FINAL REPORT

Ion Exchange Membranes and Fibers as Passive Samplers for Chemically-diverse PFAS

ESTCP Project ER20-1073

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14. ABSTRACT

The overall goal of this project was to develop ion-exchange membrane and fiber strategies for passive sampling of chemically diverse PFAS. The project was developed to address DoD's needs with respect to measurement and remediation of PFAS. The specific objectives were as follows: (1) develop ion-exchange membrane and fiber passive samplers capable of concentrating short- and long-chain PFAS with varying log D values; (2) establish selectivity coefficients for 19 PFAS of concern in the ion exchange-based samplers to quantitatively describe PFAS uptake and partitioning; (3) confirm that the ion-exchange materials are capable of effective deployment and performance in synthetic and real groundwater and surface water matrices; (4) investigate ion exchange-based passive samplers for cationic, zwitterionic, and anionic PFAS; (5) ensure consistent performance of the samplers in single- and multi-sorbate scenarios; (6) characterize effects of solution pH, ionic strength, background ions, temperature, and dissolved organic matter on the passive samplers; and, (7) deploy the passive samplers in laboratory-based mesocosms to confirm their ability to resolve spatiotemporal variations in PFAS concentration.

15. SUBJECT TERMS
PFAS, per- and polyfluoroalkyl substances, passive sampler, toxic contaminants, analytical methods, ion exchange, membranes

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LIST OF ACRONYMS

Acronym	Full name
ACE	Army Corps of Engineers
DI	Deionized
DoD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FtS 4:2	Fluorotelomer sulfonic acid 4:2
FtS 6:2	Fluorotelomer sulfonic acid 6:2
FtS 8:2	Fluorotelomer sulfonic acid 8:2
HDPE	High-density polyethylene
LC-MS/MS	Liquid chromatography with tandem mass spectrometry
LCS	Laboratory control sample
LOD	Limit of detection
LOQ	Limit of quantitation
MeOH	Methanol
MPFAS	Mass-labeled PFAS
MQL	Method quantitation limit
MW	Molecular weight
NEtFOSAA	2-(N-Ethylperfluorooctanesulfonamido) acetic acid
NMeFOSAA	2-(N-Methylperfluorooctanesulfonamido) acetic acid
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecanesulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFNS	Perfluorononanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFOSA	Perfluorooctanesulfonamide
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentanesulfonic acid
PFTreA	Perfluorotetradecanoic acid
PFTriA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid
POCIS	Polar organic chemical integrative samplers
PP	Polypropylene
QA	Quality assurance
QC	Quality control
QSM	Quality Systems Manual
RPD	Relative percent difference
RT	Retention time

Acronym	Full name
SDVB	Polystyrene-divinylbenzene
SERDP	Strategic Environmental Research and Development Program
SPE	Solid-phase etxraction
UMBC	University of Maryland Baltimore County
US	United States
WAX	Weak-anion exchange

KEYWORDS

PFAS
Ion exchange
Passive sampler
Sorption
Extraction

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ABSTRACT

Project Number: ER20-1073

Project Title: Ion exchange membranes and fibers as passive samplers for chemically-diverse PFAS

Lead Principal Investigator: Lee Blaney, PhD

Lead Organization: University of Maryland Baltimore County (UMBC)

Objective: The overall goal of this project was to develop ion-exchange membrane and fiber strategies for passive sampling of chemically diverse PFAS. The project was developed to address DoD's needs with respect to measurement and remediation of PFAS. The specific objectives were as follows: (1) develop ion-exchange membrane and fiber passive samplers capable of concentrating short- and long-chain PFAS with varying log D values; (2) establish selectivity coefficients for 19 PFAS of concern in the ion exchange-based samplers to quantitatively describe PFAS uptake and partitioning; (3) confirm that the ion-exchange materials are capable of effective deployment and performance in synthetic and real groundwater and surface water matrices; (4) investigate ion exchange-based passive samplers for cationic, zwitterionic, and anionic PFAS; (5) ensure consistent performance of the samplers in single- and multi-sorbate scenarios; (6) characterize effects of solution pH, ionic strength, background ions, temperature, and dissolved organic matter on the passive samplers; and, (7) deploy the passive samplers in laboratory-based mesocosms to confirm their ability to resolve spatiotemporal variations in PFAS concentration.

Technical Approach: Ion-exchange membranes and fibers represent a paradigm shift in passive sampling strategies for organic contaminants and PFAS, in particular. This shift stems from the wide-ranging physicochemical properties of PFAS, which complicate traditional passive sampling strategies. The specific objectives were achieved through (i) batch sorption tests to identify selectivity coefficients, competitive effects, and impacts of interfering substances on PFAS uptake by the sampler and (ii) mesocosm studies using synthetic and real water matrices. The limited-scope portion of the project was focused on Objectives 1, 2, and 3.

Results: Our findings indicated that PFAS uptake into the ion-exchange membranes was fairly rapid, namely 2-3 days under well-mixed conditions and 2-4 weeks under static conditions; furthermore, these results were confirmed in large-volume studies using a real groundwater and pond water. We confirmed through both sorption and desorption studies that ion exchange was the primary mechanism of uptake for short- and long-chain PFAS with different head groups. The uptake capacity, selectivity coefficients, and PFAS recovery (extraction) were measured for ten ion-exchange membranes and one set of ion-exchange fibers. Based on the aggregate results, the FAD-PET-75 membrane was selected as the optimal choice for follow-on work. The selectivity coefficients for PFAS over chloride ranged from 1.57 (PFBA) to 4.90 (PFOS), and 1-4 cm^2 membrane coupons were able to accumulate enough PFAS for downstream analysis. The selectivity coefficients demonstrated trends with chain-length and head group. The total dissolved solids concentration (related to ionic strength) in real groundwater and pond water affected the observed selectivity coefficients, which increased with salt content, but these parameters were successfully corrected using Setschenow constants. The FAD-PET-75 membrane was effectively dissolved in methanol to achieve high recovery of short- and long-chain PFAS (*e.g.*, 87% PFBA, 104% PFOA). We also developed prototype samplers that will continue to be refined for field deployments in the proposed follow-on work.

Benefits: Given the increased importance of PFAS to ongoing cleanup and remediation efforts at DoD facilities, new strategies are required to enable monitoring of PFAS. The limit-scope portion of this project provided proof-of-concept evidence for ion exchange-based strategies, and follow-on work will continue to develop, evaluate, and test innovative ion exchange-based materials for passive sampling of PFAS. Due to the ion-exchange mechanism, the passive samplers offer robust solutions for the full range of PFAS of interest. The results of this project contributed new scientific understanding to the use of ion-exchange passive samplers, which may also be useful for other DoD-relevant contaminants.

1. INTRODUCTION

This project aimed to develop novel passive sampling methods to accurately measure environmental concentrations of 19 priority per- and polyfluoroalkyl substances (PFAS) identified by the United States (US) Department of Defense (DoD) in groundwater, surface water, stormwater, and porewater. The outcomes of this work include (i) improved capabilities for accurate, precise, and repeatable measurements of PFAS, (ii) better sample collection, handling, and analysis of PFAS at DoD sites, and (iii) enhanced opportunities to understand spatiotemporal trends in PFAS occurrence, fate, and transport in diverse environmental media.

2. OBJECTIVES

The overall goal of this project was to develop ion-exchange membrane and ion-exchange fiber strategies for passive sampling of chemically diverse PFAS. The project aligns with DoD's increased focus on measurement and remediation of PFAS. The project goal will be accomplished through investigation of the specific objectives illustrated in Figure 1 and listed below:

1. Develop ion-exchange membrane and ion-exchange fiber passive samplers capable of concentrating short- and long-chain PFAS with varying log D values;
2. Establish selectivity coefficients for 19 PFAS of concern in the ion-exchange membrane and ion-exchange fiber samplers to quantitatively describe PFAS uptake and partitioning;
3. Confirm that the ion-exchange membrane and ion-exchange fiber passive samplers are capable of effective deployment and performance in synthetic and real groundwater, surface water, stormwater, and porewater from DoD facilities;
4. Investigate ion exchange-based passive samplers for cationic, zwitterionic, and anionic PFAS;
5. Ensure consistent ion-exchange membrane and ion-exchange fiber performance for single- and multi-sorbate scenarios;
6. Characterize effects of solution pH, ionic strength, background ions (*e.g.*, Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-}, HCO_3^{-}, Cl^{-}, etc.), temperature, and dissolved organic matter on passive samplers; and,
7. Deploy passive samplers in laboratory-based mesocosms to confirm their ability to resolve spatiotemporal variations in PFAS concentration.

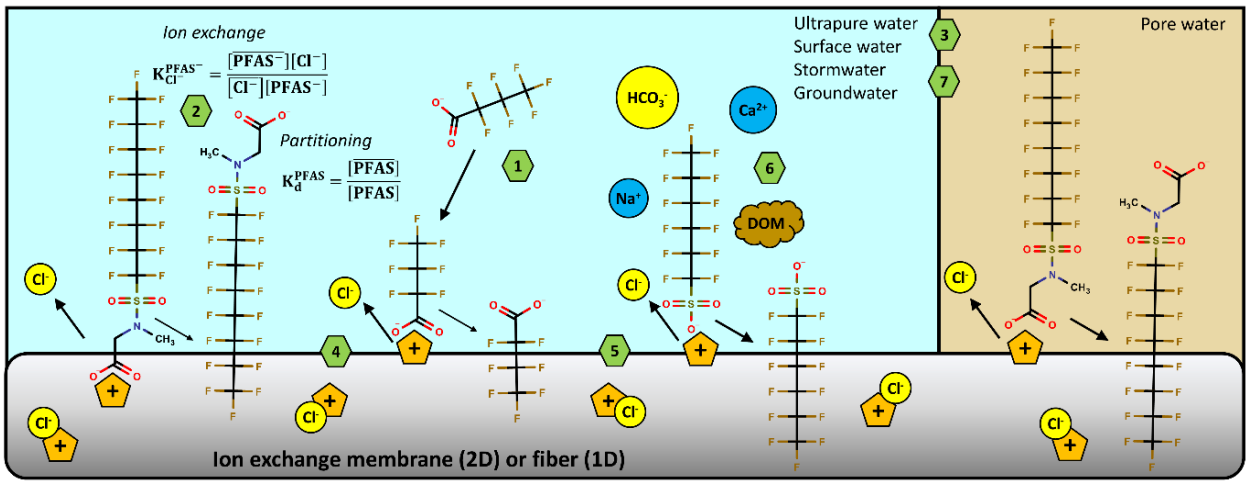

Figure 1. Overview of ER20-1073. Orange pentagons are ion-exchange sites, yellow circles are potentially competitive background anions, and blue circles are cations. The numbers in the green hexagons correspond to the specific objectives.

The limited scope portion of the project (Phase 1) was specifically focused on experimental investigation of Objectives 1-3. A "go/no go" decision will be evaluated based on the associated results to plan for deeper investigation of Objectives 4-7 and other next steps in Phase 2. In the original proposal, a "go" decision was defined as (i) successful application of ion-exchange membranes and ion-exchange fibers for passive sampling of PFAS, (ii) successful determination of selectivity coefficients for PFAS to the ion-exchange materials, and (iii) successful deployment of the ion-exchange membranes and ion-exchange fibers for PFAS passive sampling in synthetic and real water sources from DoD sites.

3. BACKGROUND

The physicochemical characteristics of PFAS vary widely. This variability has critical implications for efforts to develop passive samplers. Traditional passive samplers have mostly focused on hydrophobic persistent organic pollutants (*e.g.*, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, pesticides) with log D values greater than 3.0 [1, 2]. Note that log D is similar to log K_{ow} (*i.e.*, the log-transformed octanol-water partitioning coefficient) but accounts for acid dissociation reactions, which are relevant to PFAS chemistry in water. As suggested by Figure 2, traditional techniques pose challenges for some PFAS. Generally, molecules are described as hydrophobic if the log D value is greater than 2.0. According to this criterion, the extent of PFAS sorption in typical passive sampling polymers is limited; in fact, only 12 of the 24 priority PFAS would be expected to partition into traditional samplers. This situation was confirmed by preliminary data (included in original proposal) collected using an innovative syringe pump setup with various filter media. The more hydrophilic PFOA (log D = 1.58 at pH 7) and 6:2 FtS (log D = 1.54 at pH 7) molecules were not retained by glass fiber, nylon, polypropylene, polyvinylidene fluoride, surfactant-free cellulose acetate, or polyethersulfone membranes, whereas the more hydrophobic PFOS (log D = 3.05 at pH 7) showed varying retention based on membrane properties.

Polar organic chemical integrative samplers (POCIS) have been explored for compounds with log D values less than 3.0; however, POCIS involves kinetic sampling, which complicates efforts to validate, deploy, and measure PFAS in diverse water sources [3-5]. Given the toxicity concerns associated with short-chain and alternative PFAS [6-8], passive sampling methodologies must be able to sorb diverse PFAS. Because previous passive sampling approaches have inherent issues for uptake of chemically diverse PFAS, we explored a new paradigm for passive sampling of PFAS using ion-exchange materials. Our approach was supported by ongoing research showing effective removal of PFAS from surface water, wastewater, and groundwater by ion-exchange resins [9-11]. For example, Zaggia *et al.* [9] demonstrated concomitant removal of PFBA, PFBS, PFOA, and PFOS in pilot-scale experiments with three different resins. While the relative removal varied (*i.e.*, PFBA eluted first, PFOS eluted last), all four molecules were effectively sorbed, which suggests that ion exchangers can serve as effective passive samplers. In fact, ion exchange-based techniques have been explored for passive sampling of other chemicals [12-14]. Oemisch *et al.* [14] concluded that ion-exchange membranes have the potential to measure freely dissolved concentrations of 4-ethylbenzene-1-sulfonate and 2,4-dichlorophenoxy-

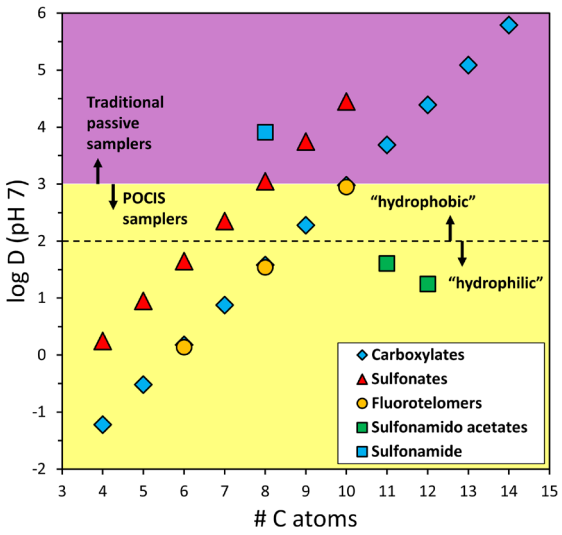

Figure 2. The log D values (at pH 7) for the 24 PFAS of concern plotted against the number of carbon atoms in the molecule. Traditional passive samplers and POCIS samplers are not expected to work for the full range of priority PFAS identified by DoD. The purple and yellow backgrounds correspond to the range of log D values that have been employed for traditional passive samplers and POCIS samplers, respectively. The dashed line shows the conventional definition of hydrophobic (log D > 2) and hydrophilic (log D < 2).

acetic acid, two molecules with similar ionic groups as the PFAS of interest. While PFAS exhibit wide-ranging log D values, the charged moiety is conserved at environmentally relevant pH conditions. This property allows anionic PFAS to interact with positively charged functionalities on anion exchangers. The relative affinity of anion-exchange sites for various PFAS has not been established, although some differences have been noted by previous researchers [9, 15, 16].

4. TECHNICAL APPROACH

The activities included in Phase 1 studies involved batch sorption experiments, and the relevant details are provided in the narrative of the Results and Discussion and the Supplemental Materials available in Appendices A and B. All experimental data are available in Appendix D, and additional details can be provided upon request.

5. RESULTS AND DISCUSSION

5.1. Objective 1

Our experimental efforts focused on the following tasks associated with Objective 1: (1.1) characterize the deployment time required to reach equilibrium between PFAS concentrations in water and the passive sampler; (1.2) identify the most appropriate isotherm model for PFAS equilibrium between water and passive samplers; and, (1.3) compare the performance of ion-exchange membranes and ion-exchange fibers as passive samplers for PFAS.

5.1.1. Evaluation of equilibrium times

Initially, we examined the equilibrium time using batch reactors containing 100 mL of synthetic groundwater with 100 mM NaCl and a mixture of 12 PFAS (*i.e.*, PFBA, PFBS, PFHxA, PFHxS, PFOA, FtS 6:2, PFOS, PFDA, NEtFOSAA, PFOSA, PFDoA, PFTreA). The initial concentration of each PFAS was 100 μg L^{-1}, except for NEtFOSAA (10 μg L^{-1}) due to the higher chemical costs. The batch reactors also contained a trace amount of methanol stemming from the PFAS stock solutions, but the total methanol content was less than 1%. Control experiments demonstrated that NEtFOSAA, PFOSA, PFDoA, and PFTreA interacted with the walls of the 125-mL high-density polyethylene (HDPE) containers, and so these PFAS were excluded from further time-based analysis; however, these interactions did not affect calculation of equilibrium relationships. Anion-exchange membrane coupons were added to the batch reactors, and aqueous samples were collected at pre-determined times. The anion-exchange membranes included AMI-7001 (AMI) and FAA-3-PK-130 (FAA). The dimensions of the AMI and FAA membrane coupons were 2 × 2 cm^2 (270 mg) and 1 × 1 cm^2 (10 mg), respectively. Both membranes had a similar anion-exchange capacity (*i.e.*, 1.25-1.30 meq g^{-1}), but the AMI membranes were approximately 4× thicker. The experimental results in Figure 3 highlighted the relatively fast uptake of PFAS onto the anion-exchange membranes. In a moderate mixing regime of 200 rpm, PFAS content reach equilibrium in the membranes after 48 h or less. More than 80 h was required for PFAS accumulation in anion-exchange membranes in slower mixing regimes. Although the AMI and FAA membranes had similar exchange capacities, we observed much higher uptake of PFAS into the FAA membranes (up to 3250 nmol g^{-1} for PFBS) for the experimental conditions; note, the higher capacity guided our decision to use smaller FAA membrane coupons. Additional kinetics results are provided for AMI in solutions with 10 mM and 100 mM NaCl in Section A1.1 of Appendix A.

Separate batch reactors were run at different conditions to confirm the equilibrium partitioning between the aqueous phase and passive sampler for longer contact times. Figure 4 reports the selectivity coefficients for PFAS over chloride (Eq. 1) for two anion-exchange membranes, namely FAD-PET-75 (labeled as FAD-75, below) and AMI-7001, at 3 d and 30 d of contact time. For these contact times, minor changes in the selectivity coefficient were observed for smaller, more hydrophilic PFAS, whereas greater changes were recorded for the larger, more hydrophobic PFAS analytes. Similar trends were observed with both membranes. Importantly, the 30-d contact time also resulted in improved precision.

The median relative standard deviations for the FAD-75 selectivity coefficients were 25% at 3 d and 8% at 30 d; similarly, the relative standard deviations for the AMI-7001 selectivity coefficients were 19% at 3 d and 7% at 30 d. Note, additional timepoints were measured between 3 d and 30 d, and equilibrium was confirmed at 30 d. The aggregate data demonstrated strong accumulation of mid-chain PFAS (*i.e.*, PFPeS to N-EtFOSAA in Figure 4) and satisfactory uptake of the other PFAS.

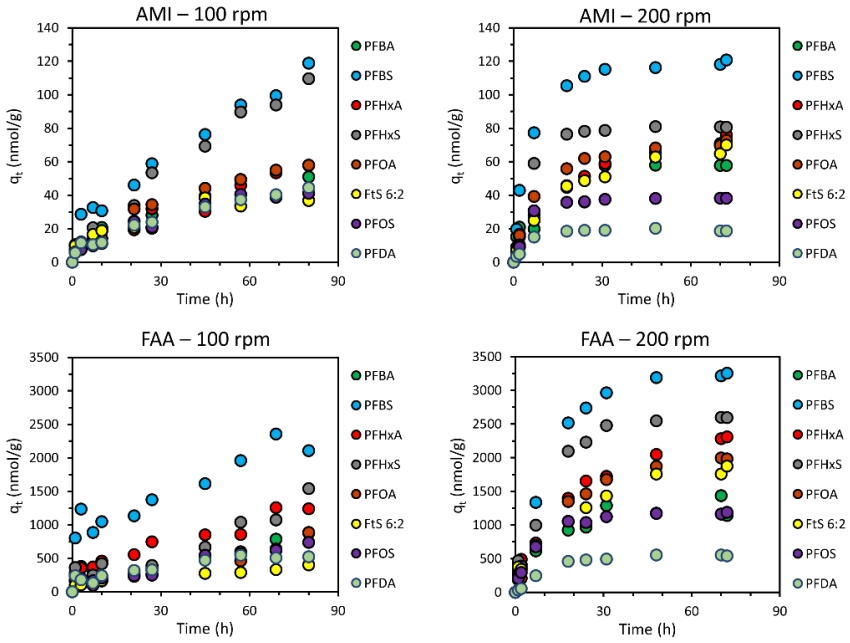

Figure 3. Preliminary results for PFAS uptake into AMI (top) and FAA (bottom) anion-exchange membranes as a function of time. The mixing speed was varied from 100 rpm (left) to 200 rpm (right) to determine the time needed to reach equilibrium under different mixing regimes.

$$K_{Cl}^{PFAS} = \frac{[PFAS^-]_{mem}[Cl^-]_{aq}}{[Cl^-]_{mem}[PFAS^-]_{aq}} \quad \text{(Eq. 1)}$$

In Eq. 1, K_{Cl}^{PFAS} is the selectivity coefficient, $[PFAS^-]_{mem}$ is the membrane-phase PFAS concentration, $[PFAS^-]_{aq}$ is the aqueous-phase PFAS concentration, $[Cl^-]_{mem}$ is the membrane-phase Cl^- concentration, and $[Cl^-]_{aq}$ is the aqueous-phase concentration of Cl^-.

5.1.2. PFAS sorption isotherms

Sorption isotherm experiments were conducted using five 100-mL solutions containing 10 mM NaCl and initial PFAS concentrations of 1.0, 2.5, 5.0, 7.5, and 10.0 mg L^{-1}. The initial PFAS concentrations were fairly high to avoid concerns about mass limitations stemming from the nearly complete uptake of PFAS from the solution into the membrane. The same 12 PFAS of concern were used in these experiments. The reactors were mixed at 200 rpm for over 100 h before measurement of the aqueous-phase PFAS concentrations. The resultant data are shown in Figure 5. Note the favorable uptake of perfluoroalkyl sulfonates, followed by fluorotelomer sulfonates, perfluoroalkyl carboxylates, PFOSA, and NEtFOSAA. Based on the shape of the data in Figure 5, we postulated the appropriateness of the Langmuir adsorption isotherm (see Eq. 2).

$$[PFAS^-]_{mem} = \frac{Q_L K_L [PFAS^-]_{aq}}{1 + K_L[PFAS^-]_{aq}} \quad \text{(Eq. 2)}$$

In Eq. 2, Q_L is the capacity of anion-exchange membrane for each PFAS (μeq g^{-1}), and K_L is a Langmuir constant for each PFAS (L $μeq^{-1}$).

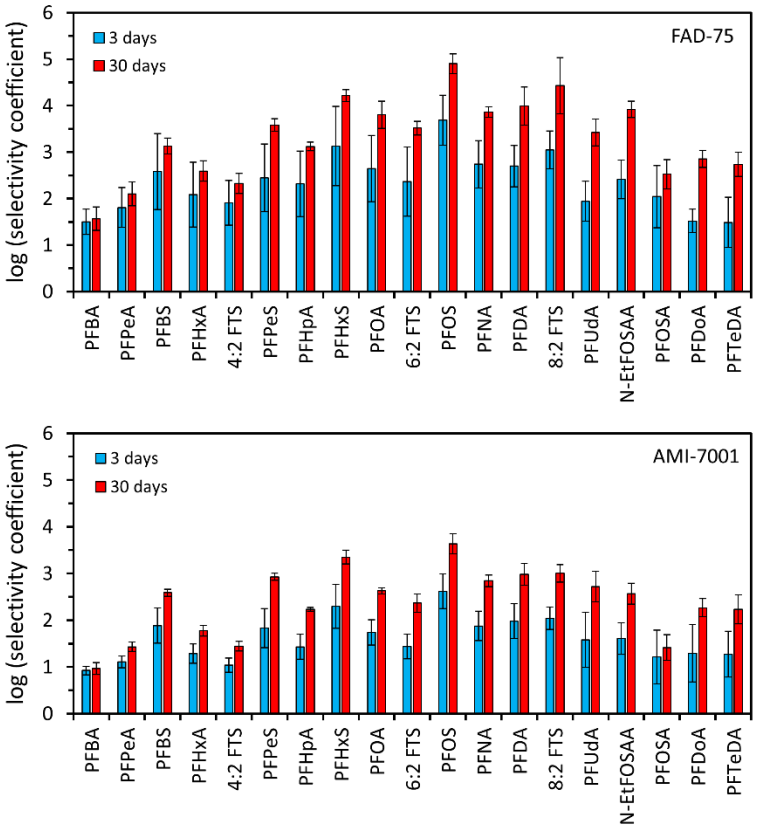

Figure 4. Selectivity coefficients for the FAD-75 and AMI-7001 anion-exchange membranes after 3 d and 30 d in batch reactors. The selectivity coefficients were evaluated at seven different conditions, and the data are reported as average (columns) ± standard deviation (error bars). The experiments involved 1 × 1 cm^2 membrane coupons (initially in Cl^- form), 50-1500 μg L^{-1} (initial, each) PFAS, and 10 mM (initial) NaCl.

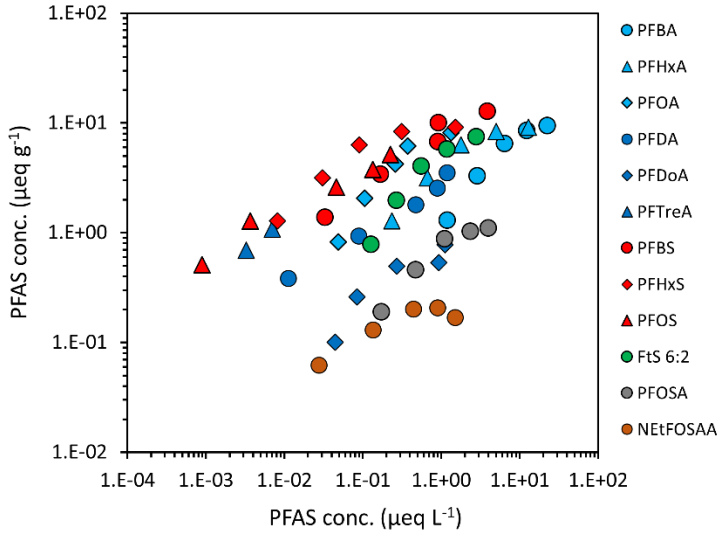

Figure 5. Adsorption isotherm data for AMI-7001. The 2 × 2 cm^2 coupon of AMI-7001 was equilibrated with a pH 6.0 solution that contained 10 mM NaCl. PFAS "mass" is reported in μeq to better identify differences in PFAS adsorption using a fair metric across all PFAS.

The PFAS of concern demonstrated a good fit to the Langmuir isotherm, as indicated in Figure 6a, which shows the membrane-phase PFAS concentrations calculated by the isotherm plotted against experimental data. Since the majority of the data points fall along the 1:1 line, the model provides a reasonable fit to the experimental data. The individual isotherm curves are shown in Figure 6b. For clarity, the curves are shown without experimental data for most PFAS of concern; however, the experimental data were included for PFOA, PFOS, and FtS 6:2 to show the goodness of fit in different concentration regimes. The selectivity coefficients corresponding to experimental data for the 10 mM and 100 mM NaCl solutions are further described in Section A1.2 of Appendix A.

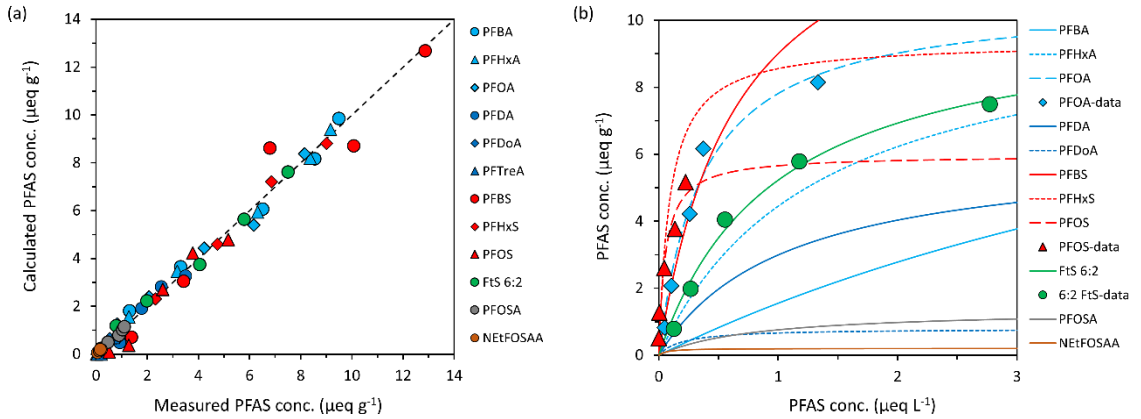

Figure 6. (a) a 1:1 plot highlighting the goodness of fit for PFAS uptake according to the Langmuir isotherm; (b) the isotherm models for the PFAS of concern in a pH 6.0 solution with 10 mM NaCl. PFAS "mass" is reported in µeq for the reasons documented in Figure 5.

5.1.3. Performance of anion-exchange fibers as passive samplers for PFAS

Due to the low selectivity of the anion-exchange fibers for PFAS, the fiber-based approach was not further considered. More details are available in Section A1.3 of Appendix A.

5.2. Objective 2 Results

Our experimental efforts focused on the following tasks associated with Objective 2: (2.1) confirm the dominant uptake mechanism for 19 PFAS with ion-exchange membrane passive samplers; (2.2) compare the performance of different ion-exchange membranes for PFAS uptake; (2.3) calculate apparent distribution coefficients ($K_{d,app}$) and selectivity coefficients ($K_{ex,app}$) for the 19 PFAS with ion-exchange membranes; and, (2.4) investigate trends in PFAS uptake to the ion-exchange based passive samplers as a function of molecular properties, including chain-length and hydrophilic group.

5.2.1. The dominant uptake mechanism was confirmed to be ion exchange

Using the data collected after 30 d of contact time (Figure 4), we evaluated the fit of the Langmuir and linear isotherms for each PFAS analyte in the FAD-75 and AMI-7001 anion-exchange membranes. The isotherms for each analyte are reported in Figure A6 of Appendix A. The isotherms provided excellent fits to the experimental data. In every case, the FAD-75 membrane outperformed the AMI-7001 membrane with respect to the magnitude of PFAS concentrations in the passive sampler. These trends were expected given the higher selectivity coefficients recorded for the FAD-75 membrane (Figure 4). Importantly, these findings confirmed ion exchange as the dominant PFAS uptake mechanism.

5.2.2. Comparison of different anion-exchange membranes

During the project, we evaluated ten different anion-exchange membranes. More details are available in Section A2.2 of Appendix A. The results confirmed that the FAD-75 membrane was the best option for use in passive samplers.

5.2.3. Trends in selectivity coefficients for PFAS over chloride

Using the 30 d equilibrium data (Figure A6 in Appendix A), we evaluated trends in selectivity coefficients as a function of class (*i.e.*, perfluorocarboxylates (PFCA), perfluorosulfonates (PFSA), fluorotelomer sulfonates (FtS), and other (*i.e.*, N-EtFOSAA, PFOSA)) and carbon number. As indicated in Figure 7, the selectivity coefficients of the PFSA and FtS analytes increased with chain length. The selectivity coefficients of the PFCA analytes increased from PFBA to PFDA but decreased from PFDA to PFTeDA. This unexpected trend may stem from steric or diffusion limitations associated with long-chain PFAS or micelle formation in the water phase. This finding is important, because long-chain PFAS would otherwise be expected to show much higher selectivity coefficients. Nevertheless, the uptake of long-chain PFAS is still sufficient for quantitation via passive sampling. The selectivity coefficients of PFCA and FtS analytes were similar for the same chain length; however, the selectivity coefficients for PFSA analytes are approximately 1.5 orders of magnitude higher. It is interesting to note that the same trends for PFCA analytes were observed in the FAD-75 and AMI-7001 anion-exchange membranes. Additional data are available for FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 in Section A2.3 of Appendix A.

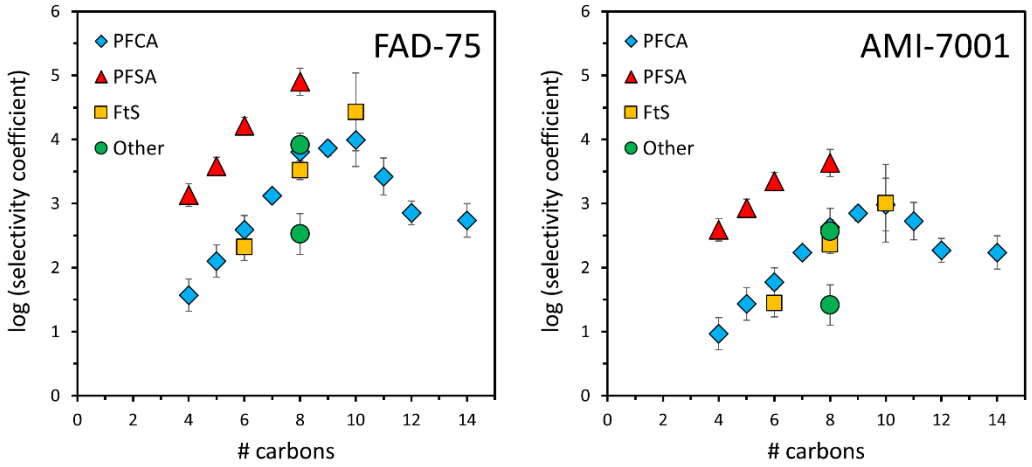

Figure 7. The trends in selectivity coefficient vs. chain length for PFCA, PFSA, FtS, and other PFAS analytes in the FAD-75 and AMI-7001 anion-exchange membranes. Note, the "Other" category includes N-EtFOSAA and PFOSA; N-EtFOSAA demonstrated a higher selectivity coefficient than PFOSA for both membranes.

5.2.4. Further confirmation of ion-exchange mechanism via desorption studies

Sequential extraction tests were conducted to further confirm that ion exchange was the dominant sorption mechanism. Additional details are available in Section A2.4 of Appendix A.

5.3. Objective 3 Results

Our experimental efforts focused on the following tasks associated with Objective 3: (3.1) confirm long-term stability of ion-exchange passive samplers in real waters; (3.2) verify calibration of passive samplers over long deployment times; and, (3.3) demonstrate ion-exchange passive samplers with real water from contaminated sites.

5.3.1. Passive sampler performance in real water matrices

To determine the ability of the anion-exchange membrane passive samplers to perform in source waters with different chemistry, we conducted experiments in (i) a groundwater collected from a US Army Corps of Engineers site and (ii) a pond water collected from the UMBC campus. The chloride (Cl^-) concentration in the groundwater (10 mg L^{-1}) was more than an order of magnitude lower than that of the

pond water (400 mg L^{-1}). Cl^- was the dominant anion in both solutions, although the pond water also contained 30 mg L^{-1} HCO_3^-, 5 mg L^{-1} NO_3^-, 5 mg L^{-1} SO_4^{2-}, and 2.1 mg_C L^{-1} of dissolved organic matter.

Approximately 40-mL aliquots of groundwater and 100-mL aliquots of pond water were added to polypropylene centrifuge tubes and HDPE bottles, respectively, and spiked with a mixture of 19 PFAS. The initial PFAS concentrations ranged from 10 to 750 µg L^{-1} in the groundwater and from 50 to 1500 µg L^{-1} in the pond water. The solutions were rapidly mixed, and then a 1×1 cm^2 coupon of the FAD-PET-75 anion-exchange membrane was added to each reactor. Controls were run with the same initial PFAS concentration but no FAD-PET-75 membrane to account for PFAS sorption to the container. Samples were collected on a weekly basis. The sampler-phase concentrations (neq g^{-1}) are plotted against the aqueous-phase concentrations (neq L^{-1}) in Figure 8 for three representative PFAS. The data in Figure 8a highlight the relatively long equilibration time for PFBA and PFBS in the groundwater matrix. In general, the PFBA concentration in the sampler decreased with time, presumably due to displacement by more preferred PFAS. For related reasons, the PFBS concentrations in the passive sampler tended to increase with time. No clear trends were apparent for PFOA, suggesting quicker equilibration of long-chain PFAS.

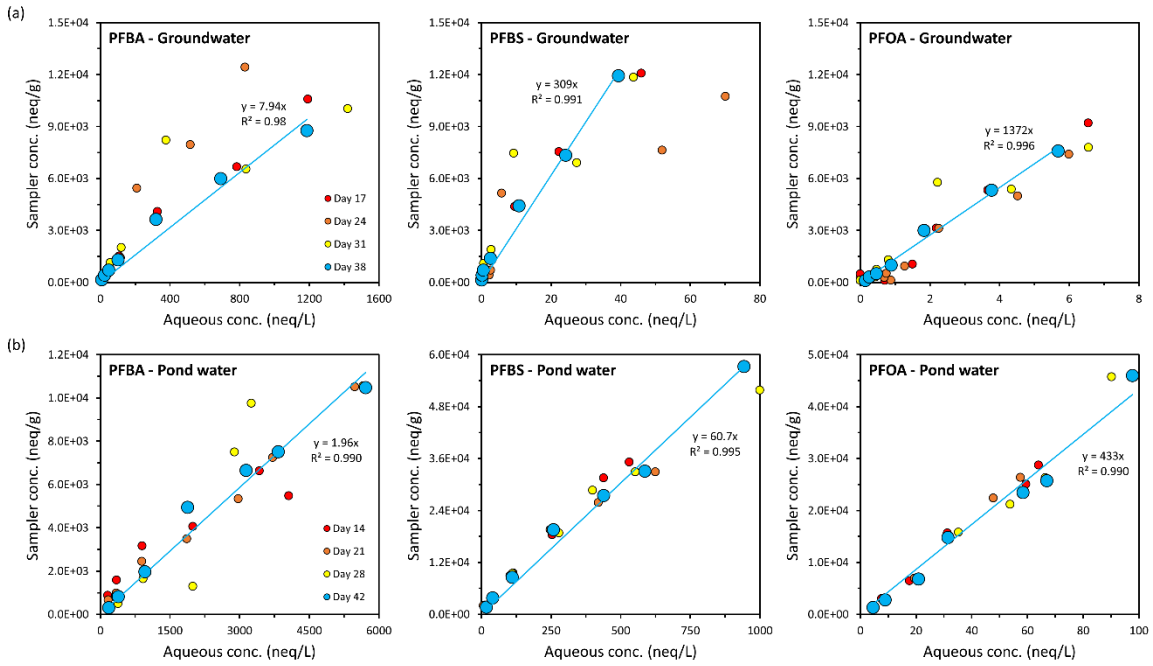

Figure 8. PFAS concentrations in the FAD-PET-75 passive sampler plotted against PFAS concentrations in (a) groundwater and (b) pond water for different contact times.

In the pond water matrix, the PFAS concentrations in the passive sampler were similar after 14, 21, 28, and 42 days (Figure 8b). These results suggest that the more complex pond water matrix, which exerts more competition for anion-exchange sites, provides a quicker equilibration period for PFAS uptake. As noted above, the pond water contained more Cl^- than the groundwater and resulted in more competitive effects. The slope of the sampler-phase concentration plotted against the aqueous-phase concentration is equal to the apparent distribution coefficient (K_d value). For ion-exchange reactions, the K_d parameter is clearly influenced by the source water chemistry.

5.3.2. Matrix effects on selectivity coefficients for PFAS over chloride

We conducted additional studies with the groundwater solution spiked with 10 mM NaCl, and the details are available in Figure A13 of Appendix A. The results indicated that the selectivity coefficient changed between groundwater and groundwater + 10 mM NaCl. While the selectivity coefficient is not directly affected by competition from other anions (Eq. 1), this parameter can be influenced by water quality. For

example, the selectivity coefficient is a function of the total salt concentration. This dependence stems from changes in PFAS activity coefficients in solutions with higher ionic strength. The activity coefficient of PFAS in salty solutions ($\gamma_{PFAS,w,salt}$) can be related to that in dilute solutions ($\gamma_{PFAS,w}$) using Eq. 4, wherein K^s_{PFAS} is the Setschenow constant and $[salt]_{tot}$ is the total salt concentration. According to Eq. 4, a higher salt concentration increases the activity coefficient of PFAS in water, leading to "salting out effects" which have been widely reported for other systems and contaminants. The Setschenow constant can be used to adjust the selectivity coefficient for solutions with different salt content (Eq. 5).

$$\gamma_{PFAS,w,salt} = \left(10^{+K^s_{PFAS}[salt]_{tot}}\right) \gamma_{PFAS,w} \quad \text{(Eq. 4)}$$

$$K^{PFAS}_{Cl}\big|_{salt} = \left(10^{+K^s_{PFAS}[salt]_{tot}}\right) K^{PFAS}_{Cl} \quad \text{(Eq. 5)}$$

The selectivity coefficients of 19 PFAS in the groundwater, groundwater + 10 mM NaCl, and pond water systems are plotted against those in deionized (DI) water + 10 mM NaCl in Figure 9. The as-measured selectivity coefficients were lower in groundwater than in the groundwater + 10 mM NaCl and DI water + 10 mM NaCl systems (Figure 9a). The selectivity coefficients in the groundwater were corrected to a 10 mM NaCl baseline by calculating one K^s_{PFAS} value for all PFAS. The fitted K^s_{PFAS} value was equal to 151, and the resulting selectivity coefficients aligned with the groundwater + 10 mM NaCl and DI water + 10 mM NaCl systems (Figure 9b). In Figure 9c, the selectivity coefficients for PFAS over chloride in pond water were similar for differently sized membrane coupons (*i.e.*, 1×1 cm^2, 2×1 cm^2) and well aligned with the DI water + 10 mM NaCl system. Figure 9d reinforces the appropriate application of one (salt-corrected) selectivity coefficient to describe PFAS equilibrium in different source waters.

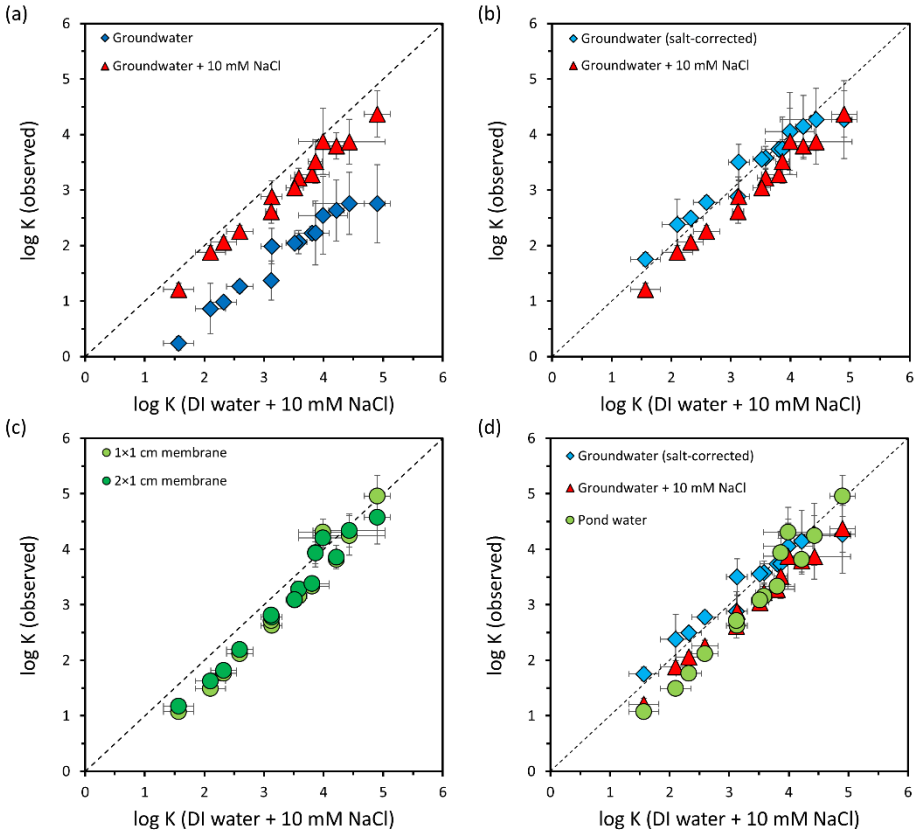

Figure 9. The selectivity coefficients for 19 PFAS over Cl^- in (a,b,d) groundwater, (a,b,d) groundwater + 10 mM NaCl, and (c,d) pond water plotted against those in DI water with 10 mM NaCl. The dashed lines indicate the 1:1 relationship, wherein the selectivity coefficients measured in real water matrices were equivalent to those in

DI water + 10 mM NaCl. Since the data group around the 1:1 line, the passive samplers can be calibrated in clean synthetic solutions and effectively applied to real source waters.

5.3.3. Improving PFAS extraction from the passive samplers

Effective extraction of PFAS from the passive samplers is crucial for accurate quantitation of PFAS concentrations. Our initial efforts with the AMI-7001 anion-exchange membrane focused on extractants containing salt (*e.g.*, NH_4Ac, NaCl) and solvent (*e.g.*, methanol, acetonitrile); however, we were not achieving high recovery of all PFAS. An improved protocol was developed for the FAD-75 membrane by dissolving the membrane in methanol, which effectively released all PFAS. More details are available in Section A3.2 of Appendix A.

5.4. Objective 4 Results

No specific tasks were identified for Objective 4 since this objective was planned to be studied in Phase 2. However, we believe that our successful deployment of anion-exchange membranes for passive sampling of anionic PFAS provides important validation of the proof-of-concept that cation-exchange membranes can also be used as passive samplers for cationic and/or zwitterionic PFAS.

5.5. Objective 5 Results

Objective 5 involves the accurate performance of ion exchange-based passive samplers in both single- and multi-solute systems. While Objective 5 was not planned for inclusion in Phase 1, we were able to evaluate this concept using data collected from Objective 2 activities. Additional details are available in Section A4 of Appendix A.

5.6. Objective 6 Results

No specific tasks were identified for Objective 6 since this objective was planned to be studied in Phase 2. This objective is meant to assess the effects of solution pH, ionic strength, background ions (*e.g.*, Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-}, HCO_3^{-}, Cl^{-}, etc.), temperature, and dissolved organic matter on passive sampling of PFAS with ion-exchange membranes. Some of our Objective 3 data speak to these effects. In particular, experiments with groundwater and pond water highlighted that the major impacts of real water quality parameters stemmed from ionic strength (see Figure 8, Figure 9, and others in Appendix A).

5.7. Objective 7 Results

The main goal of Objective 7 is to validate the performance of the ion-exchange membrane passive samplers in laboratory-based mesocosms. In this regard, we have developed prototype samplers and deployed them in large-volume equilibrium studies. Additional details are available in Section A5 of Appendix A.

6. IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Based on the aggregate experimental results and findings from the Phase 1 (May 2020 to August 2021) studies, we are excited to continue this project. We were able to successfully (i) apply ion-exchange membranes for passive sampling of PFAS, (ii) determine selectivity coefficients for PFAS to the ion-exchange membranes, and (iii) deploy the ion-exchange membranes in bench- and prototype-scale configurations for PFAS passive sampling in synthetic and real water sources. As these three criteria were central to the "go/no go" decision planned to inform the decision about whether we would proceed from Phase 1 to Phase 2, we hope that SERDP agrees with the promise of our novel approach to passive sampling of PFAS. We are eager to continue this work and look forward to receiving feedback on our Phase 1 work and interest in a Phase 2 proposal. In the meantime, we will be happy to address any questions or concerns. We prioritized this report over publications, but we are currently preparing manuscripts documenting the results of Phase 1 studies.

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APPENDIX A: SUPPORTING DATA

A1. Additional Results and Discussion from Objective 1

A1.1. Evaluation of equilibrium times

Batch kinetics tests were conducted with 100 µg L^{-1} (each) of 12 PFAS in 10 and 100 mM NaCl solutions. For these experiments, we focused on six perfluoroalkyl carboxylates (*i.e.*, PFBA, PFHxA, PFOA, PFDA, PFDoA, and PFTreA), three perfluoroalkyl sulfonates (*i.e.*, PFBS, PFHxS, and PFOS), FtS 6:2, PFOSA, and NEtFOSAA. The change in aqueous-phase concentration over time is shown for 10/12 PFAS in Figure A1. Note, PFHxA and PFHxS demonstrated high signal suppression for this particular experiment and were, therefore, excluded from this time-based analysis. The analytical issues with PFHxA and PFHxS were resolved, and these compounds are reported elsewhere in this report.

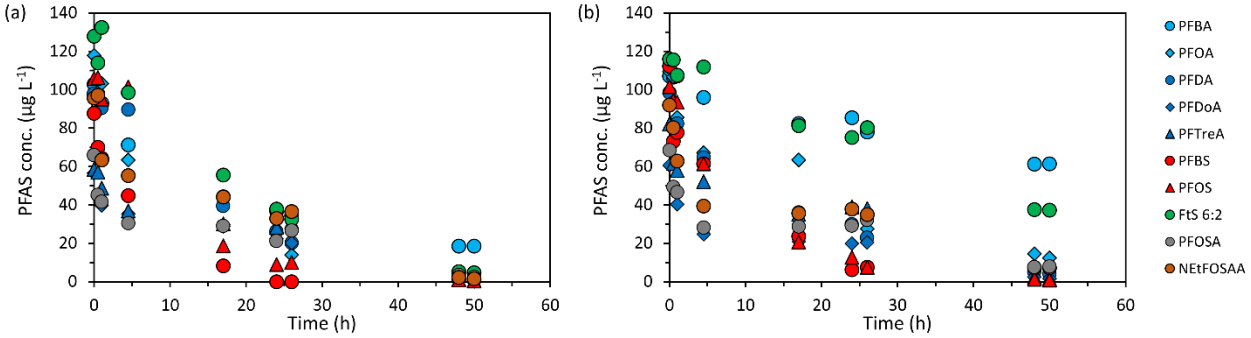

Figure A1. Sorption kinetics of select PFAS to the AMI-7001 membrane in (a) 10 mM NaCl and (b) 100 mM NaCl. The nominal initial PFAS concentration was 100 µg L^{-1} (each), and the pH was approximately 6.0. Quality control experiments suggested that PFDoA, PFTreA, PFOSA, and NEtFOSAA interacted with the high-density polyethylene (HDPE) containers; therefore, the change in concentration for these PFAS involved both uptake by the anion-exchange membranes and interactions with the containers. For this reason, PFDoA, PFTreA, PFOSA, and NEtFOSAA were not included in kinetics analysis (as described above).

The data in Figure A1 indicated the rapid uptake of PFAS by the AMI-7001 anion-exchange membrane for solutions with background matrices comprised of 10 mM NaCl and 100 mM NaCl. The two different NaCl concentrations were used to determine the effects of background anions on PFAS uptake. As expected, Cl^- exhibited more competition in the 100 mM NaCl solution, leading to slower PFAS sorption kinetics and lower membrane-phase concentrations after 50 h of contact for most of the PFAS. These results reinforced ion exchange as the primary uptake mechanism, since the higher ionic strength of the 100 mM NaCl solution did not cause "salting out" of PFAS, which would be expected for partitioning mechanisms. For the 100 mM NaCl solution, PFAS uptake was still fairly high, ranging from 17 µg g^{-1} (for PFBA) to 39 µg g^{-1} (for PFBS), indicating the strong membrane affinity for PFAS over background inorganic anions and the relatively consistent uptake of PFAS with different polar head groups and chain lengths (another expected outcome of ion-exchange mechanisms). These characteristics are necessary aspects of passive samplers for chemically diverse PFAS. In fact, more than 95% of all PFAS, except PFBA (82%) were adsorbed by the anion-exchange membranes in the 10 mM NaCl condition. These findings suggest that the PFAS concentrations in the membrane phase may have been limited by the initial mass of PFAS added to the solution. In the 100 mM NaCl solution, PFOS, PFDA, PFDoA, and PFTreA were the only PFAS that exhibited more than 95% adsorption. As we discuss below, these molecules demonstrated higher affinities for the quaternary ammonium anion-exchange groups of the membrane.

A1.2. PFAS sorption isotherms

The selectivity coefficient, which is the equilibrium constant associated with Rxn. 1, serves as the fundamental parameter that guides PFAS uptake by the anion-exchange membranes. Therefore, we calculated selectivity coefficients for PFAS anions over chloride (see Eq. 1). The PFAS selectivity coefficients for the 10 mM NaCl and 100 mM NaCl solutions are reported in Figure A2.

$$\overline{R^+Cl^-} + PFAS^- \rightleftharpoons \overline{R^+PFAS^-} + Cl^- \qquad \text{(Rxn. 1)}$$

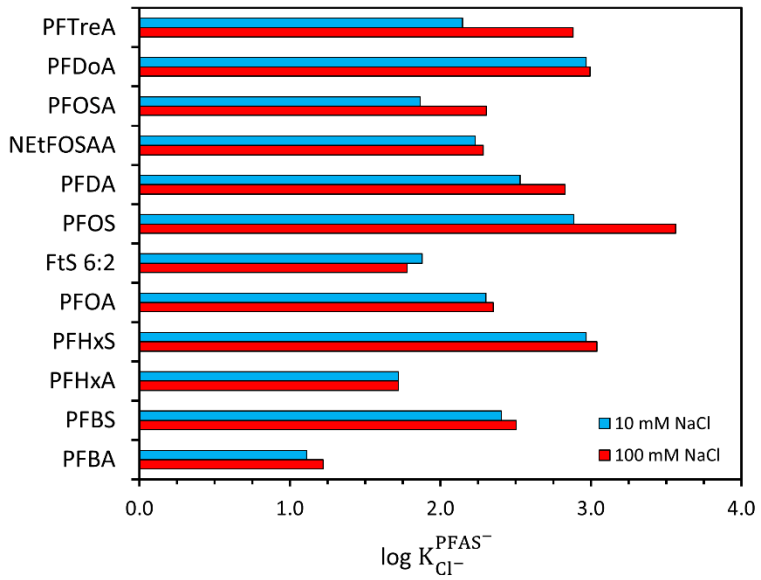

Figure A2. Selectivity coefficients of the AMI-7001 anion-exchange membrane for PFAS over chloride in 10 mM NaCl and 100 mM NaCl solutions.

The data in Figure A2 demonstrated the strong potential of anion-exchange membranes to serve as "global" passive samplers for chemically diverse PFAS. In particular, the log values of the selectivity coefficients were in the 1.5-3.0 range for most PFAS. These results indicated the highly selective uptake of PFAS over background anions like Cl^-. The experimental results in Figure A1 validated these conclusions and further highlighted the relatively rapid uptake kinetics of PFAS into anion-exchange membranes. Nevertheless, we hypothesized that the PFAS uptake capacity, and potentially selectivity coefficients, could be improved through the use of anion-exchange fibers, which have a higher surface area-to-volume ratio than anion-exchange membranes.

A1.3. Performance of anion-exchange fibers as passive samplers for PFAS

Batch sorption tests were conducted to determine PFAS uptake kinetics onto Mion AK-22 anion-exchange fibers. HDPE bottles were loaded with 100-mL solutions containing 12 PFAS of concern, namely PFBA, PFBS, PFHxA, PFHxS, PFOA, FtS 6:2, PFOS, PFDA, NEtFOSAA, PFOSA, PFDoA, and PFTreA. The nominal initial concentration of each PFAS was 100 µg L^{-1}; however, control studies indicated that NEtFOSAA, PFOSA, PFDoA, and PFTreA interacted with the HDPE containers (same as above). Due to these interfering effects, the uptake and selectivity of these four PFAS by the anion-exchange fibers were not quantified for this initial set of experiments. All experiments were completed at pH ~6 and room temperature (22 ± 3) °C. All conditions were tested in triplicate, and samples were periodically extracted to measure aqueous-phase PFAS concentrations.

Data for PFOS and PFDA (as two representative PFAS) are shown below in Figure A3. The data in Figure A3a correspond to a solution containing 100 µg L^{-1} (each) of the 12 PFAS of concern, 100 mM

Cl^-, and 100 mg of anion-exchange fibers. The background Cl^- concentration was meant to represent a high-salinity solution with maximum competition for ion-exchange sites. The data from this experiment suggested that PFAS achieved a rapid equilibrium in the anion-exchange fibers, specifically within 24 hr. The sorption capacities were approximately 30 µg g^{-1} for PFOS and PFDA, indicating that even in high-salinity solutions, 1 g of anion-exchange fibers could accumulate 30 µg of individual PFAS molecules. This mass is sufficient for the subsequent quantitation and back-calculation of aqueous-phase concentrations needed for passive sampling protocols. The experimental results in Figure A3b highlighted similar findings for solutions with 10 mM Cl^-. Overall, minor differences were observed in PFAS uptake kinetics and capacities in the presence of different background Cl^- concentrations.

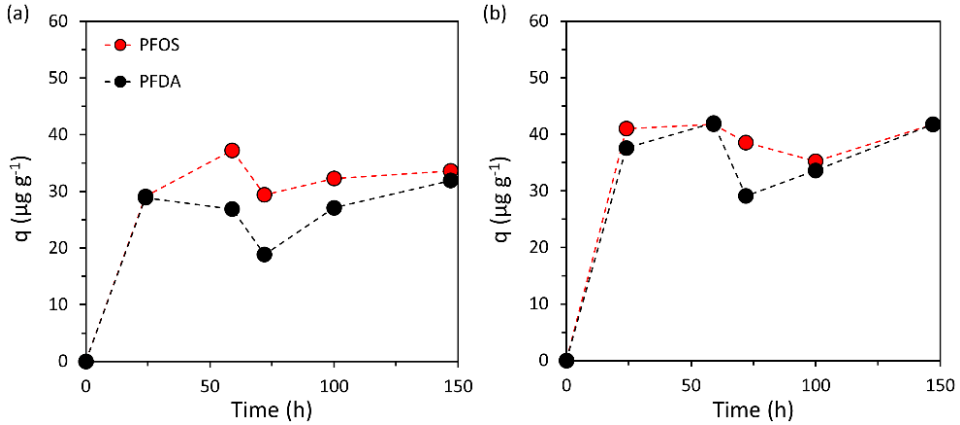

Figure A3. The anion-exchange fiber-phase PFAS concentrations with (a) 100 mM and (b) 10 mM NaCl with 100 mg of anion-exchange fibers.

Data from the aforementioned experiments were used to calculate selectivity coefficients for the anion-exchange fibers using Eq. 1. The selectivity coefficients for PFDA, PFOS, FtS 6:2, PFOA, PFHxS, PFHxA, and PFBS are shown in Figure A4 for the 10 mM NaCl and 100 mM NaCl solutions. The selectivity coefficients inconsistently varied in the presence of the higher Cl^- solution, suggesting that the performance of the anion-exchange fibers for PFAS uptake was prone to water quality effects. Based on these findings, we concluded that anion-exchange fibers were not suitable for environmental applications and ceased investigation of the fibers.

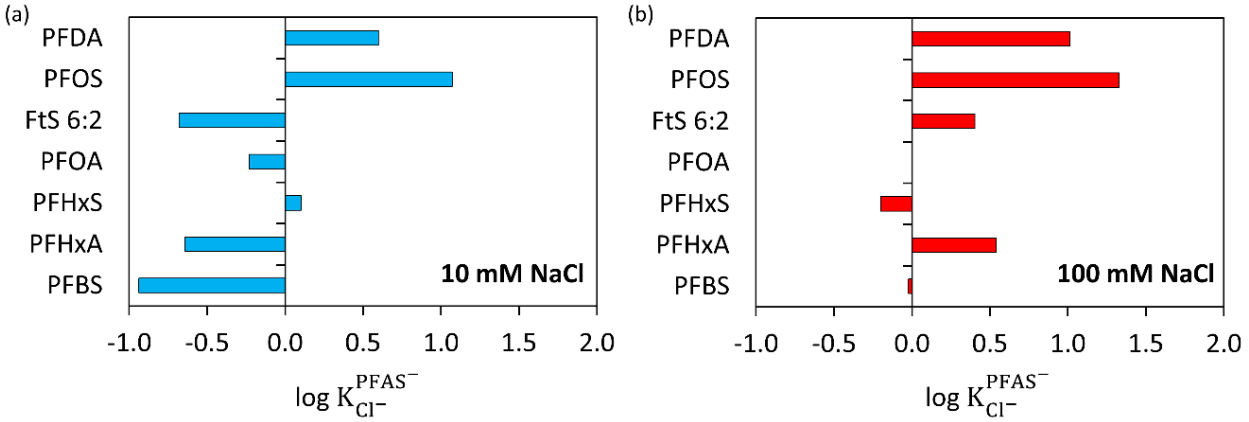

Figure A4. Apparent selectivity coefficients for PFAS over chloride for Mion AK-22 anion-exchange fibers. The anion-exchange fibers (100 mg) were exposed to a mixture of PFAS for 147 hours in (a) 10 mM NaCl or (b) 100 mM NaCl.

To determine whether anion-exchange fibers have any advantage over anion-exchange membranes, we compared the selectivity coefficients for the Mion AK-22 anion-exchange fibers to two anion-exchange membranes, namely AMI-7001 and FAA-3-PK-130. All tests were conducted in 100-mL solutions with 12 PFAS at 100 µg L^{-1} (each) and 100 mM NaCl. The mass of anion-exchange fibers was 100 mg (equivalent to ~ 0.57 meq of exchange capacity); similarly, the AMI-7001 and FAA-3-PK-130 membrane coupons (2 cm × 2 cm) were prepared with ~0.35 meq and ~0.06 meq, respectively, of exchange capacity. The data in Figure A5 showcase the superior selectivity of anion-exchange membranes compared to anion-exchange fibers. The anion-exchange fibers did exhibit better uptake kinetics; however, the anion-exchange membranes are still able to provide much faster PFAS uptake compared to traditional passive sampling materials (*e.g.*, polyethylene). In addition, the anion-exchange fibers were fairly loose and tended to shed in the reactors, raising concerns about their robustness for use in environmental applications. The relative benefits of the faster uptake kinetics by the anion-exchange fibers were, therefore, deemed less important than the greater robustness and selectivity for PFAS of the anion-exchange membranes.

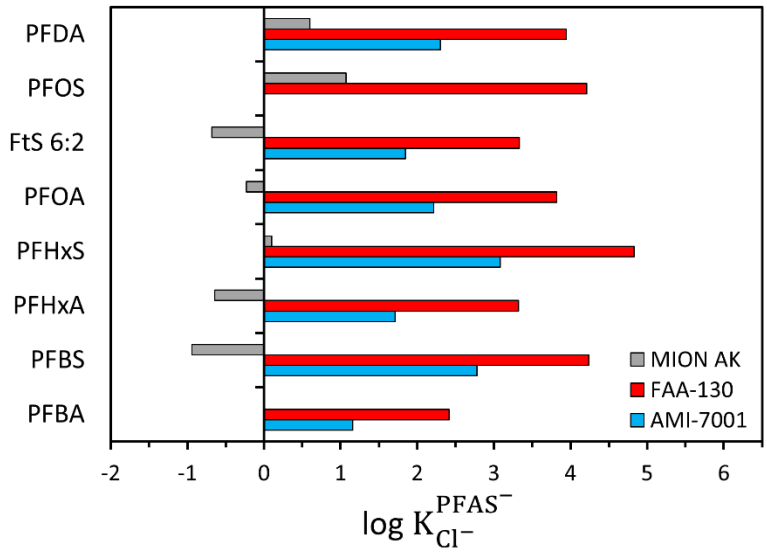

Figure A5. Selectivity coefficients for select PFAS in the Mion AK-22 anion-exchange fibers and FAA-3-PK-130 and AMI-7001 anion-exchange membranes for solutions with 100 µg L^{-1} PFAS and 100 mM NaCl.

A2. Additional Results and Discussion from Objective 2

A.2.1. The dominant uptake mechanism was confirmed to be ion exchange

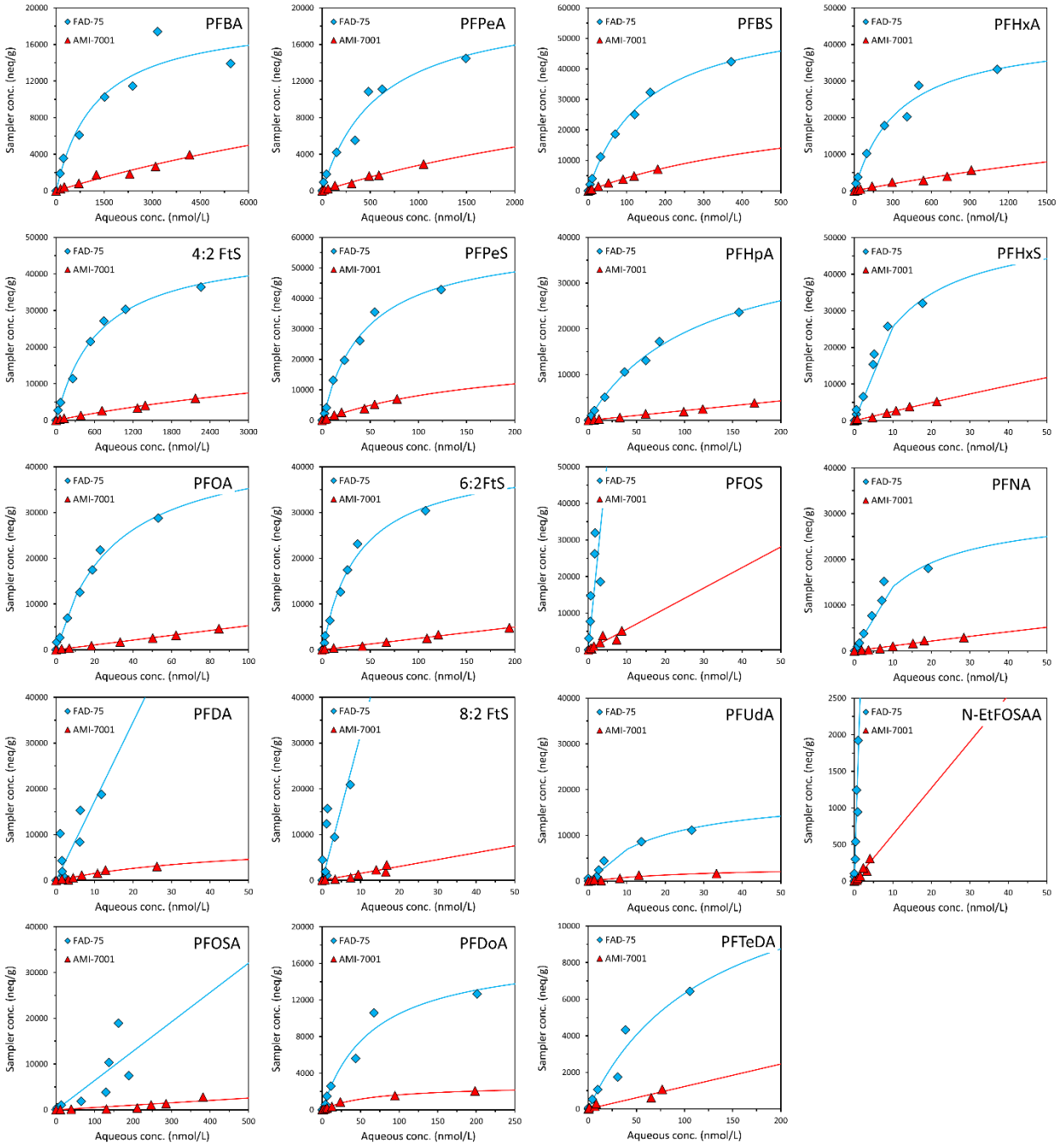

Figure A6. Sorption isotherms for the PFAS analytes in the FAD-75 and AMI-7001 membranes. These isotherms were developed using data from 30 d of contact time. For most cases, the Langmuir isotherm was fit to the experimental data. For the following cases, the linear isotherm was employed: PFOS (FAD-75 and AMI-7001); PFDA (FAD-75); 8:2 FtS (FAD-75 and AMI-7001); N-EtFOSAA (FAD-75 and AMI-7001); PFOSA (FAD-75 and AMI-7001); and, PFTeDA (AMI-7001). The linear isotherms were generally applied to PFAS that exhibited low aqueous-phase concentrations for the tested conditions. As such conditions overlap with the linear portion of the Langmuir isotherm, we do not have concerns about differences in uptake mechanism. For typical environmental PFAS concentrations, passive samplers will likely operate in the linear range of the Langmuir isotherm.

A2.2. Comparison of different anion-exchange membranes

Based on the strong performance of FAD-75 (above), we wanted to evaluate similar membrane chemistries to determine the optimal properties of anion-exchange membranes with respect to their use as passive samplers for PFAS. In this regard, we procured nine different anion-exchange membranes (see Table A1). These particular membranes were selected for study due to the differences in anion-exchange capacity, membrane thickness, and reinforcement material. The differences in anion-exchange capacity were expected to not only affect the overall uptake of PFAS by the membrane, but also the selectivity of the membranes for PFAS over background anions. The membrane thickness impacts the overall capacity (*e.g.*, µg of PFAS), but membrane thickness and reinforcement material also play a crucial role in membrane robustness for environmental applications.

Table A1. Manufacturer reported properties of nine anion-exchange membranes. Note that the first set of letters in the membrane name corresponds to the specific ion-exchange polymer, the second set of letters corresponds to the composition of the reinforcement material, and the last number corresponds to the membrane thickness.

Membrane name	FAA-3-PK-75	FAA-3-PK-130	FAB-PK-130	FAD-PET-75	FAAM-15	FAS-50	FAA-3-PE-30	FAA-3-50	FAP-450
Anion-exchange capacity (meq g^{-1})	1.2 – 1.4	1.25 ± 0.15	0.7 - 1.0	2.0 - 2.3	-	1.6 – 2.0	1.4 - 1.6	2.02	-
Mass per area (mg cm^{-2})	7.0 – 9.0	10 – 13	10 – 13	7.0 – 8.5	-	6.0 – 8.5	2.0 – 2.8	-	7.5 – 8.5
Chemical stability (pH)	0 - 14	0 – 14	0 -14	-	-	-	-	-	-
Standard thickness (µm)	70 - 80	110 - 130	110 - 140	60 - 80	13 - 17	45 - 55	20 - 30	50	50
Reinforcement	PK [a]	PK	PK	PET [b]	None	None	PE [c]	PET	Paper

a: polyketone; b: polyethylene terephthalate; c: polyethylene

In this section, we have focused our discussion on four particular membranes (*i.e.*, FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, FAD-PET-75). We generated 100-mL solutions containing 100 µg L^{-1} of 19 PFAS (*i.e.*, PFBA, PFPeA, PFBS, PFHxA, 4:2 FtS, PFPeS, PFHpA, PFHxS, PFOA, 6:2 FtS, PFNA, PFOS, PFDA, 8:2 FtS, PFUdA, NEtFOSAA, PFOSA, PFDoA, PFTeDA). The solutions also contained 1 mM NaCl or 100 mM NaCl, and the pH was approximately 6.0. Membrane coupons were cut to add a similar amount of anion-exchange sites into each reactor; in particular, the size of the membrane coupons were selected to achieve 0.007-0.027 meq of exchange sites in the 1 mM NaCl solution and 0.008-0.051 meq of exchange sites in the 100 mM NaCl solution. The membranes were generally cut into 1×1, 1×2, or 2×2 cm^2 coupons. Samples were collected at predetermined times to determine the PFAS concentrations in the aqueous phase. A separate control reactor (no anion-exchange membrane) was included.

Figure A7 reports the change in aqueous-phase concentration for 15/19 PFAS over a 10-d experiment; the other four compounds (*e.g.*, NEtFOSAA, PFOSA, PFDoA, PFTeDA) were excluded from this time-based analysis for the reasons noted above. In general, the aqueous-phase PFAS concentrations in Figure A7 highlighted the variable sorption of short-chain molecules (less removal) compared to long-chain molecules (high removal). In addition, the data suggested that FAB-PK-130 had a lower potential to sorb PFAS from water compared to FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75. For FAA-3-PK-130

and FAD-PET-75, only minor changes in PFAS concentration were observed between 72 h and 240 h. These results suggest that equilibrium was rapidly established, reinforcing the conclusions from the aforementioned experiments with AMI-7001.

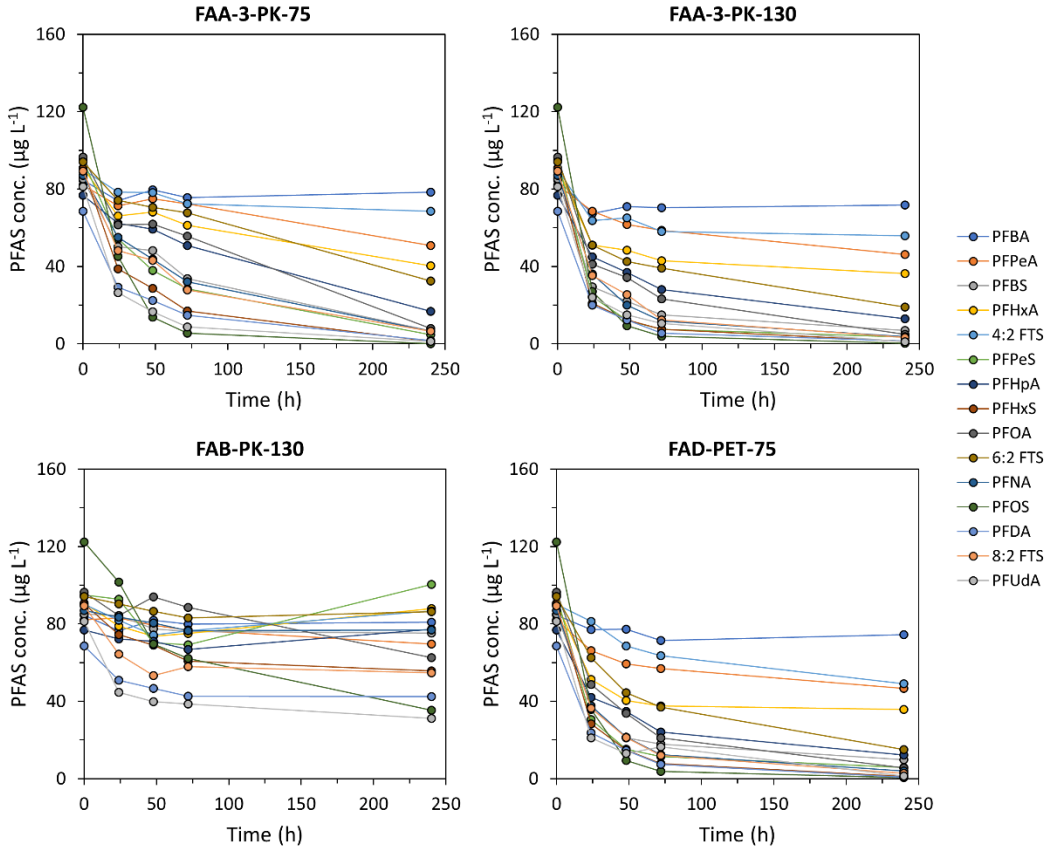

Figure A7. Aqueous-phase PFAS concentration profiles for FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 anion-exchange membranes in 100 mM NaCl solutions.

The decrease in aqueous-phase PFAS concentrations shown in Figure A7 provided insight into membrane performance; however, the differences between membrane performance are more clearly highlighted in Figure A8. The lower PFAS uptake in FAB-PK-130 was verified and indicated that this membrane will not be suitable for environmental analysis of PFAS via passive sampling. The FAA-3-PK-130 and FAD-PET-75 membranes exhibited similar performance, with maximum sorption capacities of 1070-1080 µg g^{-1} for PFOS. In fact, PFOS was the most preferred PFAS for all four membranes. The higher PFOS concentrations in FAA-3-PK-75 (up to 1950 µg g^{-1}) stemmed from the thinner membrane, which caused less "dilution" of the sorbed PFAS in the membrane phase. A deeper analysis of the PFOS concentrations suggested mass limitations related to the analytical limits of quantitation. To assess these limits, we plotted the equilibrium capacity for all 15 PFAS in all four membranes, along with the capacity calculated for complete PFAS accumulation (*i.e.*, the scenario wherein 100% of the PFAS mass added to the solution is taken up in the anion-exchange membrane), in Figure A9.

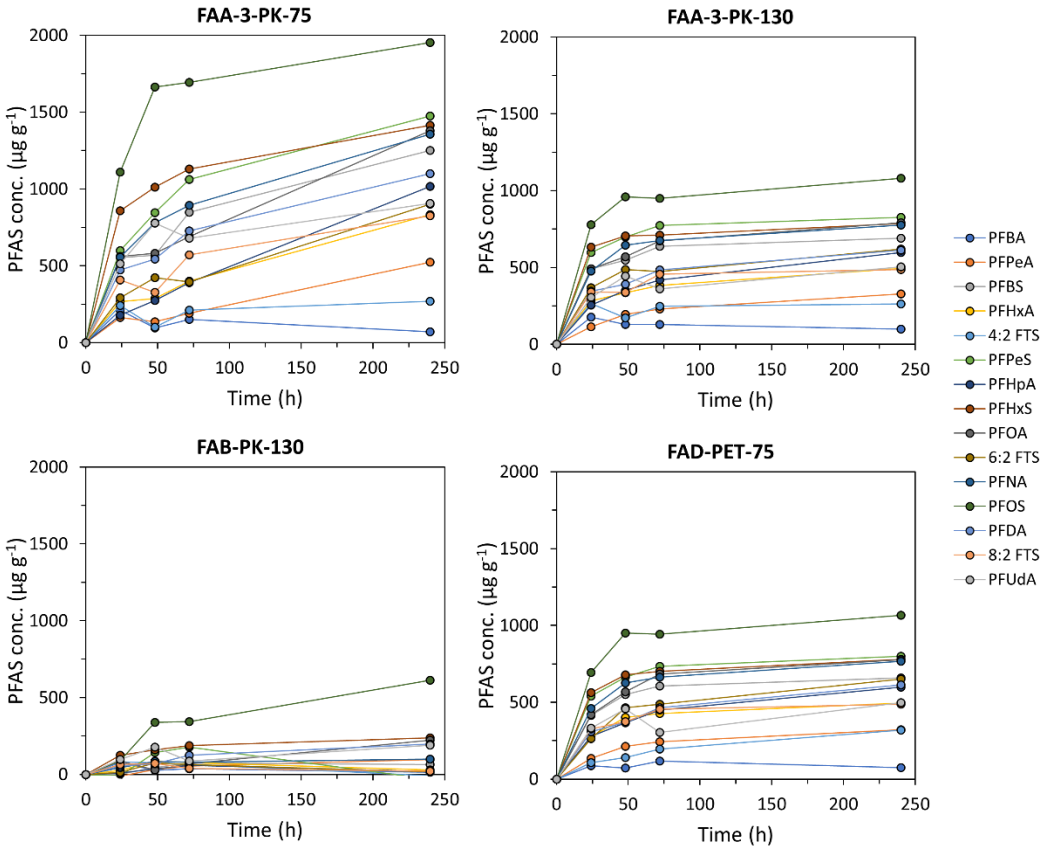

Figure A8. Membrane-phase PFAS concentration profiles for FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 anion-exchange membranes in 100 mM NaCl solutions.

The data in Figure A9 indicate that the perfluorosulfonic acids were almost completely taken up by the FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75 anion-exchange membranes. Similar results were recorded for perfluorocarboxylic acids with eight or more carbons (*i.e.*, PFOA, PFNA, PFDA, PFUdA). On the other hand, the short-chain perfluorocarboxylic acids (*i.e.*, PFBA, PFPeA, PFHxA, PFHpA) and fluorotelomer sulfonates (*i.e.*, FtS 4:2, FtS 6:2) were only partially sorbed. Overall, these results were promising and suggested that FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75 may all serve as potential options for development as PFAS passive samplers.

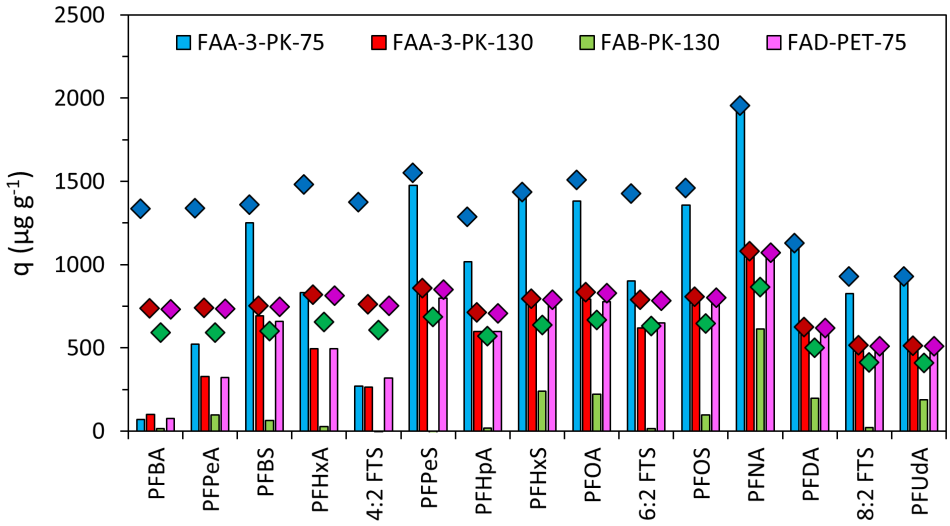

Figure A9. The equilibrium capacity of the FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 anion-exchange membranes for 15 PFAS (columns) are plotted with the capacity calculated for 100% PFAS uptake into the anion-exchange membranes (diamonds). The initial solutions contained 100 µg L^{-1} PFAS, 0.008-0.051 meq of exchange sites (dependent on membrane and coupon size), and 100 mM NaCl.

A2.3. Trends in selectivity coefficients for PFAS over chloride

Based on the good performance of the FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75 anion-exchange membranes, we calculated the selectivity coefficients for the PFAS of concern in these membranes using Eq. 1. The results are shown in Figure A10 as a function of carbon number and class (*i.e.*, perfluoro-carboxylic acids, perfluorosulfonic acids, and fluorotelomer sulfonates). The results indicated that the selectivity coefficients for the three anion-exchange membranes collapsed onto each other (with two exceptions, PFDA and PFOS). Furthermore, the data in Figure A10 showed obvious trends with carbon number, providing key information that enables extension of these results to other PFAS. This result supports further development of anion-exchange membrane based passive samplers due to the potential for model development to account for selectivity coefficients of non-target PFAS molecules.

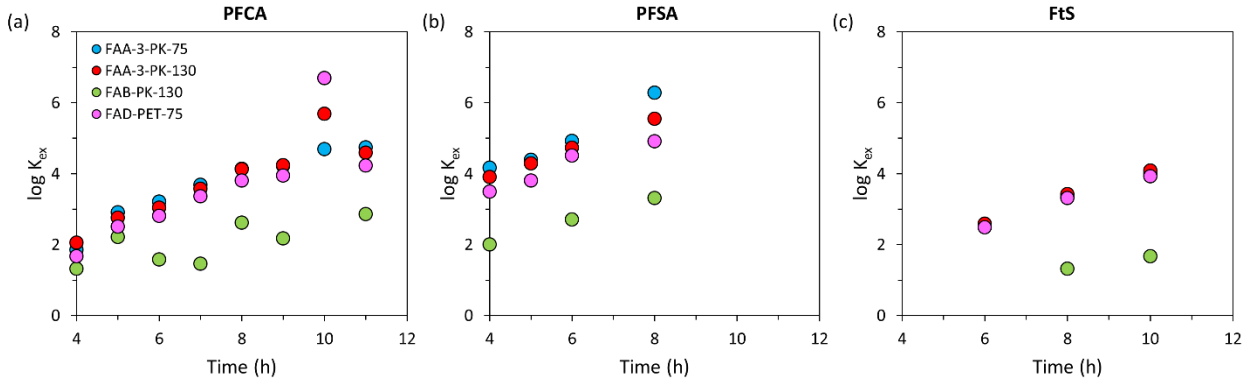

Figure A10. Trends in PFAS selectivity coefficients in the FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 anion-exchange membranes as a function of class and carbon number.

Given the observed selectivity coefficients for PFAS anions over Cl^- in the 100 mM NaCl solution, we decided to lower the background solution to 1 mM NaCl to identify the impacts of the competing anion concentration. The data shown in Figure A11 indicated that the FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75 anion-exchange membranes effectively sorbed all of the PFAS added into the solution

(considering the limits of quantitation), with the exception of PFBA (90-91%). This performance clearly showcased the impact of Cl^- competition on PFBA, PFPeA, PFHxA, PFHpA, FtS 4:2, and FtS 6:2 in the 100 mM NaCl solution. Even with the lower NaCl concentration, the FAB-PK-130 anion-exchange membrane demonstrated a much lower sorption capacity for PFAS. This result may stem from the lower anion-exchange capacity of FAB-PK-130 (0.85 meq g^{-1}) in relation to the other membranes (1.2 – 2.3 meq g^{-1}), but the mechanistic reasons for the large differences in uptake are unknown. Overall, the experimental results for the FAA-3-PK-75, FAA-3-PK-130, and FAD-PET-75 anion-exchange membranes reinforce the strong potential for use as passive samplers for PFAS.

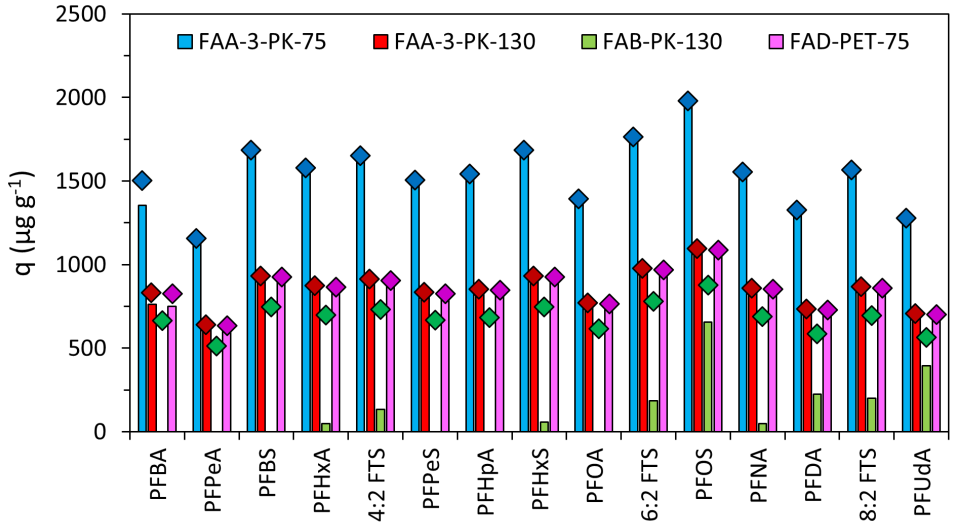

Figure A11. The equilibrium capacity of the FAA-3-PK-75, FAA-3-PK-130, FAB-PK-130, and FAD-PET-75 anion-exchange membranes for 15 PFAS (columns) are plotted with the capacity calculated for 100% PFAS accumulation in the anion-exchange membranes (diamonds). The initial solutions contained 100 µg L^{-1} PFAS, 0.007-0.027 meq of exchange sites (dependent on membrane and coupon size), and 1 mM NaCl.

A2.4. Further confirmation of ion-exchange mechanism via desorption studies

The aforementioned data suggested that ion-exchange mechanisms were prevalent; however, due to the properties of PFAS, both electrostatic and hydrophobic partitioning reactions are theoretically possible. For that reason, we conducted a series of sequential PFAS extractions from anion-exchange membranes that had been previously loaded with a mixture of PFAS. This approach allowed us to separately assess the ion exchange and hydrophobic partitioning mechanisms. The results in Figure A12 confirmed that ion exchange was the primary sorption mechanism, but methanol was required to facilitate desorption of longer-chain PFAS.

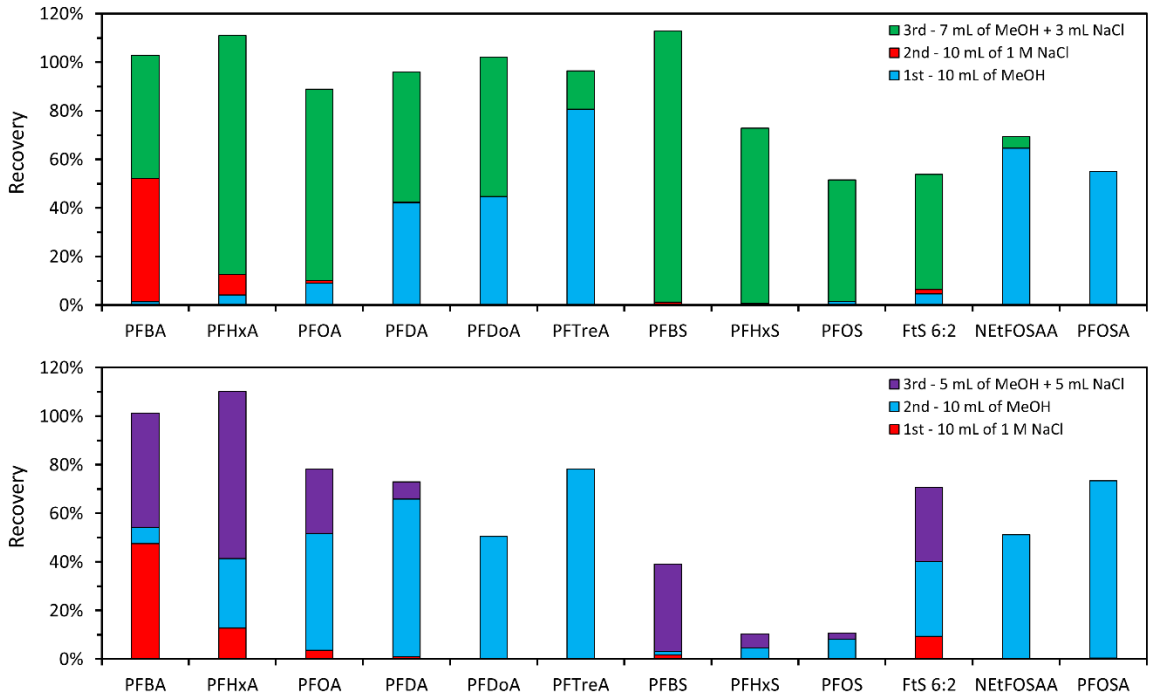

Figure A12. PFAS recovery efficiency from FAA membranes for the sequential extraction steps: (top) 10 mL methanol, followed by 10 mL of 1 M NaCl, followed by a mixture of 7 mL methanol and 3 mL 1 M NaCl; and, (bottom) 10 mL of 1 M NaCl, followed by 10 mL methanol, followed by a mixture of 5 mL methanol and 5 mL 1 M NaCl.

A3. Additional Results and Discussion from Objective 3

A3.1. Matrix effects on selectivity coefficients for PFAS over chloride

As noted above, the apparent K_d value varied in the groundwater and pond water matrices. This result was expected due to the different chemistries of the two source waters. In particular, the apparent K_d value was affected by the presence of other anions that compete with PFAS for the quaternary ammonium sites of the anion-exchange membrane. To highlight these effects, we conducted additional studies with the groundwater solution spiked with 10 mM NaCl. In Figure A13, the sampler-phase PFAS concentrations are plotted against the aqueous-phase PFAS concentrations for the original groundwater and the groundwater with 10 mM NaCl. Note, the scale of the x- and y-axes were held constant for each PFAS in Figure A13 to highlight the effects of the additional Cl^- on PFAS uptake in the passive sampler. A careful examination indicated that the apparent K_d values decreased by a factor of ~3.3 when 10 mM NaCl was spiked into the groundwater. Interestingly, the PFBA and PFBS concentrations in the membrane stabilized much faster in the presence of higher Cl^- concentrations, similar to the results reported for the pond water system in Figure 8b. This finding suggests faster equilibration in real waters, a potential benefit of the anion-exchange membrane passive samplers. Importantly, the data also emphasize the stability of PFAS in the ion-exchange membrane over longer deployment times.

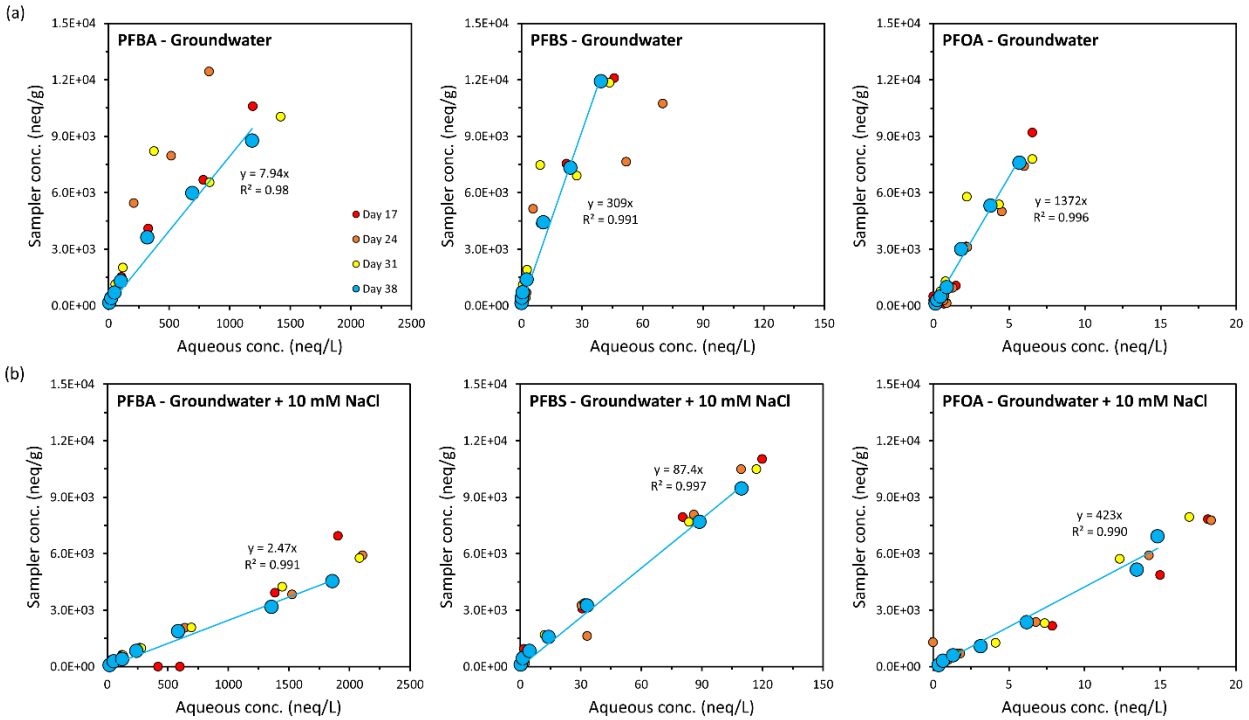

Figure A13. PFAS concentrations in the passive sampler plotted against the aqueous-phase concentrations in (a) groundwater and (b) groundwater with 10 mM NaCl. Note, the x- and y-axes are identically scaled in (a) and (b) to emphasize the change in PFAS uptake with the added NaCl. The legend in (a) also applies to (b).

In general, the K_d values described above are only appropriate for passive sampling reactions that resemble Rxn. 2. The ion-exchange reactions involved with the reported passive sampler can be better represented by Rxn. 1 (above), and the corresponding equilibrium constant is the selectivity coefficient.

$$PFAS_{aq} \rightleftharpoons PFAS_{mem} \qquad \text{(Rxn. 2)}$$

A3.2. Improving PFAS extraction from the passive samplers

Effective extraction of PFAS from the passive samplers is crucial for accurate quantitation of PFAS concentrations. Our initial efforts with the AMI-7001 anion-exchange membrane focused on extractants containing salt (*e.g.*, NH_4Ac, NaCl) and solvent (*e.g.*, methanol, acetonitrile). This approach was informed by current strategies for regenerating ion-exchange resins laden with PFAS. Importantly, the results of that work helped to confirm that ion exchange is the primary uptake mechanism. Since we decided to focus on the FAD-PET-75 anion-exchange membrane as our primary passive sampler, we revisited the PFAS extraction protocols. Figure A14 reports the baseline performance with 1 M NH_4Ac and, separately, methanol for five representative PFAS. As expected, the salt-only (NH_4Ac) extractant only provided partial removal of PFBA and 4:2 FtS, which have the lowest selectivity coefficients, for the AMI and FAD membranes. The methanol-only extract did not provide PFAS release from the AMI membrane, because the ion-exchange mechanism was inhibited in pure solvent due to electroneutrality constraints. In contrast, high extraction efficiencies (*e.g.*, 89-180%) were observed for methanol-based extraction of FAD membranes, but this result was driven by membrane dissolution in methanol. This finding changed our approach to PFAS quantitation in the membrane phase since the passive samplers will not be reused.

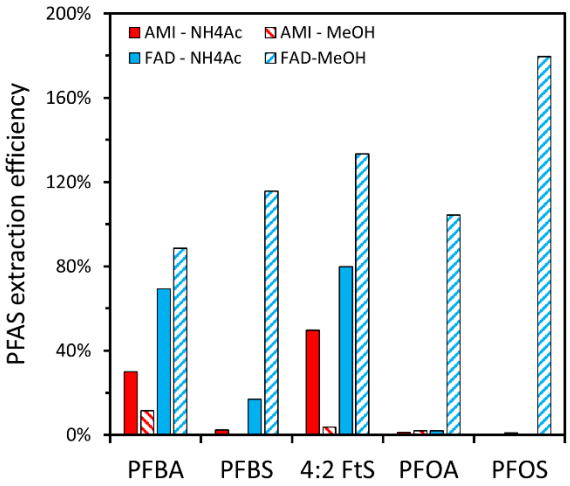

Figure A14. PFAS extraction from the AMI-7001 (AMI) and FAD-PET-75 (FAD) anion-exchange membranes with 1 M NH_4Ac and methanol (MeOH). Note, the FAD membrane dissolved in methanol, releasing the bound PFAS and ensuring high recovery.

A4. Additional Results and Discussion from Objective 5

Selectivity coefficients determined from multi-solute experiments were plotted against those from single-solute experiments with PFBA, PFBS, 4:2 FtS, PFOA, and PFOS. These experiments were conducted at seven conditions (for each PFAS), designed using the equilibrium relationships identified from the multi-solute tests. Figure A15 shows the relationships between the selectivity coefficients determined from single- and multi-solute experiments. As suggested by the figure, the selectivity coefficients were in good agreement with each other, reinforcing our approach to calculate these parameters using the multi-solute experiments (to save time and resources). More importantly, the relationship in Figure A15 indicates that PFAS will not interfere with each other in ion exchange-based passive samplers.

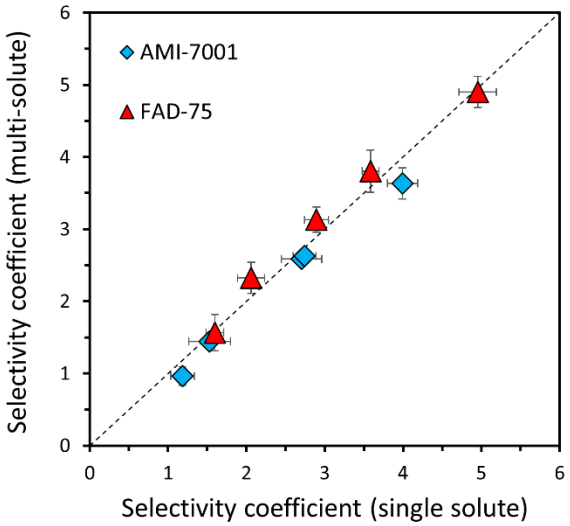

Figure A15. The selectivity coefficients calculated for PFBA, PFBS, 4:2FtS, PFOA, and PFOS in multi-solute experiments plotted against the same values determined by single-solute experiments. The good agreement confirms that the selectivity coefficients (Figure 4) and isotherms (Figure A6) reported above for multi-solute experiments can be applied to other conditions. The data in this figure generally stemmed from seven test conditions; however, the PFOA and PFOS data sets were more limited due to the low aqueous-phase concentrations, which prevented accurate calculation of selectivity coefficients for some conditions.

A5. Additional Results and Discussion from Objective 7

As shown in Figure A16, we have developed prototype passive sampling devices with FAD-75 membranes secured in stainless steel rings. These devices can be deployed in surface water, wells, sewers, or other locations. We have also constructed passive samplers with protective stainless steel (200 mesh, shown) and copper (not shown) screens to prevent damage to the membranes.

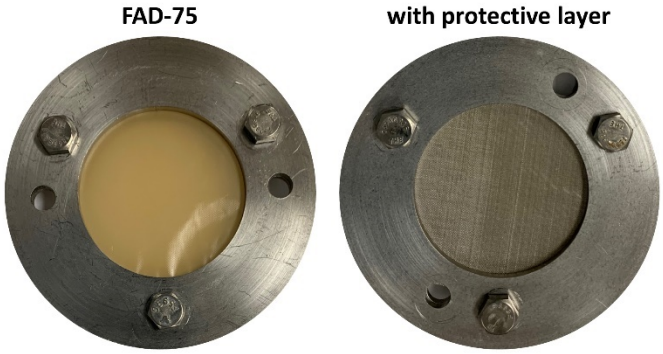

Figure A16. Passive sampler prototype devices for water sampling.

Figure A17 shows results from an experiment that employed three separate 1×1 cm^2 FAD coupons embedded in the passive sampler prototype device. The solution was comprised of pond water spiked with 10 PFAS at initial concentrations of 50-400 µg L^{-1}. The PFAS concentrations were designed to ensure quantitation of aqueous- and membrane-phase concentrations at equilibrium. The total solution volume was 10 L. After 21 d of contact, one of the FAD coupons was removed and analyzed for the sampler-phase PFAS concentrations. The relatively high concentrations of PFOS, 8:2 FtS, and PFHxS in the sampler were not surprising, because these PFAS analytes were spiked at higher initial concentrations (*i.e.*, 400, 250, and 100 µg L^{-1}, respectively). This decision stemmed from the greater selectivity coefficients of PFOS, 8:2 FtS, and PFHxS, which required higher initial concentrations to ensure accurate quantitation of the final equilibrium concentrations in the aqueous phase. Besides PFDA (100 µg L^{-1}) and the compounds noted above, all other PFAS were initially spiked at 50 µg L^{-1}. Importantly, all PFAS accumulated in the membranes at concentrations appropriate for quantitation.

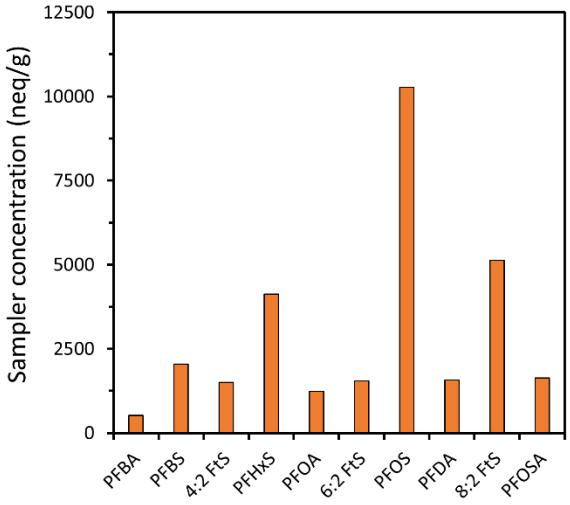

Figure A17. PFAS accumulation in FAD-based passive sampler prototype devices after 21 d contact in a relatively static 10 L solution containing 50-400 µg L^{-1} of 10 PFAS.

APPENDIX B: STANDARD OPERATING PROCEDURES

Note, the SOP document was slightly updated to fit the final Report format. In particular, Appendix A (References) from the original document was removed, and all reference information is available in the preceding pages. In addition, the section, table, and figure numbers were all appended with "B#" to prevent confusion with the corresponding items in the Final Report.

B1. Scope and Application

This white paper describes a liquid chromatography with triple quadrupole tandem mass spectrometry (LC-MS/MS) method capable of analyzing 24 per- and polyfluoroalkyl substances (PFAS) in aqueous samples and ion-exchange membranes with proper pretreatment and extraction. The complete list of 24 target PFAS is summarized in Table B1.

Table B1. PFAS to be measured in this project.

Analyte Name	Acronym	CAS Number
Perfluorotetradecanoic acid	PFTreA	376-06-7
Perfluorotridecanoic acid	PFTriA	72629-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorooctanesulfonamide	PFOSA	754-91-6
Fluorotelomer sulfonic acid 8:2	FtS 8:2	39108-34-4
Fluorotelomer sulfonic acid 6:2	FtS 6:2	27619-97-2
Fluorotelomer sulfonic acid 4:2	FtS 4:2	757124-72-4
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	NEtFOSAA	2991-50-6
2-(N-Methylperfluorooctanesulfonamido) acetic acid	NMeFOSAA	2355-31-9

PFAS-contaminated groundwater and experimental water samples (*i.e.*, aqueous samples) will be prepared for LC-MS/MS analysis by isotope dilution and/or solid-phase extraction (SPE) as described in Section 5.1. PFAS will be extracted from ion-exchange membranes and fibers with a mixture of methanol and 2 M ammonium acetate (or similar) followed by isotope dilution (see Section 5.2).

The reported methodology was established based on best practices and guidelines for PFAS analysis from the Department of Defense and the Department of Energy Consolidated Quality Systems Manual Version 5.3 (DoD/DOE QSM 5.3) [17], the requirements for SERDP & ESTCP projects addressing PFAS-related issues (November 2018), the U.S. Environmental Protection Agency (EPA) Method 537.1, the journal paper based on EPA Method 537 [18], and Wellington Laboratories Certificate of Analysis Documentation [19] (see Appendices A and B). The data presented in this white paper are representative of the method and based on analytical standards obtained from Wellington Laboratories and PFAS-

contaminated groundwater samples provided by the US Army Corps of Engineers (ACE). Detailed information about the US ACE samples can be provided upon request.

B2. Summary of the Method

The aqueous samples will be prepared for analysis by isotope dilution and/or SPE. For isotope dilution, 100 µL of sample, 150 µL of 20 mM ammonium acetate prepared in deionized (DI) water, 200 µL of methanol, and 50 µL of an internal standard solution containing 50 µg/L of mass-labeled PFAS (MPFAS) in methanol will be transferred into a 750-µL polypropylene (PP) LC vial and mixed before analysis. For SPE, a 10-mL aqueous sample will be fortified with 50 µL of a solution containing surrogates (*i.e.*, 5 ng of MPFAS), vortexed, and passed through an SPE cartridge containing polystyrene-divinylbenzene (SDVB) polymer to extract PFAS and MPFAS. These analytes will be eluted with 5 mL of methanol used to rinse the sampler container (*i.e.*, a 15-mL HDPE centrifuge tube). The extract will be evaporated to dryness under nitrogen, reconstituted with 0.5 mL methanol containing internal standards (*i.e.*, MPFAS at 10 µg/L), and adjusted to 1 mL with DI water. Alternative SPE protocols will employ WAX cartridges. PFAS in the ion-exchange membranes and fibers will be extracted with a mixture of methanol and 2 M ammonium acetate, and then isotope dilution will be performed using similar protocols as those described above. Detailed descriptions of the sample preparation protocols are provided in Section 5. The final reconstituted samples and extracts (50 µL) will be injected into an LC-MS/MS, and the target PFAS will be identified by retention time and multiple ion transitions (see Section 6). PFAS concentrations will be determined by internal standard calibrations, and surrogates will be used to track the recovery, accuracy, and precision of the method. The applicable quality control (QC) checks listed in DoD/DOE QSM 5.3 Table B-15 (referred to as Table B-15, below) are discussed below.

B3. Chemicals, Supplies, and Equipment

B3.1. PFAS and MPFAS standards

A PFAS mixture containing the 24 analytes listed in Table B1 was purchased from Wellington Laboratories (product code: PFAC-24PAR) and used to create analytical standards. The concentration of individual PFAS in the mixture was 2 mg/L, but some PFAS were present in the salt form and/or contained isomers (*i.e.*, branched, linear). To avoid confusion, measured PFAS concentrations will be reported for the anionic species after proper mass-based correction of the salt and isomer proportions. Detailed information about the standard mixture is available in the product certificate document from Wellington Laboratories (see Appendix B1). PFAS standard solutions will be prepared at different concentrations via serial dilution with methanol and/or DI water, and these standards will be used to confirm/optimize ion transitions, build the calibration standards (for "Initial calibration (ICAL)" requirements in Table B-15), check the instrument sensitivity, verify the calibration, and spike standards.

In total, 19 MPFAS were obtained from Wellington Laboratories for use as internal standards, surrogates, or "extracted internal standard analytes" (from Table B-15). These molecules include the following: perfluoro-n-[$^{13}C_4$]butanoic acid (MPFBA); perfluoro-n-[$^{13}C_5$]pentanoic acid (M5PFPeA); perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (MPFHxA); perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid (M4PFHpA); perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA); perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid (MPFNA); perfluoro-n-[1,2-$^{13}C_2$]decanoic acid (MPFDA); perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid (MPFUdA); perfluoro-n-[1,2-$^{13}C_2$]dodecanioc acid (MPFDoA); perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid (M2PFTeDA); sodium perfluoro-1-[2,3,4-$^{13}C_3$]butane sulfonate (M3PFBS); sodium perfluoro-1-hexanme[$^{18}O_2$]sulfonate (MPFHxS); sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate (MPFOS); perfluoro-1-[$^{13}C_8$]octane sulfonamide (M8FOSA-I); sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]hexane sulfonate (M2-4:2FTS); sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C_2]octane sulfonate (M2-6:2FTS); sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$]decane sulfonate (M2-8:2FTS); n-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid (d_3-N-MeFOSAA); and, n-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid (d_5-N-EtFOSAA). The 19 MPFAS were provided in separate containers at 50 mg/L. The internal standard or surrogate solutions

will be prepared at different concentrations (*e.g.*, 50 µg/L, 100 µg/L, etc.) after serial dilution with 96% methanol. Some of the MPFAS are in the salt form, but concentration correction is not necessary for their application as internal standards or surrogates. Detailed information about the MPFAS solutions is available in the product certificates from Wellington Laboratories (see Appendix B2). Note, the MPFAS acronyms were defined by Wellington Laboratories and some of them are slightly different from DoD/DOE acronyms.

B3.2. Other chemicals

Other chemicals used in this method include the following: LC-MS grade water, methanol, and ammonium acetate; reagent grade ammonium acetate and sodium chloride; polytyrosine1,3,6; Trizma; ultra-high purity nitrogen gas; 96% methanol; and, DI water. DI water was generated from tap water run through in-house adsorption, ion exchange, reverse osmosis, and UV irradiation processes. The 96% methanol was prepared by transferring 40 mL of DI water into a 1-L volumetric flask and filling the flask to the 1-L mark with LC-MS grade methanol. All chemicals were purchased from Fisher Scientific (Pittsburgh, PA) or Sigma-Aldrich (St. Louis, MO), and detailed product information can be provided upon request.

B3.3. Supplies

The following supplies were used in this method: 10-, 50-, 100-, and 1000-mL high-density polyethylene (HDPE) bottles; 15- and 50-mL HDPE centrifuge tubes; 50-, 100-, 250-, 500-, and 1000-mL PP volumetric flasks; 750-µL PP LC vials with PP caps; 10-, 100-, and 1000-µL PP pipette tips; ISOLUTE ENV+ (200 mg, 6 cm^3) SPE cartridges; Waters XBridge BEH C18 (2.1×5 mm, 2.5 µm) guard LC column; Waters XBridge BEH C18 (2.1×150 mm, 2.5 µm) analytical LC column; PP tubing for sample loading during SPE; glass test tubes (rinsed with methanol and baked prior to use) for eluate collection during SPE; and, personal protective equipment. All supplies were procured from Fisher Scientific or Waters Corp. (Milford, MA), and detailed product information can be provided upon request.

B3.4. Instrumentation

The 20-position SPE manifold was purchased from Waters Corp. and operated by vacuum pump. Samples were centrifuged using an Avanti JXN-30 high-performance centrifuge system (Beckman Coulter; Brea, CA) and sonicated using a Fisher Scientific digital ultrasonic cleaner (Pittsburgh, PA). PFAS concentrations were quantified using an UltiMate 3000 LC connected to a Thermo TSQ Quantum Access Max triple quadrupole MS/MS (Thermo; Waltham, MA). The Xcalibur 3.0 and LCquan 2.0 software were used to control the LC-MS/MS and process data, respectively.

B4. Sample Collection

The aqueous samples and PFAS-loaded ion-exchange membranes and fibers will be generated from experimental studies. All sample extracts and other QC samples will be stored in HDPE containers in a 4 °C refrigerator.

B5. Sample Preparation

B5.1. Aqueous samples

Aqueous samples will include groundwater samples, experimental water samples, and QC water samples. Aqueous samples will be placed on a clean bench, allowed to reach room temperature (*i.e.*, 20-23 °C), sonicated for 5 min to minimize potential PFAS interactions with the container walls, and vortexed. Then, 50 mL of the aqueous samples will be transferred into 50-mL centrifuge tubes and centrifuged at 6000*g* for 10 min at room temperature. After centrifugation, the supernatant will be collected and prepared for isotope dilution and/or SPE. Typically, isotope dilution and/or SPE will occur immediately after the centrifugation step; however, if the supernatant has to be stored, additional sonication and vortex steps will be applied before further processing. PFAS that are still bound to particles after sonication and

centrifugation will not be quantified; however, the suspended solids concentrations will be minimal for the limited-scope portion of this project.

B5.1.1. Isotope dilution

The specific dilution factor will be determined based on the estimated PFAS concentration (*e.g.*, 1-100 µg/L for select experiments) and the validated calibration ranges summarized in Table B2 (*e.g.*, 0.25-25 µg/L for PFOS). In general, 5× isotope dilution will be used as the starting point and achieved by mixing 100 µL of aqueous sample, 150 µL of 20 mM ammonium acetate, 200 µL of methanol, and 50 µL of the 50 µg/L internal standard solution (in methanol). Serial dilution will be conducted as necessary to ensure that (i) the measured PFAS concentration is within the validated calibration range and (ii) the concentration of internal standards is 5 µg/L in the final sample. Isotope dilution will be conducted in triplicate, and the final sample will be prepared in 750-µL PP LC vials and stored at room temperature before analysis, which will happen within 48 h.

In each batch of isotope dilution samples, internal standard solutions prepared at 5 µg/L with 50% methanol will be used as the method blank, and no analytes should be detected at concentrations greater than one-half of the corresponding limit of quantitation (LOQ). In addition, standard solutions prepared at 5 µg/L with 50% methanol will be used as laboratory control samples (LCS), and the calculated concentrations should be within ± 30% of the true values (*i.e.*, 3.5-6.5 µg/L). The lower and upper control limits for the 24 PFAS are summarized in QSM 5.3 Table C-44. A post-spike sample will be prepared to validate whether the PFAS concentrations are less than the LOQs but higher than the limits of detection (LODs) for isotope dilution analyses. Specifically, target PFAS will be spiked at the LOQs, and the calculated concentrations should be within ± 30% of the true concentrations. Note, these criteria have been met during analysis of US ACE samples but, if necessary, the corresponding corrective actions from Table B-15 will be followed during analysis of samples from this project.

For aqueous samples, SPE pretreatment will be conducted if a lower LOQ is required for experimental sensitivity or if matrix effects exceed 50% (in accordance with the "Extracted internal standard analytes" requirements from Table B-15). Matrix effects will be calculated using the peak area of the internal standards in the isotope diluted samples and the peak area of the same internal standards in the initial calibration midpoint standard (*i.e.*, the 5 µg/L standard).

Table B2. LC-MS/MS operational parameters and select method performance metrics for the 24 PFAS.

Compound	MW [a]	Ion transitions [b]	Ratio [c]	RT (min) [d]	LOQ (µg L^{-1}) [e]	LOD (µg L^{-1}) [f]	MQL (µg L^{-1}) [g]	R^2	Internal standard [h]
PFBA	214	212.9 → 168.9	-	3.57	0.1	0.03	0.01	0.996	MPFBA
PFPeA	264	262.9 → 218.9	-	6.47	0.5	0.15	0.05	0.998	M5PFPeA
PFHxA	314	312.9 → 268.9 312.9 → 118.9	0.01	8.98	0.5	0.15	0.05	0.996	MPFHxA
PFHpA	364	362.9 → 318.9 362.9 → 168.9	0.15	9.66	0.1	0.03	0.01	0.997	M4PFHpA
PFOA	414	412.9 → 368.9 412.9 → 168.9	0.20	10.25	0.5	0.15	0.05	0.998	MPFOA
PFNA	464	462.9 → 418.9 462.9 → 168.9	0.20	10.59	0.25	0.08	0.03	0.994	MPFNA
PFDA	514	512.9 → 468.9 512.9 → 218.9	0.10	11.03	0.5	0.15	0.05	0.993	MPFDA
PFUnA	564	562.9 → 518.9 562.9 → 168.9	0.05	11.36	0.5	0.15	0.05	0.998	MPFUdA
PFDoA	614	612.9 → 568.9 612.9 → 168.9	0.05	11.71	0.5	0.15	0.05	0.998	MPFDoA
PFTriA	664	662.9 → 618.9 662.9 → 168.9	0.10	12.21	0.25	0.08	0.03	0.996	MPFDoA
PFTreA	714	712.9 → 668.9 712.9 → 168.9	0.10	12.63	0.5	0.15	0.05	0.993	M2PFTeDA
PFBS	300	298.9 → 80.0 298.9 → 98.9	0.40	7.21	0.5	0.15	0.05	0.999	M3PFBS
PFPeS	350	348.9 → 80.0 348.9 → 98.9	0.60	9.12	0.25	0.08	0.03	0.999	M3PFBS
PFHxS	400	398.9 → 80.0 398.9 → 98.9	0.80	9.73	0.75	0.23	0.08	0.997	MPFHxS
PFHpS	450	448.9 → 80.0 448.9 → 98.9	0.70	10.23	0.5	0.15	0.05	0.993	MPFOS
PFOS	500	498.9 → 80.0 498.9 → 98.9	0.50	10.62	0.25	0.08	0.03	0.997	MPFOS
PFNS	550	548.9 → 80.0 548.9 → 98.9	0.60	11.02	0.25	0.08	0.03	0.995	MPFOS
PFDS	600	598.9 → 80.0 598.9 → 98.9	0.40	11.34	0.5	0.15	0.05	0.993	MPFOS

Compound	MW [a]	Ion transitions [b]	Ratio [c]	RT (min) [d]	LOQ (µg L^{-1}) [e]	LOD (µg L^{-1}) [f]	MQL (µg L^{-1}) [g]	R^2	Internal standard [h]
PFOSA	499	497.9 → 78.0 497.9 → 168.9	0.05	11.45	0.5	0.15	0.05	0.996	M8FOSA-I
FtS 4:2	328	326.9 → 306.9 326.9 → 81.0	0.15	8.95	0.1	0.03	0.01	0.999	M2-4:2FTS
FtS 6:2	428	426.9 → 406.9 426.9 → 81.0	0.15	10.24	0.25	0.08	0.03	0.993	M2-6:2FTS
FtS 8:2	528	526.9 → 506.9 526.9 → 81.0	0.15	10.97	0.5	0.15	0.05	0.999	M2-8:2FTS
NMeFOSAA	571	569.9 → 418.9 569.9 → 511.9	0.40	11.24	0.25	0.08	0.03	0.999	d_3-NMeFOSAA
NEtFOSAA	585	583.9 → 418.9 583.9 → 525.9	0.80	11.40	0.25	0.08	0.03	0.998	d_5-NEtFOSAA

a: Molecular weight (Da)
b: The **first ion transition** was used for quantitation, and the *second ion transition* was used for confirmation
c: Ratio is defined as the response of the confirmation ion over the response of the quantitation ion; based on requirements in Table B-15, a tolerance range of 50-150% of the expected ratio was applied for confirmation purposes
d: Retention time
e: LOQs determined using the method blank, first calibration standard with a calculated concentration that is 70-130% of the true value, and a signal-to-noise ratio greater than 10
f: LODs were calculated by dividing the corresponding LOQs by 3.3
g: Method quantitation limit (MQL) for aqueous samples with a 10-mL loading volume
h: Some of the MPFAS will be used as surrogates during SPE and liquid (*e.g.*, ion-exchange membranes and fibers) extraction protocols; detailed information is provided in Appendix B3

B5.1.2. SPE

SPE is designed to not only concentrate analytes, but also remove interfering substances. The sample loading volume will be adjusted based on LOQ requirements. Based on groundwater samples from US ACE, LOQs of 10-100 ng/L can be achieved for the 24 PFAS using 10-mL loading volumes. The main operational procedures are as follows. A 10-mL water sample will be fortified with 5 ng of surrogates and vortexed. SPE cartridges will be conditioned with 5 mL of methanol followed by 10 mL of DI water. Samples will be loaded at 2-4 mL/min by adjusting the vacuum level. Just before loading, an additional 5 mL of DI water will be added to the loading sample container to minimize residue loss. Another 5 mL of DI water will be used for washing. Then, 5 mL of methanol will be used to rinse the sample container (*i.e.*, "bottle rinsate" from Table B-15); furthermore, this 5 mL of methanol will be used to elute analytes from the SPE cartridge by gravity. The final extract will be evaporated to dryness under nitrogen, reconstituted with 0.5 mL of 96% methanol containing 10 μg/L of internal standards, vortexed to ensure uniform conditions, adjusted to 1 mL with 20 mM ammonium acetate solution, and vortexed again. The reconstituted samples will be transferred into 750-μL PP LC vials and stored at room temperature before analysis, which will occur within 48 h. If the measured concentration of a target analyte is above the calibration range, additional dilution will be conducted with proper spiking of internal standards (*i.e.*, the concentration of internal standards will be 5 μg/L in each sample). All SPE operations will be conducted in triplicate.

For each batch of SPE samples, a method blank (*i.e.*, 10 mL DI water), an LCS (*i.e.*, 10 mL DI water with PFAS spiked at 0.5 μg/L), and at least two matrix spike samples (*i.e.*, 10 mL aqueous samples with PFAS spiked at 0.5 μg/L) will be prepared and processed with exactly the same procedure as the aqueous samples. The spiking concentration will be adjusted if the loading volume changes due to LOQ requirements (see above). In all cases, the spiked mass of an individual PFAS will be set to 5 ng to meet the requirement for spiking concentrations to be greater than or equal to the LOQ and less than or equal to the mid-level calibration concentration.

The method blank, LCS, and matrix spike samples have been investigated during analysis of US ACE groundwater samples. With the exception of perfluorooctanesulfonamide (PFOSA), all PFAS concentrations in the method blank were less than the LODs. PFOSA was occasionally detected at concentrations above the LOQ. In those cases, the corrective action from Table B-15 has been followed. Specifically, the method blank has been re-extracted and if PFOSA concentrations were still greater than one-half of the LOQ, the analyte was flagged with a specific narrative description. The same procedures and operations will be followed for extracts from ion-exchange membranes and fibers. Note, the method blank for isotope dilution was always acceptable, which suggests that the potential contamination of PFOSA came from the SPE cartridge and/or the SPE manifold. These issues will be carefully explored to prevent convoluting effects on experimental findings from this project.

Typical recoveries of the 24 PFAS spiked in DI water (*i.e.*, LCS) and US ACE groundwater (*i.e.*, matrix spike) are presented in Figure B1. In general, PFAS recovery from US ACE groundwater samples was similar to or better than PFAS recovery from DI water. The mean recovery ranged from 63% to 101% and most PFAS were within the lower and upper control limits summarized in DoD/DOE QSM 5.3 Table C-44. The slightly lower recoveries of select PFAS (*e.g.*, NMeFOSAA, NEtFOSAA) could be attributed to the lack of a methanol rinse of the sample loading containers [18]. The methanol rinse has now been added into the SPE protocol, as described above. The method performance will be re-investigated with the aqueous samples from this project, and corrective actions from Table B-15 will be followed as needed. Results from the overall SPE protocol were highly reproducible, and the highest standard deviation was 18% (PFOA). The relative percent difference (RPD) between the matrix spike and matrix spike duplicate was less than 30% for all 24 PFAS. This criterion (*i.e.*, RPD ≤ 30%) will be applied to future analysis, and corrective actions will be taken if necessary.

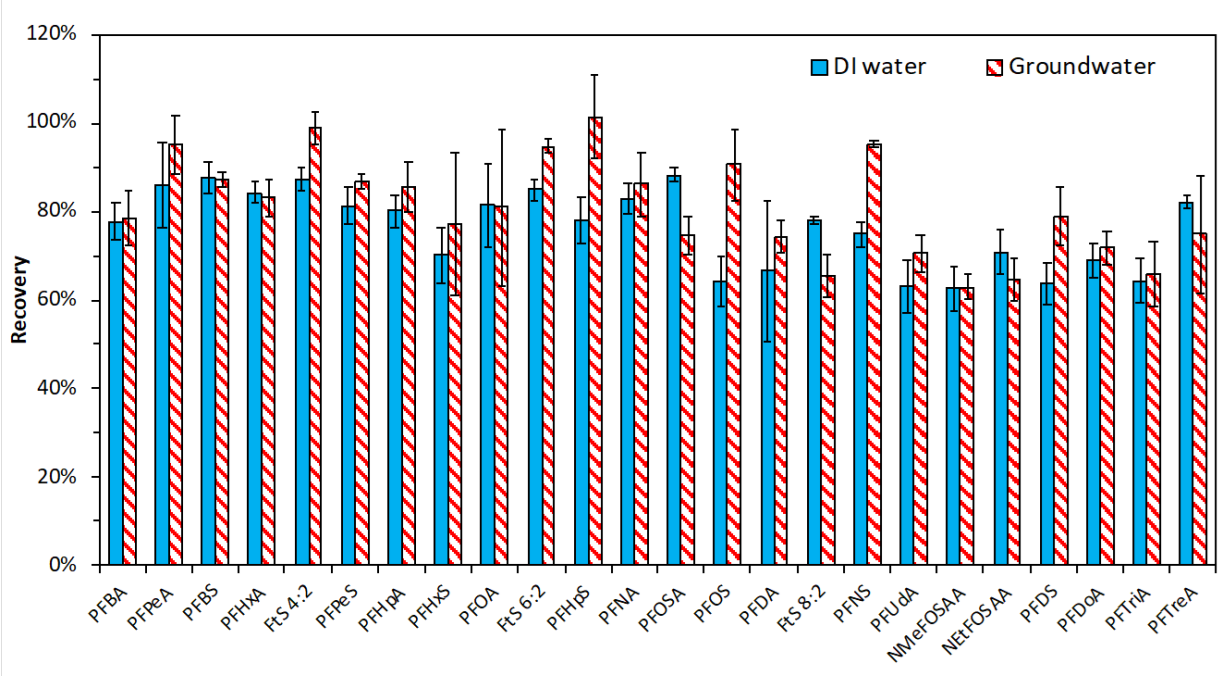

Figure B1. Absolute recovery (n = 3; error bars are standard deviation) for 5 ng of PFAS spiked into 10 mL of DI water (as LCS) and 10 mL of groundwater from US ACE (as matrix spike) during SPE.

Post-SPE matrix effects will be examined using the same methodology reported above for isotope dilution and if matrix effects exceed 50%, the proper corrective actions from Table B-15 will be taken (*e.g.*, dilution of the aqueous samples before SPE). The recoveries of surrogates are expected to be in the 70-130% range, based on the matrix spike results summarized in Figure B1; however, these recoveries will be confirmed (using the additional methanol rinse step) during analysis of samples from this project.

EPA Method 537.1 highlighted the need to spike a dechlorinating agent (*i.e.*, Trizma at 5 g/L) before SPE of drinking water samples. As the experimental water samples from this project are not expected to contain chlorine, this step will not be necessary. Recent studies have reported improved recovery with WAX SPE cartridges [20, 21], which will also be considered in this project.

B5.2. Ion-exchange membrane and fiber extracts

PFAS concentrations on the ion-exchange membranes and fibers deployed during experimentation will be analyzed following liquid extraction. First, the ion-exchange membranes and fibers will be washed with DI water and air-dried. Ion-exchange membrane coupons or fiber bundles will be transferred into a 50-mL HDPE centrifuge tube and submerged in a mixture of 7 mL methanol and 3 mL of 2 M ammonium acetate. The centrifuge tube will be transferred to a shaker at 200 rpm for at least 24 h. Our preliminary results have showed some promising recovery for 12 PFAS with one cycle, but performance will be optimized for different conditions in this project. Extractant composition, serial extractions, and the ratio of membrane or fiber mass to extractant volume will be adjusted based on experimental conditions. Following PFAS extraction from the ion exchangers, we will employ isotope dilution protocols similar to those described above. If the measured concentration of a target analyte exceeds the calibration range, the extracts will be diluted and re-analyzed. The potential sorption of PFAS onto the HDPE containers will also be investigated. After each experiment, the HDPE containers will be rinsed with 10 mL of methanol to quantify the mass of PFAS on the container wall. This process will be repeated until no PFAS are present in the bottle rinsate. Although DoD/DOE QSM 5.3 does not provide specific guidance for ion-exchange membranes and fibers, the general QA/QC principles will be followed, and proper corrective actions will be followed as needed.

B6. LC-MS/MS Analysis

B6.1. Mass calibration and instrument method

Mass calibration of the LC-MS/MS system has been routinely conducted with the reference compound polytyrosine 1,3,6 as suggested by Thermo Scientific (Waltham, MA). The m/z accuracy has been maintained at ≤ 0.2 and validated for the PFAS analytes. Detailed information about the mass calibration process can be provided upon request.

The 24 PFAS and 19 MPFAS were measured with one LC-MS/MS method. Samples (50 µL) were injected onto the guard column, which was connected in series to the analytical column. The analytes were separated using an 18-min gradient elution method with (A) methanol with 10 mM ammonium acetate and (B) water with 10 mM ammonium acetate (pH 6.8). The elution scheme was as follows: 45% A for 1.5 min; ramp to 90% A over 2 min; constant at 90% for 6 min; ramp to 45% A within 1 min; and, constant at 45% A for 7.5 min. For 0–3.0 min, the LC mobile phase was passed through the column and sent to the waste to flush background ions that were present in the sample. With the 200 µL min^{-1} flow rate, a total of 600 µL of mobile phase (12× the sample injection volume) was used to flush out potential interferences. At 3.0 min, a switching valve was used to send the LC mobile phase to the MS/MS detector. The column temperature was set at 40 °C. Negative electrospray ionization was employed for all analytes. At least one product ion was selected for quantitation, and one product ion was selected for confirmation; PFBA, PFPeA, MPFBA, and M5PFPeA were exceptions in accordance with Table B-15 and EPA Method 537.1. The molecular weight, retention times, specific ion transitions, and ion transition ratios are presented in Table B2 for the 24 PFAS and Appendix B3 for the 19 MPFAS. The scan time was set to 0.05 s (*i.e.*, 20 scan events per second), and the scanning window was set to 4 min with the retention time as the midpoint. In this 15-min method, at least 15 scans were acquired across the chromatographic peak of each analyte. Other analytical parameters associated with electrospray ionization and MS/MS detection were similar to previously reported methods and will be provided upon the request. As indicated in Table B2 and Appendix B3, the retention times for the PFAS and the corresponding MPFAS were always within 0.1 min of each other. For analysis of experimental samples, the recorded retention time of individual analytes will be routinely checked for confirmation with the 0.4 min tolerance required by Table B-15.

B6.2. LODs, LOQs, and calibrations

The instrumental LODs and LOQs were determined based on the responses of (i) PFAS standard solutions prepared in DI water and (ii) instrumental blanks (*i.e.*, DI water with internal standards) for multiple injections (n = 6). Specifically, LODs and LOQs were calculated for signal-to-noise ratios of 3 and 10, respectively. Instrumental blanks were also used to confirm the absence of PFAS contamination in the LC-MS/MS system prior to sample analysis. The method detection limits (MDLs) and MQLs were determined using the LODs and LOQs, the SPE concentration factors (or extraction factors for sediment), and analyte recovery (assuming 100% recovery for these estimates, but the actual recovery will be used during analysis). The LOQs and MQLs are summarized in Table B2; note that LODs and MDLs can be calculated by dividing the LOQs and MQLs by 3.3, respectively.

Eleven calibration standards (*i.e.*, ICAL from Table B-15) were generated at 0.1, 0.25, 0.5, 0.75, 1.0, 2.5, 5.0, 7.5, 10, 15, and 25 µg/L. The calibration curves and linearity (as coefficient of determination, or R^2) are summarized in Figure B2 and Table B2. The R^2 values were greater than 0.99 for all PFAS. In accordance with Table B-15, the instrument sensitivity check (ISC) was identified as the lowest concentration within 70-130% of the true value and with a signal-to-noise ratio greater than 10. The specific LODs, LOQs, and MQLs are summarized in Table B2.

B6.3. Sequence and data analysis

Sample analysis will be conducted in an appropriate order to ensure QA/QC. An example sequence is shown in Appendix B4, and future sequences will be ordered as follows: at least two DI water injections;

one instrumental blank; 11 calibration standards, ordered from the lowest to highest concentrations; one instrumental blank (to confirm the absence of analyte carry-over); an initial calibration verification (ICV; PFAS standard solution); one DI water injection; nine experimental samples, ordered from low to high concentrations (if known); at least one continuing calibration verification (CCV; PFAS standard solution); and, one instrumental blank. For analysis of more than nine samples within one run, the above sequence will be repeated without re-analysis of the 11 calibration standards until all experimental samples have been analyzed. A standard solution containing 0.10 to 0.75 µg L^{-1} of each PFAS will be used as the ISC, and the complete set of calibration standards will be processed before each batch of samples. The instrumental blanks, ISC, ICV, and CCV will be separately prepared as the PP caps on the LC vials are not suitable for multiple injections. The calculated concentrations in the ISC, ICV, and CCV should be within ± 30% of the true values. Corrective actions from Table B-15 will be performed as needed.

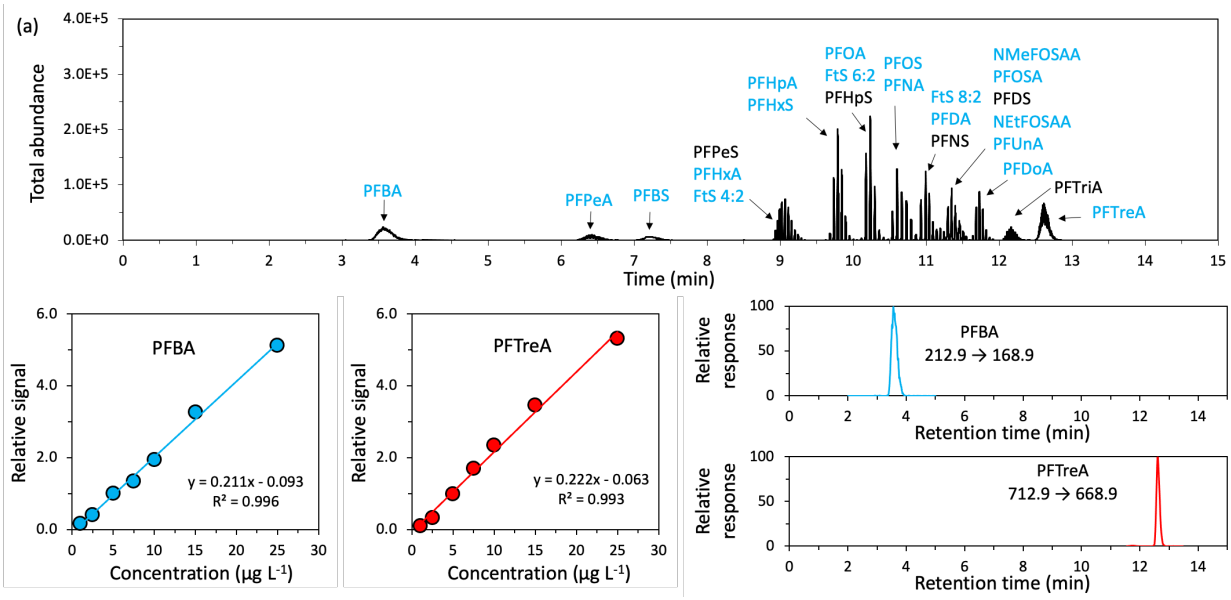

Figure B2. (a) The total ion current for a solution containing 10 µg L^{-1} of 24 PFAS (black and blue labels) and 5 µg L^{-1} of 19 mass-labeled internal standards (blue labels); (b) calibration curves for select PFAS in the 1-25 µg L^{-1} range; and, (c) chromatograms for the same PFAS.

Data analysis was carried out using the LCquan 2.0 software, and a screenshot is provided in Appendix B4. Several important parameters (*e.g.*, retention time, calibration linearity, ion transition ratio, and calculated concentrations) are provided after data processing; furthermore, all data processing was manually checked for accuracy. Measured concentrations will be converted to report all PFAS concentrations for the anionic species (Eq. S1) and linear/branched isomers.

$$C_{anion} = C_{measured} \left(\frac{MW_{anion}}{MW_{salt}} \right) \quad \text{(Eq. S1)}$$

In Eq. S1, MW_{anion} is the molecular weight of the PFAS anion and MW_{salt} is the molecular weight of the PFAS salt. For PFAS with isomers, a detailed description will be included in the narrative to confirm the concentrations of branched and linear isomers.

APPENDIX B1: PRODUCT CERTIFICATE FOR THE MIXTURE OF 24 PFAS

Table A: **PFAC-24PAR; Components and Concentrations (ng/ml, ± 5% in Methanol / Isopropanol (4%) / Water (<1%))**

Compound	Abbreviation	Concentration *** (ng/ml)	Peak Assignment in Figure 1
Perfluoro-n-butanoic acid	PFBA	2000	A
Perfluoro-n-pentanoic acid	PFPeA	2000	B
Perfluoro-n-hexanoic acid	PFHxA	2000	E
Perfluoro-n-heptanoic acid	PFHpA	2000	G
Perfluoro-n-octanoic acid	PFOA	2000	K
Perfluoro-n-nonanoic acid	PFNA	2000	M
Perfluoro-n-decanoic acid	PFDA	2000	Q
Perfluoro-n-undecanoic acid	PFUdA	2000	V
Perfluoro-n-dodecanoic acid	PFDoA	2000	X
Perfluoro-n-tridecanoic acid	PFTrDA	2000	Y
Perfluoro-n-tetradecanoic acid	PFTeDA	2000	Z
Perfluoro-1-octanesulfonamide	FOSA	2000	T
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2000	S
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2000	U

Compound	Abbreviation	Concentration *** (ng/ml)		Peak Assignment in Figure 1
		as the salt	as the anion	
Potassium perfluoro-1-butanesulfonate	L-PFBS	2000	1770	C
Sodium perfluoro-1-pentanesulfonate	L-PFPeS	2000	1880	F
Potassium perfluorohexanesulfonate*	PFHxSK: linear isomer	1620	1480	I
	PFHxSK: ∑ branched isomers	378	344	H
Sodium perfluoro-1-heptanesulfonate	L-PFHpS	2000	1900	L
Potassium perfluorooctanesulfonate**	PFOSK: linear isomer	1580	1460	O
	PFOSK: ∑ branched isomers	422	391	N
Sodium perfluoro-1-nonanesulfonate	L-PFNS	2000	1920	R
Sodium perfluoro-1-decanesulfonate	L-PFDS	2000	1930	W
Sodium 1H,1H,2H,2H-perfluoro-1-hexanesulfonate	4:2FTS	2000	1870	D
Sodium 1H,1H,2H,2H-perfluoro-1-octanesulfonate	6:2FTS	2000	1900	J
Sodium 1H,1H,2H,2H-perfluoro-1-decanesulfonate	8:2FTS	2000	1920	P

* See Table B for percent composition of linear and branched PFHxSK isomers.
** See Table C for percent composition of linear and branched PFOSK isomers.
*** Concentrations have been rounded to three significant figures.

APPENDIX B2: PRODUCT CERTIFICATES FOR THE 19 MPFAS

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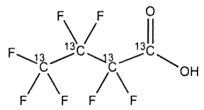
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFBA	**LOT NUMBER:**	MPFBA0417
COMPOUND:	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid		
STRUCTURE:		**CAS #:**	Not available
MOLECULAR FORMULA:	$^{13}C_4HF_7O_2$	**MOLECULAR WEIGHT:**	218.01
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2,3,4$-$^{13}C_4$)
LAST TESTED: (mm/dd/yyyy)	04/12/2017		
EXPIRY DATE: (mm/dd/yyyy)	04/12/2022		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 04/20/2017 (mm/dd/yyyy)
B.G. Chittim, General Manager

Wellington Laboratories Inc., 345 Southgate Dr. Guelph ON N1G 3M5 CANADA
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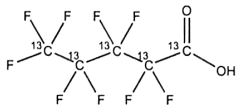
Form#:27, Issued 2004-11-10
Revision#:4, Revised 2017-03-06

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M5PFPeA	**LOT NUMBER:**	M5PFPeA1018
COMPOUND:	Perfluoro-n-[$^{13}C_5$]pentanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_5HF_9O_2$	**MOLECULAR WEIGHT:**	269.01
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($^{13}C_5$)
LAST TESTED: (mm/dd/yyyy)	10/10/2018		
EXPIRY DATE: (mm/dd/yyyy)	10/10/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Contains < 0.1% of perfluoro-n-pentanoic acid.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 10/17/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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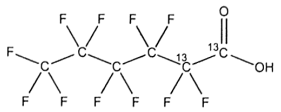
Form#:27, Issued 2004-11-10
Revision#:6, Revised 2018-08-14

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFHxA	**LOT NUMBER:**	MPFHxA1017
COMPOUND:	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_4HF_{11}O_2$	**MOLECULAR WEIGHT:**	316.04
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99%^{13}C (1,2-$^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	10/27/2017		
EXPIRY DATE: (mm/dd/yyyy)	10/27/2022		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Contains < 0.1% of perfluoro-n-hexanoic acid and < 0.3% of perfluoro-n-octanoic acid.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 10/30/2017 (mm/dd/yyyy)
B.G. Chittim, General Manager

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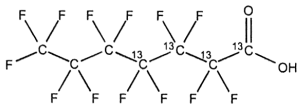
Form#:27, Issued 2004-11-10
Revision#:4, Revised 2017-03-06

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M4PFHpA	**LOT NUMBER:**	M4PFHpA0618
COMPOUND:	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_4{}^{12}C_3HF_{13}O_2$	**MOLECULAR WEIGHT:**	368.03
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2,3,4\text{-}^{13}C_4$)
LAST TESTED: (mm/dd/yyyy)	07/06/2018		
EXPIRY DATE: (mm/dd/yyyy)	07/06/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Contains ~ 0.04% of perfluoro-n-heptanoic acid.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 07/09/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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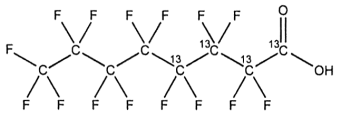
WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFOA	**LOT NUMBER:**	MPFOA0918
COMPOUND:	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid		
STRUCTURE:		**CAS #:**	960315-48-4



MOLECULAR FORMULA:	$^{13}C_4{}^{12}C_4HF_{15}O_2$	**MOLECULAR WEIGHT:**	418.04
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C (1,2,3,4-$^{13}C_4$)
LAST TESTED: (mm/dd/yyyy)	09/11/2018		
EXPIRY DATE: (mm/dd/yyyy)	09/11/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Contains ~ 0.1% of native perfluoro-n-octanoic acid (PFOA).

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Certified By: _____ **Date:** 09/12/2018 (mm/dd/yyyy)
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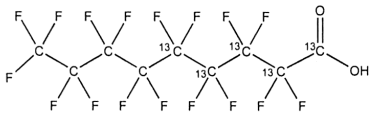
Form#:27, Issued 2004-11-10
Revision#:6, Revised 2018-08-14

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFNA	**LOT NUMBER:**	MPFNA1217
COMPOUND:	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_5{}^{12}C_4HF_{17}O_2$	**MOLECULAR WEIGHT:**	469.04
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C (1,2,3,4,5-$^{13}C_5$)
LAST TESTED: (mm/dd/yyyy)	12/14/2017		
EXPIRY DATE: (mm/dd/yyyy)	12/14/2022		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.

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Certified By: _____ **Date:** 12/19/2017 (mm/dd/yyyy)
B.G. Chittim, General Manager

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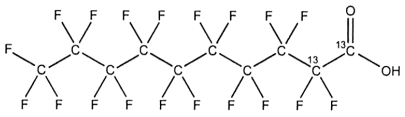
Revision#:4, Revised 2017-03-06

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFDA	**LOT NUMBER:**	MPFDA0218
COMPOUND:	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_8HF_{19}O_2$	**MOLECULAR WEIGHT:**	516.07
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	02/16/2018		
EXPIRY DATE: (mm/dd/yyyy)	02/16/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Contains < 0.1% of $^{13}C_1$-PFNA.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 03/07/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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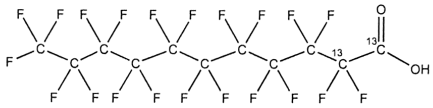
CERTIFICATE OF ANALYSIS DOCUMENTATION

PRODUCT CODE:	MPFUdA	**LOT NUMBER:**	MPFUdA1116
COMPOUND:	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_9HF_{21}O_2$	**MOLECULAR WEIGHT:**	566.08
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	11/22/2016		
EXPIRY DATE: (mm/dd/yyyy)	11/22/2021		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.
- Presence of 1-$^{13}C_1$-PFUdA (~1%; see Figure 2), 2-$^{13}C_1$-PFUdA (~1%), and PFUdA (~0.2%; see Figure 2) are due to the isotopic purity of the ^{13}C-precursor.

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Certified By: B.G. Chittim **Date:** 12/07/2016 (mm/dd/yyyy)

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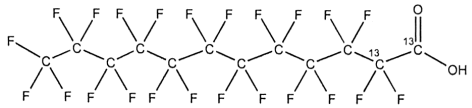
Form#:27, Issued 2004-11-10
Revision#:3, Revised 2015-03-24

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFDoA	**LOT NUMBER:**	MPFDoA0218
COMPOUND:	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	**MOLECULAR WEIGHT:**	616.08
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	02/16/2018		
EXPIRY DATE: (mm/dd/yyyy)	02/16/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 02/23/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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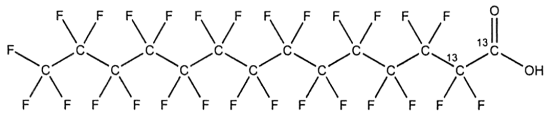
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M2PFTeDA	**LOT NUMBER:**	M2PFTeDA1218
COMPOUND:	Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_{12}HF_{27}O_2$	**MOLECULAR WEIGHT:**	716.10
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	12/11/2018		
EXPIRY DATE: (mm/dd/yyyy)	12/11/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent conversion of the carboxylic acid to the methyl ester.

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Certified By: _____ **Date:** 12/20/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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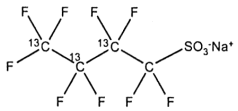
Form#:27, Issued 2004-11-10
Revision#:6, Revised 2018-08-14

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M3PFBS	**LOT NUMBER:**	M3PFBS1218
COMPOUND:	Sodium perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_3{}^{12}CF_9SO_3Na$	**MOLECULAR WEIGHT:**	325.06
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt) 46.5 ± 2.3 µg/ml (M3PFBS anion)	**SOLVENT(S):**	Methanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($2,3,4\text{-}^{13}C_3$)
LAST TESTED: (mm/dd/yyyy)	12/10/2018		
EXPIRY DATE: (mm/dd/yyyy)	12/10/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.

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Certified By: _____ **Date:** 12/13/2018 (mm/dd/yyyy)
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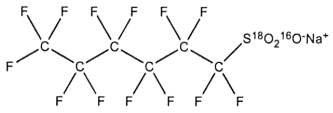
Form#:27, Issued 2004-11-10
Revision#:6, Revised 2018-08-14

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFHxS	**LOT NUMBER:**	MPFHxS0318
COMPOUND:	Sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$C_6F_{13}S^{18}O_2{}^{16}ONa$	**MOLECULAR WEIGHT:**	426.10
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt) 47.3 ± 2.4 µg/ml (MPFHxS anion)	**SOLVENT(S):**	Methanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	>94% ($^{18}O_2$)
LAST TESTED: (mm/dd/yyyy)	03/22/2018		
EXPIRY DATE: (mm/dd/yyyy)	03/22/2023		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- The response factor for MPFHxS ($C_6F_{13}S^{18}O_2{}^{16}O^-$) has been observed to be up to 10% lower than for PFHxS ($C_6F_{13}S^{16}O_3^-$) when both compounds are injected together. This difference may vary between instruments.
- Contains ~ 1.0% of sodium perfluoro-1-octane[$^{18}O_2$]sulfonate ($^{18}O_2$-PFOS) and ~ 0.3% of sodium perfluoro-1-heptane[$^{18}O_2$]sulfonate ($^{18}O_2$-PFHpS).
- Due to the isotopic purity of the starting material ($^{18}O_2$ >94%), MPFHxS contains ~ 0.3% of PFHxS. This value agrees with the theoretical percent relative abundance that is expected based on the stated isotopic purity.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 03/27/2018 (mm/dd/yyyy)
B.G. Chittim, General Manager

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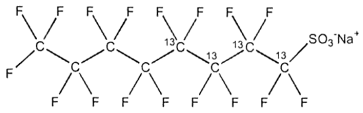
WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	MPFOS	**LOT NUMBER:**	MPFOS1017
COMPOUND:	Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_4{}^{12}C_4F_{17}SO_3Na$	**MOLECULAR WEIGHT:**	526.08
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt) 47.8 ± 2.4 µg/ml (MPFOS anion)	**SOLVENT(S):**	Methanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2,3,4$-$^{13}C_4$)
LAST TESTED: (mm/dd/yyyy)	10/17/2017		
EXPIRY DATE: (mm/dd/yyyy)	10/17/2022		
RECOMMENDED STORAGE:	Store ampoule in a cool, dark place		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains ~ 0.4% Sodium perfluoro-1-[1,2,3-$^{13}C_3$]heptanesulfonate.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 10/18/2017 (mm/dd/yyyy)
B.G. Chittim, General Manager

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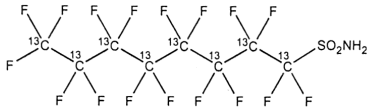
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M8FOSA-I	**LOT NUMBER:**	M8FOSA1017I
COMPOUND:	Perfluoro-1-[$^{13}C_8$]octanesulfonamide		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_8H_2F_{17}NO_2S$	**MOLECULAR WEIGHT:**	507.09
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Isopropanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($^{13}C_8$)
LAST TESTED: (mm/dd/yyyy)	10/11/2017		
EXPIRY DATE: (mm/dd/yyyy)	10/11/2022		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains ~ 1.1% of perfluoro-1-[$^{13}C_4$]octanesulfonamide and ~ 0.01% of perfluoro-1-[$^{13}C_7$]heptanesulfonamide.

FOR LABORATORY USE ONLY: NOT FOR HUMAN OR DRUG USE

Certified By: _____ **Date:** 10/20/2017 (mm/dd/yyyy)
B.G. Chittim, General Manager

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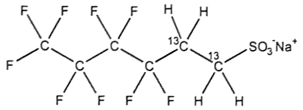
Revision#:4, Revised 2017-03-06

WELLINGTON LABORATORIES

CERTIFICATE OF ANALYSIS DOCUMENTATION

PRODUCT CODE:	M2-4:2FTS	**LOT NUMBER:**	M242FTS0119
COMPOUND:	Sodium 1H,1H,2H,2H-perfluoro-[1,2-$^{13}C_2$]hexane sulfonate		
STRUCTURE:		**CAS #:**	Not available
MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_4H_4F_9SO_3Na$	**MOLECULAR WEIGHT:**	352.12
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt) 46.7 ± 2.3 µg/ml (M2-4:2FTS anion)	**SOLVENT(S):**	Methanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	01/10/2019		
EXPIRY DATE: (mm/dd/yyyy)	01/10/2024		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- The native 4:2FTS contains 4.22% of ^{34}S (due to natural isotopic abundance) therefore both native 4:2FTS and M2-4:2FTS will produce signals in the m/z 329 to m/z 309 channel during SRM analysis. We recommend using the m/z 329 to m/z 81 transition to monitor for M2-4:2FTS during quantitative analysis as it will be free of any native contribution (see Figure 2).

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Certified By: _____ **Date:** 01/22/2019 (mm/dd/yyyy)
B.G. Chittim, General Manager

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Revision#:6, Revised 2018-08-14

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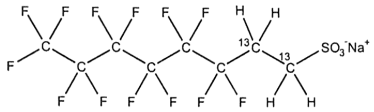
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M2-6:2FTS	**LOT NUMBER:**	M262FTS0218
COMPOUND:	Sodium 1H,1H,2H,2H-perfluoro-[1,2-$^{13}C_2$]octane sulfonate		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_6H_4F_{13}SO_3Na$	**MOLECULAR WEIGHT:**	452.13
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt)	**SOLVENT(S):**	Methanol
	47.5 ± 2.4 µg/ml (M2-6:2FTS anion)		
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	02/16/2018		
EXPIRY DATE: (mm/dd/yyyy)	02/16/2023		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- The native 6:2FTS contains 4.22% of ^{34}S (due to natural isotopic abundance) therefore both native 6:2FTS and M2-6:2FTS will produce signals in the m/z 429 to m/z 409 channel during SRM analysis. We recommend using the m/z 429 to m/z 81 transition to monitor for M2-6:2FTS during quantitative analysis as it will be free of any native contribution (see Figure 2).

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Certified By: _____ **Date:** 03/07/2018 (mm/dd/yyyy)
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Revision#:5, Revised 2018-01-22

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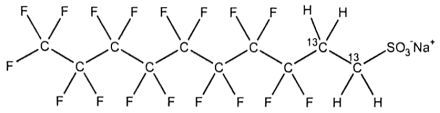
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	M2-8:2FTS	**LOT NUMBER:**	M282FTS0118
COMPOUND:	Sodium 1H,1H,2H,2H-perfluoro-[1,2-$^{13}C_2$]decane sulfonate		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$^{13}C_2{}^{12}C_8H_4F_{17}SO_3Na$	**MOLECULAR WEIGHT:**	552.15
CONCENTRATION:	50.0 ± 2.5 µg/ml (Na salt) 47.9 ± 2.4 µg/ml (M2-8:2FTS anion)	**SOLVENT(S):**	Methanol
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥99% ^{13}C ($1,2\text{-}^{13}C_2$)
LAST TESTED: (mm/dd/yyyy)	01/24/2018		
EXPIRY DATE: (mm/dd/yyyy)	01/24/2023		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- The native 8:2FTS contains 4.22% of ^{34}S (due to natural isotopic abundance) therefore both native 8:2FTS and M2-8:2FTS will produce signals in the m/z 529 to m/z 509 channel during SRM analysis. We recommend using the m/z 529 to m/z 81 transition to monitor for M2-8:2FTS during quantitative analysis as it will be free of any native contribution (see Figure 2).

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Revision#:5, Revised 2018-01-22

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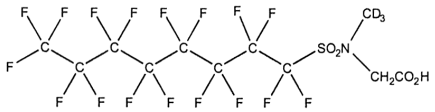
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	d3-N-MeFOSAA	**LOT NUMBER:**	d3NMeFOSAA0119
COMPOUND:	N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$C_{11}D_3H_3F_{17}NO_4S$	**MOLECULAR WEIGHT:**	574.23
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥98% $^2H_3$
LAST TESTED: (mm/dd/yyyy)	01/09/2019		
EXPIRY DATE: (mm/dd/yyyy)	01/09/2024		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent the conversion of the acetic acid moiety to the methyl ester.

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Certified By: _____ **Date:** 01/11/2019 (mm/dd/yyyy)
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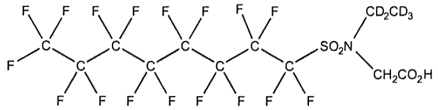
CERTIFICATE OF ANALYSIS
DOCUMENTATION

PRODUCT CODE:	d5-N-EtFOSAA	**LOT NUMBER:**	d5NEtFOSAA0119
COMPOUND:	N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid		
STRUCTURE:		**CAS #:**	Not available



MOLECULAR FORMULA:	$C_{12}D_5H_3F_{17}NO_4S$	**MOLECULAR WEIGHT:**	590.26
CONCENTRATION:	50 ± 2.5 µg/ml	**SOLVENT(S):**	Methanol Water (<1%)
CHEMICAL PURITY:	>98%	**ISOTOPIC PURITY:**	≥98% $^2H_5$
LAST TESTED: (mm/dd/yyyy)	01/23/2019		
EXPIRY DATE: (mm/dd/yyyy)	01/23/2024		
RECOMMENDED STORAGE:	Refrigerate ampoule		

DOCUMENTATION/ DATA ATTACHED:

Figure 1: LC/MS Data (TIC and Mass Spectrum)
Figure 2: LC/MS/MS Data (Selected MRM Transitions)

ADDITIONAL INFORMATION:

- See page 2 for further details.
- Contains 4 mole eq. of NaOH to prevent the conversion of the acetic acid moiety to the methyl ester.

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Certified By: _____ **Date:** 01/28/2019 (mm/dd/yyyy)
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Form#:27, Issued 2004-11-10
Revision#:6, Revised 2018-08-14

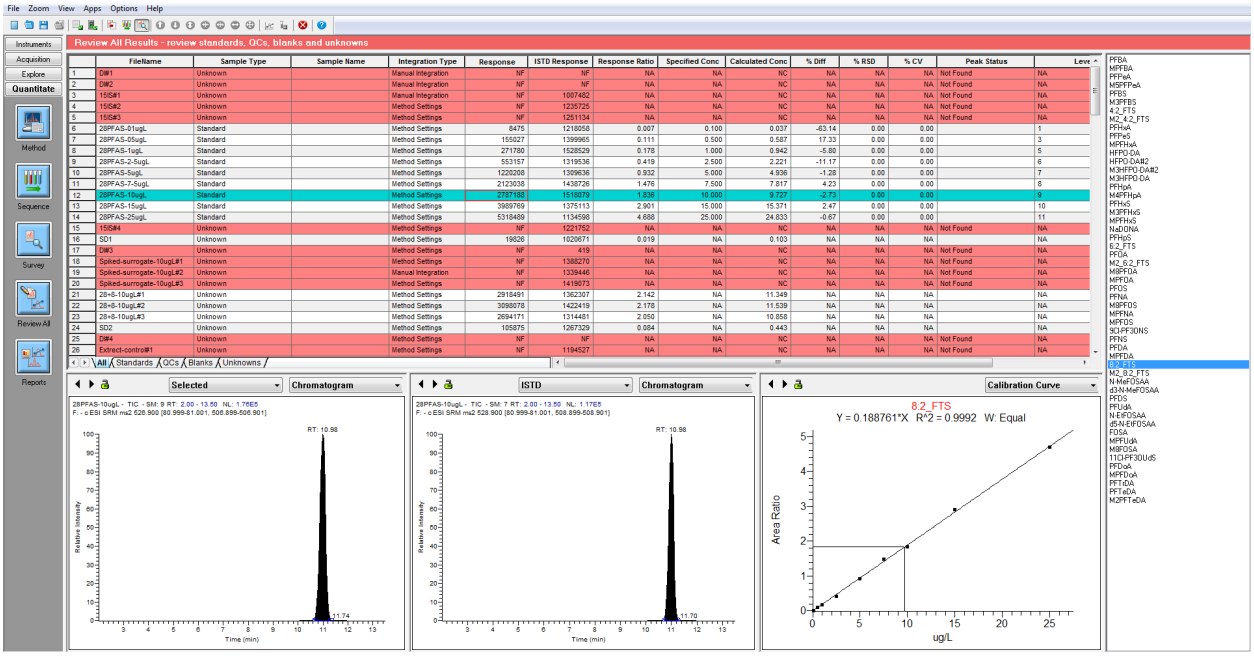
APPENDIX B3: LC-MS/MS PARAMETERS FOR THE 19 MPFAS

Compound	MW [a]	Ion transitions [b]	Ratio [c]	RT (min) [d]	Concentration as IS (µg/L) [e]	Spiked mass as surrogate (ng) [f]
MPFBA	218	216.9 → 171.9 -	-	3.59	5	-
M5PFPeA	269	267.9 → 222.9 -	-	6.45	5	-
MPFHxA	316	314.9 → 269.9 314.9 → 118.9	0.01	8.95	5	-
M4PFHpA	368	366.9 → 321.9 366.9 → 168.9	0.15	9.64	5	5
MPFOA	418	416.9 → 371.9 416.9 → 168.9	0.20	10.26	5	-
MPFNA	469	467.9 → 422.9 467.9 → 168.9	0.20	10.61	5	5
MPFDA	516	514.9 → 469.9 514.9 → 218.9	0.10	11.08	5	-
MPFUdA	566	564.9 → 519.9 564.9 → 168.9	0.05	11.37	5	-
MPFDoA	616	614.9 → 569.9 614.9 → 168.9	0.05	11.70	5	5
M2PFTreA	716	714.9 → 669.9 714.9 → 168.9	0.10	12.64	5	-
M3PFBS	303	301.9 → 80.0 301.9 → 98.9	0.40	7.13	5	-
MPFHxS	404	402.9 → 84.0 402.9 → 102.9	0.80	9.76	5	5
MPFOS	504	502.9 → 80.0 502.9 → 98.9	0.50	10.65	5	-
M8FOSA-I	507	505.9 → 78.0 505.9 → 171.9	0.05	11.47	5	-
M2-FtS 4:2	330	328.9 → 308.9 328.9 → 81.0	0.15	8.99	5	-
M2-FtS 6:2	430	428.9 → 408.9 428.9 → 81.0	0.15	10.23	5	5
M2-FtS 8:2	530	528.9 → 508.9 528.9 → 81.0	0.15	10.98	5	-
d_3-NMeFOSAA	574	572.9 → 418.9 569.9 → 514.9	0.40	11.20	5	-
d_5-NEtFOSAA	590	588.9 → 418.9 588.9 → 530.9	0.80	11.42	5	5

a: Molecular weight (Da)
b: The **first ion transition** was used for quantitation; the *second ion transition* was used for confirmation
c: Ratio is the response of the confirmation ion over that of the quantitation ion; a tolerance range of 50-150% of the expected ratio was applied for confirmation purposes (Table B-15)
d: Retention time
e: MPFAS concentration when used as internal standard
f: Spiked mass of MPFAS when used as surrogates during SPE and sediment extraction

APPENDIX B4: EXAMPLE PFAS ANALYSIS SEQUENCE

FtS 8:2 is the representative compound in this case, and the corresponding chromatogram is presented in the bottom left panel. The chromatogram in the bottom central panel is for the M2-FtS 8:2 internal standard. The FtS 8:2 calibration curve is presented in the bottom right panel.



APPENDIX B5: RESPONSE TO SOP COMMENTS

In January 2021, we responded to the following comments on our SOP document.

Document Comments

Revision Requested, No Further Review

Thank you for submitting the Standard Operating Procedures; comments are provided below. Please review these comments and provide a response to each in SEMS. Responses should include a discussion of the comment as well as a notation as to how the comment was incorporated into the revised document. Once the document is updated, submit the revised version to the Program Office under the (V2) task in SEMS. No further review of the document is required.

If you have any questions regarding this review, contact Andrea at Andrea.Leeson.civ@mail.mil.

We are extremely grateful for the feedback, which has helped us to improve the clarity and quality of our Standard Operating Procedures (SOP). We have carefully considered each comment and changed the SOP accordingly. Our specific responses to each comment, the corresponding changes made to the SOP, and a revised version of the SOP have all been submitted through SEMS.

Comment #1. LOD & LOQs

Please provide the LOD and LOQs for each analyte. It cannot be determined if the calibration curve and instrument sensitivity check (ISC) are the appropriate concentrations since this depends on these values.

Changes: An updated Table B2 (Table R1, below) has been added to the revised SOP document with the complete set of LODs and LOQs for each PFAS analyte. As noted in the table, the LOQs ranged from 0.10 to 0.75 µg L^{-1}, in agreement with the concentrations used for the calibration curves (0.10 – 25 µg L^{-1}) and the instrument sensitivity checks (ISCs; 0.10 – 0.75 µg L^{-1}). These points have been clarified by revising the following sentences at the end of Section 6.2: "In accordance with Table B-15, the instrument sensitivity check (ISC) was identified as the lowest concentration within 70-130% of the true value and with a signal-to-noise ratio greater than 10. The specific LODs, LOQs, and MQLs are summarized in Table B2." We also added the following sentence to the middle of Section 6.3: "A standard solution containing 0.10 to 0.75 µg L^{-1} of each PFAS will be used as the ISC, and the complete set of calibration standards will be processed before each batch of samples."

Table R1. LC-MS/MS operational parameters and select method performance metrics for the 24 PFAS.

Compound	MW [a]	Ion transitions [b]	Ratio [c]	RT (min) [d]	LOQ (µg L^{-1}) [e]	LOD (µg L^{-1}) [f]	MQL (µg L^{-1}) [g]	R^2	Internal standard [h]
PFBA	214	**212.9 → 168.9**	-	3.57	0.1	0.03	0.01	0.996	MPFBA
PFPeA	264	**262.9 → 218.9**	-	6.47	0.5	0.15	0.05	0.998	M5PFPeA
PFHxA	314	**312.9 → 268.9** *312.9 → 118.9*	0.01	8.98	0.5	0.15	0.05	0.996	MPFHxA
PFHpA	364	**362.9 → 318.9** *362.9 → 168.9*	0.15	9.66	0.1	0.03	0.01	0.997	M4PFHpA
PFOA	414	**412.9 → 368.9** *412.9 → 168.9*	0.20	10.25	0.5	0.15	0.05	0.998	MPFOA
PFNA	464	**462.9 → 418.9** *462.9 → 168.9*	0.20	10.59	0.25	0.08	0.03	0.994	MPFNA
PFDA	514	**512.9 → 468.9** *512.9 → 218.9*	0.10	11.03	0.5	0.15	0.05	0.993	MPFDA
PFUnA	564	**562.9 → 518.9** *562.9 → 168.9*	0.05	11.36	0.5	0.15	0.05	0.998	MPFUdA
PFDoA	614	**612.9 → 568.9** *612.9 → 168.9*	0.05	11.71	0.5	0.15	0.05	0.998	MPFDoA
PFTriA	664	**662.9 → 618.9** *662.9 → 168.9*	0.10	12.21	0.25	0.08	0.03	0.996	MPFDoA
PFTreA	714	**712.9 → 668.9** *712.9 → 168.9*	0.10	12.63	0.5	0.15	0.05	0.993	M2PFTeDA
PFBS	300	**298.9 → 80.0** *298.9 → 98.9*	0.40	7.21	0.5	0.15	0.05	0.999	M3PFBS
PFPeS	350	**348.9 → 80.0** *348.9 → 98.9*	0.60	9.12	0.25	0.08	0.03	0.999	M3PFBS
PFHxS	400	**398.9 → 80.0** *398.9 → 98.9*	0.80	9.73	0.75	0.23	0.08	0.997	MPFHxS
PFHpS	450	**448.9 → 80.0** *448.9 → 98.9*	0.70	10.23	0.5	0.15	0.05	0.993	MPFOS
PFOS	500	**498.9 → 80.0** *498.9 → 98.9*	0.50	10.62	0.25	0.08	0.03	0.997	MPFOS
PFNS	550	**548.9 → 80.0** *548.9 → 98.9*	0.60	11.02	0.25	0.08	0.03	0.995	MPFOS
PFDS	600	**598.9 → 80.0** *598.9 → 98.9*	0.40	11.34	0.5	0.15	0.05	0.993	MPFOS

Compound	MW [a]	Ion transitions [b]	Ratio [c]	RT (min) [d]	LOQ (µg L^{-1}) [e]	LOD (µg L^{-1}) [f]	MQL (µg L^{-1}) [g]	R^2	Internal standard [h]
PFOSA	499	**497.9 → 78.0** *497.9 → 168.9*	0.05	11.45	0.5	0.15	0.05	0.996	M8FOSA-I
FtS 4:2	328	**326.9 → 306.9** *326.9 → 81.0*	0.15	8.95	0.1	0.03	0.01	0.999	M2-4:2FTS
FtS 6:2	428	**426.9 → 406.9** *426.9 → 81.0*	0.15	10.24	0.25	0.08	0.03	0.993	M2-6:2FTS
FtS 8:2	528	**526.9 → 506.9** *526.9 → 81.0*	0.15	10.97	0.5	0.15	0.05	0.999	M2-8:2FTS
NMeFOSAA	571	**569.9 → 418.9** *569.9 → 511.9*	0.40	11.24	0.25	0.08	0.03	0.999	d_3-NMeFOSAA
NEtFOSAA	585	**583.9 → 418.9** *583.9 → 525.9*	0.80	11.40	0.25	0.08	0.03	0.998	d_5-NEtFOSAA

a: Molecular weight (Da)
b: The **first ion transition** was used for quantitation, and the *second ion transition* was used for confirmation
c: Ratio is defined as the response of the confirmation ion over the response of the quantitation ion; based on requirements in Table B-15, a tolerance range of 50-150% of the expected ratio was applied for confirmation purposes
d: Retention time
e: LOQs determined using the method blank, first calibration standard with a calculated concentration that is 70-130% of the true value, and a signal-to-noise ratio greater than 10
f: LODs were calculated by dividing the corresponding LOQs by 3.3
g: Method quantitation limit (MQL) for aqueous samples with a 10-mL loading volume
h: Some of the MPFAS will be used as surrogates during SPE and liquid (*e.g.*, ion-exchange membranes and fibers) extraction protocols; detailed information is provided in Appendix B3

Comment #2. Section 5.1

We recommend that all water samples be extracted by SPE techniques. Please comment on this issue.

We thank the reviewers for this suggestion, which speaks to the need to either (i) concentrate PFAS for analysis or (ii) decrease matrix effects that suppress PFAS ionization during LC-MS analysis. In these regards, we have closely followed the isotope dilution protocols described in Section 5.1.1: "SPE pretreatment will be conducted if a lower LOQ is required for experimental sensitivity or if matrix effects exceed 50% (in accordance with the "Extracted internal standard analytes" requirements from Table B-15)". Because the background ions (*e.g.*, Na^+, Cl^-) in our experimental design could potentially affect PFAS ionization, we have adjusted our LC-MS/MS method to operate more like an online-SPE process. In particular, we adjusted the mobile phase conditions to increase the retention time of the first analyte (*i.e.*, PFBA) from 2.37 min to 3.57 min; note, the new retention times have also been updated in Table B2. For 0–3.0 min, the LC mobile phase was passed through the column and sent to the waste to flush background ions that were present in the sample. With the 200 µL min^{-1} flow rate, a total of 600 µL of mobile phase (12× the sample injection volume) was used to flush out potential interferences. At 3.0 min, a switching valve was used to send the LC mobile phase to the MS/MS detector. The performance of this method was evaluated by analyzing PFAS in solutions containing 0 mM NaCl (baseline condition) and 100 mM NaCl (representative of the most extreme conditions to be tested in this project). The matrix effects reported in Figure R1 (below) were always less than 50%, in accordance with guidance from Table B-15. Given the low preponderance of matrix effects, as well as the lower potential for analyte loss during isotope dilution compared to SPE, we believe that this strategy is preferred; however, we will continue to monitor matrix effects and take the appropriate actions with respect to the need for SPE according to Table B-15. Importantly, this approach increases our analytical throughput.

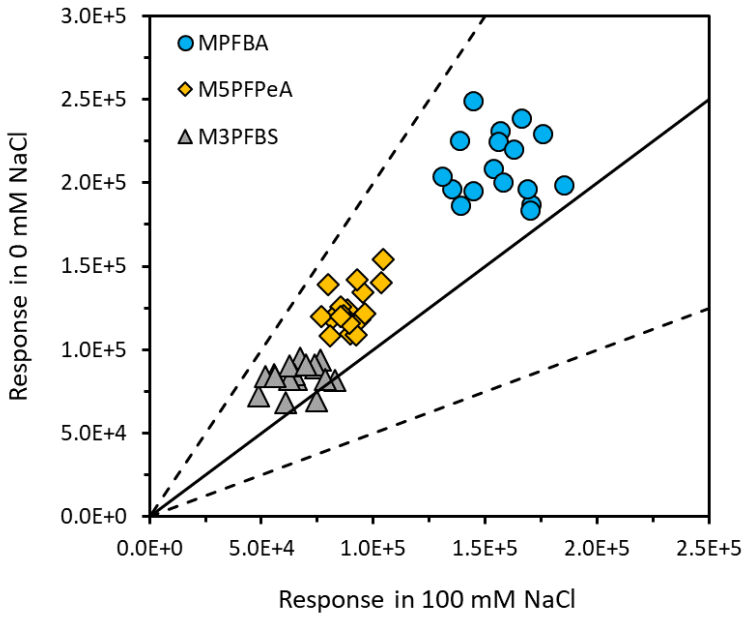


Figure R1. The MS/MS responses of 5 µg L^{-1} of three internal standards (*i.e.*, MPFBA, M5PFPeA, and M3PFBS) in solutions with 0 and 100 mM NaCl. The solid line is the 1:1 line, and the dashed lines represent the 50% matrix effects boundaries for signal suppression (upper) and enhancement (lower). These three MPFAS correspond to the earliest eluting PFAS, which are more subject to matrix effects.

Changes: Figure R2 (below) has been updated to reflect the modified LC-MS/MS method described above.

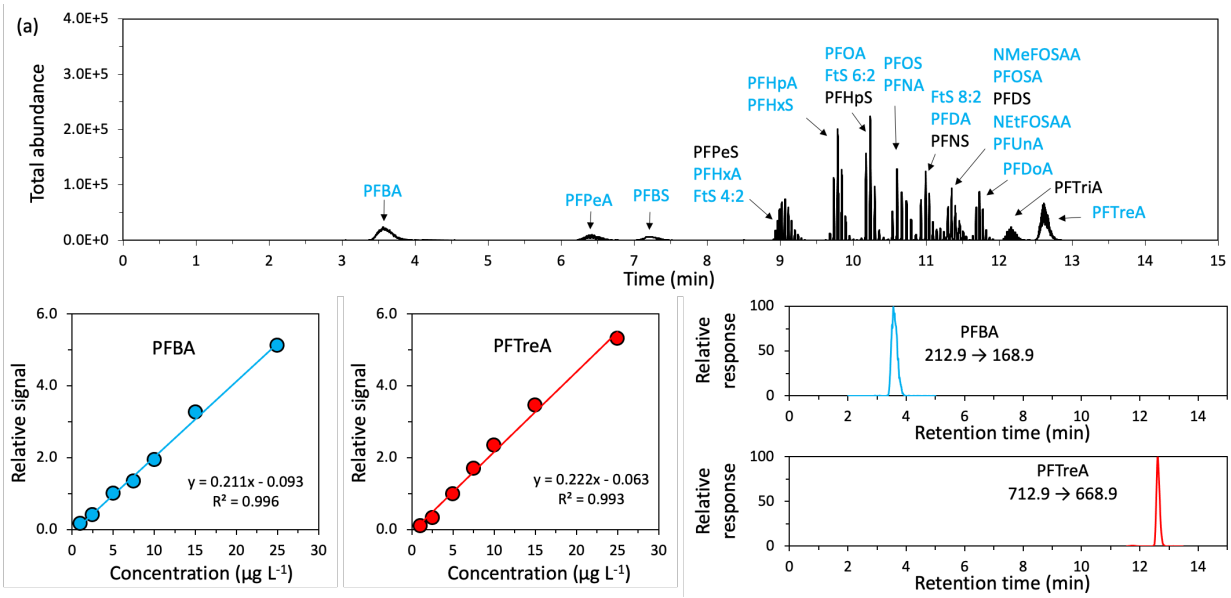


Figure R2. (a) The total ion current for a solution containing 10 µg L^{-1} of 24 PFAS (black and blue labels) and 5 µg L^{-1} of 19 mass-labeled internal standards (blue labels); (b) calibration curves for select PFAS in the 1-25 µg L^{-1} range; and, (c) chromatograms for the same PFAS.

The description of the LC elution scheme has been updated in Section 6.1: "The elution scheme was as follows: 45% A for 1.5 min; ramp to 90% A over 2 min; constant at 90% for 6 min; ramp to 45% A within 1 min; and, constant at 45% A for 7.5 min."

A new sentence has been added to Section 6.1 to describe the switching valve timing: "For 0–3.0 min, the LC mobile phase was passed through the column and sent to the waste to flush background ions that were present in the sample. With the 200 µL min^{-1} flow rate, a total of 600 µL of mobile phase (12× the sample injection volume) was used to flush out potential interferences. At 3.0 min, a switching valve was used to send the LC mobile phase to the MS/MS detector."

Comment #3. Section 5.2

When extracting the IEM coupons or fiber bundles in the HDPE centrifuge tube, please consider multiple extractions (your document indicates you will evaluate that), but also that the HDPE tubes themselves are adequately extracted with additional MeOH/ammonium acetate rinses to ensure any PFAS adhering to the tube wall is captured. Please discuss this issue.

The reviewers made an excellent point here. The concerns about potential PFAS interactions with the HDPE centrifuge tube walls were discussed for SPE procedures in Section 5.1.2 ("bottle rinsate"), and we will take a similar approach for analysis of experimental samples that contain ion-exchange membrane coupons or ion-exchange fiber bundles (Section 5.2). In this case, the experimental procedures need to separately account for PFAS on the ion-exchange materials and the centrifuge tube wall to avoid improper calculation of the equilibrium partitioning between the water and ion-exchanger phases. For this reason, the ion-exchange materials will be transferred into a "new" HDPE centrifuge tube for extraction and measurement of the PFAS concentrations in the ion-exchange materials. The water in the "original" HDPE container will be analyzed for PFAS concentrations, and the emptied "original" HDPE container will be separately extracted to account for PFAS mass on the container walls. In addition, separate

controls will be conducted without ion-exchange materials to evaluate PFAS interactions with the tube walls in the absence of ion-exchange reactions. The three measurements, namely PFAS in the ion-exchange materials, PFAS in the water, and PFAS on the container, allow proper evaluation of the PFAS mass distribution in experimental samples. PFAS extraction from the ion-exchange materials will employ 7 mL of methanol and 3 mL of 2 M ammonium acetate in accordance with literature-reported protocols. PFAS extraction from the HDPE containers will involve methanol, and the need for multiple rinses will be evaluated to ensure proper accounting of the PFAS mass balance.

Changes: The following sentences have been incorporated into Section 5.2: “The potential sorption of PFAS onto the HDPE containers will also be investigated. After each experiment, the HDPE containers will be rinsed with 10 mL of methanol to quantify the mass of PFAS on the container wall. This process will be repeated until no PFAS are present in the bottle rinsate.”

APPENDIX C: RESPONSE TO FINAL REPORT COMMENTS

In December 2021, we responded to the following comments on our Final Report v1 document.

Overview

Thank you for the feedback on our final report for ER20-1073. We have copied the feedback below (blue text) and appended our responses (black text). We thought it would be useful to keep all of our feedback in one document for review purposes, but we will also add our responses into the associated response boxes in SEMS. Appropriate changes have also been made to the Final Report, which will be uploaded under the V2 task in SEMS. If you have additional questions or requests, please do not hesitate to reach out to us.

Comment #1:

Thank you for submitting the Final Report; comments are provided below. Please review these comments and provide a response to each in SEMS in the associated response box below. Responses should include a discussion of the comment as well as a notation as to how the comment was incorporated into the revised document. Once the document is updated, submit the revised version in Word format to the Program Office under the (V2) task in SEMS. Include a completed SF298 form as page 2 of your submittal.

In order to close out the project, instruct your financial office to submit the final invoice as soon as possible so that the contract can be closed out. Final invoices must be marked as such in order to be processed correctly. The Program Office will publish the final version of the report and it will be available for users to download from the SERDP & ESTCP web page (www.serdp-estcp.org). If you have any questions regarding this review, contact Andrea at Andrea.Leeson.civ@mail.mil. Thank you for your effort in completing this important research project.

Response #1:

We have responded to all comments below and in the associated response boxes in SEMS. The revised version of the Final Report has been uploaded under the V2 task in SEMS. In addition, this document has been added to the Final Report as Appendix C. A completed SF298 form was included as page 2 of the Final Report V2 submission. I have instructed my financial office to submit the final invoice as soon as possible. We have no questions at this time.

Comment #2:

Abstract. Please update the abstract to include a section on results. This should be a brief 2 – 3 paragraph summary.

Response #2:

We have updated the content of the abstract to include a section on results as shown on the next page. The abstract was kept to one page in accordance with the Final Report guidance.

ABSTRACT

Project Number: ER20-1073

Project Title: Ion exchange membranes and fibers as passive samplers for chemically-diverse PFAS

Lead Principal Investigator: Lee Blaney, PhD

Lead Organization: University of Maryland Baltimore County (UMBC)

Objective: The overall goal of this project was to develop ion-exchange membrane and fiber strategies for passive sampling of chemically diverse PFAS. The project was developed to address DoD's needs with respect to measurement and remediation of PFAS. The specific objectives were as follows: (1) develop ion-exchange membrane and fiber passive samplers capable of concentrating short- and long-chain PFAS with varying log D values; (2) establish selectivity coefficients for 19 PFAS of concern in the ion exchange-based samplers to quantitatively describe PFAS uptake and partitioning; (3) confirm that the ion-exchange materials are capable of effective deployment and performance in synthetic and real groundwater and surface water matrices; (4) investigate ion exchange-based passive samplers for cationic, zwitterionic, and anionic PFAS; (5) ensure consistent performance of the samplers in single- and multi-sorbate scenarios; (6) characterize effects of solution pH, ionic strength, background ions, temperature, and dissolved organic matter on the passive samplers; and, (7) deploy the passive samplers in laboratory-based mesocosms to confirm their ability to resolve spatiotemporal variations in PFAS concentration.

Technical Approach: Ion-exchange membranes and fibers represent a paradigm shift in passive sampling strategies for organic contaminants and PFAS, in particular. This shift stems from the wide-ranging physicochemical properties of PFAS, which complicate traditional passive sampling strategies. The specific objectives were achieved through (i) batch sorption tests to identify selectivity coefficients, competitive effects, and impacts of interfering substances on PFAS uptake by the sampler and (ii) mesocosm studies using synthetic and real water matrices. The limited-scope portion of the project was focused on Objectives 1, 2, and 3.

Results: Our findings indicated that PFAS uptake into the ion-exchange membranes was fairly rapid, namely 2-3 days under well-mixed conditions and 2-4 weeks under static conditions; furthermore, these results were confirmed in large-volume studies using a real groundwater and pond water. We confirmed through both sorption and desorption studies that ion exchange was the primary mechanism of uptake for short- and long-chain PFAS with different head groups. The uptake capacity, selectivity coefficients, and PFAS recovery (extraction) were measured for ten ion-exchange membranes and one set of ion-exchange fibers. Based on the aggregate results, the FAD-PET-75 membrane was selected as the optimal choice for follow-on work. The selectivity coefficients for PFAS over chloride ranged from 1.57 (PFBA) to 4.90 (PFOS), and 1-4 cm^2 membrane coupons were able to accumulate enough PFAS for downstream analysis. The selectivity coefficients demonstrated trends with chain-length and head group. The total dissolved solids concentration (related to ionic strength) in real groundwater and pond water affected the observed selectivity coefficients, which increased with salt content, but these parameters were successfully corrected using Setschenow constants. The FAD-PET-75 membrane was effectively dissolved in methanol to achieve high recovery of short- and long-chain PFAS (*e.g.*, 87% PFBA, 104% PFOA). We also developed prototype samplers that will continue to be refined for field deployments in the proposed follow-on work.

Benefits: Given the increased importance of PFAS to ongoing cleanup and remediation efforts at DoD facilities, new strategies are required to enable monitoring of PFAS. The limit-scope portion of this project provided proof-of-concept evidence for ion exchange-based strategies, and follow-on work will continue to develop, evaluate, and test innovative ion exchange-based materials for passive sampling of PFAS. Due to the ion-exchange mechanism, the passive samplers offer robust solutions for the full range of PFAS of interest. The results of this project contributed new scientific understanding to the use of ion-exchange passive samplers, which may also be useful for other DoD-relevant contaminants.

Comment #3

Analytical Methods. Any future effort must follow the analytical procedures found in EPA's Method 1633- https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf We have some concern with the method extraction, cleanup procedures (see below), and detection limits. For example, the report states that "Control experiments demonstrated that NEtFOSAA, PFOSA, PFDoA, and PFTreA interacted with the walls of the 125-mL high-density polyethylene (HDPE) containers, and so these PFAS were excluded from further analysis". This phenomenon is not unknown; the EPA method would have additional methanol rinses of the vessel container (HDPE) to extract the additional sorbed materials.

We also have concerns regarding the FAD membrane dissolution by MeOH. It would appear this is a "dissolve and shoot" directly into the LC-MS/MS. If there was a cleanup step used (and there should have been), that is not discussed in the report. EPA 1633 has a requirement for cleanup with SPE that is appropriate here. An addition of PAC and then SPE may also be necessary in this specific case.

Response #3

We appreciate the reviewers' feedback here. The EPA 1633 method was released after our experimental work was completed for the limited scope portion of this project, but we have carefully reviewed the method to ensure future compliance in our follow-on work. The reviewers have asked good questions about our analytical methods, and we appreciate the opportunity to respond here.

Container rinse. We thank the reviewers for acknowledging that interactions between long-chain PFAS (*e.g.*, NEtFOSAA, PFOSA, PFDoA, PFTreA) and HDPE containers have been observed in previous studies. For analysis of real samples collected in HDPE containers, these interactions are important to ensure the accuracy of measured PFAS concentrations by accounting for potential losses to the container. In that respect, a methanol rinse of the container is appropriate, as the reviewers indicated. We regularly employ this approach in our laboratory for most analyses.

The experiments where we indicated that NEtFOSAA, PFOSA, PFDoA, and PFTreA were excluded from further analysis were focused on uptake kinetics (*e.g.*, Figure 3, Figure A1, Figure A7). For these experiments, we established batch reactors in HDPE containers and collected water samples at predetermined times to evaluate the uptake kinetics of PFAS from the aqueous phase to the membrane phase. To incorporate a container rinse, we would need to transfer the solution and membrane from one container to another after every sample is collected. We believe that such a process would add extra uncertainty from the large number of transfers between bottles. Alternatively, we could design an experiment with multiple bottles that are sacrificed at specific times, but this approach is generally discouraged for kinetics analysis since the solutions and membranes will differ from sample to sample, adding uncertainty. Importantly, our experimental results did not show major differences in the uptake kinetics for short- and long-chain PFAS with different head groups. This result is consistent with the literature for PFAS uptake in ion-exchange resins (Liu and Sun, 2021, *Water Research*, 207, 117781). Therefore, the main conclusions from the uptake kinetics experiments, namely 2-3 d equilibration under well-mixed conditions and 2-4 week equilibration under static conditions, were considered to be applicable to NEtFOSAA, PFOSA, PFDoA, PFTreA, and other PFAS of concern.

Importantly, our other experiments were mostly aimed at measuring PFAS equilibrium between the aqueous and membrane phases. For these experiments, the interactions of PFAS with the container walls are less important, because they do not affect the equilibrium conditions related to the ion-exchange reaction (Rxn. 1) or calculation of the corresponding selectivity coefficient (Eq. 1); however, it is necessary for the PFAS concentrations to be quantifiable in both the water and membrane phases. We did calculate the selectivity coefficients of NEtFOSAA, PFOSA, PFDoA, and PFTreA (*e.g.*, Figure 4, Figure 5, Figure 7, Figure 9, and others in the Appendix) after measuring their concentrations in the water and

membrane phases. To be clear, the water-phase concentrations are most appropriate here since PFAS accumulated on the container are not involved in the ion-exchange reaction (Rxn. 1).

$$\overline{R^+Cl^-} + PFAS^- \rightleftharpoons \overline{R^+PFAS^-} + Cl^- \quad \text{(Rxn. 1)}$$

$$K_{Cl}^{PFAS} = \frac{[PFAS^-]_{mem}[Cl^-]_{aq}}{[Cl^-]_{mem}[PFAS^-]_{aq}} \quad \text{(Eq. 1)}$$

For the reasons discussed above, we believe that our approach to the kinetics and equilibrium experiments were appropriate to achieve the desired outcomes, namely estimating the deployment times and accurately measuring the selectivity coefficients.

PFAS analysis in ion-exchange membranes. The reviewers raised an important point about potential matrix effects during analysis of membrane-phase PFAS concentrations. We were also concerned about these effects and conducted rigorous analysis, quality assurance, and quality control to confirm that the approach was appropriate. Importantly, our approach to passive sampling of PFAS with ion-exchange membranes is, in many respects, the same as solid-phase extraction (SPE) with weak anion-exchange sorbents. In this regard, many matrix effects are eliminated through PFAS uptake by the ion-exchange membranes, and so an additional SPE step is somewhat redundant. The extraction process was normalized for all samples, further reducing matrix effects from one membrane to another (*i.e.*, between samples), providing the same benefits from conventional SPE protocols. However, we were still concerned about whether PFAS ionization was suppressed in the final extracts, which contained 10 mM NH_4Ac and 50% methanol; note, all matrix effects were corrected using internal standards and so the major concerns here are impacts on the limits of detection and quantitation.

The ion-exchange membranes were dissolved in methanol at concentrations of less than 1 g L^{-1}. Due to the high uptake of PFAS by the ion-exchange membranes and the incompatibility of methanol-based samples with chromatographic separation, the methanol extracts were diluted at least 50× with 10 mM NH_4Ac to achieve PFAS concentrations in the $0.1 - 25$ μg L^{-1} range and a final methanol content of 50%. No precipitates were observed in the diluted extracts. We incorporated an online SPE step in the LC method (Appendix B of the Final Report) to prevent suppression issues in the ionization chamber. The method run time was extended to 15 min (longer than EPA Method 1633) to further improve analytical sensitivity by achieving better separation of PFAS and more scan events for each PFAS. The matrix effects were thoroughly checked using mass-labeled PFAS for each batch of samples and were always lower than 50% (and lower than 25% for most cases). For example, Figure R3 shows the responses of mass-labeled standards in a diluted FAD-PET-75 extract plotted against those in solutions with the same NH_4Ac and methanol contents (but no FAD-PET-75 residue); note, these data stem from the experiment shown in Figure 8 of the Final Report. These outcomes align with the quality assurance and quality control guidance from Table B-15 of the DoD QSM v5.3 document. In follow-on work, we will also specifically check that the measured matrix effects are in compliance with EPA Method 1633. If the matrix effects are too high/low, we will take the appropriate corrective actions specified in the protocols.

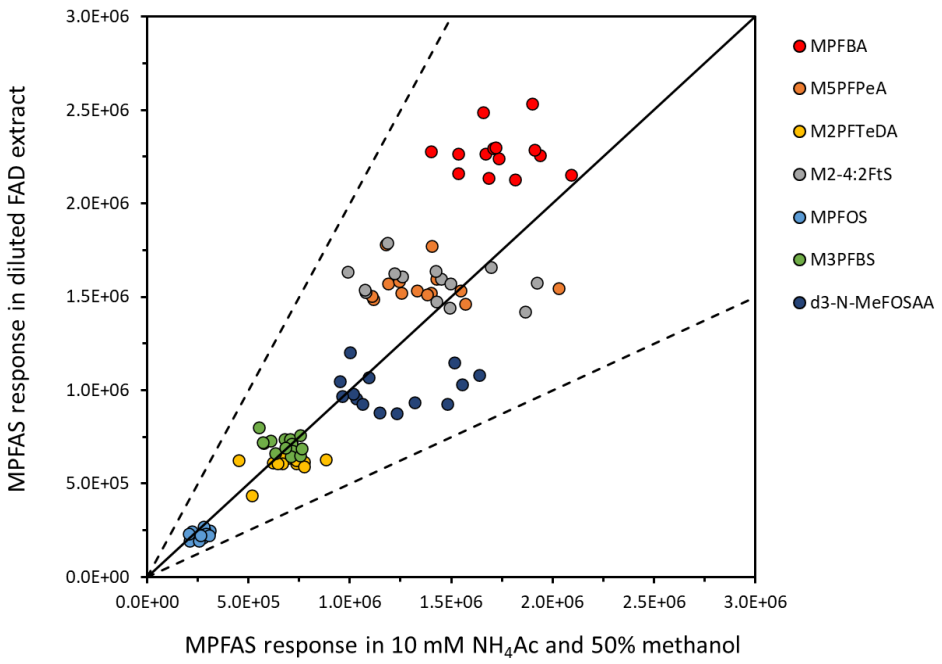


Figure R3. The response of mass-labeled PFAS (MPFAS) in a diluted FAD-PET-75 extract, which contained 10 mM NH_4Ac and 50% methanol, plotted against the response of the same mass-labeled PFAS in 10 mM NH_4Ac with 50% methanol. Based on guidance from DoD QSM v5.3, the matrix effects should be less than 50%, otherwise, additional cleanup steps are required. The upper and lower dashed lines represent 50% signal enhancement and suppression, respectively. Given the good agreement between mass-labeled PFAS responses in the FAD-PET-75 extract and clean solutions, no additional cleanup steps were required.

Comment #4

Consistent Reporting of PFAS. There is an inconsistency in the number of PFAS reported that should be reconciled in a revised report. The original proposal indicates that 24 PFAS would be tested, but varying numbers of PFAS are reported. For example:

- Figure 3 - 8 PFAS
- Figure 4 - 19 PFAS
- Figure 5 - 12 PFAS
- Figure 8 - 3 PFAS whereas the text indicates there were 19 PFAS in the groundwater
- Figure A.1 - 10 PFAS
- Figure A.4 - 7 PFAS

The point is that in order to fully evaluate the efficacy of the passive sampling method we need to be able to see all of the data for all PFAS. There may be good reasons why certain PFAS were not reported (e.g., non-detected), but that has to be articulated in the report.

Response #4

We thank the reviewers for their detailed review of our report, and we understand this concern. The reasons for these differences mostly involved (i) availability of bulk chemicals, (ii) experimentation with a "preliminary suite" and the "full suite" of analytes, and (iii) an abundance of data that could not be cohesively integrated into a single figure.

Availability of bulk chemicals. We had initially proposed 24 PFAS of concern, but we were unable to purchase bulk amounts of five compounds (*i.e.*, PFTriA, PFHpS, PFNS, PFDS, NMeFOSAA). Given the large number of experiments, the use of analytical standard-grade chemicals for experimental purposes was not feasible. For this reason, several of the figures (*e.g.*, Figure 4, Figure 7) only included 19 PFAS. To avoid confusion, we have replaced "24" with "19" throughout the Final Report.

Preliminary and full suites. Some experiments were conducted with a preliminary suite of compounds designed to capture the range of PFAS of concern according to chain-length and hydrophilic head group. In particular, the data shown in Figure 3 (uptake kinetics), Figure 4 (selectivity coefficients), and Figure 5 (sorption isotherms) were collected from experiments that included a mixture of 12 PFAS (*i.e.*, PFBA, PFBS, PFHxA, PFHxS, PFOA, FtS 6:2, PFOS, PFDA, NEtFOSAA, PFOSA, PFDoA, PFTreA). The results for NEtFOSAA, PFOSA, PFDoA, and PFTreA were not included in the uptake kinetics figure (Figure 3) for the reasons discussed in the Final Report and elaborated in our response to Comment #3 (above). To provide further clarity, we have edited the statements in question to make this point clear.

- Section 5.1.1: "Control experiments demonstrated that NEtFOSAA, PFOSA, PFDoA, and PFTreA interacted with the walls of the 125-mL high-density polyethylene (HDPE) containers, and so these PFAS were excluded from further time-based analysis".
- Section A1.1: "Quality control experiments suggested that PFDoA, PFTreA, PFOSA, and NEtFOSAA interacted with the high-density polyethylene (HDPE) containers; therefore, the change in concentration for these PFAS involved both uptake by the anion-exchange membranes and interactions with the containers. For this reason, PFDoA, PFTreA, PFOSA, and NEtFOSAA were not included in kinetics analysis (as described above)."
- Section A2.2: "Figure A7 reports the change in aqueous-phase concentration for 15/19 PFAS over a 10-d experiment; the other four compounds (*e.g.*, NEtFOSAA, PFOSA, PFDoA, PFTeDA) were excluded from this time-based analysis for the reasons noted above."

The results for NEtFOSAA, PFOSA, PFDoA, and PFTreA were included in the selectivity coefficient (Figure 4) and sorption isotherm (Figure 5) figures for the reasons described in our response to Comment #3 (above). The above explanations also apply to Figures 6, 7, 8, 9, A1, A2, A3, A4, A5, A6, A7, A8, A9, A10, A11, A12, A13, A14, A15, and A17.

Abundance of data. For some experiments, we collected more data than could be easily integrated into cohesive figures. For example, we highlighted the equilibration of three representative compounds in the groundwater and pond water matrices in Figure 8. These three PFAS highlighted our takeaway points about equilibration time, impacts of background matrix, and effective uptake of chemically diverse PFAS. However, we understand the need for transparency and data availability. For this reason, we have included the full dataset from these experiments in the attached Excel file (see Comment #4) and added the following statement.

- Section 4: "All experimental data are available in Appendix D, and additional details can be provided upon request."

The above explanations also apply to Figures A3 and A13.

Other issues. As indicated in the Final Report, PFHxA and PFHxS demonstrated high signal suppression for the experiment shown in Figure A1. This phenomenon was not observed in other experiments or samples. To provide further clarity, we have edited the statement in question to make this point clear.

- Section A1.1: "Note, PFHxA and PFHxS demonstrated high signal suppression for this particular experiment and were, therefore, excluded from this time-based analysis."

Comment #5

Analytical Data. Provide the underlying analytical data used to create each of the graphics in the report. As these graphics appear to have been created using Excel (or equivalent), the supporting data should already exist as a table you could provide as an Appendix or Attachment. In those tables, indicate with a header the report figure number (e.g., Figure 3), the membrane tested (e.g., AMI 100 rpm, FAA 100 rpm), the PFAS, the measured PFAS concentration at each time interval, the conversion to nmole/g.

An emphasis needs to be on the actual measured concentrations - not the concentrations converted to mols or C0 vs Ct. We need to be able to follow the numbers and calculations through a table and then to the figures themselves.

Tables of data are needed to understand aggregated PFAS data represented in Figures 7 and 9. Which PFAS, what are the measured values, and in the case of Figure 9 - showing the salt-correction calculations. We are especially interested in looking at the latter in more detail.

Response #5

Thank you for this comment. We have assembled the requested tables in the attached Excel file, which is referred to as Appendix D in the Final Report V2. The data are separated into distinct tabs corresponding to each figure. All data tabs show the raw data and corresponding calculations used to develop the figures. Some figures from Final Report V1 were updated using the data shown in Appendix D. As indicated in our response to Comment #4 (above), we have also added a statement in Section 4 to indicate the availability of all experimental data in Appendix D.

APPENDIX D: EXPERIMENTAL DATA

See attached Excel file for all experimental data and calculations.

APPENDIX E: LIST OF SCIENTIFIC/TECHNICAL PUBLICATIONS

1. Blaney, L.; He, K. Ion-exchange membranes and fibers as passive samplers for chemically-diverse PFAS (ER20-1073). SERDP & ESTCP Symposium 2020 (virtual), December 1, 2020.

2. Blaney, L.; He, K. Ion-exchange membranes and fibers as passive samplers for chemically-diverse PFAS (ER20-1073). SERDP & ESTCP Project Meeting on PFAS Ecotoxicity, Analyses, Fate, Transport, Treatment (San Pedro, CA), July 19-22, 2021.