Laboratory Validation of an Integrative Passive Sampler for Per- and Polyfluoroalkyl Substances in Water

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Perfluoroalkyl substances (PFAS) are an emerging class of environmental contaminants. This research involves the design and characterization of a passive sampler to measure PFAS in natural waters. Passive samplers have utility in measuring difficult to access areas or waters that have variable concentrations with time.

Laboratory Validation of an Integrative Passive Sampler for Per- and Polyfluoroalkyl Substances in Water

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Abstract

A passive sampler for per- and polyfluoroalkyl substances (PFAS) in water has been developed which uses a porous organosilica adsorbent. Some performance characteristics, which remained incompletely answered after prior lab-and field-based testing, were assessed. The integrated response mode of the sampler was verified in bench-scale experiments where the aqueous phase concentration was varied 50-fold in the flow across the passive samplers. It was found that passive samplers were able to accumulate analytes and provide an accurate time-averaged concentration in situations where the PFAS concentration changed significantly over time. The integrated response is facilitated by an average 40-fold slower back diffusion rate compared to PFAS adsorption rates, attributed to in-particle diffusion. Maximum deployment time was assessed using a multi-month laboratory-based sampling event. It was found that the integrated response was maintained over 90 days except for perfluorobutanoic acid (PFBA) and perfluorodecanoic acid PFDA where adsorption reached equilibrium after 45 and 60 days of total sampling time, respectively. The mechanism of PFAS adsorption was explored using a column breakthrough curve in combination with previously reported adsorption isotherm data. The use of isotopic dilution for PFAS measurement was studied by measuring the adsorption, recovery, and stability of mass labeled surrogates in laboratory analysis. Surrogates were quantitatively bound and determined to be stable for at least 4-weeks in the adsorbed state. Sampling rates for EPA Method 1633 compounds *N*-methyl perfluorooctanesulfonamidoacetic acid and *N*-methyl

perfluorooctanesulfonamide were also measured, expanding the existing sampling rate database to a total of 21 PFAS species.

Introduction

Measurement of per- and polyfluoroalkyl substances (PFAS) in the hydrosphere is becoming widely performed for the purpose of environmental monitoring. Passive samplers are an alternative to discrete sampling and offer advantages of convenience and the ability to measure time-averaged concentrations. Several PFAS passive samplers have been reported[1–8] providing the monitoring community new tools for PFAS measurements. Previously, we reported the development and field evaluation of an integrative PFAS passive sampler using an organosilica-based adsorbent specifically designed to bind PFAS from water[9]. The sampler design and characteristics have been previously described [9]and field evaluations conducted to determine performance under a variety of conditions[10]. Here, we report accompanying laboratory studies required to validate integrated passive sampling performance, establish practical guidelines for use, and understand adsorption mechanisms. Specifically, the integrative response was tested by conducting controlled experiments where PFAS was varied. Validating integrative response important for the field of passive sampling by providing methodology and evidence that devices do deliver an time-averaged concentration.

The passive sampler discussed herein is comprised of a high-density polyethylene housing with PFAS adsorbent resin held in place by open mesh polypropylene screens[9]. The adsorbent is swellable organically modified silica (SOMS)[11] encapsulating polyethylenimine (PEI, Figure 1), an amine containing weak ion exchange polymer. In addition, the Cu(II) ions are complexed by the PEI amine groups to increase the valency and density of cationic sites in the resin. SOMS is a hydrophobic porous matrix prepared by the polycondensation of bis(trimethoxysilylethyl)benzene (Figure 1). The SOMS matrix can be reversibly swollen 3x in geometric volume by the absorption of organic solvents[12]. PEI is added to the swollen SOMS pore network and crosslinked within to ensure irreversible encapsulation. Amine groups on the PEI spontaneously complex Cu(II) ions leading to the final adsorbent termed Cu(II)-PEI-SOMS. PFAS adsorption is facilitated by interactions with the hydrophobic matrix, weak ion exchange sites of the PEI, and ionic interactions with immobilized Cu(II) ions. SOMS is commercially available as Osorb® and the completed passive sampler is available as the Sentinel™ passive sampler.

Passive samplers can be based on either an integrative (kinetic) or equilibrium (thermodynamic) mode[13] of sampling (Figure 2). Integrative-based sampling[14] is performed in regime where analyte adsorption is occurring prior to equilibrium and has the advantage of providing a time-weighted average concentration if adsorption is pseudo-irreversible. Maintaining analyte adsorption in the kinetic regime is accomplished by limiting the diffusion rate by a membrane or other type of physical barrier and/or using an adsorbent with a high adsorption capacity[15]. The aqueous phase concentration, C_w, using an integrative passive sampler is calculated using a measured rate constant termed a sampling rate, R_s, (L/d) for a particular analyte via:

$$C_w = \frac{ng\ accumulated}{R_s(\frac{L}{d}) \times\ time\ (days)} \tag{1}$$

with the resulting concentration units being ng/L. Knowing the sampling rates for analytes at the deployment conditions is an important requirement for integrative passive sampling requiring laboratory measurements in addition to field-based studies. Sampling rates for the Sentinel sampler have been measured previously and are in the general range of 0.02 L/d.

Equilibrium-based passive sampling[16] functions by having deployment lengths long enough that analyte partitioning reaches a maximum based on equilibrium with the water column. Equilibrium devices can be more easily calibrated to calculate C_w from the mass adsorbed by measuring the equilibrium partition constants for the adsorbent. Equilibrium samplers can be deployed for long periods of time to ensure equilibrium is reached, thus maximizing adsorption, improving detection limits, and reducing corrections for site-specific changes in adsorption kinetics. Despite the potential advantages of equilibrium sampling including ease calibration and better sensitivity, such devices cannot provide a time-weighted average concentration.

Testing of Cu(II)-PEI-SOMS passive samplers in initial development work demonstrated efficacy to adsorb both short-chain and long-chain PFAS compounds. Devices using Cu(II)-PEI-SOMS were found to be integrative over periods of >12 days in initial testing, however, upper limits of integrative performance were not determined. Sentinel™ passive samplers were subsequently evaluated in field tests in both groundwater and surface water contexts[10]. Deployment times ranged from 3-30 days. Results of field evaluations corresponded to an integrative response and showed strong correlation with co-collected grab samples. Several important questions arose during the previous prototype development, laboratory validation, and field evaluation phases. First, further evidence was needed to confirm whether the integrative passive samplers provided a time-averaged concentration that would accurately measure systems where the concentration vs. time profile was highly variable, which is difficult to reliably do in the field. Specifically, reversibility of adsorption needed to be understood and how adsorption/desorption kinetics would affect the calculated aqueous phase PFAS time-averaged concentration C_w. Responses to variable concentration can be more precisely controlled in bench-scale studies. Second, the maximum deployment time needed to be established. Longer deployment times allow for more comprehensive measurements and lower limits of detection since mass continues to accumulate in the integrative mode. However, the saturation of the adsorbent would cause the device to reach equilibrium with PFAS in the water and thus the integrative response to be lost leading to systematic errors when calculating C_w. Saturation would lead to a systematic error since calculations are based on an integrative response model[14] using pre-established sampling rates. Thirdly, adsorption rate during long deployments (>60 days) in groundwater needed to be investigated to understand potential effect such as blinding due by biofilm growth or the presence of naturally occurring dissolved salts. Finally, lab analysis methodologies using isotopic dilution were assessed.

Materials and Methods

Materials. The list of PFAS analytes and isotopically labeled surrogates are provided in supplemental information (Table S1) along with the abbreviations.. HPLC-MS grade methanol was obtained from J.T.Baker. Osorb® (SOMS) was obtained from Aquanex Technologies. All other reagents were obtained from Sigma-Aldrich. Avantor^{TM} polyethylene centrifuge tubes (50 mL) were obtained from VWR.

Adsorbent synthesis. Preparation of the Cu(II)-PEI-SOMS was done as described previously[9]. Briefly, 1 g of SOMS was swollen with 5.5 mL methanol, placed in 5.0 mL a 10% wt/vol solution of PEI. After being shaken for 24 h, the resulting material was rinsed with deionized (DI) water and dried at 25˚C. A solution of 0.5% vol/vol 1,6-diisocyanatohexane in acetone was applied to the SOMS-PEI until fully wet. The slurry heated to 60˚C for 5 min in water bath, and allowed to react at room temperature for 18 h to crosslink amine groups. The resulting material was rinsed sequentially with water, 10 mL of 20 mg/mL $CuCl_{2\ in}$ DI water, and water. After completion of the synthesis Cu(II)-PEI-SOMS was Soxhlet extracted with methanol for 2 hr to remove any non-crosslinked polymer or other residues, rinsed with DI water, and stored in 40% glycerol solution.

Copper adsorption capacity. The amount of Cu(II) bound to PEI-modified SOMS was measured by a solution depletion experiment. Following the crossing-linking step, 10 mL of 20 mg/mL of $CuCl_2$ solution was added to 2.5 of PEI-SOMS and equilibrated for 0.5 hr. Samples of the Cu(II) solution were taken prior to mixing and after adsorption and measured by atomic absorbance spectrometry using a Thermo SOLAAR M-Series instrument. The amount of Cu(II) bound to the resin was determined by difference.

Column breakthrough experiment. A 2.0 g amount of Cu(II)-PEI-SOMS was added to 16 mm Pharmacia column. The resin was rinsed for 30 min with DI water to remove residual glycerol storage solution. A mixture of 12 PFAS compounds with a total concentration of 5,000 μg/L (see supplemental Table S2 for individual concentrations) was passed through the bed at a flow rate of 0.5 bed volumes/min. Aliquots (250 μL) were collected at intervals and mixed with 750 μL of methanol containing internal standards. PFAS concentrations were measured using high performance liquid chromatography tandem mass spectrometry HPLC-MS/MS.

Passive sampler construction. The PFAS passive sampler design been described previously [9] and is summarized. The device is constructed of polyethylene (2.5 cm wide by 4.5 cm long by 0.2 mm thick) containing 100 mg swellable Cu(II)-PEI-SOMS (180-250 µm particle size). The adsorbent is housed in direct contact with the water inside a 1 cm through-hole held in place by polyethylene mesh screens on opposite sides (Figure 3). The Cu(II)-PEI-SOMS is pre-wetted with 40% glycerol during sampler construction which precludes the need for preconditioning. Two ¼” threaded mounting points allow for modes of attachment.

Laboratory passive sampler measurements. Passive samplers (n=3) were rinsed in DI water and placed in series within a 26-mm diameter Pharmacia XK glass column attached to a Pharmacia P-500 pump. Polyethylene tubing and containers were used for all fluid handling. A solution containing 11 PFASs (2.5 µg/L each) in simulated groundwater was prepared (see supplementary information and Table S3 for water solute composition). The PFAS solution was passed through the column at a linear flow rate 0.38 cm/min, and at a temperature of 25˚C. At 25, 60, and 90-day intervals one of passive samplers was removed starting with the sampler furthest downstream of the flow. After removal from the water stream, the sampler was placed in 15.0 mL of DI water containing 3.30 ng/mL of each 11 PFAS surrogates and equilibrated for 7 hr. Analytes were extracted with 20 mL of methanol with 1% ammonium hydroxide as described previous and used similarly for soil[9,17]. Extracts were dried under nitrogen, reconstituted in 1.0 mL of methanol containing internal standards (M8PFOA, M8PFOA, and d3-MeFOSA), and analyzed by HPLC-MS/MS. The mass of PFAS adsorbed by the sampler was determined by isotopic dilution.

For variable concentration experiments the concentration of PFAS was varied over time by mixing two streams of high (10,000 ng/L each) and low (200 ng/L each) solutions prepared in simulated groundwater. A separate pump and tubing system were used for each solution which was combined prior the columns holding passive samplers. An in-line mixer was used at the confluence of each solution to ensure mixing prior to reaching the sampling chamber. A Pharmacia LCC-501 flow controller was used to create the desired concentration profile. Two flow experiments were performed where PFAS concentration was varied with time. The first was a steady stream of 200 ng/L concentration PFAS interrupted by a 24 hr pulse where the concentration was raised to 10,000 ng/L. After the pulse of high concertation, the levels were returned to the lower 200 ng/L amount and maintained for 163 hr. A passive sampler was placed in the stream for the duration to test if back diffusion led to the loss of PFAS adsorbed during the high concentration time-period. Samplers were also deployed: 1) at the beginning and removed immediately after the high concentration event; and 2) after the high concentration pulse for sampling during the post-pulse time-period. A second column flow experiment used a multi-pulse variable PFAS concentration profile. In both experiments, the theoretical mass accumulation was modeled using the previously determined sampling rates (R_s).Effluent samples were collected at intervals and measured using EPA Method 537.1 to monitor the concentration profile.

Measurement of sampling rates (R_s) of previously untested analytes was done by placing 3 samplers in a 0.38 cm/min flowing stream of simulated groundwater containing 25 μg/L PFNA, 50 μg/L N-MeFOSA, 21 μg/L N-MeFOSAA , and 1.0 mg/L humic acid at 25°C. Samplers were removed at 2, 7, and 14 days and measured as described above by adsorption of surrogates, methanol desorption, and analysis by HPLC-MS/MS.

Surrogate adsorption and recovery testing. Samplers were placed in 15.0 mL of DI water contain 50 ng each of isotopically labeled mass surrogates. The uptake of surrogates was measured by removing 250 μL aliquots, combining them with 750 μL of methanol containing 50 ng/mL internal standards, and measurement by HPLC-MS/MS. Recovery was measured by equilibrating passive sampler with a 3.3 ng/mL solution of isotopically labeled surrogates measuring uptake by direct injection by HPLC-MS/MS. A control experiment was performed by measuring surrogate concentration in the absence of a sampler. After removing the samplers from the surrogate solution and removing residual water by centrifugation at 1,500 rpm, the samplers were then extracted with 20 mL of methanol containing 1% v/v ammonium hydroxide. The solutions were dried under nitrogen and reconstituted in 1.0 mL of methanol. The amount of mass labeled surrogates recovered was determined by HPLC-MS/MS via comparison to a calibration curve (see supplemental information Table S5).

Analytical measurements. Measurement of PFAS concentrations was performed using an Agilent 1200/6410 HPLC-MS/MS via multiple reaction monitoring as described previously[18].

Calibration curves, method blanks, and laboratory validation standards were run with each workflow. Peak areas of internal standards fell with 10% of expectation. The MRM transitions are provided in supplemental information Table S4. HPLC parameters and limits of detection are provided in supplemental information Tables S6 and S7, respectively. Analyte concentrations were determined by isotopic dilution using co-adsorbed surrogates matched to each analyte (Table S1).

Results and Discussion

Adsorption Capacity of Cu(II)-PEI-SOMS receiving phase. Integrative passive samplers require that a receiving phase possess sufficiently high adsorption capacity to maintain analyte accumulation in a kinetic regime during the sampling interval so as not come to equilibrium. Cu(II)-PEI-SOMS (surface area 260 m^2/g; pore volume 0.28 mL/g) was previously evaluated using adsorption isotherms[9]. Adsorption isotherms for both C4-C9 perfluorocarboxylates and C4-C8 perfluorosulfonates measured in simulated groundwater were all linear and did not approach saturation even at maximal equilibrium concentrations of 300-1500 g/L. However, it was difficult to estimate the capacity of the adsorbent through equilibrium adsorption. Column experiments were used to measure the breakthrough capacity of Cu(II)-PEI-SOMS for a mixture of 11 PFAS compounds (Figure 4) with a total concentration of 5,000 μg/L in deionized water (~500 μg/L each). Breakthrough of shorter-chain perfluorocarboxylates (ex. PFBA, capacity 3.3 mg/g) occurred first compared to longer-chain compounds (ex PFOS, capacity 6.6 mg/g). Breakthrough of short chain PFAS has also been observed for activated carbon and ion exchange resins[19–22]. It is hypothesized that the hydrophobic fluoroalkyl chain provides additional synergistic modes of adsorption beyond an ionic interaction, increasing total capacity[23,24]. Hydrophobic aromatic residues from the SOMS likely aid in the adsorption of hydrophobic long-chain PFAS[18]. Often competitive displacement of short-chain adsorbates on ion exchange resins[25,26] occurs as longer-chain PFAS continue to bind leading to C/C_0 (i.e. concentration effluent / concentration influent) values greater than 1[21]. Competitive displacement has also been observed with other SOMS-based adsorbents[18]. Such competitive adsorption dynamics would lead to systematic errors in passive sampling when mixtures of short and long-chain compounds are present. However, Cu(II)-PEI-SOMS shows minimal displacement of PFBA and PFPeA occur after reaching breakthrough (Figure 4). Retention of short chain compounds is hypothesized to be due to the divalent Cu(II) ions leading to stronger electrostatic interactions compared to mono-valent ion exchange resins. Interestingly, improved binding of short-chain PFAS is reestablished after initial breakthrough. Improvement of short chain adsorption may be due to accumulation of PFAS adsorbed to surfaces which leads to synergistic adsorbate-adsorbate interactions.

The amount of Cu(II) ions in the resin was measured using the depletion method. It was found that 0.17 mmol/g of Cu(II) was bound in Cu(II)-PEI-SOMS. The amount of copper ions was compared to the amount of PFAS bound. In comparison, at the discontinuation of the column breakthrough experiment 0.22 mmol/g of PFAS compounds were bound. It is noted that long-chain compounds such as PFDA had not reached breakthrough so full capacity had not been achieved. Regardless, based on the ratio of PFAS bound to Cu(II) there was an excess of bound PFAS compared to number Cu(II) ions on the resin (0.22 vs. 0.17 mmol/g). The extended capacity was to limited to the retention longer chain compounds beyond stochiometric equivalency with Cu(II) and suggests that other adsorption mechanisms, such as hydrophobic interactions, are occurring. Shorter chain compounds such as PFBA and PFPeA are likely adsorbed primarily through ionic interactions and their breakthrough near stoichiometric equivalency to Cu(II) supports this hypothesis. Overall, there is reasonable capacity for PFAS adsorption for passive sampling applications, however, adsorption capacity for shorter chain compounds based on ion exchange capacity was found to be the limiting factor for extended deployment times.

Upper limits on deployment time were evaluated using laboratory-based passive samplers in flowing water conducted over a duration of 90-days. Longer sampling times can improve detection limits through the accumulation of analyte, but if capacity is ultimately reached, then the sampler would cease acting as an integrative device. The 90-day exposure test was completed with a mixture of 11 PFAS compounds at 2.5 μg/L each in simulated groundwater (Figure 5, supplemental information Figure S1). Samplers were removed at 25, 60 and 90 days. Only PFBA and PFDA deviated from integrative response over the 90-day period as evidenced by the approach to full capacity (pseudo-equilibrium) after an estimated 45 days. All the other 9 PFAS did not reach capacity and thus maintained a steady rate of accumulation. Interestingly, PFHxS and PFOS showed an increase in sampling rate at times >60 days. The increased uptake rate may be due to adsorption of these compounds to previously bound PFAS in the pores of the resin. Adsorbate-adsorbate interactions between PFOS at surfaces has been detected both by electrochemical measurements[27] and adsorption isotherms.[28] . In contrast, PFBA adsorption may be due mote exclusively to ion exchange interactions with the resin and thus is limited by number of accessible Cu(II) sites. PFDA adsorption rates at long time scales may be reduced by diffusional barriers since the stronger hydrophobic interactions likely aid in uptake but also limit mobility to reach interior pores[29,30]. Regardless of some potential mechanistic constraints, the capacity of Cu(II)-PEI-SOMS allows deployment times longer than 30-45 days if integrative measurement of PFBA is not a requirement. During deployments time >45 days PFBA should be assumed to come to maximum capacity. Since adsorption isotherms are linear it is hypothesized that the capacity scales directly with concentration meaning that if lower concentrations of PFAS are found the water being monitored it will not extend the time to equilibrium. Sampling rates (determined from the slopes of the curves) matched those determined previously indicating consistency of the design (see supplemental information Table S8).

Surrogate adsorption and recovery. Standard methods to measure PFAS in water use solid phase extraction coupled with the use of surrogates for isotopic dilution measurements. Co-measurement of surrogates via HPLC-MS/MS allows for improved accuracy in analyte concentration determination when recoveries are variable. The analysis method of the Sentinel sampler uses a similar isotopic dilution method. When the samplers are returned to the lab the devices which fit in 50 mL centrifuge tubes are soaked in a DI water solution containing an appropriate amount of isotopically labeled surrogates. The time needed to quantitative adsorb the surrogates was measured and found optimally to be 5-10 hr (see supplemental information Figure S2). After 18 hr, surrogates back-diffuse slightly potentially along with PFAS analytes, thus longer duration surrogate adsorption times (i.e. >8 hr)is not advisable.

The fraction of surrogate was measured after a 7 hr equilibration time using direct injection HPLC-MS/MS. Near quantitative adsorption of the surrogates (91-99% uptake) were observed for 19 different PFAS types (Table 1). Following adsorption of the surrogates the passive samplers were extracted with methanol containing 1% ammonium hydroxide and the recovery of the bound surrogates was measured using the mass balance (Table 1). Good recovery of C4-C8 perfluorocarboxylates and perfluorosulfonates (87-103% recovery) was observed. Reduced levels of recovery were obtained for long-chain perfluorocarboxylates, the neutral PFOSA, *N*-MeFOSA, *N*-EtFOSA, *N*-MeFOSE, and *N*-EtFOSE which were in the 10-25% range. The long chain C-14 perfluorotetradecanoic acid (PFTeDA) showed only a 10% recovery. A control experiment was used to assess if the poor recovery of certain compounds was due to loss of surrogate due to adsorption to the walls of the centrifuge tube. No reduction of PFAS surrogates was observed over 8 hr. After 24 hr there was a 5-15% drop in PFTeDA, PFOSA, and PFOS. Based on the data it appears the more hydrophobic long-chain compounds are strongly adsorbed and difficult to extract with methanol. Data also suggest that prolonged surrogate exposure should be avoided to prevent losses to competitive adsorption to labware. Other solvent systems or use of sonication may be more effective in desorption which can be explored in future work. It would be useful to understand if the reduced recovery of neutral PFAS is due to poor solubility in methanol, increased adsorption affinity, or a combination of both effects. Incomplete recovery highlights the utility of isotopic dilution measurements in passive sampler methods similar standard methods for discrete samples.

PFAS stability during storage. After samplers are returned to a laboratory from field deployment there may be a time interval where the devices are stored prior to measurement[31–33]. During the storage time the passive samplers should remain sealed to prevent them from fully drying out. Since the PFAS is adsorbed to the resin, it was hypothesized that analytes should be stabilized against degradation. The stability was examined by binding 19 mass labeled PFAS compounds and measuring uptake by the passive sampler by direct injection of the depleted water. Samplers were stored at 4˚C and processed at 1-week intervals. The change in recovered PFAS mass was monitored as ΔPFAS recovered vs time (Table 1). Most PFAS compounds (17/19) had less than a 5% difference in recovery over the 4-week span. Of the two with larger variations, PFBA showed a 19% increase in recovery over 4 weeks and 8:2-FTS had a slope of -8.2% per week over time. However, measured stability (slope of recovery vs. time) for both compounds were influence by single data points that were outside of a linear trend (supplemental information Figure S3) and it is estimated that both are stable after adsorption. Overall, the data indicate that the samplers can be stored for at least 4 weeks at 4˚C prior to analysis.

Response to variable concentrations. One of the advantages of passive sampling over discrete grab sampling is the ability to measure a time-averaged concentration[34,35]. There are two requirements in the use of passive samplers where concentrations vary quickly and significantly: *i*) a rapid enough analyte adsorption rate is needed to bind PFAS during pulsed changes in concentration; and *ii*) the ability to retain analytes in a low concentration regime is needed after cessation of a high concentration pulse. Previous measurements have shown that the Rs values for Cu(II)-PEI-SOMS do not vary with PFAS concentration.[9] laboratory system was used to generate flow with a controlled and variable concentration of PFAS over time[36].

Two separate flow experiments were performed where PFAS concentration varied (Figure 6). The first concentration profile to be considered is the system with a single 24 hr pulsed change in concentration (Figure 6A). The experiment was used to determine the degree back diffusion. Measurement of the accumulated mass after the deployment was compared to the theoretical mass that would be accumulated (Table 1). The sampler that was deployed for the duration (Figure 6A) had a final accumulated mass only slightly less compared to theoretical (16%, laveragel) and -2% on average). The high retention is notable since this sampler was maintained in the stream 163 hr after the high concentration pulse. A higher difference in expected vs measured concentration was noted for PFOSA and HFPO-DA. It is noted that spiked aqueous phase concentrations of these compounds were much lower (due to lower availability of these compounds). Also, PFBA and PFPeA had larger deviations which may be due the lower affinity of these compounds to the adsorbent.

The other two samplers which were present during the duration and after the concentration spike (Figure 6B&C) had accumulated masses that matched predicted amounts based on established R_s values (Table 2). The second column flow experiment used a multi-pulse variable PFAS concentration profile (Figure 6D) which also indicated integrative response (Table 1) as predicted integrated PFAS amounts matched those measured. Based the difference between actual final mass vs. predicted mass the R_s(off) rate (e.g. back diffusion sampling rate) for each PFAS was estimated (supplemental Table S9) assuming a linear desorption rate (i.e. $R_{s,\text{off}} = (\text{ng}_{\text{measured}} - \text{ng}_{\text{predicted}})/\text{time}$). Interesting, the back diffusion rates were found to be on average 40-fold slower than the adsorption rate. Mechanisms that explain the difference between on/off rates are discussed below. The data also suggest that adsorption rate is fast enough to sample a pulse change in concentration 24 hr duration and yield an accurate time-averaged concentration. The data can be used to guide field use. As long as deployment times are less than 10 days following a high concentration event the high mass accumulation from a high concentration event should be retained in the sampler to extended that an accuracy of+/-30%. A recommendation is that in flashly systems total deployment times should not exceed 10-14 days to ensure that back diffusion does not eliminate accumulation of an early high concentration signal.

An outlier of the variable concentration experiment is the observation that PFBA and PFPeA consistently exhibited a higher concentration as measured by the passive sampler compared to the effluent as measured by standard methods. One explanation is that the R_s need to be better refined for shorter-duration measurements. Also, there may have been some loss of these compounds prior to elution from the passive sampling column which was the location where water samples were obtained for independent measurement of the aqueous phase concentration.

One of the features of the sentinel passive sampler design is that the Cu(II)-PEI-SOMS receiving phase particles are in direct contact with the water (i.e. not using a membrane to separate the adsorbent from the water). An open polyethylene mesh holds the 180-250 μm particles in a through-hole allowing water to pass directly across and through the bed. The design has some advantages. After deployment PFAS can be extracted from the sampler without the need for disassembly, speeding up lab workflows post-deployment. In addition, the direct contact approach eliminates intentional diffusional barriers to adsorption such as a membrane potentially allowing sampling of short duration spikes in concentration. In order to test the response rate to short duration pulses in concentration and gradual changes in concentration, a more complicated PFAS profile was generated using the laboratory flow system (Figure 6D). Two duplicate passive samplers were deployed for the duration of the time period/profile. The mass accumulated in the passive samplers closely match the predicted mass. All measured PFAS concentration by passive sampling match the predicted concentration within ±25%. Similar to the first variable concentration experiment PFBA exhibited the larger difference (-19%); also, PFHpA exhibited a larger difference (-23%) . Overall, the data obtained here indicate that the passive sampler design acts in a truly integrative made allowing application to water streams with variable PFAS concentration profiles.

Features of the Sentinel passive sampler allow broad use of the sampler possible. For example, the ability to accurately sample changing systems suggests the passive sampler would be useful for stormwater and variable surface water monitoring. Since the sampler is pre-wetted makes it logistically useful for deployment ahead of a storm event. Initial ad hoc experiments have shown that the samplers can be placed in a stormwater infrastructure while dry and accumulated PFAS when flow arises. Some of the technical difficulties in such a flashy system include determining the flow rate and duration. Performance reference compounds may be useful in future work to help calibrate total flow exposure in flashy systems.

Sampling rates for N-MeFOSA and N-MeFOSAA. Sampling rates are determined by using eq (1) measuring accumulated mass over time for a known C_w. Additional PFAS analytes are being added to analysis methods such as EPA Method 1633[37]. Sampling rates (R_s) for N-MeFOSA and N-MeFOSAA were measured in 14-day continuous flow experiments using simulated groundwater containing 1.0 mg/L humic acid at 25˚C. PFNA uptake was measured in tandem with these analytes to serve as internal reference point to ensure there was no variability sampler-sampler. The measured R_s value for N-MeFOSA was 0.0125+/- 0.009 L/day which is nearly identical that previously measured for PFNA, PFOA, and PFOS. In contrast, the R_s value for N-MeFOSAA was lower: 0.0063+/-0.008 L/day (see supplemental information Figure S4 for accumulation plots). N-MeFOSAA differs from other PFAS analytes by having a sulfonamide acetate group that is separated from the induction of fluoroalkyl chain and has a p*K*a of 3.92[38]. The weakly acid carboxylic acid group of N-MeFOSAA is unique to PFASs measured to date and may indicate that a different mode of interaction with the resin. These data highlight the need to measure R_s values for analytes for each analyte which is planned for all Method 1633 analytes as standards become available. The current list of R_s values for 21 PFASs measured to date is provided in supplemental information Table S10.

Water samples are taken at intervals during the time-course of passive sampler exposure and measured using direct injection LC-MS and quantified using external standards. Observations made during the accumulation experiments are reported to benefit other practitioners. A significant decline in the concentration of N-MeFOSA and N-MeFOSAA over time in the water reservoir was observed (supplemental information Figure S5). It is hypothesized that the compounds were partitioning to the sides of the container or the air-water interface. In particular, N-MeFOSA will be found in a neutral form, as it possesses which has no ionizable functional group had a 95% decrease in concentration over the 14-day period. N-MeFOSAA which has a weakly acidic functional group showed a 40% decline in concentration during the same period. Similarly, loss of these analytes has been reported in laboratory sample stability studies[32,33]. In contrast, PFNA showed no appreciable change in concentration which has also be found to be true for other perfluorinated PFAS compounds measured in this work.

These data indicated careful monitoring of solutes is needed when conducting long-term calibrations, especially for emerging PFAS compounds.

Adsorption mechanisms. Extended capacity of an adsorbent placed in direct contact a water stream that requires >90 days to reach equilibrium is not an intuitive result. Understanding the mechanism of adsorption is important for the application of passive sampling and PFAS removal, in general. Compared to other commercial adsorbents such as Oasis WAX which is made of fine 30 um particles, Cu(II)-PEI-SOMS is has much larger 250-300 μm particle size. The first step of the adsorption process is hypothesized to be binding of PFAS to surface sites in an adsorbent. Adsorption to surface sites is relatively rapid. The rapid adsorption process for Cu(II)-PEI-SOMS is manifest in the kinetic plots where there is a step-wise mass accumulation of PFAS at the beginning of the deployment which appears as a non-zero intercept in the plot of mass vs. time at 3-10 sampling times[9]. After adsorption to the surface or near surface sites, a PFAS analyte is hypothesized to be able diffuse the particle interior. SOMS is a continuously porous material[39] that is "filled" with PEI polymer (~20% w/w). Previous results have shown that small molecules can freely diffuse across >5 mm distances within SOMS with diffusion coefficients of 3×10^{-8} cm^2/s[40]. It is hypothesized that after PFAS is initially adsorbed to surface sites of Cu(II)-PEI-SOMS molecules then undergo intraparticle diffusion. Diffusion into the interior of the particle would thus be competition for back diffusion into the water, thus explaining the retention of PFAS after a high concentration sampling event. Since the resin interior has high surface area and pore volume (0.28 mL/g) there is sufficient interior pore space to accommodate PFAS (and other adsorbates) via accumulation. Overall, the interior pore capacity for PFAS coupled with a slow intraparticle diffusion rate may explain why equilibration times are long and uptake is consistently steady and well-suited for integrative passive sampling. Future work could study the intraparticle diffusion coefficients of PFAS.

High adsorption capacity may be further explained PFAS aggregation in the pores[41]. Aggregates may be accommodated by the swelling of SOMS. PFAS has previously been shown to macroaggregate in ion exchange resins presumably driven by the intermolecular affinity of fluoroalkyl groups[42–44]. Aggregation would be more prominent in long-chain PFAS compounds (e.g., more $-CF_2-$ units) which may explain the high adsorption capacity of these compounds. . Aggregation may be facilitated by positive charges at PEI and Cu(II) sites which would neutralize localized charge buildup by PFAS anions leading to charge-charge repulsion, that would otherwise destabilize aggregation. Aggregate formation would also be a separate sink for adsorbed PFAS which would add another kinetic barrier to back-diffusion enhancing the integrative response of the adsorbent for passive sampling.

Biofilm development on the surface of the Cu(II)-PEI-SOMS particles would potentially inhibit mass accumulation by acting as a diffusional barrier to initial PFAS adsorption from the water[45]. In passive sampler evaluations simulated groundwater with 1 mg/L humic acid was used. Despite the presence of organic matter in the water, visible development biofilms were never observed (though water became turbid over long periods of time). Linear uptake in mass accumulations over a period 90 d was observed. . It is hypothesized that the geometry and chemical composition of Cu(II)-PEI-SOMS prevents challenges associated with biofilm development or other fouling mechanisms. First, the lack of a membrane or other microporous barrier is helpful as such materials can become clogged with fine particles or microorganisms from the water. The Sentinel design places the adsorbent particles in direct contact with water in what can be simply described as a thin pouch. Thus, in fast flowing water the particles can tumble and fine particles can be removed by turbulent flow. Second, the Cu(II) ions while provided sites for PFAS adsorption may also have biocidal activity limiting biofilm formation.

Third, SOMS is a micro-mechanically flexible material[12] that may also help to prevent biofilm development. Overall, the unique feature of SOMS (continuous porosity, high pore volume, mechanically flexible matrix architecture, and loading with copper ions) allows for unique ways to construct passive samplers.

Conclusions

Integrative mode passive sampling is useful in providing a time-weighted average analyte concentration in flows with varying amounts of analyte. Passive samplers using a Cu(II)-PEI-SOMS receiving phase demonstrated an integrative response >90 days for most PFAS tested. The integrative response was confirmed to provide a time-weighted average concentration over at least 7-days even when PFAS concentration changed by an order of magnitude during the sampling interval. Adsorbed PFAS was preserved in the resin after aqueous phase concentrations decreased by slow back diffusion kinetics. Slower back diffusion rates relative to adsorption rates were attributed to intraparticle diffusional sink into the interior pore structure of SOMS and potential formation of PFAS aggregates in the adsorbed fraction. Sampling rates for PFAS range between 0.004-0.020 L/day for groundwater like systems. Accumulation rate of PFAS in the receive phase was controlled by to adsorption kinetics since the passive sampler places the resin in direct contact with the water.

Conflict of interest: Possibly; authors E. Carter, K. Toth, and C. Divine are employed by Arcadis which is the assignee in pending patent applications related to the described sampler. Osorb is patented by The College of Wooster where Paul Edmiston (inventor) is employed.

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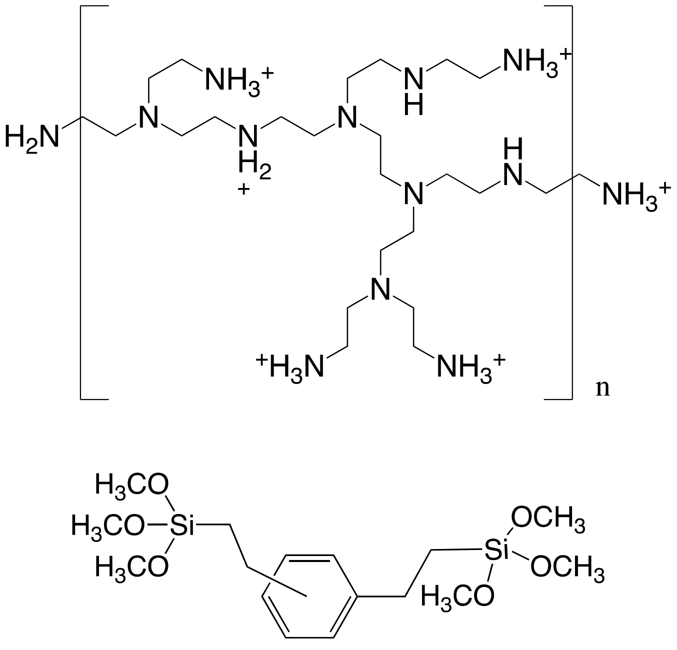

Fig 1. Chemical structure of (top) PEI weak ion exchange polymer and (bottom) BTEB sol-gel precursor .

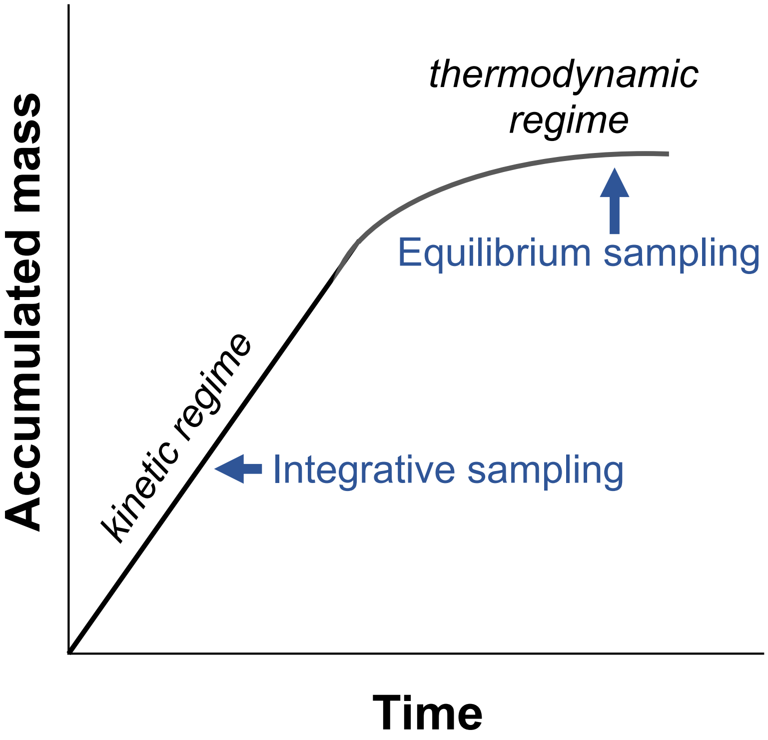

Fig 2. Mass accumulation vs time profile comparing integrative and equilibrium-based (capacity threshold) passive sampling.

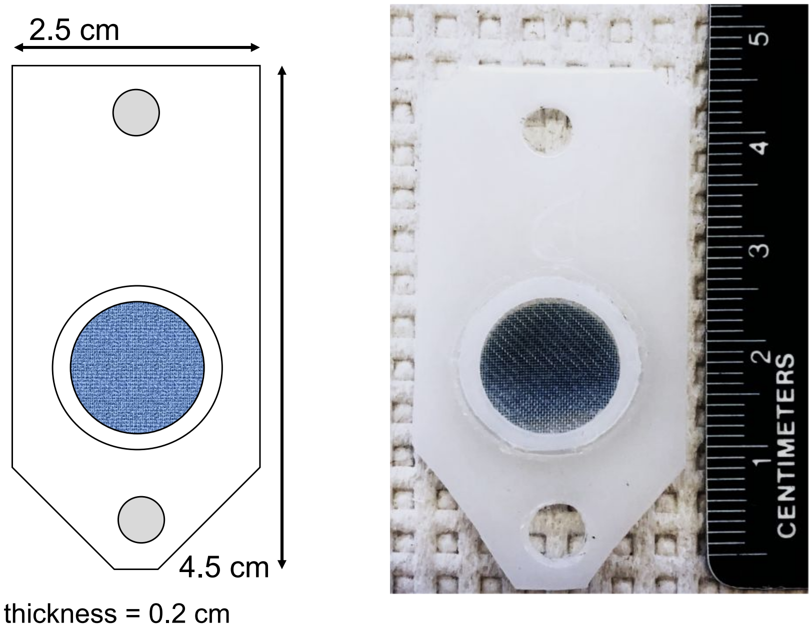

Fig 3. Schematic (left) and photograph (right) of the passive sampler constructed of HDPE.

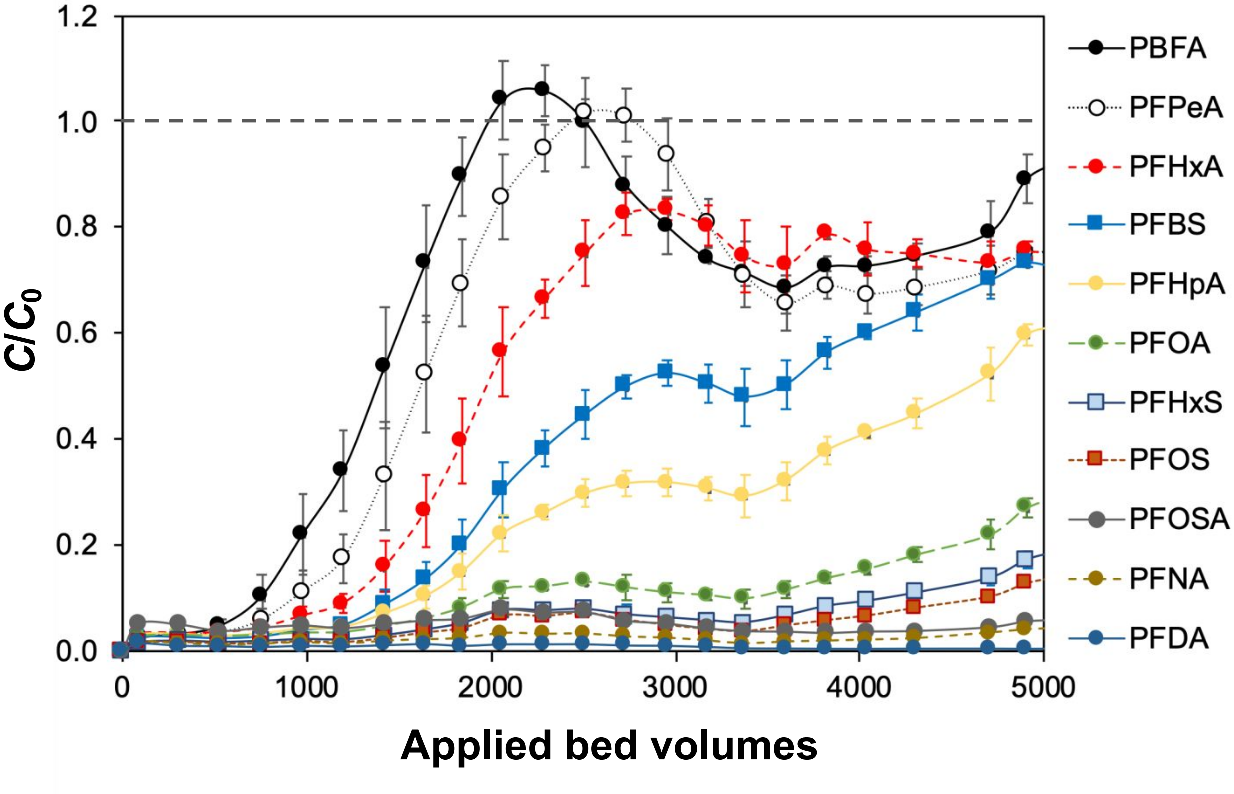

Fig 4. Breakthrough curves for Cu(II)-PEI-SOMS with total PFAS concentration 5,000 μg/L, *T*= 25˚C , and flow rate = 0.5 bed vol/min.

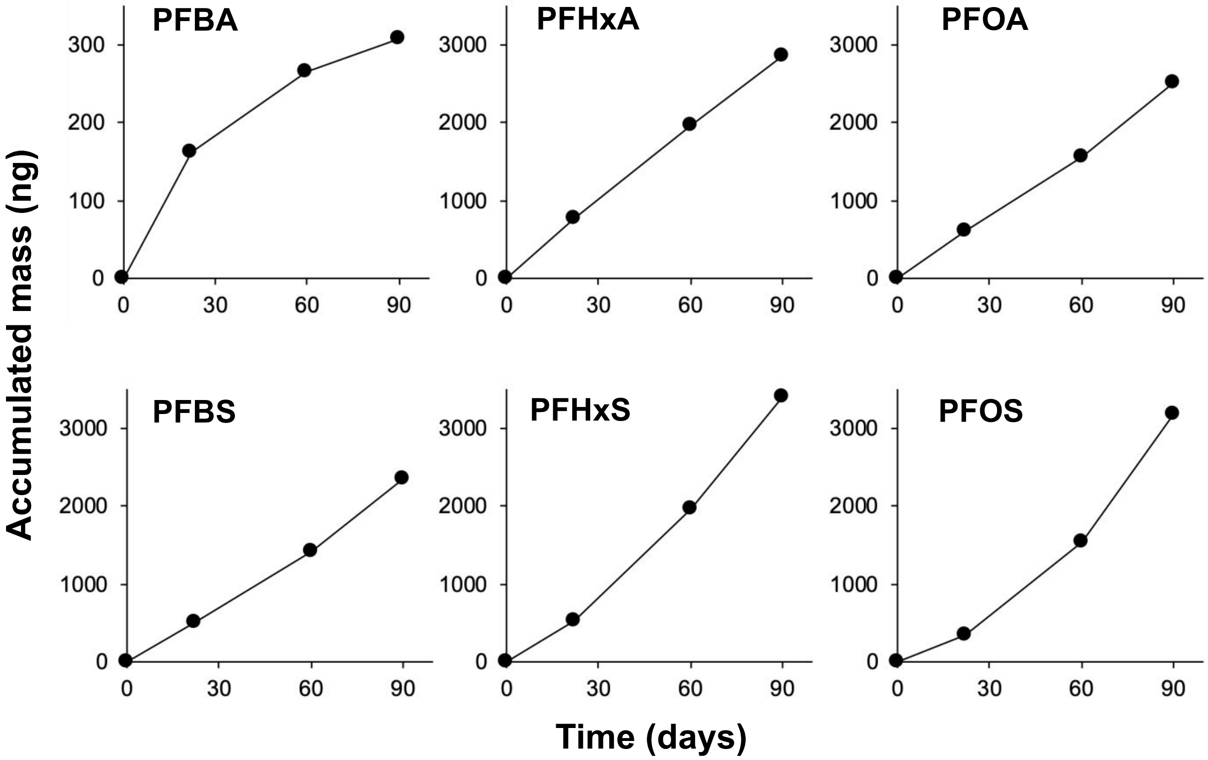

Fig 5. Mass accumulations by passive samplers over 90-days (2.5 μg/L each PFAS).

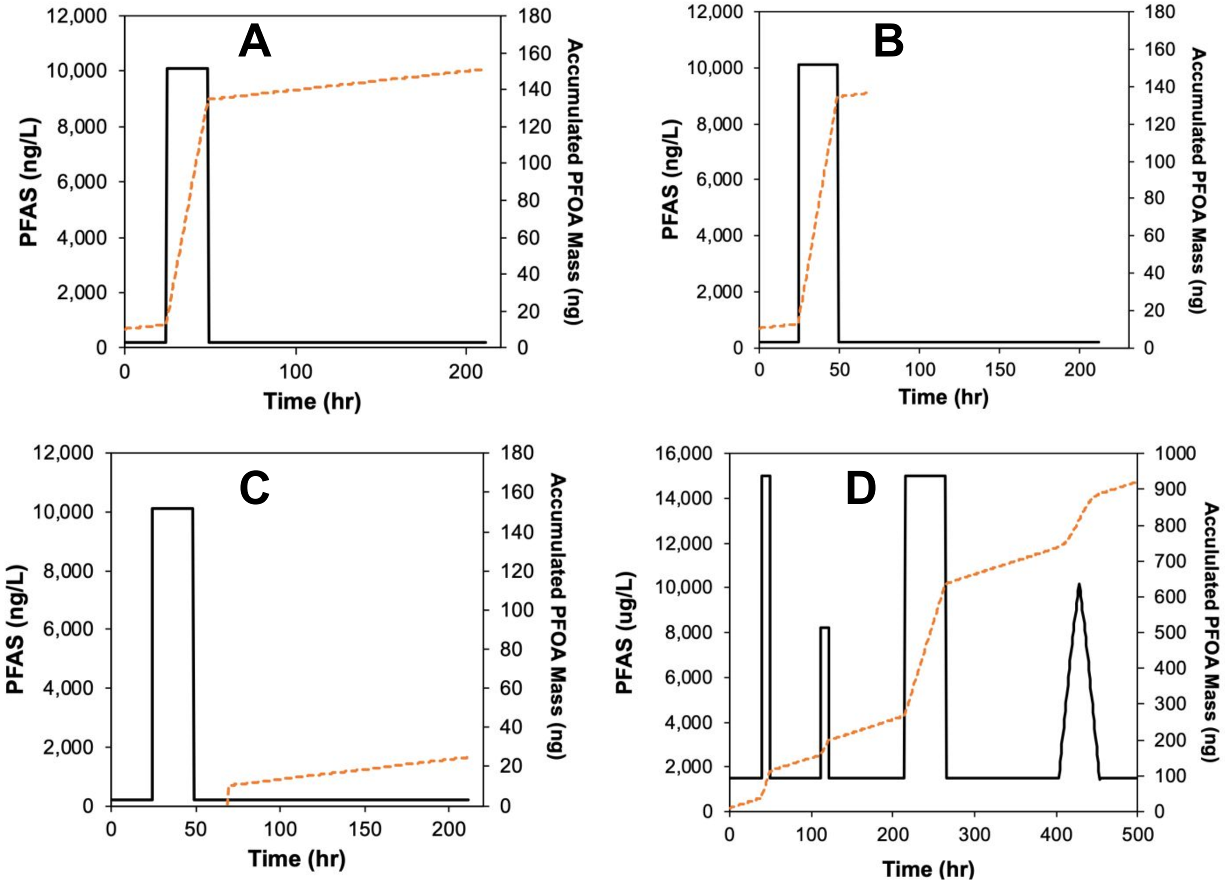

Fig 6. Concentration profiles and calculated theoretical PFOA mass accumulations by passive samplers. Dotted lines depict the theoretical mass of PFOA adsorbing assuming fully integrative response. A-C represent an experiment with a pulsed change in concentrations where samplers were deployed at across different times.

Table 1: PFAS surrogate adsorption extent, recovery, and stability.

Surrogate	**Percent Adsorbed**	**Percent Recovery**	**Stability Δ%Recovery/ Week**
[M]4:2 FTS	96 ± 6	93 ± 11	-0.4
[M]6:2 FTS	95 ± 5	105 ± 15	-3.6
[M]8:2 FTS	93 ± 6	99 ± 12	-8.2
[M]FOSA	94 ± 6	25 ± 4	+2.7
d_3-N-MeFOSA	94 ± 8	14 ± 2	n/m
d_3-N-EtFOSA	95 ± 7	18 ± 3	n/m
d_3-N-MeFOSAA	95 ± 6	21 ± 10	n/m
[M]HFPO-DA	95 ± 4	67 ± 24	+3.6
[M]PFBA	97 ± 5	103 ± 26	+19
[M5]PFPeA	96 ± 5	103 ± 10	+4.3
[M]PFHxA	95 ± 6	90 ± 8	+4.1
[M4]PFHpA	94 ± 5	93 ± 7	-0.6
[M]PFOA	94 ± 5	92 ± 7	-0.2
[M]PFNA	93± 4	41 ± 3	+0.5
[M]PFDA	92 ± 4	32 ± 3	+4.1
[M]PFUdA	91 ± 7	26 ± 2	-1.0
[M]PFDoA	82 ± 9	23± 5	-2.9
[M]PFTeDA	99 ± 9	10 ± 2	-1.5
[M]PFBS	95 ± 5	104 ± 12	-4.1
[M]PFHxS	93 ± 6	105 ± 11	-4.0
[M]PFOS	92 ± 2	87 ± 9	-4.5
d_7-N-MeFOSE	94 ± 5	15 ± 2	n/m
d_9-N-EtFOSE	93 ± 6	15 ± 2	n/m

(n=5); n/m = not measured

Table 2: Time-averaged PFAS concentrations predicted by an integrative model compared to those measured by the passive sampler.

Analyte	*R*s (L/day)	Concentration (ng/L)											
		Sampler A[1]			**Sampler B**			**Sampler C**			**Sampler D**		
		Predicted[2]	Measured	Δ%[3]	Predicted	Measured	Δ%	Predicted	Measured	Δ%	Predicted	Measured[4]	Δ%
PFOSA	0.013	180	108	-40	12	17	42	69	31	-55	920	750±50	-19
HFPO-DA	0.014	22	30	36	0	-		7	10	43	940	770±50	-19
PFBA	0.008	2,890	4,780	65	174	290	67	1,070	1,210	13	1,000	840±50	-16
PFPeA	0.010	3,130	4,590	47	179	290	62	1,150	1,380	20	935	1,040±110	11
PFHxA	0.013	3,640	4,160	14	208	280	35	1,340	1,320	-1	1,060	1,090±140	3
PFHpA	0.014	3,370	3,590	7	187	210	12	1,240	1,210	-2	1,160	900±90	-23
PFOA	0.016	3,670	3,580	-2	207	237	14	1,350	1,280	-5	1,450	1,580±170	9
PFNA	0.013	3,990	3,860	-3	230	260	13	1,470	1,330	-10	2,120	2,110±190	-1
PFDA	0.013	3,710	3,540	-5	214	200	-7	1,370	1,180	-14	2,570	2,660±350	4
PFBS	0.013	3,770	4,620	23	218	205	-6	1,390	1,520	9	2,160	2,330±10	8
PFHxS	0.014	3,370	3,540	5	201	190	-5	1,250	1,200	-4	1,810	1,580±60	-13
PFOS	0.016	3,190	3,080	-3	188	95	6	1,180	1,020	-14	1,360	1,620±90	19

[1] Sampler identifier matches Figure 5.

[2] Predicted is the average aqueous phase concentration (ng/L) in simulated groundwater of the during the sampler exposure period as measured in the water by SPE with HPLC-MS/MS detection.

[3] Percent difference between predicted vs. measured by passive sampler.

[4] Average of two duplicate passive samplers.