



Abstract

Background. Per- and Polyfluoroalkyl Substances (PFAS) have emerged as a concern in the environment as the historical use of aqueous film-forming foam (AFFF) in emergency response and firefighter training has resulted in the release of PFAS into groundwater, sediment, pore water and surface water. As PFAS are persistent, bioaccumulate in living organisms and have demonstrated toxicity, there is a critical need to understand migration pathways and bioavailability of PFAS to ensure proper delineation and risk characterization. The established sampling protocols and PFAS concentration only captures the total concentration at a single timepoint and represents the entire mass of PFAS present, which may result in an overestimation of the bioavailable PFAS exposure to human and ecological receptors.

Approach. A simple equilibrium dialysis passive sampler, consisting of ultrapure water contained in an inert container capped by a semipermeable membrane for monitoring PFAS in sediment pore water and surface water was developed and validated through a series of laboratory and field experiments. A series of bench-scale experiments were designed to monitor for key PFAS compounds followed by field validation via two *in situ* field pilots where samplers were deployed in both the sediment and overlying water.

Results. This study demonstrated that the sampler materials were inert with regards to PFAS and that the rate of PFAS uptake described by Fick's law of diffusion. Targeted analytical results (modified EPA 537, draft EPA 1633) suggested that the concentration of PFAS in the sampled medium can be readily calculated based on the PFAS concentration in the receiving phase and the mass transfer coefficient. PFAS equilibrium was reached in 14 days for surface water, and average of 75% equilibrium for all target compounds detected in pore water after 28 days and were all within a factor of 2 or less with averaged grab sample results. Non-targeted results analyzed by UHPLC Orbitrap mass spectrometry suggests that the sampler can be used to detect and quantify novel PFAS analytes beyond the EPA regulated list.

Background

The extensive use of per and polyfluoroalkyl substances (PFAS) in the last several decades including aqueous film-forming foams (AFFF), fluoropolymers, cosmetics, food packaging, carpets and textiles has resulted in the contamination of water, air, land, and biota by these uniquely persistent and potentially toxic organic compounds. Therefore, the need for a simple device to monitor PFAS in the environment has resulted in significant research and development effort. Equilibrium passive sampling is a powerful tool for simple and effective detection and quantification of environmental contaminants and hold great promise for the PFAS.



FIGURE 1: PFAS Passive Sampler in 3D Printed Frame

Sampler Design

- High-density Polyethylene container filled with ultrapure water (receiving solution)
- Membrane Filters tested to determine the ideal diffusion rate-limiting barrier
- Polyethylene terephthalate glycol frame (for easy field deployment)
- The polycarbonate membrane with the other sampler materials were inert with regards to PFAS (i.e., neither source nor sink).

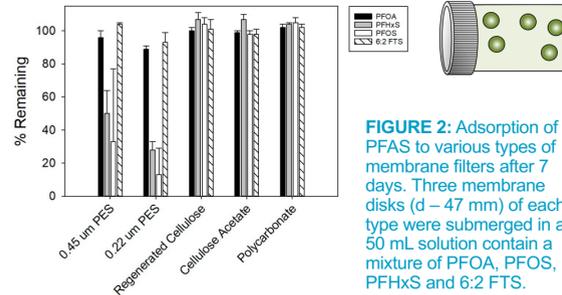


FIGURE 2: Adsorption of PFAS to various types of membrane filters after 7 days. Three membrane disks (d = 47 mm) of each type were submerged in a 50 mL solution containing a mixture of PFOA, PFOS, PFHxS and 6:2 FTS.

PFAS Uptake

- Series of mesocosm experiments to investigate the uptake of model compounds into the sampler and determine equilibrium time
- Concentrations of the PFAS analytes rose and fell exponentially, membrane rate limiting barrier followed Fick's second law of diffusion.
- Equilibrium achieved after 2 weeks

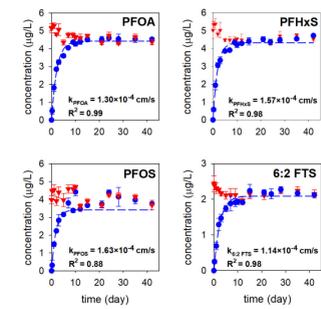


FIGURE 3: The concentration-time profiles of PFAS analytes. Red Triangles: the concentrations in the solution in the jar. Blue Circles: the concentration in the sampler receiving solution.

Reverse Tracer

- Series of Mesocosm experiment to investigate the migration of spiked tracer compounds from the sampler to the bulk solution
- Tracer compounds (performance reference compounds; PRCs) fell exponentially, membrane rate limiting barrier followed second law of diffusion

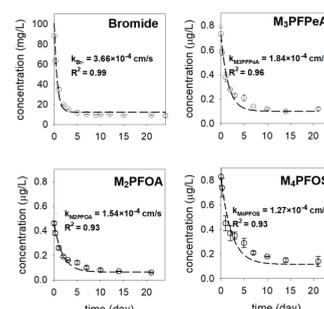


FIGURE 4: The concentration-time profiles of reverse tracer (performance reference compounds; PRCs) in the receiving solution of the sample.

Field Validation

Samplers were deployed in sediment pore water and lake water at Lake Niapenco (Hamilton, Ontario, Canada) which is part of the Welland River watershed and located downstream of the John C. Munro Hamilton International Airport in Fall 2021 and Spring 2022. PFAS has been present and characterized in surface water, bulk sediment and biota in this watershed, presumably due to the use of AFFF in fire-fighter training activities at the airport. Targeted investigations (modified EPA 537 / draft EPA 1633) and non-targeted methods were undertaken to validate the applicability of this sampler for field investigations.

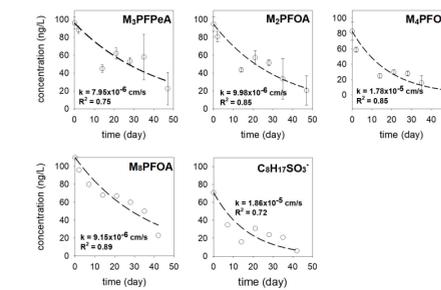


FIGURE 5: The concentration-time profile of the PRCs in the samplers deployed in sediment at Lake Niapenco. Additional PRCs tested include M3PFOA and 1-Octanesulfonate.

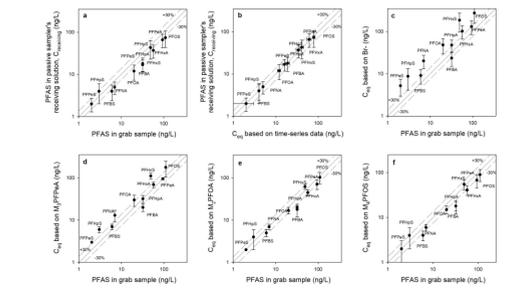


FIGURE 6: The concentration of detected PFAS in sediment pore water as indicated by passive samplers, compared to the concentration of in mechanically extracted sediment pore water (a), time series data (b) and four different PRCs (c – f) to predict the equilibrium concentration.

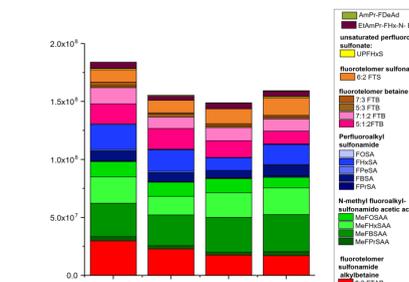


FIGURE 7: Area counts of novel PFAS identified in passive samplers deployed in surface water (SW) and pore water (PW) by non-targeted mass spectrometry.

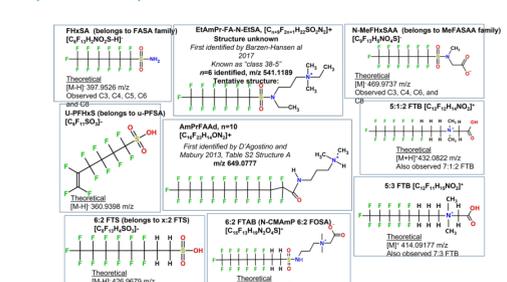


FIGURE 8: Example structures of novel PFAS structures identified during the field deployment of the passive samplers.

The observed mass transfer coefficient $k_{PFAS, experimental}$ and $k_{PRC, experimental}$ across the membrane was fitted to the following equations:

$$\text{For PFAS Analytes: } C_s(t) = C_b(0) \times \left(\frac{V_j}{V_j + V_s} \right) \times \left(1 - \exp \left(- \frac{A k_{PFAS, experimental} t}{V_s V_j / (V_j + V_s)} \right) \right)$$

$$\text{For PRCs: } C_{PRC}(t) = \frac{V_s C_{PRC}(0)}{V_j + V_s} + \left[\left(C_{PRC}(0) - \frac{V_s C_{PRC}(0)}{V_j + V_s} \right) \times \exp \left(- \frac{A k_{PRC, experimental} t}{V_s V_j / (V_j + V_s)} \right) \right]$$

$$k_{PFAS, calculated} = k_{PRC, experimental} \times \frac{D_{PFAS}}{D_{PRC}}$$

$$\% \text{ difference} = \frac{k_{PFAS, calculated} - k_{PFAS, experimental}}{k_{PFAS, experimental}} \times 100\%$$

PFAS	$k_{experimental}$ (cm/s)	Based on Br-		Based on M ₃ PFPeA		Based on M ₂ PFOA		Based on M ₄ PFOS	
		$k_{calculated}$ (cm/s)	% Difference	$k_{calculated}$ (cm/s)	% Difference	$k_{calculated}$ (cm/s)	% Difference	$k_{calculated}$ (cm/s)	% Difference
PFOA	1.30×10 ⁻⁴	8.83×10 ⁻⁵	-32%	7.51×10 ⁻⁵	-42%	1.54×10 ⁻⁴	19%	1.15×10 ⁻⁴	-11%
PFHxS	1.57×10 ⁻⁴	8.11×10 ⁻⁵	-48%	6.90×10 ⁻⁵	-56%	1.41×10 ⁻⁴	-10%	1.06×10 ⁻⁴	-33%
PFOS	1.63×10 ⁻⁴	9.74×10 ⁻⁵	-40%	8.28×10 ⁻⁵	-49%	1.70×10 ⁻⁴	4%	1.27×10 ⁻⁴	-22%
6:2 FTS	1.14×10 ⁻⁴	7.57×10 ⁻⁵	-34%	6.44×10 ⁻⁵	-43%	1.32×10 ⁻⁴	16%	9.88×10 ⁻⁵	-13%

Summary

A simple and robust equilibrium passive sampler for monitoring PFAS in sediment pore water and lake water has been validated. The sampler materials were inert with regards to PFAS, the rate of uptake can be described by Fick's law of diffusion and equilibrium concentrations of targeted PFAS analytes (modified EPA 537, draft EPA 1633) can be calculated with the incorporation of PRCs.

Additional non-targeted mass spectral analyses of field-deployed samplers suggests that the sampler can be used to detect and quantify a diverse set of PFAS analytes beyond the EPA targeted list if required.

Future work includes the adaption and validation of the sampler for low flow environments such as groundwater and correlation with PFAS uptake by aquatic biota.