

## EMERGING CONTAMINANT ARTICLE

## TOPICAL COLLECTION ON PFAS ANALYTICS AND TREATMENT

# Passive sampler designed for per- and polyfluoroalkyl substances using polymer-modified organosilica adsorbent

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**Abstract**

A passive sampler designed to measure per- and polyfluoroalkyl substances (PFAS) was evaluated to determine chemical uptake rates under a variety of conditions. The sampler design is simple and robust, using organosilica modified with cross-linked amine polymer in an high density polyethylene housing retained with polypropylene mesh. The addition of amine groups as a weak ion-exchange resin in combination with Cu<sup>2+</sup> was designed to promote binding of short-chain PFAS. A five-fold improvement in perfluorobutanoic acid adsorption was measured when Cu<sup>2+</sup> was added to the polyethylenimine polymer. The samplers showed an integrated response to all analytes tested except for short-chain PFAS. Sampling rates of PFAS analytes from simulated groundwater were on average 10 mL/day at flow rates of 0.038–1.9 cm/min. Relatively low variability in sampling rate was observed over the range of laboratory tested conditions (representing common conditions in environmental waters) including elevated ionic strength, sulfate concentration, and humic acid content.

**KEYWORDS**

adsorption, passive sampling, PFAS

## 1 | INTRODUCTION

Per and polyfluoroalkyl substances (PFAS) are aqueous contaminants of emerging concern due to the possibility of impacts on human health and the environment (Ankley et al., 2021; Lee et al., 2020; Zeng et al., 2019). PFAS are a diverse class of compounds comprising anionic, cationic, and neutral species, each with a range of fluoroalkyl chain lengths (Barzen-Hanson et al., 2017; Buck et al., 2011). The chemical and biological stability of PFAS combined with their ongoing transport via the atmosphere (Tian et al., 2018) and hydrosphere

(Xiao, 2017) has led to routine detections in drinking water (Boone et al., 2019; Hu et al., 2016) and in humans (Jian et al., 2018; Olsen et al., 2017). For example, numerous sites contain groundwater, surface water, and stormwater run-off contaminated with PFAS from the historical use of aqueous film forming foam for firefighter training and emergency response (Anderson et al., 2016; Houtz et al., 2013). Measuring PFAS in environmental waters (e.g., stormwater, streams, lakes, wetlands, and groundwater) is of growing importance in understanding fate and transport, assessing risk and monitoring remedy performance.

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Passive samplers have been widely employed to measure a large range of contaminants and can offer several advantages compared with traditional grab samples (Barceló & Ruan, 2019; Greenwood et al., 2007). In site investigation work, passive sampling can reduce the labor costs and health and safety risk associated with sampling, amount of materials shipped for analysis, and investigation-derived waste generated (Valenzuela et al., 2020). Grab sampling provides water quality data at a specific time, but may not be representative of a time weighted average if transient variations in analyte concentration are missed. Integrative passive samplers can provide a more efficient means to measure time weighted average concentration vs. multi-time point direct water sampling (Salim & Górecki, 2019). Additionally, there are some circumstances such as stormwater events where grab sampling is inconvenient due to unpredictable timing of storm-driven flows and high concentration variability. For these applications, a wide variety of passive sampling design strategies have been developed by many others to convert the amount of accumulated analyte to the concentration in water (Booij et al., 2016).

Several studies (Lai et al., 2018) have tested passive sampling systems to measure aqueous PFAS concentration including the polar organic chemical integrative sampler (POCIS) (Kaserzon et al., 2014; Kaserzon et al., 2019; Li et al., 2016; Persson, 2015), diffusive gradient thin film (Challis, 2018), and use of specialized adsorbents (Wang et al., 2017). POCIS samplers use a small particle size adsorbent placed behind diffusion-limiting (sub-micron pore size) membranes, which contact the water. Such samplers have been generally successful in measuring PFAS in aqueous samples. However, uptake rates can vary depending on flow rate and pH (Li et al., 2016). Performance reference compounds can be preloaded standards with known desorption rates to correct for flow rate dependences (Liu et al., 2013). Unfortunately, the use of performance reference compounds with commercial adsorbents has been unsuccessful with PFAS (Kaserzon et al., 2014). POCIS designs have some practical disadvantages, for instance, standard sampling systems are relatively large in size, making them harder to deploy in narrow well casings. Also, the slow rates of analyte diffusion through the membrane may preclude sampling dynamic stormwater events. Alternative designs using thin films hosting adsorbent resins have also shown promise (Challis, 2018). New types of PFAS-specific adsorbents, including sol-gel derived media with ionic sites, have demonstrated that adsorption can be tailored (Wang et al., 2017; Yang et al., 2020).

Adsorbents are the functional ingredient in passive samplers. Ion exchange (Chularueangksorn et al., 2013) and amine-based adsorbents (Ateia et al., 2019) have been

### Article Impact Statement

Measuring per- and polyfluoroalkyl substances in environmental samples is important for monitoring. Passive samplers can offer practical advantages for making measurements.

shown to adsorb PFAS from aqueous solutions. Our efforts to create PFAS adsorbents have resulted in modified swellable organically modified silica (SOMS) with amine polymers. SOMS is a sol-gel derived porous adsorbent that has been investigated for adsorbing dissolved organics from water (Edmiston & Underwood, 2009). SOMS is synthesized from the polycondensation of bis(trimethoxysilylethyl) benzene (BTEB, Figure 1a) under specific conditions that provide a microscopic structure that has the ability to reversibly swell 6 ml/g upon contact with organic solvents (Burkett et al., 2008) creating >20 nm pores. The bridging  $-(CH_2)_2-Ar-(CH_2)_2$  group provides flexibility and makes SOMS hydrophobic and thus unable to swell upon contact with water. Previously, the capability of SOMS to swell and re-constrict was used to physically entrap a quaternary amine cationic polymer (poly[(3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone)] in the hydrophobic pores to create a hybrid material (poly-QA-SOMS) that adsorbed PFAS solutes from water (Stebel et al., 2019). Although poly-QA-SOMS was able to adsorb both short-chain PFAS (e.g.,  $C_4$ , perfluorobutanoic acid [PFBA]) and long-chain compounds (e.g.,  $C_8$ , perfluorooctanoic acid, PFOA), the adsorbent had higher capacity for longer-chain PFAS adsorbates and was sensitive to changes in ionic strength. Overall, ion-exchange was found to be important in promoting PFAS binding, especially short-chain compounds.

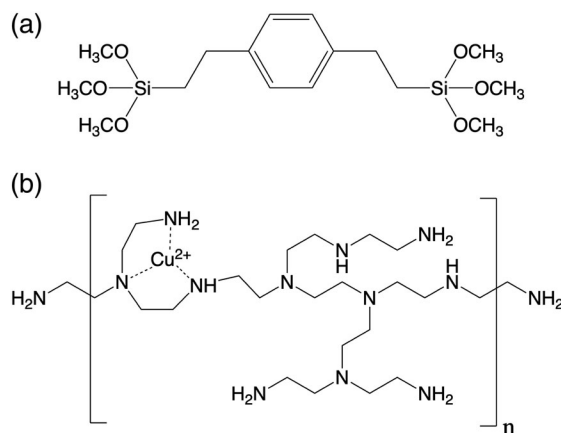


FIGURE 1 (a) Structure of bis(trimethoxysilylethyl) benzene silane precursor. (b) Structure of polyethylenimine polymer modifier with potential Cu<sup>2+</sup> binding site indicated

The overall goal of this work was to create a PFAS-optimized passive sampler that could be used in a wide range of environmental contexts. Five objectives were completed. First, a SOMS-based PFAS adsorbent was created by modifying the pores with polyethylenimine (PEI, Figure 1b), a weak ion-exchange polymer with a high density of amine sites. The advantages to PEI compared with a quaternary amine polymer were that the PEI could be chemically cross-linked with a bifunctional linker to irreversibly immobilize the polymer in the pore network, preventing leaching upon solvent rinse. Also, the amine groups could act as ligands to bind polyvalent metal ions ( $\text{Cu}^{2+}$ ) to increase valency in an ion exchange role. Second, a small, all-polyethylene passive sampler that could fit into all sizes of groundwater wells and surface waters was designed, built, and tested. Third, uptake of PFAS as a function of time and concentration was measured to determine if response was integrative or equilibrium-based. PFAS tested were a mixture of  $\text{C}_4$ – $\text{C}_9$  perfluorocarboxylates and  $\text{C}_4$ ,  $\text{C}_6$ , and  $\text{C}_8$  perfluorosulfonates, perfluorooctane sulfonamide, and hexafluoropropylene oxide dimer acid (see Table S1 for a complete analyte list). Fourth, the sampler was tested across a range of water conditions varying flow rate, pH, oxidation-reduction potential (ORP), temperature, ionic strength, sulfate concentration, and amount of dissolved humic acid. These conditions were designed to represent common conditions in environmental waters. Fifth, the co-adsorption isotopically labeled surrogates post-deployment was evaluated. Surrogates allow for isotopic dilution to be performed potentially, allowing SOMS-based samplers to be integrated into workflows of laboratories using the EPA 537.1 method of PFAS analysis.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

PEI (MW 1300; 50% in  $\text{H}_2\text{O}$ ), 1,6-diisocyanatohexane, copper (II) chloride, glycerol, humic acid, and neat PFAS were obtained from Aldrich. PFAS standards were obtained from Wellington Laboratories. Oasis<sup>®</sup> HLB solid-phase extraction (SPE) cartridges were obtained from Waters. BTEB and dimethydimethoxysilane was purchased from Gelest. All other solvents and reagents were obtained from Thermo-Fisher.

### 2.2 | Cu(II)-PEI-SOMS synthesis

SOMS was synthesized as previously described (Burkett et al., 2008) using a 9:1 mol ratio of BTEB:

dimethydimethoxysilane as the precursor mixture. After preparation, the material was ground and sieved to a 60–80 mesh (180–250  $\mu\text{m}$  particle size). SOMS was swollen in methanol, placed in a 10% wt/vol solution of PEI (5 ml solution per g SOMS), and the mixture shaken for 24 h. The material was then rinsed with water and dried at 25 °C. A solution of 0.5% vol/vol solution of 1,6-diisocyanatohexane in acetone was applied to the SOMS-PEI until fully wet, the slurry heated to 60 °C for 2 min, and allowed to react at room temperature for 18 h. The resulting material was Soxhlet extracted with methanol for 2 h to remove residual reagents. SOMS-PEI was rinsed sequentially with water saturated with  $\text{CuCl}_2$ , deionized (DI) water, and 50% glycerol solution to create Cu(II)-PEI-SOMS.

### 2.3 | Characterization

Surface area and pore volume were measured by  $\text{N}_2$  adsorption at 77 °K using a Beckman Coulter SA-3100 instrument following outgassing at 120 °C for 120 min prior to measurement. Surface area was calculated using the BET method (Brunauer et al., 1938) and the pore size distribution was calculated using the BJH method (Barrett et al., 1951). Fourier transform infrared spectra (FT-IR) were taken using a Nicolet 6700 FT-IR using a diamond-attenuated total reflectance accessory.

### 2.4 | Passive sampler construction

The passive sampler body was constructed high density polyethylene (HDPE) 2.5 cm wide by 4.5 cm long by

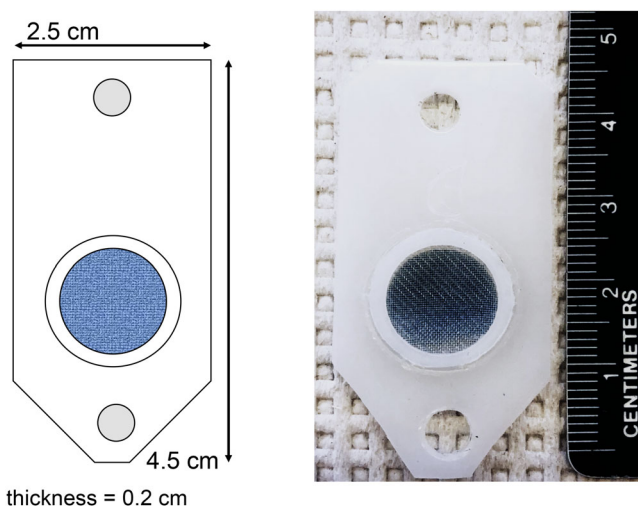


FIGURE 2 Schematic (left) and photograph (right) of the passive sampler constructed of high density polyethylene

TABLE 1 Adsorbent surface area, pore volume, and pore size distribution

Adsorbent	Surface area (m <sup>2</sup> /g)	Pore volume (ml/g)	Pore size distribution (%)							
			<6 nm	6–8 nm	8–10 nm	10–12 nm	12–16 nm	16–20 nm	20–80 nm	>80 nm
SOMS	425	0.49	78	16	1.8	0.9	0.8	0.6	1.5	0.4
Cu(II)-PEI-SOMS	260	0.28	88	6.2	1.2	0.7	0.7	0.5	1.6	0.7

Abbreviations: PEI, polyethylenimine; SOMS, swellable organically modified silica.

0.2 mm thick with a 1 cm through-hole for adsorbent (Figure 2). Each sampler had two 1/4-inch-threaded attachment points. Adsorbent (60 mg) was contained between 98 × 98 polypropylene mesh screens (150 μm opening with a 34% open area), which were heat welded onto the opposite faces of HDPE using a thin ring of HDPE plastic. The adsorbent was wetted with 50% glycerol:DI water, allowing the samplers to be placed in the sampling matrix without any pre-treatment steps. The 250 μm particle size of Cu(II)-PEI-SOMS allowed the resin to be retained within open mesh screens, allowing direct contact with the water to be sampled. The sampler is sized and tapered at one end to fit into a standard 50 ml centrifuge tube, allowing minimal handling during sample collection, transport, and analysis. If removal of the adsorbent resin is needed, the mesh windows snap off by forcefully bending the sampler by hand.

## 2.5 | Passive sampler ruggedness

The passive sampler design considered ruggedness and durability and field application requirements. Design testing included repeatedly deploying the sampler into a simulated monitoring well (2-inch PVC pipe and slotted well screen) installed in a bucket of filter pack sand saturated with tap water. A stainless steel screw was attached to the sampler as a weight, and nylon string was used to deploy the sampler in the well. In 100 deployment and retrieval tests, the sampler did not snag on the screen or otherwise experience visible damage. Additionally, tests simulating stream and stormwater sampling conditions were conducted to evaluate for potential damage to the weld in the HDPE mesh that might occur due to flowing water. Two samplers were installed in fixed position within a 3-inch PVC pipe. One sampler was positioned parallel to and one perpendicular to the flow of water in the pipe. Field-site (from Peterson Air Force Base, Colorado) water containing a PFAS mixture was recirculated through the pipe at a flow velocity of approximately 20 cm/s.

## 2.6 | Adsorption measurements

Equilibrium constants and isotherms were measured as previously described (Stebel et al., 2019) using adsorbent dosages of 40 mg/L (20 mg in 500 ml). Adsorbents were pre-wetted with sequentially with methanol and water prior to addition to solutions of PFAS. All measurements were in duplicate. Prior to the addition of the adsorbent, 250 μl sample was taken and added to 750 μl of methanol. After equilibrium had been achieved (72 h active shaking), an aliquot was taken, filtered through 0.44 μm cellulose acetate to remove adsorbent, and then diluted with 250–750 μl of methanol. Isotopically labeled PFOA internal standard was added to at least three samples per set. Samples were run by direct injection by HPLC-MS/MS.

## 2.7 | Laboratory calibration measurements

Passive samplers were rinsed in DI water and placed with the face parallel to continuous flow in a 26-mm diameter Pharmacia XK glass column attached to a pump system. Polyethylene tubing was used for all fluid handling. The standard condition was 1.0 μg/L of each PFAS analyte, a linear flow rate 0.38 cm/min, and at a temperature of 25 °C. A standard simulated groundwater matrix was used, which contained a mixture of dissolved solids commonly found in groundwater and 1 mg/L humic acid (see supplementary information and Table 2). The water chemistry, temperature, and flow rate were varied by using the same flow system and changing one variable at a time. To determine sampling rate, passive samplers were exposed to a particular condition for 3, 6, and 12 days and the accumulated mass measured. In order to measure the accumulated mass of PFAS, the sampler was removed from the matrix, rinsed with DI water, and placed in 15 ml solution of DI water containing 3.3 ng/ml of each 11 surrogates (see supplementary information for list of analyte and surrogate). After equilibrating the surrogate mixture by shaking for

TABLE 2 Adsorption equilibrium constants

Adsorbent	Matrix	$K_d$ (L/g)										
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFBS	PFHxS	PFOS	HFPO-DA	
Oasis® WAX	DI water	21 ± 3	90 ± 40	330 ± 120	1200 ± 400	3800 ± 900	10,500	310 ± 30	6200	32,000	480 ± 200	
	Groundwater	1.5 ± 1.2	1.8 ± 1.3	2.9 ± 1.3	7.7 ± 1.6	25 ± 3	116 ± 13	4.5 ± 0.7	38 ± 3	720 ± 190	1.0 ± 0.8	
Cu(II)-PEI-SOMS	DI water	70 ± 10	210 ± 30	630 ± 60	1290 ± 150	1550 ± 290	1400	770 ± 240	4250 ± 50	7500 ± 900	300 ± 40	
	Groundwater	6.8 ± 1.5	8.1 ± 1.9	23 ± 1	46 ± 2	95 ± 10	170 ± 18	26 ± 3	140 ± 13	510 ± 110	28 ± 3	

Abbreviations: PEI, polyethylenimine; PFBA, perfluorobutanoic acid; PFOA, perfluorooctanoic acid; SOMS, swellable organically modified silica. Error is standard deviation, n=3.

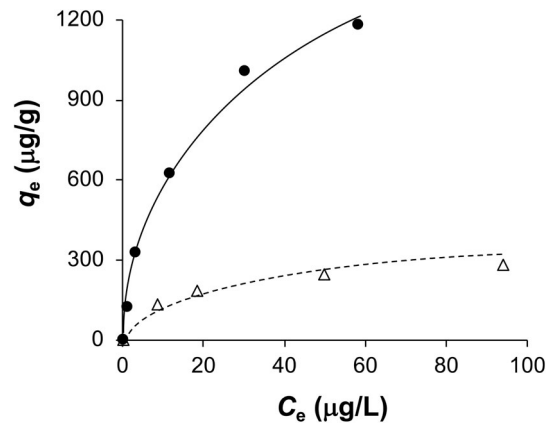


FIGURE 3 Adsorption isotherms of PFBA to Cu(II)-PEI-SOMS (•) and PEI-SOMS (Δ) at 25 °C. PEI, polyethylenimine; PFBA, perfluorobutanoic acid; SOMS, swellable organically modified silica

18 h, the sampler was removed, centrifuged at 1500 rpm to dry, and extracted in 15 ml of methanol with 0.1% vol/vol ammonium hydroxide. The methanol was evaporated under nitrogen gas and reconstituted with 1 ml methanol with 50 ng/ml each of three internal standards (see supplemental information).

## 2.8 | Simulated aquifer tank test

A simulated aquifer tank was used for additional laboratory testing of the passive samplers. The tank test setup is described in detail in previous work (Ulrich et al., 2021), and was modified slightly from a single-pass flow-through design to recirculation. The simulated aquifer tank consisted of a glass aquarium tank (46 cm wide, 122 cm long, and 41 cm tall), filled with 10 lateral centimeters of gravel (Imagitarium Nutmeg Aquarium Gravel) on each end and Ottawa sand in the body of the tank (Humboldt Manufacturing, Chicago, Illinois) mixed with 0.5 weight percent sand-sized limestone chips. The tank was designed to accommodate five 2-inch diameter slotted PVC well screens. Ulrich et al. (2021) operated the tank in a single-pass flow-through design; however, for this study, the effluent was collected and recirculated via a peristaltic pump. A three-pronged injection apparatus was built from 1/8-inch stainless steel Swagelok® tubing, a four-way tee fitting, and two 90° elbow fittings. The injection apparatus was inserted into the gravel zone on the upgradient side. The tank effluent was collected through a glass wool filled bulkhead fitting in the tank wall on the downgradient side of the tank.

The simulated aquifer contained reduced ferrous sulfides (precipitated in a previous experiment) and cultured sulfate-reducing bacteria. Similar geochemical (i.e., low



redox) reducing conditions could potentially exist in field sites where hydrocarbon releases have occurred. Reducing conditions were maintained over the duration of the experiment to avoid large shifts in geochemical parameters that could potentially affect adsorption processes on the passive samplers. A removable plexiglass cover was placed on top of the tank to reduce contact with ambient air. Nitrogen was applied to the headspace via tubing from a liquid nitrogen dewar through a 1/4-inch Swagelok® port

in the cover to maintain a positive pressure nitrogen headspace for the majority of the test. Collection of samples required the removal of the cover for brief amounts of time. In the third month of the 3-month test, a syringe pump injected sodium lactate was injected to maintain reducing conditions in-line using a combination of flexible tubing and 1/8-inch Swagelok® stainless steel tubing.

Prior to initiation of this experiment, the tank was drained of previous experimental solution, flushed

TABLE 3 Extraction recovery from Cu(II)-PEI-SOMS passive samplers

Percent recovery (%)									
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFNA	PFBS	PFHxS	PFOS
64 ± 10	67 ± 13	67 ± 11	60 ± 9	64 ± 9	61 ± 5	72 ± 12	71 ± 12	65 ± 8	65 ± 5

Abbreviations: PEI, polyethylenimine; PFBA, perfluorobutanoic acid; PFOA, perfluorooctanoic acid; SOMS, swellable organically modified silica. Error is standard deviation, n=5.

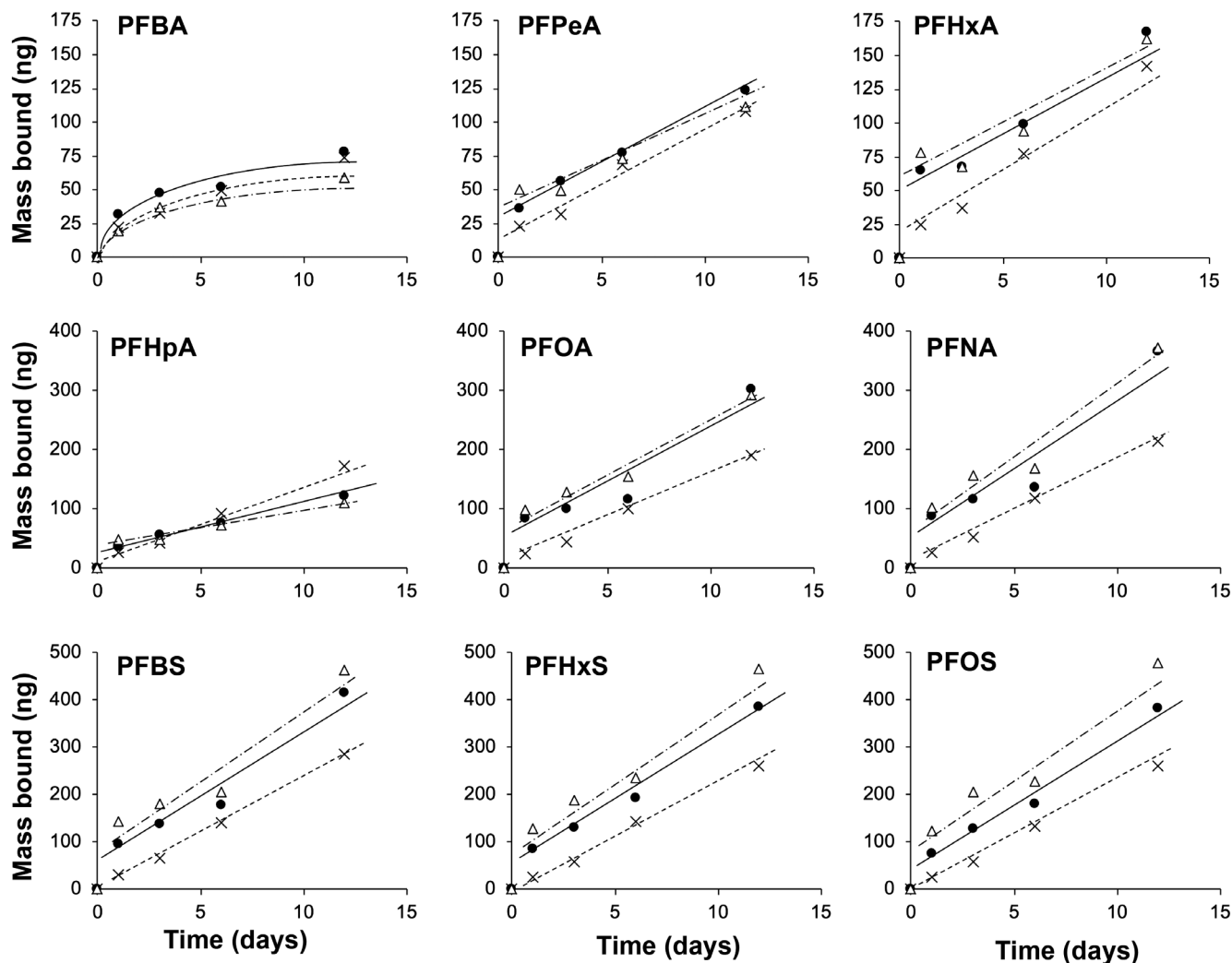


FIGURE 4 Mass accumulated as a function of time for Cu(II)-PEI-SOMS passive samplers deployed in simulated groundwater, concentration PFAS = 1 µg/L each,  $T = 25^{\circ}\text{C}$ . Flow rate 0.038 cm/min (cross, dashed line); 0.38 cm/min (circles, solid line); 1.9 cm/min (triangles, dot dash line). PEI, polyethylenimine; PFBA, perfluorobutanoic acid; SOMS, swellable organically modified silica

with municipal tap water to reduce residual total dissolved solids, and finally flushed with approximately 10 gallons of site water from Peterson Air Force Base containing a PFAS mixture. A recirculation rate of approximately 7.2 L/day was applied through the tank with a peristaltic pump. This flow rate equates to an average pore velocity range of 15–25 cm/day (based on bulk or mobile porosity estimates). Two paired passive samplers, one with Cu(II)-PEI-SOMS and one with PEI-SOMS were suspended in each of three simulated monitoring wells. The samplers were removed after approximately 1, 2, and 3 months of deployment in the recirculating aquifer tank and analyzed for PFAS. Grab water samples were collected from the tank after the first and third months of recirculation and analyzed for PFAS.

## 2.9 | Extraction efficiency measurements

Samplers were placed in 15 ml DI water containing 3.3 ng/ml of a combination of 11 surrogates and shaken for 18 h. After equilibration, the water was sampled and measured by LC-MS/MS to verify the complete adsorption of surrogates. The samplers were extracted as described above, and the amount of recovered surrogates was measured by LC-MS/MS.

## 2.10 | Analytical measurements

The concentrations of PFAS in calibration solution used in each continuous flow experiment were confirmed by

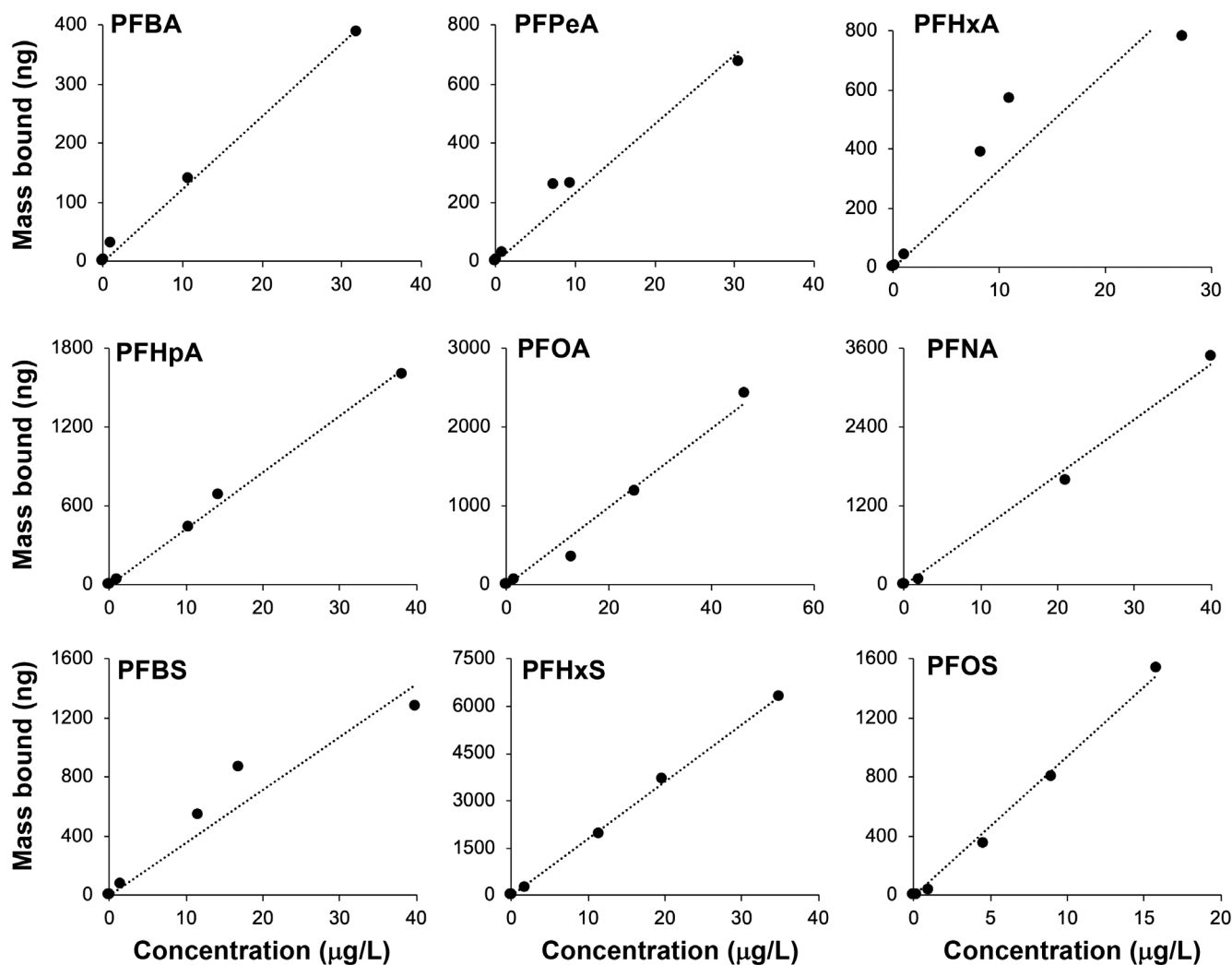


FIGURE 5 Mass accumulated as a function of concentration Cu(II)-PEI-SOMS passive samplers deployed for 3 days in simulated groundwater, all PFAS mixed, flow rate = 0.38 cm/min,  $T = 25^\circ\text{C}$ . PEI, polyethylenimine; PFBA, perfluorobutanoic acid; SOMS, swellable organically modified silica

TABLE 4 Sampling rates of Cu(II)-PEI-SOMS passive samplers at various conditions

Varied parameter	Sampling rate L/day ( $\times 10^3$ )										
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFBS	PFHxS	PFOS	HFPO-DA	FOSA
Standard condition <sup>a</sup>	2.7 ± 0.1 <sup>b</sup>	6.0 ± 0.3 <sup>b</sup>	8.0 ± 1.2	9.2 ± 0.2	11.1 ± 3.2	11.4 ± 3.5	11.9 ± 3.9	20 ± 11	11.6 ± 3.2	15 ± 10	10.6 ± 1.6
Na <sub>2</sub> SO <sub>4</sub> 250 mg/L	4.6 <sup>b</sup>	9.7	13.0	14.1	13.3	13.0	15.5	43.1	13.2	11.9	17.7
NaCl 5000 mg/L	1.7 <sup>b</sup>	5.7	9.2	12.1	13.1	14.2	3.5	34.5	14.2	6.9	16.7
Humic acid, 75 mg/L	2.2 <sup>b</sup>	3.9 <sup>b</sup>	5.7	6.7	7.2	7.6	7.3	30.9	9.5	6.1	10.4
ascorbic acid, 250 mg/L	9.8 <sup>b</sup>	14.2 <sup>b</sup>	16.8	17.1	16.9	16.4	19.2	53.7	15.9	13.5	9.4
T = 14°C	5.3 ± 0.5 <sup>b</sup>	6.4 ± 1.2 <sup>b</sup>	7.7 ± 1.3	6.3 ± 1.1	6.1 ± 1.5	5.3 ± 2.8	6.9 ± 0.2	7.1 ± 0.8	5.7 ± 2.1	4.8 ± 0.5	11 ± 9
T = 4°C	4.3 ± 0.5 <sup>b</sup>	5.3 ± 0.6 <sup>b</sup>	6.7 ± 0.1	4.6 ± 0.3	5.0 ± 0.2	5.7 ± 3.2	7.9 ± 1.2	7.5 ± 1.2	5.5 ± 0.8	5.4 ± 0.1	5.2 ± 0.8
pH = 5.5	6.0	8.9	16.0	11.5	13.3	13.4	12.1	20.8	16.4	16.1	15.1
pH = 9.5	3.4	5.9	13.0	8.8	10.0	11.0	8.3	16.9	12.8	14.9	20
Simulated well <sup>c</sup>	0.1 <sup>b</sup>	0.8	1.1	3.1	3.0	71.9	3.9	1.9	9.7	-	-
Flow rate, 0.038 cm/min	3.7 <sup>b</sup>	7.1	8.1	8.8	9.8	9.0	11.9	9.8	10.8	25.4	7.6
Flow rate, 1.9 cm/min	>5 <sup>b</sup>	5.4 <sup>b</sup>	6.1	7.8	11.1	12.4	14.8	13.7	15.7	30.5	7.0

Abbreviations: AFFF, aqueous film forming foam; PEI, polyethylenimine; PFBA, perfluorobutanoic acid; PFOA, perfluorooctanoic acid; SOMS, swellable organically modified silica. Error is standard deviation, n=2.  
<sup>a</sup>Standard simulated ground water: Ca<sup>2+</sup> = 10 mg/L; Mg<sup>2+</sup> = 1.5 mg/L Na<sup>+</sup> = 14 mg/L; HCO<sub>3</sub><sup>-</sup> = 25 mg/L; Cl<sup>-</sup> = 22 mg/L; HSO<sub>4</sub><sup>-</sup> = 10 mg/L; humic acid = 1.0 mg/L; pH = 7.2; flow rate 0.38 cm/min, T = 25 °C; PFAS = 2000 ng/L each.

<sup>b</sup>Equilibrium reached within 12 days.

<sup>c</sup>Tank with field obtained AFFF impacted groundwater; flow rate of 0.007–0.018 cm/min.



solid-phase extraction. Water samples (250 ml) were spiked with 50  $\mu\text{l}$  isotopically labeled surrogate solution (1.0  $\mu\text{g}/\text{ml}$ ). Oasis<sup>®</sup> WAX 6 cc/150 mg cartridges were conditioned with 4 ml of 0.1% ammonium in methanol, 4 ml of methanol, and finally 5 ml of nanopure water. Samples were drawn through the SPE cartridges using a vacuum manifold. After the sample was added to the cartridges, the cartridges were then rinsed with 5 ml of DI water. The elution was 4 ml of 0.1% vol/vol ammonium in methanol. Sample bottles were rinsed with 5 ml of elution solvent, which was also passed through the SPE cartridge. Eluents were then evaporated by nitrogen gas and reconstituted with 1.0 ml methanol internal standard (50 ng/ml).

PFAS concentrations were analyzed by LC-MS using an Agilent 1200/6410 HPLC-MS/MS (QqQ) using Infinity Lab C18 Poroshell 120 21  $\times$  100 mm column, particle size 2.7  $\mu\text{m}$  with a Restek PFAS delay column. Mobile phases were A: 5 mM ammonium acetate in water B: 95% methanol +5 mM ammonium acetate with a flow rate of 0.250 ml/min at a temperature of 35  $^{\circ}\text{C}$ . Injection volumes were 5  $\mu\text{l}$ . The mobile phase was ramped to 40% water from 3 to 5 min. During the period from 5 to 21 min, the mobile was ramped linearly from 40% water to 20% water, followed by a rapid ramp to 0% water at 23 min. The mobile phase was held constant at 100% methanol (95%) for an additional 2 min.

Adsorption isotherms of PFAS analytes with expected concentrations  $>2 \mu\text{g}/\text{L}$  were measured using direct injection with MRM detection utilizing both quantitative and qualitative transitions of analytes and internal standards (see Table S3 for parameters). SPE extraction was completed on at least one aliquot of every batch of PFAS simulated groundwater used for passive sampler calibrations. Mixtures of PFAS analytes were analyzed using gradient elution (for example chromatogram see Figure S1). A laboratory reagent blank and laboratory control sample were run before each set of samples and several times during each daily worklist. A laboratory control was run with each sample subset or experimental method or set of samples. The limit of quantitation was 0.65–6.5  $\mu\text{g}/\text{L}$  in direct injection mode with replicate precision  $<3\%$ .

## 3 | RESULTS AND DISCUSSION

### 3.1 | Adsorbent characterization

Initial work was conducted to measure the physical properties of the Cu(II)-PEI-SOMS and the resin's affinity for PFAS solutes. Incorporation of the PEI polymer into the pores led to a loss of dry state surface area and pore volume (Table 1). FT-IR spectra indicate the

presence of the polymer in the SOMS (Figure S2). Based on integrated peak areas of the N–H bending peak (1620  $\text{cm}^{-1}$ ) vs Si–O–Si (1150  $\text{cm}^{-1}$ ), the amount of polymer to SOMS is approximately 5%–10%. The swelling of the polymer-modified material is significantly less than unmodified SOMS, reduced to 1.1 ml/g compared with 6.0 ml/g, respectively. The spontaneous swelling due to matrix expansion is likely reduced in the PEI-modified version due to the presence of the cross-linked polymer throughout the pore structure. SOMS fully swollen with methanol has a tensile strength of approximately 0.5 MPa compared with 10–20 MPa when dry as measured by shearing the particles with a load cell. Although the loss in pore size when not fully swollen may reduce adsorbent capacity under conditions of high-concentration PFAS solutions, the improved physical stability of the modified resin is helpful for field applications. The binding affinity of PFAS by Cu(II)-PEI-SOMS was maintained as compared with other SOMS materials (Stebel et al., 2019).

The effect of Cu(II) ion addition was studied by measuring the adsorption isotherm of PFBA of PEI-SOMS in deionized water with and without bound copper ion. PFBA was selected since the short perfluoroalkyl group chain length means that an ionic interaction is the predominant binding mechanism. The incorporation of Cu(II) led to approximately five-fold increase in adsorption capacity of PFBA in the range of 1–50  $\mu\text{g}/\text{L}$  (Figure 3). The higher affinity is attributed to the increased charge density provided by the complexed Cu(II) sites. Improving the affinity for short-chain PFAS is helpful in balancing the equilibrium adsorption affinity and thus sampler uptake rates across the chain lengths, especially since long-chain PFAS generally have higher binding affinity.

Adsorption isotherms were measured for C<sub>4</sub>–C<sub>9</sub> perfluorocarboxylates and C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> perfluorosulfonates in simulated groundwater containing standard dissolved solids with a pH 7.2 (see Table S3 for solute concentration). The Freundlich parameters and adsorption isotherms are provided in Table S5, Figure S3. Adsorption isotherms for Cu(II)-PEI-SOMS showed the resin did not become saturated in the equilibrium concentrations ( $C_e$ ) of 10–1500  $\mu\text{g}/\text{L}$ , similar to previous versions of modified SOMS for PFAS. The ability to further bind PFAS as the concentration increases (i.e. large numbers of binding sites) allows the sampler to achieve a wider dynamic range and yielding an integrative response under the relatively low flow conditions examined here. Acceptable binding affinity for all PFAS solutes was observed for Cu(II)-PEI-SOMS as demonstrated by the adsorption equilibrium values ( $K_d$ , L/g) measured for  $C_0 = 250 \mu\text{g}/\text{L}$  (Table 2). Binding affinity to Cu(II)-PEI-SOMS was impacted (average 20-fold reduction)

when the matrix was switched from DI water to simulated groundwater containing dissolved ions (Table 2, notes and Table S3) and 1.0 mg/L humic acid. In contrast to Cu(II)-PEI-SOMS, Oasis<sup>®</sup> WAX showed higher affinity for PFAS in DI water, in particular long-chain PFAS such as PFOS with a  $K_d > 10,000$  L/g. Interestingly, PFAS adsorption affinity by Oasis<sup>®</sup> WAX was reduced at least 50-fold in simulated groundwater compared with DI water demonstrating a high degree of sensitivity to water chemistry. The chemistry of the Oasis<sup>®</sup> WAX is a mix-mode weak ion-exchange resin. The cation exchange capacity of Oasis<sup>®</sup> WAX is due to protonation of 1,4-diazacyclohexane amine groups (pKa's of  $\sim 6$  and  $9$ ). Cross-linked divinylbenzene and amide groups are also present. The cause of the reduced affinity of the commercial adsorbent may be due to a difference in pH between DI water and groundwater (6.5 vs 7.5, respectively) or a reduction in affinity due to increased ionic strength of the groundwater and presence of humic acid (anionic natural organic matter). It is noted that the particle size of Oasis<sup>®</sup> WAX used was 30  $\mu\text{m}$ , whereas the particle size of the SOMS adsorbent was 250  $\mu\text{m}$ . Overall, Cu(II)-PEI-SOMS showed a more consistent affinity across PFAS chain length and water chemistry with better affinity of short-chain PFAS in simulated groundwater. It is hypothesized that the combination of a hydrophobic pore, with a cationic amine polymer, and cationic metal ion can aid in binding PFAS via both hydrophobic interactions with a fluoroalkyl group and ion-ion interactions with the anionic sulfonate and carboxylate groups. Based on the desorption by methanol (see below), it is hypothesized that hydrophobic interactions may be the predominant interaction. In future work, we plan to vary the polymer structure and loading amount, in addition to the type of metal ion to determine the effect on PFAS adsorption.

### 3.2 | Passive sampler design evaluation

Samplers were unharmed after 100 consecutive repeated deployments (insertion and retrieval) in a simulated well, as evidenced by visual inspection of all welds and attachment points having no damage. Similarly, passive samplers were unharmed when placed in simulated streams with flow rates of 5 m/min. During laboratory handling, every sampler ( $n = 65$ ) remained intact during preparations, which included 24 h of active shaking, multi-hour emersion in methanol, and centrifugation up to 3000 rpm. The extent of isotopic standard adsorption was determined by sampling direct injection LC-MS of incubation solution. Adsorption of isotopic surrogates to passive samplers was observed to

come to completion after 24 h incubation even following deployment times up to 30 days in simulated groundwater. Analyte/surrogate desorption by methanol could be performed by immersing the intact sampler in 15 ml of solvent, meaning the adsorbent does not need to be removed prior to analysis. The current prototype design is robust and appears appropriate for field application.

### 3.3 | PFAS extraction recovery

High adsorption affinity for analytes is desirable to improve performance, however, strong binding can negatively impact desorption. Methanol containing 0.1% ammonia hydroxide was used to desorb PFAS directly from the Cu(II)-PEI-SOMS passive samplers. Ammonia was added to deprotonate amine groups on the PEI and helps reduce ionic interactions between the PFAS and resin. Extraction recoveries were 60%–70% across the 10 analytes (Table 3). Fluoroalkyl chain length was not a factor in the degree of recovery, suggesting unrecovered PFAS may be strongly adsorbed via ionic interaction rather than hydrophobic interactions. Surrogates were used at all times, which allow the measurements to be corrected for incomplete adsorption, so variable recovery only impacts detection limits. Sonication and use of alternative solvent mixtures will be explored in the future to promote quantitative adsorbate extraction.

### 3.4 | Passive sampler uptake rates and calibration

Three separate test regimes were used to evaluate the performance of the design: (i) accumulated mass was measured over time to determine if the response was equilibrium-based or integrative; (ii) the accumulated mass was measured as a function of PFAS concentration; and (iii) the sampling rate ( $R_s$ , L/day; ng adsorbed/day per ng/L in solution) was measured across a range of water conditions and flow rates. Experiments measuring PFAS accumulation over time and concentration were performed with standard simulated groundwater. The effect of water conditions was measured by varying one specific parameter using simulated groundwater as the solution. Adsorption as a function time shows an integrative response for all PFAS analytes except PFBA (Figure 4). Linear response was observed up to 30 days in standard simulated groundwater (Figure S4) except for PFBA and PFPeA, which showed equilibrium behavior leveling off at a constant amount of bound mass. Based on the equilibrium constants measured for

this specific prototype design, it is estimated that the sampler would have an integrative response for >55 days for all analytes except PFBA and PFPeA, which bind with the lowest adsorption capacity. A unique feature of adsorption was an observed fast initial rate during the first 24 h of exposure as demonstrated by nonzero intercepts of linear fits. Fast early-stage accumulations are attributed to a rapid adsorption step at the surface/near-surface of the Cu(II)-PEI-SOMS resin upon immersion. The integrative response is attributed to diffusion of PFAS both to the resin from the bulk water and subsequently into the pores of 250  $\mu\text{m}$  particles. The rapid initial uptake, followed by an integrative response, opens the possibility to different sampling strategies. For example, the rapid initial response may allow for “dip-and-measure” single-day sampling. The rate of accumulated mass over time was relatively consistent at the three different flow rates measured (0.038, 0.38, and 1.9 cm/min).

Linear response with respect to concentration was observed for all analytes under the conditions of all PFAS being present in combination, a flow rate of 0.38 cm/min, a matrix of simulated groundwater, and an exposure time of 3 days (Figure 5). The amount of PFAS bound during the 3-day exposure allowed for detection limits <70 ng/L for PFOA and PFOS. An interesting observation was that PFHxS exhibited the largest relative mass bound. It is hypothesized that PFHxS has the optimal combination of affinity and small enough size to diffuse into the pore matrix. The measured linear response up to 50,000 ng/L PFAS concentration indicates that the capacity for PFAS is acceptable despite the reduction in the resin's ability to swell. Inaccurate results would be achieved in a situation where one PFAS molecule would competitively displace another during the sampling period as a result of limited adsorption capacity. For instance, a longer-chain PFAS with higher affinity may displace shorter-chain analyte, leading to an underestimation of the shorter-chain analyte. Passive sampling measurements were all completed with a mixture of PFAS to assess if displacement occurs. Within the range of concentrations (up to 30  $\mu\text{g/L}$  each PFAS) and time (7 days), displacement due to competitive binding was not observed, as all response curves were linear with aqueous phase concentration. The concentrations and time are times tested are within the expectation of environmentally relevant values; however, further studies are planned in the future to determine at what loading capacity competitive binding occurs.

Adsorption of PFAS solutes by adsorbents can be affected by other water solutes. Sensitivity of sample rate,  $R_s$ , (L/day) to matrix effects and flow was measured across the set of PFAS (Table 4). The purposes of measuring sampling rate are two-fold: (i) sampling rate is the parameter used to calculate the aqueous concentration of

analyte for integrative samplers; (ii)  $R_s$  values can be compared with other passive samplers. If there are variations in the sampling rate due to matrix effects or stream flow, the dependence of such parameters could lead to challenges in relating environmental water concentration to accumulated mass. Several parameters common to groundwater and surface water monitoring were varied including temperature (4°, 14°, 25 °C), natural organic matter concentration (1.0, 75 mg/L humic acid), sulfate concentration, ionic strength (+5000 mg/L NaCl), redox potential (+250 mg/L ascorbic acid), and flow rate. Across the entire data set, there are relatively minimal variations with some exceptions. Minimal effect of sampling rate in the presence of elevated dissolved solids ( $\text{Na}_2\text{SO}_4$  and NaCl) was observed. However, elevated humic acid concentrations of 75 mg/L led to an average 30% reduction in sampling rate across all PFAS. The resin was visually discolored brown following elevated humic acid exposure suggesting that adsorption of humic acid to the outside of the particles may hinder diffusion of PFAS. The pH of the solution was varied to 5.5 and 9.5 with minimal effect on  $R_s$  values, although at pH 9.5 there was less PFAS adsorbed potentially due to less protonation of the PEI polymer. Sampling under the standard experimental conditions in simulated groundwater was repeated with a separate set of samplers constructed of a separate batch of adsorbent to test reproducibility (Table 4, line 1), reporting the standard deviation between  $R_s$  values. The results are reproducible and indicate that variations in sampling rate under different solution conditions are not significantly different or, if statistically different, the variation is relatively small.

The flow rate was varied from nearly quiescent (pore velocity estimated at 10–25 cm/day, or 0.007–0.018 cm/min) via deployment in a simulated monitoring well to 1.9 cm/min parallel across the face of the sampler in lab column flow systems. Between 0.038 and 1.9 cm/min, there is minimal change in sampling rate in column flow systems. A significant decrease in the sampling rate of shorter-chain PFAS solutes was observed in the simulated aquifer monitoring well. For example, the sampling rate of PFPeA was reduced seven-fold, whereas the rate of PFOS was dropped by less than 50%. It is noted that differences in sampling rate are only evident for certain PFAS and will need to be accounted for in calibrations. Overall, the samplers were relatively insensitive to changes in water chemistry and flow rate, supporting the hypothesis that direct exposure of resins reduces the number of variables in the kinetics of adsorption.

Sampling rates for the Cu(II)-PEI-SOMS passive samplers are equivalent to POCIS-type samplers despite the SOMS-based samplers being significantly smaller in size (sampling area: 11–17  $\text{cm}^2$  for POCIS vs 1.1  $\text{cm}^2$  for

samplers tested herein). Golelius (2019) reported  $R_s$  values 0.007–0.1 L/day for POCIS-WAX samplers (membrane surface area 45.8 cm<sup>2</sup>) under approximately equivalent concentrations (500 ng/L) used herein and flow rates of 20 cm/s. Similar  $R_s$  values (0.1–0.2 L/day) were reported for POCIS by Kaserzon (2013) using Strata™ XAW resin, (17 cm<sup>2</sup> surface area, 100 cm/s flow rate). Diffusive gradient thin film devices have  $R_s$  values of 0.007–0.020 L/day using a surface area of 3.1 cm<sup>2</sup> (Wang et al., 2021) in stirred solutions. Cu(II)-PEI-SOMS passive samplers have rates that are at 2–10x faster normalized to sampling surface area under slower flow rate regimes. The faster analyte uptake of the SOMS-based sampler is likely due to the direct contact of resin particles with the aqueous solution. Thus, the design reported here is hypothesized to be better suited to sampling short-duration events such as stormwater measurements.

## 4 | CONCLUSIONS

A passive sampler where PFAS-specific adsorbent is in direct contact with an aqueous solution was successfully built and tested. Cu(II)-PEI-SOMS adsorbent was tailored to maximize both hydrophobic and ion-exchange interactions, the latter promoted by the addition of divalent copper ions. It is possible that the amounts of PEI and Cu<sup>2+</sup> can be further optimized to create even higher affinity sorbents. Passive sampler uptake rates were relatively fast and constant even under the condition of extreme ionic strength and NOM concentrations, indicating potential applicability to a wide range of environmental water types. Integrative performance for most analytes showed a linear response to concentration with time (except for PFBA and PFPeA), which simplifies the calculation of aqueous concentrations. Sampling times as short as 3 days were necessary to reach limits-of-detection <70 ng/L for PFOA and PFOS. The Cu(II)-PEI-SOMS based passive sampler will be studied in future work to measure performance in field-based testing and accuracy to measure PFAS in various environmental waters.

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## CONFLICT OF INTEREST

The process to prepare the organosilica materials described within have been patented by The College of Wooster and

licensed to ABS Materials, Inc. A patent application for the process design of the passive sampler has been jointly submitted by The College of Wooster and Arcadis. The employers of the corresponding authors have a financial interest in the commercialization of the patents.

## AUTHOR CONTRIBUTIONS

**Heather A Hartmann:** Investigation. **Claire E Hefner:** Investigation. **Erika Carter:** Data curation; supervision; investigation; project administration; writing-review & editing. **David Liles:** Data curation; investigation; project administration; writing-review & editing. **Craig Divine:** Funding acquisition; project administration; writing-review & editing. **Paul L Edmiston:** Conceptualization; formal analysis; funding acquisition; investigation; methodology; writing - original draft; project administration; writing-review & editing.

## DATA AVAILABILITY STATEMENT

Data available on request from the authors

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