SERDP

FINAL REPORT

Osorb® Media Use in PFAS Passive Samplers

Craig Divine
Erika Carter
Kevin Toth
Arcadis

Paul Edmiston
The College of Wooster

December 2023

SERDP Project ER20-1127

DISTRIBUTION STATEMENT A
This document has been cleared for public release.

REPORT DOCUMENTATION PAGE			*Form Approved OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
08/03/2024	SERDP Final Report	7/21/2020 - 7/21/2024

4. TITLE AND SUBTITLE
Osorb® Media Use in PFAS Passive Samplers

5a. CONTRACT NUMBER
20-C-0052

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Craig Divine
Arcadis

Paul Edmiston
College of Wooster

5d. PROJECT NUMBER
ER20-1127

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Arcadis
320 Commerce, Suite 200
Irvine, CA 92602

8. PERFORMING ORGANIZATION REPORT NUMBER
ER20-1127

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of the Deputy Assistant Secretary of Defense (Energy Resilience & Optimization)
3500 Defense Pentagon, RM 5C646
Washington, DC 20301-3500

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
ER20-1127

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The additional work on the Sentinel™ passive sampler for per- and polyfluoroalkyl substances completed during the extension period for Strategic Environmental Research and Development Program Project ER20-1127 and presented herein focused in several areas – technology transfer, including commercialization of manufacturing and laboratory analysis; passive sampler calibration; and field application by United States Environmental Protection Agency researchers.

15. SUBJECT TERMS
PFAS, AFFF, sampling and analysis, passive sampling

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Craig Divine
UNCLASS	UNCLASS	UNCLASS	UNCLASS	52	**19b. TELEPHONE NUMBER** *(Include area code)* 720-308-5367

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Tables

List of Figures

List of Appendices

Acronyms and Abbreviations

%	percent
°C	degrees Celsius
CEERD	United States Army Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
HDPE	high-density polyethylene
HPLC-MS/MS	high performance liquid chromatography tandem mass spectrometry
LOD	limit of detection
mL	milliliter
ng	nanogram
ng/L	nanograms per liter
PFAS	per- and polyfluoroalkyl substances
PFHxA	perflurohexanoic acid
PFNA	perfluorononanoic acid
PFOS	perfluorooctanesulfonic acid
RPD	relative percent difference
rpm	revolutions per minute
*R*s	sampling rate
SD	standard deviation
SERDP	Strategic Environmental Research and Development Program
U.S.	United States
USEPA	United States Environmental Protection Agency

Abstract

The additional work on the Sentinel™ passive sampler for per- and polyfluoroalkyl substances (PFAS) completed during the extension period for Strategic Environmental Research and Development Program Project (SERDP) ER20-1127 and presented herein focused in several areas – technology transfer, including commercialization of manufacturing and laboratory analysis; passive sampler calibration; and field application by United States Environmental Protection Agency (USEPA) researchers.

- The Sentinel™ passive sampler is commercially available from a manufacturer, Aquanex Technologies, LLC. Slight changes to the physical design were introduced to make the sampler more durable for varied field applications (e.g., adding rivets to more securely hold the screens containing the Osorb sorbent in place), and by developing a stainless steel model intended for sediment applications (in response to suggestions from USEPA researchers).
- The laboratory methodology was adapted to facilitate commercial laboratory production and align the extraction method to USEPA Method 1633 – eliminating an evaporation step, resulting in an expedited procedure. To date ten laboratories in the United States and Europe have gained experience with the Sentinel™ passive sampler and are anticipated to offer analysis commercially in 2024.
- Additional work was also performed to refine the calibration of the sampling rate (R_s) values with respect to temperature using a Langmuir-type model. This will allow more precise reporting of PFAS concentrations based on the use of R_s values keyed to the field sample temperature, where measured. Furthermore, R_s values for sediment porewater applications were developed based on a mixture of laboratory calibration and extrapolations from previously generated data. These sediment porewater R_s values will form a starting point for additional calibration to be performed in a forthcoming Environmental Security Technology Certification Program (ESTCP) project demonstrating the sampler in sediment porewater.
- USEPA Office of Research and Development researchers deployed passive samplers (Sentinel™ samplers and two other types) in a Duluth, Minnesota field study area in conjunction with SERDP Project ER22-3202, Food-Web Exposures and Consequent Effects of PFAS on Birds. Passive samplers were deployed in three field events (2022 – 2023) in surface water and sediment with a primary goal of providing field validation of passive sampler robustness, ease of use, and field effectiveness. Laboratory analysis of the Sentinel™ passive samplers deployed by USEPA researchers revealed consistent performance compared to previous demonstrations in terms of surrogate performance and field duplicates. Slightly higher variability in field duplicates was noted for sediment porewater samples than for surface water, as would be expected in a heterogeneous sediment environment. The updated R_s values developed for sediment porewater were applied to calculate the sediment porewater PFAS concentrations. The complete comparison study results, including other passive samplers and grab samples, will be reported by USEPA. Feedback from USEPA researchers has already resulted in the manufacturer's modification of the Sentinel™ sampler design for sediment porewater applications. Additional recommendations regarding tooling for sediment deployments will be applied during the forthcoming ESTCP Project ER23-7696, Osorb Passive Sampler for Determination of PFAS in Sediment Pore Water.

The results of this work continue to support the utility of the Sentinel™ passive sampler for a wide variety of field applications.

1.0 Introduction

Continuation funding during an extension period was obtained from the Strategic Environmental Research and Development Program (SERDP) under Project ER20-1127 to perform additional field demonstrations in 2022 and 2023 through collaboration with United States (U.S.) Environmental Protection Agency (USEPA) researchers. Furthermore, additional laboratory method development, additional passive sampler calibration, and technology transition activities were performed during this extension period.

2.0 Technology Transition in Manufacturing and Laboratory Analysis

This section describes technology transition status regarding commercialization of manufacturing and analysis of the Sentinel™ passive sampler.

2.1 Commercial Passive Sampler Construction

Slight changes were made to the passive sampler morphology for commercial production.

For water applications (e.g., groundwater, surface water, storm water), the passive sampler body is constructed of high-density polyethylene (HDPE) with dimensions of 2.5 centimeters wide by 5 centimeters long (slightly longer than prototype 4.5-centimeter length), with a 1-centimeter diameter through-hole. The sorbent resin is placed between HDPE mesh screens held in place with HDPE rivets (versus the original heat-welded HDPE ring). The modified design is more rugged for field deployments. A small stainless steel tag, stamped with a unique serial number, doubles as a weight, and is included with each sampler.

A second model of the passive sampler with a stainless steel body was developed by the manufacturer for sediment applications in response to feedback from USEPA researchers (see Section 4). The stainless steel model of the passive sampler uses the same sorbent held behind HDPE mesh, which is held in place with copper rivets.

The passive sampler is commercially available as the Sentinel™ passive sampler from Aquanex Technologies, LLC at https://aquanextech.com/.

Figure 1. Commercially manufactured Sentinel™ passive sampler for water (left) and sediment (right). Source: AquanexTech.com.

2.2 Analytical Method Development

Modifications to the analytical procedure for passive sampler analysis were made in 2023 as USEPA Method 1633 began to be offered by commercial laboratories. The main goal of the procedure modification was to reduce solvent (methanol) extraction volumes and eliminate the evaporation step to be in line with USEPA Method 1633 while avoiding volatilization of certain per- and polyfluoroalkyl substances (PFAS; e.g., fluorotelomer alcohols). The modification further simplifies the analytical procedure for commercial laboratories, which may encourage them to offer the analysis.

The modified extraction procedure is shown on **Figure 2** and provided in **Appendix A**.

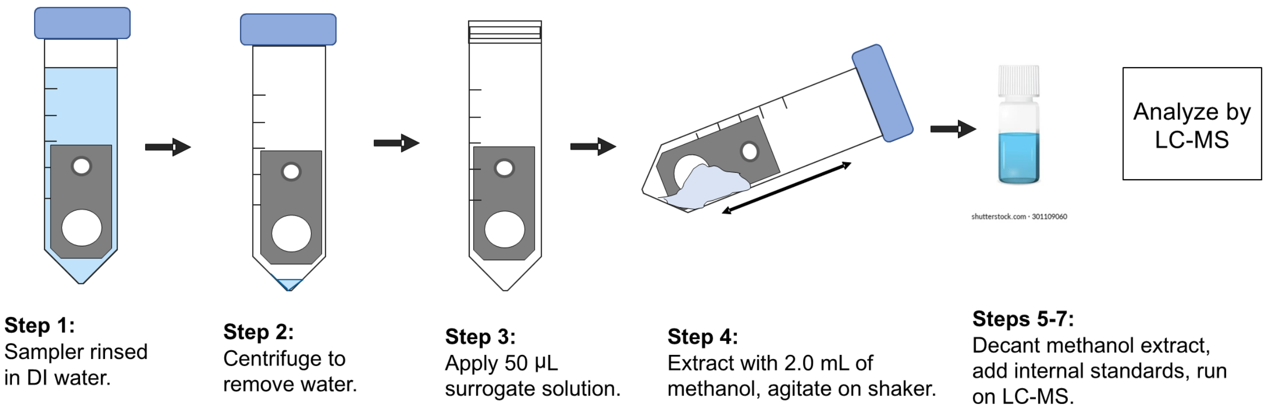


Figure 2. Updated passive sampler post-deployment extraction steps.

2.3 Laboratories with Experience in Sentinel™ Passive Sampler Analysis

Technology transfer of passive sampler analysis to commercial laboratories continued in 2022-2023, in general, led by the manufacturer. **Table 1** shows the current laboratory capabilities as of February 2024.

Table 1. Commercial laboratory capability for Sentinel™ passive sampler analysis (February 2024)

Lab Group	Location	Country	Analysis	Status	DoD Qualified?
SGS AXYS	Sidney, BC	Canada	1633	Active	Yes
SGS	Fellbach	Germany	1633	Active	No
SGS	Dayton, NJ	USA	1633	TBD 2024	No
SGS	Orlando, FL	USA	1633	TBD 2024	Yes
Pacific Rim	Vancouver, BC	Canada	1633	Active	In process
Enthalpy Analytical	Wilmington, NC	USA	1633	TBD 2024	Yes
Eurofins	Brisbane	Australia	1633	TBD 2024	No
Eurofins	Lancaster, PA	USA	1633	Pending	Yes
RTI Labs	Detroit, MI	USA	537.1	Active	No
ALS Laboratories	Hawarden	UK	1633	TBD 2024	No

3.0 Passive Sampler Calibration Updates

Laboratory analysis of the passive sampler post-deployment yields an accumulated mass of analyte bound during the sampling time. The accumulated mass (ng) is converted to the aqueous phase concentration, C_w (nanograms per liter [ng/L]), using the following equation.

$$C_w = \frac{accumulated\ mass}{R_s \times t} \qquad \text{Equation 1}$$

where R_s is the sampling rate and t is the sampling time in days.

Two updates to the sampling rates (R_s) previously developed in this project were made in the extension year, including refinements to R_s calibration with respect to temperature, and development of R_s values for sediment porewater.

3.1 Temperature Calibration

In the first years of the project, lab and field data both demonstrated a non-linear dependence on temperature, which enabled temperature effects to be grouped in two conditions for typical environmental ranges: above and below 10 degrees Celsius (°C). If water temperature at a sampling location had an average of <10°C, an analyte-specific correction factor was applied to reduce the sampling rate to account for the slower kinetics at the lower temperature regime.

Additional evaluation of the empirical data collected during the initial project work revealed that the R_s versus temperature curve could be a fit to a Langmuir-style equation as follows:

$$R_s(T) = \frac{R_{s(max)} \times K \times T}{1 + (K \times T)} \qquad \text{Equation 2}$$

where $R_s(T)$ is the R_s calculated for a specific temperature, and $R_{s(max)}$ and K are curve-fitting parameters. Use of this equation allows more precise calibration of R_s for sample locations, and thus more precise PFAS concentrations where temperature is measured. The fit curve for perfluorooctanesulfonic acid (PFOS) and calculated R_s values for temperatures between 1 and 25 °C are included as an example in **Appendix B**. An Excel-based calculator to determine temperature-adjusted R_s values for groundwater and surface water samples was developed and provided to the passive sampler manufacturer.

3.2 Calibration of R_s Values for Sediment Applications

Development of R_s values for sediment porewater was performed with the assistance of U.S. Army Engineer Research and Development Center (CEERD, Environmental Lab) and SERDP Project ER22-3392. Estuarine sediment from a relatively pristine site (99 percent [%] fines, 2.2% total organic carbon) was spiked via coated sand (solvent-free) with a mixture of perflurohexanoic acid (PFHxA), perfluorooctanoic acid, perfluorononanoic acid (PFNA), perfluorodecanoic acid, perfluoroundecanoic acid, perfluorohexanesulfonic acid, PFOS, perfluorodecane sulfonic acid, 8:2 fluorotelomer sulfonic acid, and 6:2 fluorotelomer sulfonic acid at a target concentration of 5 milligrams per kilogram dry weight for each chemical. Passive samplers were deployed in PFAS spiked sediment for 14 days. Pore water concentrations in the sediment were determined by CEERD and were used to determine the R_s values (**Table 2**). The R_s values are lower than those observed for sampling in flowing water steams which is expected as flow rate and mass transport is a key factor in PFAS uptake in integrative passive samplers. The R_s values for other USEPA 1633 analytes were extrapolated from these 11 analytes using flow rate dependency trendlines measured throughout the project. An example of the variation of measured Rs with flow rate is shown for PFHxA in **Figure 3**. The complete list of sediment porewater R_s values determined to date for USEPA Method 1633 analytes is provided in **Appendix C**. The R_s values will continue to be refined as additional pore water data are provided to the project team (e.g., USEPA deployed passive samplers, as well as anticipated future work funded through the Environmental Security Technology Certification Program [ESTCP]).

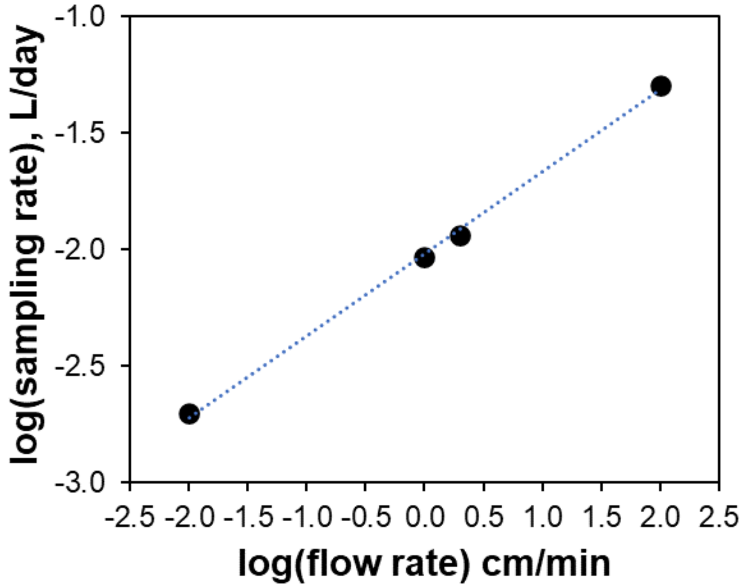


Figure 3. Measured sampling rate (R_s) versus flow rate for PFHxA

Table 2. R_s Values Measured for Sediment Porewater at 25 °C, Compared to Values for Streams

PFAS Analyte	R_s **(L/d)**	
	Stream	Sediment
6:2 Fluorotelomer sulfonic acid	0.060	0.0018
8:2 Fluorotelomer sulfonic acid	0.060	0.0011
Perflurohexanoic acid (PFHxA)	0.051	0.0020
Perfluorooctanoic acid (PFOA)	0.065	0.0022
Perfluorononanoic acid (PFNA)	0.068	0.0015
Perfluorodecanoic acid (PFDA)	0.068	0.0013
Perfluoroundecanoic acid (PFUdA)	0.065	0.0012
Perfluorohexanesulfonic acid (PFHxS)	0.070	0.0025
Perfluorooctanesulfonic acid (PFOS)	0.065	0.0011

4.0 Additional Field Deployments – Duluth, Minnesota

4.1 Introduction (project background)

Additional field deployments of the Sentinel™ passive sampler in surface water and sediment were conducted by USEPA Office of Research and Development researchers Marc Mills and Brian Crone. This work is being completed in coordination with the SERDP Project ER22-3202, Food-Web Exposures and Consequent Effects of PFAS on Birds (referred to as Avian Tools Study, with Principal Investigator Matthew Ettinger, USEPA), which began with a scoping study in 2022 and is expected to continue for three additional years. The objective of SERDP Project ER22-3202 is to improve understanding of the distribution and movement of PFAS in avian food webs and the effects of PFAS on birds. USEPA researchers Marc Mills and Brian Crone contributed additional scope to the project, including the collection of riparian spiders and deployment of several types of PFAS passive samplers. These elements were added to expand the scope of food-web characterization and evaluate PFAS passive sampler performance.

4.2 Objectives

The objectives of these additional field deployments are to compare and validate the use of passive samplers from three different manufacturers for estimating PFAS bioavailability and concentrations in surface and sediment porewater.

The USEPA team's field validation focuses on the robustness of the passive samplers, their ease of use, and effectiveness in field conditions. The comparison of passive sampler types is not intended to determine whether any one sampler is "better" than the other but rather to determine the most appropriate context and matrix application for each sampler type. The comparison of passive sampler results to measurements of PFAS in water, sediment and biota is used to determine if passive samplers can be used to estimate bioavailability as well as provide temporally integrated PFAS measurements. Lastly, the data collected from these field deployments are used to characterize the sites and sources of PFAS.

4.3 Study Area

The study area is in northeast Minnesota near the city of Duluth. Passive samplers were deployed in surface water and sediment at five field locations. Boulder Lake, Rice Lake, Martin Road, Duluth Air National Guard Base, and Boy Scout Landing were selected as field locations to better understand sources of transport and connection in relation to aquatic food webs. An additional field location near a nearby landfill was added in the second deployment year.

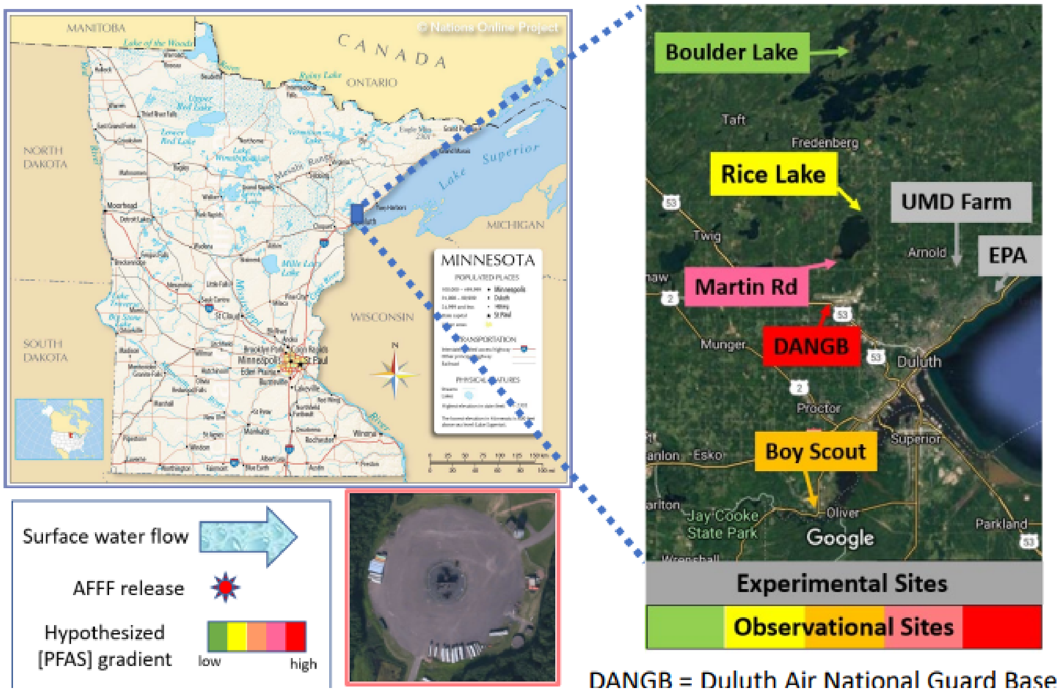


Figure 4. USEPA Study Area near Duluth, Minnesota

4.4 Field Scope and Methods

USEPA Office of Research and Development staff deployed passive samplers provided by three different organizations in surface water and porewater at locations included in the larger Avian Tools Study. The deployment of the passive samplers coincides with surface water, sediment, and biota samples being collected under the larger Avian Tools study and will be used to evaluate their effectiveness as a tool for PFAS monitoring in the environment. Characterization of the riparian spider contaminant concentrations will be used to determine if these organisms correlate well with sediment, food web, and bioaccumulation measurements, such as passive samplers.

For surface water deployments all three types of passive samplers were attached via cable ties to the rails of moorings shown in **Figure 5** (right panel). A temperature sensor was also deployed on each mooring and water quality measurements were taken with a YSI sonde both at deployment and retrieval of the samplers. Temperature data were not available for review at the time of writing this report.

For pore water deployments all three types of passive samplers were joined together as shown in **Figure 5** (left panel) and pushed completely into the sediment with a custom drive head and push rods until the top of the sampler was even with the sediment water interface.

4.4.1 <u>Field Deployments 1 and 2 – 2022</u>

The first-year scoping study, including field deployments 1 and 2, was used to evaluate station selection, in particular, evaluating the range of concentrations present and verifying that that passive sampler selected would be appropriate for measuring those concentrations. Passive samplers were deployed at 12 locations during two different deployment periods. The two deployment periods were used to evaluate temporal changes and provide overlap with other environmental measurements. The first deployment period was in June – July 2022 (54 days on average). The samples collected and analyzed from the first deployment included 12 surface water passive samplers, one field duplicate, and one trip blank. The second deployment period was in July – September 2022 (60 days on average). The samples collected and analyzed from the second deployment included 12 surface water passive samplers, eight sediment porewater passive samplers, two field duplicate passive samplers (one for surface water and one for sediment porewater), and one trip blank. During the second field deployment, in addition to the samples collected and analyzed, four sediment porewater passive samplers were damaged during deployment and could not be analyzed; and one surface water passive sampler was lost. In addition, one sediment porewater passive sampler failed laboratory quality control and its results are not reported.

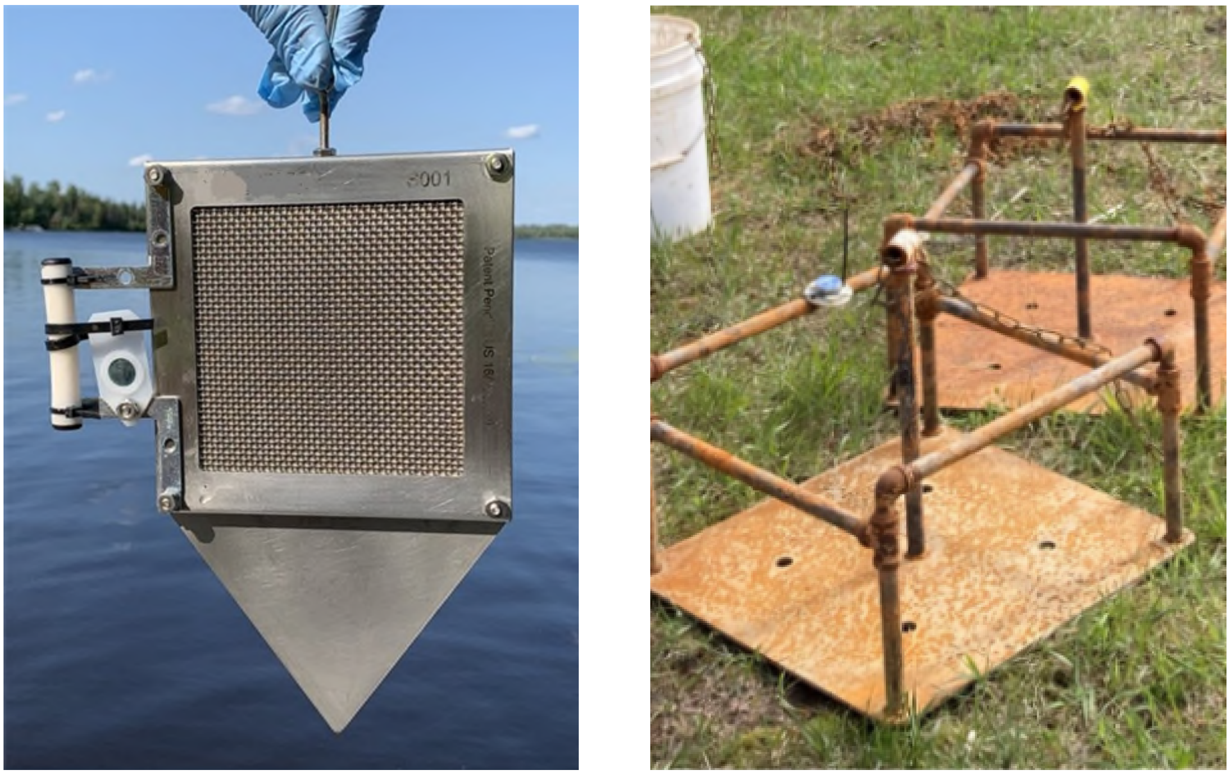


Figure 5. Photos of passive sampler deployment configuration for sediment (left) and surface water (right) in Duluth, Minnesota study area.

4.4.2 Field Deployment 3 – 2023

The scope of work for field deployment 3 included sampling at the 12 locations used in field deployments 1 and 2, as well as four additional locations and three mini-deployments. Three of the additional locations (LF-01, LF-02, SR-01) were added to evaluate whether a landfill site may be acting as an additional source of PFAS in the study area. One of the additional locations (MR-02) and three mini deployments (MD-01, MD-02, MD-03) at Martin Road were added to evaluate deployment duration. The average deployment period, excluding MD stations, was 43 days in June – July 2023. Samples collected and analyzed from the third deployment included 18 surface water samplers, 18 sediment porewater samplers, eight field duplicates for water, nine field duplicates for sediment porewater, five trip blanks for surface water, and five trip blanks for sediment porewater.

Table 3. Field Sample Summary – Duluth, Minnesota Study Area (2022-2023)

Deployment Event	Passive Samplers Analyzed				Damaged/Lost Passive Samplers
	Surface Water	Sediment Porewater	Field Duplicates	Trip Blanks	
1 (Summer 2022)	12	0	1	1	0
2 (Summer 2022)	12	8	2	1	4 sediment 1 surface water
3 (Summer 2023)	18	18	17	10	3 surface water
Total:	42	26	20	12	4 sediment 3 surface water

4.5 Laboratory Analysis of Passive Samplers

Analysis of PFAS extracted from the passive samplers generated during field deployments was performed at the College of Wooster. The samples were extracted and analyzed using a modified USEPA Method 537.1, as described in the December 2023 Final Report and below.

Upon retrieval and return to the laboratory samplers were rinsed with PFAS-free deionized water to remove debris. (Note: The adsorbent was not removed from the sampler body during analysis and all steps are performed at 25°C.) Each sampler was placed in a 50-milliliter (mL) conical centrifuge tube along with 15 mL of deionized water containing isotopically labeled surrogates (50 nanograms [ng] each) and mixed for 7-8 hours on a platform shaker table. Samplers were removed from surrogate solution and residual liquid was spun off by centrifugation for 20 seconds at 1,500 revolutions per minute (rpm). PFAS was extracted by placing each sampler in a 50 mL centrifuge tube containing 20 mL of methanol + 2% NH_4OH and shaking it 4 hours. Samplers were next removed from the methanol solution and placed in a new 50 mL centrifuge tube and centrifuged for 20 seconds at 1,500 rpm to spin down residual solution. The methanol recovered by centrifugation was combined with the extraction solution and evaporated to reduce the volume to 0.5-1.0 mL under N_2. Internal standards were added (10 µL HIF-IS) and the liquid centrifuged at 14,000 rpm to remove suspended particles prior to analysis by high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS).

PFAS analyte standards were obtained from Wellington Laboratories. Solvents were purchased from Pharmco/Aaper and used as received. Ammonium acetate (LC-MS grade) was obtained from Sigma-Aldrich. All other reagents and supplies were obtained from Fisher Scientific and used as received.

PFAS concentrations were analyzed by HPLC-MS/MS using an Agilent 1200/6410 HPLC-MS/MS (QqQ) with using Infinity Lab C18 Poroshell 120 21x100 mm column, particle size 2.7 micrometer with a Restek PFAS delay column. Mobile phases were A: 5 mM ammonium acetate in water B: 95% methanol + 5 mM ammonium acetate with a flow rate of 0.250 mL/min at temperature of 45°C. A calibration curve was measured with each batch of samples. Method blanks, instrument blanks, and 10 nanograms per milliliter laboratory control standards were run in accordance to the Department of Defense QSM Table B-15. Limits of detection (LODs) and method detection limits for each analyte are reported in Edmiston et al. (2023a); for most analytes these are <1 ng/L and <2 ng/L, respectively for water passive samplers.

The PFAS concentrations in the aqueous phase C_w (ng/L) were determined from the accumulated mass of each analyte adsorbed during deployment using Equation 1 (see Section 3). Samples received in 2022 were analyzed for 19 USEPA Method 537.1 PFAS analytes, and samples received in 2023 were analyzed for 41 USEPA Method 1633 analytes. The *Rs* values for surface water were those previously reported in the project Final Report (Divine et al. 2023). The *Rs* values for sediment porewater were those developed during the project extension (discussed in Section 3.2 and provided in **Appendix C**.

4.6 Field Deployment Results and Discussion

The following sections provide results of the 2022 and 2023 passive samplers deployments in the Duluth, Minnesota field study area sampled by the USEPA field team.

4.6.1 Results

Both surface water and sediment passive samplers were analyzed successfully. Only one passive sampler failed analytical quality assurance/quality control and its results were not reportable. PFAS results from passive samplers deployed in water and sediment in the Duluth study are provided in **Appendix D-1** through **D-3** for the three 2022-2023 deployment events, respectively.

Detected analytes primarily consisted of C4-C8 perfluorocarboxylates and perfluorosulfonates, as well as perfluorobutane sulfonamide and perfluorohexane sulfonamide. In addition, longer chain PFNA and perfluorodecanoic acid were detected in some sediment porewater samples. Detected PFAS concentrations measured in the study were generally in single digit ng/L to hundreds of ng/L. Concentrations greater than 1,000 ng/L were limited to sediment porewater samples, in particular, those from the Duluth Air National Guard Base and Martin Road sampling locations.

Field duplicates were collected from each sampling event to provide a measure of sampler to sampler variability. The field duplicate results are summarized in **Table 4**. Overall, the results of field duplicates were consistent with previous field results. It was expected that the sediment porewater passive samplers could display higher variability in results than surface water passive samplers due to heterogeneity within the porewater environment. For cases when an analyte was detected in both the parent and field duplicate sample, relative percent difference (RPD) was calculated (73 paired surface water passive sampler analyses and 95 paired sediment porewater sampler analyses). As predicted, the average RPD of sediment porewater analyses (57% [standard deviation (SD)=42]) was slightly higher than that of surface water passive samplers (32% [SD=33]). Paired non-detect values were observed very frequently (74% of analyses). Very rarely (in fewer than 3% of analyses) was an analyte detected in one passive sampler and not its paired duplicate/parent (**Table 4**).

Table 4. Summary of Passive Sampler Field Duplicate Performance – Duluth, Minnesota Study Area (2022-2023)

Parameter (Counts)	Surface Water Passive Samplers	Sediment Porewater Passive Samplers
Total Field Duplicate Pairs (Sample n)	10	10
Total Paired Analyses	386	347
Detect Analyte Pairs	73	95
Relative Percent Difference (Standard Deviation)	32% (SD=33)	57% (SD=42)
Non-Detect Analyte Pairs	306	240
Mixed Detect / Non-Detect Pair	7	12

Surrogate recoveries measured on samples from the first and third Duluth deployment events were similar to previous batches (79% and 96%, on average, respectively), while the average recoveries from the second deployment event were lower (57% on average). Surrogate recoveries are provided in **Appendix D-4**. Similar to previous observations, the highest recoveries was generally observed for C4-C8 perfluorocarboxylates and perfluorosulfonates and lower recoveries were frequently observed for long-chain perfluorocarboxylates, the neutral PFOS, N-methylperfluorooctanesulfonamide, N-EtFOSA, N-MeFOSE, and N-EtFOSE. It is noted that the third deployment event (summer 2023) used passive samplers provided by the new commercial manufacturer. Analysis of these commercial samplers yielded recoveries consistent with or better than previous results.

4.6.2 Recommendations and Lessons Learned

Feedback and recommendations were provided by the USEPA researchers regarding the Sentinel™ passive sampler field performance, especially regarding design for sediment applications.

Several changes to sediment passive sampler design were adopted by the commercial manufacturer for implementation in 2023 based on feedback from the 2022 field season (**Figure 1**). In 2022, several of the sediment porewater passive samplers flexed during deployment resulting in loss of sorbent. To increase durability, the sampler housing for sediment applications was changed from HDPE to stainless steel. In addition, the screen attachment that holds the sorbent in place was made more robust by adding rivets to the design. Another recommendation was to incorporate a means of identifying each passive sampler in the field. Accordingly, the manufacturer has attached a stainless steel identification tag with serial number to each sample, to be used for identification as well as doubling as a weight to aid the sampler in sinking. (Both the label tags and rivets were also incorporated into the commercial design for the passive sampler for water applications.)

Other USEPA recommendations included developing a supportive frame that could be used to deploy multiple passive samplers across a depth profile in sediment and also to collect multiple samples from the same depth (side-by-side samples), that could perhaps be used for duplicates or simultaneous additional analyses (e.g., composites, total oxidizer precursors, total organic fluorine). Additionally, it was recommended that a means of determining depth in sediment by direct measurement be provided. It was noted that in other types of passive samplers for sediment (e.g., polyethylene sheets), visually observed biofouling lines are often used to determine the sediment – surface water interface and accordingly how deep in the sediment the samplers were deployed (**Figure 6**). These recommendations will be used to inform future passive sampler studies.

Figure 6. Biofouling lines are marked by red arrows and delineate the sediment – surface water interface.

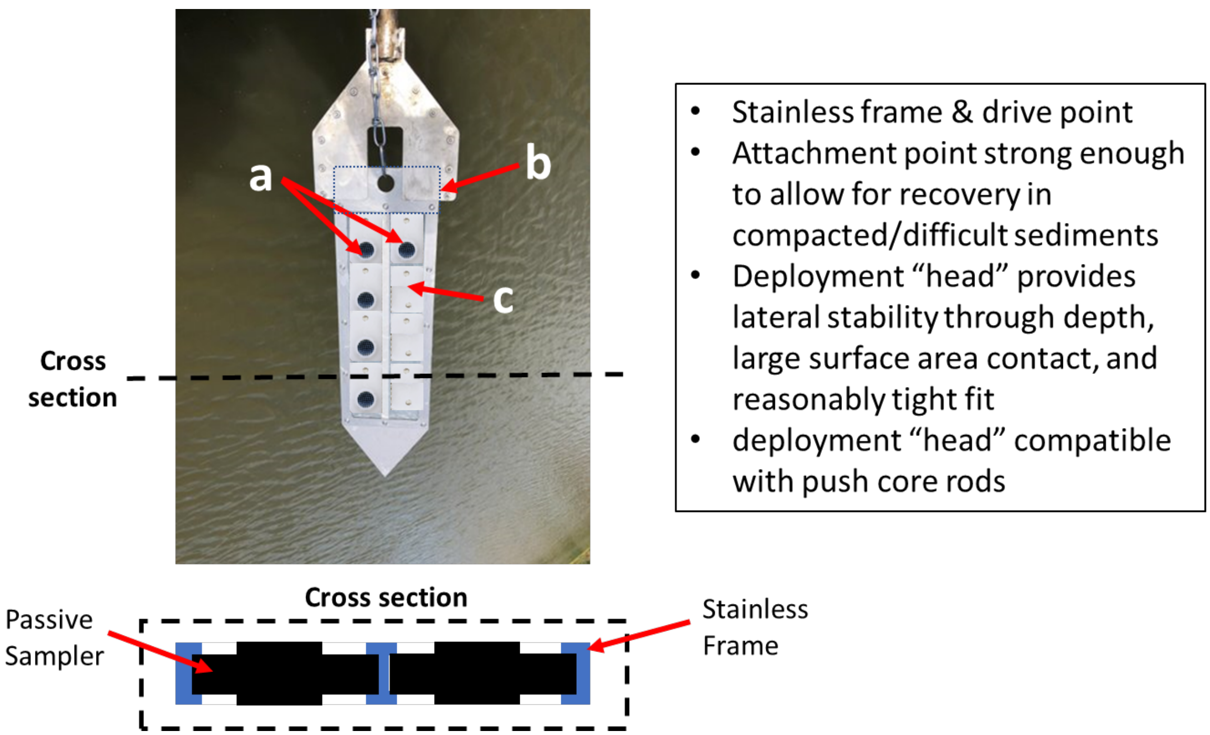


Figure 7. USEPA researcher suggestions for design of sediment passive sampler frame. a) Slotted two channel frame (one for targeted analysis and one for compositing, duplication, screening, etc.) that allows for evaluating multiple depth profiles. b) Removable "cap" to secure the samplers once they are loaded into the frame. Alternatively, samplers can be sandwiched between two frames. c) "Blank" Spacers for customizable deployment configuration.

5.0 Summary and Conclusions

The additional work completed during the extension period for SERDP Project ER20-1127 focused in several areas – technology transfer, including commercialization of manufacturing and laboratory analysis; passive sampler calibration, and field application by USEPA researchers.

- The Sentinel™ passive sampler is commercially available from a manufacturer, Aquanex Technologies, LLC. Slight changes to the physical design were introduced to make the sampler more durable for varied field applications (adding rivets to more securely hold the screens containing the Osorb sorbent in place), and by developing a stainless steel model intended for sediment applications. The stainless steel model was developed in response to suggestions from USEPA researchers during the first year of their Duluth, Minnesota field study.
- The laboratory methodology was adapted to facilitate commercial laboratory production and align the extraction method to USEPA Method 1633 – eliminating an evaporation step, resulting in an expedited procedure. To date ten laboratories in the U.S. and Europe have gained experience with the Sentinel™ passive sampler and are anticipated to offer analyses commercially in 2024.
- Additional work was also performed to refine the calibration of R_s values with respect to temperature using a Langmuir-style curve. This will allow more precise reporting of PFAS concentrations based on the use of R_s values keyed to the field sample temperature, where measured. Furthermore, R_s values for sediment porewater applications were developed based on a mixture of laboratory calibration and extrapolations from previously generated data. These sediment porewater R_s values will form a starting point for additional calibration to be performed in a forthcoming ESTCP project that will focus on demonstrating the passive sampler in sediment porewater.
- USEPA Office of Research and Development researchers deployed passive samplers (Sentinel™ passive samplers and two other types) in a Duluth, Minnesota field study area in conjunction with SERDP Project ER22-3202, Food-Web Exposures and Consequent Effects of PFAS on Birds. The passive samplers were deployed during three field events in 2022 and 2023 in surface water and sediment with a primary goal of providing field validation of the robustness of the passive samplers, their ease of use, and effectiveness in field conditions. Laboratory analysis of the Sentinel™ passive samplers deployed by USEPA researchers revealed consistent performance compared to previous field demonstrations in terms of surrogate performance and field duplicates. Slightly higher variability in field duplicates was noted for sediment porewater samples than for surface water, as would be expected in a heterogeneous sediment environment. The new R_s values developed for sediment porewater were applied to calculate the sediment porewater concentrations. The full comparison study results, including other passive samplers and grab samples, will be reported by USEPA at the conclusion of their study. Feedback from USEPA researchers has already resulted in the manufacturer's modification of the Sentinel™ passive sampler design for sediment porewater applications, including a more robust steel housing, rivets, and addition of serial numbers on identification tags that double as weights. These changes were implemented for the third field deployment event in the Duluth, Minnesota study area. Additional recommendations were regarding configuring tooling for deploying passive samplers in sediment porewater. These

recommendations will be applied during the forthcoming ESTCP Project ER23-7696, Osorb Passive Sampler for Determination of PFAS in Sediment Pore Water.

5.1 Comparison to Project Performance Objectives

Findings of the project were compared to qualitative and quantitative performance objectives in the Final Report (Divine et al. 2023). **Table 5** presents this table again, with additional findings from the current period of extension highlighted in bold type.

Table 5. Summary of Project Findings in Relation to Project Performance Objectives. Updated findings are noted in bold text.

Performance Objective	Success Criteria	Findings s (New Additions in Bold)
Quantitative Performance Objectives		
Adsorbent effective in measuring the full set of PFAS analytes	Kd values >1 liters per gram for both short-chain and long-chain analytes	Achieved
Determine if sampler has an integrative or equilibrium response	Predictable response with minimal sampler-to-sampler variability (<15% variance)	Achieved. Integrative for deployment up to 45 days
Determine detection limits of the sampler	LOD < 10 ng/L under optimal deployment conditions	Achieved. LOD of at least 2 ng/L for typical deployments of 1 week or more
Determine the effect of water chemistry on response	Predictable response with minimal impact on LOD and calibration. (<5% error when following standard operating procedures)	Achieved. Minimal impact for most environmental waters. Elevated total organic carbon (>75 milligrams per liter) and elevated pH (9.5) lower sampling rate Rs. Low redox (250 milligrams per liter ascorbic acid) increases sampling rate.
Determine the effect of temperature on response	Predictable response with minimal impact on LOD and calibration	Achieved. Some changes (5-50%) in R_s as function of temperature, accommodated by developing low-temperature R_s correction. Additional calibration could be completed if desired. **R_s values versus temperature were found to fit well to a Langmuir-type model. An *Rs* – temperature-dependence curve was developed for each PFAS analyte to facilitate more precise sampler calibration, if desired by the user.**

Performance Objective	Success Criteria	Findings s (New Additions in Bold)
Ensure PFAS recovery (desorption) is adequate and does not impact results	Predictable response meeting LOD objective and achieving >60% recovery and <30% error.	Achieved
Accurate measurements obtained with passive samplers	Results with passive samplers matched grab samples (±30% difference)	Achieved, on average based on laboratory calibration results
Qualitative Measurements		
Samplers are rugged	No damage or loss of media after 100 repeated well deployments. No damage or loss of media in high flow stream.	Achieved. Confirmed in laboratory. Ruggedness also confirmed qualitatively in field evaluation.
Quantitative Field Measurements		
Evaluate reproducibility of data obtained from passive samplers	Results between duplicate passive samplers match (±30% RPD difference) and are not statistically different at $p < 0.05$; a second line of evidence to be used is a reliability index.	Achieved and reproducibility confirmed. Average relative standard deviation of approximately 14% and 30%, respectively, for groundwater and surface water replicates for analytes with concentrations greater than 70 ng/L. For analytes detected at lower concentrations, average relative standard deviation of approximately 29 to 42% observed in surface water replicate samples. **RPD was calculated for detected analytes in 20 field duplicate samples collected by USEPA at the Duluth, Minnesota study area. An average RPD of 32% (SD=33, n=73 analyses) was measured for surface water passive samplers and average RPD of 56% (SD=44, n=94 analyses) was measured for sediment pore water passive samplers. Higher RPDs in sediment porewater samples is expected, attributed to inherent sediment heterogeneity.**

Performance Objective	Success Criteria	Findings s (New Additions in Bold)
Evaluate the comparability of data from passive samplers and paired grab samples using standard sampling methods	Understand comparability of data sets and factors that contribute to differences. Results will be considered comparable at 30% difference. Statistical significance ($p<0.05$) will be evaluated (for example, Passing-Bablok, or Two One-Sided T-Tests). A second line of evidence to be considered is a reliability index.	Achieved. Good 1:1 correspondence overall. Peterson Space Force Base groundwater passive and grab results were not statistically different. Surface water results displayed greater deviations from 1:1 correspondence, likely due in part to suspended particulates in grab samples and the dynamic nature of surface water concentrations over time. Across the four study sites, approximately two thirds of paired passive and grab sample detections matched within 2X and nearly all paired detect results matched within 5X. Grab sampling should not necessarily be the gold standard for comparison. Further, the passive sampler represents a time-weighted average compared to a grab sample which is a point-in-time sample.
Evaluate variability in passive sampler results based on depth of deployment in surface water – at surface or submerged	Paired surface / submerged results outside of expected variability (surface > 30% higher than submerged result) may reflect PFAS stratification in the stream water. Data will be evaluated qualitatively to assess whether further research is warranted.	Achieved. Statistical difference not observed, though qualitatively, some samples collected near the water surface contained the highest concentrations of some analytes (Section 4.2.5)
Confirm passive samplers are applicable to both low flow rate (groundwater) and high flow rate (stream) environmental settings, and determine whether multiple calibration procedures are required	Passive sampler results match grab sample results (±30% difference) using planned calibration procedures. If alternate calibration procedures can be developed and demonstrated in field testing, the success criterion for this objective will be considered achieved.	Achieved. Laboratory work found that two calibration regimes for R_s – one for groundwater and one for surface water were warranted. Slightly higher precision observed in groundwater versus surface water sites. **Additional work performed to develop preliminary R_s calibration for sediment porewater. These will be refined in a new ESTCP project.**

Performance Objective	Success Criteria	Findings s (New Additions in Bold)
Qualitative Field Measurements		
Identify challenges and limitations of passive sampler design	Challenges/limitations are understood and/or can be readily mitigated	Achieved. Samplers retrieved from surface water settings successfully washed in lab prior to analysis. Weights/attachments can (and should) be tailored to field conditions. Sufficient weight required in monitoring well deployment to ensure sampler remains submerged. **Additional modifications made by commercial manufacturer based on user (USEPA) feedback – developed stainless steel passive sampler for sediment applications. Added rivets to more securely hold sorbent in place. Added serial number to stainless steel weight attached to each sampler.**
Evaluate the utility of passive sampler results to inform remedial decision-making	Data from passive samplers are useful in supporting remedial decision making based on stakeholder feedback	Achieved. LODs useful for decision-making. Integrative nature of passive samplers adds value for surface water sampling.
Consolidate passive sampler performance data into technical guidance for their use	Technical guidance for the use of passive samplers and data interpretation	Achieved. Technical guidance developed for field deployment and laboratory analysis. Laboratory guidance includes tabulation of R_s values to allow calculation of concentrations in water (C_w). **Analytical technical guidance updated to align to modified USEPA Method 1633. Additional *Rs* values developed to allow calculation of concentrations in sediment porewater.**
Manufacture	Affordable final product.	Achieved. Samplers are now commercially available through Technologies, LLC. **Aquanex Technologies, LLC now offers two models of Sentinel™ passive sampler – one for deployment in water and one for deployment in sediment. In addition, as of 2024 multiple commercial laboratories in the U.S. and Europe have the capability to analyze the passive sampler.**

5.2 Benefits and Study Implications

The results of this work continue to support the immediate application of the Sentinel™ passive sampler for a wide variety of field applications. Data generated herein have provided additional calibration of R_s values with temperature for more precise concentration measurement, and have provided preliminary R_s values for sediment porewater that will be refined in future work. Technology transition has progressed, with manufacturer improvements to the passive sampler design and development of a sturdier stainless steel model for sediment applications. Furthermore laboratory methods have been aligned with USEPA Method 1633 and multiple commercial laboratories in the U.S. and Europe have been engaged in passive sampler analysis, further facilitating adoption by the practitioner community. The Sentinel™ passive sampler continues to be demonstrated as a flexible tool for sampling a variety of dynamic aqueous environments.

6.0 Acknowledgements

The authors thank Tim Siegenthaler for assistance in construction of the prototype passive samplers. The authors also thank Dr. Marc Mills and Brian Crone at USEPA Office of Research and Development for designing and performing field deployments at the Duluth, Minnesota study area, in collaboration with Dr. Matthew Ettinger's SERDP Project ER22-3202. Efforts by Dr. Kevin Berner and Ricky Bowles at Technologies, LLC to support the sampler design modifications and fabrication are greatly appreciated. We appreciate the deployment of sediment samplers in lab spiked sediment by Dr. David Moore and Dr. Guilherme Lotufo at ERDC which assisted us in determining the sediment porewater sampling rates (SERDP project ER22-3392).

7.0 Literature Cited

Divine, C., P. Edmiston, E. Carter, K. Toth. 2023. Final Report: ER20-1127. Osorb® Media Use in Per- and Polyfluoroalkyl Substances (PFAS) Passive Samplers. Revision 1.0 (Final). December 13.

Edmiston, P. L., Carter, E., Toth, K., Hershberger, R., Hill, N., Versluis, P., Hollinden, P. and Divine, C. 2023a. Field Evaluation of the Sentinel™ Integrative Passive Sampler for the Measurement of Perfluoroalkyl and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent, Groundwater Monitoring & Remediation. April. Available online: http://doi.org/10.1111/gwmr.12574

Appendix A

Sentinel™ Passive Sampler Extraction Procedure (Revision June 2023)

Sentinel™ Passive Sampler Extraction Procedure
Final Report Addendum: ER20-1127

Storage: Passive samplers can be stored at 4°C until analysis until analysis. Samplers are typically processed within 2 weeks of delivery but have shown to be stable for over 4 weeks when stored in sealed tubes.

Procedure

1. (***Rinse***) The sampler is rinsed with PFAS-free DI water to remove debris from sampling. Rinsing can be done in a tube with rapid shaking or under a constant flow of water.[1,2]
2. (***Centrifuge to Dry***). The sampler is placed in a 50 mL conical centrifuge tube (i.e. Falcon™ tube) and spun at 1,500 rpm for 3 min to remove water.[3]
3. (***Surrogate Application)*** 10 □L of surrogate solution (ex. MPFAC-HIF-ES from Wellington Laboratory) is pipetted directly onto the sampling window to dose the adsorbent. The sampler is left for 30 min in an uncapped new 50 mL conical centrifuge tube to evaporate the solvent.
4. (***Extraction***) 2.0 mL of methanol with 2% NH_4OH is added to the 50 mL centrifuge tube containing the passive sampler. The tube is placed at an ~35° angle on its side on a platform shaker and agitated for 10 min to extract bound PFAS and surrogates at room temperature. Make sure the solvent is washing across the windows of the passive sampler.[4]
5. The sampler is removed from the methanol solution and placed in a new 50 mL centrifuge tube and centrifuged for 30 seconds at 1,500 rpm to spin down residual methanol. The methanol recovered by centrifugation is combined with the extraction solution.
6. (***Internal standard addition***) 50 □L of internal standard solution (ex. MPFAC-HIF-IS from Wellington Laboratory) is added to the methanol extract.[5,6]
7. (Optional) The reconstituted solution is centrifuged in 1.5 mL centrifuge tube at 14,000 rpm to remove particulates prior to HPLC-MS/MS. Filtration per 1633 guidelines is also possible.

Notes:

(1) Adsorbent in new samplers is shipped with 50% glycerol wetting the resin. If a sampler has not been used (ex. Field Blank), the sampler should be stored in 50 mL of DI water for 24 hr to remove glycerol. The DI water can be replaced at intervals to help fully remove glycerol. Removal of glycerol improves the binding of surrogates.

(2) In extreme cases, the plastic housing of some passive samplers returned from the field is stained or coated with residues that are difficult to remove by water rinse. In such cases a KimWipe is generally successful in removing residues.

(3) Samplers are tapered on one end to fit into the bottom of a standard 50 mL centrifuge tube.

(4) If 2.0 mL of methanol is insufficient to allow rinsing across the across the windows to the sampler a larger volume of methanol can be used (ex. 3-5 mL).

(5) The procedure can be paused at the methanol extraction step.

(6) EnviCarb® 1-M-USP or equivalent can be added prior to internal standards to follow 1633.

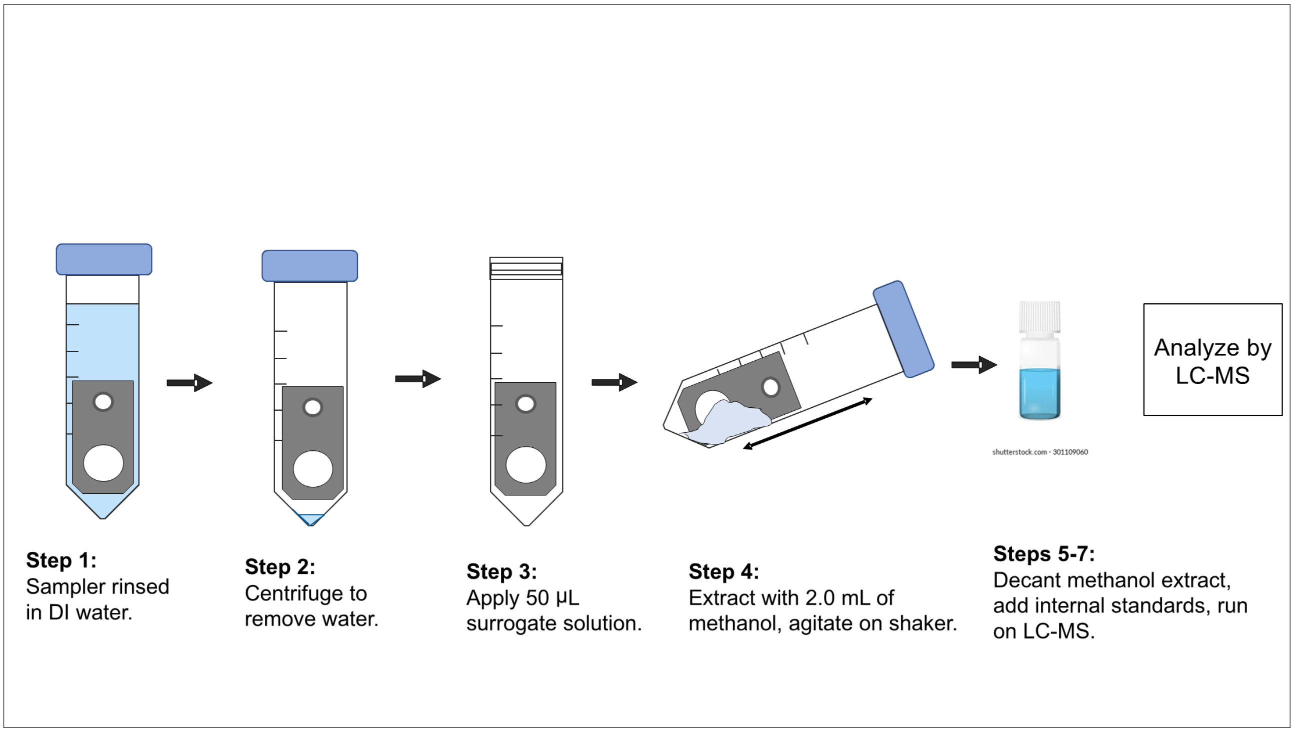


Figure 1: Diagram of the extraction process.

Passive Sampler – Converting Mass Adsorbed to the PFAS Concentration in Water

The accumulated mass (ng) recovered from the passive sampler is converted to the aqueous phase concentration, C_w (ng/L), using the following equation.

$$C_w = \frac{accumulated\ mass}{R_s \times t}$$

where R_s is the sampling rate (L/day) and t is the sampling time in days. Sampling rates were experimentally determined in bench-scale measurements and vary according to flow rate and temperature.

Appendix B

Temperature Calibration Data and Calculations for PFOS

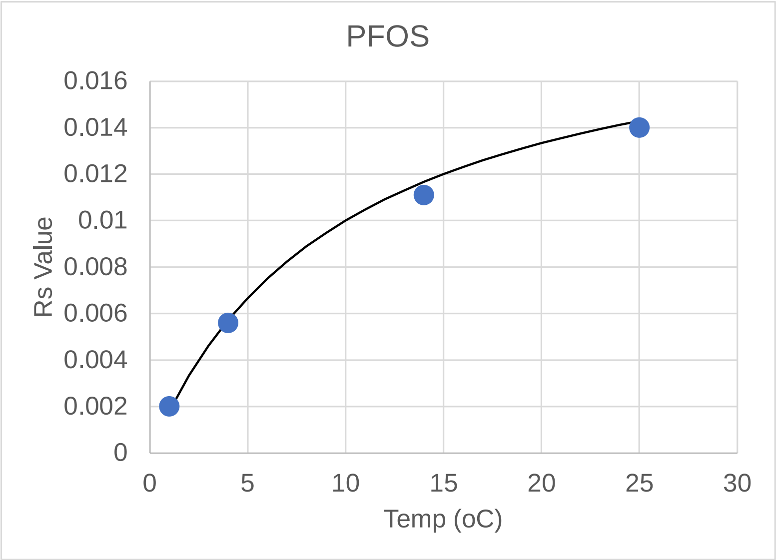
Rs values measured at 0.38 cm/min

Fitted using Langmuir Isotherm Equation

1°C values assigned

					Rs (L/d)				
Temp °C	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFBS	PFHxS	PFOS
1	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
4	0.0033	0.0033	0.00397	0.0056	0.0056	0.0066	0.0054	0.0068	0.0056
14	0.0033	0.0059	0.00735	0.00797	0.00898	0.00917	0.0132	0.012	0.0111
25	0.0033	0.0063	0.0093	0.0112	0.0124	0.0131	0.016	0.016	0.014

Max	0.0091	0.0136	0.015	0.017	0.018	0.022	0.025	0.02
K	0.13	0.1	0.13	0.12	0.11	0.1	0.085	0.1
1	0.001046903	0.001236364	0.001725664	0.001821429	0.001783784	0.002	0.001958525	0.001818182
4	0.003113158	0.003885714	0.005131579	0.005513514	0.0055	0.006285714	0.006343284	0.005714286
14	0.00587305	0.007933333	0.009680851	0.010656716	0.010913386	0.012833333	0.013584475	0.011666667
25	0.006958824	0.009714286	0.011470588	0.01275	0.0132	0.015714286	0.017	0.014285714
diff	9.08395E-07	5.8314E-07	7.52604E-08	3.18878E-08	4.67495E-08	0	1.72015E-09	3.30579E-08
	3.491E-08	7.10408E-09	2.19418E-07	7.47991E-09	0.00000121	7.8449E-07	2.0859E-07	1.30612E-08
	7.26322E-10	3.40278E-07	2.92701E-06	2.81138E-06	3.03939E-06	1.34444E-07	2.51056E-06	3.21111E-07
	4.34048E-07	1.71633E-07	7.3218E-08	1.225E-07	1E-08	8.16327E-08	0.000001	8.16327E-08
	3.4452E-07	2.75539E-07	8.23727E-07	7.43311E-07	1.07654E-06	2.50142E-07	9.30218E-07	1.12216E-07



Fitted Equation

Temp	Calculated Rs PFOS
1	0.00181818
2	0.00333333
3	0.00461538
4	0.00571429
5	0.00666667
6	0.0075
7	0.00823529
8	0.00888889
9	0.00947368
10	0.01
11	0.01047619
12	0.01090909
13	0.01130435
14	0.01166667
15	0.012
16	0.01230769
17	0.01259259
18	0.01285714
19	0.01310345
20	0.01333333
21	0.01354839
22	0.01375
23	0.01393939
24	0.01411765
25	0.01428571

Appendix C

Sampling Rate (Rs) Values for Sediment Porewater at 25°C

Appendix C - Sampling Rate (Rs) Values for Sediment Porewater at 25°C
Final Report Addendum: ER20-1127

PFAS	R_s, Sediment Porewater
4:2FTS	0.00190
6:2FTS	0.00179
8:2FTS	0.00106
FOSA	0.00150
HFPO-DA	0.00180
PFBA	0.00100
PFPeA	0.00197
PFHxA	0.00197
PFHpA	0.00200
PFOA	0.00225
PFNA	0.00154
PFDA	0.00126
PFUdA	0.00117
PFDoA	0.00090
PFTrDA	0.00090
PFTeDa	0.00090
PFBS	0.00300
PFPeS	0.00250
PFHxS	0.00251
PFHpS	0.00200
PFOS	0.00111
PFNS	0.00900
PFDS	0.00760
FBSA	0.00200
FHxSA	0.00200
N-meFOSAA	0.00200
NaDONA	0.00200
N-EtFOSA	0.00200
N-EtFOSAA	0.00200
N-EtFOSE	0.00200
NFDHA	0.00200
N-MeFOSA	0.00200
N-Me-FOSE	0.00200
PFEESA	0.00200
PFMBA	0.00200
PFMPA	0.00200
PFEESA	0.00200
9Cl-P3ONS	0.00200
11Cl-PF3OUdS	0.00200
3:3-FTCA	0.00200
5:3-FTCA	0.00225
7:3-FTCA	0.00154

Note:
Grey shading indicates Rs value measured directly in the laboratory in collaboration with SERDP Project ER22-3392. Other values extrapolated from previous laboratory data.

Appendix D

PFAS Analytical Results and Surrogate Recoveries – Duluth, Minnesota Study Area (2022-2023)

Appendix D-1 PFAS Results in Sentinel Passive Samplers for Surface Water - Duluth, Minnesota, Deployment 1, Summer 2022
Final Report Addendum: ER20-1127

	Location:	BL-01 Water		BL-02 Water		BL-03 Water		RL-01 Water		RL-02 Water		RL-02 DUP		BS-01 Water		BS-02 Water		MR-01 Water		DANG-A1 Water		DANG-A2 Water		DANG-B1 Water		DANG-B2 Water		Field Blank	
	Deployment Date / Time:	6/7/2022		6/7/2022		6/7/2022		6/7/2022		6/7/2022		6/7/2022		6/9/2022		6/9/2022		6/6/2022		6/6/2022		6/6/2022		6/6/2022		6/6/2022		6/7/2022	
	Retrieval Date / Time:	7/30/2022		7/30/2022		7/30/2022		7/31/2022		7/31/2022		7/31/2022		7/29/2022		7/29/2022		7/29/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022		6/7/2022	
	Water	Concentration (ng/L)																											
PFAS analyte	MRL (ng/L)	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual
4:2FTS	2	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U
6:2FTS	2	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	**8**		**17**		<2.0	J	**2.3**		<2.0	U
8:2FTS	2	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	U	<2.0	J	<2.0	J	<2.0	J	<2.0	J	<2.0	U
FOSA	1.8	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	U	<1.8	J	<1.8	U	<1.8	U	<1.8	U
HFPO-DA	6.8	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U	<6.8	U
PFBA	2.4	**2.6**		**1.8**	J	**3.4**		**3.7**		**2.8**		**4.2**		**2.7**		**2.5**		**15.7**		**2.9**		**2.8**		**4.3**		**5.8**		<2.4	U
PFPeA	2	**2.7**		**3.9**		**8.2**		**8**		**6.1**		**9.2**		0	U	**5.6**		**37.3**		**22.9**		**26.7**		**20.5**		**35.2**		<2.0	U
PFHxA	1.2	0.4	U	0	U	**1.4**		**4.2**		**4.3**		**6.3**		**1.5**		**0.9**	U	**20.1**		**19**		**32.7**		**14.8**		**23.7**		<1.2	U
PFHpA	1.2	**1.2**	J	**2.5**		**2.9**		**2.4**		**2.1**		**3.2**		**2.3**		**1.2**	J	**6.2**		**6.9**		**15**		**4.3**		**8.3**		<1.2	U
PFOA	1.2	**2.2**		0	U	**3.1**		**5.9**		**5.7**		**8.6**		**7.9**		**2.8**		**20.9**		**12**		**23.9**		**18.6**		**38.2**		<1.2	U
PFNA	1.2	**0.3**	J	0	U	**0.7**	J	**0.8**	J	**0.8**	J	**1.4**	J	**1.2**	J	**0.5**	U	**1.1**	J	**1.3**		**3.3**		**0.9**	J	**2**		<1.2	U
PFDA	1.2	0	U	0	U	0	U	0	U	**0.3**	U	3	U	**1.7**		0	U	0	U	**0.8**	J	**2.2**	U	**0.5**	J	**1**	J	<1.2	U
PFUdA	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	**0.4**	J	**0.6**	J	0	U	**0.2**	J	<1.2	U
PFDoA	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	**0.3**	J	**0.8**	J	0.1	U	**0.1**	U	<1.2	U
PFTrDA	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	<1.2	U
PFTeDa	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0.1	U	0.1	U	0.1	U	0	U	<1.2	U
PFBS	1.2	0	U	0	U	0	U	**3.2**		**2.8**		**3.9**		0	U	**0.5**	U	**13.5**		**12.5**		**18.7**		**7.1**		**10.4**		<1.2	U
PFPeS	1.2	0	U	0	U	0	U	**7.8**		**8.7**		**2.9**		0	U	0	U	**7.7**		**13.1**		**24.6**		**4.9**		**8.3**		<1.2	U
PFHxS	1.2	0	U	0	U	0	U	**16**		**15.7**		**23.1**		**2.4**		**0.8**	J	**59**		**84.9**		**176**		**45.5**		**86.6**		<1.2	U
PFHpS	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	**3.3**		**6.3**		**1**	J	**1.6**		<1.2	U
PFOS	1.2	0	U	0	U	0	U	**9.7**		**10**		**13.4**		**21.1**		0	U	**37.1**		**109**		**260**		**37.2**		**64.6**		<1.2	U
PFNS	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	J	**1**	J	0.1	U	0.2	U	<1.2	U
PFDS	1.2	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	0	U	**0.2**	J	0.3	U	0	U	0	U	<1.2	U
FBSA	not measured																												
FHxSA	not measured																												
N-meFOSAA	2.1	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U
NaDONA	3.2	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	U	<3.2	J	<3.2	U
N-EtFOSA	2.5	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U
N-EtFOSAA	2.1	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U	<2.1	U
N-EtFOSE	5.5	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U
NFDHA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
N-MeFOSA	2.5	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U	<2.5	U
N-Me-FOSE	5.5	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U	<5.5	U
PFEESA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
PFMBA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
PFMPA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
9Cl-P3ONS	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	J	<1.2	J	<1.2	U	<1.2	U	<1.2	U
11Cl-PF3OUdS	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
3:3-FTCA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
5:3-FTCA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U
7:3-FTCA	1.5	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U	<1.5	U

Notes and Abbreviations:

Samplers stored in cold storage following retrieval and received for analysis in April 2023.

Bold type indicates detected values.

J - Estimated concentration

MRL - Minimum reporting level

ng/L - nanograms per liter

U - Non-detect at value indicated

Appendix D-2 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 2, Summer 2022
Final Report Addendum: ER20-1127

Location:		Blank		MR-01-Water		MR-01-Sediment		RL-01-Water		RL-02-Water		BS-01-Water		BS-01-Sediment		BS-02-Water		BL-01-Water		BL-01-Sediment		BL-02-Water	
Deployment Date / Time:				7/29/2022		7/29/2022		7/30/2022		7/30/2022		7/29/2022		7/29/2022		7/29/2022		7/30/2022		7/30/2022		7/30/2022	
Retrieval Date / Time:				9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/30/2022		9/30/2022		9/30/2022	
	Water	Concentration (ng/L)																					
PFAS analyte	MRL (ng/L)	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual
4:2FTS	2	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U
6:2FTS	2	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U
8:2FTS	2	<2	U	<2	J	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U
FOSA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
HFPO-DA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFBA	2	<2	U	**57**		**20**		**2**	J	<2	J	1	U	**8**	J	**2**	J	**2**	J	**18**		**4**	
PFPeA	1.2	<1.2	U	**110**		**6**		**4**		**3**		<1.2	U	4	U	**2**		**3**		**10**		**4**	
PFHxA	1.2	<1.2	U	**100**		**23**		**4**		**4**		<1.2	U	**11**		**1**	J	**1**	J	**11**		**1**	J
PFHpA	1.2	<1.2	U	**22**		**16**		**1**	J	**2**		<1.2	U	**12**		**3**		**1**	J	**10**		**1**	J
PFOA	1.2	<1.2	U	**60**		**11**		**3**		**4**		<1.2	U	**10**		**1**	J	**1**	J	**8**		**2**	
PFNA	1.2	<1.2	U	**2**	J	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	**2**	U	<1.2	U
PFDA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFUdA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFDoA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFTrDA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFTeDa	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFBS	1.2	<1.2	U	**27**		**1**	J	**1**	J	**1**	J	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFPeS																							
PFHxS	1.2	<1.2	U	**330**		**35**		**15**		**22**		<1.2	U	**16**		<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFHpS																							
PFOS	1.2	<1.2	U	**140**		**165**		**10**		**20**		<1.2	U	**93**		<1.2	U	<1.2	U	9	U	<1.2	U
PFNS	not measured																						
PFDS	not measured																						
FBSA	not measured																						
FHxSA	not measured																						
N-meFOSAA	not measured																						
NaDONA	not measured																						
N-EtFOSA	not measured																						
N-EtFOSAA	not measured																						
N-EtFOSE	not measured																						
NFDHA	not measured																						
N-MeFOSA	not measured																						
N-Me-FOSE	not measured																						
PFEESA	not measured																						
PFMBA	not measured																						
PFMPA	not measured																						
9Cl-P3ONS	not measured																						
11Cl-PF3OUdS	not measured																						
3:3-FTCA	not measured																						
5:3-FTCA	not measured																						
7:3-FTCA	not measured																						

Appendix D-2 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 2, Summer 2022
Final Report Addendum: ER20-1127

	Location:	**BL-02-Sediment**		**BL-03-Water**		**DANG-A1-Water**		**DANG-A1-Water-DUP**		**DANG-A1-Sediment**		**DANG-A1-Sediment-DUP**		**DANG-B1-Water**		**DANG-B1-Sediment**		**DANG-B2-Water**		**DANG-B2-Sediment**	
	Deployment Date / Time:	7/30/2022		7/30/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022		8/3/2022	
	Retrieval Date / Time:	9/30/2022		9/30/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022		9/29/2022	
	Water																				
PFAS analyte	**MRL (ng/L)**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**
4:2FTS	2	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U	<2	U
6:2FTS	2	<2	U	<2	U	**4**		**8**		**74**		**44**		<2	U	<2	U	**3**		<2	U
8:2FTS	2	<2	U	<2	U	<2	U	<2	U	**32**		**11**	J	<2	U	<2	U	<2	U	<2	U
FOSA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	0	U	0	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
HFPO-DA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	0	U	0	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFBA	2	**5**	U	**2**	J	**4**		**4**		**39**		**22**		**4**		**15**	J	**12**		1	U
PFPeA	1.2	**2**	J	**2**		**23**		**29**		**91**		**68**		**9**		**15**		**30**		**2**	
PFHxA	1.2	**10**		<1.2		**26**		**47**		**269**		**190**		**16**		**55**		**56**		**18**	
PFHpA	1.2	**33**		**2**		**7**		**13**		**74**		**51**		**3**		**14**		**10**		**7**	
PFOA	1.2	**9**		<1.2	U	**10**		**22**		**99**		**59**		**21**		**44**		**74**		**19**	
PFNA	1.2	<1.2	U	<1.2	U	**1**	J	**1**	J	**17**		**9**	J	<1.2	U	<1.2	U	**1**	J	<1.2	J
PFDA	1.2	<1.2	U	<1.2	U	<1.2	J	<1.2	U	**23**		**13**	J	<1.2	U	<1.2	U	<1.2	J	<1.2	J
PFUdA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	**0**	U	**0**	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFDoA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	**6**	U	**4**	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFTrDA	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	**0**	U	**0**	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFTeDa	1.2	<1.2	U	<1.2	U	<1.2	U	<1.2	U	**0**	U	**0**	U	<1.2	U	<1.2	U	<1.2	U	<1.2	U
PFBS	1.2	<1.2	U	<1.2	U	**5**		**10**		**29**		**20**		**2**		**5**		**7**		<1.2	U
PFPeS																					
PFHxS	1.2	**6**		<1.2	U	**115**		**270**		**546**		**305**		**65**		**110**		**191**		**45**	
PFHpS																					
PFOS	1.2	**46**		<1.2	U	**140**		**385**		**2,750**		**955**		**31**		**363**		**92**		**150**	
PFNS	not measured																				
PFDS	not measured																				
FBSA	not measured																				
FHxSA	not measured																				
N-meFOSAA	not measured																				
NaDONA	not measured																				
N-EtFOSA	not measured																				
N-EtFOSAA	not measured																				
N-EtFOSE	not measured																				
NFDHA	not measured																				
N-MeFOSA	not measured																				
N-Me-FOSE	not measured																				
PFEESA	not measured																				
PFMBA	not measured																				
PFMPA	not measured																				
9Cl-P3ONS	not measured																				
11Cl-PF3OUdS	not measured																				
3:3-FTCA	not measured																				
5:3-FTCA	not measured																				
7:3-FTCA	not measured																				

Notes and Abbreviations:
Samplers received for analysis in October 2022

Samplers Damaged During Deployment:
RL-02-Sediment
BS-02-Sediment
BL-03-Sediment
Dang-A2-Sediment

Samplers Lost During Deployment:
Dang-A2-Water

Samplers Not Passing Lab QA/QC:
RL-01-Sediment

Bold type indicates detected values.
J - Estimated concentration
MRL - Minimum reporting level
ng/L - nanograms per liter
U - Non-detect at value indicated

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	BL01 water	BL01 sed	BL02 water	BL02 sed	BL03 water	BL03 sed	BS01 water	BS01 sed	BS02 water	BS02 water dup
		Deployment Date / Time:	6/13/2023 12:48	6/13/2023 12:48	6/13/2023 12:30	6/13/2023 12:30	6/13/2023 13:27	6/13/2023 13:27	6/15/2023 15:30	6/15/2023 15:30	6/15/2023 13:15	6/15/2023 13:15
		Retrieval Date / Time:	7/28/2023 16:14	7/28/2023 16:10	7/28/2023 15:52	7/28/2023 15:50	7/28/2023 16:24	7/28/2023 16:21	7/26/2023 16:05	7/26/2023 16:07	7/26/2023 15:06	7/26/2023 15:06
PFAS analyte	**Water MRL (ng/L)**	**Sediment MRL (ng/L)**	**Concentration (ng/L)**									
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	-	-	-	-	-	-	-	-
8:2FTS	0.94	39.8	-	-	-	-	-	-	-	-	-	-
FOSA	0.16	4.8	-	-	-	-	-	-	-	3.7J	-	-
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	-	-	-	-	-	-	-
PFPeA	0.42	2.7	-	-	-	-	-	13	2.1	-	1.7	1.7
PFHxA	0.13	2.5	-	-	-	-	-	-	2.5	4	-	-
PFHpA	0.05	1.1	-	2.7	-	3.6	-	-	2.1	2.7	-	-
PFOA	0.04	0.8	-	-	-	150	-	-	4	3.7	-	-
PFNA	0.04	1.3	-	3	-	8.1	-	2.8	-	-	-	-
PFDA	0.05	0.2	-	-	-	11	-	2.7	-	-	-	-
PFUdA	0.06	0.3	-	-	-	-	-	-	-	-	-	-
PFDoA	0.07	3.4	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	-	-	-	110	-	-	2.1	-	-	-
PFPeS	0.31	6.0	-	-	-	-	-	-	4.6	-	-	-
PFHxS	0.33	6.9	-	-	-	280	-	1.8J	52	12	-	-
PFHpS	0.39	9.5	-	-	-	15	-	-	-	-	-	-
PFOS	0.46	20.2	-	65	3.1	110	-	44	54	120	4.4	5.7
PFNS	0.37	18.5	-	-	-	-	-	-	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	-	-	-	-	-	-	-	-	-	-
FHxSA	0.17	3.8	-	-	-	-	-	-	35	11	-	-
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	-	-	-	-	-	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	BS02 sed	BS02 sed dup	DANGA1 water	DANGA1 sed	DANGA2 water	DANGA2 waterdup	DANGA2 sed	DANGA2 seddup	DANGB1 water	DANGB1 sed
		Deployment Date / Time:	6/15/2023 13:15	6/15/2023 13:15	6/15/2023 11:25	6/15/2023 11:25	6/15/2023 12:12	6/15/2023 12:12	6/15/2023 12:12	6/15/2023 12:12	6/15/2023 9:58	6/15/2023 9:58
		Retrieval Date / Time:	7/26/2023 15:06	7/26/2023 15:06	7/27/2023 19:37	7/27/2023 19:37	7/27/2023 19:22	7/27/2023 19:22	7/27/2023 19:22	7/27/2023 19:22	7/27/2023 18:31	7/27/2023 18:31
PFAS analyte	Water MRL (ng/L)	Sediment MRL (ng/L)										
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	3.2	12J	2.7	3.1	28	46	-	66
8:2FTS	0.94	39.8	-	-	-	4	-	-	-	7.6J	-	-
FOSA	0.16	4.8	4.2J	9.4	1.9J	4.5J	-	-	7.2J	5.9J	-	11
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	12	-	-	9.9	-	-	30
PFPeA	0.42	2.7	8.3	9.9	2.5	34	4.2	5.3	47	73	2.1	17
PFHxA	0.13	2.5	2.5	5	8.3	47	8.3	10	100	160	2.1	25
PFHpA	0.05	1.1	3.8	4.4	3.7	11	3.5	4.1	28	40	3.3	110
PFOA	0.04	0.8	-	-	24	60	23	22	85	120	6.7	180
PFNA	0.04	1.3	3.7	3.3	-	4.4	-	-	4.7	8.2	-	2100
PFDA	0.05	0.2	2.3	1.8	-	6.2	-	-	6.0	7.3	-	550
PFUdA	0.06	0.3	-	-	-	-	-	-	-	-	-	4.9
PFDoA	0.07	3.4	-	-	-	2.6J	-	-	2.1J	1.8J	-	2.3J
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	-	2.1J	13	30	8.1	9.8	60	100	-	200
PFPeS	0.31	6.0	-	-	14	21	10	11	54	88	4.2	6.4
PFHxS	0.33	6.9	4.5J	6.2J	82	110	70	71	260	420	78	660
PFHpS	0.39	9.5	-	-	6.1	6.8J	5.3	4.5	15	22	-	21
PFOS	0.46	20.2	95	110	110	430	81	95	750	1200	210	8600
PFNS	0.37	18.5	-	-	2.2	-	2.0	1.6	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	-	-	3.1	35	4.1	4.9	82	110	-	-
FHxSA	0.17	3.8	-	3J	190	230	130	150	410	600	13	-
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	15	-	-	13	20	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	DANGB2 water	DANGB2 waterdup	DANGB2 sed	DANGB2 seddup	FB1 water	FB2 water	FB3 water	FB4 water	FB5 water	FB1 sed
		Deployment Date / Time:	6/15/2023 10:30	6/15/2023 10:30	6/15/2023 10:30	6/15/2023 10:30	N/A	N/A	N/A	N/A	N/A	N/A
		Retrieval Date / Time:	7/27/2023 18:25	7/27/2023 18:25	7/27/2023 18:25	7/27/2023 18:25	6/14/2023 13:30	6/15/2023 12:33	7/26/2023 23:40	7/27/2023 18:50	7/28/2023 20:18	6/14/2023 13:30
PFAS analyte	Water MRL (ng/L)	Sediment MRL (ng/L)										
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	5.6J	42	-	-	-	-	-	-
8:2FTS	0.94	39.8	-	-	-	11J	-	-	-	-	-	-
FOSA	0.16	4.8	-	-	7.1J	11	-	-	-	-	-	-
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	-	-	-	-	-	-	-
PFPeA	0.42	2.7	1.9	2.6	9.7	17	-	-	-	-	-	6.6
PFHxA	0.13	2.5	3.1	3.3	22	110	-	-	-	-	-	-
PFHpA	0.05	1.1	2.9	2.9	8.7	80	-	-	-	-	-	3.9
PFOA	0.04	0.8	5.1	4.2	12	75	-	-	-	-	-	-
PFNA	0.04	1.3	-	-	5.2	27	-	-	-	-	-	7.3
PFDA	0.05	0.2	-	-	2.9	14	-	-	-	-	-	-
PFUdA	0.06	0.3	-	-	-	2.3	-	-	-	-	-	-
PFDoA	0.07	3.4	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	1.9	1.7	7	40	-	-	-	-	-	-
PFPeS	0.31	6.0	3.6	3.1	6.4	73	-	-	-	-	-	-
PFHxS	0.33	6.9	56	54	100	1200	-	-	-	-	-	-
PFHpS	0.39	9.5	-	-	-	18	-	-	-	-	-	-
PFOS	0.46	20.2	160	180	1300	9700	-	-	-	-	-	-
PFNS	0.37	18.5	-	-	-	-	-	-	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	-	-	3.9	15	-	-	-	-	-	-
FHxSA	0.17	3.8	11	13	120	320	-	-	-	-	-	-
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	-	-	-	-	-	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	FB2 sed	FB3 sed	FB4 sed	FB5 sed	LF01 water	LF01 waterdup	LF01 sed	LF01 seddup	LF02 water	LF02 sed	MD01 water
		Deployment Date / Time:	N/A	N/A	N/A	N/A	6/14/2023 13:21	6/14/2023 13:21	6/14/2023 13:21	6/14/2023 13:21	6/14/2023 15:00	6/14/2023 15:00	6/14/2023 10:45
		Retrieval Date / Time:	6/15/2023 12:33	7/26/2023 23:40	7/27/2023 18:50	7/28/2023 20:18	7/28/2023 23:08	7/28/2023 23:08	7/28/2023 23:08	7/28/2023 23:08	7/26/2023 18:15	7/26/2023 18:15	6/28/2023 15:06
	Water	Sediment											
PFAS analyte	MRL (ng/L)	MRL (ng/L)											
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	-	-	-	-	-	-	-	-	-
8:2FTS	0.94	39.8	-	-	-	-	-	-	-	-	-	-	-
FOSA	0.16	4.8	-	-	-	-	-	-	-	-	-	-	-
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	-	-	-	-	-	-	-	-
PFPeA	0.42	2.7	4.8	-	-	11	-	13	8.5	11	-	7.5	8.5
PFHxA	0.13	2.5	-	13	-	14	-	1.8	-	-	-	2.8	6
PFHpA	0.05	1.1	6.3	5.1	6.1	5.4	-	4.5	-	-	-	3.7	2.7
PFOA	0.04	0.8	-	-	-	-	-	-	-	-	-	-	2.7
PFNA	0.04	1.3	6.5	-	-	-	-	6.4	2	3	-	2.6	-
PFDA	0.05	0.2	-	-	-	-	-	-	-	-	-	2.0	-
PFUdA	0.06	0.3	-	-	-	-	-	-	-	-	-	-	-
PFDoA	0.07	3.4	-	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	-	-	-	18	-	4	-	-	-	-	6.1
PFPeS	0.31	6.0	-	-	-	-	-	4.7	-	-	-	-	4.4
PFHxS	0.33	6.9	-	-	-	-	-	9.5	-	-	-	12	39
PFHpS	0.39	9.5	-	-	-	-	-	-	-	-	-	-	-
PFOS	0.46	20.2	41	55	38	45	3.5	160	110	170	9.2	300	200
PFNS	0.37	18.5	-	-	-	-	-	-	-	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	-	-	-	-	-	-	-	-	-	-	-
FHxSA	0.17	3.8	-	-	-	-	-	-	-	-	-	-	-
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	-	-	-	-	-	-	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-	-

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	MD01 waterdup	MD01 seddup	MD02 sed	MD02 seddup	MD03 water	MD03 waterdup	MD03 sed	MD03 seddup	MR01 water	MR01 sed	MR02 water
		Deployment Date / Time:	6/14/2023 10:45	6/14/2023 10:45	6/14/2023 11:11	6/14/2023 11:11	6/14/2023 11:50	6/14/2023 11:50	6/14/2023 11:50	6/14/2023 11:50	6/14/2023 14:25	6/14/2023 14:25	6/14/2023 16:40
		Retrieval Date / Time:	6/28/2023 15:06	6/28/2023 15:06	7/12/2023 12:00	7/12/2023 12:00	7/27/2023 13:14	7/27/2023 13:14	7/27/2023 13:14	7/27/2023 13:14	7/26/2023 19:35	7/26/2023 19:35	7/27/2023 13:30
PFAS analyte	Water MRL (ng/L)	Sediment MRL (ng/L)											
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	-	-	-	-	-	-	-	-	-
8:2FTS	0.94	39.8	-	-	-	-	-	-	-	-	-	-	-
FOSA	0.16	4.8	-	-	-	-	-	-	-	-	-	-	-
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	-	-	-	-	-	-	-	-
PFPeA	0.42	2.7	6.7	48	14	48	2.6	2.9	15	25	2.7	-	1.9
PFHxA	0.13	2.5	4.5	130	44	82	4.2	4.6	82	110	2.7	3.2	3.7
PFHpA	0.05	1.1	2.5	79	23	44	2.5	3.5	130	63	-	1.8	2.3
PFOA	0.04	0.8	2.8	71	21	40	2.9	4.7	190	64	-	5.2	2.4
PFNA	0.04	1.3	-	24	8	15	-	-	55	22	-	2.4	-
PFDA	0.05	0.2	-	20	3.1	3.6	-	-	8.7	6.6	-	1.5	-
PFUdA	0.06	0.3	-	-	-	-	-	-	-	-	-	-	-
PFDoA	0.07	3.4	-	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	26	100	38	82	5.6	5.4	90	85	2.5	-	4.1
PFPeS	0.31	6.0	4.1	100	36	72	5.9	7.2	240	97	2.5	-	5.6
PFHxS	0.33	6.9	40	910	300	620	47	63	2400	820	21	14	45
PFHpS	0.39	9.5	-	4.7J	3.7J	6.4J	-	-	36	14	-	-	-
PFOS	0.46	20.2	280	31000	5400	5800	280	130	20000	8300	37	77	63
PFNS	0.37	18.5	-	-	-	-	-	-	-	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	-	29	7.9	22	-	-	17	16	-	-	-
FHxSA	0.17	3.8	-	-	-	-	-	-	13	4	-	-	-
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	-	-	-	-	-	-	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-	-

Appendix D-3 PFAS Results in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota, Deployment 3, Summer 2023
Final Report Addendum: ER20-1127

		Location:	MR02 sed	RL01 water	RL01 sed	RL02 water	RL02 waterdup	RL02 sed	RL02 seddup	SR01 water	SR01 waterdup	SR01 sed	SR01 seddup
		Deployment Date / Time:	6/14/2023 16:40	6/13/2023 15:35	6/13/2023 15:35	6/13/2023 16:20	6/13/2023 16:20	6/13/2023 16:20	6/13/2023 16:20	6/14/2023 15:51	6/14/2023 15:51	6/14/2023 15:51	6/14/2023 15:51
		Retrieval Date / Time:	7/27/2023 13:30	7/28/2023 18:00	7/28/2023 18:00	7/28/2023 19:50	7/28/2023 19:50	7/28/2023 19:50	7/28/2023 19:50	7/26/2023 18:44	7/26/2023 18:44	7/26/2023 18:44	7/26/2023 18:44
	Water	Sediment											
PFAS analyte	MRL (ng/L)	MRL (ng/L)											
4:2FTS	0.79	18.7	-	-	-	-	-	-	-	-	-	-	-
6:2FTS	0.80	20.2	-	-	-	-	-	-	-	-	-	-	-
8:2FTS	0.94	39.8	-	-	-	-	-	-	-	-	-	-	-
FOSA	0.16	4.8	-	-	-	-	-	-	-	-	-	-	-
HFPO-DA	0.19	4.7	-	-	-	-	-	-	-	-	-	-	-
PFBA	0.96	8.7	-	-	-	-	-	-	-	-	-	-	-
PFPeA	0.42	2.7	14	-	7	-	-	5.8	-	5.8	2.7	35	24
PFHxA	0.13	2.5	74	-	8.8	-	-	7.1	6	9.7	6.1	61	45
PFHpA	0.05	1.1	37	-	4.2	-	-	4.1	4	4.3	3.9	21	18
PFOA	0.04	0.8	22	-	2.1	-	-	2.6	-	5.6	6.7	18	20
PFNA	0.04	1.3	11	-	2.4	-	-	2.9	1.5	-	-	6.7	6.4
PFDA	0.05	0.2	1.8	-	-	-	-	-	-	-	-	-	1.7
PFUdA	0.06	0.3	-	-	-	-	-	-	-	-	-	-	-
PFDoA	0.07	3.4	-	-	-	-	-	-	-	-	-	-	-
PFTrDA	0.09	4.3	-	-	-	-	-	-	-	-	-	-	-
PFTeDa	0.07	3.7	-	-	-	-	-	-	-	-	-	-	-
PFBS	0.32	4.5	57	-	3.3J	-	-	2.8J	2.2J	9.4	5.8	22	27
PFPeS	0.31	6.0	52	-	-	-	-	-	-	11	9.9	21	25
PFHxS	0.33	6.9	430	9.7	23	8.2	7.6	22	13	89	94	240	210
PFHpS	0.39	9.5	3.7J	-	-	-	-	-	-	-	-	-	-
PFOS	0.46	20.2	1600	18	180	17	16	170	120	130	140	1400	850
PFNS	0.37	18.5	-	-	-	-	-	-	-	-	-	-	-
PFDS	0.40	23.4	-	-	-	-	-	-	-	-	-	-	-
FBSA	0.17	3.8	13	-	-	-	-	-	-	3.5	2.3	27	24
FHxSA	0.17	3.8	2.2J	-	-	-	-	1.8J	-	7.7	3.4	57	55
N-meFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
NaDONA	0.05	1.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSA	2.20	31.4	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSAA	0.93	11.2	-	-	-	-	-	-	-	-	-	-	-
N-EtFOSE	0.41	3.1	-	-	-	-	-	-	-	-	-	-	-
NFDHA	0.22	5.6	-	-	-	-	-	-	-	-	-	-	-
N-MeFOSA	1.46	36.7	-	-	-	-	-	-	-	-	-	-	-
N-Me-FOSE	0.22	2.6	-	-	-	-	-	-	-	-	-	-	-
PFEESA	0.11	2.2	-	-	-	-	-	-	-	-	-	-	-
PFMBA	0.15	3.3	-	-	-	-	-	-	-	-	-	-	-
PFMPA	0.18	4.7	-	-	-	-	-	-	-	-	-	-	-
9Cl-P3ONS	0.06	1.4	-	-	-	-	-	-	-	-	-	-	-
11Cl-PF3OUdS	0.10	2.4	-	-	-	-	-	-	-	-	-	-	-
3:3-FTCA	1.50	31.4	-	-	-	-	-	-	-	-	-	-	-
5:3-FTCA	0.07	1.4	-	-	-	-	-	-	-	-	-	-	-
7:3-FTCA	0.03	1.3	-	-	-	-	-	-	-	-	-	-	-

Notes and Abbreviations:
Samplers received for analysis in October 2023.

Samplers Lost During Deployment:
Dang-A2-Water

"-" denotes value below MRL, i.e. non-detect
J - denotes detected but below MRL
MRL - Minimum reporting level
ng/L - nanograms per liter

Appendix D-4 Surrogate Recoveries in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota (2022 - 2023)
Final Report Addendum: ER20-1127

Surrogate Recovery - Deployment 1 - Summer 2022 (April 2023 received)

	Percent Recovery															
Surrogate	**Average**	**Stdev**	BL-01	BL-02	BL-03	BS-01	BS-02	DANG-A2	DANG-A1	DANG-B1	DANG-B2	FieldBlank	MR-01	RL-01	RL-02	RL-02DUP	**Average**
[M2]4:2 FTS	**102**	**41**	103	75	76	27	99	165	103	131	88	41	83	141	152	148	**102**
[M2]6:2 FTS	**116**	**53**	110	76	75	24	114	177	124	142	105	35	94	162	184	197	**116**
[M2]8:2 FTS	**92**	**60**	71	62	55	17	75	224	90	91	64	25	51	140	194	135	**92**
[M2]PFDoA	**11**	**6**	18	4	5	9	5	12	19	7	4	20	10	8	9	18	**11**
[M2]PFTeDA	**29**	**19**	70	15	20	17	9	29	42	17	12	56	23	23	26	53	**29**
[M3]HFPO-DA	**54**	**42**	87	10	25	31	13	60	163	40	17	58	67	35	48	108	**55**
[M3] PFBS	**106**	**34**	147	123	123	33	99	138	127	120	87	41	80	122	127	113	**106**
[M4]PFBA	**94**	**40**	149	65	67	37	73	113	196	88	58	76	94	91	93	114	**94**
[M4]PFHpA	**101**	**49**	151	48	54	43	82	111	217	94	61	65	104	109	112	162	**101**
[M5]PFHxA	**98**	**47**	154	52	60	41	73	116	215	92	62	61	96	106	103	138	**98**
[M5]PFPeA	**96**	**47**	154	61	63	41	70	119	224	91	62	68	86	94	94	119	**96**
[M6]PFDA	**94**	**59**	115	33	37	38	58	138	234	73	43	60	87	106	108	181	**94**
[M7] PFUdA	**52**	**30**	74	20	22	30	27	71	123	39	22	57	49	48	55	96	**52**
[M8]PFOA	**106**	**57**	150	32	41	42	87	107	240	99	65	117	117	100	102	187	**106**
[M8]PFOS	**131**	**46**	163	136	118	40	114	151	168	151	107	49	100	176	193	174	**131**
[M8]PFOSA	**32**	**38**	54	0	0	31	17	13	118	11	6	49	45	0	0	103	**32**
[M9]PFNA	**98**	**52**	155	37	42	40	80	97	196	80	55	61	110	112	121	185	**98**
d3-N-MeFOSAA	**36**	**50**	0	0	0	22	29	0	150	30	18	54	64	0	0	138	**36**
D5N-EtFOSAA	**50**	**42**	0	29	22	54	132	25	16	60	62	27	40	141	**48**		
	79	**55**															

Surrogate Recoveries - Deployment 2 - Summer 2022

	Percent Recovery																					
Compound	**Average**	**Stdev**	RL-01_Water_A	RL-02_Water	BS-01_Water	BS-01_Sed_5	BS-02_Water_F	BL-01_Water_8	BL-01_Sed_H	BL-03_Water_9	BL-02_Sed_I	Dang-A1-Water_3	Dang-A1-Water(dup)_K	Dang-A1_Sed_B	Dang-A1_Sed(dup)_E	Dang_B1_Water_14	Dang-B1-Sed_D	Dang-B2-Water_21	Dang-B2-Sed_1	MR-01-Water_J	MR-01-Sed_13	**Average**
[M] PFBA	**65**	**24**	62	59	91	84	71	79	65	87	45	95	77	54	70	64	80	26	89	16	21	**65**
[M] PFDoA	**27**	**12**	30	20	43	12	12	23	24	47	18	49	34	24	23	25	38	13	40	21	13	**27**
[M] PFHxA	**66**	**27**	74	68	86	130	59	80	63	84	40	90	74	47	60	65	78	24	85	13	25	**66**
[M] PFNA	**54**	**21**	65	59	71	100	40	73	51	78	36	67	48	37	47	54	65	24	66	12	34	**54**
[M] PFOA	**55**	**22**	65	58	68	101	41	76	48	78	33	76	66	37	46	52	62	23	69	11	30	**55**
[M] PFOS	**50**	**16**	69	54	63	70	48	69	44	75	34	59	42	32	44	51	60	27	61	17	39	**51**
[M] PFTeDA	**13**	**5**	13	8	24	17	12	10	13	13	6	15	13	9	9	15	16	10	13	27	8	**13**
[M] PFUdA	**34**	**13**	41	32	47	24	17	37	32	54	25	60	45	26	31	32	45	18	49	15	23	**34**
[M] 6:2 FTS	**88**	**39**	138	116	85	136	53	154	68	143	46	102	125	54	76	93	83	42	90	23	54	**89**
[M] FOSA	**19**	**11**	7	23	25	30	19	36	21	40	13	29	13	13	5	17	31	7	20	4	6	**19**
[M]PFDA	**50**	**17**	60	52	63	69	32	61	45	69	32	75	63	36	43	49	59	24	63	14	32	**50**
[M] PFHxS	**60**	**23**	79	61	75	110	66	84	52	86	38	67	53	37	50	55	66	27	74	15	41	**60**
[M2] 8:2 FTS	**47**	**18**	73	59	47	59	23	68	34	64	22	64	73	30	37	52	44	38	48	15	35	**47**
[M2] -4:2 FTS	**113**	**52**	182	152	102	180	79	187	88	182	50	145	176	65	87	133	97	59	102	32	48	**113**
[M3] HFPO-DA	**59**	**28**	63	59	86	121	32	68	55	76	39	91	70	45	54	59	75	20	83	9	19	**59**
[M3] PFBS	**79**	**31**	101	74	97	144	93	105	63	109	48	107	91	48	61	75	87	37	95	21	40	**79**
[M3] PFPeA	**78**	**33**	78	73	107	152	80	89	74	93	53	110	92	60	76	73	100	28	108	15	24	**78**
[M4] PFHpA	**71**	**29**	83	77	89	140	60	98	66	98	43	88	73	49	64	70	80	28	88	13	33	**71**
	57	**35**																				

Appendix D-4 Surrogate Recoveries in Sentinel Passive Samplers for Surface Water and Sediment Porewater - Duluth, Minnesota (2022 - 2023)
Final Report Addendum: ER20-1127

Surrogate Recovery - Deployment 3 - Summer 2023

	Percent Recovery																								
Surrogate	**Average**	**Stdev**	BL01 water	BL02 water	BL03water	BL01 sed	BL02 sed	BL03 sed	BS01 water	BS02 water	BS02 water dup	BS01 sed	BS02 sed	BS02 sed dup	DANGA1 water	DANGA2 water	DANGA2 waterdup	DANGA1 sed	DANGA2 sed	DANGA2 seddup	DANGB1 water	DANGB2 water	DANGB2 waterdup	DANGB1 sed	DANGB2 sed
[M2]4:2 FTS	**90**	**38**	187	143	157	98	69	53	107	130	113	81	70	70	132	150	135	65	51	47	121	114	116	47	56
[M2]6:2 FTS	**95**	**42**	179	216	146	106	70	61	105	162	143	85	70	62	139	163	145	99	65	57	134	124	124	66	58
[M2]8:2 FTS	**113**	**55**	284	274	210	180	98	82	115	174	182	123	71	77	213	203	197	142	89	66	139	137	146	79	58
[M2]PFDoA	**113**	**25**	160	152	148	142	140	121	112	126	113	138	108	103	145	142	132	135	108	91	110	104	110	109	87
[M2]PFTeDA	**118**	**30**	172	153	152	141	158	124	129	139	123	140	122	98	157	150	132	142	116	87	106	109	120	113	89
[M3]HFPO-DA	**75**	**10**	88	77	87	85	90	83	74	73	64	81	78	70	79	81	73	74	72	62	72	67	68	76	67
[M3] PFBS	**99**	**13**	115	102	107	103	121	100	99	89	72	97	100	92	109	106	115	102	95	78	97	100	95	92	89
[M3]PFHxS	**89**	**14**	105	96	114	101	105	91	82	98	77	104	93	83	94	100	98	101	81	77	85	91	90	85	79
[M4]PFBA	**100**	**12**	98	108	106	103	111	106	94	95	90	96	101	86	123	116	107	105	104	97	112	111	98	112	102
[M4]PFHpA	**98**	**17**	120	104	118	116	115	106	94	95	79	116	95	88	114	115	108	116	99	84	93	97	98	102	86
[M5]PFHxA	**94**	**14**	109	90	106	108	104	106	88	82	75	102	95	78	118	112	105	98	94	82	95	94	94	104	80
[M5]PFPeA	**92**	**15**	109	87	104	106	110	103	93	81	69	100	94	82	114	105	107	100	99	82	88	88	84	110	80
[M6]PFDA	**94**	**21**	142	125	112	134	109	103	106	111	91	114	91	82	125	115	118	107	94	70	96	88	91	80	79
[M7] PFUdA	**114**	**26**	155	155	153	156	138	117	121	119	114	136	114	91	155	137	132	135	110	86	118	110	116	102	88
[M8]PFOA	**98**	**19**	122	109	118	115	114	104	100	99	87	113	102	89	123	115	114	110	97	80	101	98	97	96	79
[M8]PFOS	**82**	**14**	105	104	98	103	82	88	80	93	77	89	76	73	71	80	68	91	82	62	83	85	83	71	71
[M8]PFOSA	**97**	**31**	145	135	139	128	116	97	102	108	95	114	83	72	156	151	137	132	103	76	95	96	110	94	78
[M9]PFNA	**105**	**21**	141	126	133	137	119	109	112	110	94	124	110	98	97	92	92	125	104	84	101	99	103	112	81
D3N-MeFOSA	**81**	**17**	91	102	86	82	95	84	81	98	90	78	94	75	102	103	94	82	86	75	89	77	74	90	91
D5N-EtFOSA	**76**	**19**	98	106	87	86	86	79	68	78	79	86	69	70	94	87	87	82	79	58	82	73	69	72	72
D5N-EtFOSAA	**100**	**42**	165	162	171	177	118	93	116	126	112	116	92	79	175	151	148	135	103	67	112	107	116	93	68
D7N-Me-FOSE	**94**	**25**	142	133	109	115	115	96	84	97	74	108	106	97	122	114	110	102	96	73	107	100	92	109	98
D9N-EtFOSE	**85**	**24**	139	112	100	94	107	81	82	90	64	98	95	83	114	105	96	97	89	62	98	90	85	92	89

95.7391

Surrogate Recovery - Deployment 3 - Summer 2023, continued

	Percent Recovery																								
Surrogate	DANGB 2 seddup	FB1 water	FB2 water	FB3 water	FB4 water	FB5 water	FB1 sed	FB2 sed	FB3 sed	FB4 sed	FB5 sed	LF01 water	LF01 waterdup	LF02 water	LF01 sed	LF01 seddup	LF02 sed	MD01 water	MD01 waterdup	MD03 water	MD03 waterdup	MD01 seddup	MD02 sed	MD02 seddup	MD03 sed
[M2]4:2 FTS	75	61	56	59	53	51	43	47	47	44	48	171	185	109	92	104	50	108	87	83	64	87	83	69	87
[M2]6:2 FTS	70	83	71	78	76	66	53	53	40	53	52	196	202	104	101	94	61	80	68	57	56	78	75	60	76
[M2]8:2 FTS	59	121	102	108	102	93	53	56	47	52	47	187	204	114	117	101	77	74	60	59	51	77	75	72	85
[M2]PFDoA	89	129	128	118	122	90	69	65	54	69	58	151	139	101	133	135	112	94	89	81	65	94	93	84	88
[M2]PFTeDA	81	157	131	117	135	103	68	58	44	68	56	159	138	107	138	131	101	98	88	83	67	96	100	84	89
[M3]HFPO-DA	61	103	88	81	83	70	69	65	60	69	63	85	86	60	75	78	65	77	74	66	51	69	67	61	64
[M3] PFBS	86	133	104	108	100	89	85	80	75	78	80	118	136	87	96	105	84	108	100	96	73	100	93	80	83
[M3]PFHxS	73	91	93	97	92	72	74	68	57	58	64	119	121	74	102	114	78	102	96	74	64	83	84	72	76
[M4]PFBA	95	119	103	103	104	89	88	83	77	90	81	129	129	84	109	110	100	94	92	82	63	90	87	85	88
[M4]PFHpA	83	130	113	114	112	92	80	74	68	82	68	131	133	87	113	123	87	86	81	73	55	76	82	75	70
[M5]PFHxA	77	118	113	106	104	90	77	80	72	81	75	127	115	84	111	111	82	79	90	72	57	80	76	75	74
[M5]PFPeA	80	127	108	106	109	93	84	76	68	83	79	114	113	81	107	112	89	77	78	67	50	77	76	73	67
[M6]PFDA	75	107	102	104	94	82	67	65	54	62	51	127	114	84	115	111	86	78	72	64	54	73	84	64	76
[M7] PFUdA	80	126	126	111	126	88	79	69	59	81	62	165	148	107	134	142	102	99	85	72	61	92	91	82	99
[M8]PFOA	80	123	111	109	109	91	76	67	62	76	64	139	135	93	120	118	90	83	78	69	54	78	79	74	74
[M8]PFOS	74	95	88	83	86	72	53	53	57	66	53	120	109	79	110	95	74	87	73	71	66	76	82	72	76
[M8]PFOSA	60	125	105	104	108	89	61	49	33	48	47	169	159	101	127	121	88	68	64	60	48	68	61	59	58
[M9]PFNA	83	129	115	117	126	89	74	69	66	77	63	148	148	102	130	127	96	90	84	74	58	91	81	77	81
D3N-MeFOSA	62	110	91	98	86	98	53	74	56	88	67	118	98	56	86	88	74	58	61	57	34	54	46	57	44
D5N-EtFOSA	61	101	114	92	89	82	78	56	62	62	50	114	110	66	94	77	78	50	42	45	33	46	46	33	42
D5N-EtFOSAA	63	135	124	121	127	96	55	47	42	55	39	174	166	109	132	129	84	34	32	33	23	34	35	30	39
D7N-Me-FOSE	85	131	115	105	114	94	74	74	53	81	66	119	122	80	78	106	81	57	57	52	39	50	55	42	53
D9N-EtFOSE	76	129	111	112	101	86	64	62	43	66	54	117	113	71	70	95	75	52	53	47	35	43	49	31	40

Surrogate Recovery - Deployment 3 - Summer 2023, continued

	Percent Recovery														
Surrogate	MD03 seddup	MR01 water	MR02 water	MR01 sed	MR02 sed	RL01 water	RL02 water	RL02 waterdup	RL01 sed	RL02 sed	RL02 seddup	SR01 water	SR01 waterdup	SR01 sed	SR01 seddup
[M2]4:2 FTS	67	119	119	77	61	124	141	136	74	65	56	118	130	66	51
[M2]6:2 FTS	61	103	109	69	64	142	146	146	74	72	70	100	119	76	59
[M2]8:2 FTS	56	94	112	102	76	158	160	153	90	77	95	103	128	93	66
[M2]PFDoA	81	113	127	128	107	135	134	123	139	129	132	113	120	120	108
[M2]PFTeDA	84	128	148	146	113	159	136	150	140	131	140	124	135	114	107
[M3]HFPO-DA	65	84	83	82	78	79	74	79	85	81	84	81	88	80	81
[M3] PFBS	95	102	111	107	92	105	103	114	107	112	105	108	115	110	100
[M3]PFHxS	84	93	86	96	86	95	99	97	98	95	98	85	88	87	87
[M4]PFBA	89	103	106	97	100	102	97	102	100	101	106	111	114	100	105
[M4]PFHpA	75	103	102	107	96	106	101	101	114	104	111	96	105	112	103
[M5]PFHxA	74	93	100	110	94	98	95	92	97	100	104	94	102	97	100
[M5]PFPeA	71	87	91	105	93	93	88	99	101	103	103	96	100	100	98
[M6]PFDA	71	91	107	102	90	105	111	110	110	106	106	100	105	94	87
[M7] PFUdA	94	107	121	126	112	130	135	138	137	120	132	122	118	124	110
[M8]PFOA	75	102	109	108	96	107	104	104	106	109	115	114	116	107	93
[M8]PFOS	75	85	84	91	75	96	97	94	94	85	85	86	88	79	74
[M8]PFOSA	59	108	106	103	81	99	98	104	102	109	91	104	125	94	91
[M9]PFNA	79	104	116	111	98	122	120	118	134	114	131	109	115	108	105
D3N-MeFOSA	51	75	80	95	82	97	89	86	91	83	94	86	83	92	96
D5N-EtFOSA	42	92	89	94	62	87	82	83	94	85	78	71	99	78	82
D5N-EtFOSAA	35	106	112	105	85	122	120	134	119	99	106	102	127	107	86
D7N-Me-FOSE	42	104	108	112	105	102	107	102	118	101	118	89	121	106	105
D9N-EtFOSE	33	100	99	103	90	83	95	88	100	90	106	87	110	97	92