

## Development of an Equilibrium Passive Sampler for PFAS Detection and Quantification in Aqueous Environments

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**Background/Objectives.** Per- and polyfluoroalkyl substances (PFAS) have emerged as a concern in the environment due to their persistence, bioaccumulation in living organisms, and toxicity. 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, porewater, and surface water. As PFAS are persistent, bioaccumulate in living organisms, and have demonstrated toxicity in laboratory animals, there is a critical need to understand migration pathways and bioavailability of PFAS to ensure proper delineation and risk characterization. The established sampling protocols only capture the total concentration at a single timepoint and PFAS concentrations measured represent the entire mass of PFAS present, which may result in an overestimation of the bioavailable PFAS exposure to human and ecological receptors. Therefore, a technique, tool, and/or technology that can assess bioavailability and risk of PFAS in the environment is required.

**Approach/Activities.** Traditional sampling methods for sediment, porewater, surface water and groundwater quantify total concentrations of chemicals present in that media by physical extraction. The use of total concentrations in risk assessments may result in an overestimation of risk, as only the bioavailable fraction of the chemical can bioaccumulate into organism tissues, resulting in exposures to human and ecological receptors. Although biota and tissue samples could be collected to assess this risk, these methods are time-consuming and costly. Equilibrium passive sampling is a popular approach used by practitioners and regulators to assess bioavailability and risk through the dissolved phase of contaminants, including metals, persistent organic pollutants (i.e., PCBs, PAHs, and pesticides), nutrients and pharmaceuticals. In contrast, PFAS are emerging contaminants and researchers have only started investigating potential passive sampling solutions. Given their partial water-solubility and the ability of analytical laboratories to detect trace amounts of PFAS in water, a diffusion-based equilibrium passive sampler was developed. When deployed, analytes dissolved in the water or sediment porewater equilibrate with the water in the sampler through the membrane. Through a series of bench-scale laboratory experiments, factors affecting the migration of several carboxylate and sulfonate PFAS into a diffusion cell were tested including the type of membrane filter, filter pore size, and solution chemistry. The results of these experiments suggested that the uptake of PFAS into the sampler was the fastest with polycarbonate membrane-based samplers, that the solution chemistry did not influence the PFAS uptake, that PFAS were not lost to sorption, that PFAS were not produced from sampler materials and that this sampler could be used to monitor

multiple PFAS compounds.

**Results/Lessons Learned.** The laboratory validated sampler was further tested via two in situ field pilots to measure PFAS in sediment porewater and surface water and two in situ deployments for groundwater. Targeted analytical results (Modified EPA 537, EPA 1633) indicated that equilibrium was reached in 14 days for surface water and after 28 days in porewater an average 75% equilibrium for all target compounds was reached and equilibrium concentrations can be determined with the incorporation of reverse tracers. Also, all data were within a factor of 2 or less with averaged grab sample results. Non-targeted analysis from the samplers showed more diversity in species and the applicability for detection of additional PFAS analytes with this sampler. Samplers deployed in groundwater monitoring wells agreed with dialysis bags designed for PFAS sampling as well as groundwater grab samples, providing an alternative sampling device for quarterly groundwater monitoring. Future experiments include direct comparison with tissue samples to further validate the relationship between passive sampling results and exposure, risk, and bioaccumulation.