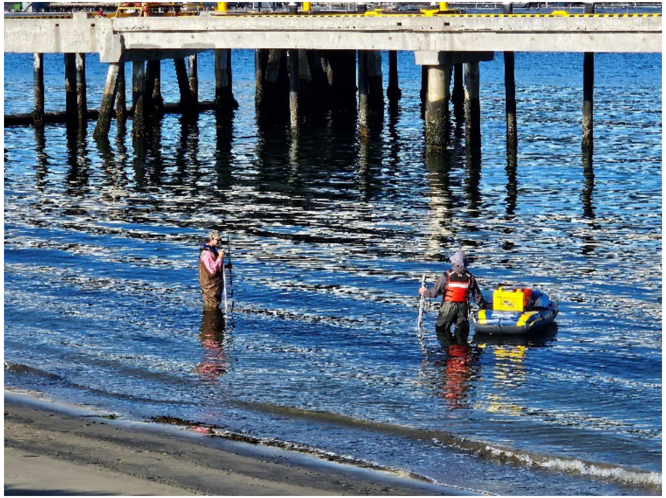


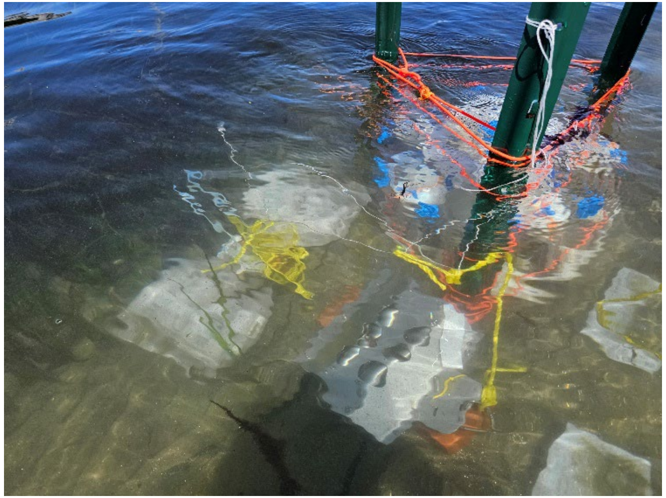


PFASsive™: ESTCP ER23-7741

ESTCP

Tidally influenced, marine water





Questions?

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PFASsive™: Solution for PFAS Monitoring!

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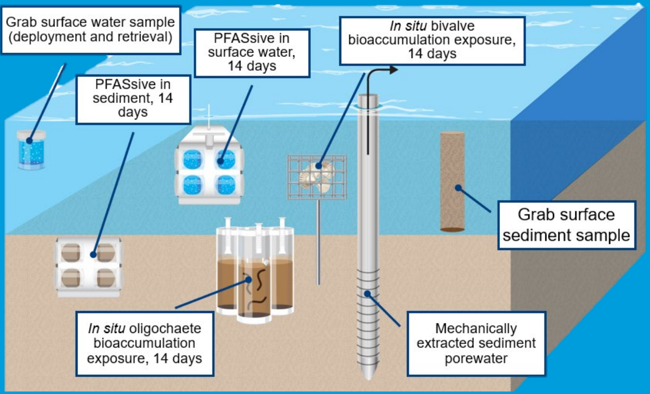
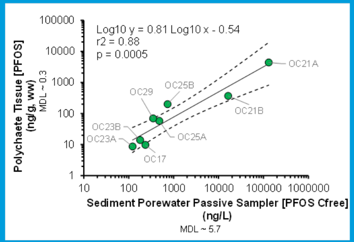
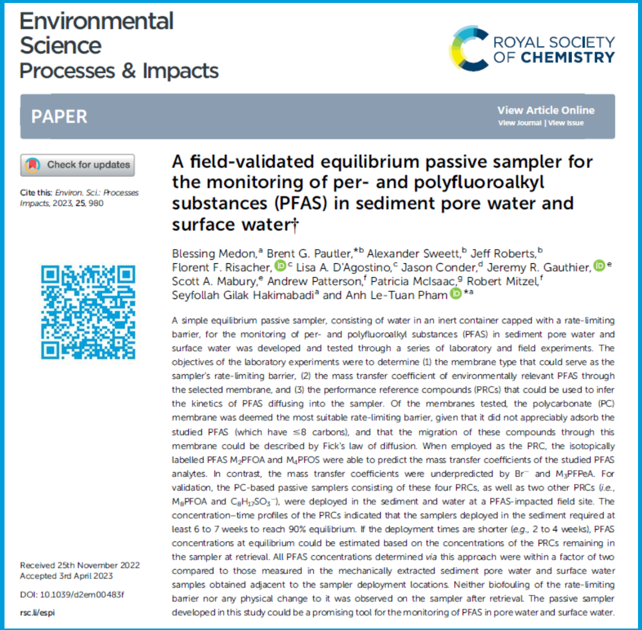
ESTCP







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A field-validated equilibrium passive sampler for the monitoring of per- and polyfluoroalkyl substances (PFAS) in sediment pore water and surface water†

Blessing Medon,[a] Brent G. Pautler,*[b] Alexander Sweett,[b] Jeff Roberts,[b] Florent F. Risacher,[c] Lisa A. D'Agostino,[c] Jason Conder,[d] Jeremy R. Gauthier,[e] Scott A. Mabury,[e] Andrew Patterson,[f] Patricia McIsaac,[g] Robert Mitzel,[f] Seyfollah Gilak Hakimabadi[a] and Anh Le-Tuan Pham*[a]

A simple equilibrium passive sampler, consisting of water in an inert container capped with a rate-limiting barrier, for the monitoring of per- and polyfluoroalkyl substances (PFAS) in sediment pore water and surface water was developed and tested through a series of laboratory and field experiments. The objectives of the laboratory experiments were to determine (1) the membrane type that could serve as the sampler's rate-limiting barrier, (2) the mass transfer coefficient of environmentally relevant PFAS through the selected membrane, and (3) the performance reference compounds (PRCs) that could be used to infer the kinetics of PFAS diffusing into the sampler. Of the membranes tested, the polycarbonate (PC) membrane was deemed the most suitable rate-limiting barrier, given that it did not appreciably adsorb the studied PFAS (which have ≤8 carbons), and that the migration of these compounds through this membrane could be described by Fick's law of diffusion. When employed as the PRC, the isotopically labelled PFAS M_2PFOA and M_4PFOS were able to predict the mass transfer coefficients of the studied PFAS analytes. In contrast, the mass transfer coefficients were underpredicted by Br^- and M_3PFPeA. For validation, the PC-based passive samplers consisting of these four PRCs, as well as two other PRCs (*i.e.*, M_8PFOA and $C_8H_{17}SO_3^-$), were deployed in the sediment and water at a PFAS-impacted field site. The concentration–time profiles of the PRCs indicated that the samplers deployed in the sediment required at least 6 to 7 weeks to reach 90% equilibrium. If the deployment times are shorter (*e.g.*, 2 to 4 weeks), PFAS concentrations at equilibrium could be estimated based on the concentrations of the PRCs remaining in the sampler at retrieval. All PFAS concentrations determined *via* this approach were within a factor of two compared to those measured in the mechanically extracted sediment pore water and surface water samples obtained adjacent to the sampler deployment locations. Neither biofouling of the rate-limiting barrier nor any physical change to it was observed on the sampler after retrieval. The passive sampler developed in this study could be a promising tool for the monitoring of PFAS in pore water and surface water.

Received 25th November 2022
Accepted 3rd April 2023

DOI: 10.1039/d2em00483f

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