TECHNICAL REPORT

Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 (Volume II): Soils and Sediments

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Abstract

This report is the second in a series presenting the results of a multi-laboratory validation study (MLVS) designed to validate the EPA's draft Office of Water (OW) *Method 1633: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS* (the Study). The Study was conducted as a joint effort by the U.S. Department of Defense (DoD) and the Environmental Protection Agency (EPA).

This report is the second in the series of MLVS reports to be published. The first report, titled *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633: Wastewater, Surface Water, and Groundwater Matrices* (herein identified as *Volume I*) provides the detailed project information that applies to this and subsequent reports in addition to this report. That report provides the project background, the overall project management structure, data validation, and data management procedures. The processes, evaluation, and procedures of the previous report are incorporated by reference.

The objective of the Study was to demonstrate the efficacy of the method using PFAS-spiked environmental samples. Solid matrices were prepared by shaking an aliquot of the sample with methanolic ammonium hydroxide, followed by carbon clean-up, and then concentrated via solid-phase extraction (SPE). Analyte concentrations were determined using either an isotope dilution or extracted internal standard (EIS) quantification schemes; both of which utilize isotopically labeled compounds that are added to the samples prior to extraction. Injection internal standards (IISs), referred to as non-extracted internal standards (NISs) in EPA Method 1633, were also used to determine EIS compound recoveries and provide a general indicator of overall analytical quality. The method includes 40 target analytes, 24 EIS compounds, and 7 NIS compounds. Analytes were quantified and reported as their acid form.

Ten laboratories participated in the Study: eight commercial laboratories and two state laboratories. All laboratories had previously demonstrated their initial calibrations (ICAL) and were required to complete an initial demonstration of capabilities study for solid media. Upon successful completion, unspiked, and PFAS-spiked soil and sediment samples were sent to each of the laboratories. Three soil and three sediment sample series were analyzed, each series consisting of an unspiked sample, three replicate low-spiked samples, and three replicate high-spiked samples, for a total of 42 (21 soil + 21 sediment) analyses for each participating laboratory.

All data packages were reviewed for completeness and compliance with the requirements of the MLVS Method and the Study Data Validation Guidelines (DVGs); the validation team and process is described in detail in *Volume I*.

Evaluation of the calibration demonstrations submitted by each laboratory as part of Phase 3 of the Study is included in *Volume I*. For soils and sediment, the laboratories conducted an initial demonstration of capabilities (IDC) that included of a method detection limit (MDL) determination, an Initial Precision and Recovery (IPR) study, and the limit of quantitation verification (LOQVER). The pooled average MDL for all laboratories was less than 1 µg/kg, and generally less than 0.4 µg/kg for most PFAS. For PFOA and PFOS the pooled MDL was less than 0.1 µg/kg. MDLs were highest for the three FTCA compounds. All laboratories met the Study IPR NIS compound target criterion of >30% recovery, and the EIS compound target acceptance criteria

of 20–150%. All of the valid target analyte results reported from IPRs were within the study target analyte criterion of between 40–150%. For the LOQVER, of the nine laboratories included in the statistical analysis, all met the Study NIS compound target acceptance criterion of >30% recovery. Of the valid target analyte results reported from the LOQVERs, less than 1% of the results exceeded the target criterion of 40–150%. Of the valid EIS compound results reported from LOQVERs, the failure rate relative to the EIS compound acceptance criterion of 20–150% was less than 0.5%.

For soils, three individual soil matrices were analyzed for an unspiked sample, three low-spiked samples and three high-spiked samples, for a total of 21 samples per laboratory. All sample results from the 10 laboratories were evaluated. The combined (pooled) average percent recoveries results for all laboratories and all PFAS using both the low spike and high spike samples were between 71.5–107%. For EIS compounds, individual laboratories higher variability were found for $^{13}C_4$-PFBA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE. For the 10 laboratories the pooled average EIS compound percent recovery ranged between 50.9% (D_5-NEtFOSA) to 112.9% ($^{13}C_2$-8:2FTS). For the pooled soil EIS compound percent recovery, all mean percent recoveries were within the MLVS method-specified target recovery.

For sediments, the results were similar to those for soils, with somewhat higher variability. The pooled (low-spiked/high-spiked samples) average percent recoveries were between 68.2% and 92.4%. The individual laboratory results for all PFAS averaged from 18% to 131.5%. For the pooled EIS compound data, most of the recoveries were greater than 80%. For the low- and high-spiked samples, the proportion of all values that were between 20% and 150% of the spike concentrations is >88%. The one exception is $^{13}C_2$-8:2FTS, for which 71% (116 of 164 measures) were between 20-150% recovery, with the other recoveries > 130%. In a comparison of individual laboratory EIS compound performance, all laboratories were within the acceptance criteria range, with the exception of $^{13}C_4$-PFBA where lower recoveries were observed.

Matrix spike recoveries were statistically evaluated by Analysis of Variance (ANOVA) as described in *Volume I.* All main effects were significant with greater than 99% confidence. On average all PFAS were observed with mean recoveries 70-130% of the target spike concentration. Matrix, Spike Concentration, and Laboratory main effects were also relatively consistent and close to the target spike concentration (i.e., 100% recovery).

Based on the data from the Study, EPA developed quality control (QC) acceptance criteria for soils and sediment following the same methods used in *Volume I.* These QC specifications included those to be applied to IPRs, OPRs, LLOPRs, EIS compound, and NIS compound recoveries.

The results for the soil and sediment samples support a finding that EPA Method 1633 measures PFAS concentrations as well as or better than most EPA methods for similar sized organic contaminants in real-world samples of these matrices.

EXECUTIVE SUMMARY

E.S.1 INTRODUCTION

This report is the second in a series presenting the results of a multi-laboratory validation study (MLVS) designed to validate the Environmental Protection Agency's (EPA) draft Office of Water (OW) *Method 1633: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS* (EPA Method 1633). This project was designed to validate EPA Method 1633 and were undertaken through the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP).

The MLVS was undertaken cooperatively as the MLVS Team, which included SERDP/ Environmental Security Technology Certification Program (ESTCP); EPA's Offices of Water, of Land and Emergency Management, of Research and Development; the U.S. Navy; the U.S. Air Force; and the U.S. Army Corps of Engineers (USACE). SERDP/ESTCP, EPA OW, the U.S. Navy, the U.S. Air Force and the USACE approved and are co-signers to the Study Plan developed for the project.

E.S.2 OBJECTIVES

The Study was designed to evaluate the robustness of EPA Method 1633 when performed by suitable laboratories using similar instruments of different manufacturers and models, as well as provide information on the range of precision and accuracy of quantitation that is achievable by suitable laboratories.

This report is focused on demonstrating EPA 1633 for soils and sediments. The first report, *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume I: Wastewater, Surface Water, and Groundwater Matrices*, (*Volume I*), provides the detailed project information that applies to this and subsequent reports.

The focus of the MLVS was to generate the necessary data to document the precision and accuracy and overall performance of the analytical method for quantitation of PFAS in environmental matrices. The primary objectives of in this report were to:

- Identify and quantify up to 40 per- and polyfluoroalkyl substances (PFAS) in solids (soil, and sediment) using the isotope dilution liquid chromatography–tandem mass spectrometry (LC-MS/MS) method.
- Achieve a low parts per billion (ppb) method detection limits and levels of quantitation in soil and sediment.
- Demonstrate that the method can be implemented at a typical mid-sized full-service environmental laboratory.
- Validate the method using spiked real-world soil and sediment.

Volume I provided validation of EPA Method 1633 for wastewater, surface water, and groundwater. This Volume 2 provides validation of the method for soils and sediment. Volume 3 will evaluate landfill leachate and biosolids, while Volume 4 will evaluate fish and shellfish tissue.

E.S.3 METHOD DESCRIPTION

Methods followed are detailed in the *Volume I* report. Briefly, soil and sediment were prepared via solvent extraction and SPE, followed by carbon clean-up processes. The method utilized liquid chromatography–tandem mass spectrometry (LC-MS/MS) in multiple reaction monitoring (MRM) mode to evaluate quantification and confirmation (where applicable) of ions of each of the 40 target analytes. Analyte concentrations were determined using either an isotope dilution or extracted internal standard (EIS) quantification scheme; both utilized isotopically labeled compounds that were added to the samples prior to extraction. Analytes were quantified and reported as their acid form. Seven non-extracted internal standards (NIS)[1] were used to determine EIS recoveries and provide a general indicator of overall analytical quality. A list of the 40 target analytes, 24 EIS compounds, and seven NIS compounds are provided in the Report.

E.S.4 TECHNICAL APPROACH

The analytical method for this study was the one validated and included in the report, *Single-Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS* (SERDP 2020 and 2021), and defined in the August 2021 draft of EPA 1633. Updates reflecting those changes was have been iteratively released by EPA, the most recent is the 4th Draft Method 1633 (EPA 2023). The complete method used for this study is provided in Appendix A to the *Volume I*.

Ten laboratories (eight commercial contract laboratories and two state laboratories) participated in the Study. For the purposes of this study, the laboratories were randomly assigned numbers, which were used to maintain the anonymity of the results. All laboratories had previously demonstrated their initial calibrations (ICAL) (*Volume I*) and were required to complete an initial demonstration of capabilities study for solid media. Upon successful completion, unspiked, and PFAS-spiked soil and sediment samples were sent to each of the laboratories.

All data packages were reviewed for completeness and compliance with the requirements of the MLVS Method and the Study Data Validation Guidelines (DVGs); the validation team and process is described in detail in *Volume I*. All ten laboratories contributed data packages for the solid IDC and spiked soils evaluation, but only 8 laboratories contributed data for the sediment evaluation. One laboratory declined to participate, and one laboratory's data did not pass the quality assurance requirements.

E.S.5 SOLID IDOC FINDINGS

Initial Demonstration of Capabilities

The laboratories next submitted documentation of an IDOC that consisted of a method detection limit (MDL) determination, an Initial Precision and Recovery (IPR) study, and the limit of quantitation verification (LOQVER). The process for setting the MDL is discussed in more detail in *Volume I*.

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[1] NIS were referred to in the SLVS Report as Injected Internal Standards (IIS). EPA used the *NIS* in the draft EPA Method 1633; NIS is adopted for this MLVS report.

Solid Method Detection Limits

MDLs for all 40 target analytes were determined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. The pooled average MDL for all laboratories was less than 1 µg/kg, and generally less than 0.4 µg/kg for most PFAS compounds. For PFOA and PFOS, the pooled MDL was less than 0.1 µg/kg. MDLs were highest for the three FTCA compounds. These results confirmed that results in the low parts per billion can be achieved for solids with Method 1633.

Solid Initial Precision and Recovery

For the IPR studies, four aliquots of 5 g of PFAS-free Ottawa or reagent-grade sand were spiked with all 40 target analytes such that the final concentration of each PFAS in the IPR were greater than or equal to the LOQ and less than or equal to the midpoint of the laboratory's calibration. All laboratories met the Study IPR NIS compound target recovery criterion of >30% recovery, and the EIS compound target recovery criterion of 20–150%. All of the valid target analyte results reported from IPRs were within the study target analyte criterion of between 40–150%.

Solid Limits of Quantitation Verification Analyses

A single aliquot of 5 g of PFAS-free Ottawa or reagent-grade sand was spiked with all 40 target analytes such that the final concentration of each PFAS for the LOQVER was one and two times the laboratory's LOQ. One laboratory did not identify their LOQVER sample as required by the Study in their submittal; therefore, only nine laboratories were included in the statistical analysis. Of the submitted LOQVERs all met the Study NIS target recovery criterion of >30% recovery. Of the valid target analyte results reported from the LOQVERs, less than 1% of the results exceeded the target recovery criterion of 40–150%. Of the valid EIS compound results reported from LOQVERs, the failure rate relative to the EIS compound recovery criterion of 20–150% was less than 0.5%.

E.S. 6 SOIL PERFORMANCE EVALUATION

The results demonstrated the efficacy of EPA Method 1633 to accurately report PFAS concentrations in real-world soil samples. Three individual soil matrices were analyzed for an unspiked sample, three low-spiked samples and three high-spiked samples, for a total of 21 samples per laboratory. All sample results from the 10 laboratories were evaluated.

For the low-spiked samples, >95% of all 40 spiked PFAS were recovered between 40–150% of the spiked concentration With the exception of the FTCA compounds, most of those percent recoveries were between 70–130%. For the FTCA compounds, 2–5% of the reported recoveries were less than 40%, 31–47% were between 40 to 70%, with 56.2% between 70–130%. For the high-spike samples the results were similar: >95% of all 40 spiked PFAS were recovered between 40–150% of the spiked concentration. The results for the FTCA compounds in the high-spike sample were similar to that observed in the low-spike samples. The combined (pooled) average percent recoveries results for all laboratories and all PFAS using both the low-spiked and high-spiked samples were between 71.5–107%.

For EIS compounds, the MLVS Method did not prescribe definitive acceptance criteria, but did have a target percent recovery set at 20–150%. EIS compound recoveries were evaluated by individual laboratories, as well as the combined results for the minimum, maximum, and average percent recovery. For the individual laboratories, the higher variability were found in $^{13}C_4$-PFBA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE. Three laboratories showed overall lower EIS compound recovery. One laboratory had poor and highly variable recovery for $^{13}C_4$-PFBA, with a low of 5% recovery in a single sample. Two other laboratories had lower recoveries for almost all of the EIS compounds. For the 10 laboratories the pooled average EIS compound percent recovery ranged between 50.9% (D_5-NEtFOSA) and 112.9% ($^{13}C_2$-8:2FTS). For the pooled soil EIS compound percent recovery, all mean percent recoveries were within the MLVS method-specified target recovery.

E.S. 7 SEDIMENT PERFORMANCE EVALUATION

The results for the spiked sediment samples are similar to those found for the soils. Of the 10 laboratories, one of the state laboratories dropped out of the study after conducting the soil analysis. Three individual sediment matrices were analyzed for an unspiked sample, three low-spiked samples and three high-spiked samples. While 21 samples were sent to the laboratories, for one laboratory and one sample, the data had to be excluded due to a spiking error.

The observed trends in spiked results were similar to that observed for soil, but with more variability. The low-spiked sample mean percent recovery for each target analyte fell between 67.6–92.1%. For the high-spiked samples, the range was 68.7–120%, with the combined low/high-spiked data from 68.2–92.4%. Variability, as indicated by the pooled between-laboratory standard deviation (s_b) was slightly greater in the high-spiked samples than in the low-spiked samples (31 of the 40 target analytes). The highest pooled between-laboratory standard deviation PFTrDA. One possible reason why this pooled between-laboratory standard deviation is significantly greater than that of any other target analyte may be the fact that for this target analyte only, laboratories used different EIS compounds for quantification. Due to software limitations, some laboratories did not utilize the average of $^{13}C_2$-PFDoA and $^{13}C_2$-PFTeDA to quantitate PFTrDA, as stated in the method. Some laboratories used $^{13}C_2$-PFTeDA only, while others used $^{13}C_2$-PFDoA only.

The range of concentrations of EIS compounds used by the laboratories were the same as those for the soils. For the 8 laboratories the pooled average EIS compound percent recovery ranged between 45.1% (D_5-NEtFOSA) and 132.9% ($^{13}C_2$-8:2FTS). The range of values by individual laboratories ranges from 6.6 - 279%. The highest variability in EIS compound recoveries for all laboratories were associated with the same EIS compounds ($^{13}C_4$-PFBA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE) as in soil samples. Two laboratories had poor and highly variable recovery for $^{13}C_4$-PFBA.

E.S. 9 COMBINED SOIL AND SEDIMENT PERFORMANCE EVALUATION

MLVS results demonstrated the ability of laboratories to routinely achieve the MLVS target acceptance criteria for sample preparation batch QC samples (Method Blank, OPR, and LLOPR). The concentration of each target analyte in the method blank was required to be <½ the laboratory's LOQ and < 1/10th the concentration of the target method in associated samples. The low rate of detection in method blanks demonstrated by this study, 13 out of 1,228 target analytes reported (1.06%) indicates the processes described in the method are successful in reducing the potential for bias associated with contamination. Method blank contamination resulted in the "B" qualification of 29 results out of 14,791 soil and sediment sample results reported. Thus, these measured concentrations were only sufficient to warrant "B" flags for what ultimately represented <0.196% of the final data set. The method blanks demonstrate that any bias associated with background contamination introduced during sample preparation was negligible.

OPR recoveries across all media for all laboratories were relatively tight, generally at or above 90% with narrow pooled between-laboratory standard deviation (s_b), within-laboratory standard deviation (s_w), and Relative Standard Deviation (RSD). Of the OPRs included in the statistical analysis, all met the Study NIS criterion (>30% recovery). Of the 1,264 valid target analyte results reported from OPRs, two failed to meet the target analyte criterion (40–150%), resulting in a failure rate of 0.158%. Of the 759 valid EIS compound results reported from OPRs, seven failed to meet the EIS compound acceptance criterion (20–150%), resulting in a failure rate of 0.92%.

All LLOPRs included in the statistical analysis met the Study LLOPR NIS compound recovery criterion (>30%). Of the 1,186 valid target analyte results reported from LLOPRs, five failed to meet the target analyte criterion (40 – 150%), resulting in a failure rate of 0.42%.

Matrix spike recoveries were statistically evaluated by Analysis of Variance (ANOVA) as described in *Volume I.* All main effects were significant with greater than 99% confidence. On average all PFAS were observed with mean recoveries 70-130% of the target spike concentration. Matrix, Spike Concentration, and Laboratory main effects were also relatively consistent and close to the target spike concentration (i.e., 100% recovery). While there were statistically significant differences among the various levels of each main effect evaluated, the overall method accuracy and precision was quantified. Method accuracy was calculated as the mean percent bias (% recovery – 100%) for each spike concentration and laboratory and matrix averaging over the method analytes. Precision was calculated as the inter-laboratory percent relative standard deviation (RSD) among replicate measures of the various spiked samples.

Based on the data from the Study, EPA developed quality control (QC) acceptance criteria for soils and sediment following the same methods used in *Volume I.* These QC specifications included those to be applied to IPRs, OPRs, LLOPRs, EIS compound, and NIS compound recoveries.

E.S.10 CONCLUSION

The objectives of this MLVS were achieved: validation of EPA Method 1633 and the production of a method that can be implemented at a typical mid-sized full-service environmental laboratory. Overall, the data generated during the MLVS demonstrated that EPA Method 1633, as written, is robust enough to be performed by suitable laboratories using similar instruments of different manufacturers and models. The results generated by participating laboratories in this study routinely met the requirements stated in the method for:

- Mass calibration and mass calibration verification,
- Initial calibration and calibration verification,
- Determination of MDLs and LOQs,
- Initial Precision and Recovery, ,
- Preparatory batch QC samples (MB, OPR, LLOPR), and
- Quantitative and qualitative analyte identification criteria.

The suitability of EPA Method 1633 to detect and quantify the 40 target analytes in soil and sediment was successfully demonstrated through the analysis of spiked real-world samples of those matrix types. Method blank results demonstrated that there was negligible bias associated with background contamination introduced during sample preparation was negligible. The IPR, OPR, and LLOPR recoveries and the EIS and NIS compound recoveries associated with study samples were used to derive QC acceptance criteria for inclusion in the finalized method.

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LIST OF ACRONYMS AND ABBREVIATIONS

AFCEC	Air Force Civil Engineer Center
AFFF	aqueous film-forming foam
ANOVA	analysis of variance
ATP	alternate test procedure
CASRN	CAS registry number
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CV	calibration verification
DoD	U.S. Department of Defense
EDD	electronic data deliverable
EIS	extracted internal standard
ELAP	Environmental Laboratory Accreditation Program
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Exa	Exa Data & Mapping Services, Inc.
GDIT	General Dynamics Information Technology
HGL	HydroGeoLogic, Inc.
ICAL	initial calibration
ID	isotope dilution
IDA	Institute for Defense Analyses
IDOC	initial demonstration of capability
IPR	initial precision and recovery
ISC	instrument sensitivity check
LC-MS/MS	liquid chromatography–tandem mass spectrometry
LCS	laboratory control sample
LHA	lifetime health advisory
LLOPR	low level ongoing precision and recovery
LOD	limit of detection
LOQ	limit of quantitation
LLOQ	lower limit of quantitation
LOQVER	limit of quantitation verification
m/z	mass to charge ratio
MB	method blank
MDL	method detection limit
MDL_b	MDL based on method blank
MDL_s	MDL based on spiked samples
MLVS	Multi-Laboratory Validation Study

MRM	multiple reaction monitoring
MS	matrix spike
MSD	matrix spike duplicate
NAVSEA	Naval Sea Systems Command
NIS	non-extracted internal standard
OLEM	Office of Land and Emergency Management
OPR	ongoing precision and recovery
ORD	Office of Research and Development
OW	[EPA] Office of Water
PFAS	per- and polyfluoroalkyl substances
PFAS acronyms	**see** Table 1-1
ppb	parts per billion
QA	quality assurance
QC	quality control
QSM	quality systems manual
RF	response factor
RF_s	response factor of each EIS
RR	response ratio
RSD	relative standard deviation
RSE	relative standard error
SD	Sediment
SEE	Science and Engineering for the Environment, LLC
SERDP	Strategic Environmental Research and Development Program
SGS AXYS	SGS AXYS Analytical Services, Ltd. (Sidney, BC, Canada)
SLVS	Single-Laboratory Validation Study
SOW	statement of work
SPE	solid-phase extraction
SS	Soil
SW	surface water
µg/kg	microgram per kilogram
USACE	U.S. Army Corps of Engineers
Waters ERA	ERA – A Waters Company
Wellington	Wellington Laboratories, LLC

1 INTRODUCTION

This report is the second in a series presenting the results of a multi-laboratory validation study (MLVS) designed to validate the Environmental Protection Agency's (EPA) draft Office of Water (OW) *Method 1633: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS* (EPA Method 1633). A project designed to validate EPA Method 1633 was undertaken through the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP). Conducted as a joint effort by SERDP, the DoD, and the EPA, the objectives of this project were to:

- Identify and quantify up to 40 per- and polyfluoroalkyl substances (PFAS) in aqueous matrices (groundwater, surface water, landfill leachate, and wastewater), solids (soil, sediment, and biosolids), and tissues using the isotope dilution liquid chromatography–tandem mass spectrometry (LC-MS/MS) method.
- Achieve a low parts per trillion (ppt) limit of quantitation (LOQ) in aqueous matrices and parts per billion (ppb) in solids and tissues.
- Produce a method that can be implemented at a typical mid-sized full-service environmental laboratory.
- Conduct single- and multi-laboratory validation studies of the draft EPA Method 1633.

A standard operating procedure was developed, tested on eight environmental matrices and a Single-Laboratory Validation Study (SLVS) was completed with a report published in January 2022. That report, *Single-Laboratory Validation Study of PFAS by Isotope Dilution LC-MS/MS* resulted in the EPA OW publishing the draft EPA Method 1633 in September 2021, with updates of the method in June 2022, and December 2022. Subsequently, a Multi-Laboratory Validation Study (MLVS or "the Study") was undertaken with the first report titled *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume I: Wastewater, Surface Water, and Groundwater Matrices*, completed and published in July 2023. With publication of *Volume I*, the 4th Draft Method 1633 (EPA 2023) was finalized for the aqueous matrices: wastewater, surface water, and groundwater. The method is still draft for the remaining matrices (soil, sediments, biosolids, landfill leachate, and tissue). This report addresses the multi-laboratory study results for the solid matrices of soils and sediment[2]. Additional reports will be published at a later date for all other matrices included in the scope of the method.

The importance of the publication of the draft EPA Method 1633 (and by extension the Study) is reflected in the DoD's December 7, 2021, *Memorandum for the Update for Establishing a Constituent Methodology for the Analysis of Per- and Polyfluoroalkyl Substances in Media Other than Drinking Water*. This memorandum required that all new contracts and task orders after December 31, 2021, use draft EPA Method 1633 for the analysis for PFAS in matrices other than drinking water, using a laboratory accredited to the method/matrix/analyte by the DoD Environmental Laboratory Accreditation Program (DoD ELAP).

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[2] For the purposes of this report, solid matrices will refer to soils and sediments. Biosolids are included in the MLVS but will be presented in a subsequent report.

The MLVS was designed to evaluate the robustness of EPA Method 1633 when performed by suitable laboratories using similar instruments of different manufacturers and models, as well as provide information on the range of precision and accuracy of quantitation that is achievable by those laboratories. This was achieved through the evaluation of data generated from PFAS-spiked environmental samples (herein identified as study samples). A Study Plan which documented the procedures to be used throughout the entire study, including the creation and shipment of study samples, the preparation and analysis of study samples, the reporting, validation, and statistical analysis of the data generated by the Study. The laboratory sample preparation and analysis procedure was EPA Method 1633 with interim quality assurance and quality control criteria included (*Volume I*, MLVS Method, Appendix A). This Study was undertaken using EPA's *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program* (2018) as guidance where applicable. This Study was not an Alternate Test Procedure, so the guidance is not relevant for some steps. The Study follows all of the steps EPA's Clean Water Act Method Program has done for previous new EPA methods.

Evaluation of the data collected, as well as consideration of feedback from the participating laboratories, is documented herein to provide the basis for revisions to draft EPA Method 1633. This report and subsequent reports, along with all pertinent MLVS documentation needed to support publication of draft EPA Method 1633 as a final method, will be provided to the EPA OW. Additionally, the information and data from this MLVS will also be submitted to the EPA Office of Land and Emergency Management (OLEM) for the future development of an EPA solid waste (SW)-846 method.

This report is the second in the series of MLVS reports to be published. The first report, *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume I: Wastewater, Surface Water, and Groundwater Matrices*, provides the detailed project information that applies to this and subsequent reports in addition to this report. That report provides the project background, the overall project management structure, data validation, and data management procedures. Further, it describes the processes for laboratory selection, selection of study sample sources, and study sample creation and delivery. In addition, it includes results from evaluation of the overall EPA Method 1633 capabilities of each laboratory. This included the evaluation of each laboratory's standard operating procedure and documentation of Initial Calibrations (ICAL), the Initial Demonstration of Capabilities (IDOC), method detection limit (MDL) determination, and verification of their sample LOQ for aqueous matrices. The processes, evaluation, and procedures of the previous report are incorporated herein by reference and will not be repeated.

1.1 BACKGROUND

The use of man-made organofluorine chemicals, including various PFAS, fluorinated pharmaceuticals, and fluorinated pesticides, is widespread. Of this group of chemicals, PFAS are of particular concern due to their persistence in the environment. There are challenges to providing a single comprehensive definition for PFAS, but as a class, they are generally molecules with a carbon-carbon alkyl chain with multiple carbon-fluorine bonds. PFAS comprise a group of thousands of man-made chemicals that have been in production since the 1940s and are found in a variety of consumer products such as cookware, food packaging, and water-repellent fabrics.

The potential human health and environmental effects of PFAS are discussed in *Volume I*. EPA recognized the need to develop analytical methods for PFAS for other matrices that are regulated under the Clean Water Act, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and the Toxic Substance Control Act, as well as other ongoing efforts to demonstrate potential clean-up and PFAS-containing waste disposal (EPA, 2019; 2020). In 2022 EPA proposed designation of PFOA and PFAS as hazardous substances under CERCLA (40 CFR Part 302). The DoD has environmental management responsibilities for PFAS released to the environment associated with the use of aqueous film-forming foam (AFFF) (Leeson et al., 2020; Anderson et al., 2020). The use of AFFF has resulted in the widespread occurrence of PFAS in groundwater, drinking water, soils, sediments, receiving waters, and ecological receptors at many current and former military installations as well as more broadly throughout the community.

Because PFAS are ubiquitous in the environment, EPA and the DoD determined the need for a robust method that can quantify as many PFAS as practical in a variety of environmental matrices. Recognizing this challenge and opportunity, the EPA and DoD collaborated on the development of an isotope dilution method for non-drinking water aqueous matrices (surface water, groundwater, wastewater influent/effluent, landfill leachate), solids (soil, sediment, biosolids), and tissues (fish and clam). A project team was formed, headed by the SERDP/ESTCP, the DoD, and in conjunction with EPA, led by the OW and with contributions from the EPA OLEM and Office of Research and Development (ORD) to develop and validate what is Method 1633.

1.2 METHOD SUMMARY

The analytical method for this Study was validated and included in the report, *Single-Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS* (SERDP 2020 and 2021), and defined in the August 2021 draft of EPA 1633. Refinements to that method were made based on interactions and feedback from the 10 laboratories that participated in this MLVS. Updates reflecting those changes was have been iteratively released by EPA, the most recent is the 4th Draft Method 1633 (EPA 2023). The complete method used for this Study is provided in Appendix A to the *Volume I*.

The analytical method includes both sample preparation and sample analysis procedures that are applicable to a variety of environmental matrices. The matrices evaluated by the Study include wastewater, surface water, groundwater, landfill leachate, soil, sediment, biosolids, and tissue. The aqueous matrices are prepared via solid-phase extraction (SPE) and carbon clean-up processes. Soil, sediment, biosolids, and tissue matrices are prepared via solvent extraction followed by carbon clean-up and concentration via solid-phase extraction (SPE). The method utilized liquid chromatography–tandem mass spectrometry (LC-MS/MS) in multiple reaction monitoring (MRM) mode to evaluate quantification and confirmation (where applicable) of ions of each of the 40 target analytes (Table 1-1). Analyte concentrations were determined using either an isotope dilution or extracted internal standard (EIS) quantification scheme; both utilized isotopically labeled compounds that were added to the samples prior to extraction. At the time of validation, only 24 isotopically labeled analogs of the 40 target analytes were commercially available, and therefore only 24 target analytes could be quantified using isotope dilution quantitation. All other analytes were quantified using EIS quantitation with these isotopically labeled analogs. Recovery of both quantification schemes corrects the analyte results. Analytes were quantified and reported as their acid form.

Seven non-extracted internal standards (NIS) were used to determine EIS recoveries and provide a general indicator of overall analytical quality. A list of the 40 target analytes, 24 EIS compounds, and seven NIS compounds is provided in Table 1-1.

1.3 SUMMARY OF THE RESULTS OF THE AQUEOUS MLVS

The results of the MLVS for wastewater, groundwater and surface water was deemed a success because it met EPA's three goals for the Study, namely:

1. *Identify and quantify up to 40 PFAS in aqueous matrices (groundwater, surface water, landfill leachate, and wastewater, using the isotope dilution LC-MS/MS method.*

The Study generated method performance data for wastewater, surface water and groundwater. Of the 594 matrix spiked samples analyzed during the multi-laboratory study:

- 99.3 percent of the wastewater samples achieved recoveries between 70–130% (285 out of 287 samples); 84.9% of the wastewater results achieved recoveries between 70–130% (9468 out of 11154 results).
- 100 percent of the surface water samples achieved recoveries between 70–130% (162 out of 162 samples); 88.3% of the surface water results achieved recoveries between 70–130% (5615 out of 6360 results).
- 100 percent of the groundwater samples achieved recoveries between 70–130% (138 out of 138 samples; 92.2% of the groundwater results achieved recoveries between 70–130% (4685 out of 5083 results).

The MLVS results demonstrated that this method can identify and quantify individual PFAS.

2. *Achieve a low ppt LOQ in aqueous matrices.* The MLVS results demonstrated that the method could quantify 40 PFAS at levels between 0.712 and 100 ng/L in a 500-mL aqueous sample.

EPA's third goal for the multi-laboratory study was to show that:

3. *The method can be implemented at a typical mid-sized full-service environmental laboratory.*

Because all of the required instrumentation for this method has become commonplace in many full-service environmental laboratories, the results of the single-laboratory study demonstrate that this goal is achievable. The multi-laboratory validation study will determine how well a typical full-service laboratory can perform the method.

Table 1-1. Names, Abbreviations, and Chemical Abstract Service Registry Numbers (CASRN) for Target PFAS, Extracted Internal Standards, and Non-extracted Internal Standards

Analyte Name	Abbreviation	CASRN
Target Analytes		
Perfluoroalkyl carboxylic acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluoroalkyl sulfonic acids		
Acid Form		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Fluorotelomer sulfonic acids		
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4
Perfluorooctane sulfonamides		
Perfluorooctanesulfonamide	PFOSA	754-91-6
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2
Perfluorooctane sulfonamidoacetic acids		
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
Perfluorooctane sulfonamide ethanols		
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2
Per- and Polyfluoroether carboxylic acids		
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA	919005-14-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Ether sulfonic acids		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OudS	763051-92-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7

Table 1-1. Names, Abbreviations, and Chemical Abstract Service Registry Numbers (CASRN) for Target PFAS, Extracted Internal Standards, and Non-extracted Internal Standards (Continued)

Analyte Name	Abbreviation	CASRN
Fluorotelomer carboxylic acids		
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA	914637-49-3
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4
Extracted Internal Standard (EIS) Compounds		
Perfluoro-n-[$^{13}C_4$]butanoic acid	$^{13}C_4$-PFBA	NA
Perfluoro-n-[$^{13}C_5$]pentanoic acid	$^{13}C_5$-PFPeA	
Perfluoro-n-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	$^{13}C_5$-PFHxA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	$^{13}C_4$-PFHpA	
Perfluoro-n-[$^{13}C_8$]octanoic acid	$^{13}C_8$-PFOA	
Perfluoro-n-[$^{13}C_9$]nonanoic acid	$^{13}C_9$-PFNA	
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	$^{13}C_6$-PFDA	
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	$^{13}C_7$-PFUnA	
Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	$^{13}C_2$-PFDoA	
Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid	$^{13}C_2$-PFTeDA	
Perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonic acid	$^{13}C_3$-PFBS	
Perfluoro-1-[1,2,3-$^{13}C_3$]hexanesulfonic acid	$^{13}C_3$-PFHxS	
Perfluoro-1-[$^{13}C_8$]octanesulfonic acid	$^{13}C_8$-PFOS	
Perfluoro-1-[$^{13}C_8$]octanesulfonamide	$^{13}C_8$-PFOSA	
N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	D_3-NMeFOSAA	
N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	D_5-NEtFOSAA	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-$^{13}C_2$]hexanesulfonic acid	$^{13}C_2$-4:2FTS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-$^{13}C_2$]octanesulfonic acid	$^{13}C_2$-6:2FTS	
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-[1,2-$^{13}C_2$]decanesulfonic acid	$^{13}C_2$-8:2FTS	
Tetrafluoro-2-heptafluoropropoxy-$^{13}C_3$-propanoic acid	$^{13}C_3$-HFPO-DA	
N-methyl-d_7-perfluorooctanesulfonamidoethanol	D_7-NMeFOSE	
N-ethyl-d_9-perfluorooctanesulfonamidoethanol	D_9-NEtFOSE	
N-methyl-d_3-perfluoro-1-octanesulfonamide	D_3-NMeFOSA	
N-ethyl-d_5-perfluoro-1-octanesulfonamide	D_5-NEtFOSA	
Non-extracted Internal Standard (NIS) Compounds		
Perfluoro-n-[2,3,4-$^{13}C_3$]butanoic acid	$^{13}C_3$-PFBA	NA
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	$^{13}C_4$-PFOA	
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	$^{13}C_2$-PFDA	
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanesulfonic acid	$^{13}C_4$-PFOS	
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$^{13}C_5$-PFNA	
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	$^{13}C_2$-PFHxA	
Perfluoro-1-hexane[$^{18}O_2$]sulfonic acid	$^{18}O_2$-PFHxS	

Notes:
The target analyte names are for the acid and neutral forms of the analytes. See Table 8 in the draft EPA Method 1633, Analysis of PFAS in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS for the names and CASRN of the corresponding anion forms, where applicable.
CASRN = Chemical Abstracts Service Registry Number.
LC-MS/MS = liquid chromatography mass spectrometry/mass spectrometry.
NA = Not applicable; NIS and EIS compounds do not have CASRN.
PFAS = Per- and Polyfluoroalkyl Substances.

2 STUDY MANAGEMENT, OBJECTIVES, DESIGN, AND IMPLEMENTATION

The Study objectives and design are described in the Study Plan *for Multi-Laboratory Validation of Draft EPA Method 1633 – PFAS in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS* (Study Plan), which is included as Appendix A to *Volume I*. The overall study was designed to resemble that of the *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater under EPA's Alternate Test Procedure Program* (EPA Office of Water, 2018). While this MLVS is not designed to support an alternate test procedure (ATP) application, the number of matrices and statistical analyses of the data mirror what would be required for an ATP for national use.

2.1 STUDY MANAGEMENT: PFAS METHOD VALIDATION TEAM

A joint EPA and DoD PFAS Method Validation Team was formed to oversee the PFAS analytical method development and validation. Study management was done cooperatively as the MLVS Team, which included SERDP/Environmental Security Technology Certification Program (ESTCP); the U.S. Army Corps of Engineers (USACE); EPA's Offices of Water, of Land and Emergency Management, of Research and Development; the U.S. Navy; and the U.S. Air Force. SERDP/ESTCP, the USACE, EPA OW, the U.S. Navy, and the U.S. Air Force approved and are co-signers to the *Study Plan*.

Funding for this project was provided by SERDP/ESTCP to the USACE, which in turn contracted with HydroGeoLogic, Inc. (HGL) to serve as the Oversight Contractor for the project. SERDP/ESTCP also established contracts with Science and Engineering for the Environment LLC (SEE), for program management; Exa Data & Mapping Services, Inc., (Exa) for data management; and the following firms for independent, third-party data validation: Jacobs Engineering Group, Inc.; and Pyron Environmental Inc. The Institute for Defense Analyses (IDA) conducted statistical analyses on the resulting data. The funding for both the single-laboratory and the multiple-laboratory validation studies was provided by SERDP.

Ten laboratories (eight commercial contract laboratories and two state laboratories) agreed to participate in the Study. The ten laboratories participating are listed in Table 2-1. For the purposes of this Study, the laboratories were randomly assigned numbers, which were used to maintain the anonymity of the results. Not all laboratories participated in all media; two laboratories opted out of participating in the Study for landfill leachate, biosolids, and tissues, with one laboratory also opting out of the sediments (Table 2-2).

The laboratories were contracted to HGL, which also managed the contracting for sample spiking and shipment and received all deliverables from the laboratories. HGL also contracted a commercial vendor, Wellington Laboratories, LLC (Wellington), to provide analytical standard mixtures and individual, high-concentration PFAS analytical standards as defined by the MLVS Team to the laboratories participating in the Study. Another commercial vendor, Waters ERA, which specializes in proficiency testing samples, prepared and shipped the Study Samples using "real-world" environmental sample matrices.

2.2 STUDY OBJECTIVE AND DESIGN

The overall MLVS objectives and design are detailed in Section 2 of *Volume I*. In the evaluation of solid matrices, the design articulated in the Study Plan involved:

- Ten laboratories, with a goal of complete soil and sediment sample data sets from at least six of those laboratories.
- Three soil and three sediment samples of varying physical/chemical characteristics including pH, grain size, percent moisture, and total organic carbon. Sediment samples included two freshwater, and one marine site.
- Multi-point calibration of the target analytes by each laboratory.
- IDOC in solid media by each laboratory.
- Determination of MDLs by each laboratory.
- Analyses of matrix spiked samples prepared from each of the soil/sediment samples.

Initial Calibration studies were conducted by each laboratory; those results are discussed in Section 4 of *Volume I*.

2.3 MATRICES AND SAMPLE SELECTION

The MLVS was designed to provide a test of the method by analyses of real-world environmental matrices. To obtain a wide diversity and sufficient quantity of matrices and samples, SERDP and EPA coordinated with municipal, state, and EPA Regional contacts to obtain sufficient volumes/mass used in the Study.

The list of all soil and sediment samples acquired for this Study is found in the Study Plan ***(****Volume I*, Appendix A, Attachment 2***)***. The specific samples used are provided in Table 2-3. Samples and sources are discussed briefly below.

EPA provided seven individual soil samples from sites in California, Illinois, Montana, New Mexico, Tennessee, and Utah. These samples were collected as part of other on-going EPA site investigations and sent under chain of custody to ERA-Waters in Colorado. All soil samples were analyzed for PFAS and for grain size, pH, and total organic carbon (TOC). While the original intent was to use all seven soil samples, the Study Plan opted to run only three. Based on the PFAS and conventional analyses, the three soil samples selected were from Tennessee (SSW), Montana (SSR), and New Mexico (SST) (Table 2-3). Levels of PFAS measured in those three samples are provided in Table 2-4. The results of the conventional analyses are provided in Table 2-5. PFAS native concentrations were low, principally below detection limits for the three soil samples. The SSW sample had detectable levels of several PFAS, but in all cases these were less than 0.2 µg/kg. Table 2-5 shows a wide range of TOC from 2,900 (SST), 15,000 (SSW), and 34,000 (SSR) mg/kg. Table 2-5 also shows these samples have a range of percent sand/silt/clay fractions: SSR at 51/43/6 %; SST at 62.5/25/12.5 %, and SSW at 8/84/8 % fractions.[3] Three sediments were collected by

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[3] EPA Method 1633 states that units should be reported as ng/g, but in the MLVS Work Plan the decision was made to have the laboratories report the solid results in µg/kg dry weight. As the units are equivalent, the tables in this report are stated as µg/kg.

SEE and sent via chain of custody to Waters ERA in CO. Two freshwater samples, one silty-sand (SDY), and one sandy (SDZ) sediment were collected from Burley Creek near Gig Harbor, WA. Burley Creek is a wild-salmon creek that has no known sources of PFAS or other contaminants of concern. PFAS in those two samples were either just at, or below the detection limits. TOC levels were 21,000 and 7,300 mg/kg, respectively in the two Burley Creek samples. A marine silty-sand sediment sample was collected from Sequim Bay, WA. The TOC in this sample was 33,000 mg/kg.

The MLVS design specified that each of the soil and sediment field-collected samples were sub-sampled to create a pre-spiked characterization sample, an unspiked (or “native”) sample, three replicates at a low-spiked concentration, and three replicates at a high-spiked concentration (Table 2-3). Each sample was assigned a matrix code: soils SS and sediments SD. To distinguish individual samples, a single letter sample identifier was assigned. The native sample was assigned the number 0, the unspiked study sample assigned the number 1, low-spiked replicates 2–4, and the high-spiked replicates 5–7.

2.4 SELECTION OF SPIKING LEVELS AND SOLID MEDIA

All of the soils and sediments were screened for baseline PFAS levels. ERA-Waters homogenized all sample matrices and shipped aliquots of composite samples collected from each to SGS AXYS for native PFAS analyses and to Eurofins-TestAmerica (ETA)-Denver for conventional physical and chemical analyses.

Results of the baseline target PFAS in the solid media samples are presented in Table 2-4. From these results, the EPA and the Study Quality Assurance (QA) Manager determined appropriate low-spiked, and high-spiked concentrations for each target PFAS. The intent was to bracket the range of PFAS concentrations observed in the test samples while keeping the concentrations within the calibration range provided in the method. Table 2-4 also shows the appropriate target calibration level set of each PFAS by EPA and the DoD.

2.5 PREPARATION OF STUDY SAMPLES

Preparation of all selected study samples was performed by Waters ERA, and followed the general procedures documented in the Study Plan. Specific spiking procedures for solids followed at Waters ERA are provided in Appendix A.

High and low spiking levels were set by the Study QA Manager and EPA based upon review of the baseline (background) PFAS concentrations for the solid samples (Table 2-4).

Study samples of 5.0 grams dry-weight basis were spiked by Waters ERA at two concentrations per analyte using spiking concentrates prepared from concentrated stock solutions procured from Wellington. Bulk matrices were homogenized prior to packaging. Spiking concentrates were vortexed prior to use. Once the aliquots were spiked, they were sealed and segregated to a designated area of Waters ERA to prevent double spiking accidents. Samples were typically spiked during the week prior to shipping, frozen at -20º C through the weekend, and packed and shipped the following Monday.

Waters ERA issued Certificates of Spiking for all matrices and all spiked samples (high and low). An example certificate is shown in Figure 2-1.

Samples were shipped directly from Waters ERA to each participating laboratory, in cooler boxes with frozen blue gel packs to keep the samples cool during shipping. Each laboratory received seven 24-mL amber glass screw-top vials of each of the soil and sediment samples: one bottle for analyses of the unspiked sample, three bottles spiked at a low-spiked level, and three bottles spiked at a high-spiked level. Any remaining sample volume was stored at Waters ERA in case they were needed at a later date. HGL tracked all sample shipments and confirmed receipt and condition with each laboratory.

The sample preparation procedure found in the MLV Study Method was followed, with the following exceptions:

- Instead of homogenizing the sample and weighing out an aliquot of the sample, the laboratories were instructed to transfer the entire contents (5.0 g) of the container received to a 50-mL polypropylene centrifuge tube.
- Percent moisture was not performed by the laboratories. The amount of sample in each container took into account the % moisture of the sample and 5.0 g dry weight of each sample.
- The laboratories were instructed to record 5.0 g as the mass of sample prepared and 0% moisture as the % moisture for each sample. Further, the instructions were to use that weight and percent moisture when calculating PFAS concentrations in each sample.
- The soil/sediment sample container was rinsed with 10 mL of 0.3% methanolic ammonium hydroxide, vortexed, and then that solution was transferred to the centrifuge tube as described in Section 11.3.4 of EPA Method 1633.
- Laboratories were instructed to report the results in µg/kg.

2.5.1 Soil Samples

The soil samples prepared and shipped by Waters ERA are listed in Table 2-3. The three parent soil matrices were each prepared as one unspiked, three replicates at the low-spiked level, and three replicate at the high-spiked level (Table 2-4). This resulted in 21 individual soil samples at each laboratory for analysis.

Soil samples were spiked on 19 July 2022, frozen at -20° C over the weekend, shipped on 25–26 July under chain of custody, and generally arrived within one day of shipment, and below 6° C. Upon check-in, the samples were immediately stored at -20° C until preparation. The date of arrival, along with confirmation that the samples remained under that Study Plan-specified temperature of < 6° C, were confirmed during the data validation review. A set of soil and sediment sample preparation guidelines accompanied each shipment to the laboratory (Figure 2-2).

One set of soils samples sent to Laboratory 1 was delayed in transit by one day but arrived at the laboratory under temperature. Another set of soil samples to Laboratory 2 arrived on-time, but multiple samples were above 6° C; these samples were not used in the Study. A second set was sent to Laboratory 2 on 1 August and arrived 2 August 2023 on time and under temperature and were used in the Study.

An additional set of samples (soils and sediments) had to be sent to Laboratory 8. At the bench, the chemist did not follow directions and took approximately 2.0 g for determining percent moisture and extracted the remaining 3 g for PFAS analysis. The laboratory did not realize that mistake until after the PFAS analyses were complete and reported the error to HGL; these results were not used in the Study. Arrangements were made for a second set of soil and sediment samples to be sent out on 9 August 2023 and arriving the following day. Laboratory 8 extracted those resent samples on the day received.

2.5.2 Sediment Samples

The sediment samples prepared and shipped by Waters ERA are listed in Table 2-3. The three parent soil matrices were each prepared as one unspiked, three replicates at the low-spike level, and three replicates at the high-spiked level. This resulted in 21 individual sediment samples at each laboratory for analysis.

Sediment samples were spiked on 19 July, frozen at -20° C, shipped 25 - 26 July 2023 under chain of custody, and arrived within one day of shipment with temperatures at or below 6° C. Upon check-in, the samples were immediately stored at -20° C until preparation. The date of arrival, along with confirmation that the samples remained under the < 6° C temperature specified in the Study Plan, were confirmed during the data validation review.

Only nine laboratories participated in the sediment analyses. Laboratory 2 opted out of the Study for sediments, and all other remaining MLVS matrices.

Table 2-1. Participating Laboratories

Laboratory/Supplier	**Location**	**Role**
Participating MLVS Laboratories		
Alpha Analytical [1]	Mansfield, MA	MLVS Participant Laboratory (laboratories were randomly assigned numbers 1 to 10 in the remainder of this report)
Battelle Memorial Institute	Norwell, MA	
California EPA	Pasadena, CA	
Eurofins Lancaster	Lancaster, PA	
Eurofins-TestAmerica (ETA) West Sacramento	West Sacramento, CA	
GEL Laboratories	Charleston, SC	
Pace Analytical	Baton Rouge, LA	
Maryland Department of Health	Baltimore, MD	
SGS North America	Orlando, FL	
Vista Analytical Laboratory [1]	El Dorado Hills, CA	
Ancillary Laboratories		
Waters ERA	Golden, CO	PFAS-spiked matrices and sample shipment for all aqueous, solid and tissues
SGS AXYS Analytical Services, Ltd.	Sydney, BC, Canada	Native PFAS measures for all aqueous, solid, and tissue samples
Eurofins-TestAmerica (ETA) Denver	Arvada, CO	Ancillary analytical measures for wastewater, surface water, groundwater, soils, solids, and tissue
Wellington Laboratories, LLC	Overland Park, KS	Provider of all PFAS standards for matrix spiking, calibration, as well as Extracted Internal Standards and Non-extracted Internal Standards

Notes:

1. During the MLVS Alpha Analytical was purchased by Pace Analytical. Vista Analytical Laboratory was purchased by Enthalpy Analytical.

Table 2-2. Participant Laboratory Number and Matrices Analyzed

Laboratory Number	**PFAS Matrix Analyses**												
	Initial Calibration	**Initial Dem. Capabilities**			**Aqueous Matrices**				**Solid Matrices**			**Tissue Matrices**	
		Aqueous	**Solid**	**Tissue**	**Wastewater**	**Surface Water**	**Ground Water**	**Landfill Leachate**	**Soil**	**Sediment**	**Solid Matrices - Biosolids**	**Fish**	**Shellfish**
1	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
2	✓	✓	✓	✗	✓	✓	✓	✗	✓	✗	✗	✗	✗
3	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
4	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
5	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
7	✓	✓	✓	✗	✓	✓	✓	✗	✓	✓	✗	✗	✗
8	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
9	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
10	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Notes:

✓ indicates participated in specific media/matrices.

✗ indicates did not participate in specific media/matrices.

Table 2-3. Soil and Sediments Used for the Low/High PFAS Matrix Spikes

Sample Name	**Description**	**Matrix Code**	**Sample Identifier**	**Characterization Pre-Spike**	**MLVS Sample IDs**							**Sample Spike Date**
					Unspiked	**Low**			**High**			
						Replicate 1	**Replicate 2**	**Replicate 3**	**Replicate 1**	**Replicate 2**	**Replicate 3**	
Soil												
Musselshell, Clark Co. MT	AA (2016-106), L32547-2	SS	R	SSR0	SSR1	SSR2	SSR3	SSR4	SSR5	SSR6	SSR7	7/19/2022
Fruitland, San Juan Co. NM	CC (2018-105), L32547-4	SS	T	SST0	SST1	SST2	SST3	SST4	SST5	SST6	SST7	7/19/2022
Brock, Wheatley Co. TN	FF (2019-110) L32547-7	SS	W	SSW0	SSW1	SSW2	SSW3	SSW4	SSW5	SSW6	SSW7	7/19/2022
Sediment												
Burley 1 Sed. Burley Creek, WA	Freshwater silty sand	SD	Y	SDY0	SDY1	SDY2	SDY3	SDY4	SDY5	SDY6	SDY7	7/19/2022
Burley 2 Sed. Burley Creek, WA	Freshwater sandy	SD	Z	SDZ0	SDZ1	SDZ2	SDZ3	SDZ4	SDZ5	SDZ6	SDZ7	7/19/2022
Sequim Bay Sediment	Marine sediment	SD	AA	SDAA0	SDAA1	SDAA2	SDAA3	SDAA4	SDAA5	SDAA6	SDAA7	7/19/2022

Table 2-4. Target Low/High PFAS Spiked Concentrations and Calibration Range based on Native PFAS Analyses in Soils and Sediments

Target PFAS	Target PFAS Spike Concentrations		Target Calibration		PFAS Target Compound Analytical Results					
			5.0 g Sample		Soil Samples (µg/kg)			Sediment Samples (µg/kg)		
	Low Spike[1]	High Spike[1]	Low Cal	High Cal	SSR0	SST0	SSW0	SDY0	SDZ0	SDAA0
PFBA	4	50	0.64	200	< 0.1503	< 0.1478	< 0.1455	< 0.1694	< 0.1526	< 0.1462
PFPeA	4	50	0.32	100	< 0.07516	< 0.07391	< 0.07274	< 0.08471	< 0.07628	< 0.07309
PFHxA	4	25	0.16	50	0.03848	< 0.03696	0.04811	0.05227	< 0.03814	< 0.03655
PFHpA	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFOA	4	25	0.16	50	< 0.03758	< 0.03696	0.052	< 0.04235	< 0.03814	< 0.03655
PFNA	4	25	0.16	50	< 0.03758	< 0.03696	0.1897	< 0.04235	< 0.03814	< 0.03655
PFDA	4	25	0.16	50	< 0.03758	< 0.03696	0.04634	0.0555	< 0.03814	< 0.03655
PFUnA	4	25	0.16	50	< 0.03758	< 0.03696	0.1977	< 0.04235	< 0.03814	< 0.03655
PFDoA	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	0.05082	< 0.03814	< 0.03655
PFTrDA	4	25	0.16	50	< 0.03758	< 0.03696	0.05908	< 0.04235	< 0.03814	< 0.03655
PFTeDA	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFBS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFPeS	4	25	0.16	50	< 0.03777	< 0.03714	< 0.03655	< 0.04256	< 0.03833	< 0.03673
PFHxS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFHpS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFOS	4	25	0.16	50	0.09389	< 0.03696	0.1325	0.3066	0.03941	< 0.03655
PFNS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFDS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	0.05664	< 0.03814	< 0.03655
PFDoS	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
4:2FTS	4	25	0.64	40	< 0.1503	< 0.1478	< 0.1455	< 0.1694	< 0.1526	< 0.1462
6:2FTS	4	25	0.64	40	< 0.1355	< 0.1332	< 0.1311	< 0.1527	< 0.1375	< 0.1317
8:2FTS	4	25	0.64	40	< 0.1503	< 0.1478	< 0.1455	< 0.1694	< 0.1526	< 0.1462
PFOSA	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
NMeFOSA	4	25	0.4	50	< 0.04322	< 0.04250	< 0.04183	< 0.04871	< 0.04386	< 0.04203
NEtFOSA	4	25	0.4	50	< 0.09395	< 0.09239	< 0.09093	< 0.1059	< 0.09535	< 0.09137

Table 2-4. Target Low/High PFAS Spiked Concentrations and Calibration Range based on Native PFAS Analyses in Soils and Sediments (continued)

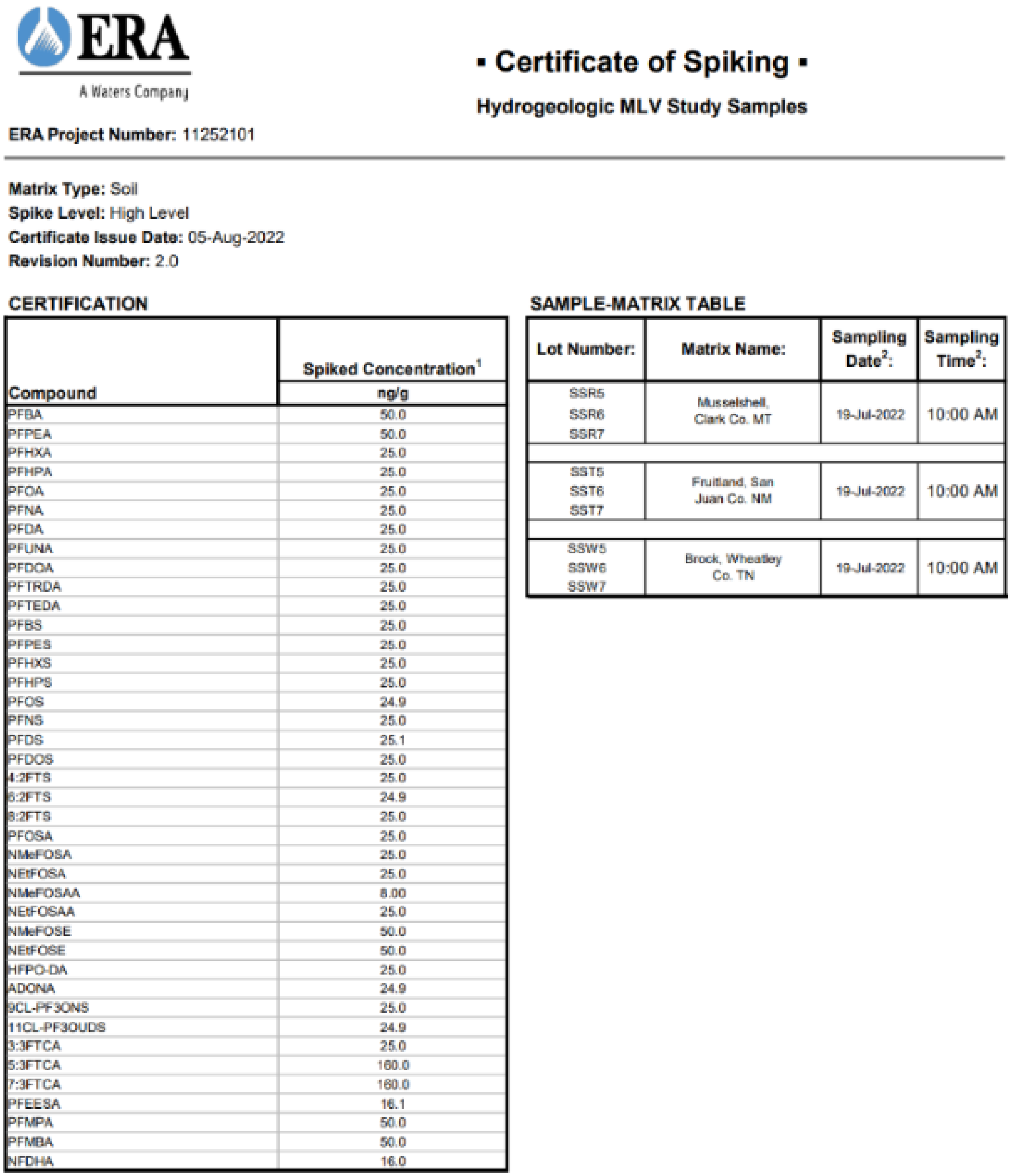
Target PFAS	Target PFAS Spike Concentrations		Target Calibration		PFAS Target Compound Analytical Results					
			5.0 g Sample		Soil Samples (µg/kg)			Sediment Samples (µg/kg)		
	Low Spike[1]	High Spike[1]	Low Cal	High Cal	SSR0	SST0	SSW0	SDY0	SDZ0	SDAA0
NMeFOSAA	4	8	0.4	10	< 0.03758	< 0.03696	< 0.03637	0.07156	< 0.03814	< 0.03655
NEtFOSAA	4	25	0.16	50	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
NMeFOSE	10	50	1.6	100	< 0.3758	< 0.3696	< 0.3637	< 0.4235	< 0.3814	< 0.3655
NEtFOSE	10	50	1.6	100	< 0.2811	< 0.2764	< 0.2721	< 0.3168	< 0.2853	< 0.2734
HFPO-DA	4	25	0.64	40	< 0.1428	< 0.1404	< 0.1382	< 0.1609	< 0.1449	< 0.1389
ADONA	4	25	0.64	40	< 0.1503	< 0.1478	< 0.1455	< 0.1694	< 0.1526	< 0.1462
9CL-PF3ONS	4	25	0.64	40	< 0.1507	< 0.1482	< 0.1459	< 0.1698	< 0.1529	< 0.1466
11CL-PF3OudS	4	25	0.64	40	< 0.1505	< 0.1480	< 0.1457	< 0.1696	< 0.1527	< 0.1464
3:3FTCA	4	25	0.8	40	< 0.1503	0.1582	< 0.1455	< 0.1694	< 0.1526	< 0.1462
5:3FTCA	20	160	4	250	< 0.9395	< 0.9239	< 0.9093	< 1.059	< 0.9535	< 0.9137
7:3FTCA	20	160	4	250	< 0.9395	< 0.9239	< 0.9093	< 1.059	< 0.9535	< 0.9137
PFEESA	4	16	0.32	20	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
PFMPA	4	50	0.32	100	< 0.07516	< 0.07391	< 0.07274	< 0.08471	< 0.07628	< 0.07309
PFMBA	4	50	0.32	100	< 0.03758	< 0.03696	< 0.03637	< 0.04235	< 0.03814	< 0.03655
NFDHA	0.8	20	4	16	< 0.07516	< 0.07391	< 0.07274	< 0.08471	< 0.07628	< 0.07309

Notes:
[1] All spiked concentrations are presented as acid concentrations; as final concentration in sample in µg/kg.

Table 2-5. Results of Conventional Analyses for the Candidate Soil and Sediment Samples

Analyte	**Unit**	**Soil - SSR0 Result**	**Soil - SST0 Result**	**Soil - SSW0 Result**	**Sediment - SDY0 Result**	**Sediment - SDZ0 Result**	**Sediment - SDAA0 Result**
Salinity	unitless	---	---	---	< 20 [1]	< 20 [1]	30
pH adj. to 25 deg C	SU	8.0	7.8	5.6	6	6.8	7.8
Specific Conductance	umhos/cm	---	---	---	120	110	5600
Total Organic Carbon	mg/kg	34,000	2,900	15,000	21,000	7,300	3,300
Percent Moisture	percent	3.1	1.3	1.5	55.5	14	24.6
Sand (>0.064 mm - 75 mm)	percent	51	62.5	8	77.5	92	88
Silt	percent	43	25	84	22	7	11.5
Clay	percent	6.0	12.5	8.0	0.5	1.0	0.5

Notes:
1. Sediment samples SDY and SDZ were collected in a freshwater creek. The laboratories detection limit for salinity is 20. Converting the specific conductivity to salinity the salinity of samples SDY0 and SDZ0 are less than < 0.1 mg/L, while SDAA0 is 32 mg/L as NaCl.



ERA
A Waters Company

▪ Certificate of Spiking ▪

Hydrogeologic MLV Study Samples

ERA Project Number: 11252101

Matrix Type: Soil
Spike Level: High Level
Certificate Issue Date: 05-Aug-2022
Revision Number: 2.0

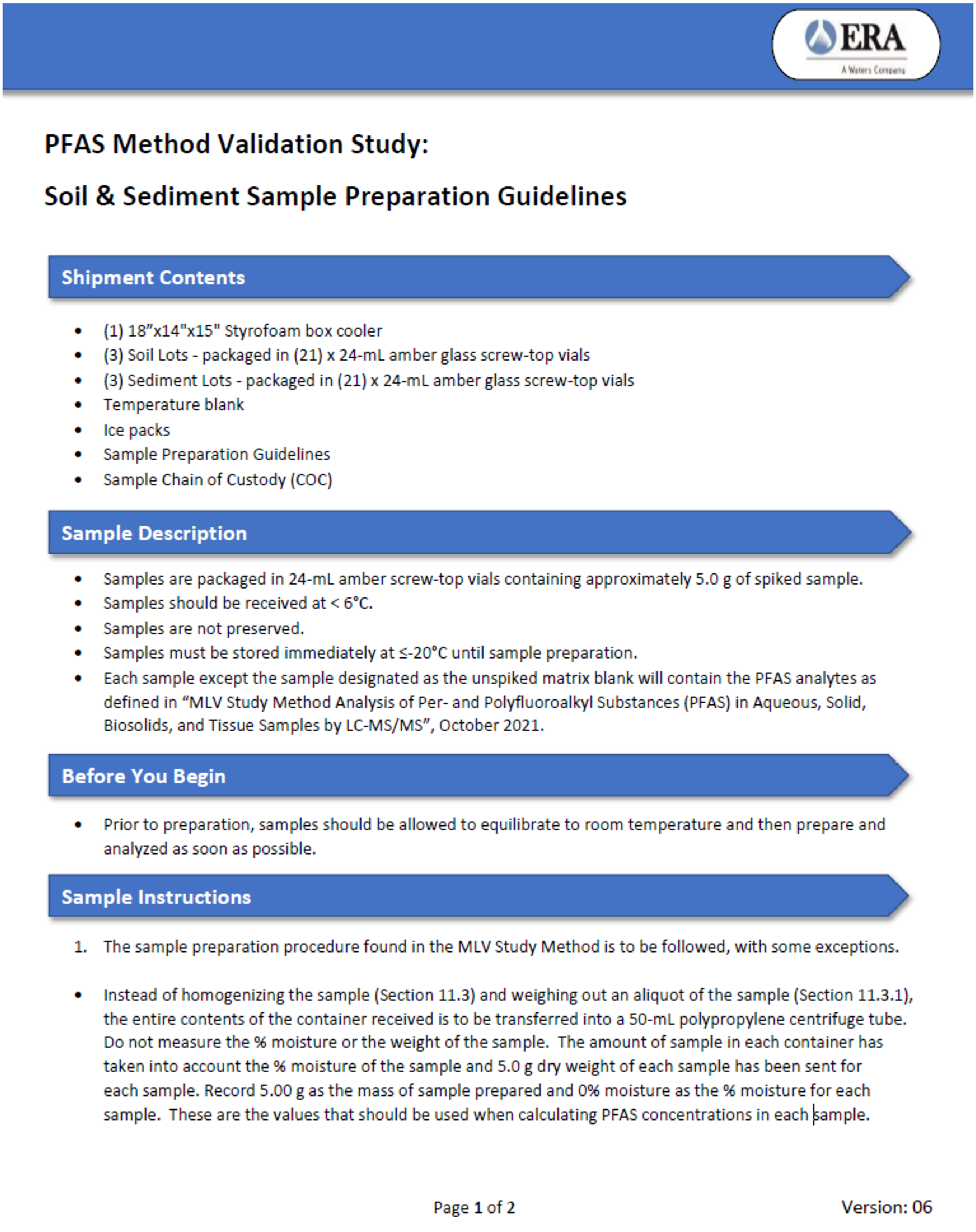
CERTIFICATION

Compound	Spiked Concentration[1] ng/g
PFBA	50.0
PFPEA	50.0
PFHXA	25.0
PFHPA	25.0
PFOA	25.0
PFNA	25.0
PFDA	25.0
PFUNA	25.0
PFDOA	25.0
PFTRDA	25.0
PFTEDA	25.0
PFBS	25.0
PFPES	25.0
PFHXS	25.0
PFHPS	25.0
PFOS	24.9
PFNS	25.0
PFDS	25.1
PFDOS	25.0
4:2FTS	25.0
6:2FTS	24.9
8:2FTS	25.0
PFOSA	25.0
NMeFOSA	25.0
NEtFOSA	25.0
NMeFOSAA	8.00
NEtFOSAA	25.0
NMeFOSE	50.0
NEtFOSE	50.0
HFPO-DA	25.0
ADONA	24.9
9CL-PF3ONS	25.0
11CL-PF3OUDS	24.9
3:3FTCA	25.0
5:3FTCA	160.0
7:3FTCA	160.0
PFEESA	16.1
PFMPA	50.0
PFMBA	50.0
NFDHA	16.0

SAMPLE-MATRIX TABLE

Lot Number:	Matrix Name:	Sampling Date[2]:	Sampling Time[2]:
SSR5 SSR6 SSR7	Musselshell, Clark Co. MT	19-Jul-2022	10:00 AM
SST5 SST6 SST7	Fruitland, San Juan Co. NM	19-Jul-2022	10:00 AM
SSW5 SSW6 SSW7	Brock, Wheatley Co. TN	19-Jul-2022	10:00 AM

Figure 2-1. Example Soil Certificate of Spiking



PFAS Method Validation Study:

Soil & Sediment Sample Preparation Guidelines

Shipment Contents

- (1) 18"x14"x15" Styrofoam box cooler
- (3) Soil Lots - packaged in (21) x 24-mL amber glass screw-top vials
- (3) Sediment Lots - packaged in (21) x 24-mL amber glass screw-top vials
- Temperature blank
- Ice packs
- Sample Preparation Guidelines
- Sample Chain of Custody (COC)

Sample Description

- Samples are packaged in 24-mL amber screw-top vials containing approximately 5.0 g of spiked sample.
- Samples should be received at < 6°C.
- Samples are not preserved.
- Samples must be stored immediately at ≤-20°C until sample preparation.
- Each sample except the sample designated as the unspiked matrix blank will contain the PFAS analytes as defined in "MLV Study Method Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS", October 2021.

Before You Begin

- Prior to preparation, samples should be allowed to equilibrate to room temperature and then prepare and analyzed as soon as possible.

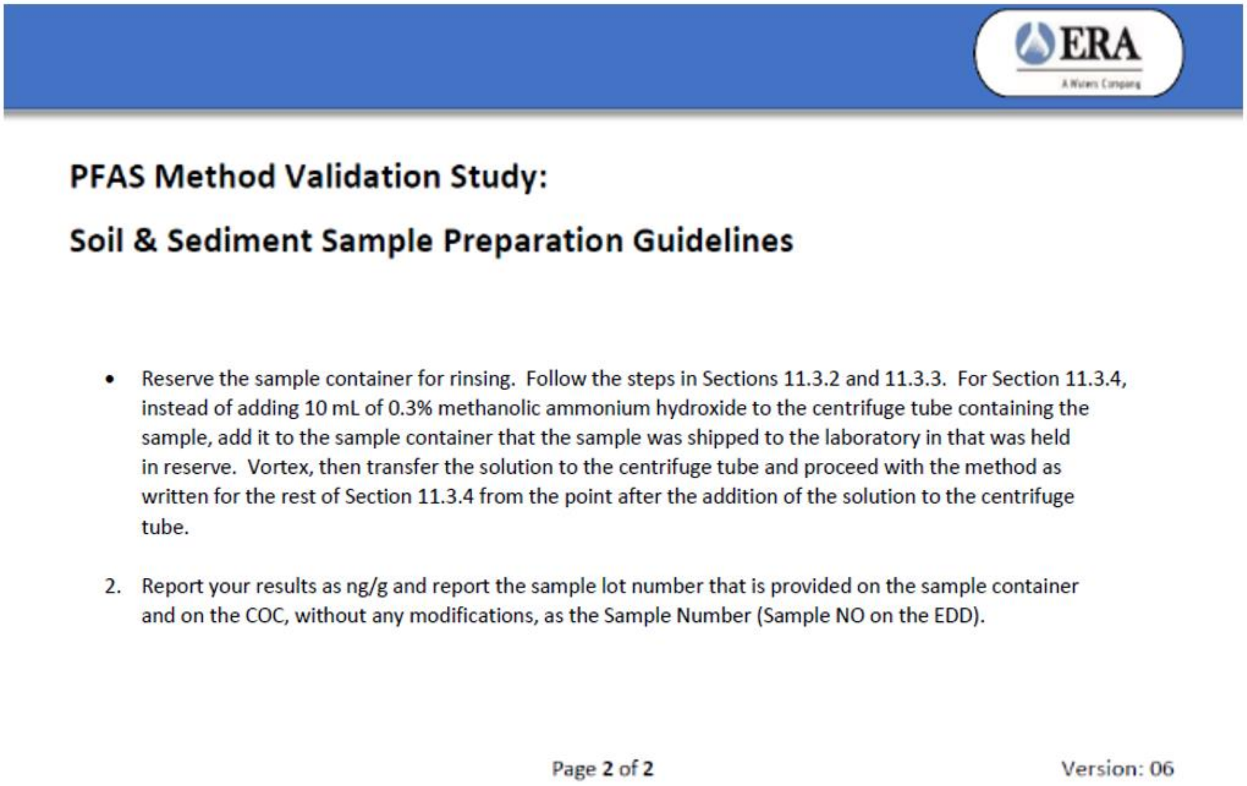
Sample Instructions

1. The sample preparation procedure found in the MLV Study Method is to be followed, with some exceptions.

- Instead of homogenizing the sample (Section 11.3) and weighing out an aliquot of the sample (Section 11.3.1), the entire contents of the container received is to be transferred into a 50-mL polypropylene centrifuge tube. Do not measure the % moisture or the weight of the sample. The amount of sample in each container has taken into account the % moisture of the sample and 5.0 g dry weight of each sample has been sent for each sample. Record 5.00 g as the mass of sample prepared and 0% moisture as the % moisture for each sample. These are the values that should be used when calculating PFAS concentrations in each sample.

Page **1** of **2**　　Version: 06

Figure 2-2. Example Soil Sample Preparation Guideline Form



PFAS Method Validation Study:

Soil & Sediment Sample Preparation Guidelines

- Reserve the sample container for rinsing. Follow the steps in Sections 11.3.2 and 11.3.3. For Section 11.3.4, instead of adding 10 mL of 0.3% methanolic ammonium hydroxide to the centrifuge tube containing the sample, add it to the sample container that the sample was shipped to the laboratory in that was held in reserve. Vortex, then transfer the solution to the centrifuge tube and proceed with the method as written for the rest of Section 11.3.4 from the point after the addition of the solution to the centrifuge tube.

2. Report your results as ng/g and report the sample lot number that is provided on the sample container and on the COC, without any modifications, as the Sample Number (Sample NO on the EDD).

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Figure 2-2. Example Soil Sample Preparation Guideline Form. (continued)

3 DATA MANAGEMENT, DATA VALIDATION, AND DATA RULES FOR STATISTICAL ANALYSES

Procedures were established in the Study Plan for data management (project and analytical data), data validation after receipt of the laboratory packages, and compilation of a validated Project Database from the individual validated electronic data deliverables (EDD) for each of the laboratories. The procedures for data management and data validation are described in *Volume I* Section 3 and in the Study Plan (*Volume I, Appendix A*).

This chapter briefly recaps the procedures and quality assurance/quality control checks (QA/QC) for data management, validation, creation of a Project Database, and rules and procedures that governed the solids data used for the statistical analyses. The final data validation reports for each laboratory and each matrix are archived separate from this report. Rules established for the export of data to IDA for statistical analyses are discussed here; application of those data are presented in Appendix B (IDA Report) and the subsequent chapters of this report.

3.1 DATA MANAGEMENT

Procedures for Data Management are detailed in the Data Management Report (*Volume I*, Appendix C). Data Management included the processes and procedures for the transmission, tracking, verification, review, storage, and delivery of laboratory data, and the associated validation. After approval of the final data validation reports and EDDs, Data Management procedures were employed for the assembly and maintenance of the overall project database (all data, all matrices), and the subsequent export of data for statistical analyses.

All raw data and reporting forms were provided electronically by the laboratories. These data packages were in a *.pdf format and contained all elements that would be required for Level IV hardcopy data package (i.e., raw data are provided, and all supporting data is present such that a 3rd party could recalculate all of the results from the raw data). EDDs were submitted in Excel format. Multiple data packages and EDDs were submitted for each phase of the Study, and all of them were reviewed for completeness and data quality.

Upon receipt of an individual laboratory EDD, detailed checks were performed prior to providing the data to the validators. These checks were conducted in the project database using automated processes that generated error messages that were subsequently communicated back to the laboratory. Approximately sixty different checks were executed, in seven different error categories: completeness, units, formatting, nulls/placeholders, sample coding, qualifiers, and calculations. Of these many checks that were executed on each EDD, there were several errors that were regularly found. This included issues with the codes applied to describe the sample and blank entries in fields needed to ensure accurate querying of the resulting database. Details of the EDD checking procedures are included in *Volume I*, Appendix C.

3.2 DATA VALIDATION

All data packages were reviewed for completeness and compliance with the requirements of the MLVS Method (*Volume I*, Appendix A), and the Study Data Validation Guidelines (DVGs) (*Volume I*, Attachment 5 to the Study Plan). While not explicitly cited in the Study Plan, the validation procedure also utilized the *Data Validation Guidelines Module 6: Data Validation*

Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-24 (DoD 2022) specifically to support the Study.

Data validation was conducted by the Jacobs Engineering Group, Inc. (Jacobs), and Pyron Environmental, Inc (Pyron). Specific laboratories were assigned to each validation firm for efficiency as well as to facilitate review of the laboratory data packages and familiarity with laboratory personnel. A data validation report (DVR) and an amended EDD with the addition of data qualifiers as appropriate was submitted for each laboratory and matrix. These were subsequently reviewed by the Study QA Manager and EPA's contractor GDIT. If/where necessary, additional information was required from the laboratories, and the DVRs and EDDs amended.

As was done in the previous report, a common reporting format was used for the checklist, the DVRs, and the calculation confirmation spreadsheet following the MLVS DVG, and QSM Table B-24. These documents were reviewed by the Study QA Manager and EPA and were consistently used throughout the Study.

For most laboratories, the data validation process was generally much improved as compared to the review of the aqueous matrices included in the previous report. For some laboratories the problems were seemingly intractable and required a stubbornly iterative process. Despite the clear guidance in EPA Method 1633, the requirements for reporting in the Study Plan, the specific training provided online to all participants, the EDD-reporting requirements, and having been through the validation process for the wastewater, surface water, and groundwater matrices, laboratory deliverables often contained errors. These errors included, but were not limited to:

- Chromatograms not included in the data package needed for manual integrations (confirmation).
- Miscalculation or non-reported percent recoveries.
- Incorrect EIS compound associations (e.g., PFTrDA quantified using $^{13}C_2$-PFTeDA, not an average of $^{13}C_2$-PFDoA and $^{13}C_2$-PFTeDA or being quantified using $^{13}C_3$-PFDoA).
- Retention time outside of acceptance criteria for target and EIS compounds.
- Incorrect or missing ion transition summaries.
- Incorrect manual integration of peaks from chromatographs with an inability to confirm the laboratories' calculations.

The participating laboratories were generally helpful and responsive to correcting problems in the laboratory deliverables. Often, the laboratory provided a completely new version of the data package and EDD. In some cases, the laboratory errors were sufficiently significant that the data would be rejected. These included incorrect extraction volumes, failure to spike EIS compounds correctly, and incorrect calculations from chromatographs. Rejected data are discussed in subsequent sections of this report.

After submittal of the DVR and EDD by the validators, there was an additional iterative process of review by the Study QA Manager and EPA. Problems were identified by the agencies and returned to the validator for additional review and correction. Each submittal was given an updated version number (V0, V1, etc.), which was tracked by Exa. The process was repeated until the Agency concerns were fully resolved.

In the review of the validator-submitted EDD, EPA and the Study QA Manager reviewed the validator-added qualifiers, and either confirmed, nulled, or added a different data qualifier after additional review of the laboratory report. The qualifiers and the reason for the changes are fully documented in the Study QA Manager-approved EDDs, and in the Project Database.

The final validated study results comprise the documents listed in the General List of Documents and are maintained in the Project record.

General List of Documents comprising the final validated study report.

- PFAS Laboratory Study Completeness Checklist (HGL)
- Matrix-specific validator Checklist (Jacobs or Pyron)
- Matrix-specific validator calculation verification spreadsheet (Jacobs or Pyron)
- Matrix-Specific Data Validation Report (Jacobs or Pyron)
- Validated Electronic Data Deliverable
- Study QA Manager/EPA Review(s) and final concurrence memo
- Validator response(s) to Study QA Manager /EPA Review(s)
- Final EDD approved by Study QA Manager/EPA.

Table 3-1 present a summary of the total type and number of analyses reviewed for the soil and sediment study. A total of 56,339 individual results were submitted by the laboratories for the IDC, soil, and sediment samples. Of those submitted data, 53,270 data points passed all quality assurance reviews and were advanced for statistical analyses.

3.3 DATA USED IN THE STATISTICAL ANALYSES

The IDA Statistical Data Analysis Report for Solid Media is Appendix B to this volume. Statistical analyses of the laboratory data generally followed that listed in the EPA's *Alternate Procedures Test Procedures Program* (EPA 2018, Appendix G), where applicable, the procedures described in the report, *Single- Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS,* (SERDP and ESTCP 2021). Additional statistical analyses were conducted by the Air Forces Civil Engineering Center (AFCEC and EPA's contractor General Dynamics Information Technology (GDIT). The AFCEC and GDIT findings are reported separately in Sections 7.4 and 8.4 (AFCEC) and 9.5 (GDIT) of this report.

Once all data had been validated, and the final EDDs were approved by Study QA Manager and EPA, the data were considered complete and ready to initiate the statistical analyses. Exa prepared an export from the Project Database for each individual matrix (solid IDC, soils, and sediments), which underwent review by the MLVS Team. Principally, the purpose of this final review was to ensure the dataset was correct and complete, there was a single result reported for a matrix sample/compound pair (i.e., no duplicates), and the matrix spiked percent recovery calculations conducted by Exa were correctly reported. Upon approval, the final export was prepared, and the results provided to IDA and EPA for analysis.

The details of the final data review process, calculation of percent recoveries, and the rules regarding the calculation of the percent recovery in the PFAS-spiked samples is presented in *Volume I,* Section 3.4. For most cases, Equation 1 describes how the percent recovery was calculated. The equation is based on the concentrations measured in the spiked samples, relative to the concentrations in the unspiked sample run at each laboratory, and the spike concentration added by Waters ERA prior to the individual matrix samples.

Equation 1. Calculation of Percent Recovery for Spiked Matrices

$$\left[\frac{\text{Final Result Spiked Sample [Analyte]} - \text{Final Result Unspiked Measured Native Sample [Analyte]}}{\text{Spike [Analyte]Added]}}\right] * 100$$

Where [Analyte] is a specific PFAS target compound (e.g., PFBS, PFOA, 6:2FTS, etc.)

Additional calculation rules were developed to account for cases in which values were undetected, when the unspiked samples were excluded (X-flagged), where measured unspiked sample concentrations exceed the spiked level, or where the calculation of the percent recovery resulted in a negative value. Table 3-2 shows the seven cases determined for these conditions, how the percent recovery was calculated, and whether the percent recovery result for those specific instances were excluded from the statistical analysis.

The final data sets used for the statistical analyses by IDA, EPA, and AFCEC are in the MLVS Project electronic repository and are not included with this report. As indicated above, 52,270 data points out of 56,339, approximately 94% of the analytical data generated, were used for the statistical analyses.

Table 3-1. Summary of Type and Number of Analyses Reviewed

Sample Type	**Number of Laboratories**	**Total # Results Submitted by Laboratories[1]**	**Number Post-validation Results used in Statistical Analysis[2]**				
			Samples	**Target Analyte Results**	**EIS Compound Results**	**NIS Compound Results**	**Total Results Reviewed**
ICAL and IDC: Ottawa Sand or PFAS-free sand							
MDL Study (7 method blanks [MDL$_B$])	10	5,833	81	3,217	1,930	576	5,723
MDL Study (7 MDL spiked samples [MDL$_S$])	10	5,619	79	3,137	1,880	560	5,577
Initial Precision and Recovery (IPR) Study	10	2,927	41	1,626	978	295	2,899
Method Blanks	10	2,063	29	1,155	695	205	2,055
Limit of Quantification Verification	9	1,279	18	718	430	127	1,275
Ongoing Precision and Recovery	5	852	12	473	282	84	839
Low-Level Ongoing Precision and Recovery	3	355	5	199	120	35	354
Soil							
Unspiked Samples	10	2,345	30	1,190	715	211	2,116
Low-Level Spike	10	6,538	89	3,525	2,121	627	6,273
High-Level Spike	10	6,612	90	3,567	2,145	633	6,345
Low-Level Ongoing Precision and Recovery	10	1,495	20	790	479	142	1,411
Method Blanks	10	1,634	21	833	500	148	1,481
Ongoing Precision and Recovery	10	1,634	22	869	522	155	1,546
Sediment							
Unspiked Samples	8	1,996	24	953	571	169	1,693
Low-Level Spike	8	5,544	72	2,856	1,713	507	5,076
High-Level Spike	8	5,631	68	2,700	1,621	477	4,798
Low-Level Ongoing Precision and Recovery	8	1,280	18	712	429	127	1,268
Method Blanks	8	1,422	18	716	429	127	1,272
Ongoing Precision and Recovery	8	1,280	18	713	429	127	1,269
Total Number of Results		**56,339**	**755**	**29,949**	**17,989**	**5,332**	**53,270**

Version: Summary_tables_Exa_CH3_10312023.xlsx

Notes:
[1] Number of results submitted by the laboratories (i.e., pre-validation).
[2] Post-validation results included in the dataset used in statistical analysis.
[3] Due to laboratories batching soil and sediment samples in the same preparation batch, results for some Method Blanks, Low-Level Ongoing Precision and Recovery and Ongoing Precision and Recovery samples have been included in both the counts for soil and sediment analyses.

Table 3-2. Data Rules for Calculating Percent Matrix Spike Recoveries

Case	**Unspiked Sample**	**Spiked Sample**	**Calculation of MS Spike Recovery**	**Data for Statistical Analyses**
1	detected	detected	Base case. Use Equation 1	All resultant values used
2	not detected	detected	**(**Final Result Spiked Sample [ ] / (Spike [ ] Added]**)** * 100	All resultant values used
3	not detected/X-flagged	not detected/X-flagged	when spiked sample is X or U, it is excluded, and %recovery is not calculated	No % recovery value for that sample and analyte pair
4	not detected/X-flagged	detected	**(**Final Result Spiked Sample [ ] / (Spike [ ] Added]**)** * 100	All resultant values used
5	detected/X-flagged	detected	**(**Final Result Spiked Sample [ ] / (Spike [ ] Added]**)** * 100	Values were reviewed on a case-by-case basis for inclusion or rejection.
6	detected [ ] > spiked level	detected	Not calculated	No % recovery value for that sample and analyte pair
7	detected	< Unspiked [ ]	Calculated, but results in negative % recovery.	Negative % Recovery values excluded from statistical analyses

Notes:
[ ] - reported analyte concentration

4 CALIBRATION AND QUANTIFICATION: SOIL AND SEDIMENT MEDIA

Soil and sediment media sample extracts were analyzed by LC-MS/MS in MRM mode. Section 4 of *Volume I* provides a description of the calibration and quantification scheme used. Since the publication of *Volume I*, two more qualitative standards have become commercially available. These are for PFOA and PFNA. Therefore, since the completion of this Study, seven additional quantitative isomeric standards have become commercially available for the target analytes (PFOA, PFNA, PFOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE). In accordance with EPA Method 1633, these standards must be used when creating calibration standards, calibration verification standards, and spiking solutions and these seven PFAS compounds were eliminated from the qualitative identification standard required by the method.

4.1 MASS CALIBRATION AND MASS CALIBRATION VERIFICATION

Each laboratory performed mass calibration and mass calibration verification in accordance with the instrument manufacturer's instructions. Please see *Volume I*, Section 4.1 for additional details on the mass calibration and mass calibration verification.

4.2 MULTI-POINT INITIAL CALIBRATION

Discussion on the multi-point initial calibrations evaluated in Phase 3 of the MLVS can be found in *Volume I*, Section 4.2. It should be noted that while data from Laboratory 8 was eliminated from the evaluation due to a spiking error, ICALs used for quantitation of the solid IDC and soil and sediment samples were spiked correctly. Therefore, data from Laboratory 8 was included in the statistical analysis of data for the solid IDC and soil and sediment samples.

4.3 QUALITATIVE STANDARDS

Volume I, Section 4.3 contains information on the Qualitative Standard used in the Study.

4.4 CALIBRATION VERIFICATION

The calibration verification (CV) standards reported by each laboratory were created using the Wellington standard mixtures provided by the MLVS. CVs were analyzed daily, prior to analysis of samples, after every 10 study samples or less, and at the end of each analytical sequence. The concentration of the CV was approximately the mid-level of the calibration curve used by each laboratory. Target analytes and EIS compounds were required to recover within ±30% of their true value. Data submitted from all laboratories met this criterion with the exception of one laboratory. Laboratory 10 reported one instance of CV standards failing to meet this criterion that affected the data that was reported (Table 4-1). Two target analytes, 6:2FTS and NMeFOSAA in one CV failed criteria. These two analytes were not detected in the affected samples, SST1 and SSW1. In this instance, the lower limit of the acceptance criterion was exceeded for these two target analytes, indicating the concentration reported for these target analytes in the samples that were bracketed by these CVs are potentially biased low. Per the Study Plan, the concentrations detected in these samples were retained and qualified with a "J" qualifier. No sample results were eliminated from the Study due to CV failures. The low CV failure rate documented by this Study indicates the MLVS CV % recovery criteria is routinely achievable.

Table 4-1. Summary of Instances of CV Recoveries Outside of MLVS Acceptance Criteria Range

Laboratory #	Matrix	Target Analyte	Target Analyte % Recovery	Number of Affected Samples
10	SS	6:2FTS	66	2
10	SS	NMeFOSAA	68.8	2

Source files: Soil and Sediment DVRs

4.5 INSTRUMENT SENSITIVITY CHECK

Each laboratory created instrument sensitivity check (ISC) standards using the Wellington standard mixtures provided for the MLVS. The ISC standard was required to contain the target analytes at a concentration equal to the laboratory's LOQ concentrations, and be analyzed daily, prior to sample analysis, to verify the sensitivity of the instrument. All laboratories met this criteria with the exception of Laboratory 1. The concentration of the ISCs associated with soils and sediment sample analysis were at a concentration that was 0.25 times their LOQ. This data was not excluded from the evaluation of ISC standards, and no sample results were eliminated from the Study due to this nonconformance. Target analytes and EIS compounds were required to recover within ±30% of their true value. Data submitted from all laboratories met this criteria with only one exception. There were two instances of ISC standards failing to meet this criterion that affected the data that was reported by Laboratory 3 (Table 4-2). One of these failures were associated with sediment samples (fourteen samples) only while the other affected both soil and sediment samples (fourteen samples total). Per the Study Plan, samples that were bracketed by ISC standards whose % recoveries exceeded the acceptance criteria were retained and qualified with a "J+" qualifier in instances when the affected analyte was detected in the sample and a "J" in instances when it was not. No sample results were eliminated from the Study due to ISC failures. The low ISC failure rate documented by this Study indicates the ISC % recovery acceptance criteria required by this Study is routinely achievable.

Table 4-2. Summary of Instances of ISC Recoveries Outside of MLVS Acceptance Criteria Range

Laboratory #	Matrix	Target Analyte	Target Analyte % Recovery	Number of Affected Samples
3	SS	NMeFOSAA	146.7	7
3	SD	NMeFOSAA	146.7	7
3	SD	NMeFOSAA	141.5	14

Source files: Soil and Sediment DVRs

5 INITIAL DEMONSTRATION OF CAPABILITIES

In addition to performing a minimum of three initial multi-point calibrations, laboratories submitted documentation of an IDOC that was compliant with requirements of Phase 3 of the Study Plan (*Volume I*, Appendix A). The IDOC consisted of the IPR study, MDL determination, and the limit of quantitation verification (LOQVER). All IDOC samples were created using the Wellington standard mixtures provided for the MLVS. The IDOC was performed in accordance with the requirements of EPA Method 1633.

5.1 METHOD DETECTION LIMITS

As part of Phase 3 of the MLVS, each laboratory was required to determine the MDLs for all 40 PFAS target analytes. MDLs were determined using the revised MDL procedure promulgated by EPA in 2017. The revised procedure defines the MDL as:

> *"... the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results."*

The procedure consists of two parts: determination of the MDL based on method blanks (called MDL_b), and determination of the MDL based on spiked samples (called MDL_s). Both MDL_b and MDL_s are determined in a reference matrix using at least seven replicates prepared and analyzed on three non-consecutive days.

The MDL_b is calculated as:

$$MDL_b = \overline{X} + t_{(n-1,\ 1-\propto=0.99)} S_b$$

where:

$\overline{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1,\ 1-\alpha = 0.99)}$ = Student's *t*-value appropriate for the single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom

S_b = sample standard deviation of the replicate method blank sample analyses

Note: The equation above is used when all the method blanks for an individual analyte give numerical results. If some (but not all) of the method blank results give numerical results, then the MDL_b is set equal to the highest method blank result.

The MDL_s is calculated as:

$$MDL_s = t_{(n-1,\ 1-\propto=0.99)} S_s$$

where:

$t_{(n-1,\ 1-\alpha = 0.99)}$ = Student's *t*-value appropriate for a single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom
S_s = sample standard deviation of the replicate spiked sample analyses

PFAS-free Ottawa or reagent-grade sand was the reference media used to prepare the seven MDL method blank replicates. Each was spiked with the 24 EIS and seven NIS compounds to create seven MDL method blanks. Seven MDL spiked replicates were prepared in the same manner as the MDL method blanks except the 40 target analytes were also added to each MDL spiked replicate. All MDL method blanks, and MDL spiked samples were prepared per EPA Method 1633 (*Volume I*, Appendix A), in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. The EIS and NIS compounds were spiked at the same concentrations as in the ICAL standards. The MDL values based on method blanks (MDL_b) and spiked samples (MDL_S) were calculated by each laboratory following data review, and an initial MDL was determined as the higher of these two values.

During the validation process, it was discovered that an error had occurred in the MDL Study submitted by Laboratory 8 that affected the quantitation of NMeFOSA, NEtFOSA, D_3-NMeFOSA, and D_5-NEtFOSA. Incorrect peak area associations had been made for D_3-NMeFOSA, and D_5-NEtFOSA, rendering their recoveries and the quantitation of their associated target analytes, NMeFOSA and NEtFOSA, incorrect. Due to this error, all data for these two analytes and two EIS compounds have been eliminated from the rest of the IDC as well as the soil and sediment statistical analyses.

The MDL Study from Laboratory 5 exhibited gross laboratory contamination of 6:2FTS in every MDL_b sample. The MDL calculated for 6:2FTS calculated from these MDL_b samples was four times greater than the highest LOQ reported by any laboratory. Additionally, the final MDL for 6:2FTS for Laboratory 5, 6.69 µg/kg, was greater than the concentration of the low spike in the soil and sediment samples. Because of this, all data for 6:2FTS reported by Laboratory 5 was omitted from the solid IDC, soil, and sediment statistical analysis.

Table 5-1 shows the pooled results of the MDL study. The table includes the maximum MDL_s or MDL_b, the minimum and maximum reported MDL, the number of laboratories using the MDL_b as the final MDL, and the pooled MDL across the laboratories. Of the 10 laboratories, only Laboratory 1 and Laboratory 3 reported MDL_b detections (Table 5-2), and these were for 6:2FTS and NMeFOSA. Figure 5-1 shows the distribution of individual laboratory MDLs relative to the pooled value calculated in Table 5-1. The figures shows that the individual MDLs reported by the laboratories are relatively similar and clustered around the pooled MDL for PFBA through PFMPA. Beginning at NFDHA and continuing through the FTCAs, a much wider distribution of MDLs is seen. This is also reflected in the minimum and maximum MDL for those same PFAS in Table 5-1.

Table 5-1. Solids Method Detection Limit Study Results

Target Analyte	Number of Labs[1]	Max MDL$_s$[2]	Max MDL$_b$[3]	Minimum Concentration of MDL (µg/kg)[4]	Maximum Concentration of MDL (µg/kg)[5]	# Labs Using MDL$_b$ as Final MDL[6]	Pooled MDL[7]
PFBA	10	0.309	U	0.0455	0.309	0	0.15
PFPeA	10	0.137	U	0.0395	0.137	0	0.0707
PFHxA	10	0.127	U	0.0227	0.127	0	0.0638
PFHpA	10	0.107	U	0.0232	0.107	0	0.05
PFOA	10	0.156	0.0138	0.0337	0.156	0	0.069
PFNA	10	0.565	U	0.0384	0.565	0	0.136
PFDA	10	0.128	U	0.0356	0.128	0	0.0586
PFUnA	10	0.457	U	0.0255	0.457	0	0.119
PFDoA	10	0.11	U	0.0264	0.11	0	0.0573
PFTrDA	10	0.192	U	0.0211	0.192	0	0.0705
PFTeDA	10	0.105	U	0.0242	0.105	0	0.0454
PFBS	10	0.0884	U	0.0227	0.0884	0	0.0447
PFPeS	10	0.162	U	0.0149	0.162	0	0.0753
PFHxS	10	0.159	U	0.0146	0.159	0	0.0757
PFHpS	10	0.145	U	0.0234	0.145	0	0.0655
PFOS	10	0.135	0.0102	0.0166	0.135	0	0.0681
PFNS	10	0.181	U	0.0213	0.181	0	0.0672
PFDS	10	0.175	U	0.0239	0.175	0	0.0762
PFDoS	10	0.15	U	0.0272	0.15	0	0.0559
4:2FTS	10	0.397	U	0.0805	0.397	0	0.198
6:2FTS	9	0.763	0.215	0.139	0.763	1	0.312
8:2FTS	10	0.613	U	0.0724	0.613	0	0.313
PFOSA	10	0.0979	0.0671	0.0142	0.0979	0	0.0393
NMeFOSA	9	0.136	0.104	0.029	0.136	1	0.0706
NEtFOSA	9	0.127	0.104	0.0101	0.127	0	0.066
NMeFOSAA	10	0.158	U	0.0304	0.158	0	0.0822
NEtFOSAA	10	0.197	U	0.0252	0.197	0	0.0771
NMeFOSE	10	1.0	0.0199	0.154	1.0	0	0.357
NEtFOSE	10	0.831	0.0238	0.0613	0.831	0	0.345
PFMPA	10	0.115	U	0.0383	0.115	0	0.0693
PFMBA	10	0.101	U	0.0317	0.101	0	0.054
NFDHA	10	0.473	U	0.0596	0.473	0	0.181
HFPO-DA	10	0.542	0.0373	0.0514	0.542	0	0.252
ADONA	10	0.497	U	0.0797	0.497	0	0.23
PFEESA	10	0.157	U	0.0345	0.157	0	0.0778
9Cl-PF3ONS	10	0.44	U	0.0779	0.44	0	0.224
11Cl-PF3OUdS	10	0.363	U	0.0881	0.363	0	0.18
3:3FTCA	10	0.509	U	0.103	0.509	0	0.231
5:3FTCA	10	1.57	U	0.446	1.57	0	0.858
7:3FTCA	10	1.76	U	0.561	1.76	0	0.869

Source**:** OS_MDL_results_V1_231109_095126.csv

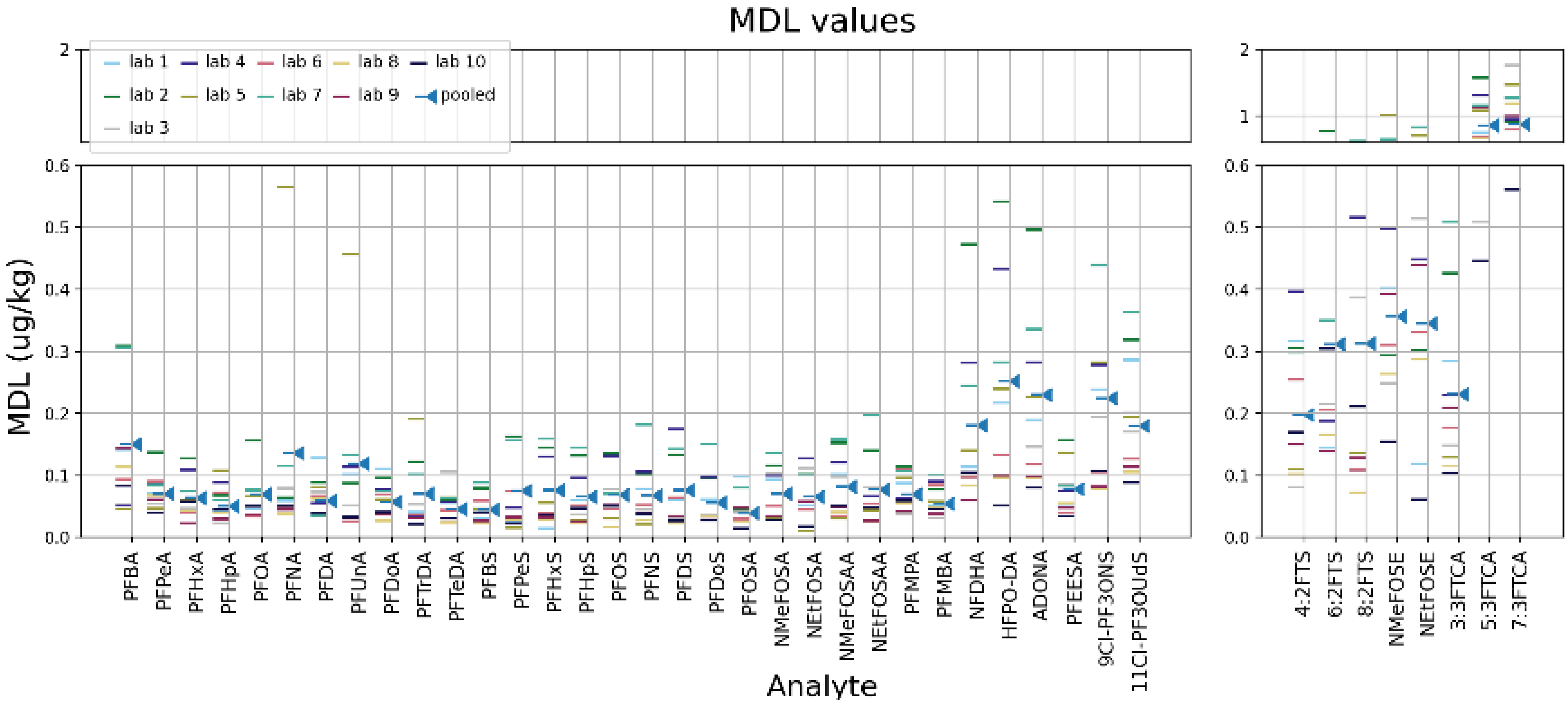
Notes:
1 The number of laboratories for which an MDL value was calculated.
2 The maximum MDLs value across individual spiked samples.
3 The maximum MDLb value across individual spiked samples. "U" indicates analyte was not detected.
4 The minimum MDL across the values calculated for each laboratory.
5 The maximum MDL across the values calculated for each laboratory.
6 The number of laboratories for which the MDLb value was the final MDL value.
7 Pooled MDL using the individual laboratory MDL values calculated. Equation from EPA 821-B-18-001 page G-22.

Table 5-2. Frequency of Detection in Solids MDL_b by Laboratory

# MDL_b Detections	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5[1]	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
	20	0	9	0	0	0	0	0	0	0

Version: Summary_tables_Exa_CH5_10312023.xlsx

[1] Data from Laboratory 5 for 6:2FTS was not included in this table since the MDL was determined to be invalid.



Source File: OS_MDL_Plot_V1_231109_095126

Figure 5-1. Solids Method Detection Limit Study Results.
Figure includes individual and pooled Results (Table 5-1)

5.2 INITIAL PRECISION AND RECOVERY (IPR) RESULTS

IPR studies were performed in the solid matrices. Four aliquots of 5.0 grams dry-weight of PFAS-free Ottawa or reagent-grade sand were spiked with all 40 target analytes such that the final concentration of each PFAS in the IPR was greater than or equal to the LOQ and less than or equal to the midpoint of the laboratory's calibration. These spiked aliquots were prepared and analyzed in exactly the same manner as study samples, per EPA Method 1633.

A total of 41 IPRs were included in the statistical analysis. The mean percent recovery, standard deviations, and RSD of recoveries are presented in Table 5-3. All 41 IPRs met the Study IPR NIS criteria (>30% recovery). All of the 1,626 valid target analyte results reported from IPRs were within the target analyte criteria (40–150%). The lowest reported percent recovery was 54%, reported by Laboratory 9 for 3:3FTCA in a single IPR sample and the highest reported percent recovery was 144%, reported by Laboratory 4 for both NMeFOSA and NFDHA. All of the 978 valid EIS compound results reported from IPRs met the target EIS compound acceptance criteria (20–150%). The lowest reported percent recovery was 22.7%, reported by Laboratory 4 for D_5-NEtFOSA in a single IPR sample and the highest reported percent recovery was 146%, reported by Laboratory 2 for $^{13}C_2$-8:2FTS.

Most of the highest target analyte recoveries were associated with Laboratories 4 and 6 (Figure 5-2). None of these results can be explained by their EIS compound recoveries since they were not statistically different than those from the other laboratories. The lowest mean recovery was associated with PFDoS, 92%, while the highest mean recovery was associated with 6:2FTS. All but 5 mean target analyte recoveries were at or greater than 100%.

A graphical representation of the performance of the variance in the soil IPR results across all laboratories, all analytes, and concentrations is given in Figure 5-3. From the data presented in Table 5-3, the plot shows the percent relative standard deviation (%RSD) of the 4 replicates analyzed by each laboratory, pooled vs. concentration. The shaded area in the plot represents the minimum (2.13) and maximum (13.5) %RSDs, with a median for the pooled data 7.3%. The preponderance of the points in Figure 5-3 are below 20% RSD for each analyte by laboratory; the exceptions to that are observed for Laboratories 4 and 6, as discussed above. Figure 5-3 also shows that variance tends to increase as analyte concentration nears the limit of detection for a method/instrument which could explain the slight rise in %RSD for lower analyte concentrations in the IPR data.

Table 5-3. Solid IPR Results

Analyte	Number of Labs[1]	Number of Results[2]	Mean % Recovery[3]	Pooled Between-Lab std. dev. $(s_b)^4$	Pooled Within-Lab std. dev. $(s_w)^5$	Pooled Between- and Within-Lab std. dev. $(s_c)^6$	RSD $(s_w)^7$
Target Analytes							
PFBA	10	41	104	11.3	2.22	11.9	2.13
PFPeA	10	41	103	11.8	4.4	12.4	4.29
PFHxA	10	41	103	8.76	6.98	9.21	6.76
PFHpA	10	41	103	8.92	4.86	9.36	4.7
PFOA	10	41	105	9.25	6.95	9.72	6.59
PFNA	10	41	105	11.5	8.91	12	8.47
PFDA	10	41	103	12	5.83	12.6	5.67
PFUnA	10	41	102	11	6.62	11.5	6.5
PFDoA	10	41	104	11.2	6.33	11.7	6.07
PFTrDA	10	41	101	14.9	5.6	15.6	5.54
PFTeDA	10	41	104	10.8	5.32	11.3	5.13
PFBS	10	41	104	8.9	9.48	9.36	9.1
PFPeS	10	41	107	11.2	7.74	11.8	7.23
PFHxS	10	41	104	12.2	7.8	12.8	7.52
PFHpS	10	41	105	10.1	8.85	10.6	8.45
PFOS	10	41	106	10.8	6.37	11.4	6.02
PFNS	10	41	104	10.3	8.67	10.8	8.36
PFDS	10	41	100	9.31	8.5	9.79	8.47
PFDoS	10	41	92	10.8	6.72	11.3	7.3
4:2FTS	10	41	106	7.56	8.02	7.95	7.57
6:2FTS	9	37	111	10.1	9.46	10.6	8.52
8:2FTS	10	41	108	7.82	12.5	8.26	11.6
PFOSA	10	41	105	9.78	4.11	10.3	3.92
NMeFOSA	9	36	110	10.1	7.13	10.7	6.47
NEtFOSA	9	36	107	6.98	6.2	7.35	5.77

Table 5-3. Solid IPR Results (Continued)

Analyte	Number of Labs[1]	Number of Results[2]	Mean % Recovery[3]	Pooled Between-Lab std. dev. (s_b)[4]	Pooled Within-Lab std. dev. (s_w)[5]	Pooled Between- and Within-Lab std. dev. (s_c)[6]	RSD (s_w)[7]
NMeFOSAA	10	41	103	11.9	9.66	12.5	9.38
NEtFOSAA	10	41	98.7	12.7	7.82	13.3	7.93
NMeFOSE	10	41	106	7.88	5.35	8.28	5.04
NEtFOSE	10	41	105	9.49	3.54	9.96	3.38
PFMPA	10	41	101	14.6	5.47	15.3	5.41
PFMBA	10	41	103	12.6	6.78	13.3	6.56
NFDHA	10	41	104	16.5	12.3	17.3	11.8
HFPO-DA	10	41	105	11.8	6.91	12.4	6.57
ADONA	10	41	110	14.6	7.46	15.4	6.78
PFEESA	10	41	107	12.1	5.94	12.7	5.56
9Cl-PF3ONS	10	41	106	11	7.94	11.6	7.46
11Cl-PF3OUdS	10	41	102	11.2	7.67	11.8	7.53
3:3FTCA	10	41	94.4	16.3	6.64	17.1	7.03
5:3FTCA	10	41	98.9	15.7	6.87	16.5	6.94
7:3FTCA	10	41	93.8	15.9	6.03	16.7	6.43
EIS Compounds							
$^{13}C_4$-PFBA	10	41	94.3	18.8	9.71	19.7	10.3
$^{13}C_5$-PFPeA	10	41	96.4	18.5	5.46	19.4	5.67
$^{13}C_5$-PFHxA	10	41	95.5	16.6	6.34	17.4	6.64
$^{13}C_4$-PFHpA	10	41	95.1	18.3	5.02	19.2	5.28
$^{13}C_8$-PFOA	10	41	96.8	18.2	9.47	19.1	9.78
$^{13}C_9$-PFNA	10	41	93.7	17	7.27	17.8	7.75
$^{13}C_6$-PFDA	10	41	97.4	17.8	7.54	18.7	7.74
$^{13}C_7$-PFUnA	10	41	98	17.1	7.82	18	7.98
$^{13}C_2$-PFDoA	10	41	89.8	16.2	6.82	17	7.59
$^{13}C_2$-PFTeDA	10	41	83.2	18.5	8.41	19.4	10.1

Table 5-3. Solid IPR Results (Continued)

Analyte	**Number of Labs[1]**	**Number of Results[2]**	**Mean % Recovery[3]**	**Pooled Between-Lab std. dev. (s_b)[4]**	**Pooled Within-Lab std. dev. (s_w)[5]**	**Pooled Between- and Within-Lab std. dev. (s_c)[6]**	**RSD (s_w)[7]**
$^{13}C_3$-PFBS	10	41	94.6	18.3	9.19	19.2	9.71
$^{13}C_3$-PFHxS	10	41	93.9	16.9	9.25	17.7	9.85
$^{13}C_8$-PFOS	10	41	95	19	6.24	19.9	6.57
$^{13}C_2$-4:2FTS	10	41	101	19.7	8.2	20.6	8.16
$^{13}C_2$-6:2FTS	10	41	98.7	16.4	11.7	17.2	11.9
$^{13}C_2$-8:2FTS	10	41	101	15.2	13.7	16	13.5
$^{13}C_8$-PFOSA	10	41	86.8	21.8	5.96	22.8	6.87
D_3-NMeFOSA	9	36	58.3	20.8	4.67	21.9	8.01
D_5-NEtFOSA	9	36	56.7	20.9	4.42	22	7.79
D_3-NMeFOSAA	10	41	95.9	19.1	5.95	20	6.2
D_5-NEtFOSAA	10	41	96	15.5	6.99	16.3	7.28
D_7-NMeFOSE	10	41	70.8	14.6	5.17	15.4	7.29
D_9-NEtFOSE	10	41	71	18.3	5.18	19.1	7.29
$^{13}C_3$-HFPO-DA	10	41	93.8	21.1	6.52	22.1	6.95

Source: OS_IPR_results_V1_231109_095126.csv

Notes:
1 The number of laboratories reporting initial precision recovery (IPR) results.
2 The number of individual IPR results that do not have a U flag included in the calculations.
3 Mean % Recovery - The mean percent recovery for IPR samples across all labs for the given analyte.
4 The combined within and between laboratory standard deviations. Equation from EPA 821-B-18-001 page G-25.
5 The pooled between-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
6 The combined within and between laboratory standard deviations. Equation from EPA 821-B-18-001 page G-25.
7 The pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100).

Table 5-4. Solid LOQVER Summary

Target Analyte	**Number of Laboratories**[1]	**Minimum Concentration (µg/kg)**[2]	**Maximum Concentration (µg/kg)**[3]	**Minimum Percent Recovery**[4]	**Maximum Percent Recovery**[5]
Target Analyte					
PFBA	9	0.445	8.47	81.8	120
PFPeA	9	0.215	4.15	68.3	150
PFHxA	9	0.125	2.63	68.4	134
PFHpA	9	0.117	2.14	72.8	122
PFOA	9	0.108	2.6	76.8	139
PFNA	9	0.106	2.28	81.2	133
PFDA	9	0.108	2.35	81.2	150
PFUnA	9	0.106	2.67	76.4	133
PFDoA	9	0.109	2.45	84.5	140
PFTrDA	9	0.104	2.79	84.4	122
PFTeDA	9	0.112	2.5	73.6	129
PFBS	9	0.095	1.69	69.2	136
PFPeS	9	0.104	2.4	59.1	176
PFHxS	9	0.097	2.3	60.7	142
PFHpS	9	0.106	2.36	71.4	134
PFOS	9	0.129	2.14	74.1	170
PFNS	9	0.103	2.35	60.9	114
PFDS	9	0.117	2.21	38.5	121
PFDoS	9	0.084	2.54	41.4	114
4:2FTS	9	0.422	8.6	59.9	126
6:2FTS	9	0.414	9.11	61.1	156
8:2FTS	9	0.412	11.8	81.2	139
PFOSA	9	0.121	2.47	78	121
NMeFOSA	8	0.117	2.39	77.2	136
NEtFOSA	8	0.114	2.14	75.2	129
NMeFOSAA	9	0.096	2.31	81.6	150

Table 5-4. Solid LOQVER Summary (Continued)

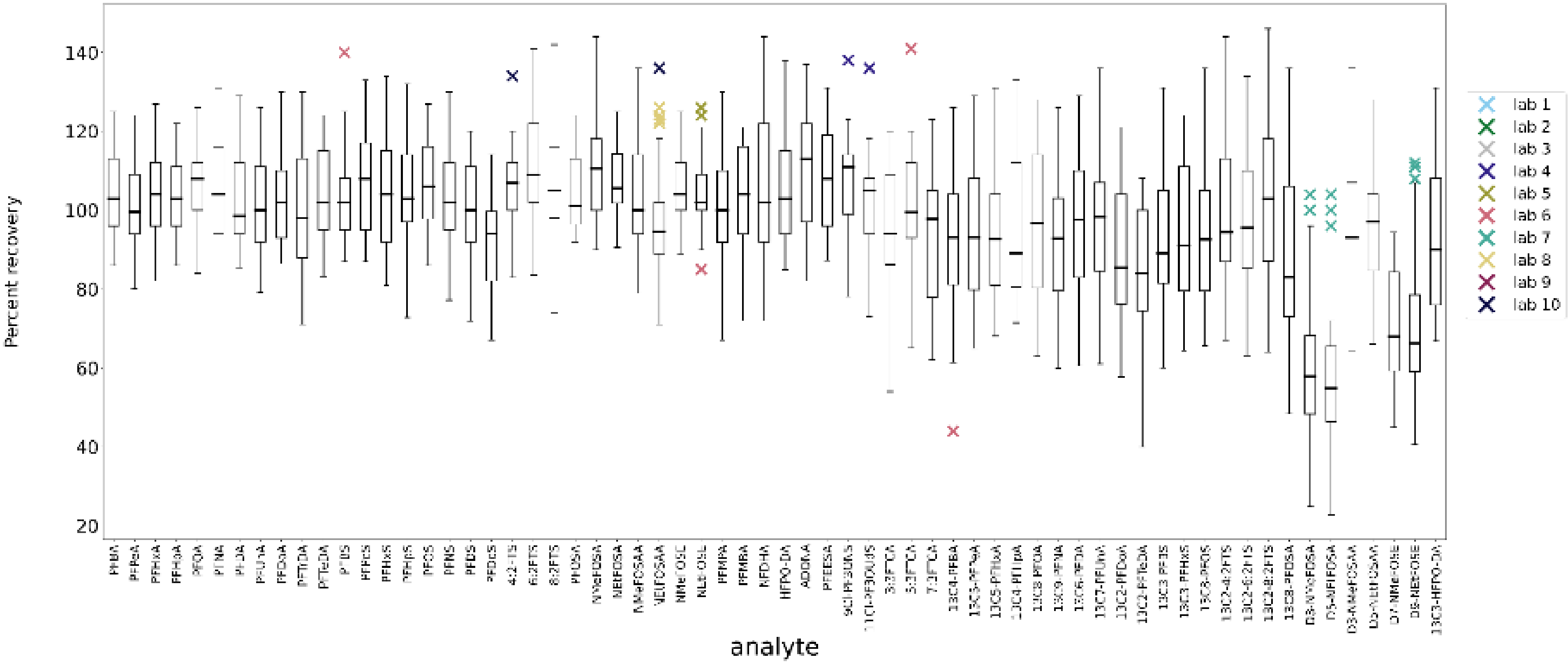
Target Analyte	**Number of Laboratories[1]**	**Minimum Concentration (ng/kg)[2]**	**Maximum Concentration (ng/kg)[3]**	**Minimum Percent Recovery[4]**	**Maximum Percent Recovery[5]**
NEtFOSAA	9	0.1	1.92	67.6	158
NMeFOSE	9	1.15	26	76.8	121
NEtFOSE	9	1.16	21.4	75.2	121
PFMPA	9	0.181	3.97	73.7	118
PFMBA	9	0.183	4.57	64.5	120
NFDHA	9	0.22	4.74	73.4	144
HFPO-DA	9	0.428	9.48	73.6	139
ADONA	9	0.369	9.16	90.5	152
PFEESA	9	0.169	4.12	75.5	118
9Cl-PF3ONS	9	0.372	9.07	81.1	143
11Cl-PF3OUdS	9	0.334	8.98	51.7	131
3:3FTCA	9	0.42	9.37	68.2	113
5:3FTCA	9	2.02	63.6	68	118
7:3FTCA	9	1.96	57.8	67.2	146
EIS Compound					
13C4-PFBA	9	6.05	9.62	70.5	109
13C5-PFPeA	9	3.16	4.87	64.4	112
13C5-PFHxA	9	1.54	2.34	72	109
13C4-PFHpA	9	1.63	2.36	66.8	104
13C8-PFOA	9	1.5	2.62	71.6	115
13C9-PFNA	9	0.754	1.23	60.3	113
13C6-PFDA	9	0.81	1.23	68.2	108
13C7-PFUnA	9	0.742	1.21	72.2	112
13C2-PFDoA	9	0.652	1.16	65.2	96.1
13C2-PFTeDA	9	0.481	1.12	48.1	96.6
13C3-PFBS	9	1.39	2.36	59.7	127
13C3-PFHxS	9	1.23	2.4	62	120
13C8-PFOS	9	1.57	2.57	71.5	134

Table 5-4. Solid LOQVER Summary (Continued)

Target Analyte	Number of Laboratories[1]	Minimum Concentration (ng/kg)[2]	Maximum Concentration (ng/kg)[3]	Minimum Percent Recovery[4]	Maximum Percent Recovery[5]
13C2-4:2FTS	9	2.85	5.52	75.1	147
13C2-6:2FTS	9	2.82	4.95	74.2	130
13C2-8:2FTS	9	2.64	5.15	68.8	134
13C8-PFOSA	9	1.29	2.33	60.8	116
D3-NMeFOSA	8	0.531	1.9	26.6	76
D5-NEtFOSA	8	0.318	1.7	15.9	68
D3-NMeFOSAA	9	3.08	4.76	69.6	113
D5-NEtFOSAA	9	2.63	5	65.8	125
D7-NMeFOSE	9	6.79	35.2	34	176
D9-NEtFOSE	9	5.74	21.9	28.7	110

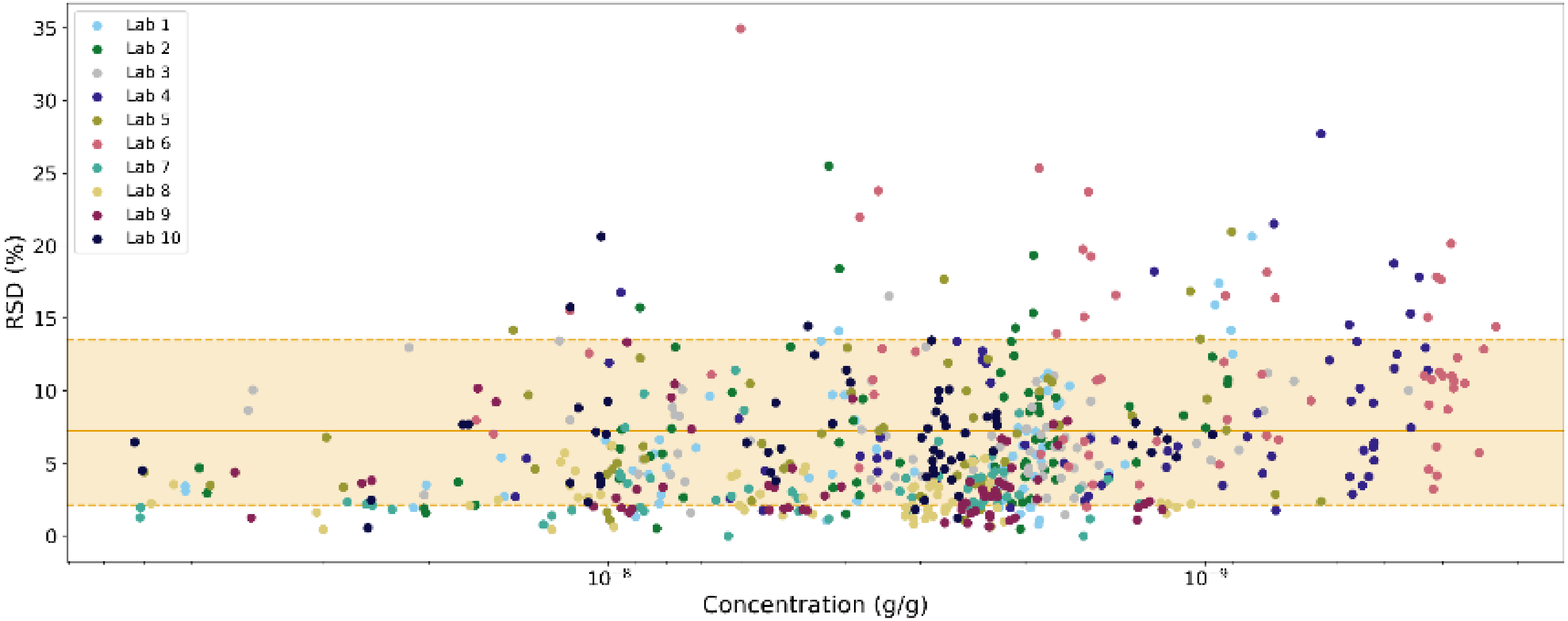
Source: OS_LOQVER_results_V1_231109_095.csv

Notes:
[1] The number of laboratories reporting limit of quantitation verification (LOQVER) results.
[2] The minimum concentration measured across all laboratories.
[3] The maximum concentration measured across all laboratories.
[4] The minimum percent recovery across all laboratories.
[5] The maximum percent recovery across all laboratories.



Source File: OS_IPR_Boxplot_V1_231109_095126

Figure 5-2. Initial Precision and Recovery (IPR) Results by Analyte by Laboratory
Figure includes both target compound recoveries, and EIS compound recoveries.



Source File: OS_IPR_Horwitz_V1_231109_095126

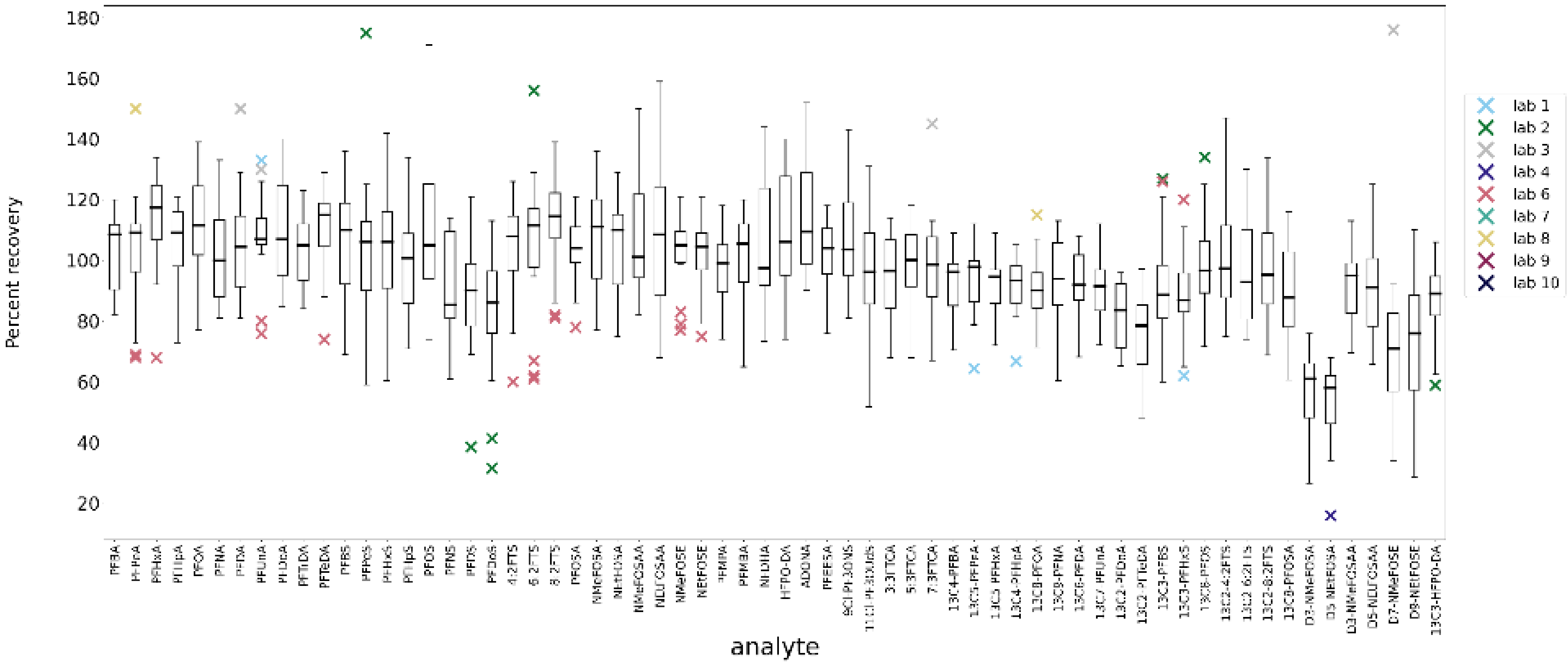
Figure 5-3. Individual Laboratory and Pooled IPR Relative Standard Deviation (from Table 5-3)
Shaded Area is the range (minimum and maximum) IPR RSD from Table 5-3. Solid line is the median %RSD
Figure includes both target compound recoveries, and EIS compound recoveries.
The concentrations on the Y-axis is arrayed from highest to lowest. Limits of detection would be at the right tail of the graphic.

5.3 SOLIDS LIMIT OF QUANTITATION VERIFICATION ANALYSES

Since a low level ongoing precision and recovery (LLOPR) is not included in EPA IDOC requirements, the Study Plan required laboratories to analyze an LOQVER sample in order to verify their stated LOQs. A single aliquot of 5 grams of PFAS-free Ottawa or reagent-grade sand was spiked with all 40 target analytes such that the final concentration of each PFAS in the LOQVER was one and two times the LOQ. This spiked aliquot was prepared and analyzed in exactly the same manner as study samples, per EPA Method 1633 (Appendix A). While laboratories were required to prepare and analyze only one LOQVER per the Study Plan, some laboratories chose to prepare and analyze as many as seven. Laboratory 5 did not identify an LOQVER sample in their submittal; therefore, no data from Laboratory 5 was included in the statistical analysis. It should be noted that the laboratory did submit an LLOPR sample, which must be spiked at two times the LOQ, whereas the LOQVER sample can be spiked at one to two times the LOQ. All data submitted for LOQVER samples was included in the statistical analysis.

A total of 18 LOQVERs were included in the statistical analysis. Table 5-4 shows the pooled results across all laboratories by PFAS; the results are graphically shown in Figure 5-4. All 18 LOQVERs met the Study NIS target acceptance criteria (>30% recovery). Of the 718 valid target analyte results reported from LOQVERs, seven target analytes recoveries exceeded the target criteria (40–150%), resulting in an exceedance rate of 0.97%. All seven exceedances were reported by Laboratory 2: PFDoS (31.5%), PFDS (38.5%), ADONA (152%), 6:2FTS (156%), NEtFOSAA (159%), PFOS (171%), and PFPeS (175%). Of the valid 430 EIS compound results reported from LOQVERs, two recoveries exceeded the EIS compound acceptance criteria (20–150%), resulting in a failure rate of 0.47%. The exceedances were reported by Laboratory 4 for D_5-NEtFOSA, and Laboratory 3 for D7-NMeFOSE, at 15.9% and 176%, respectively.

Table 5-5 provides the range of LOQs the laboratories used to report soil and sediment samples in this Study. Concentrations are based on a sample mass of 5 grams; LOQs that were elevated due to extract dilutions prior to analysis were omitted from the summary.



Source file: OS_LOQVER_Boxplot_V2_231121_101003

Figure 5-4. Limit of Quantitation Verification (LOQVER) Results by Analyte by Laboratory
Figure includes both target compound recoveries, and EIS compound recoveries.

Table 5-5. Summary of Verified LOQs

Target Analyte	Number of Laboratories	LOQ Minimum Concentration (µg/kg) [1]	LOQ Maximum Concentration (µg/kg) [1]
PFBA	10	0.64	1.6
PFPeA	10	0.32	0.8
PFHxA	10	0.16	0.4
PFHpA	10	0.16	0.4
PFOA	10	0.16	0.4
PFNA	10	0.16	1.25
PFDA	10	0.16	0.4
PFUnA	10	0.16	0.5
PFDoA	10	0.16	0.4
PFTrDA	10	0.16	0.4
PFTeDA	10	0.16	0.4
PFBS	10	0.16	0.355
PFPeS	10	0.16	0.376
PFHxS	10	0.16	0.366
PFHpS	10	0.16	0.381
PFOS	10	0.16	0.375
PFNS	10	0.16	0.385
PFDS	10	0.16	0.386
PFDoS	10	0.16	0.388
4:2FTS	10	0.64	1.5
6:2FTS	9	0.64	1.52
8:2FTS	10	0.64	1.54
PFOSA	10	0.16	0.4
NMeFOSA	9	0.16	0.4
NEtFOSA	9	0.16	0.4
NMeFOSAA	10	0.16	0.4
NEtFOSAA	10	0.16	0.4
NMeFOSE	10	1.6	4
NEtFOSE	10	1.6	4
PFMPA	10	0.32	0.8
PFMBA	10	0.32	0.8
NFDHA	10	0.32	0.8
HFPO-DA	10	0.64	1.6
ADONA	10	0.64	1.51
PFEESA	10	0.32	0.712
9Cl-PF3ONS	10	0.64	1.5
11Cl-PF3OUdS	10	0.64	1.51
3:3FTCA	10	0.8	5
5:3FTCA	10	4	10
7:3FTCA	10	4	10

Version: Summary_tables_Exa_CH5_11072023.xlsx

Notes:
[1] Concentrations based on a sample mass of 5 grams

6 SOILS

A total of 21study samples were created and shipped to each participating laboratory as described in Section 2 of this report. These included one native (unspiked), three low-spiked, and three high-spiked samples. All soil study samples were prepared and analyzed by each laboratory as required by EPA Method 1633.

Data were reported and validated in accordance with the requirements of the Study Plan. The rules used for omission of individual analyte results are presented in Section 3 of this report. As noted in Section 5, during the validation process, an error was identified in Laboratory 8 data that affected the quantitation of NMeFOSA, NEtFOSA, D_3-NMeFOSA, and D_5-NEtFOSA. Due to this error, all data for these two analytes and two EIS compounds have been eliminated from the soil and sediment statistical analyses. In addition, data for 6:2FTS from Laboratory 5 was omitted from the soil statistical analysis.

The methods used to calculate the percent recoveries, within-laboratory standard deviation, within- and between-laboratory standard deviation, and within-laboratory RSDs followed the ATP-prescribed methods (EPA 2018). The specific detailed methods followed are presented in *Volume I, Appendix D*. Methods adapted for evaluating the soils and sediments are found in Appendix B of this report.

6.1 PFAS CONCENTRATIONS IN UNSPIKED SOILS

Each laboratory received and analyzed a single sample of each soil sample (Table 2-3). The concentrations detected in this sample were considered the background or “native” concentration for each of the environmental matrices for each laboratory. Table 6-1 also includes the results of the reconnaissance analysis (by SGS AXYS) used to set the low/high-spiked concentrations (Table 2-2). The total number of PFAS target analytes detected by at least one laboratory is given in Table 6-2. PFBA, PFOA, and NetFOSAA were detected by at least one laboratory in all three native soil samples. PFOS was detected by most laboratories in the SSR sample (Musselshell, Clark Co. MT) and the SSW sample (Brock, Wheatley Co. TN), but not in the SST sample (Fruitland, San Juan Co., NM). A summary of the minimum and maximum reported values across all laboratories is found in Appendix Table C-1.

Table 6-1 also shows that the detections of PFAS reported from the three soil samples across the 10 laboratories ranged from five (Laboratories 7 and 8) to 15 (Laboratory 2); the reconnaissance laboratory reported nine detected PFAS. The majority of detections were between the laboratory-derived MDL and LOQ, therefore are estimated values, as indicated by the “J” data qualifier.

6.2 SOIL MATRIX SPIKE RESULTS

The compiled PFAS-spiked soil sample results from the 10 laboratories are given in Table 6-3. Overall, the pooled laboratory mean percent recoveries were greater than 90% for most compounds in both the low- and high-spiked samples (Figures 6-1 and 6-2), except as discussed below.

For the low-spiked soils samples (Table 6-3), the pooled mean percent recovery was 94% across all 40 PFAS analyzed, with a range of 68% (3:3FTCA) and 106% (8:2FTS). The inter- and intra-laboratory variability was low. (The pooled between-laboratory standard deviation (s_b) for the 40 PFAS ranged between 8.1–18.2%, with a median of 12.2%. The pooled within-laboratory standard deviation (s_w) was also relatively narrow: 5.8–16.2%, with a median of 8.8%. The RSD on the s_w was relatively narrow at approximately 9%. Pooled mean percent recoveries are noted for 3:3FTCA (68%), 5:3FTCA (76.2%), and 7:3FTCA (77.2%).

As evident in Figure 6-1, there are differences in reported recoveries by individual laboratories and specific compounds (data in Appendix C, Table C-2):

- For PFMPA, the pooled average percent recovery was 92%. Laboratories 3, 6, and 9 all reported recoveries for at least one sample at less than 50%, while Laboratory 5 had one sample reported at greater than 138%.
- For 9Cl-PF3ONS and 11Cl-PF3OUdS, the pooled average percent recovery was 103.3 and 95.2%, respectively. Laboratory 2's overall average for the measured soils were similar to the pooled percent recovery, but had single sample recoveries of 17.6 and 39.9%, respectively. Laboratories 5 and 10, by contrast, reported recoveries greater than 140%.
- For the three FTCA (3:3, 5:3, and 7:3), Laboratories 1, 2, and 7-10 had lower percent recoveries, with at least one sample less than 50%.
- Laboratory 5 in particular had elevated recoveries for all 40 compounds. (Figure 6-1 and Appendix C, Table C-2 and C-3).

For the pooled high-spiked samples (Table 6-3), the pooled recoveries were similar to that observed in the low-spiked samples. The pooled mean % recovery was between 71.5 (3:3FTCA) to 107% (8:2FTS), averaging 97.9% across all 40 PFAS analyzed. The pooled between-laboratory standard deviation (s_b) for the 40 PFAS ranged between 8.1–25.1%, with a median of 13.5%. The pooled within-laboratory standard deviation (s_w) was also relatively narrow: 7–38%, with a median of 10.9%. The RSD on the s_w is relatively narrow at approximately 13%.

Figure 6-2 shows the notable differences for individual laboratories and specific target analytes (data in Appendix C, Table C-3):

- For PFHxA, PFHpA, and PFOSA, Laboratory 8 reported greater than 600% recovery from the same sample. Those anomalous reported values skewed the higher pooled mean percent recoveries and standard deviations for the three compounds (Table 6-3).
- For 9Cl-PF3ONS and 11Cl-PF3OUdS the pooled average percent recoveries were 105 and 95.2%, respectively. Laboratory 2's overall averages were again similar to the pooled percent recovery but had single-sample recoveries of 18.1 and 4.9%, respectively.
- For the three FTCA (3:3, 5:3, and 7:3), while percent recoveries were improved over the low-spiked results, Laboratory 7 had recoveries of 16.4, 20.9 and 26.1% respectively.

The combined low/high-spiked sample statistical results are given in Table 6-3 and shown on Figure 6-3. The mean percent recoveries were between 71.5% (3:3FTCA) and 107% (8:2FTS), both of which fall within the targeted recovery range (70–130%). With the exception of the three FTCAs, the remaining pooled recoveries were greater than 90%.

Results comparing the three different soils samples using the pooled laboratory results are given in Table 6-4. Generally, the mean percent recoveries were similar for all target PFAS across the three soil samples. These data suggest that there were no specific matrix interferences associated with the differences in soil type, grain size, or TOC identified in Table 2-5. The FTCAs are the exception to that, with lower recoveries observed in the SSW (58-68%) sample relative to samples SSR and SST (78–88%). Data in Table 2-5 show that sample SSW is a slightly sandy silt (84% silt), whereas SSR and SST are silty sands (43/51% and 25/62.5%, respectively).

6.3 SOIL EXTRACTED INTERNAL STANDARD RESULTS

Per EPA Method 1633, EIS compounds were spiked into each sample prior to preparation. The amount of each EIS compound added to each sample varied slightly, depending on the target analyte and laboratory. The range of the EIS compound concentrations used by the laboratories is presented in Table 6-5. Since concentration levels between laboratories are not significantly different from one another, any interlaboratory variability observed in their recoveries cannot be attributed to concentration differences.

The MLVS Method did not prescribe definitive acceptance criteria for EIS compound recoveries; however, it did provide target acceptance criteria. The target percent recovery for EIS compounds in this Study are 20–150%. These target criteria were based on the results from the SLVS. Since the statistical evaluation from the MLVS will be the basis for the acceptance criteria included in future versions of EPA Method 1633, each laboratory was instructed to follow their routine corrective action process when the target criteria were not met. This includes reanalysis and dilution. If the reanalysis or dilution met the target criteria, the reanalysis was reported, otherwise, the first analysis was reported. By doing so, results that were extremely biased due to events such as a mis-injection or carryover, were eliminated from the statistical analysis.

The combined results for the minimum, maximum, and average percent recovery are given in Table 6-6. Supporting individual laboratory results are provided in Appendix C, Table C-4. For the 10 laboratories, the pooled average EIS percent recovery ranged between 50.9 (D_5-NEtFOSA) and 112.9% ($^{13}C_2$-8:2FTS). Table 6-7 presents the pooled soil EIS percent recovery; all mean percent recoveries were within the MLVS method-specified target recovery.

Figures 6-4 show that the highest variability in EIS compound recoveries for all laboratories were for $^{13}C_4$-PFBA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE. Three laboratories showed overall lower EIS recovery. Laboratory 9 had poor and highly variable recovery for $^{13}C_4$-PFBA, with a low of 5% recovery in a single sample. Laboratories 2 and 8 had lower recoveries for almost all of the EIS compounds.

While all EIS compound data were retained to evaluate the EIS performance, the only target analyte data retained for statistical evaluation is where the associated EIS compounds was ≥ 10%.

Table 6-1. Summary of Target Analytes Detected in Unspiked Soil Samples in µg/kg

Analyte	Number of Labs	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7		Lab 8		Lab 9		Lab 10		SGS-AXYS Baseline	
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual [1]
SSR1 - Musselshell, Clark Co. MT																							
PFBA	10	0.14	U	0.128	J	0.096	J	0.0514	U	0.19	J	0.0872	U	0.31	U	0.267	U	0.148	J	0.083	U	0.1503	U
PFHxA	10	0.0795	J	0.107	U	0.046	U	0.109	U	0.101	J	0.0375	U	0.075	U	0.0667	U	0.078	U	0.204	J+B	0.03848	
PFOA	10	0.0663	J	0.187	U	0.096	J	0.0821	J	0.0929	J	0.0315	U	0.076	U	0.0667	U	0.036	U	0.113	J+	0.03758	U
PFOS	10	0.141	J	0.166	U	0.2		0.132	U	0.122	J	0.132	J	0.1	J	0.134	J	--	X	0.135	J	0.09389	
PFOSA	10	0.0977	U	0.259	J	0.043	U	0.0305	U	0.127	U	0.0273	U	0.08	U	0.0667	U	0.047	U	0.014	U	0.03758	U
NMeFOSA	10	0.0933	U	0.2	J	0.1	U	0.1	U	0.0467	U	0.0468	U	0.14	U	--	X	0.034	U	0.029	U	0.04322	U
NEtFOSA	10	0.0515	U	0.185	J	0.112	U	0.128	U	0.0664	U	0.0417	U	0.1	U	--	X	0.059	U	0.017	U	0.09395	U
NEtFOSAA	10	0.0541	U	0.179	J	0.082	U	0.0674	UJ	0.0441	U	0.051	U	0.2	U	0.0667	U	0.026	U	0.047	U	0.03758	U
NMeFOSE	10	0.403	U	0.44	J	0.25	U	0.497	U	1.0	U	0.29	U	0.64	U	0.667	U	0.396	U	0.151	U	0.3758	U
5:3FTCA	10	0.748	U	0.929	J	0.505	U	1.31	U	1.08	U	0.645	U	1.2	U	0.133	U	1.11	U	0.443	U	0.9395	U
7:3FTCA	10	1	U	2.7	J	1.76	U	0.948	U	1.47	U	0.741	U	1.3	U	1.33	U	0.998	U	0.563	U	0.9395	U
SST1 - Fruitland, San Juan Co. NM																							
PFBA	10	0.14	U	0.102	U	0.05	U	0.0514	U	0.101	J	0.0872	U	0.31	U	0.267	U	0.144	U	0.083	U	0.1478	U
PFOA	10	0.0453	U	0.268	IJ	0.052	U	0.0509	U	0.0788	U	0.0315	U	0.076	U	0.0667	U	0.036	U	0.0626	J+	0.03696	U
NEtFOSAA	10	0.0541	U	0.156	U	0.152	J	0.0674	UJ	0.0441	U	0.051	U	0.2	U	0.0667	U	0.026	U	0.047	U	0.03696	U
SSW1 - Brock, Wheatley Co. TN																							
PFBA	10	0.14	U	0.108	J	0.05	U	0.0514	U	0.322	J	0.0872	U	0.31	U	0.267	U	0.144	U	0.083	U	0.1455	U
PFPeA	10	0.0715	U	0.0986	U	0.056	U	0.0857	U	0.0636	J	0.0842	U	0.085	U	0.133	U	0.062	U	0.039	U	0.07274	U
PFHxA	10	0.0579	U	0.107	U	0.046	U	0.109	U	0.132	J	0.0375	U	0.075	U	0.0667	U	0.078	U	0.273	J+B	0.04811	Q
PFHpA	10	0.0429	U	0.0528	U	0.023	U	0.0886	U	0.112	U	0.0675	U	0.06	U	0.0667	U	0.032	J	0.061	J	0.03637	U
PFOA	10	0.0539	J	0.187	U	0.052	U	0.0783	J	0.114	J	0.0748	J	0.076	U	0.0698	J	0.059	J	0.18	J+	0.052	
PFNA	10	0.166	J	0.189	J	0.078	U	0.22		0.565	U	0.24		0.17	J	0.239		0.184	J	0.263		0.1897	
PFDA	10	0.128	U	0.0744	U	0.075	U	0.0669	IJ	0.0807	U	0.0618	U	0.058	BJ+	0.0667	U	0.038	U	0.039	U	0.04634	Q
PFUnA	10	0.142	J	0.246	J	0.051	U	0.202		0.457	U	0.208		0.16	J	0.268		0.181	J	0.248		0.1977	
PFTrDA	10	0.0403	U	0.174	U	0.053	U	0.047	J	0.192	U	0.0339	U	0.1	U	0.0667	U	0.044	J	0.0457	J	0.05908	
PFOS	10	0.15	J	0.166	U	0.256		0.159	J	0.16	J	0.128	J	0.093	J	0.16	J	0.137	J	0.161	J	0.1325	
4:2FTS	10	0.317	U	0.272	U	0.081	U	0.397	U	0.169	J	0.238	U	0.3	U	0.25	U	0.151	U	0.17	U	0.1455	U
6:2FTS	10	0.144	U	0.51	U	0.28	U	0.187	U	--	X	0.36	J+	0.35	U	0.253	U	0.139	U	0.305	UJ	0.1311	U
PFOSA	10	0.0977	U	0.066	U	0.043	U	0.0305	U	0.127	U	0.0273	U	0.08	U	0.0667	U	0.05	J	0.0306	JI	0.03637	U
NMeFOSA	10	0.0933	U	0.113	U	0.1	U	0.1	U	0.0467	U	0.0468	U	0.14	U	--	X	0.034	U	0.0452	J	0.04183	U
NMeFOSAA	10	0.101	U	0.136	U	0.136	J+	0.12	U	0.0304	U	0.0318	U	0.16	U	0.0667	U	0.049	U	0.05	U	0.03637	U
NEtFOSAA	10	0.0541	U	0.191	J	0.082	U	0.0674	U	0.0441	U	0.051	U	0.2	U	0.0667	U	0.026	U	0.047	U	0.03637	U
NEtFOSE	10	0.12	U	0.466	U	0.51	U	0.444	U	0.703	U	0.309	U	0.83	U	0.667	U	0.442	U	0.0931	J	0.2721	U
5:3FTCA	10	0.748	U	1.35	J	0.505	U	1.31	U	1.08	U	0.645	U	1.2	U	0.133	U	1.11	U	0.443	U	0.9093	U
7:3FTCA	10	1.0	U	1.67	J	1.76	U	0.948	U	1.47	U	0.741	U	1.3	U	1.33	U	0.998	U	0.563	U	0.9093	U
Total # Analytes Reported Across All Samples		7		15		6		7		11		6		5		5		8		14		9	

Version: Summary_tables_Exa_CH6_10312023.xlsx

Notes:
'—" = X-qualified results

Table 6-2. Numbers of Detected Analytes by Soil Sample

Unspiked Soil Sample	**Total Number of Analytes Detected by at least One Laboratory**
SSR1 - Musselshell, Clark Co. MT	12
SST1 - Fruitland, San Juan Co. NM	6
SSW1 - Brock, Wheatley Co. TN	19

Source file: Summary_tables_Exa_CH6_10312023.xlsx

Table 6-3. Pooled Laboratory PFAS-Spiked Soil Samples Results. Low-spiked, High-spiked, and Combined Low/High-Spiked Samples

Analyte	Number of Labs	Low-Spiked Samples					High-Spiked Samples					Combined Low/High-Spiked Samples				
		Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)
PFBA	10	86	100	12.4	7.0	7.0	87	103	10.3	5.4	5.3	173	101	11.1	6.59	6.5
PFPeA	10	89	101	12.8	5.6	5.5	90	101	8.98	7.6	7.5	179	101	10.2	7.72	7.64
PFHxA	10	89	98	7.7	4.9	5.0	90	105	26.2	55.8	53.0	179	102	16.2	40	39.3
PFHpA	10	89	97.2	8.51	5.2	5.3	90	106	28.2	60.6	57.4	179	101	17.3	43.4	42.8
PFOA	10	89	96.9	9.65	5.9	6.1	90	100	8.72	7.7	7.7	179	98.6	9.08	7.02	7.11
PFNA	10	89	96.8	11.1	7.7	8.0	90	101	12.6	9.5	9.4	179	98.8	11.7	8.92	9.02
PFDA	10	89	99.9	11.5	7.4	7.4	90	102	9.68	10.2	10.0	179	101	10.3	9.15	9.07
PFUnA	10	89	97.8	11.4	7.7	7.8	90	102	12.5	8.2	8.1	179	99.8	11.7	8.26	8.28
PFDoA	10	89	101	12.7	9.0	8.9	90	101	10.7	10.3	10.2	179	101	11.5	9.66	9.59
PFTrDA	10	89	97.8	10.6	9.5	9.7	90	102	13	11.2	11.0	179	99.7	11.7	10.4	10.4
PFTeDA	10	88	97.1	9.7	9.7	10.0	89	96.6	10.9	8.3	8.6	177	96.8	10	9	9.29
PFBS	10	89	95.3	8.47	6.7	7.0	90	101	11.2	7.8	7.7	179	98	9.51	8.03	8.19
PFPeS	10	89	96.9	13.2	7.2	7.5	90	102	12.3	8.0	7.8	179	99.6	12.6	8.08	8.11
PFHxS	10	89	98.5	10.1	5.8	5.9	90	102	11.6	8.5	8.4	179	100	10.6	7.68	7.66
PFHpS	10	89	99.6	14.7	9.9	9.9	90	104	11.9	9.4	9.0	179	102	12.8	10.1	9.94
PFOS	10	89	97.7	10.2	7.1	7.2	90	101	8.41	7.8	7.7	179	99.5	9.04	7.77	7.81
PFNS	10	89	95.5	11.5	6.2	6.5	90	98.9	10.7	8.8	8.8	179	97.2	10.9	7.88	8.1
PFDS	10	89	91.1	15.4	8.2	9.0	90	94.2	13.7	10.2	10.9	179	92.7	14.3	9.57	10.3
PFDoS	10	89	86.1	18.2	11.2	13.0	90	90.1	17.1	13.2	14.7	179	88.1	17.4	12.3	14
4:2FTS	10	89	91.7	12.1	8.0	8.8	90	97.9	8.81	10.0	10.2	179	94.8	10	9.91	10.5
6:2FTS	9	81	96.2	9.28	11.2	11.7	81	102	10.7	12.8	12.6	162	99	9.47	12.5	12.6
8:2FTS	10	89	106	12.8	11.1	10.5	90	108	13.7	12.3	11.3	179	107	12.8	11.9	11.1
PFOSA	10	89	99	11.2	5.8	5.9	90	107	25.1	53.5	50.2	179	103	17.6	38	36.9
NMeFOSA	9	79	96.5	8.86	6.8	7.1	81	98	8.39	7.6	7.7	160	97.2	8.33	7.31	7.52
NEtFOSA	9	77	98.5	10.4	6.6	6.8	80	101	8.08	8.0	7.9	157	100	9	7.66	7.66
NMeFOSAA	10	89	95.3	14	6.7	7.0	90	99.2	14.9	9.9	10.0	179	97.3	14.4	8.63	8.87
NEtFOSAA	10	89	99	15.2	6.8	6.8	90	101	13.6	10.0	10.0	179	100	14.3	8.63	8.63
NMeFOSE	10	89	95.9	12.4	6.9	7.2	90	99	10.9	6.6	6.7	179	97.5	11.5	6.96	7.14
NEtFOSE	10	88	97.5	10.7	7.0	7.2	89	98.4	8.17	7.9	8.1	177	98	9.17	7.65	7.8
PFMPA	10	89	92	17.4	13.5	14.7	90	93.9	19.8	19.5	20.8	179	93	18.3	16.7	17.9
PFMBA	10	89	100	8.09	9.0	9.0	90	105	9.31	10.5	10.0	179	102	8.63	9.84	9.61
NFDHA	10	89	97.7	12.3	12.8	13.1	90	100	11.4	12.1	12.1	179	98.9	11.1	12.7	12.8
HFPO-DA	10	89	97.5	8.54	8.1	8.3	90	101	8.16	8.6	8.5	179	99.4	8.15	8.51	8.56

Table 6-3. Pooled Laboratory PFAS-Spiked Soil Samples Results. Low-spiked, High-spiked, and Combined Low/High-Spiked Samples (Continued)

Analyte	**Number of Labs**	**Low-Spiked Samples**					**High-Spiked Samples**					**Combined Low/High-Spiked Samples**				
		Number of Results	**Mean % Recovery**	**Pooled Between-Lab std. dev. (s_b)**	**Pooled Within-Lab std. dev. (s_w)**	**RSD (s_w)**	**Number of Results**	**Mean % Recovery**	**Pooled Between-Lab std. dev. (s_b)**	**Pooled Within-Lab std. dev. (s_w)**	**RSD (s_w)**	**Number of Results**	**Mean % Recovery**	**Pooled Between-Lab std. dev. (s_b)**	**Pooled Within-Lab std. dev. (s_w)**	**RSD (s_w)**
ADONA	10	89	103	13.8	8.6	8.3	90	105	16.3	9.4	8.9	179	104	14.8	9.38	8.98
PFEESA	10	89	96.1	10.9	8.6	8.9	90	103	13.4	7.3	7.1	179	99.5	11.8	9.09	9.14
9Cl-PF3ONS	10	89	103	10.6	16.7	16.2	90	105	13.7	15.8	15.0	179	104	11.4	16.4	15.7
11Cl-PF3OUdS	10	88	95.2	13.2	13.3	14.0	90	99.7	19.7	16.1	16.1	178	97.5	16.1	15.4	15.8
3:3FTCA	10	89	68	10.1	12.6	18.5	90	74.9	13.2	15.0	20.1	179	71.5	11.6	14	19.6
5:3FTCA	10	89	76.2	13.1	11.9	15.6	90	81.3	14.8	13.3	16.3	179	78.8	13.7	12.8	16.2
7:3FTCA	10	89	77.2	16	13.8	17.8	90	84.1	21.1	14.6	17.3	179	80.6	18.3	14.7	18.2

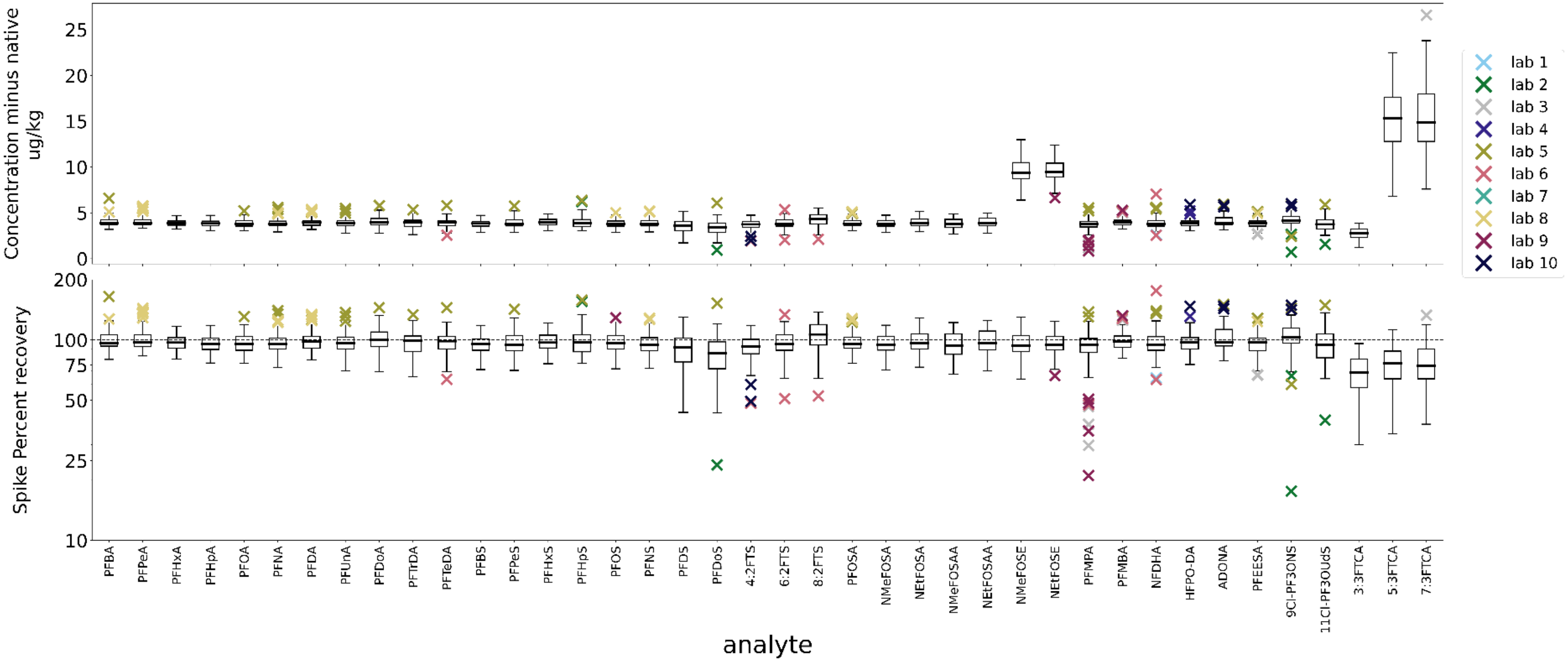
Source file: SS_Matrix_compiled_results_V1_2.cvs

Table 6-4. PFAS-Spiked Samples Results by Individual Soil Sample

Analyte	SSR					SST					SSW				
	Number of Labs	**Number of Results**	**Mean % Recovery**	**Min % Recovery**	**Max % Recovery**	**Number of Labs**	**Number of Results**	**Mean % Recovery**	**Min % Recovery**	**Max % Recovery**	**Number of Labs**	**Number of Results**	**Mean % Recovery**	**Min % Recovery**	**Max % Recovery**
PFBA	10	58	102	80	128	10	60	100	80	124	10	55	102	66.8	165
PFPeA	10	60	102	81.4	144	10	60	101	73.2	138	10	59	99.8	74.6	138
PFHxA	10	60	100	80	126	10	60	98.8	80.2	115	10	59	106	73.6	**644**
PFHpA	10	60	98.9	80.4	127	10	60	98.2	68	123	10	59	107	66.8	**688**
PFOA	10	60	99.8	80.8	123	10	60	97.2	72.1	131	10	59	98.9	72.8	119
PFNA	10	60	99.3	78.2	129	10	60	96.9	60.4	146	10	59	100	76.1	140
PFDA	10	60	103	79.2	156	10	60	97.8	67.6	122	10	59	102	78.8	134
PFUnA	10	60	100	70	158	10	60	98	76.8	129	10	59	101	82	137
PFDoA	10	60	102	58	145	10	60	99	72.4	126	10	59	101	68.4	132
PFTrDA	10	60	99.1	65.5	130	10	60	97.3	71.2	142	10	59	103	58	145
PFTeDA	10	59	95.9	69.5	122	10	59	97	66.8	145	10	59	97.6	63.2	128
PFBS	10	60	96.1	71.2	120	10	60	99.8	70.8	125	10	59	98.1	62.4	128
PFPeS	10	60	97.8	74.3	130	10	60	100	75.6	137	10	59	101	70.5	142
PFHxS	10	60	101	78.1	126	10	60	101	76.1	133	10	59	99.4	74	126
PFHpS	10	60	103	77.6	155	10	60	101	72	147	10	59	102	76.6	158
PFOS	10	60	103	79	129	10	60	97.9	73.5	120	10	59	97.8	71.8	125
PFNS	10	60	98.6	72.3	129	10	60	95.8	62	119	10	59	97.4	68	128
PFDS	10	60	94.6	43.5	123	10	60	90.2	33.6	130	10	59	93.1	62.9	126
PFDoS	10	60	89.8	23.8	122	10	60	85.4	14.1	152	10	59	89.3	50.8	124
4:2FTS	10	60	95.3	49.4	122	10	60	95.9	63.6	123	10	59	93.2	48.4	125
6:2FTS	9	54	101	64.5	134	9	54	98	69.8	168	9	54	98.3	51	145
8:2FTS	10	60	108	64.3	136	10	60	106	68.8	152	10	59	108	52.6	138
PFOSA	10	60	101	76.5	128	10	60	98.5	59.2	123	10	59	109	78	**620**
NMeFOSA	9	54	97.3	71	118	9	53	96.5	69.6	116	9	53	97.9	80	116
NEtFOSA	9	51	100	73.2	129	9	53	100	69.2	122	9	53	99.5	76	122
NMeFOSAA	10	60	97.3	68.2	124	10	60	95.8	63.6	126	10	59	98.6	28.7	125
NEtFOSAA	10	60	100	70	137	10	60	99.3	70	132	10	59	100	32.4	125
NMeFOSE	10	60	95.9	63.9	124	10	60	98	69.4	124	10	59	98.5	77.3	130
NEtFOSE	10	59	97.8	66.5	124	10	59	97.6	64.4	119	10	59	98.5	77.2	124
PFMPA	10	60	92.9	20.4	130	10	60	95.3	33.2	128	10	59	90.6	23	138
PFMBA	10	60	103	81	128	10	60	102	84.8	135	10	59	102	71.6	149
NFDHA	10	60	99.6	64.8	176	10	60	100	66.9	150	10	59	96.7	63.5	130
HFPO-DA	10	60	101	80	126	10	60	98	81	134	10	59	98.8	75.5	148
ADONA	10	60	105	83.5	155	10	60	103	82.7	152	10	59	105	64.7	161
PFEESA	10	60	96.2	69.8	132	10	60	103	77.6	132	10	59	99.8	66.8	129
9Cl-PF3ONS	10	60	106	17.6	144	10	60	105	18.1	150	10	59	102	60.2	149
11Cl-PF3OUdS	10	59	100	39.9	149	10	60	95.7	4.9	149	10	59	96.3	64.1	162
3:3FTCA	10	60	78.3	45	118	10	60	77.6	48.5	114	10	59	58.3	16.4	103
5:3FTCA	10	60	86.5	51.5	119	10	60	83.8	59	126	10	59	65.8	20.9	97.5
7:3FTCA	10	60	88.2	38	137	10	60	85.2	50	166	10	59	68.4	26.1	132

Source file: SS_Matrix_sample_results_V1_230928_173420.csv

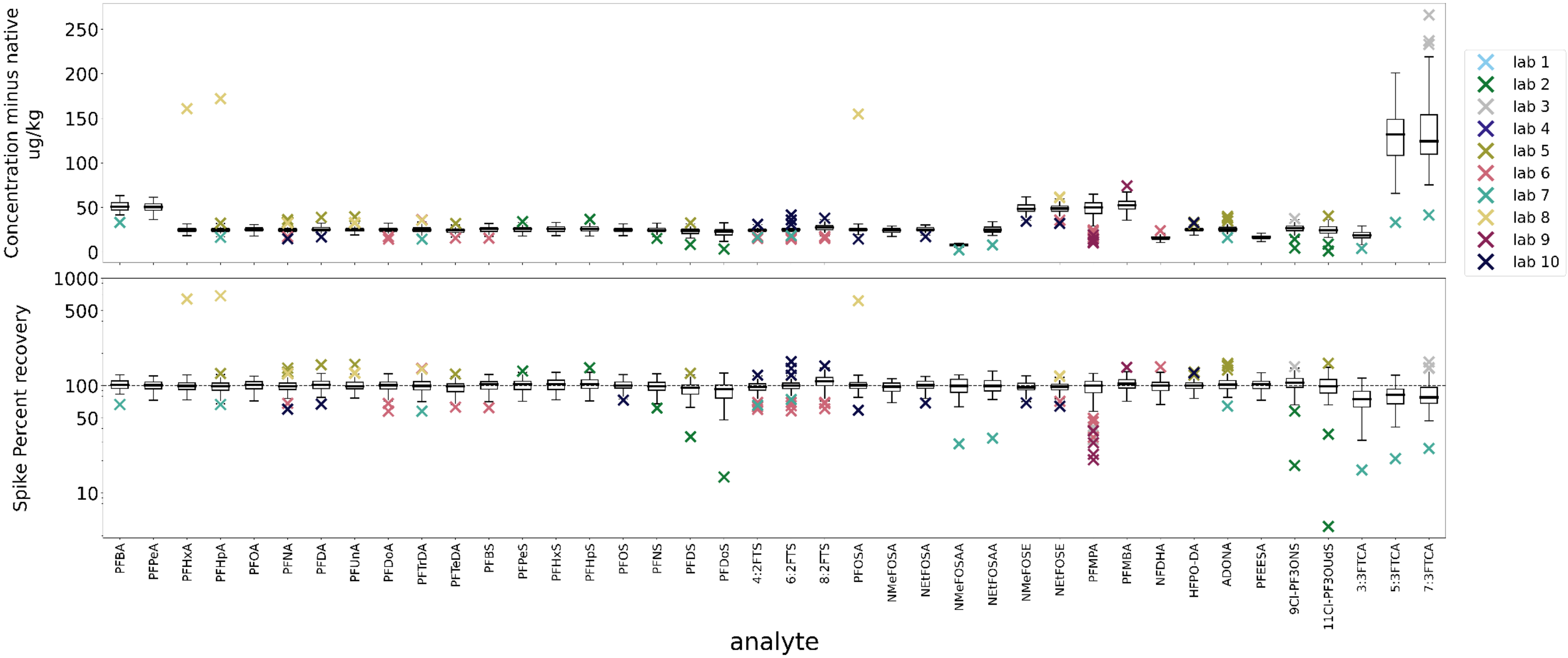
Notes:
Number of Labs - The number of laboratories reporting matrix spiked sample results.
Number of Results - The total number of matrix sample results categorized as low-spiked concentration (indicated in Row 1) that do not have a U flag.
Mean % Recovery - The mean percent recovery for spiked samples across all laboratories.
Min % Recovery - The minimum percent recovery for the matrix spiked samples across all laboratories.
Max % Recovery - The maximum percent recovery for the matrix spiked samples across all laboratories.



Source File: SS_LowSpike_Boxplot_V2_231122_095457

Figure 6-1. Soil Low Matrix Spiked Results by Analyte by Laboratory

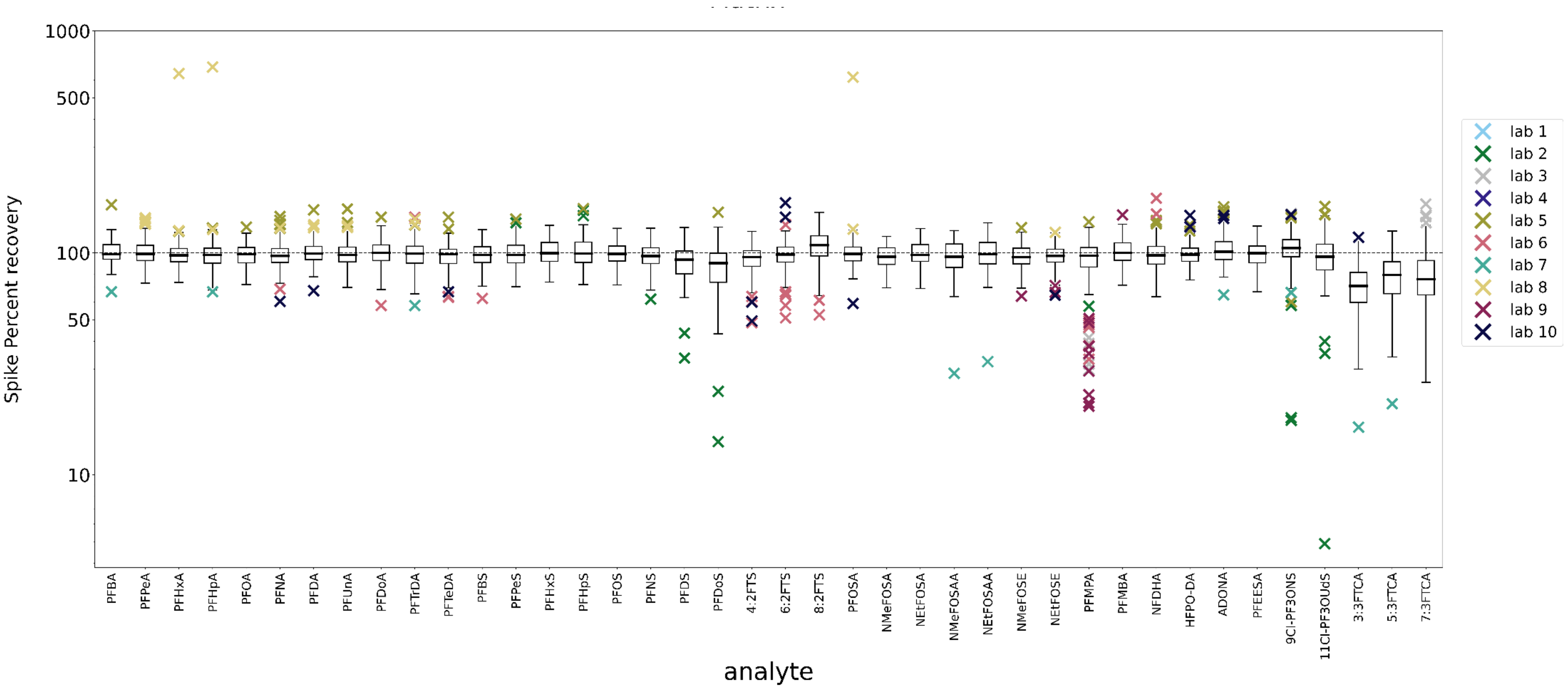
(A) Spiked concentration minus the laboratory-reported native concentration. (B) Low-spiked percent recovery.



Source File: SS_HighSpike_Boxplot_V2_231122_095457

Figure 6-2. Soil High Matrix Spiked Results by Analyte by Laboratory

(A) Spiked concentration minus the laboratory-reported native concentration. (B) High-spiked percent recovery.



Source File: SS_LowHighCombinedSpike_Boxplot_V2_231122_095457

Figure 6-3. Pooled Low- and High-spiked Soil Percent Recovery Results by Analyte by Laboratory

Table 6-5. Range of Concentrations of EIS Compounds Used by All Laboratories

EIS Compound	Minimum Concentration (μg/kg)	Maximum Concentration (μg/kg)
$^{13}C_4$-PFBA	8.00	10.00
$^{13}C_5$-PFPeA	4.00	5.00
$^{13}C_5$-PFHxA	2.00	2.50
$^{13}C_4$-PFHpA	2.00	2.50
$^{13}C_8$-PFOA	2.00	2.50
$^{13}C_9$-PFNA	1.00	1.25
$^{13}C_6$-PFDA	1.00	1.25
$^{13}C_7$-PFUnA	1.00	1.25
$^{13}C_2$-PFDoA	1.00	1.25
$^{13}C_2$-PFTeDA	1.00	1.25
$^{13}C_3$-PFBS	1.86	2.50
$^{13}C_3$-PFHxS	1.90	2.50
$^{13}C_8$-PFOS	1.92	2.50
$^{13}C_2$-4:2FTS	3.75	5.00
$^{13}C_2$-6:2FTS	3.80	5.00
$^{13}C_2$-8:2FTS	3.84	5.00
$^{13}C_8$-PFOSA	2.00	2.50
D_3-NMeFOSA	2.00	2.50
D_5-NEtFOSA	2.00	2.50
D_3-NMeFOSAA	4.00	5.00
D_5-NEtFOSAA	4.00	5.00
D_7-NMeFOSE	20.00	25.00
D_9-NEtFOSE	20.00	25.00
$^{13}C_3$-HFPO-DA	8.00	10.00

Version: Summary_tables_Exa_CH6_10312023.xlsx

Table 6-6. Summary of EIS Compound Percent Recovery in Soil Samples for All Laboratories

EIS Compound [1]	**All Laboratories % Recovery**			
	n	**Min**	**Max**	**Mean**
$^{13}C_4$-PFBA	209	5	116	77.5
$^{13}C_5$-PFPeA	209	27	122	82.5
$^{13}C_5$-PFHxA	216	34.3	121	87
$^{13}C_4$-PFHpA	209	30	121	86.4
$^{13}C_8$-PFOA	209	26.1	115	85.9
$^{13}C_9$-PFNA	209	20.2	115	84.9
$^{13}C_6$-PFDA	209	18.3	112	83.5
$^{13}C_7$-PFUnA	209	13.2	125	85.5
$^{13}C_2$-PFDoA	209	12.1	129	80.6
$^{13}C_2$-PFTeDA	209	7.38	144	76.2
$^{13}C_3$-PFBS	209	33	127	85.7
$^{13}C_3$-PFHxS	209	25.9	119	85.5
$^{13}C_8$-PFOS	209	17.9	115	85.8
$^{13}C_2$-4:2FTS	209	41.2	253	105.5
$^{13}C_2$-6:2FTS	209	35.5	193	100.6
$^{13}C_2$-8:2FTS	209	27.5	295	112.9
$^{13}C_8$-PFOSA	209	19.4	117	79.6
D_3-NMeFOSA	188	8.7	94.8	56.6
D_5-NEtFOSA	188	7.2	90	50.9
D_3-NMeFOSAA	209	20.6	184	85.6
D_5-NEtFOSAA	209	20	154	85.3
D_7-NMeFOSE	209	12	115	65.3
D_9-NEtFOSE	209	8.71	105	63.3
$^{13}C_3$-HFPO-DA	209	28.6	126	86.5

Version: Summary_tables_Exa_CH6_10312023.xlsx

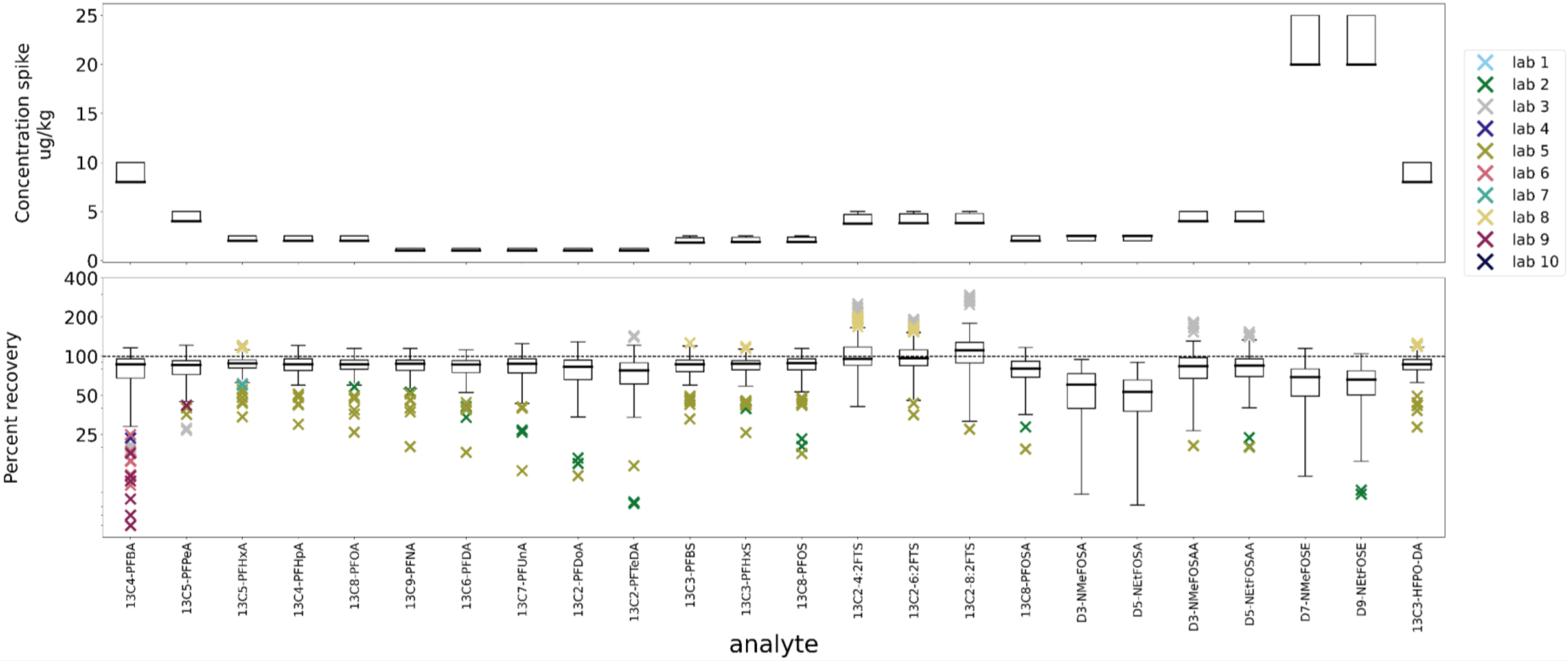
[1] Based on validated data. Does not include MB, OPR, LLOPR QC samples.

Table 6-7. Statistical Evaluation of EIS Compound Results Associated with Soil Samples

Analyte	**Number of Labs**	**Number of Results**	**Mean % Recovery**	**Pooled Between-Lab std. dev. (s_b)**	**Pooled Within-Lab std. dev. (s_w)**	**RSD (s_w)**
$^{13}C_4$-PFBA	10	209	77.5	18.9	20.1	25.9
$^{13}C_5$-PFPeA	10	209	82.4	13.9	13.2	16
$^{13}C_5$-PFHxA	10	216	86.9	9.62	10.4	11.9
$^{13}C_4$-PFHpA	10	209	86.4	9.92	11	12.7
$^{13}C_8$-PFOA	10	209	85.8	9.77	10.3	12
$^{13}C_9$-PFNA	10	209	84.9	11.4	10.3	12.1
$^{13}C_6$-PFDA	10	209	83.5	10.7	11.3	13.5
$^{13}C_7$-PFUnA	10	209	85.5	12.6	13.3	15.5
$^{13}C_2$-PFDoA	10	209	80.6	15	13.6	16.9
$^{13}C_2$-PFTeDA	10	209	76.2	16.7	14.4	18.9
$^{13}C_3$-PFBS	10	209	85.8	11.8	10.8	12.6
$^{13}C_3$-PFHxS	10	209	85.4	10.6	10.8	12.6
$^{13}C_8$-PFOS	10	209	85.8	11.5	12.1	14
$^{13}C_2$-4:2FTS	10	209	105	29.6	24.3	23
$^{13}C_2$-6:2FTS	10	209	101	23.1	19.2	19.1
$^{13}C_2$-8:2FTS	10	209	113	34.6	27.9	24.7
$^{13}C_8$-PFOSA	10	209	79.6	11.9	13.1	16.4
D_3-NMeFOSA	9	188	56.5	18.3	11.4	20.2
D_5-NEtFOSA	9	188	50.9	16.6	10.8	21.1
D_3-NMeFOSAA	10	209	85.5	20.7	17.4	20.3
D_5-NEtFOSAA	10	209	85.4	15.6	16.7	19.6
D_7-NMeFOSE	10	209	65.3	19.5	12.5	19.1
D_9-NEtFOSE	10	209	63.3	15.9	13.3	21
$^{13}C_3$-HFPO-DA	10	209	86.5	11.9	9.73	11.3

Source file: SS_EIS_results_V1_230928_173420.cvs

Notes:
Number of Labs - The number of laboratories reporting matrix (native & spiked) results.
Number of Results - The total number of matrix results that do not have a U flag.
Mean % Recovery - The mean percent recovery across all of the EIS compound individual samples across all laboratories for the given analyte.
s_b - The pooled between-laboratory standard deviation. Equation from EPA 821-B-18-001page G-25.
s_w - The pooled within-laboratory standard deviation. Equation from EPA 821-B-18-001page G-25.
RSD - The pooled within-laboratory relative standard deviation (RSD, (s_w / (mean % recovery) *100).



Source File: SS_EIS_Boxplot_V2_231122_095457

Figure 6-4. Soil EIS Compound Results by Compound by Laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.

6.4 SOIL SUMMARY

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world soil samples. The pooled (low-spiked/high-spiked samples) average percent recoveries as shown in Table 6-4 were between 71.5–107%.

Tables 6-8 and 6-9 provide summaries of the relative proportions of the spiked sample recoveries for all laboratories that fell between the target percent recovery acceptance criteria of 40–150% that was used to evaluate the OPR and LLOPR (40–150%).

For the low-spiked samples, >95% of all 40 spiked PFAS were recovered between 40–150% of the spiked concentration (Table 6-8). With the exception of the FTCA compounds, most of those percent recoveries were between 70–130%. For example, in Table 6-4 for PFBA, 85 out of 89 reported values had greater than 70% recovery. For PFDoS, 70 out of 89 reported values had greater than 70% recovery. For the FTCA compounds, 2–5% of the reported recoveries were less than 40%, 31–47% were between 40–70%, with 56.2% between 70–130%. For the high-spiked samples the results were the same: >95% of all 40 spiked PFAS were recovered between 40–150% of the spiked concentration (Table 6-9). The results for the FTCA compounds were also similar to that observed in the low-spiked samples.

Table 6-10 provides a summary of the relative proportions of the pooled low-/high-spiked results for all laboratories that met the Study target percent recovery acceptance criteria. For the low- and high-spiked samples, the proportion of all values that were between 20–150% of the spiked concentrations was >88%.

Finally, Table 6-11 provides a comparison of the mean individual laboratory EIS percent recoveries relative to the acceptance limits for EIS compounds that EPA determined for all aquatic matrices and QC samples in the most recent draft of EPA Method 1633 (Version 4, Table 6). For that comparison, average EIS percent recoveries for all compounds and all laboratories were solidly within the acceptance criteria range.

Table 6-8. Proportion of Soil Matrix Spiked Percent Recovery Results for Target Analytes within Ranges (Low-Spiked Samples)

Analyte	Low-Spiked Samples						
	n	<40%	≥40% to <70%	≥70% to <130%	≥130% to <150%	≥150% to <200%	≥200%
PFBA	86	0	0	98.8	0	1.2	0
PFPeA	89	0	0	93.3	6.7	0	0
PFHxA	89	0	0	100	0	0	0
PFHpA	89	0	0	100	0	0	0
PFOA	89	0	0	98.9	1.1	0	0
PFNA	89	0	0	97.8	2.2	0	0
PFDA	89	0	0	95.5	4.5	0	0
PFUnA	89	0	0	97.8	2.2	0	0
PFDoA	89	0	1.1	95.5	3.4	0	0
PFTrDA	89	0	2.2	96.6	1.1	0	0
PFTeDA	88	0	2.3	96.6	1.1	0	0
PFBS	89	0	0	100	0	0	0
PFPeS	89	0	0	98.9	1.1	0	0
PFHxS	89	0	0	100	0	0	0
PFHpS	89	0	0	93.3	4.5	2.2	0
PFOS	89	0	0	100	0	0	0
PFNS	89	0	0	100	0	0	0
PFDS	89	0	6.7	92.1	1.1	0	0
PFDoS	89	1.1	19.1	78.7	0	1.1	0
4:2FTS	89	0	5.6	94.4	0	0	0
6:2FTS	81	0	4.9	93.8	1.2	0	0
8:2FTS	89	0	2.2	94.4	3.4	0	0
PFOSA	89	0	0	100	0	0	0
NMeFOSA	79	0	0	100	0	0	0
NEtFOSA	77	0	0	100	0	0	0
NMeFOSAA	89	0	2.2	97.8	0	0	0
NEtFOSAA	89	0	0	100	0	0	0
NMeFOSE	89	0	2.2	96.6	1.1	0	0
NEtFOSE	88	0	1.1	98.9	0	0	0
PFMPA	89	4.5	6.7	86.5	2.2	0	0
PFMBA	89	0	0	97.8	2.2	0	0
NFDHA	89	0	2.2	93.3	3.4	1.1	0
HFPO-DA	89	0	0	97.8	2.2	0	0
ADONA	89	0	0	93.3	5.6	1.1	0
PFEESA	89	0	3.4	96.6	0	0	0
9Cl-PF3ONS	89	1.1	3.4	88.8	6.7	0	0
11Cl-PF3OUdS	88	1.1	3.4	93.2	2.3	0	0
3:3FTCA	89	5.6	47.2	47.2	0	0	0
5:3FTCA	89	3.4	31.5	65.2	0	0	0
7:3FTCA	89	2.2	40.4	56.2	1.1	0	0

Version: Summary_tables_Exa_CH6_10312023.xlsx

[1] Based on validated data. Does not include MB, OPR, LLOPR QC samples.

Table 6-9. Proportion of Soil Matrix Spiked Percent Recovery Results for Target Analytes within Ranges (High-Spiked Samples)

Analyte	All Labs Proportion % Recovery						
	n	<40%	≥40% to <70%	≥70% to <130%	≥130% to <150%	≥150% to <200%	≥200%
PFBA	87	0	1.1	98.9	0	0	0
PFPeA	90	0	0	100	0	0	0
PFHxA	90	0	0	98.9	0	0	1.1
PFHpA	90	0	2.2	96.7	0	0	1.1
PFOA	90	0	0	100	0	0	0
PFNA	90	0	2.2	93.3	4.4	0	0
PFDA	90	0	1.1	96.7	1.1	1.1	0
PFUnA	90	0	0	95.6	3.3	1.1	0
PFDoA	90	0	2.2	97.8	0	0	0
PFTrDA	90	0	1.1	91.1	7.8	0	0
PFTeDA	89	0	2.2	97.8	0	0	0
PFBS	90	0	1.1	98.9	0	0	0
PFPeS	90	0	0	97.8	2.2	0	0
PFHxS	90	0	0	98.9	1.1	0	0
PFHpS	90	0	0	97.8	2.2	0	0
PFOS	90	0	0	100	0	0	0
PFNS	90	0	3.3	96.7	0	0	0
PFDS	90	1.1	4.4	92.2	2.2	0	0
PFDoS	90	1.1	15.6	82.2	1.1	0	0
4:2FTS	90	0	3.3	96.7	0	0	0
6:2FTS	81	0	2.5	95.1	1.2	1.2	0
8:2FTS	90	0	3.3	86.7	8.9	1.1	0
PFOSA	90	0	1.1	97.8	0	0	1.1
NMeFOSA	81	0	1.2	98.8	0	0	0
NEtFOSA	80	0	1.2	98.8	0	0	0
NMeFOSAA	90	1.1	1.1	97.8	0	0	0
NEtFOSAA	90	1.1	0	95.6	3.3	0	0
NMeFOSE	90	0	1.1	98.9	0	0	0
NEtFOSE	89	0	1.1	98.9	0	0	0
PFMPA	90	8.9	6.7	83.3	1.1	0	0
PFMBA	90	0	0	97.8	2.2	0	0
NFDHA	90	0	2.2	94.4	2.2	1.1	0
HFPO-DA	90	0	0	97.8	2.2	0	0
ADONA	90	0	1.1	88.9	5.6	4.4	0
PFEESA	90	0	0	96.7	3.3	0	0
9Cl-PF3ONS	90	1.1	2.2	87.8	7.8	1.1	0
11Cl-PF3OUdS	90	2.2	4.4	83.3	8.9	1.1	0
3:3FTCA	90	3.3	40	56.7	0	0	0
5:3FTCA	90	1.1	31.1	67.8	0	0	0
7:3FTCA	90	1.1	25.6	66.7	5.6	1.1	0

Version: Summary_tables_Exa_CH6_10312023.xlsx

[1] Based on validated data. Does not include MB, OPR, LLOPR QC samples.

Table 6-10. Proportion of Soil Percent Recovery Results for EIS Compounds within Ranges

EIS Compound	**All Labs Proportion % Recovery**					
	n	**<10%**	**≥10% to <20%**	**≥20% to <150%**	**≥150% to 200%**	**≥200%**
$^{13}C_4$-PFBA	209	2.4	4.3	93.3	0	0
$^{13}C_5$-PFPeA	209	0	0	100	0	0
$^{13}C_5$-PFHxA	216	0	0	100	0	0
$^{13}C_4$-PFHpA	209	0	0	100	0	0
$^{13}C_8$-PFOA	209	0	0	100	0	0
$^{13}C_9$-PFNA	209	0	0	100	0	0
$^{13}C_6$-PFDA	209	0	0.5	99.5	0	0
$^{13}C_7$-PFUnA	209	0	0.5	99.5	0	0
$^{13}C_2$-PFDoA	209	0	1.4	98.6	0	0
$^{13}C_2$-PFTeDA	209	1	0.5	98.6	0	0
$^{13}C_3$-PFBS	209	0	0	100	0	0
$^{13}C_3$-PFHxS	209	0	0	100	0	0
$^{13}C_8$-PFOS	209	0	0.5	99.5	0	0
$^{13}C_2$-4:2FTS	209	0	0	89	7.2	3.8
$^{13}C_2$-6:2FTS	209	0	0	91.9	8.1	0
$^{13}C_2$-8:2FTS	209	0	0	88	8.6	3.3
$^{13}C_8$-PFOSA	209	0	0.5	99.5	0	0
D_3-NMeFOSA	188	0.5	5.9	93.6	0	0
D_5-NEtFOSA	188	2.1	4.8	93.1	0	0
D_3-NMeFOSAA	209	0	0	96.7	3.3	0
D_5-NEtFOSAA	209	0	0	99.5	0.5	0
D_7-NMeFOSE	209	0	1.4	98.6	0	0
D_9-NEtFOSE	209	1	0.5	98.6	0	0
$^{13}C_3$-HFPO-DA	209	0	0	100	0	0

Version: Summary_tables_Exa_CH6_10312023.xlsx

[1] Based on validated data. Does not include MB, OPR, LLOPR QC samples.

Table 6-11. Soil Percent Recovery Results for EIS Compounds Compared to Acceptance Limits for Aqueous Matrices in EPA Method 1633

EIS Compound	Acceptance Limits for EIS Compounds in All Aqueous Matrices and QC Samples [1]		Average EIS % Recovery by Laboratory for Soils (Appendix C-4)										All Labs % recovery	
			Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10	n	Avg
$^{13}C_4$-PFBA	52	130	77.1	94	54.4	81.2	77.2	54.4	72.8	109.6	56.9	97.4	209	77.5
$^{13}C_5$-PFPeA	40	130	83.6	93.6	64.4	88.1	78.5	70.6	63.2	103.1	79.9	99.5	209	82.5
$^{13}C_5$-PFHxA	40	130	85.2	93.3	85	88.5	83.6	78.1	68.7	104.6	88.1	94	216	87
$^{13}C_4$-PFHpA	40	130	79.4	90.2	92.9	86.5	79.9	79.3	68.1	102.7	87.7	96.8	209	86.4
$^{13}C_8$-PFOA	40	130	82.6	85.1	90	88.7	75	78.6	71.1	105.5	87.3	94.2	209	85.9
$^{13}C_9$-PFNA	40	130	81.2	89.7	94	88.5	69.5	77.6	66.5	103.6	86	91.8	209	84.9
$^{13}C_6$-PFDA	40	130	77.1	84.1	92.4	87	70	77.2	67.1	101.5	86.3	92	209	83.5
$^{13}C_7$-PFUnA	30	130	72	83.2	106.8	92.1	74.7	75.3	70.5	101.8	90.1	88.1	209	85.5
$^{13}C_2$-PFDoA	10	130	64.7	76	107	84.7	67.7	70.5	60.9	95.5	90	88.5	209	80.6
$^{13}C_2$-PFTeDA	10	130	61.8	73.2	111.3	79.2	68.8	57.5	57	83.2	91.1	78.2	209	76.2
$^{13}C_3$-PFBS	40	135	77.5	90.7	85.8	84.3	78.8	78.2	70.1	113	84	94.4	209	85.7
$^{13}C_3$-PFHxS	40	130	83.9	85.8	92.7	85.6	75.2	76.2	69	105.9	86.2	93.7	209	85.5
$^{13}C_8$-PFOS	40	130	81.6	79.8	91	91.8	75.5	80.1	67	105.5	85.5	100	209	85.8
$^{13}C_2$-4:2FTS	40	200	89.6	122.1	142.4	98.7	74.1	85.2	69.6	162.3	102.9	106.1	209	105.5
$^{13}C_2$-6:2FTS	40	200	96.4	93.7	124.1	106.6	77.2	87.2	64.2	146	105.8	104	209	100.6
$^{13}C_2$-8:2FTS	40	300	123.8	113.6	187.5	108.8	84.8	102.6	59	140.9	115	91.4	209	112.9
$^{13}C_8$-PFOSA	40	130	71.4	85.9	91.8	77.5	78.3	65.6	58.5	98.1	84.4	84.5	209	79.6
D_3-NMeFOSA	10	130	64.8	70	80.2	21.2	52.5	54.4	38.3	**--** [2]	72.8	54.7	188	56.6
D_5-NEtFOSA	10	130	62.3	62.4	75.5	17.9	50.1	50.5	35.6	**--**	51.5	52.5	188	50.9
D_3-NMeFOSAA	40	170	63.2	94.3	133	86.9	82.3	66	63.9	91	80.6	94.6	209	85.6
D_5-NEtFOSAA	25	135	63.4	97.4	117.3	87.9	82.3	67.6	73.5	90.9	81.8	91.2	209	85.3
D_7-NMeFOSE	10	130	58.4	72.7	100.2	42	62.7	56.2	32.2	78.5	76.6	73.6	209	65.3
D_9-NEtFOSE	10	130	62.1	74.5	85.4	41.1	62.9	56.3	33.9	72.1	73.1	71.7	209	63.3
$^{13}C_3$-HFPO-DA	40	130	82.5	91.5	86	86.4	71.1	80.4	72.2	113.5	89.8	90.7	209	86.5

Notes:

1 EIS Limits from EPA Method 1633 Ver 4. Table 6.
2 EIS data rejected for QC failures.

7 SEDIMENTS

A total of 21 study samples were shipped to each participating laboratory, as described in Section 2 of this report. This included a single unspiked sample, triplicate low- and triplicate high-spiked samples, in two freshwater sediment and one marine sediment samples. All sediment samples were prepared and analyzed by EPA Method 1633. As stated in Section 2, Laboratory 2 did participate in the sediment phase of this project. In addition, data from Laboratory 5 was omitted from the statistical analysis due to a calculation error that could not be rectified. Results for sample SDZ5 submitted by Laboratory 9 were omitted due to an apparent spiking error (concentrations detected at approximately two times stated spike concentrations). Data were reported and validated in accordance with the requirements of the Study Plan. The rules for use/omission of individual analyte results are presented in *Volume I*, Section 3.

7.1 NATIVE PFAS CONCENTRATIONS IN SEDIMENTS

The background native concentrations first measured prior to setting the spiking concentrations were done by SGS AXYS. Each laboratory received and analyzed a single sample of each sediment sample. The concentrations measured by the eight individual laboratories are given in Table 7-1, which also includes the original background concentration measured by SGS AXYS for comparison. The concentrations detected in this sample were considered the background or "native" concentration for each of the environmental matrices for each laboratory.

Table 7-2 summarizes the detections reported by each laboratory for the three sediment samples, as well as the results from the reconnaissance analysis.

Of the 40 PFAS target analytes in the draft EPA Method 1633, 25 were not detected in any of the three sediment samples by any of the eight laboratories included in the statistical analysis of the sediment portion of the validation study, nor by the reconnaissance laboratory. The 15 detected target analytes were: PFOA, PFHxS, PFOS, PFDoS, 6:2FTS, PFBA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFTrDA, PFOSA, NMeFOSAA, and NEtFOSE. The majority of detections were between the laboratory-derived MDL and LOQ, therefore are estimated values, as indicated by the "J" data qualifier. Of the six detections reported for sample SDAA1, only one detection, for PFOA, reported by Laboratory 1, was reported at a concentration above the laboratory's LOQ.

Although there was considerable overall agreement across all of the laboratories, the results for the unspiked samples did vary across both the samples and the laboratories. Across the three soil samples, five to eighteen of the target analytes were reported by at least one of the eight laboratories that completed the aqueous portion of the Study, as shown in Table 7-2. Of the 40 PFAS target analytes in the draft EPA Method 1633, PFOS was the only target analyte detected by every laboratory in a sample (SDY1).

7.2 SEDIMENT MATRIX SPIKE RESULTS

The spiked sediment samples were evaluated to demonstrate the precision and accuracy of EPA Method 1633 on real-world samples. Isotope dilution methods typically do not include the use of matrix spike (MS) and matrix spike duplicate (MSD) samples as part of the sample preparation batch QC elements. An objective of this Study was to demonstrate performance of the method in real-world samples that contain target analytes.

As detailed in Section 2 of this report, the matrix spike samples created by Waters ERA were prepared and analyzed by each laboratory in accordance with EPA Method 1633. Preparation methods for the PFAS-spiked matrices are in Appendix A. A total of 21 sediment samples were sent to each laboratory. Three individual sediment matrices were analyzed for an unspiked sample, three low-spiked samples and three high-spiked samples. While 21 samples were sent to the laboratories, as noted previously sample results from Laboratory 9 for sample SDZ5 were excluded from the final data set due to spiking error.

The methods used by IDA to calculate the percent recoveries, within-laboratory standard deviation, within and between laboratory standard deviation and within-laboratory RSDs followed the ATP-prescribed methods (EPA 2018); these are presented in, Appendix D. The rules applied to the sediment data set for statistical analyses were described in Section 3.4. The results of the determination of the matrix spike recoveries for the individual samples are presented in Appendix D.

The compiled (all laboratory) PFAS-spiked sediment samples are given in Table 7-3, organized as low-spiked samples, high-spiked samples, and the combined low- and high-spiked sample results. Results are also shown in Figures 7-1 and 7-2. Supporting individual laboratory spike recovery data are given in Appendix D, Tables D-1 (low-spiked) and D-2 (high-spiked).

The trends in spiked results were similar to that observed for soil, with some exceptions. The low-spiked sample mean percent recovery for each target analyte fell between 67.6–92.1% (PFDoS and PFMBA, respectively) (Table 7-3). For the high-spiked samples, the range was 68.7–120% (PFDoS and NEtFOSAA, respectively), with the combined low/high-spiked data from 68.2–92.4% (PFDoS and PFMBA, respectively). Variability, as indicated by the pooled between-laboratory standard deviation (s_b) was slightly greater in the high-spiked samples than in the low-spiked samples (31 of the 40 target analytes). The pooled within-laboratory standard deviation (s_w) was slightly greater in the low-spiked samples than in the high-spiked samples for most target analytes (26 of the 40 target analytes).

The highest pooled between-laboratory standard deviation in the low-spiked, high-spiked, and combined low- and high-spiked samples was observed for PFTrDA; 30.7, 30.2, and 30.5, respectively. One possible reason why this pooled between-laboratory standard deviation is significantly greater than that of any other target analyte may be the fact that for this target analyte only, laboratories used different EIS compounds for quantification. Due to software limitations, some laboratories did not utilize the average of $^{13}C_2$-PFDoA and $^{13}C_2$-PFTeDA to quantitate PFTrDA, as stated in the method. Some laboratories used $^{13}C_2$-PFTeDA only, while others used $^{13}C_2$-PFDoA only.

The highest pooled within-laboratory standard deviation in the low-spiked, high-spiked, and combined low- and high-spiked samples was observed for 6:2FTS; 14.6, 14.7, and 18.5, respectively. These elevated pooled within-laboratory standard deviations can be attributed to Laboratories 6 and 8 (Figures 7-1 and 7-2).

In general, the variability observed in the low-spiked samples were also observed in the high-spiked samples. In some instances, high variability can be attributed to the results from specific laboratories. This is the case for the variability associated with PFDoS, 6:2FTS, and PFMPA. Laboratories 1 and 10 exhibited very low recoveries for PFDoS when compared to all other laboratories. The recoveries for PFDoS from Laboratories 1 and 10 where almost all less than 40% (100% and 88.9%, respectively for the low-spiked samples and 55.6% and 66.7% respectively for high-spiked samples), while no other laboratories had recoveries that were less than 40% for PFDoS except for one recovery reported by Laboratory 6. Laboratories 6 and 8 exhibited statistically different recoveries than all other laboratories for 6:2FTS in that 50% of the low-spiked recoveries reported by Laboratory 8 were less than 40% when no other laboratories reported values below this threshold and Laboratories 6 and 8 had recoveries greater than 130% when no other laboratories reported values above this threshold. A third of the recoveries for PFMPA reported by Laboratory 6 were below 40%, while no other laboratories had recoveries that were less than 40% for PFMPA, except for one recovery reported by Laboratory 4.

Comparison of the results for the two freshwater sediment samples and the one marine sediment sample is shown in Table 7-4. Generally, the mean % recoveries were similar for all compounds across all three samples.

7.3 SEDIMENT EXTRACTED INTERNAL STANDARD RESULTS

The range of concentrations of EIS used by the laboratories were the same as those for the soils (Table 6-5). The limits for EIS compounds defined by the MLVS Method were 20–150%. The combined results for the minimum, maximum, and average percent recovery is given in Table 7-5. Supporting individual laboratory results are in Appendix Table D-4. For the 8 laboratories the pooled average EIS percent recovery ranged between 45.1% (D_5-NEtFOSA) and 132.9% ($^{13}C_2$-8:2FTS). The range of values by individual laboratories ranges from 6.6–279%. Table 7-6 presents the pooled sediment EIS percent recovery; all mean percent recoveries were within the MLVS method-specified target recovery.

Figures 7-4 show that the highest variability in EIS compound recoveries for all laboratories were associated with the same EIS compounds ($^{13}C_4$-PFBA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE) as in soil samples. Three laboratories showed overall lower EIS recovery. Laboratories 6 and 9 had poor and highly variable recovery for $^{13}C_4$-PFBA, with recoveries as low as 8.1 and 10%, respectively.

Table 7-1. Summary of Target Analytes Detected in Unspiked Sediment Samples in µg/kg

Analyte	Number of Labs	Lab 1		Lab 3		Lab 4		Lab 6		Lab 7		Lab 8		Lab 9		Lab 10		Axys-SGS Baseline
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	
SDAA1 - Sequim Bay Sediment																		
PFOA	8	0.215		0.052	U	0.0509	U	0.0315	U	0.076	U	0.0667	U	0.036	U	0.051	U	< 0.03655
PFHxS	8	0.015	U	0.059	U	0.13	U	0.0363	U	0.16	U	0.0609	U	0.082	J	0.036	U	< 0.03655
PFOS	8	0.0414	U	0.079	U	0.132	U	0.0426	U	0.07	U	0.0619	U	0.086	J	0.051	U	< 0.03655
PFDoS	8	0.059	U	0.038	U	0.0976	U	0.0309	U	0.15	U	0.0647	U	0.069	JI	0.027	U	< 0.03655
6:2FTS	8	0.259	J	0.28	U	0.187	U	0.193	U	0.35	U	3.53	J	0.139	U	0.305	UJ	< 0.1317
SDY1 - Burley 1 Sed. Burley Creek, WA																		
PFBA	8	0.14	U	0.072	J	0.0514	U	0.0872	U	0.31	U	0.267	U	0.144	U	0.083	U	< 0.1694
PFHxA	8	0.0579	U	0.056	J	0.109	U	0.0375	U	0.075	U	0.0667	U	0.078	U	0.297	BJ+	Q 0.05227
PFHpA	8	0.0429	U	0.04	J	0.0886	U	0.0675	U	0.06	U	0.0667	U	0.03	U	0.044	U	< 0.04235
PFOA	8	0.0453	U	0.064	J	0.0509	U	0.0315	U	0.076	U	0.0667	U	0.036	U	0.0896	BJ+	< 0.04235
PFNA	8	0.0583	U	0.208		0.0444	U	0.0459	U	0.12	U	0.0667	U	0.044	U	0.05	U	< 0.04235
PFDA	8	0.128	U	0.075	U	0.0559	U	0.0618	U	0.036	U	0.0667	U	0.038	U	0.0395	JI	Q 0.05550
PFUnA	8	0.102	U	0.232		0.115	U	0.024	U	0.13	U	0.0667	U	0.03	U	0.031	U	< 0.04235
PFTrDA	8	0.0403	U	0.056	J	0.0323	U	0.0339	U	0.1	U	0.0667	U	0.031	U	0.022	U	< 0.04235
PFHxS	8	0.015	U	0.059	U	0.13	U	0.0363	U	0.16	U	0.0609	U	0.045	J	0.036	U	< 0.04235
PFOS	8	0.253		0.176	J	0.307		0.328		0.36		0.367		0.243		0.367		0.3066
PFDoS	8	0.059	U	0.112	JI	0.0976	U	0.0309	U	0.15	U	0.0647	U	0.028	U	0.027	U	< 0.04235
6:2FTS	8	0.144	U	0.28	U	0.187	U	0.193	U	0.35	U	4.21	J	0.139	U	0.305	UJ	< 0.1527
PFOSA	8	0.0977	U	0.043	U	0.0305	U	0.0273	U	0.08	U	0.0667	U	0.064	J	0.014	U	< 0.04235
NMeFOSAA	8	0.101	U	0.1	UJ	0.12	U	0.0318	U	0.16	U	0.0916	J	0.07	J	0.108	J	0.0716
SDZ1 - Burley 2 Sed. Burley Creek, WA																		
PFHxA	8	0.0579	U	0.046	U	0.109	U	0.0375	U	0.075	U	0.0667	U	0.078	U	0.168	BJ+I	< 0.03814
PFOA	8	0.172	J	0.052	U	0.0849	JI	0.0315	U	0.076	U	0.0667	U	0.036	U	0.0941	BJ+	< 0.03814
PFHxS	8	0.0159	J	0.059	U	0.13	U	0.0363	U	0.16	U	0.0609	U	0.033	U	0.036	U	< 0.03814
PFOS	8	0.0822	J	0.079	U	0.132	U	0.0426	U	0.07	U	0.0619	U	0.052	U	0.051	U	0.03941

Table 7-1. Summary of Target Analytes Detected in Unspiked Sediment Samples in µg/kg (Continued)

Analyte	**Number of Labs**	**Lab 1**		**Lab 3**		**Lab 4**		**Lab 6**		**Lab 7**		**Lab 8**		**Lab 9**		**Lab 10**		**Axys-SGS Baseline**
		Conc	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	**Conc**	**Qual**	
6:2FTS	8	0.144	U	0.536	J	0.187	U	0.193	U	0.35	U	3.58	J	0.139	U	0.305	U	< 0.1375
NEtFOSE	8	0.165	J	0.51	U	0.444	U	0.309	U	0.83	U	0.667	U	0.442	U	0.063	U	< 0.2853
Total # Analytes Reported Across All samples		7		10		2		1		1		5		7		7		5

Version: Summary_tables_Exa_CH7_10312023.xlsx

Table 7-2. Numbers of Detected Analytes in Unspiked Sediment Samples

Sediment Sample	**Total Number of Analytes Detected by at least One Laboratory**
SDAA1 - Sequim Bay Sediment	5
SDY1 - Burley 1 Sed. Burley Creek, WA	14
SDZ1 - Burley 2 Sed. Burley Creek, WA	6

Version: Summary_tables_Exa_CH7_10312023.xlsx

Table 7-3. Pooled Laboratory PFAS-Spiked Sediment Samples Results. Low-spiked, High-spiked, and Combined Low/High-Spiked Samples

Analyte	Number of Labs	Low-Spiked Samples					High-Spiked Samples					Combined Low/High-Spiked Samples				
		Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)
PFBA	8	69	89.7	15	6.0	6.7	64	93.4	14.1	6.1	6.5	133	91.5	14.2	7.05	7.71
PFPeA	8	72	91.3	14.4	7.4	8.1	68	91.3	16.2	6.5	7.2	140	91.3	15	7.44	8.15
PFHxA	8	72	90.8	16.3	7.5	8.3	68	89.7	15.3	7.2	8.0	140	90.3	15.7	7.62	8.44
PFHpA	8	72	86.8	14.5	7.0	8.1	68	89	16.1	7.1	8.0	140	87.8	15	7.33	8.35
PFOA	8	72	87.4	16.9	8.4	9.7	68	88.8	16.4	7.7	8.7	140	88.1	16.5	8.11	9.21
PFNA	8	72	85.4	19.3	6.9	8.1	68	84.9	21	8.0	9.5	140	85.1	20	7.6	8.93
PFDA	8	72	87.7	21.5	10.7	12.3	68	87.5	23.4	9.7	11.1	140	87.6	22.3	10.3	11.8
PFUnA	8	72	85.1	21.2	11.0	13.0	68	83.8	24.8	9.9	11.8	140	84.5	22.6	10.8	12.7
PFDoA	8	72	85.6	24.9	9.8	11.4	68	82.3	26.5	10.4	12.6	140	84	25.6	10.1	12
PFTrDA	8	72	87.1	30.7	10.6	12.2	68	83.8	30.2	14.0	16.7	140	85.5	30.5	12.2	14.2
PFTeDA	8	72	84.5	26	11.0	13.0	68	81.3	26.3	11.1	13.6	140	83	26.1	10.9	13.2
PFBS	8	72	90.5	14.9	6.6	7.3	68	91.7	19.7	8.9	9.7	140	91.1	16.6	8.77	9.63
PFPeS	8	72	89.8	17	6.0	6.7	68	92.9	15.9	8.3	8.9	140	91.3	16.3	7.69	8.42
PFHxS	8	72	90.7	16.4	6.8	7.5	68	93.1	19.1	7.8	8.3	140	91.9	17.5	7.79	8.48
PFHpS	8	72	87.7	17.9	7.7	8.8	68	90.8	18.2	6.9	7.6	140	89.2	17.6	8.01	8.98
PFOS	8	72	84.4	17.5	7.3	8.6	68	86.1	18.6	7.6	8.8	140	85.2	17.8	7.84	9.19
PFNS	8	72	84.4	23	9.9	11.7	68	85.1	24.9	8.5	10.0	140	84.7	23.8	9.28	11
PFDS	8	72	77.7	21.8	10.7	13.8	68	77.8	22.8	8.6	11.1	140	77.8	22.1	9.81	12.6
PFDoS	8	72	67.7	25.1	10.5	15.5	68	68.7	25.2	11.7	17.0	140	68.2	25	10.9	16
4:2FTS	8	72	86.2	15.4	9.1	10.6	68	88.3	14.4	8.8	10.0	140	87.2	14.7	9.26	10.6
6:2FTS	8	69	83.6	15.8	14.4	17.2	68	92	18	14.7	16.0	137	87.8	12.8	18.5	21.1
8:2FTS	8	72	91.3	21.9	13.0	14.3	68	92.4	23.7	12.6	13.6	140	91.8	22.4	13.1	14.3
PFOSA	8	72	83.8	17.6	7.6	9.0	68	83.5	19	8.2	9.8	140	83.7	18.1	8.12	9.71

Table 7-3. Pooled Laboratory PFAS-Spiked Sediment Samples Results. Low-spiked, High-spiked, and Combined Low/High-spiked Samples (Continued)

Analyte	Number of Labs	Low-Spiked Samples					High-Spiked Samples					Combined Low/High-spiked Samples				
		Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)
NMeFOSA	7	63	80.3	17.8	9.2	11.5	60	79.7	19.7	9.9	12.4	123	80	18.5	9.76	12.2
NEtFOSA	7	60	82.2	19.5	9.2	11.1	60	83.4	21.9	10.3	12.4	120	82.8	20.3	10.1	12.2
NMeFOSAA	8	72	83.6	24	7.8	9.4	68	84.7	26.3	9.9	11.7	140	84.1	24.9	8.9	10.6
NEtFOSAA	8	72	86.2	20.9	8.7	10.1	68	84.4	21.9	11.0	13.0	140	85.4	21.2	9.97	11.7
NMeFOSE	8	72	82.3	22.4	9.0	11.0	68	81.3	25.1	10.6	13.1	140	81.8	23.5	9.95	12.2
NEtFOSE	8	72	83.7	23.8	9.3	11.1	68	81.4	25.9	10.5	13.0	140	82.6	24.7	9.95	12.1
PFMPA	8	72	86.9	19.1	11.9	13.7	68	85.1	21.2	15.0	17.7	140	86	20.1	13.4	15.5
PFMBA	8	72	92.1	16.5	8.9	9.6	68	92.8	17.1	8.9	9.6	140	92.4	16.4	9.25	10
NFDHA	8	72	87	14	12.9	14.8	68	90.5	15.4	11.2	12.4	140	88.7	14.3	12.4	13.9
HFPO-DA	8	72	89.4	14.6	7.6	8.5	68	92.3	13.5	8.0	8.7	140	90.8	13.9	8.01	8.82
ADONA	8	72	90.5	14	8.8	9.8	68	91.7	14.8	8.0	8.7	140	91.1	14.1	8.72	9.58
PFEESA	8	72	88.9	15.9	7.1	8.0	68	91.5	18	7.1	7.8	140	90.2	16.6	7.58	8.41
9Cl-PF3ONS	8	72	89.9	17	10.9	12.1	68	89.2	15.6	10.0	11.2	140	89.6	16.1	10.5	11.8
11Cl-PF3OUdS	8	72	77.8	19.4	13.0	16.8	68	79.4	20.3	10.8	13.5	140	78.6	19.5	11.9	15.2
3:3FTCA	8	72	78.1	15	9.1	11.6	68	85.6	16.3	12.6	14.8	140	81.8	15.3	11.8	14.5
5:3FTCA	8	72	78.4	20.1	12.3	15.7	68	83.3	18.5	10.5	12.6	140	80.8	19	12.4	15.4
7:3FTCA	8	72	81.8	20.7	12.9	15.8	68	86.6	24.3	12.3	14.2	140	84.1	22.1	13.3	15.8

Source: SD_Matrix_compiled_results_V0_2.csv

Notes:
Number of Labs - The number of laboratories reporting matrix spiked sample results.
Number of Results - The total number of matrix sample results categorized as low/high-spiked concentration that do not have a U flag.
Mean % Recovery - The mean percent recovery for low/high-spiked samples across all laboratories.
s_b - The pooled between-laboratory standard deviation of the percent recovery for low-spiked samples. Equation from EPA 821-B-18-001 page G-25.
s_w - The pooled within-laboratory standard deviation of the percent recovery for low-spiked samples. Equation from EPA 821-B-18-001 page G-25.
RSD - The pooled within-laboratory relative standard deviation for low/high-spiked samples (RSD, (sw / (mean % recovery) *100)).

Table 7-4. PFAS-Spiked Samples Results by Individual Sediment Sample

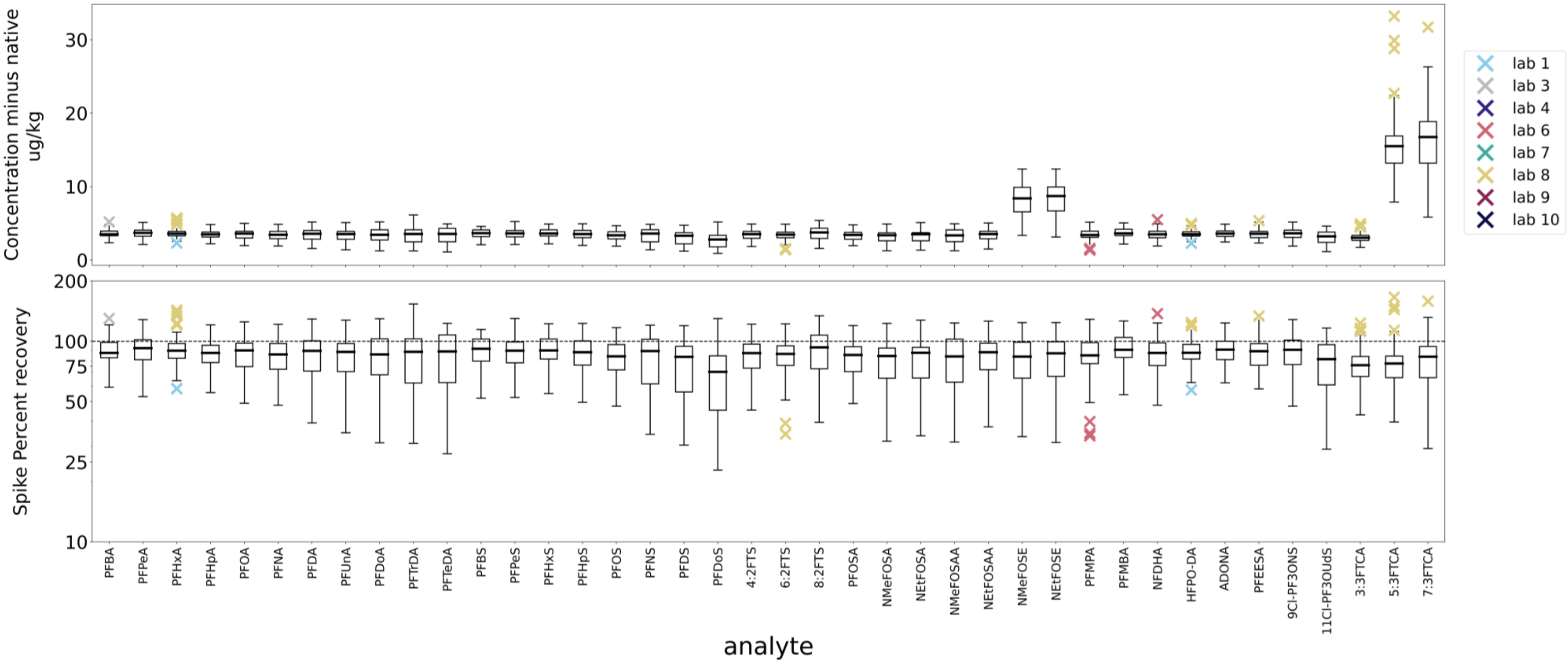
Analyte	SDAA				SDY				SDZ			
	Sequim Bay Marine Sediment				Burley Creek 1 Freshwater Sediment				Burley Creek 2 Freshwater Sediment			
	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery
PFBA	7	42	95.0	67.5 - 120	8	45	89.0	59 - 130	8	46	90.7	64 - 123
PFPeA	8	48	93.3	68.2 - 125	8	45	90.1	60.5 - 128	8	47	90.5	53 - 120
PFHxA	8	48	91.8	66.5 - 126	8	45	90.3	57.6 - 143	8	47	88.8	65.3 - 124
PFHpA	8	48	89.6	56.5 - 119	8	45	85.3	55.5 - 104	8	47	88.4	60.8 - 126
PFOA	8	48	86.4	49.1 - 116	8	45	91.1	60 - 125	8	47	86.8	58.4 - 129
PFNA	8	48	83.9	46.4 - 121	8	45	86.2	51.2 - 118	8	47	85.4	53.2 - 126
PFDA	8	48	84.6	39.2 - 134	8	45	89.8	61.3 - 128	8	47	88.5	54.4 - 129
PFUnA	8	48	79.8	35 - 128	8	45	86.3	47 - 120	8	47	87.5	56.8 - 135
PFDoA	8	48	80.5	29.1 - 124	8	45	84.3	44.8 - 123	8	47	87.2	47.6 - 130
PFTrDA	8	48	80.7	31 - 145	8	45	87.4	48.4 - 166	8	47	88.6	48.8 - 163
PFTeDA	8	48	78.6	27.5 - 125	8	45	84.1	46 - 123	8	47	86.3	49.2 - 122
PFBS	8	48	95.1	59 - 128	8	45	86.6	52 - 120	8	47	91.2	64 - 126
PFPeS	8	48	92.5	61.9 - 131	8	45	89.2	52.5 - 121	8	47	92.1	65.3 - 130
PFHxS	8	48	92.4	54.9 - 135	8	45	90.6	55.1 - 134	8	47	92.5	63.9 - 133
PFHpS	8	48	88.5	49.6 - 126	8	45	89.8	54.1 - 123	8	47	89.4	59.6 - 122
PFOS	8	48	83.7	47.5 - 122	8	45	85.2	56.4 - 115	8	47	86.8	59.5 - 122
PFNS	8	48	82.3	34.4 - 132	8	45	84.8	46.8 - 122	8	47	87.1	54.8 - 131
PFDS	8	48	74.1	30.4 - 113	8	45	80.1	31.8 - 120	8	47	79.2	42.8 - 116
PFDoS	8	48	67.4	23.5 - 122	8	45	67.2	18 - 130	8	47	69.9	28.6 - 116
4:2FTS	8	48	89.6	55.1 - 114	8	45	85.0	41.6 - 122	8	47	86.9	45.4 - 112
6:2FTS	8	48	88.4	39 - 166	7	42	87.7	54.8 - 150	8	47	87.2	34.5 - 123
8:2FTS	8	48	85.5	39.5 - 137	8	45	93.8	58 - 134	8	47	96.3	57.1 - 132
PFOSA	8	48	80.3	49 - 110	8	45	84.6	54.4 - 119	8	47	86.2	50.4 - 120
NMeFOSA	7	42	75.7	31.8 - 113	7	40	84.1	51.6 - 123	7	41	80.5	46 - 106
NEtFOSA	7	42	77.8	33.8 - 128	7	37	86.9	52 - 128	7	41	84.1	46.8 - 118

Table 7-4. PFAS-Spiked Samples Results by Individual Sediment Sample (Continued)

Analyte	SDAA				SDY				SDZ			
	Sequim Bay Marine Sediment				Burley Creek 1 Freshwater Sediment				Burley Creek 2 Freshwater Sediment			
	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery
NMeFOSAA	8	48	81.6	29.2 - 126	8	45	84.5	46.5 - 120	8	47	86.4	45.8 - 126
NEtFOSAA	8	48	82.3	33.2 - 122	8	45	86.1	49.6 - 126	8	47	87.8	52.8 - 121
NMeFOSE	8	48	80.5	33.5 - 132	8	45	80.8	43.2 - 122	8	47	84.1	47.4 - 127
NEtFOSE	8	48	80.5	31.3 - 123	8	45	81.5	41.4 - 124	8	47	85.7	47.6 - 122
PFMPA	8	48	87.9	33.2 - 132	8	45	87.8	51.6 - 123	8	47	82.5	31.4 - 129
PFMBA	8	48	94.6	65.2 - 129	8	45	90.8	56.8 - 119	8	47	91.7	54.2 - 127
NFDHA	8	48	92.6	55.5 - 143	8	45	87.1	48 - 138	8	47	86.3	54.2 - 115
HFPO-DA	8	48	92.8	64.8 - 120	8	45	88.8	57.2 - 119	8	47	90.7	63.5 - 126
ADONA	8	48	92.4	62.4 - 124	8	45	90.8	58.2 - 118	8	47	89.9	68.2 - 124
PFEESA	8	48	92.9	66.6 - 134	8	45	89.3	57.9 - 134	8	47	88.3	59.8 - 136
9Cl-PF3ONS	8	48	89.7	47.5 - 121	8	45	88.9	52.5 - 128	8	47	90.1	63.2 - 121
11Cl-PF3OUdS	8	48	76.2	29 - 122	8	45	79.5	38.4 - 116	8	47	80.1	44.2 - 121
3:3FTCA	8	48	88.5	63.2 - 123	8	45	75.8	43 - 108	8	47	80.5	50.7 - 122
5:3FTCA	8	48	87.5	53 - 133	8	45	80.7	39.6 - 166	8	47	74.1	46.8 - 119
7:3FTCA	8	48	87	43.5 - 131	8	45	88.9	46.4 - 158	8	47	76.6	29.2 - 120

Source file: SD_Matrix_sample_results_V0.csv

Notes:
Number of Labs - The number of laboratories reporting matrix spiked sample results.
Number of Results - The total number of results for the samples that do not have a U flag.
Mean % Recovery - The mean percent recovery for samples across all laboratories.
Range % Recovery - The minimum to maximum percent recovery for samples across all laboratories.



Source file: SD_LowSpike_Boxplot_V1_231122_100457

Figure 7-1. Sediment Low-spiked Results by Analyte by Laboratory

(A) Spiked concentration minus the laboratory-reported native concentration. (B) Calculated percent recovery.

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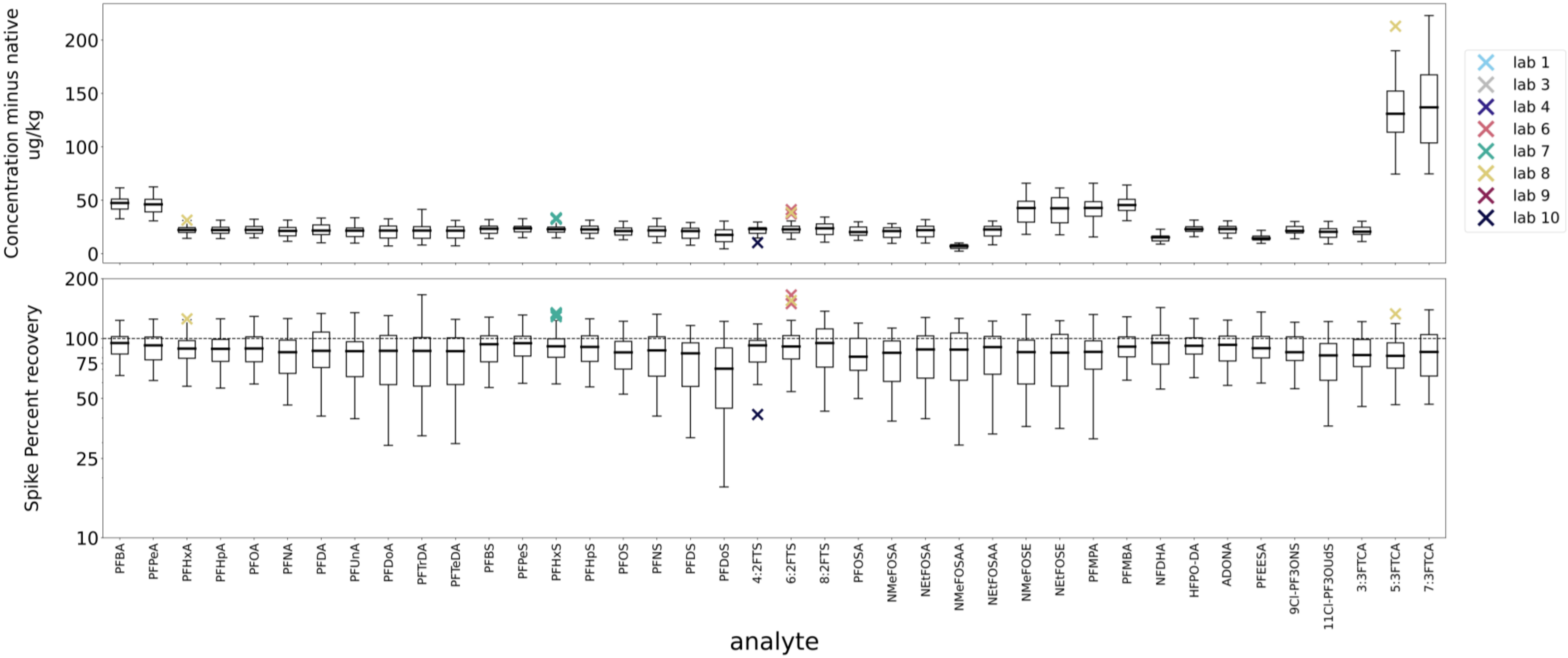
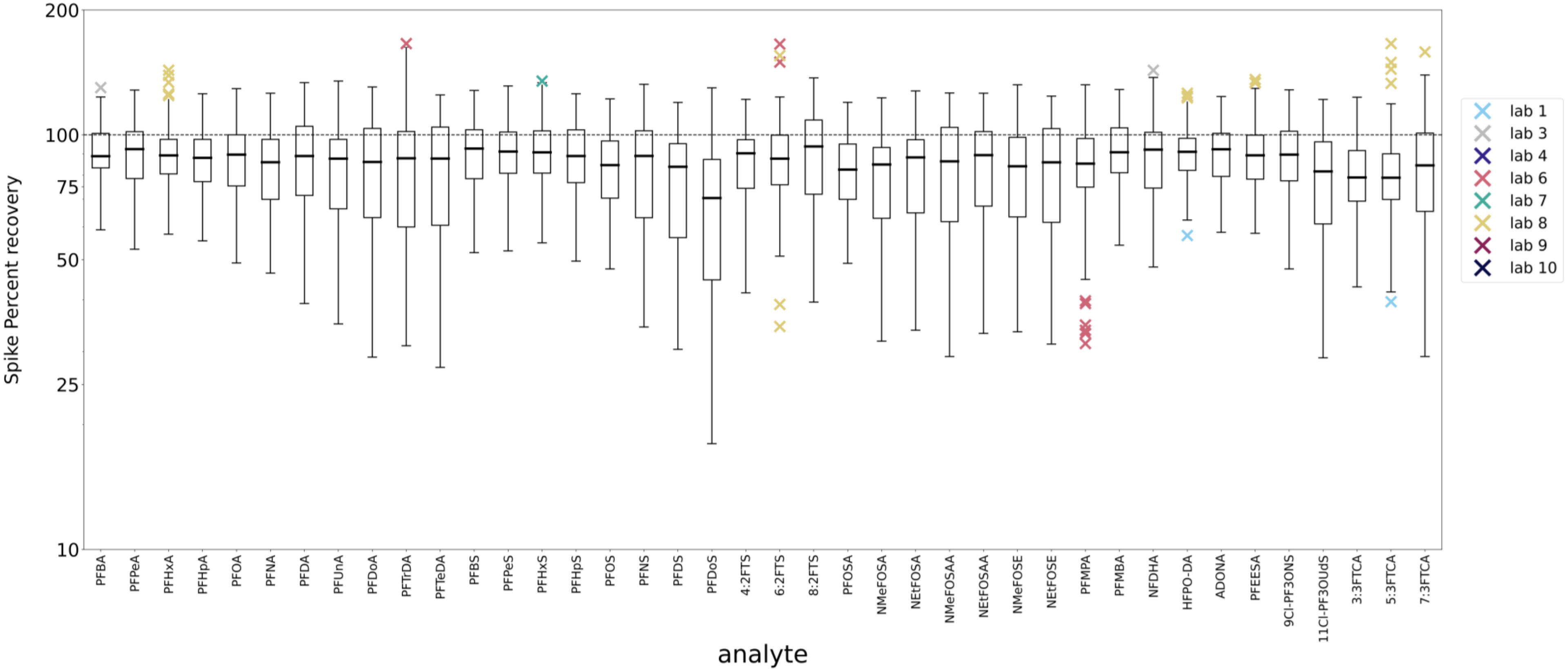


Source file: SD_HighSpike_Boxplot_V1_231122_100457

Figure 7-2. Sediment High-spiked Results by Analyte by Laboratory

(A) Spiked concentration minus the laboratory-reported native concentration. (B) Calculated percent recovery.



Source file: SD_LowHighCombinedSpike_Boxplot_V1_231122_100457

Figure 7-3. Pooled Low- and High-spiked Sediment Percent Recovery Results by Analyte by Laboratory

Table 7-5. Summary of EIS Compound Percent Recovery in Sediment Samples for all Laboratories

EIS Compound	All Laboratories			
	n	Min	Max	Mean
$^{13}C_4$-PFBA	164	8.09	116	77.9
$^{13}C_5$-PFPeA	164	32.2	135	84.4
$^{13}C_5$-PFHxA	171	45.3	128	88.4
$^{13}C_4$-PFHpA	164	44.4	126	87.3
$^{13}C_8$-PFOA	162	51	126	86.8
$^{13}C_9$-PFNA	164	53	128	87.2
$^{13}C_6$-PFDA	164	53.3	115	85.2
$^{13}C_7$-PFUnA	164	35	129	85.4
$^{13}C_2$-PFDoA	164	35	132	81.2
$^{13}C_2$-PFTeDA	164	20.4	132	69.9
$^{13}C_3$-PFBS	164	55	145	90.2
$^{13}C_3$-PFHxS	164	45.4	128	88.2
$^{13}C_8$-PFOS	164	55	120	88.4
$^{13}C_2$-4:2FTS	164	45	272	115.7
$^{13}C_2$-6:2FTS	164	51	279	116.1
$^{13}C_2$-8:2FTS	164	50	276	132.9
$^{13}C_8$-PFOSA	164	40.7	122	80.5
D_3-NMeFOSA	146	6.7	101	52
D_5-NEtFOSA	146	6.6	90	45.1
D_3-NMeFOSAA	164	49.5	182	94
D_5-NEtFOSAA	164	36.7	184	93.1
D_7-NMeFOSE	164	16	133	61.9
D_9-NEtFOSE	164	16	122	58.4
$^{13}C_3$-HFPO-DA	164	49	138	87.7

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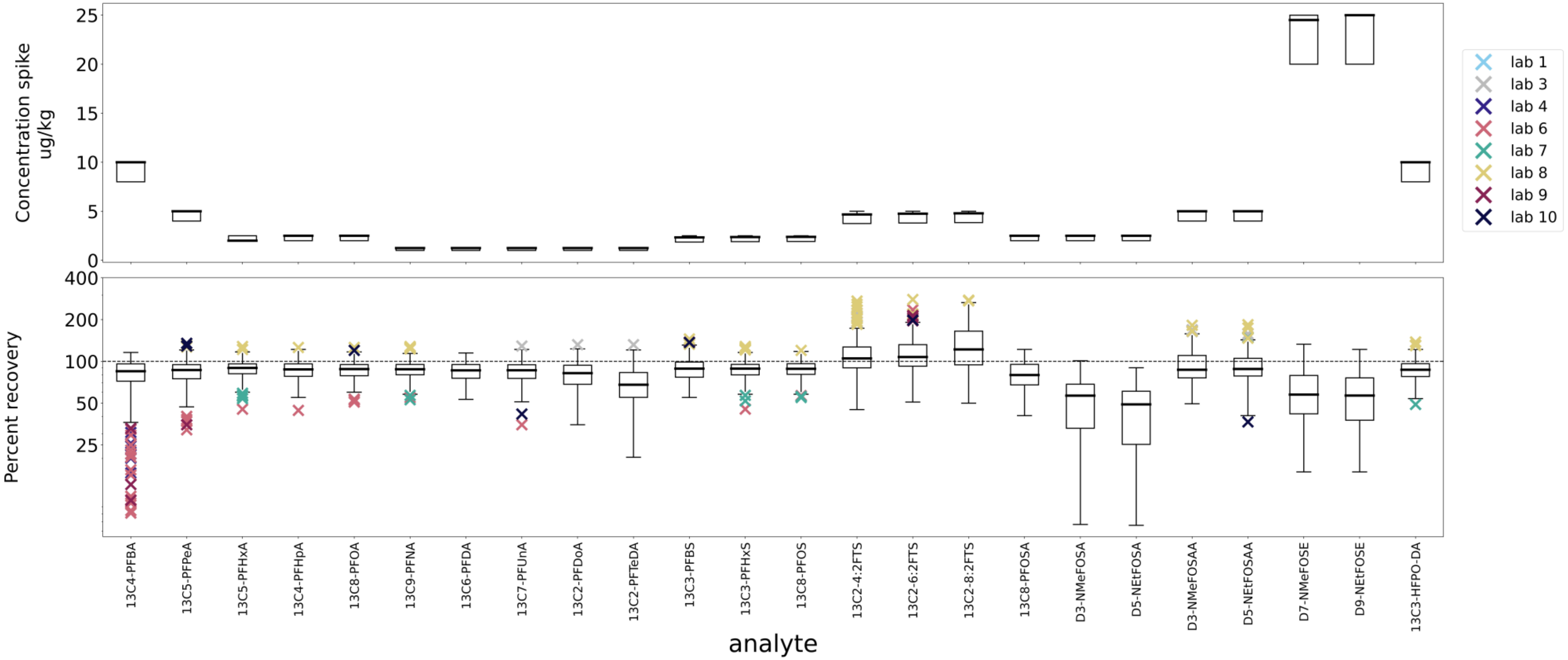
Does not include MB, OPR, LLOPR QC samples.

Table 7-6. EIS Results Associated with Sediment Samples

EIS Compounds	Number of Labs	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)
$^{13}C_4$-PFBA	8	164	77.9	22.8	18.5	23.7
$^{13}C_5$-PFPeA	8	164	84.4	18.8	10.5	12.5
$^{13}C_5$-PFHxA	8	171	88.3	13.7	7.73	8.75
$^{13}C_4$-PFHpA	8	164	87.3	12.8	8.75	10
$^{13}C_8$-PFOA	8	162	86.8	12	8.11	9.35
$^{13}C_9$-PFNA	8	164	87.2	13	8.15	9.34
$^{13}C_6$-PFDA	8	164	85.2	11.9	8.79	10.3
$^{13}C_7$-PFUnA	8	164	85.4	12.6	11.3	13.3
$^{13}C_2$-PFDoA	8	164	81.2	13.1	12.5	15.4
$^{13}C_2$-PFTeDA	8	164	69.9	18.1	13.9	19.9
$^{13}C_3$-PFBS	8	164	90.2	16.3	10.3	11.4
$^{13}C_3$-PFHxS	8	164	88.1	13	8.6	9.76
$^{13}C_8$-PFOS	8	164	88.3	14.3	7.42	8.4
$^{13}C_2$-4:2FTS	8	164	116	39.1	26.2	22.6
$^{13}C_2$-6:2FTS	8	164	116	32.9	28.9	24.9
$^{13}C_2$-8:2FTS	8	164	133	42.7	38.1	28.7
$^{13}C_8$-PFOSA	8	164	80.5	13.8	14.4	17.9
D_3-NMeFOSA	7	146	52	19.4	15.3	29.5
D_5-NEtFOSA	7	146	45.1	16.9	14.6	32.4
D_3-NMeFOSAA	8	164	94	22	16.7	17.7
D_5-NEtFOSAA	8	164	93.1	18.2	18.4	19.8
D_7-NMeFOSE	8	164	61.8	25.7	13.8	22.3
D_9-NEtFOSE	8	164	58.4	22.8	14.5	24.8
$^{13}C_3$-HFPO-DA	8	164	87.7	14.4	9.28	10.6

Source file: SD_EIS_results_V0.csv

Notes:
Number of Labs - The number of laboratories reporting matrix (native & spiked) results.
Number of Results - The total number of matrix results that do not have a U flag.
Mean % Recovery - The mean percent recovery across all of the EIS compound individual samples across all laboratories for the given analyte.
s_b - The pooled between-laboratory standard deviation. Equation from EPA 821-B-18-001page G-25.
s_w - The pooled within-laboratory standard deviation. Equation from EPA 821-B-18-001page G-25.
RSD - The pooled within-laboratory relative standard deviation (RSD, (s_w / (mean % recovery) *100).



Source file: SD_EIS_Boxplot_V1_231122_100457

Figure 7-4. Sediment EIS Compound Results by Compound by Laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.

7.4 SEDIMENT SUMMARY

The results for the spiked sediment samples are similar to those found for the soils and support a finding that EPA Method 1633 adequately measures PFAS concentrations in real-world surface samples. Results for both the low-spiked and the high-spiked samples were very similar (Figure 7-3). The pooled (low-spiked/high-spiked samples) average percent recoveries shown in Table 7-3 were between 68.2–92.4%. The individual laboratory results for all PFAS averaged from 18% (PFDoS, Laboratory 10) to 131.5% (PFTrDA, Laboratory 6) (Appendix D, Table D-3). The pooled between-laboratory standard deviations (s_b) were at 30%, the pooled within-laboratory standard deviations (s_w) less than 20%, with the RSD on s_w at 20%.

Tables 7-7 and 7-8 provides a summary of the relative proportions for all laboratories that fell between the Study's target percent recovery acceptance criteria of 40–150% that is used to evaluate the OPR and LLOPR (40–150%).

For the low-spiked samples, for 39 of the 40 PFAS-spiked samples, pooled matrix spiked samples were recovered at greater than 90% for between 40–150% of the spiked concentration (Table 7-7). The one exception was PFDoS for which 76.4% of the reported values (55 of 72) were within the target range. Also, for PFDoS, approximately 24% of the reported recovery values were less than 40% (17 of 72). Like soils, most of the reported recovery values were between 40–130%, but sediments were different from soils in that a larger portion occurred in the 40–70% range. For the high-spiked samples the results were the same: 39 of the 40 PFAS-spiked samples, pooled matrix spiked samples were recovered at greater than 90% for between 40–150% of the spiked concentration, with the exception of PFDoS.

Table 7-9 provides a summary of the relative proportions of the pooled low/high-spiked sample EIS compound recoveries. For these pooled EIS data, most of the recoveries were greater than 80%. For the low- and high-spiked samples, the proportion of all values that were between 20–150% of the spiked concentrations is >88%. The one exception is $^{13}C_2$-8:2FTS, for which 71% (116 of 164 measures) were between 20–150% recovery, with the other recoveries > 130%.

A comparison of the mean individual laboratory EIS percent recoveries relative to the acceptance limits for EIS compounds that EPA determined for all aquatic matrices and QC samples in the most recent draft of EPA Method 1633 (Version 4, Table 6) for the sediment evaluations is given in Table 7-10. For that comparison, average EIS percent recoveries for all compounds and all laboratories were within the acceptance criteria range, with the exception of $^{13}C_4$-PFBA and Laboratory 6 for which the average recovery was 36.6%.

Table 7-7. Proportion of Sediment Matrix Spiked Percent Recovery Results for Target Analytes within Ranges (Low-spiked Samples)

Analyte	All Labs Proportion % Recovery						
	n	<40%	≥40% to <70%	≥70% to <130%	≥130% to <150%	≥150% to <200%	≥200%
PFBA	69	0	10.1	88.4	1.4	0	0
PFPeA	72	0	6.9	93.1	0	0	0
PFHxA	72	0	9.7	86.1	4.2	0	0
PFHpA	72	0	15.3	84.7	0	0	0
PFOA	72	0	19.4	80.6	0	0	0
PFNA	72	0	22.2	77.8	0	0	0
PFDA	72	2.8	20.8	76.4	0	0	0
PFUnA	72	4.2	19.4	76.4	0	0	0
PFDoA	72	5.6	20.8	73.6	0	0	0
PFTrDA	72	4.2	27.8	55.6	11.1	1.4	0
PFTeDA	72	5.6	25	69.4	0	0	0
PFBS	72	0	13.9	86.1	0	0	0
PFPeS	72	0	16.7	81.9	1.4	0	0
PFHxS	72	0	13.9	86.1	0	0	0
PFHpS	72	0	18.1	81.9	0	0	0
PFOS	72	0	22.2	77.8	0	0	0
PFNS	72	2.8	26.4	70.8	0	0	0
PFDS	72	5.6	29.2	65.3	0	0	0
PFDoS	72	23.6	23.6	52.8	0	0	0
4:2FTS	72	0	20.8	79.2	0	0	0
6:2FTS	69	4.3	14.5	81.2	0	0	0
8:2FTS	72	1.4	22.2	73.6	2.8	0	0
PFOSA	72	0	25	75	0	0	0
NMeFOSA	63	3.2	25.4	71.4	0	0	0
NEtFOSA	60	3.3	25	71.7	0	0	0
NMeFOSAA	72	2.8	27.8	69.4	0	0	0
NEtFOSAA	72	1.4	23.6	75	0	0	0
NMeFOSE	72	2.8	26.4	70.8	0	0	0
NEtFOSE	72	5.6	23.6	70.8	0	0	0
PFMPA	72	4.2	11.1	84.7	0	0	0
PFMBA	72	0	9.7	90.3	0	0	0
NFDHA	72	0	16.7	81.9	1.4	0	0
HFPO-DA	72	0	11.1	88.9	0	0	0
ADONA	72	0	15.3	84.7	0	0	0
PFEESA	72	0	11.1	87.5	1.4	0	0
9Cl-PF3ONS	72	0	15.3	84.7	0	0	0
11Cl-PF3OUdS	72	6.9	25	68.1	0	0	0
3:3FTCA	72	0	30.6	69.4	0	0	0
5:3FTCA	72	1.4	27.8	66.7	2.8	1.4	0
7:3FTCA	72	2.8	29.2	65.3	1.4	1.4	0

Version: Summary_tables_Exa_CH7_10312023.xlsx

Note: Does not include MB, OPR, LLOPR QC samples.

Table 7-8. Proportion of Sediment Matrix Spiked Percent Recovery Results for Target Analytes within Ranges (High-spiked Samples)

Analyte	All Labs Proportion % Recovery						
	n	<40%	≥40% to <70%	≥70% to <130%	≥130% to <150%	≥150% to <200%	≥200%
PFBA	64	0	4.7	95.3	0	0	0
PFPeA	68	0	10.3	89.7	0	0	0
PFHxA	68	0	7.4	92.6	0	0	0
PFHpA	68	0	8.8	91.2	0	0	0
PFOA	68	0	20.6	79.4	0	0	0
PFNA	68	0	27.9	72.1	0	0	0
PFDA	68	0	22.1	76.5	1.5	0	0
PFUnA	68	1.5	30.9	66.2	1.5	0	0
PFDoA	68	2.9	30.9	64.7	1.5	0	0
PFTrDA	68	7.4	25	60.3	4.4	2.9	0
PFTeDA	68	8.8	25	66.2	0	0	0
PFBS	68	0	17.6	82.4	0	0	0
PFPeS	68	0	8.8	89.7	1.5	0	0
PFHxS	68	0	11.8	82.4	5.9	0	0
PFHpS	68	0	14.7	85.3	0	0	0
PFOS	68	0	22.1	77.9	0	0	0
PFNS	68	0	32.4	64.7	2.9	0	0
PFDS	68	7.4	27.9	64.7	0	0	0
PFDoS	68	17.6	30.9	51.5	0	0	0
4:2FTS	68	0	13.2	86.8	0	0	0
6:2FTS	68	0	17.6	77.9	1.5	2.9	0
8:2FTS	68	0	22.1	73.5	4.4	0	0
PFOSA	68	0	25	75	0	0	0
NMeFOSA	60	1.7	31.7	66.7	0	0	0
NEtFOSA	60	1.7	31.7	66.7	0	0	0
NMeFOSAA	68	1.5	30.9	67.6	0	0	0
NEtFOSAA	68	1.5	27.9	70.6	0	0	0
NMeFOSE	68	2.9	27.9	67.6	1.5	0	0
NEtFOSE	68	5.9	29.4	64.7	0	0	0
PFMPA	68	5.9	17.6	75	1.5	0	0
PFMBA	68	0	7.4	92.6	0	0	0
NFDHA	68	0	16.2	82.4	1.5	0	0
HFPO-DA	68	0	4.4	95.6	0	0	0
ADONA	68	0	7.4	92.6	0	0	0
PFEESA	68	0	7.4	89.7	2.9	0	0
9Cl-PF3ONS	68	0	11.8	88.2	0	0	0
11Cl-PF3OUdS	68	5.9	27.9	66.2	0	0	0
3:3FTCA	68	0	22.1	77.9	0	0	0
5:3FTCA	68	0	20.6	77.9	1.5	0	0
7:3FTCA	68	0	32.4	63.2	4.4	0	0

Version: Summary_tables_Exa_CH7_10312023.xlsx

Note: Does not include MB, OPR, LLOPR QC samples.

Table 7-9. Proportion of Sediment Percent Recovery Results for EIS Compounds within Ranges

EIS Compound	All Laboratories Proportion % Recovery					
	n	<10%	≥10% to <20%	≥20% to <150%	≥150% to <200%	≥200%
$^{13}C_4$-PFBA	164	1.8	4.3	93.9	0	0
$^{13}C_5$-PFPeA	164	0	0	100	0	0
$^{13}C_5$-PFHxA	171	0	0	100	0	0
$^{13}C_4$-PFHpA	164	0	0	100	0	0
$^{13}C_8$-PFOA	162	0	0	100	0	0
$^{13}C_9$-PFNA	164	0	0	100	0	0
$^{13}C_6$-PFDA	164	0	0	100	0	0
$^{13}C_7$-PFUnA	164	0	0	100	0	0
$^{13}C_2$-PFDoA	164	0	0	100	0	0
$^{13}C_2$-PFTeDA	164	0	0	100	0	0
$^{13}C_3$-PFBS	164	0	0	100	0	0
$^{13}C_3$-PFHxS	164	0	0	100	0	0
$^{13}C_8$-PFOS	164	0	0	100	0	0
$^{13}C_2$-4:2FTS	164	0	0	84.1	8.5	7.3
$^{13}C_2$-6:2FTS	164	0	0	82.3	12.8	4.9
$^{13}C_2$-8:2FTS	164	0	0	70.7	16.5	12.8
$^{13}C_8$-PFOSA	164	0	0	100	0	0
D_3-NMeFOSA	146	0.7	9.6	89.7	0	0
D_5-NEtFOSA	146	2.7	12.3	84.9	0	0
D_3-NMeFOSAA	164	0	0	94.5	5.5	0
D_5-NEtFOSAA	164	0	0	96.3	3.7	0
D_7-NMeFOSE	164	0	0.6	99.4	0	0
D_9-NEtFOSE	164	0	3.7	96.3	0	0
$^{13}C_3$-HFPO-DA	164	0	0	100	0	0

Version: Summary_tables_Exa_CH7_10312023.xlsx

Note: Does not include MB, OPR, LLOPR QC samples.

Table 7-10. Sediment Percent Recovery Results for EIS Compounds Compared to Acceptance Limits for Aqueous Matrices in EPA Method 1633

EIS Compound	**Acceptance Limits for EIS Compounds in All Aqueous Matrices and QC Samples** [1]		**Average EIS % Recovery by Laboratory for Sediments (Appendix D-4)**								**All Labs % recovery**	
			Lab 1	**Lab 3**	**Lab 4**	**Lab 6**	**Lab 7**	**Lab 8**	**Lab 9**	**Lab 10**	**n**	**Avg**
$^{13}C_4$-PFBA	52	130	82.6	88.4	60.3	36.6	74.3	108.1	75.8	101.7	164	77.9
$^{13}C_5$-PFPeA	40	130	85.1	82.9	90	58.9	58.3	108	87.4	107.9	164	84.4
$^{13}C_5$-PFHxA	40	130	83.5	90	91.8	75.7	65.9	109.1	92.2	101.1	171	88.4
$^{13}C_4$-PFHpA	40	130	80.1	92	88.9	75.2	67.4	106.3	91.2	100.2	164	87.3
$^{13}C_8$-PFOA	40	130	81.6	91.4	88.5	70.6	73.2	107.3	91.4	95.3	162	86.8
$^{13}C_9$-PFNA	40	130	80.7	90	90.2	79.2	65	109	91.3	95.7	164	87.2
$^{13}C_6$-PFDA	40	130	78.8	88	87.2	76	65.3	104	91.8	93.2	164	85.2
$^{13}C_7$-PFUnA	30	130	77.9	101.9	86.7	77.2	67.8	102.7	93.6	78.6	164	85.4
$^{13}C_2$-PFDoA	10	130	67.9	100.3	85	74.9	64.6	92.5	92.8	73.7	164	81.2
$^{13}C_2$-PFTeDA	10	130	60	102.4	77.3	57.3	49.8	65.3	89	58.2	164	69.9
$^{13}C_3$-PFBS	40	135	79.2	93.4	89	80.5	67.7	121.2	91.7	103	164	90.2
$^{13}C_3$-PFHxS	40	130	84.5	91	88	78.2	66.9	110.5	92.4	97.9	164	88.2
$^{13}C_8$-PFOS	40	130	82.3	89	87.3	82.2	64.3	112.9	91.1	101.5	164	88.4
$^{13}C_2$-4:2FTS	40	200	96.3	153.2	99.2	90.3	66	189.8	124	117.5	164	115.7
$^{13}C_2$-6:2FTS	40	200	108.1	111.8	97.5	104.8	66.4	175.8	144	130.4	164	116.1
$^{13}C_2$-8:2FTS	40	300	138.8	195.7	106.2	119.5	65.6	171.9	166.2	106.4	164	132.9
$^{13}C_8$-PFOSA	40	130	69.5	95.7	78.8	71.1	59.6	89.9	99.8	81.6	164	80.5
D_3-NMeFOSA	10	130	60.1	83.1	27.4	53.6	31.8	--	64.6	44.3	146	52
D_5-NEtFOSA	10	130	56	73.9	25.1	47.9	26.9	--	44.9	40.7	146	45.1
D_3-NMeFOSAA	40	170	72.8	130.4	84.8	80.9	75	124.2	100.7	88	164	94
D_5-NEtFOSAA	25	135	72.3	122.2	84.6	83.7	85.6	115.6	104.7	79.8	164	93.1
D_7-NMeFOSE	10	130	61.6	116.1	52.3	53.8	24.9	51.6	65.8	67.8	164	61.9
D_9-NEtFOSE	10	130	58.9	105.6	46.7	56.6	26	45.4	63	63.1	164	58.4
$^{13}C_3$-HFPO-DA	40	130	80.4	89.2	87.6	79.6	66.7	116.5	91.9	94.3	164	87.7

Notes:
1 EIS Limits from EPA Method 1633 Ver 4. Table 6.

8 SUMMARY FOR SOILS AND SEDIMENTS

8.1 PREPARATORY BATCH QC

Per EPA Method 1633, a sample preparation batch consists of up to 20 study samples, a method blank, an OPR sample, and an LLOPR sample.

The MLVS Method did not prescribe definitive acceptance criteria for OPR, LLOPR, NIS, and EIS compound recoveries; however, it did provide target acceptance criteria. The target percent recovery for target analytes was 40–150% in OPRs and LLOPRs, 20–150% for EIS compounds, and greater than 30% for NIS compounds. These target criteria were based on the results from the SLVS. Since the statistical evaluation from the MLVS will be the basis for the acceptance criteria included in future versions of EPA Method 1633, the laboratories were instructed to follow their routine corrective action process when the target criteria were not met. This included reanalysis and dilution. If the reanalysis or dilution met the target criteria, the reanalysis was reported; otherwise, the first analysis was reported. By doing so, results that were extremely biased due to events such as a miss-injection or carryover, were eliminated from the statistical analysis.

8.1.1 Method Blank

Method blanks are included in the method to evaluate the potential for background contamination to be introduced during sample preparation in the laboratory. A 5.0 g aliquot of PFAS-free Ottawa or reagent-grade sand was used to prepare each method blank associated with soil and sediment samples and all were prepared in exactly the same manner as study samples. A total of 31 method blanks were included in the statistical analysis.

Of these 31 method blanks, included detections of target analytes concentrations above the laboratories' MDLs. A total of seven target analytes were detected. All but three of these reported concentrations were above the laboratories' MDL, but below the laboratories' LOQ. Six of the thirteen detections in method blanks were associated with method blanks reported by Laboratory 10 and the seven others were reported by Laboratories 2, 5, 6, 7, and 8 (Table 8-1). The most frequent detection was of 6:2FTS, with four instances and detections by three laboratories. The low rate of detection in method blanks demonstrated by this Study, 13 out of 1,228 target analytes reported (1.06%) indicates the processes described in the method are successful in reducing the potential for bias associated with contamination.

The concentration of each target analyte in the method blank was required to be <½ the laboratory's LOQ or <1/10th the concentration of the target method in associated samples, whichever is greater. When a method blank failed to meet this criterion, the laboratory applied a "B" data qualifier to the result for the affected target method in the associated sample. Four out of the 31 method blanks reported failed to meet the Study criteria. Laboratories 6 and 8 failed to meet the Study criteria in one method blank each while Laboratories 10 failed to meet the criteria in two method blanks. There were 25 results for 6:2FTS that were "B" qualified, 3 by Laboratory 6 and 22 by Laboratory 10. The 6:2FTS failure reported by Laboratory 8 did not affect any study samples; only a single LLOPR result. Four results for PFHxA reported by Laboratory 10 were also "B" qualified.

In cases where the concentration of the detected target analyte in the method blank was greater than 1/5th the concentration of the target method in these sample, per the data validation guidelines, a "J+" data qualifier was applied to the target analyte in these samples to indicate these results were potentially biased high. As a result, all but four of the "B" qualified results were also "J+" qualified. A summary of the affected data is presented in Table 8-2.

Method blank contamination resulted in the "B" qualification of 29 results out of 14,791 soil and sediment sample results reported. Thus, these measured concentrations were only sufficient to warrant "B" flags for what ultimately represented <0.196% of the final data set. The method blanks demonstrate that any bias associated with background contamination introduced during sample preparation was negligible.

Table 8-1. Method Blank Detection Summary

Matrix of Associated Samples	Laboratory ID	Target Analyte	# of Occurrences	Concentrations (µg/kg)
Soil	2	NEeFOSA	1	0.124 J
Soil	2	NMeFOSA	1	0.121 J
Soil & Sediment	5	PFBA	1	0.0855 J
Soil	6	6:2FTS	1	1.31 B
Soil & Sediment	7	PFDA	2	0.064 J, 0.057 J
Sediment	8	6:2FTS	1	0.363 JB
Soil & Sediment	10	6:2FTS	2	2.41 B, 1.55 B
Soil & Sediment	10	PFHxA	2	0.166 JB, 0.147 JB
Soil & Sediment	10	PFOA	2	0.0902 J, 0.0744 JI

Source File: Chapter 8 Soil_Sed Summary 12112023.xlx

Notes:
J = Analyte concentration >MDL but <LOQ; estimated value.
B = The concentration found in the method blank was ≥ ½ LOQ or ≥ 1/10th the concentration of the target analyte in an associated sample, whichever is greatest.
I = Ion abundance ratio did not meet acceptance criteria

Table 8-2. Study Samples Qualified Due to Method Blank Contamination

Sample Number	Laboratory Number	Target Analyte	Target Analyte Concentration (µg/kg)	Associated Method Blank Concentration (µg/kg)
SSR1	10	PFHxA	0.204 J+B	0.147 JB
SSR2	10	6:2FTS	4.87 J+B	2.41 B
SSR3	10	6:2FTS	3.75 J+B	2.41 B
SSR4	10	6:2FTS	4.47 J+B	2.41 B
SST2	10	6:2FTS	4.16 J+B	1.55 B
SST3	10	6:2FTS	3.04 J+B	1.55 B
SST4	10	6:2FTS	3.55 J+B	1.55 B
SSW1	10	PFHxA	0.273 J+B	0.166 JB
SSW2	10	6:2FTS	3.98 J+B	1.55 B
SSW2	6	6:2FTS	4.92 J+B	1.31 B
SSW3	10	6:2FTS	4.28 J+B	1.55 B
SSW3	6	6:2FTS	3.03 J+B	1.31 B
SSW4	10	6:2FTS	3.77 J+B	1.55 B
SSW4	6	6:2FTS	2.4 J+B	1.31 B
SDY1	10	PFHxA	0.297 J+B	0.166 JB
SDY2	10	6:2FTS	2.74 J+B	1.55 B
SDY3	10	6:2FTS	3.34 J+B	1.55 B
SDY4	10	6:2FTS	2.84 J+B	1.55 B
SDY5	10	6:2FTS	14.5JB	1.55 B
SDZ1	10	PFHxA	0.168 J+BI	2.41 B
SDZ2	10	6:2FTS	2.34 J+B	2.41 B
SDZ3	10	6:2FTS	4.44 J+B	2.41 B
SDZ4	10	6:2FTS	4.28 J+B	2.41 B
SDZ5	10	6:2FTS	16.5B	2.41 B
SDZ6	10	6:2FTS	18.7B	2.41 B
SDZ7	10	6:2FTS	20.4B	2.41 B
SDAA2	10	6:2FTS	2.04 J+B	2.41 B
SDAA3	10	6:2FTS	3.34 J+B	2.41 B
SDAA4	10	6:2FTS	3.07 J+B	2.41 B

Source: Chapter 8 Soil_Sed Summary 12112023.xlx

Notes:
J = Analyte concentration >MDL but <LOQ; estimated value.
J+ = Estimated value due analyte concentration being greater than the MDL but less than or equal to five times the concentration detected in the Method Blank.
B = The concentration found in the method blank was ≥ ½ LOQ and ≥ 1/10th the concentration of the target analyte in an associated sample.

8.1.2 Ongoing Precision and Recovery Analyses

OPR samples, sometimes referred to in other methods as Laboratory Control Samples (LCS), were included in the method to evaluate the efficiency of the sample preparation process. An OPR was included in each preparation batch, which consisted of a 5-g aliquot of PFAS-free Ottawa or reagent-grade sand that was spiked with all 40 target analytes such that the final concentration of each PFAS in the OPR was greater than or equal to the LOQ and less than or equal to the midpoint of the laboratory's calibration. This spiked aliquot was prepared and analyzed in exactly the same manner as study samples.

OPR recoveries across all media for all laboratories was relatively tight, generally at or above 90% with narrow pooled between-laboratory standard deviation (s_b), within-laboratory standard deviation (s_w), and RSD. (Table 8-3, Figure 8-1B). The concentration at which the OPR was spiked by each laboratory did not vary greatly (Figure 8-1A).

A total of 32 OPRs were included in the statistical analysis. All 32 OPRs met the Study NIS criteria (>30% recovery). Of the 1,264 valid target analyte results reported from OPRs, two failed to meet the target analyte criteria (40–150%), resulting in a failure rate of 0.158%. Laboratory 4 reported one target analyte exceedances in one OPR: NMeFOSA (151%), and Laboratory 5 reported one target analyte exceedance in one OPR: 11Cl-PF3OUdS (156%). Of the 759 valid EIS compound results reported from OPRs, seven failed to meet the EIS compound acceptance criteria (20–150%), resulting in a failure rate of 0.92%. Laboratory 4 reported four EIS compound exceedances in one OPR; D_3-NMeFOSA (10.9%), D_5-NEtFOSA (6.1%), D_7-NMeFOSE (17.5%), and D_9-NEtFOSE (13.7%). Laboratory 6 reported one EIS compound exceedance in two OPRs: $^{13}C_4$-PFBA (8.89% and 15.1%). Laboratory 7 reported a single EIS compound exceedance in one OPR: D_5-NEtFOSA (6.1%). Overall, the recoveries of Laboratory 6 OPR recoveries trended lower than all other laboratories, while those of Laboratory 8 exhibited slightly higher OPR recoveries than most (Figure 8-1B).

Following EPA guidance (EPA 821-B-18-001), lower and upper percent recovery limits for target analytes were generated (Table 8-4). The lower percent recovery limit is the mean % recovery minus two times the RSD and the upper percent recovery limit is the mean % recovery plus two times the RSD. All statistically derived lower control limits are greater than the MLVS target lower limit of 40% and all upper control limits are lower than the MLVS target upper limit of 150%. In addition, all lower limits are greater than 70% with the exception of PFDoS (66.8%), and all upper limits were less than or equal to 130% with the exception of 8:2FTS (130.9%), NMeFOSAA (132.2%), and NFDHA (134.2%).

8.1.3 Low-Level Ongoing Precision and Recovery Analyses

LLOPR samples were included in the method to evaluate the efficiency of the sample preparation process near the quantitation limit. An LLOPR was included in each preparation batch, consisting of a 5-g aliquot of PFAS-free Ottawa or reagent-grade sand that was spiked with all 40 target analytes such that the final concentration of each PFAS in the LLOPR was two times the laboratory's LOQ. This spiked aliquot was prepared and analyzed in exactly the same manner as study samples.

All of the 30 LLOPRs included in the statistical analysis met the Study LLOPR NIS compound recovery criteria (>30%). Of the 1,186 valid target analyte results reported from LLOPRs, five failed to meet the target analyte criteria (40–150%), resulting in a failure rate of 0.42%. Laboratory 3 reported one target analyte exceedances in one LLOPR: PFMPA (30%). Laboratory 5 reported two exceedances in one LLOPR: PFDS (151%) and PFDoS (163%). Laboratory 8 reported one exceedance in two LLOPRs: 6:2FTS (168% and 306%). Of the 716 valid EIS compound results reported from LLOPRs, eleven failed to meet the EIS compound criteria (20-150%), resulting in a failure rate of 1.54%. Laboratory 4 reported four EIS compound exceedances in one LLOPR; D_3-NMeFOSA (13.2%), D_5-NEtFOSA (5.2%), D_7-NMeFOSE (16.8%), and D_9-NEtFOSE (13.2%). These are the same EIS compounds that failed in a single OPR reported by Laboratory 4, with similar recoveries for each. Laboratories 1 and 3 both reported two EIS compound exceedances in one LLOPR; $^{13}C_4$-PFBA (4%), $^{13}C_5$-PFPeA (15%), D_3-NMeFOSA (18.5%) and D_5-NEtFOSA (18.2%), respectively. Laboratory 6 reported one EIS compound exceedance in one LLOPR: $^{13}C_4$-PFBA (19.4%). This is the same EIS compound that exceeded criteria in two OPRs reported by Laboratory 6. Laboratory 7 reported a single EIS compound exceedance in one OPR: D_5-NEtFOSA (19%). This is the same EIS compound that exceeded criteria in one OPRs reported by Laboratory 7. These low failure rates demonstrate the target criteria adopted by this Study are routinely achievable. A summary of the LLOPR target analyte and EIS compound recoveries is presented in Table 8-5. Overall, the recoveries of Laboratory 6 LLOPR recoveries trended lower than all other laboratories, while those of Laboratories 5 and 8 exhibited slightly higher LLOPR recoveries than most (Figure 8-2B).

Following EPA guidance (EPA 821-B-18-001), the LLOPR percent recovery and RSD values in Table 8-5 were used to calculate lower and upper percent recovery limits for target analytes.

The lower percent recovery limit is the mean percent recovery minus two times the RSD and the upper percent recovery limit is the mean percent recovery plus two times the RSD. All statistically derived lower control limits are greater than MLVS target lower limit of 40% and all statistically derived upper control limits are lower than the MLVS target upper limit of 150% with the exception of 6:2FTS (182.2%).

All of the statistically derived lower and upper LLOPR control limits were within the lower and upper OPR control limits, indicating a single percent recovery acceptance criteria range; that of the OPR, could be utilized for both OPR and LLOPRs.

Table 8-3. Summary of Soil and Sediment OPR Percent Recoveries

Analyte	Number of Labs	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
PFBA	10	31	108	8.9	5.6	5.2	10.4
PFPeA	10	32	110	9.9	7.4	6.7	12.0
PFHxA	10	32	107	6.8	6.0	5.6	8.7
PFHpA	10	32	108	8.8	10.4	9.6	12.7
PFOA	10	32	108	6.4	9.1	8.4	10.1
PFNA	10	32	109	8.6	7.7	7.1	11.1
PFDA	10	32	110	10.5	10.9	10.0	14.2
PFUnA	10	32	109	10.6	9.9	9.0	13.8
PFDoA	10	32	113	10.4	6.8	6.0	12.3
PFTrDA	10	32	111	14.7	9.0	8.1	17.2
PFTeDA	10	32	111	10.5	8.1	7.3	12.9
PFBS	10	32	107	7.2	8.1	7.5	10.1
PFPeS	10	32	109	11.2	7.1	6.5	13.1
PFHxS	10	32	108	9.1	8.8	8.2	12.0
PFHpS	10	32	112	9.8	8.3	7.5	12.4
PFOS	10	32	108	8.0	7.7	7.1	10.6
PFNS	10	32	107	9.0	9.1	8.5	12.1
PFDS	10	32	103	15.3	8.8	8.5	17.6
PFDoS	10	32	93.2	16.1	12.3	13.2	19.7
4:2FTS	10	32	108	11.2	9.7	9.0	14.3
6:2FTS	9	28	108	10.5	10.4	9.6	14.0
8:2FTS	10	32	113	8.7	10.1	8.9	12.3
PFOSA	10	32	109	10.1	6.6	6.0	11.9
NMeFOSA	9	27	104	9.4	10.5	10.0	13.1
NEtFOSA	9	26	103	5.7	5.3	5.1	7.4
NMeFOSAA	10	32	108	10.3	13.1	12.1	15.3

Table 8-3. Summary of Soil and Sediment OPR Percent Recoveries (Continued)

Analyte	Number of Labs	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
NEtFOSAA	10	32	108	12.3	7.3	6.7	14.3
NMeFOSE	10	32	110	10.0	6.5	5.9	11.8
NEtFOSE	10	32	108	6.7	7.0	6.5	9.2
PFMPA	10	32	100	15.7	14.4	14.3	20.3
PFMBA	10	32	111	9.3	10.0	9.0	12.8
NFDHA	10	32	109	11.0	13.8	12.6	16.2
HFPO-DA	10	32	106	6.4	9.7	9.1	10.5
ADONA	10	32	112	12.1	7.4	6.7	14.1
PFEESA	10	32	108	8.8	5.5	5.0	10.3
9Cl-PF3ONS	10	32	110	9.8	10.4	9.5	13.4
11Cl-PF3OUdS	10	32	102	17.7	12.7	12.5	21.3
3:3FTCA	10	32	98.8	10.7	10.4	10.5	14.1
5:3FTCA	10	32	102	8.2	5.0	4.9	9.5
7:3FTCA	10	32	95.8	12.5	8.1	8.5	14.7
$^{13}C_4$-PFBA	10	32	88	20.4	13.9	15.7	24.3
$^{13}C_5$-PFPeA	10	32	91.9	11.2	6.0	6.5	12.8
$^{13}C_5$-PFHxA	10	33	96.3	8.8	6.7	6.9	10.8
$^{13}C_4$-PFHpA	10	32	94	7.4	7.4	7.9	9.9
$^{13}C_8$-PFOA	10	32	93.4	7.6	6.9	7.4	9.8
$^{13}C_9$-PFNA	10	32	91.1	10.2	7.5	8.2	12.3
$^{13}C_6$-PFDA	10	32	89.4	7.9	8.6	9.6	10.9
$^{13}C_7$-PFUnA	10	32	89.3	7.7	10.2	11.4	11.7
$^{13}C_2$-PFDoA	10	32	80.2	9.5	10.7	13.3	13.3
$^{13}C_2$-PFTeDA	10	32	74	11.5	12.6	17.1	16.0
$^{13}C_3$-PFBS	10	32	94.9	10.3	6.6	6.9	12.1
$^{13}C_3$-PFHxS	10	32	93.5	8.5	5.7	6.1	10.1

Table 8-3. Summary of Soil and Sediment OPR Percent Recoveries (Continued)

Analyte	Number of Labs	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
$^{13}C_8$-PFOS	10	32	90.5	7.9	6.3	6.9	9.8
$^{13}C_2$-4:2FTS	10	32	101	15.1	9.9	9.8	17.8
$^{13}C_2$-6:2FTS	10	32	98.3	11.3	8.8	9.0	14.0
$^{13}C_2$-8:2FTS	10	32	97.4	13.9	11.6	11.9	17.5
$^{13}C_8$-PFOSA	10	32	83.6	13.9	8.3	9.9	16.2
D_3-NMeFOSA	9	27	54.6	16.3	10.9	20.0	19.4
D_5-NEtFOSA	9	27	50.1	16.9	12.0	24.0	20.3
D_3-NMeFOSAA	10	32	91.6	13.1	11.7	12.8	16.9
D_5-NEtFOSAA	10	32	89.2	12.0	8.9	10.0	14.6
D_7-NMeFOSE	10	32	65.4	19.5	11.3	17.2	22.5
D_9-NEtFOSE	10	32	63.2	17.9	13.8	21.8	22.0
$^{13}C_3$-HFPO-DA	10	32	92.8	8.7	6.9	7.4	10.8

Source IDA file: SS_SD_EXPORT_V1_20230927.csv

Notes:
Number of Results - The number of individual OPR results that do not have a U flag included in the calculations.
Mean % Recovery - The mean percent recovery for OPR samples across all labs for the given analyte.
sb - The pooled between-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
sw - The pooled within-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
sc - The combined within- and between-laboratory standard deviations. Equation from EPA 821-B-18-001 page G-26.
RSD - The pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100). Equation from EPA 821-B-18-001 page G-26.

Table 8-4. Statistically Derived Soil and Sediment OPR Acceptance Criteria

Analytes	Mean % Recovery	2 x RSD[1]	LCL[2]	UCL[3]
PFBA	108	10.38	97.62	118.40
PFPeA	110	13.46	96.54	123.50
PFHxA	107	11.20	95.80	118.20
PFHpA	108	19.22	88.78	127.20
PFOA	108	16.78	91.22	124.80
PFNA	109	14.20	94.80	123.20
PFDA	110	19.90	90.10	129.90
PFUnA	109	18.04	90.96	127.00
PFDoA	113	12.08	100.92	125.10
PFTrDA	111	16.16	94.84	127.20
PFTeDA	111	14.54	96.46	125.50
PFBS	107	15.08	91.92	122.10
PFPeS	109	13.06	95.94	122.10
PFHxS	108	16.34	91.66	124.30
PFHpS	112	14.92	97.08	126.90
PFOS	108	14.20	93.80	122.20
PFNS	107	16.96	90.04	124.00
PFDS	103	17.04	85.96	120.00
PFDoS	93.2	26.40	66.80	119.60
4:2FTS	108	17.94	90.06	125.90
6:2FTS	108	19.26	88.74	127.30
8:2FTS	113	17.86	95.14	130.90
PFOSA	109	12.06	96.94	121.10
NMeFOSA	104	20.00	84.00	124.00
NEtFOSA	103	10.24	92.76	113.20
NMeFOSAA	108	24.20	83.80	132.20
NEtFOSAA	108	13.40	94.60	121.40
NMeFOSE	110	11.86	98.14	121.90
NEtFOSE	108	13.04	94.96	121.00
PFMPA	100	28.60	71.40	128.60
PFMBA	111	17.90	93.10	128.90
NFDHA	109	25.20	83.80	134.20
HFPO-DA	106	18.22	87.78	124.20
ADONA	112	13.32	98.68	125.30
PFEESA	108	10.08	97.92	118.10
9Cl-PF3ONS	110	18.94	91.06	128.90
11Cl-PF3OUdS	102	25.00	77.00	127.00
3:3FTCA	98.8	21.00	77.80	119.80
5:3FTCA	102	9.80	92.20	111.80
7:3FTCA	95.8	17.00	78.80	112.80

Source File: dervied from Table 8-3 and IDA file: SS_SD_EXPORT_V1_20230927.csv

Notes:

[1] Two times the pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100)

[2] Lower % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.

[3] Upper % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.

Table 8-5. Soil and Sediment LLOPR Results Summary

Analyte	Number of Labs	Number of Results	Min Concentration µg/kg	Max Concentration µg/kg	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
PFBA	10	29	0.722	1.99	104	9.51	7.07	6.77	11.5
PFPeA	10	30	0.294	1.01	106	5.85	11.2	10.6	11
PFHxA	9	27	0.172	0.502	109	8.23	8.87	8.13	11.3
PFHpA	10	30	0.186	0.544	106	8.36	10	9.41	12
PFOA	10	30	0.171	0.584	111	12.7	9.95	8.98	15.6
PFNA	9	27	0.177	0.582	106	8.44	8.25	7.82	11.2
PFDA	10	30	0.18	0.58	111	10.5	9.81	8.87	13.7
PFUnA	10	30	0.166	0.525	109	10.6	14.2	13.1	16.1
PFDoA	10	30	0.182	0.53	109	10.4	12.5	11.4	14.9
PFTrDA	10	30	0.173	0.552	110	14.7	14.5	13.3	19.5
PFTeDA	10	30	0.175	0.569	108	7.25	13.2	12.2	13.2
PFBS	10	30	0.158	0.447	109	7.01	6.95	6.35	9.29
PFPeS	10	30	0.156	0.51	106	11.2	12.1	11.4	15.4
PFHxS	10	30	0.162	0.514	108	9.15	11.7	10.9	13.5
PFHpS	10	30	0.158	0.569	106	11.8	9.77	9.2	14.7
PFOS	10	30	0.171	0.458	108	7.52	8.89	8.2	10.7
PFNS	10	30	0.169	0.478	106	8.63	8.72	8.24	11.5
PFDS	10	30	0.16	0.582	102	18.2	8.26	8.06	20.2
PFDoS	10	30	0.139	0.631	91.5	20.5	13	14.2	24
4:2FTS	10	30	0.669	1.86	102	12.3	7	6.86	14.1
6:2FTS	8	24	0.661	3.72	119	31.5	37.5	31.6	45.3
8:2FTS	10	30	0.656	2.07	112	8.58	11.3	10.1	12.9
PFOSA	10	30	0.177	0.518	109	10.4	9.16	8.4	13.2
NMeFOSA	9	27	0.183	0.529	104	10.8	14.7	14.2	16.5

Table 8-5. Soil and Sediment LLOPR Results Summary (Continued)

Analyte	Number of Labs	Number of Results	Min Concentration µg/kg	Max Concentration µg/kg	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
NEtFOSA	9	27	0.189	0.508	104	8.81	9.91	9.54	12.3
NMeFOSAA	10	30	0.172	0.496	106	10.8	14.9	14	16.6
NEtFOSAA	10	30	0.162	0.59	109	14	13.2	12.1	18.2
NMeFOSE	10	30	1.74	5.33	106	8.66	9.74	9.18	12.1
NEtFOSE	10	30	1.76	4.68	105	5.81	8.1	7.73	9
PFMPA	10	30	0.192	1.02	95.3	15.6	17.7	18.6	21.8
PFMBA	10	30	0.344	1.01	108	4.29	13.3	12.3	11.8
NFDHA	10	30	0.333	1.18	110	11.6	15.4	14	17.5
HFPO-DA	10	30	0.554	2.07	105	7.09	11.3	10.8	11.8
ADONA	10	30	0.666	2.22	110	13.1	8.92	8.1	15.5
PFEESA	10	30	0.309	0.896	105	7.82	6.95	6.6	9.97
9Cl-PF3ONS	10	30	0.674	2.09	108	7.6	10.8	10	11.9
11Cl-PF3OUdS	10	30	0.591	2.23	100	15.3	9.71	9.69	17.9
3:3FTCA	10	30	0.519	2.27	94.6	11.6	12	12.7	15.6
5:3FTCA	10	30	3.39	11.4	99.1	7.03	6.62	6.68	9.15
7:3FTCA	10	30	3.2	12.1	91.2	12.8	9.32	10.2	15.5
13C4-PFBA	10	30	0.304	10.3	80.7	21.4	24.4	30.3	30
13C5-PFPeA	10	30	0.616	6.13	86	14.7	19.1	22.2	21.9
13C5-PFHxA	10	31	1.43	2.86	93	11.5	8.18	8.8	13.8
13C4-PFHpA	10	30	1.44	2.63	90.5	9.59	8.41	9.29	12.2
13C8-PFOA	10	30	1.39	2.58	91.2	9.14	7.25	7.95	11.3
13C9-PFNA	10	30	0.651	1.31	91	12.1	8.67	9.53	14.5
13C6-PFDA	10	30	0.708	1.29	89.4	11.7	6.74	7.54	13.4
13C7-PFUnA	10	30	0.72	1.54	92.5	11.7	7.77	8.4	13.8

Table 8-5. Soil and Sediment LLOPR Results Summary (Continued)

Analyte	Number of Labs	Number of Results	Min Concentration µg/kg	Max Concentration µg/kg	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)	Combined std. dev. (s_c)
13C2-PFDoA	10	30	0.589	1.27	82.8	10.7	9.7	11.7	13.7
13C2-PFTeDA	10	31	0.43	1.38	75.7	14.3	12.5	16.6	18.2
13C3-PFBS	10	30	1.27	2.57	90.3	9.65	9.23	10.2	12.6
13C3-PFHxS	10	30	1.28	2.55	91.6	8.73	9.98	10.9	12.3
13C8-PFOS	10	30	1.36	2.64	90.9	10.2	7.44	8.19	12.3
13C2-4:2FTS	10	30	2.69	5.76	101	14.2	11.6	11.5	17.6
13C2-6:2FTS	10	30	2.7	5.56	98.6	12.8	13.9	14.1	17.6
13C2-8:2FTS	10	30	2.24	6.31	98.8	13.1	16.4	16.6	19.2
13C8-PFOSA	10	30	1.23	2.54	83.2	16.4	7.46	8.98	18.3
D3-NMeFOSA	9	27	0.263	2.24	53.9	19.6	10.6	19.8	22.4
D5-NEtFOSA	9	27	0.103	2.16	49	19.8	12.1	24.6	23
D3-NMeFOSAA	10	30	2.57	5.89	91.9	15.8	10.9	11.9	18.8
D5-NEtFOSAA	10	30	2.41	5.97	90.5	17.3	9.79	10.8	19.8
D7-NMeFOSE	10	30	3.36	24.7	64.3	20.2	11.5	17.9	23.1
D9-NEtFOSE	10	30	2.64	23.6	62.3	18.7	14	22.4	22.7
13C3-HFPO-DA	10	30	5.36	10.3	90.2	9.98	8.23	9.13	12.4

Source File: IDA file: SS_SD_EXPORT_V1_20230927.csv

Notes:
Number of Results - The number of individual OPR results that do not have a U flag included in the calculations.
Mean % Recovery - The mean percent recovery for OPR samples across all labs for the given analyte.
sb - The pooled between-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
sw - The pooled within-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
sc - The combined within- and between-laboratory standard deviations. Equation from EPA 821-B-18-001 page G-26.

Table 8-6. Statistically Derived Soil and Sediment LLOPR Acceptance Criteria

Analyte	Mean % Recovery	2 x RSD[1]	LCL[2]	UCL[3]
PFBA	104	13.54	90.46	117.50
PFPeA	106	21.20	84.80	127.20
PFHxA	109	16.26	92.74	125.30
PFHpA	106	18.82	87.18	124.80
PFOA	111	17.96	93.04	129.00
PFNA	106	15.64	90.36	121.60
PFDA	111	17.74	93.26	128.70
PFUnA	109	26.20	82.80	135.20
PFDoA	109	22.80	86.20	131.80
PFTrDA	110	26.60	83.40	136.60
PFTeDA	108	24.40	83.60	132.40
PFBS	109	12.70	96.30	121.70
PFPeS	106	22.80	83.20	128.80
PFHxS	108	21.80	86.20	129.80
PFHpS	106	18.40	87.60	124.40
PFOS	108	16.40	91.60	124.40
PFNS	106	16.48	89.52	122.50
PFDS	102	16.12	85.88	118.10
PFDoS	91.5	28.40	63.10	119.90
4:2FTS	102	13.72	88.28	115.70
6:2FTS	119	63.20	55.80	182.20
8:2FTS	112	20.20	91.80	132.20
PFOSA	109	16.80	92.20	125.80
NMeFOSA	104	28.40	75.60	132.40
NEtFOSA	104	19.08	84.92	123.10
NMeFOSAA	106	28.00	78.00	134.00
NEtFOSAA	109	24.20	84.80	133.20
NMeFOSE	106	18.36	87.64	124.40
NEtFOSE	105	15.46	89.54	120.50
PFMPA	95.3	37.20	58.10	132.50
PFMBA	108	24.60	83.40	132.60
NFDHA	110	28.00	82.00	138.00
HFPO-DA	105	21.60	83.40	126.60
ADONA	110	16.20	93.80	126.20
PFEESA	105	13.20	91.80	118.20
9Cl-PF3ONS	108	20.00	88.00	128.00
11Cl-PF3OUdS	100	19.38	80.62	119.40
3:3FTCA	94.6	25.40	69.20	120.00
5:3FTCA	99.1	13.36	85.74	112.46
7:3FTCA	91.2	20.40	70.80	111.60

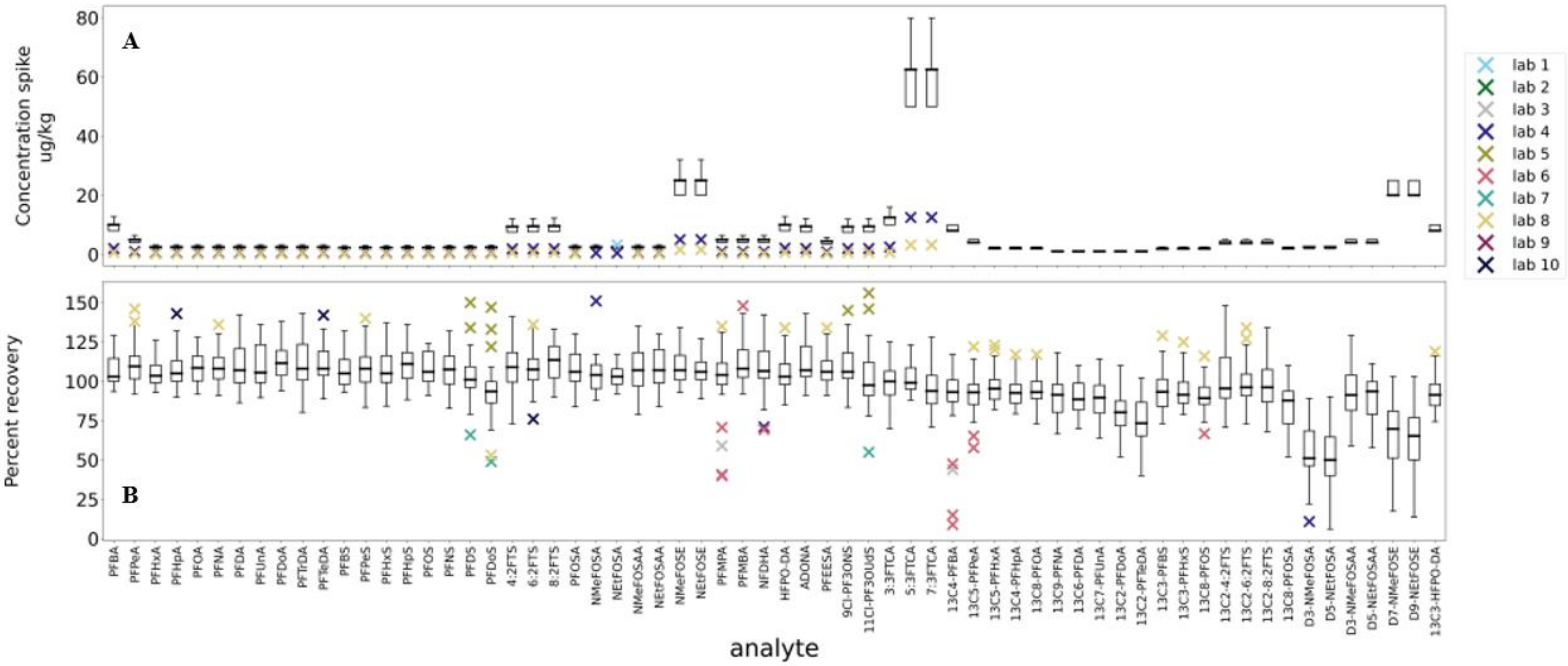
Source File: derived from Table 8-5 and IDA file: SS_SD_EXPORT_V1_20230927.csv

Notes:

[1] Two times the pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100)

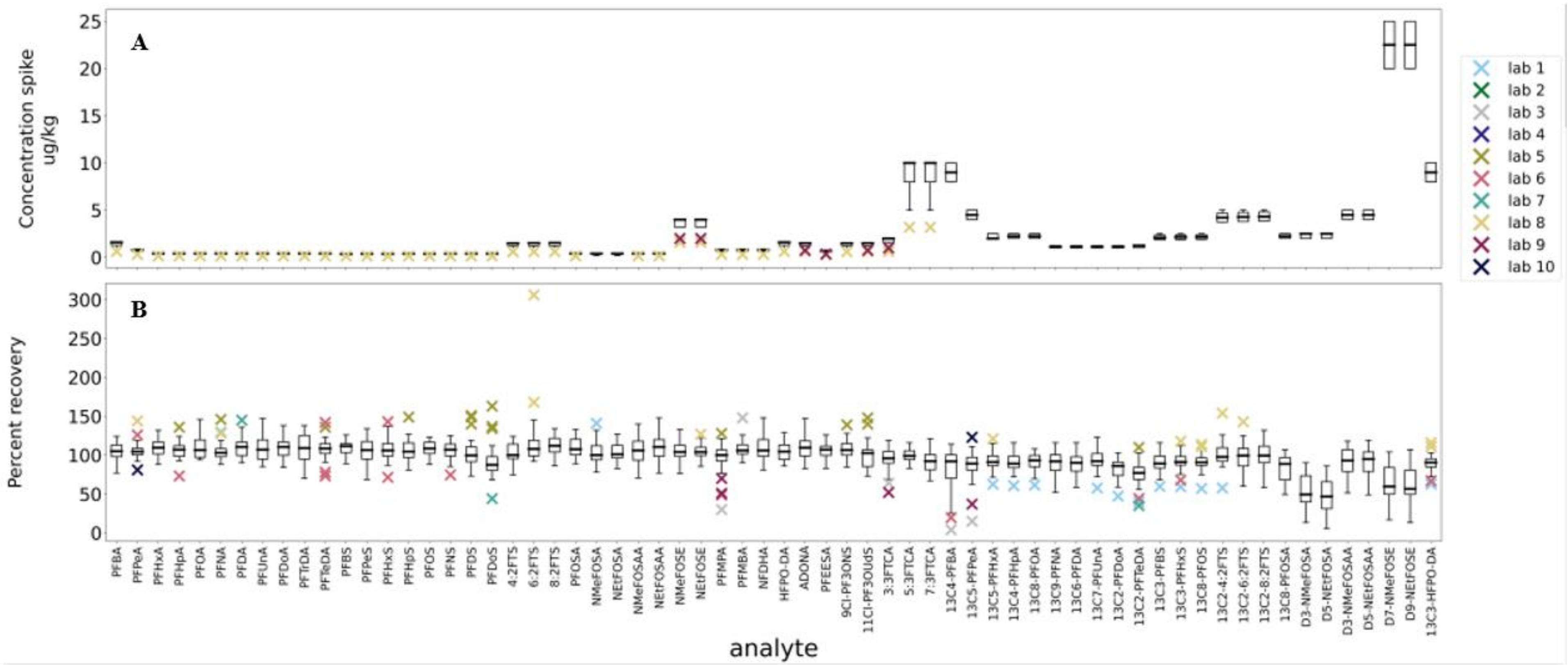
[2] Lower % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.

[3] Upper % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.



Source file: ALL_OPR_Boxplot_V0_231005_084136

Figure 8-1. Soil and Sediment OPR Results by Compound by Laboratory
(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all OPR data batched with unspiked and spiked samples.



Source file: ALL_LLOPR_Boxplot_V0_231005_084136

Figure 8-2. Soil and Sediment LLOPR Results by Compound by Laboratory
(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all LLOPR data batched with unspiked and spiked samples.

8.2 EXTRACTED INTERNAL STANDARDS

One of the most important aspects of draft EPA Method 1633 is its use of isotope dilution quantitation to determine the concentrations of the target analytes. As described in Section 4 of this report, each sample to be analyzed is spiked with a suite of 24 labeled analogs of the target PFAS that are used as quantitation reference standards for both true isotope dilution quantitation and a modified form of isotope dilution for other target analytes. Those 24 labeled compounds are referred to as EIS compounds in EPA Method 1633. They are exact analogs of 24 of the 40 target analytes. Further discussion of the relationship EIS compounds to the target analytes, their use in quantification, and the benefits of their use is spelled out in Section 4 of *Volume I*.

EIS compound recovery data was compiled from all analyses of spiked and unspiked soil and sediment samples.

EIS compound recovery data was compiled from all analyses of spiked and unspiked aqueous samples. The EIS compound recoveries from the ten laboratories that completed the soil and sediment sample portion of the Study are summarized in Table 8-7 below. These data represent the analyses of the unspiked samples and matrix spike aliquots of all 6 samples (three soils, 3 sediments) at two spiking levels (“low” and “high”), for a total of 334 to 387 observations for each EIS compound (8,886 observations in all). The only data which were not included were in situations that were identified in previous sections of this report, which were caused by spiking errors or extraction errors. Table 8-7 includes outliers identified in previous sections. The table contains the observed mean, minimum, and maximum recoveries from those observations for each labeled compound, across all of the ten laboratories, except for D_3-NMeFOSA and D_5-NEtFOSA due to the previously mentioned calculation error by Laboratory 8. Table 8-8 provides a summary of the relative proportions for all laboratories that fell between the Study EIS compound target percent recovery acceptance criteria.

8.3 NON-EXTRACTED INTERNAL STANDARD RECOVERY ANALYSES

The seven NIS compounds are: $^{13}C_3$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{18}O_2$-PFHxS, and $^{13}C_4$-PFOS. These labeled standards are added to the final sample extract shortly before the instrumental analysis, in a manner similar to the use of the “internal standards” in many EPA non-isotope dilution methods for organic contaminants that rely on mass spectrometric determination (e.g., EPA Methods 624.1 and 625.1).

The responses of the seven NIS compounds are used to calibrate the 24 EIS compounds and to calculate the recoveries of those EIS compounds in samples. Further discussion of the relationship of the NIS compounds to the EIS compounds, their use as a diagnostic tool to assess instrument sensitivity, and the benefits of their use is spelled out in Section 4 of *Volume I*.

Table 8-7. Soil and Sediment EIS Compound Recovery Analysis

Analyte	**Number of Labs**	**Number of Results**	**Mean % Recovery**	**Pooled Between-Lab std. dev. (s_b)**	**Pooled Within-Lab std. dev. (s_w)**	**RSD (s_w)**
$^{13}C_4$-PFBA	10	373	77.7	18.2	20.4	26.3
$^{13}C_5$-PFPeA	10	373	83.3	15.0	13.4	16.1
$^{13}C_5$-PFHxA	10	387	87.6	10.9	10.7	12.3
$^{13}C_4$-PFHpA	10	373	86.8	10.7	11.3	13.0
$^{13}C_8$-PFOA	10	371	86.2	10.4	10.7	12.4
$^{13}C_9$-PFNA	10	373	85.9	12.0	10.6	12.3
$^{13}C_6$-PFDA	10	373	84.3	11.1	11.7	13.9
$^{13}C_7$-PFUnA	10	373	85.5	11.9	14.2	16.6
$^{13}C_2$-PFDoA	10	373	80.9	13.5	14.7	18.2
$^{13}C_2$-PFTeDA	10	373	73.4	15.9	16.2	22.0
$^{13}C_3$-PFBS	10	373	87.7	13.2	11.8	13.4
$^{13}C_3$-PFHxS	10	373	86.6	11.3	11.3	13.1
$^{13}C_8$-PFOS	10	373	86.9	12.4	12.3	14.2
$^{13}C_2$-4:2FTS	10	373	110.0	33.0	24.9	22.7
$^{13}C_2$-6:2FTS	10	373	107.0	26.5	25.0	23.3
$^{13}C_2$-8:2FTS	10	373	122.0	36.9	33.7	27.7
$^{13}C_8$-PFOSA	10	373	80.0	11.8	15.0	18.8
D_3-NMeFOSA	9	334	54.6	17.9	14.2	26.0
D_5-NEtFOSA	9	334	48.4	15.9	13.5	28.0
D_3-NMeFOSAA	10	373	89.3	19.1	19.4	21.7
D_5-NEtFOSAA	10	373	88.8	14.9	19.9	22.5
D_7-NMeFOSE	10	373	63.8	20.5	15.3	24.0
D_9-NEtFOSE	10	373	61.1	17.5	16.2	26.5
^{13}C3-HFPO-DA	10	373	87.0	12.8	10.3	11.9

Source File: \\isi\IDA\Projects\5056 PFAS\Results\Phase4\EIS\231005_084136

Notes:

Number of Results - The total number of matrix results that do not have a U flag.
Mean % Recovery - The mean percent recovery across all individual matrix samples and labs for the given analyte.
s_b - The pooled between-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
s_w - The pooled within-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
RSD - The pooled within-laboratory relative standard deviation (RSD, (s_w/(mean % recovery) *100). Equation from EPA 821-B-18-001 page G-26.

Table 8-8. Proportion of All Soil and Sediment Media % Recovery Results for EIS Compounds within Ranges

EIS Compound	n	<10%	≥10% to <20%	≥20% to <150%	≥150% to <200%	≥200%
$^{13}C_4$-PFBA	373	2.1	4.3	93.6	0.0	0.0
$^{13}C_5$-PFPeA	373	0.0	0.0	100.0	0.0	0.0
$^{13}C_5$-PFHxA	387	0.0	0.0	100.0	0.0	0.0
$^{13}C_4$-PFHpA	373	0.0	0.0	100.0	0.0	0.0
$^{13}C_8$-PFOA	371	0.0	0.0	100.0	0.0	0.0
$^{13}C_9$-PFNA	373	0.0	0.0	100.0	0.0	0.0
$^{13}C_6$-PFDA	373	0.0	0.3	99.7	0.0	0.0
$^{13}C_7$-PFUnA	373	0.0	0.3	99.7	0.0	0.0
$^{13}C_2$-PFDoA	373	0.0	0.8	99.2	0.0	0.0
$^{13}C_2$-PFTeDA	373	0.5	0.3	99.2	0.0	0.0
$^{13}C_3$-PFBS	373	0.0	0.0	100.0	0.0	0.0
$^{13}C_3$-PFHxS	373	0.0	0.0	100.0	0.0	0.0
$^{13}C_8$-PFOS	373	0.0	0.3	99.7	0.0	0.0
$^{13}C_2$-4:2FTS	373	0.0	0.0	86.9	7.8	5.4
$^{13}C_2$-6:2FTS	373	0.0	0.0	87.7	10.2	2.1
$^{13}C_2$-8:2FTS	373	0.0	0.0	80.4	12.1	7.5
$^{13}C_8$-PFOSA	373	0.0	0.3	99.7	0.0	0.0
D_3-NMeFOSA	334	0.6	7.5	91.9	0.0	0.0
D_5-NEtFOSA	334	2.4	8.1	89.5	0.0	0.0
D_3-NMeFOSAA	373	0.0	0.0	95.7	4.3	0.0
D_5-NEtFOSAA	373	0.0	0.0	98.1	1.9	0.0
D_7-NMeFOSE	373	0.0	1.1	98.9	0.0	0.0
D_9-NEtFOSE	373	0.5	1.9	97.6	0.0	0.0
$^{13}C_3$-HFPO-DA	373	0.0	0.0	100.0	0.0	0.0

Source file: Summary_tables_Exa_CH8_10312023.xlsx

Some non-isotope dilution methods place bounds on the responses of the internal standards as a factor of two around the mean response in most recent ICAL (e.g., the area of internal standard X in Sample Y must be within 50–200% of its mean area in the ICAL standards). For the purposes of the EPA Method 1633 validation study, DoD required the laboratories to normalize their NIS compound responses against the mean responses in the ICAL and report the normalized responses as “recoveries.” A target lower limit of recovery of greater than or equal to 30% was utilized in the MLVS; no target upper limit was provided to the laboratories.

All of the NIS compound “recovery” data from the unspiked and spiked soil and sediment samples were compiled and descriptive statistics for each NIS compound were generated across all soil and sediment samples. Table 8-9 summarizes 2,624 NIS compound recoveries data across all soil and sediment samples and ten laboratories, reported to the nearest percent. All NIS compound recoveries met the target recovery criteria (>30%). All five of the NIS recoveries reported below

50% were reported by Laboratory 2 and of the 77 NIS compound recoveries reported at or below 66%, all but one result (Laboratory 6), were reported by Laboratories 2 (61 recoveries) and 5 (15 recoveries). Figure 8-3 clearly illustrates that recoveries reported by Laboratories 2 and 5 are statistically different than those reported by the other laboratories. All 12 of the NIS compound recoveries that exceeded 200% were reported by Laboratory 5. In addition, 39 of the 61 NIS compound recoveries that exceeded 150% were reported by Laboratory 5.

Table 8-9. All Soil and Sediment Media Samples NIS Compound Recovery Analysis

Analyte	Number of Labs	Number of Results	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	RSD (s_w)
$^{13}C_3$-PFBA	10	373	102	19.6	18.0	17.7
$^{13}C_2$-PFHxA	10	387	100	15.6	20.9	20.9
$^{13}C_4$-PFOA	10	371	102	14.5	20.9	20.5
$^{13}C_5$-PFNA	10	373	103	15.4	20.4	19.8
$^{13}C_2$-PFDA	10	373	104	14.8	20.9	20.1
$^{18}O_2$-PFHxS	10	373	101	16.9	21.4	21.2
$^{13}C_4$-PFOS	10	374	101	16.1	20.4	20.1

Source File: \\isi\IDA\Projects\5056 PFAS\Results\Phase4\NIS\231005_084136

Notes:
[1] Analysis does not include recoveries associated with samples extracts that required dilution prior to analysis.
Mean % Recovery - The mean percent recovery across all individual matrix samples and labs for the given analyte.
sb - The pooled between-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
sw - The pooled within-laboratory standard deviation of the percent recoveries. Equation from EPA 821-B-18-001 page G-25.
RSD - The pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100). Equation from EPA 821-B-18-001 page G-26.

Following EPA guidance (EPA 821-B-18-001), lower and upper percent recovery limits for NIS compounds were generated (Table 8-10). The lower percent recovery limit is the mean percent recovery minus two times the RSD and the upper percent recovery limit is the mean percent recovery plus two times the RSD. All statistically derived lower control limits are greater than MLVS target lower limit of 30%.

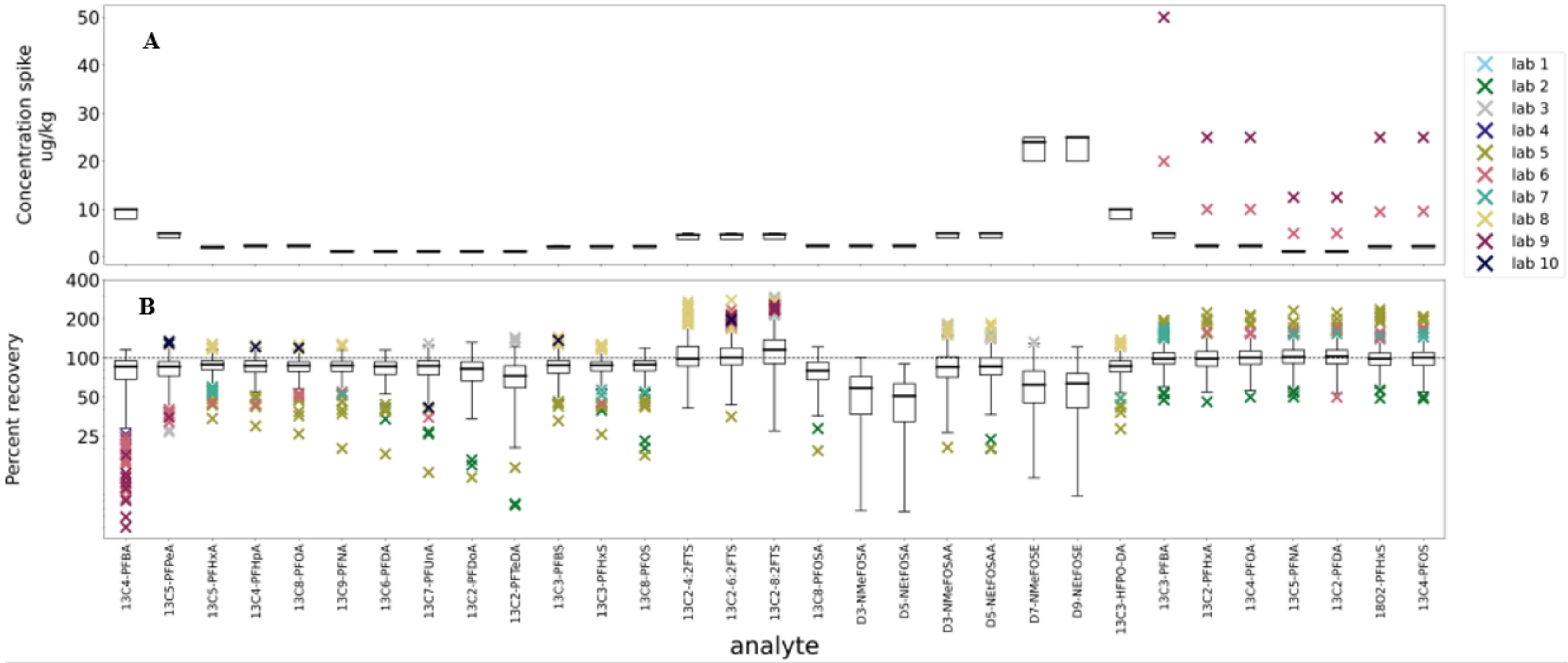
Table 8-10. Statistically-Derived NIS Compound Recovery Acceptance Criteria

NIS Compound	Mean % Recovery	2 x RSD[1]	LCL[2]	UCL[3]
$^{13}C_3$-PFBA	102	35.4	66.6	137.4
$^{13}C_2$-PFHxA	100	41.8	58.2	141.8
$^{13}C_4$-PFOA	102	41.0	61	143
$^{13}C_5$-PFNA	103	39.6	63.4	142.6
$^{13}C_2$-PFDA	104	40.2	63.8	144.2
$^{18}O_2$-PFHxS	101	42.4	58.6	143.4
$^{13}C_4$-PFOS	101	40.2	60.8	141.2

Source File: \ Source File: Calculated from data in Table 8-9.

Notes:

[1] Two times the pooled within-laboratory relative standard deviation (RSD, (sw/(mean % recovery) *100)
[2] Lower % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.
[3] Upper % Recovery acceptance limit calculated as the Mean % Recovery – (2 x RSD) expressed as whole number.



Source file: ALL_NIS_Boxplot_V0_231005_084136

Figure 8-3. Soil and Sediment NIS and EIS Compound Results by Compound by Laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.

Figure includes all EIS and NIS compound data from unspiked and spiked samples.

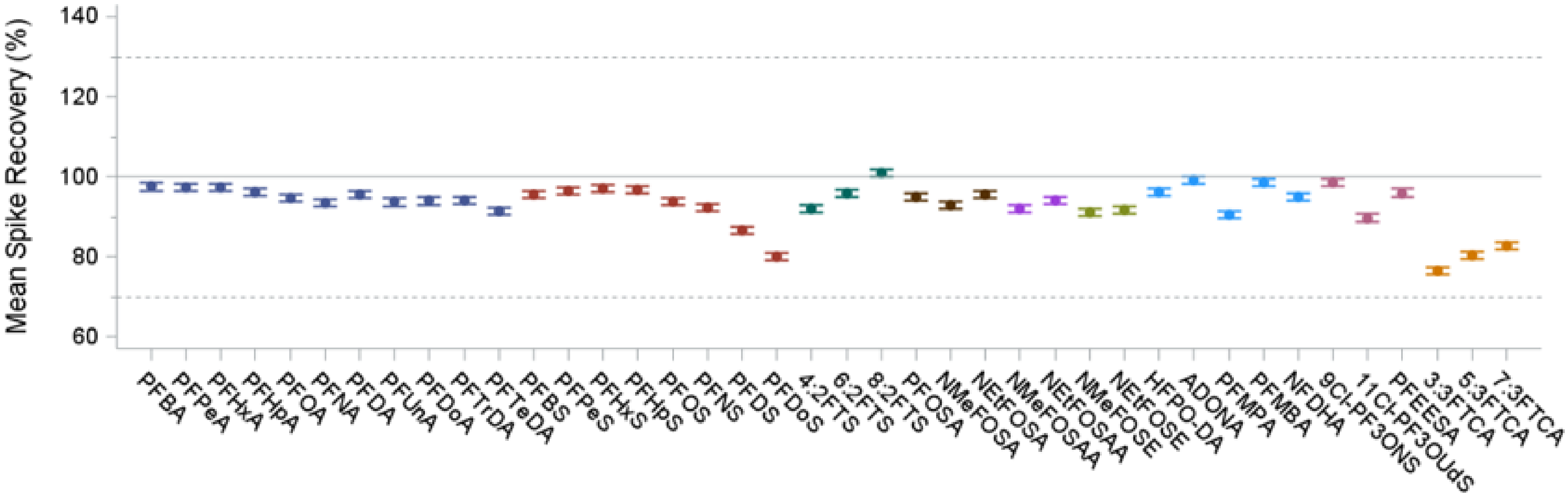
8.4 MATRIX SPIKE ANALYSES

Matrix spike recoveries were statistically evaluated by Analysis of Variance (ANOVA) to test for differences among the various independent experimental factors (i.e., main effects). Main effects included the target analytes ("PFAS"), the different matrices ("Matrix"), laboratories ("Lab"), and spike concentrations ("Spike Conc."). Because the final working dataset consisted of missing permutations of main effects, 1) no interaction effects were evaluated and 2) the Least Squares Means from the ANOVA predictions are reported to more accurately reflect mean differences (i.e., marginal means that control for other model parameters). All main effects were significant with greater than 99% confidence (Table 8-11). On average all PFAS were observed with mean recoveries 70-130% of the target spike concentration (Figure 8-4). Matrix, Spike Conc., and Lab main effects were also relatively consistent and close to the target spike concentration (i.e., 100% recovery) (Figure 8-5).

Despite statistically significant differences among the various levels of each main effect evaluated, the overall method accuracy and precision was quantified. Method accuracy was calculated as the mean percent bias (% recovery – 100%) for each spike concentration and laboratory and matrix averaging over the method analytes to avoid an impracticable number of permutations. Similarly, precision was calculated as the inter-laboratory %RSD among replicate measures of the various spiked samples. Figure 8-6 illustrates the calculated accuracy and precision on a unit scale such that the results can be interpreted quantitively (i.e., a literal bullseye target). The analysis of MS data included all data, including those that were identified in the IDA statistical analyses as outliers.

Table 8-11. Accuracy Analysis: ANOVA Results for the Observed Matrix Spike Recoveries

Effect	**F Value**	**P Value**
Matrix	874.6	<0.0001
Laboratory	681.3	<0.0001
PFAS	34.22	<0.0001
Spiked Concentration	99.59	<0.0001



● Perfluoroalkyl carboxylic acids
● Perfluoroalkyl sulfonic acids
● Fluorotelomer sulfonic acids
● Perfluorooctane sulfonamides
● Perfluorooctane sulfonamidoacetic acids
● Perfluorooctane sulfonamide ethanols
● Per- and Polyfluoroether carboxylic acids
● Ether sulfonic acids
● Fluorotelomer carboxylic acids

Figure 8-4. Mean Spike Recoveries Summarized for Each Target Analyte (i.e., the “PFAS” Effect)

Error bars reflect one standard error. Reference lines are provided ± 30% of the target spike concentration for illustration only.

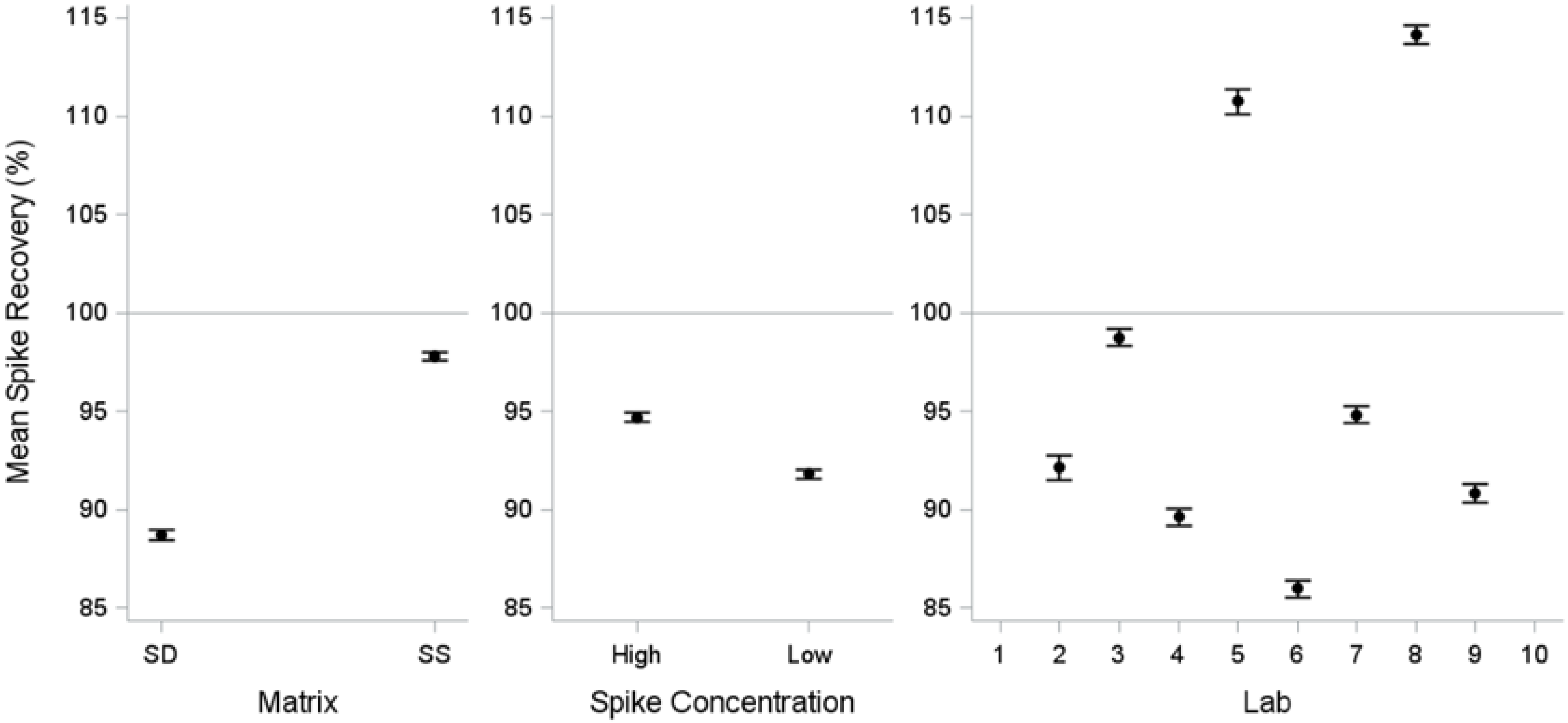


Figure 8-5. Mean Spike Recoveries Summarized for Each Matrix, Spike Concentration, and Laboratory (i.e., the "Matrix", "Spike Conc." and "Lab" Effects)

Error bars reflect one standard error.

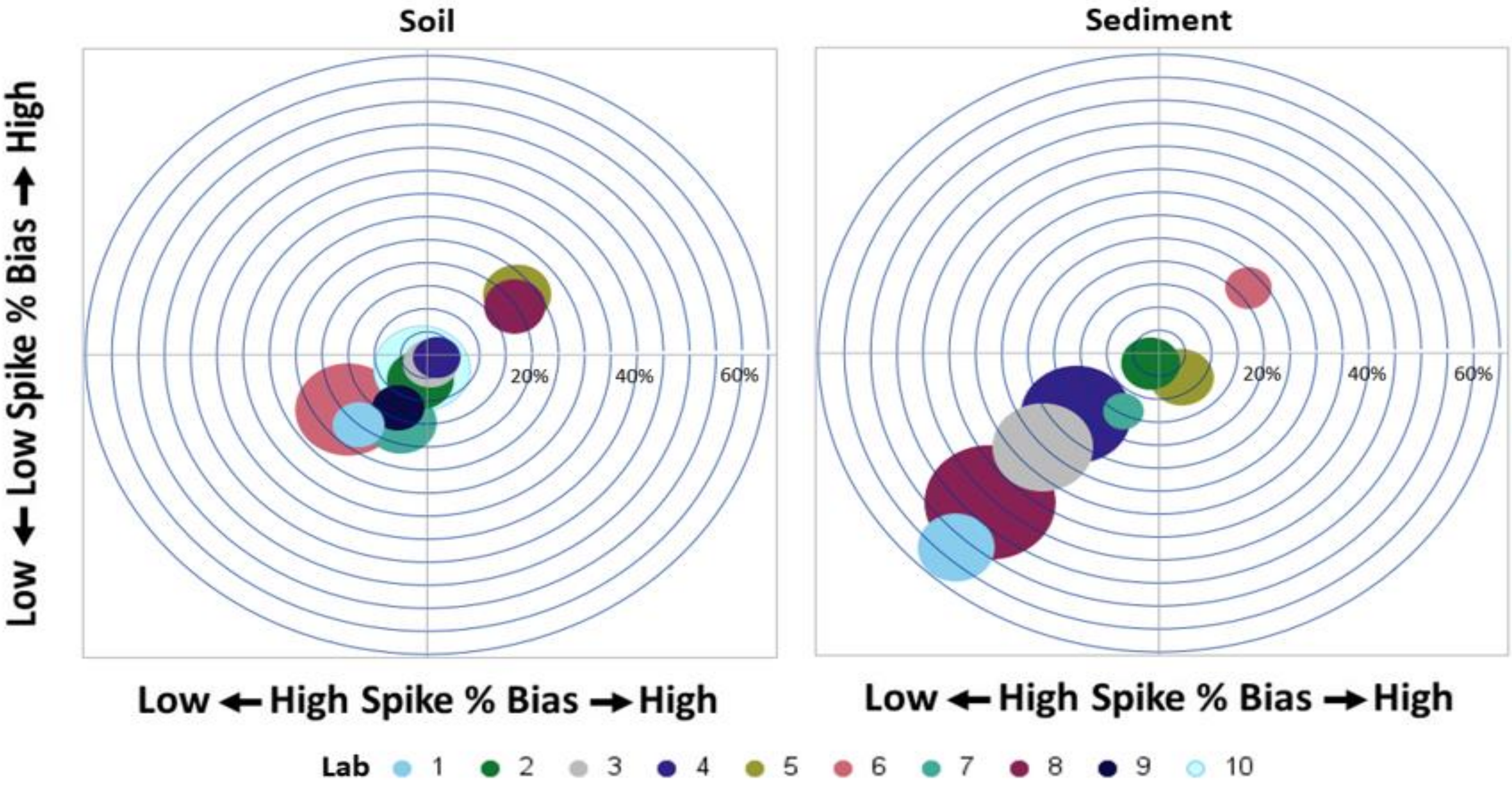


Figure 8-6. Summary Illustration of the Overall Method Accuracy and Precision

Bubble sizes reflect precision calculated as the intra-laboratory %RSD among replicate measures of the various spiked samples. Bubble centroids reflect mean bias (% recovery - 100%). The RSDs are scaled to the axes such that the illustration can be interpreted quantitatively.

8.5 DETERMINATION OF FINAL QC SPECIFICATIONS FOR METHOD 1633

EPA and DoD used the same approach to determine the QC acceptance criteria for the solid samples that they used for the results from the *Volume I* (Section 9.5). Following completion of the statistical calculations, EPA and DoD examined the initial acceptance limits and agreed to take several additional steps that allowed EPA to establish the final QC specifications for Method 1633 for IPRs, OPRs, LLOPRs, EIS compound, and NIS compound recoveries. This was in part, due to the fact there appeared to be true outliers included in the final data set and the resulting acceptance criteria were more stringent than the acceptance criteria included in EPA Method 1633 for analytical standards that did not undergo sample preparation. Among those steps were:

- Additional analyses using statistical procedures previously applied to evaluate IPR and OPR QC acceptance criteria to inter-laboratory validation studies of EPA Methods 1600 and 1603. These calculation routines developed by GDIT in the Statistical Analysis Software (SAS) package, were conducted on the final MLVS data set and includes an allowance for simultaneous testing of multiple analytes.
- Combining the IPR, OPR, and LLOPR data from soil and sediment matrix types because the IPR, OPR, and LLOPR aliquots are all prepared in reference sand (e.g., Ottawa Sand or silica powder), so there is no risk of a “matrix effect” related to these solid matrix types for the associated study samples. This step would allow EPA to develop a single set of QC specifications that could be applied to both matrix types, thus simplifying the implementation of the method in laboratories.
- Similarly combining the EIS compound data from these two matrix types and all QC and study samples and developing a single set of EIS compound QC specifications that was applied to all study samples and QC samples, further simplifying the implementation of the method in laboratories.
- Comparing the newly calculated limits to the Study data set and where appropriate, applying professional judgement to manually establish QC limits that cutoff at the 1st and 99th percentiles of the observed data, and then rounding those values to the nearest multiple of 5%.

8.5.1 Initial SAS Calculations

Table 8-12 contains the initial SAS calculations of the IPR and OPR limits for the 40 target analytes using the entire data set (all 10 laboratories and both soil and sediment reference QC matrix analyses), with the calculated recoveries, RSDs, minimum, and maximum observed recoveries rounded to the nearest 1%.

Table 8-12. Initial SAS Calculations of the IPR and OPR Limits for the 40 Target Analytes Using the Entire Data Set

Analyte	n	# labs	Mean	Max. RSD	IPR Lower Limit (%)	IPR Upper Limit (%)	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	Min. Obs. Rec.	Max. Obs. Rec.
PFBA	105	69	142	66	144	77	124	144	77	124
PFPeA	106	72	139	61	150	68	150	150	68	150
PFHxA	107	80	134	69	145	68	134	145	68	134
PFHpA	106	73	138	66	145	73	136	145	73	136
PFOA	109	77	140	67	150	77	146	150	77	146
PFNA	106	67	146	60	153	81	146	153	81	146
PFDA	107	70	144	60	154	81	150	154	81	150
PFUnA	107	71	143	61	153	76	147	153	76	147
PFDoA	109	71	147	62	155	84	140	155	84	140
PFTrDA	106	55	158	49	163	70	138	163	70	138
PFTeDA	108	72	143	64	151	73	142	151	73	142
PFBS	106	76	136	65	147	69	136	147	69	136
PFPeS	107	68	146	56	158	59	175	158	59	175
PFHxS	106	71	140	59	153	61	143	153	61	143
PFHpS	106	73	139	61	151	71	149	151	71	149
PFOS	108	80	136	65	150	74	171	150	74	171
PFNS	103	70	137	59	148	61	125	148	61	125
PFDS	100	51	148	43	156	39	151	156	39	151
PFDoS	91	40	141	28	153	32	163	153	32	163
4:2FTS	105	76	134	62	148	60	126	148	60	126
6:2FTS	111	62	161	32	190	61	306	190	61	306
8:2FTS	111	83	139	68	154	81	139	154	81	139
PFOSA	107	73	140	68	145	78	133	145	78	133
NMeFOSA	106	67	146	59	153	77	141	153	77	141
NEtFOSA	105	74	137	69	142	75	129	142	75	129
NMeFOSAA	106	67	144	54	157	71	150	157	71	150
NEtFOSAA	105	59	151	48	162	68	159	162	68	159
NMeFOSE	107	75	139	69	144	77	133	144	77	133
NEtFOSE	105	76	134	72	139	75	127	139	75	127
PFMPA	99	44	154	37	161	30	128	150	74	140
PFMBA	106	78	135	62	150	65	148	162	83	152
NFDHA	107	71	143	48	166	73	148	151	81	143
HFPO-DA	106	72	140	62	150	74	140	157	52	148
ADONA	111	69	154	60	162	83	152	149	52	119
PFEESA	106	74	138	68	144	76	126	143	68	118
9Cl-PF3ONS	108	76	140	65	151	81	143	146	67	145
11Cl-PF3OUdS	100	55	146	44	157	52	148	144	76	126
3:3FTCA	96	47	144	43	149	52	119	161	30	128
5:3FTCA	100	63	137	57	143	68	118	150	65	148
7:3FTCA	94	52	137	43	146	67	145	166	73	148

8.5.2 Final IPR, OPR, LLOPR, EIS Compound, and NIS Compound QC Acceptance Criteria for Method 1633

As was done for the aqueous portion of the Study, following the review of the statistically derived acceptance limits, EPA and DoD decided to apply both a non-parametric approach and professional judgement (e.g., elimination of results from a specific laboratory for an analyte or EIS compound) to establish the QC acceptance limits for the following:

- IPR
- Combined OPR/LLOPR limits (e.g., one set of limits for both types of OPR)
- EIS compound recoveries in study samples

The initial calculations of the IPR recoveries in Table 8-13 were generated using a 99.875% confidence interval. The 99.875% confidence level was used because it targets an overall 5% false positive probability (i.e., a compound failing the criterion despite not having any analytical problems) of at least one failure across the 40 target analytes; 99.875 = 100 - ([5/40]/100). The goal of the non-parametric approach was to set the limits such that no more than 1% of the observed results would fail either the lower or upper limits.

All of the non-parametric IPR and OPR/LLOPR recovery limits were then expressed to a multiple of 5% and the RSD limits were expressed to the nearest 1%. Some of the calculated OPR/LLOPR criteria were tightened when none of the approximately 120 OPR observed results were within 10% of the calculated values. Furthermore, none of the criteria were made more stringent than 70% for the lower recovery or 130% for the upper recovery, which are the bounds for the calibration verification criteria, as it does not make sense to make the IPR or OPR recovery more stringent than that criteria. The final IPR and OPR/LLOPR limits for the target analytes are shown in Table 8-13.

Most of the acceptance criteria in Table 8-13 are inclusive of the highest or lowest observed result from Table 8-12, which included about 120 data points from 10 laboratories for most of the analytes. Below are the exceptions:

- The lowest observed OPR result for PFDS was 39%. The calculated criteria of 40% was used (generated from the whole data set using a 99.875% confidence interval), because this one data point appeared to be an outlier.
- The highest observed OPR results for 6:2FTS are above the 200% calculated criteria. These are considered outliers because the 99.875% confidence interval calculated an upper limit of 190%.

As was done for the aqueous portion of the Study, EPA and DoD decided to develop a single set of acceptance limits for EIS compound recoveries that would be applicable to both the Study sample results and the IPR and OPR/LLOPR and other QC samples analyses (e.g., method blanks). The goal was to simplify the application of the EIS compound acceptance limits in the laboratory. The ranges of EIS compound recoveries in study samples were significantly wider than in method blanks, OPRs, and LLOPRs, so the wider of the two sets was used.

Table 8-13. Final IPR and OPR/LLOPR Acceptance Limits

Analyte	IPR Max RSD	IPR Lower Limit (%)	IPR Upper Limit (%)	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)
PFBA	17	70	140	70	140
PFPeA	26	70	140	60	150
PFHxA	23	70	135	65	140
PFHpA	21	70	140	65	145
PFOA	23	70	140	70	150
PFNA	24	65	145	70	155
PFDA	26	70	145	70	155
PFUnA	26	70	145	70	155
PFDoA	25	70	145	70	150
PFTrDA	26	55	160	65	150
PFTeDA	24	70	145	65	150
PFBS	25	60	145	65	145
PFPeS	29	65	140	55	160
PFHxS	28	65	145	60	150
PFHpS	27	70	140	65	155
PFOS	27	70	135	65	160
PFNS	27	70	140	55	140
PFDS	31	50	150	40	155
PFDoS	40	40	140	25	160
4:2FTS	27	70	135	60	150
6:2FTS	50	60	160	55	200
8:2FTS	27	70	140	70	150
PFOSA	19	70	140	70	140
NMeFOSA	26	65	145	70	155
NEtFOSA	19	70	135	70	140
NMeFOSAA	31	65	145	65	155
NEtFOSAA	31	60	150	65	165
NMeFOSE	19	70	140	70	140
NEtFOSE	17	70	135	70	135
PFMPA	25	70	140	30	140
PFMBA	33	55	145	60	150
NFDHA	27	45	145	60	155
HFPO-DA	25	70	140	70	145
ADONA	26	70	155	70	160
PFEESA	20	70	140	70	140
9Cl-PF3ONS	23	65	135	70	150
11Cl-PF3OUdS	31	50	135	45	160
3:3FTCA	32	45	155	45	130
5:3FTCA	28	70	135	60	130
7:3FTCA	39	70	145	60	150

Source files: Solids IPR and OPR-LLOPR specs 11-7-23_ah CM.xlsx and Comparison of IPR-OPR specs for aqueous and solids_ah GDIT.xlsx

The acceptance limits in Table 8-14 were developed from the entire study sample data set of 334 to 373 recoveries per EIS compound using both a non-parametric approach and professional judgement (including the decision to eliminate the EIS compound recoveries from one laboratory for a specific parameter). Also, none of the acceptance criteria were made more stringent than 40% to 130%. Professional judgement was used to prevent the worst performing laboratories from overly influencing the method criteria.

The spiked sample data from the aqueous portion of the Study demonstrated that the accuracy of the method was good when the EIS compound recovery was as low as 5%, and as high as 500%, but if the criteria were made this wide, it might encourage poor laboratory technique. Also, a very low acceptance limit could mask sample processing or instrumental issues that would reduce the method's sensitivity. The criteria below were obtainable by the overwhelming majority of the laboratories participating in the solid sample portion of the Study.

The NIS compound data were compiled only using the Study samples, which generated 371 to 387 data points for each of the NIS compound. The criteria were generated by applying professional judgement to manually establish QC acceptance limits that cutoff at the 1st and 99th percentiles of the observed data, and then rounding those values to the more inclusive multiple of 5%. Based on the percentiles shown in Table 8-15, all of the acceptance criteria were set at 50–200%, which is consistent with the approach used for the aqueous portion of the Study.

Table 8-14. Final EIS Compound Acceptance Limits Applicable to All Solid Sample Types

EIS Compound	Lower Limit (%)	Upper Limit (%)
$^{13}C_4$-PFBA	8*	130
$^{13}C_5$-PFPeA	35	130
$^{13}C_5$-PFHxA	40	130
$^{13}C_4$-PFHpA	40	130
$^{13}C_8$-PFOA	40	130
$^{13}C_9$-PFNA	40	130
$^{13}C_6$-PFDA	40	130
$^{13}C_7$-PFUnA	40	130
$^{13}C_2$-PFDoA	40	130
$^{13}C_2$-PFTeDA	20	130
$^{13}C_3$-PFBS	40	135
$^{13}C_3$-PFHxS	40	130
$^{13}C_8$-PFOS	40	130
$^{13}C_2$-4:2FTS	40	165
$^{13}C_2$-6:2FTS	40	215
$^{13}C_2$-8:2FTS	40	275
$^{13}C_8$-PFOSA	40	130
D_3-NMeFOSA	10	130
D_5-NEtFOSA	10	130
D_3-NMeFOSAA	40	135**
D_5-NEtFOSAA	40	150
D_7-NMeFOSE	20	130
D_9-NEtFOSE	15	130
$^{13}C_3$-HFPO-DA	40	130

Source file: 1633 Soil and Sed EIS & NIS Specs 2023-11-08.xlsx

* Recovery of $^{13}C_4$-PFBA can be problematic in some study samples. Although the lower limit for recovery for this EIS compound is set below 10%, laboratories should routinely track recovery of this EIS compound and take reasonable steps to ensure that recovery is at least 10% in the majority of samples.

** Most of the very high recoveries of D_3-NMeFOSAA were from Laboratory 3. After removing those recoveries from consideration, the 99th percentile dropped from 178% to 133%, which was rounded to 135%.

Table 8-15. NIS Compound Acceptance Limits Applicable to All Solid Sample Types

NIS Compound	**n**	**p1**	**p99**	**Lower Limit (%)**	**Upper Limit (%)**
$^{13}C_2$-PFDA	373	56	169	50	200
$^{13}C_2$-PFHxA	387	56	180	50	200
$^{13}C_3$-PFBA	373	54	170	50	200
$^{13}C_4$-PFOA	371	58	157	50	200
$^{13}C_4$-PFOS	374	59	172	50	200
$^{13}C_5$-PFNA	373	57	159	50	200
$^{18}O_2$-PFHxS	373	59	194	50	200

Source file: 1633 Soil and Sed EIS & NIS Specs 2023-11-08.xlsx

9 CONCLUSIONS

The objectives of this MLVS were achieved: validation of EPA Method 1633 and the production of a method that can be implemented at a typical mid-sized full-service environmental laboratory. Overall, the data generated during the MLVS demonstrated that EPA Method 1633, as written, is robust enough to be performed by suitable laboratories using similar instruments of different manufacturers and models. The results generated by participating laboratories in this Study routinely met the requirements stated in the method for:

- Mass calibration and mass calibration verification
- Initial calibration and calibration verification
- Determination of MDLs and LOQs
- Initial Precision and Recovery
- Preparatory batch QC samples (MB, OPR, LLOPR)
- Quantitative and qualitative analyte identification criteria

The suitability of EPA Method 1633 to detect and quantify the 40 target analytes in soil and sediment was successfully demonstrated through the analysis of spiked real-world samples of those matrix types. Method blank results demonstrated that there was negligible bias associated with background contamination introduced during sample preparation. The IPR, OPR, and LLOPR recoveries (Tables 5-3, 8-3, and 8-5) and the EIS and NIS compound recoveries (Tables 8-7 and 8-8) associated with study samples were used to derive QC acceptance criteria (Tables 8-13, 8-14, and 8-15) for inclusion in the finalized method.

10 REFERENCES

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Appendix A

Waters-ERA Spiking Procedures for Solids

PFAS Method Validation Study:

Soil & Sediment Sample Preparation Guidelines

Shipment Contents

- (1) 18”x14"x15" Styrofoam box cooler
- (3) Soil Lots - packaged in (21) x 24-mL amber glass screw-top vials
- (3) Sediment Lots - packaged in (21) x 24-mL amber glass screw-top vials
- Temperature blank
- Ice packs
- Sample Preparation Guidelines
- Sample Chain of Custody (COC)

Sample Description

- Samples are packaged in 24-mL amber screw-top vials containing approximately 5.0 g of spiked sample.
- Samples should be received at < 6°C.
- Samples are not preserved.
- Samples must be stored immediately at ≤-20°C until sample preparation.
- Each sample except the sample designated as the unspiked matrix blank will contain the PFAS analytes as defined in “MLV Study Method Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS”, October 2021.

Before You Begin

- Prior to preparation, samples should be allowed to equilibrate to room temperature and then prepare and analyzed as soon as possible.

Sample Instructions

1. The sample preparation procedure found in the MLV Study Method is to be followed, with some exceptions.

- Instead of homogenizing the sample (Section 11.3) and weighing out an aliquot of the sample (Section 11.3.1), the entire contents of the container received is to be transferred into a 50-mL polypropylene centrifuge tube. Do not measure the % moisture or the weight of the sample. The amount of sample in each container has taken into account the % moisture of the sample and 5.0 g dry weight of each sample has been sent for each sample. Record 5.00 g as the mass of sample prepared and 0% moisture as the % moisture for each sample. These are the values that should be used when calculating PFAS concentrations in each sample.

- Reserve the sample container for rinsing. Follow the steps in Sections 11.3.2 and 11.3.3. For Section 11.3.4, instead of adding 10 mL of 0.3% methanolic ammonium hydroxide to the centrifuge tube containing the sample, add it to the sample container that the sample was shipped to the laboratory in that was held in reserve. Vortex, then transfer the solution to the centrifuge tube and proceed with the method as written for the rest of Section 11.3.4 from the point after the addition of the solution to the centrifuge tube.

2. Report your results as ng/g and report the sample lot number that is provided on the sample container and on the COC, without any modifications, as the Sample Number (Sample NO on the EDD).

Appendix B

PFAS MLVS Institute for Defense Analyses Report

INTEROFFICE MEMORANDUM

SCIENCE & TECHNOLOGY
DIVISION

29 November 2023

To: Dr. Kimberly Spangler, Dr. Andrea Leeson, SERDP/ESTCP
CC: Mr. Timothy Thompson, Science, Engineering and the Environment, LLC
From: Dr. Allyson Buytendyk, Institute for Defense Analyses (IDA)
Subject: IDA Statistical Analyses in the PFAS Multi-Laboratory Validation (MLV)

In 2022, SERDP/ESTCP sponsored IDA to be the independent organization to conduct the statistical analyses in the joint Department of Defense (DoD) and Environmental Protection Agency (EPA) multi-laboratory validation (MLV) study of a PFAS measurement method—EPA Draft Method 1633. IDA's role in the PFAS MLV study is to statistically summarize the overall performance of the laboratories for each test. Results from the statistical analyses inform 1) the acceptance criteria for quality control (QC) samples that the EPA will establish for the method and 2) the precision and accuracy of measurements of the PFAS analytes in each environmental matrix studied.

The study plan for the PFAS MLV closely follows the process outlined in the EPA Alternate Test Procedure (ATP) guidance[1] which, describes the tests and statistical formulas for developing QC acceptance criteria based on data generated in a study. The ATP specifies three tiers of statistical formulas based on the number of laboratories analyzing each sample. The PFAS MLV study includes ten participating laboratories and three types of datasets: initial calibration (ICAL), initial demonstration of capability (IDC), and environmental matrix samples. Previously, IDA analyzed the ICAL, aqueous IDC and three aqueous environmental matrices: wastewater (WW), surface water (SW) and ground water (GW) datasets provided by the sponsor[2].

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[1] U.S. Environmental Protection Agency, Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternative Test Procedure Program, EPA 821-B-18-001. (Washington, DC: Environmental Protection Agency, February 2018). https://www.epa.gov/sites/default/files/2018-03/documents/chemical-atp-protocol_feb-2018.pdf.

[2] The results of the previous analysis of the aqueous datasets are documented in A. Buytendyk, K. Fisher, T. Pleasant, J. Shah, J. Silk, *Statistical Methods in the Multi-Laboratory Validation of a PFAS Measurement Method*. Alexandria: Institute for Defense Analyses, July 2023. IDA Product 3000051

IDA then analyzed the sponsor provided solids PFAS MLV datasets (solids IDC, soils (SS) and sediment (SD) environmental matrices) using the same statistical methods outlined in the MLV study plan/EPA's ATP at Tier 3[3] for the aqueous dataset. This memo outlines the formulas IDA used in the statistical analyses and also documents the version of the solids datasets that correspond to the tables and figures IDA generated for the PFAS MLV study.[4]

STATISTICAL FORMULAS

IDC DATASET

Method Detection Limit (MDL)

MDL for Spiked Samples for a Lab

The equation for the MDL for spiked samples for a laboratory is represented as:

Equation 1: MDL for Spiked Samples for a Lab ($MDL_{s,lab}$)[5]

$$MDL_{s,j} = S_{s,j} \cdot t_{(n-1,1-\propto=0.99)};$$

where $S_{s,j}$=sample standard deviation of spiked sample measured concentrations for lab j, $t_{(n-1,1-\propto=0.99)}$ = student' s t-value for the one tailed test at the 99% confidence level with n-1 degrees of freedom.

MDL for Blank Samples for a Lab[6]

- If none of the blank samples give a numerical result, the MDL for the blank samples for a laboratory does not apply.
- If some (but not all) of the blank samples give a numerical result, the MDL for the blank samples for a laboratory is the maximum value.
- If all of the blank samples give a numerical result, the MDL for the blank samples for a laboratory is represented as:

Equation 2: MDL for Blank Samples for a Lab ($MDL_{b,lab}$)[7]

$$MDL_{b,j} = \bar{X}_j + S_{b,j} \cdot t_{(n-1,1-\propto=0.99)};$$

where $\bar{X}_j$ = mean measured concentration of the blank samples for lab j, $S_{b,j}$= sample standard deviation, of the blank samples measured concentration for lab j, $t_{(n-1,1-\propto=0.99)}$ = student's t-value for the one tailed test at the 99% confidence level with n-1 degrees of freedom.

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[3] QC acceptance criteria at Tier 3 requires a minimum of nine laboratories. EPA, *Protocol for Review and Validation of New Methods,* G-22.

[4] IDA performs calculations on the dataset using coded scripts in Python version 3.7.8, rounds statistical values based on the number of significant figures reported in the dataset and delivers the outputs as CSV files to the sponsor.

[5] 40 CFR Part 136, Appendix B; EPA, *Protocol for Review and Validation of New Methods,* G-9.

[6] 40 CFR Part 136, Appendix B; EPA, *Protocol for Review and Validation of New Methods,* G-9.

[7] 40 CFR Part 136, Appendix B; EPA, *Protocol for Review and Validation of New Methods,* G-9.

Lab MDL

The equation for the MDL for a laboratory is represented as:

Equation 3: MDL for a Lab (MDL_{lab})[8]

$$MDL_j = \max\{MDL_{s,j}, MDL_{b,j}\};$$

where $MDL_{s,j}$ = the MDL for the spiked samples for lab j, $MDL_{b,j}$ = the MDL for the blank samples for lab j.

Pooled MDL

The equation for MDL that is pooled using individual lab MDL values is represented as:

Equation 4: Pooled MDL (MDL_{pooled})[9]

$$MDL_{pooled} = \sqrt{\sum_{j=1}^{m} \frac{n_j}{N} \left(\frac{MDL_j}{t_{(n_j, 1-\alpha=0.99)}} \right)^2} \, t_{(N, 1-\alpha=0.99)};$$

where m = number of labs, MDL_j = method detection limit for the *jth* lab, $n_{,j}$ = number of replicates for the *jth* lab, N = total number of replicates, $\boldsymbol{t_{(n,1-\alpha=0.99)}}$= student's t-value for the one tailed test at the 99% confidence level with n degrees of freedom.

Limit of Quantitation Verification (LOQVER)

The equation for percent bias of laboratory measurements near the limit of quantitation (LOQ) is represented as:

Equation 5: LOQ Percent Bias[10]

$$LOQ_{bias,j} = \frac{\text{spike concentration} - \overline{\mathrm{X}}_j}{\text{spike concentration}} \cdot 100;$$

where $\overline{\mathrm{X}}_j$ = mean of the measured sample concentrations for lab j.

Initial Precision and Recovery (IPR)

The equation for the between laboratory standard deviation is represented as:

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[8] Code of Federal Regulations (CFR), Title 40, Part 136, Appendix B.

[9] EPA, *Protocol for Review and Validation of New Methods,* G-22.

[10] Department of Defense, Department of Energy (DoD, DOE), *DoD Quality Systems Manual Version 5.4*, Module 4, Section 1.5.2 (Washington, DC: DoD, DOE, 2021), 77–78, https://www.denix.osd.mil/edqw/denix-files/sites/43/2021/10/QSM-Version-5.4-FINAL.pdf.

Equation 6: Between Lab Standard Deviation (s_b)[11]

$$s_b = \sqrt{\frac{\sum_{j=1}^{m}\left(\overline{X_j}-\overline{X}\right)^2}{\mathrm{m-1}}};$$

where m = the number of labs, $\overline{\mathrm{X}}$ = overall mean percent recovery, $\overline{X_j}$ = the mean percent recovery for the *jth* lab.

The equation for the within-laboratory standard deviation is represented as:

Equation 7: Within Lab Standard Deviation (s_w)[12]

$$s_w = \sqrt{\frac{\sum_{j=1}^{m}\left(s_j\right)^2}{\mathrm{m}}};$$

where m = the number of labs, s_j = the variance of the percent recovery values for the *jth* lab.

The equation for the combined standard deviation for IPR results in the study is represented as:

Equation 8: IPR Combined Standard Deviation (s_{IPR})[13]

$$s_{IPR} = \sqrt{\left(1+\frac{1}{m}\right)s_b^2 + \left(\frac{1}{4}-\frac{1}{n}\right)s_w^2};$$

where m = the number of labs, n = the number of data points per lab, s_b = the between lab standard deviation, s_w = the within lab standard deviation.

The equation for the relative standard deviation (RSD) across all laboratories is represented as:

Equation 9: RSD[14]

$$RSD = \frac{\mathrm{s}_w}{\overline{X}} \cdot 100;$$

where s_w = the within lab standard deviation, $\overline{X}$= mean percent recovery across all labs.

ENVIRONMENTAL MATRIX DATASET

Ongoing Precision and Recovery (OPR) & Low-Level Ongoing Precision and Recovery (LLOPR)

The equation for the combined standard deviation for the OPR and LLOPR results in the study is represented as:

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[11] EPA, *Protocol for Review and Validation of New Methods,* G-25.

[12] EPA, *Protocol for Review and Validation of New Methods,* G-25.

[13] EPA, *Protocol for Review and Validation of New Methods,* G-25.

[14] EPA, *Protocol for Review and Validation of New Methods,* G-26.

Equation 10: OPR Combined Standard Deviation (s_{OPR})[15]

$$s_{OPR} = \sqrt{\left(1 + \frac{1}{m}\right) s_b^2 + \left(1 - \frac{1}{n}\right) s_w^2}\ ;$$

where m = the number of labs, n = the number of data points per lab, s_b = the between-lab standard deviation, s_w = the within-lab standard deviation.

Equation 9 provides the formula for the RSD for the OPR test. The calculations for the LLOPR test follow those for the OPR using Equations 6, 7, 9 and 10.

Matrix Spike Recovery

The calculations for the matrix spike test include those in Equations 6 and 7 to determine s_b and s_w as well as Equation 9 to find the RSD for the matrix test.

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[15] EPA, *Protocol for Review and Validation of New Methods,* G-26.

DATASETS & IDA GENERATED PRODUCTS FILE NAMES

IDA Generated Product	
Tables	**Figures**
Solids Initial Demonstration of Capabilities Dataset OS_DBexport_V0_20231018.xlsx	
OS_IPR_results_V1_231109_095126.csv	OS_IPR_Boxplot_V2_231121_101003.png
OS_LOQVER_results_V1_231109_095126.csv	OS_IPR_Horwitz_V2_231121_101003.png
OS_MDL_results_V1_231109_095126.csv	OS_LOQVER_Boxplot_V2_231121_101003.png
	OS_MDL_Plot_V2_231121_101003.png
Sediments Matrix Dataset SD_DBexport_V0_20230921.xlsx	
SD_LLOPR_results_V0_230927_151133.csv	SD_LLOPR_Boxplot_V1_231122_100457.png
SD_OPR_results_V0_230927_151133.csv	SD_OPR_Boxplot_V1_231122_100457.png
SD_EIS_Phase4_py_log_V0_230927_151133.txt	SD_HighSpike_Boxplot_V1_231122_100457.png
SD_Matrix_sample_results_V0_230927_151133.csv	SD_LowSpike_Boxplot_V1_231122_100457.png
SD_Matrix_compiled_results_V0_230927_151133.csv	SD_LowHighCombinedSpike_Boxplot_V1_231122_100457.png
SD_MB_results_V0_230927_151133.csv	SD_EIS_Boxplot_V1_231122_100457.png
Soils Matrix Dataset SS_DBexport_V3_20230927.xlsx	
SS_LLOPR_results_V1_230928_173420.csv	SS_LLOPR_Boxplot_V2_231122_095457.png
SS_OPR_results_V1_230928_173420.csv	SS_OPR_Boxplot_V2_231122_095457.png
SS_EIS_results_V1_230928_173420.csv	SS_HighSpike_Boxplot_V2_231122_095457.png
SS_Matrix_sample_results_V1_230928_173420.csv	SS_LowSpike_Boxplot_V2_231122_095457.png
SS_Matrix_compiled_results_V1_230928_173420.csv	SS_LowHighCombinedSpike_Boxplot_V2_231122_095457.png
SS_MB_results_V1_230928_173420.csv	SS_EIS_Boxplot_V2_231122_095457.png
All Solids Matrix Dataset SS_SD_EXPORT_V1_20230927.xlsx	
ALL_LLOPR_results_V0_231005_084136.csv	ALL_LLOPR_Boxplot_V0_231005_084136.png
ALL_OPR_results_V0_231005_084136.csv	ALL_LLOPR_Horwitz_V1_231109_102618.png
ALL_EIS_results_V0_231005_084136.csv	ALL_OPR_Boxplot_V0_231005_084136.png
ALL_NIS_results_V0_231005_084136.csv	ALL_OPR_Horwitz_V1_231109_102618.png
	ALL_NIS_Boxplot_V0_231005_084136.png

Appendix C

Soil Supporting Tables

Table C-1. Target Analytes Detected in Unspiked Soil Samples by Laboratory (ug/kg).

Analyte	Number of Labs	SSR1		SST1		SSW1	
		Min	Max	Min	Max	Min	Max
PFBA	10	0.0514 U	0.31 U	0.05 U	0.31 U	0.05 U	0.322 J
PFPeA	10	0.039 U	0.133 U	0.039 U	0.133 U	0.039 U	0.133 U
PFHxA	10	0.0375 U	0.204 J+B	0.0375 U	0.109 U	0.0375 U	0.273 J+B
PFHpA	10	0.023 U	0.112 U	0.023 U	0.112 U	0.023 U	0.112 U
PFOA	10	0.0315 U	0.187 U	0.0315 U	0.268 IJ	0.052 U	0.187 U
PFNA	10	0.044 U	0.565 U	0.044 U	0.565 U	0.078 U	0.565 U
PFDA	10	0.036 U	0.128 U	0.036 U	0.128 U	0.038 U	0.128 U
PFUnA	10	0.024 U	0.457 U	0.024 U	0.457 U	0.051 U	0.457 U
PFDoA	10	0.038 U	0.12 U	0.038 U	0.12 U	0.038 U	0.12 U
PFTrDA	10	0.022 U	0.192 U	0.022 U	0.192 U	0.0339 U	0.192 U
PFTeDA	10	0.03 U	0.208 U	0.03 U	0.208 U	0.03 U	0.208 U
PFBS	10	0.027 U	0.088 U	0.027 U	0.088 U	0.027 U	0.088 U
PFPeS	10	0.0149 U	0.16 U	0.0149 U	0.16 U	0.0149 U	0.16 U
PFHxS	10	0.015 U	0.16 U	0.015 U	0.16 U	0.015 U	0.16 U
PFHpS	10	0.025 U	0.15 U	0.025 U	0.15 U	0.025 U	0.15 U
PFOS	10	0.1 J	0.2	0.0414 U	0.166 U	0.093 J	0.256
PFNS	10	0.0213 U	0.18 U	0.0213 U	0.18 U	0.0213 U	0.18 U
PFDS	10	0.027 U	0.176 U	0.027 U	0.176 U	0.027 U	0.176 U
PFDoS	10	0.027 U	0.168 U	0.027 U	0.168 U	0.027 U	0.168 U
4:2FTS	10	0.081 U	0.397 U	0.081 U	0.397 U	0.081 U	0.397 U
6:2FTS	9	0.139 U	0.51 U	0.139 U	0.51 U	0.139 U	0.51 U
8:2FTS	10	0.102 U	0.61 U	0.102 U	0.61 U	0.102 U	0.61 U
PFOSA	10	0.014 U	0.259 J	0.014 U	0.127 U	0.0273 U	0.127 U
NMeFOSA	9	0.029 U	0.2 J	0.029 U	0.14 U	0.034 U	0.14 U
NEtFOSA	9	0.017 U	0.185 J	0.017 U	0.128 U	0.017 U	0.128 U
NMeFOSAA	10	0.0304 U	0.16 U	0.0304 U	0.16 U	0.0304 U	0.16 U
NEtFOSAA	10	0.026 U	0.2 U	0.026 U	0.2 U	0.026 U	0.2 U
NMeFOSE	10	0.151 U	1 U	0.151 U	1 U	0.151 U	1 U
NEtFOSE	10	0.063 U	0.83 U	0.063 U	0.83 U	0.0931 J	0.83 U
PFMPA	10	0.041 UJ	0.133 U	0.041 UJ	0.133 U	0.041 U	0.133 U
PFMBA	10	0.031 UJ	0.133 U	0.031 UJ	0.133 U	0.031 U	0.133 U
NFDHA	10	0.06 U	0.282 U	0.06 U	0.282 U	0.06 U	0.282 U
HFPO-DA	10	0.051 U	0.432 U	0.051 U	0.432 U	0.051 U	0.432 U
ADONA	10	0.079 U	0.34 U	0.079 U	0.34 U	0.079 U	0.34 U
PFEESA	10	0.034 U	0.136 U	0.034 U	0.136 U	0.034 U	0.136 U
9Cl-PF3ONS	10	0.081 U	0.44 U	0.081 U	0.44 U	0.081 U	0.44 U
11Cl-PF3OUdS	10	0.088 U	0.36 U	0.088 U	0.36 U	0.088 U	0.36 U
3:3FTCA	10	0.103 U	0.51 U	0.103 U	0.51 U	0.103 U	0.51 U
5:3FTCA	10	0.133 U	1.31 U	0.133 U	1.31 U	0.133 U	1.35 J
7:3FTCA	10	0.563 U	2.7 J	0.563 U	1.76 U	0.563 U	1.76 U

Source: Appendix_Soil 11152023.xlsx

Table C-2. Summary of Soil Spike Percent Recoveries in Low-Spiked Samples.

Analyte	Lab 1 spike % recovery				Lab 2 spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	89.2	98	93.2	9	93.6	99	96.1	8	94.2	107.4	102.3	8	96	107	101.4
PFPeA	9	89.5	94.8	91.1	9	97	101	98.7	9	94.8	112.8	101.8	9	90	110	98.9
PFHxA	9	80.2	92	86.4	9	99.2	105.5	101.9	9	87.5	104.8	93.6	9	92	104.2	98.5
PFHpA	9	84	94.8	88.1	9	95.2	107.2	99.5	9	87	99.5	95.1	9	92.8	102.8	98.5
PFOA	9	79.8	92.6	85.8	9	95.8	109	102.9	9	95.5	109.1	103.1	9	90.5	107.8	98.0
PFNA	9	73	83.4	80.2	9	88.5	99.5	94.7	9	90	114.5	99.0	9	93.5	103.2	97.8
PFDA	9	85	111.5	94.8	9	87.2	104.8	97.3	9	94.8	117	101.8	9	90.2	104.8	98.7
PFUnA	9	82.2	98.5	90.9	9	86.5	102.1	97.8	9	82	114	96.6	9	92.5	112.7	100.9
PFDoA	9	77.5	87.5	82.7	9	99.5	109.7	103.5	9	95	115.3	104.6	9	92.5	110.8	104.6
PFTrDA	9	76.2	97.5	86.5	9	69.5	111	95.6	9	93.8	106.2	100.8	9	88	104.3	97.9
PFTeDA	9	76.5	90.2	84.0	8	98.8	105.8	102.7	9	70.8	99.8	89.5	9	94.8	108.2	101.3
PFBS	9	76.8	88.2	83.5	9	92.2	99.5	96.4	9	94.8	112.5	100.3	9	96.2	112	103.4
PFPeS	9	76	91.1	83.6	9	93.3	129.2	102.2	9	88.6	100.7	95.7	9	92.3	108.9	99.8
PFHxS	9	76.1	89.5	82.7	9	95.3	102	98.6	9	83.8	99.8	95.3	9	94.5	113	103.8
PFHpS	9	76.3	90	82.5	9	95.3	155.4	104.5	9	91.3	131.9	105.3	9	85	112	98.6
PFOS	9	80.2	99.5	87.4	9	93	112	100.5	9	90.6	102.7	97.4	9	87.5	106.2	97.3
PFNS	9	72.8	91.6	82.1	9	72.3	96.8	89.7	9	93.3	108.7	101.3	9	89.6	104.7	99.3
PFDS	9	66.6	81.8	74.8	9	43.5	93.7	82.4	9	89.9	110.1	100.3	9	81	105.8	96.2
PFDoS	9	55.8	76.9	64.9	9	23.8	91	75.1	9	96.5	114.1	106.3	9	83.2	98.2	93.5
4:2FTS	9	81.1	92.3	86.1	9	87.6	97.3	92.2	9	90.1	112.9	99.4	9	85.4	102.5	98.0
6:2FTS	9	86	92	88.6	9	92.5	107	102.6	9	93.2	109.2	99.4	9	90.5	112.8	99.2
8:2FTS	9	83.6	100.2	90.1	9	108.2	117.9	112.2	9	100.2	124.6	114.2	9	95.3	128.8	110.6
PFOSA	9	89.8	99.2	93.7	9	87.3	99.2	95.7	9	94.5	106.5	99.8	9	94.5	108.7	100.2
NMeFOSA	9	79.5	93.5	87.7	9	93.8	110	99.2	9	89.5	114.2	103.6	8	88.5	117	103.1
NEtFOSA	9	87.5	94.5	90.2	9	85.6	96.5	91.9	9	97.5	128.8	116.3	6	99	115	107.9
NMeFOSAA	9	80.5	94	85.3	9	92	100.8	96.1	9	102.8	122	111.2	9	88.2	106.7	96.1
NEtFOSAA	9	78.2	95.2	86.5	9	88	98.5	93.0	9	92.5	111.2	105.1	9	93.2	113	103.7
NMeFOSE	9	78.7	91.1	84.9	9	77.6	98.1	91.7	9	83.5	106	96.6	9	97.2	109	101.0
NEtFOSE	9	81.6	89.4	86.3	8	88.9	101	93.9	9	92.4	117	107.2	9	94.7	111	101.1
PFMPA	9	92.8	104.2	98.2	9	89.5	97.5	94.4	9	29.8	91	67.5	9	95	106.5	101.6
PFMBA	9	84.5	93.5	87.8	9	96.5	102.2	99.2	9	87.5	125.5	98.0	9	97.5	108.2	103.4
NFDHA	9	64.8	89.8	79.5	9	90.5	103.8	98.3	9	72.8	108.5	89.5	9	88.5	110.5	101.4
HFPO-DA	9	82.8	97.8	91.8	9	95.8	109.5	101.2	9	88.8	101.5	95.1	9	98	130.8	108.6
ADONA	9	86.4	102	94.9	9	88.1	107.3	99.3	9	87.1	113.1	95.8	9	96	119.4	105.0
PFEESA	9	81.3	102.2	92.5	9	73.1	103.5	93.4	9	66.8	90.5	78.1	9	90.5	105	99.2
9Cl-PF3ONS	9	84.1	100.2	96.0	9	17.6	109.2	90.3	9	69.2	125.6	92.3	9	102	130.8	114.2
11Cl-PF3OUdS	9	71.7	86.6	80.4	8	39.9	97.2	86.9	9	72	122.7	90.5	9	96.2	119.4	108.5
3:3FTCA	9	54.5	71.2	63.7	9	59.8	81.2	72.8	9	41.5	93.8	74.0	9	64.5	74.5	69.9
5:3FTCA	9	48.2	71	59.6	9	61.3	90	73.4	9	73	112.5	88.8	9	71.5	86	77.3
7:3FTCA	9	53	68.5	62.5	9	38	93	66.9	9	99.5	133	112.8	9	70.5	87	76.8

Source: Appendix_Soil 11152023.xlsx

-- : X-flagged results

Table C-2. Summary of Soil Spike Percent Recoveries in Low-Spiked Samples.

Lab 5 spike % recovery				Lab 6 spike % recovery				Lab 7 spike % recovery				Lab 8 spike % recovery			
n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
8	109.5	164.7	118.7	9	88.8	95.8	92.4	9	80	82.5	80.6	9	111.8	127.5	122.0
8	106.7	116	111.4	9	90.2	108.7	96.1	9	90	97.5	93.9	9	116.3	144	133.7
8	96.7	115.7	106.1	9	86.2	102.8	93.9	9	90	97.5	92.8	9	99.8	116.8	110.8
8	108.2	118.3	113.0	9	76.8	104.8	90.6	9	85	92.5	88.9	9	98.5	116.8	108.5
8	96.4	130.8	111.1	9	76.6	92.2	85.3	9	87.5	97.5	93.1	9	100.2	119.3	110.4
8	89.5	140.2	115.1	9	76.8	95.2	86.2	9	90	98.2	94.7	9	98.8	125.2	114.7
8	98.2	126.2	113.0	9	82.8	89.8	85.1	9	86.1	102.5	95.6	9	114.8	134.2	125.7
8	104	137	119.9	9	80.5	96.8	88.0	9	82.5	91	86.7	9	99.5	123.2	113.8
8	100.2	145	116.9	9	74.2	117.8	96.7	9	90	95	92.8	9	109.7	132.5	123.4
8	94	133.8	112.9	9	65.5	125	94.2	9	80	87.5	84.2	9	104.8	124	117.2
8	99.2	145	112.7	9	63.7	115	90.7	9	92.5	102.5	96.9	9	98.8	117	110.7
8	98	111.8	105.7	9	73	99.5	89.5	9	80	97.5	89.4	9	98.5	118.3	107.8
8	109.7	142.3	120.1	9	70.5	94.3	82.8	9	76.7	94.1	85.8	9	110.6	125.5	117.0
8	107	120.9	113.2	9	79.8	121.7	92.7	9	92.3	107.2	99.2	9	107	121.7	115.6
8	119.2	158.4	131.9	9	76.6	99.5	87.5	9	79.8	99.8	88.1	9	96.3	122.4	111.0
8	108.4	116.5	112.4	9	71.8	93	81.0	9	87.5	95.2	90.6	9	98.5	125.2	113.9
8	102.7	117.1	110.9	9	72.8	90.1	81.8	9	89.1	101.5	96.0	9	103.2	128.5	116.5
8	111.1	130.1	119.5	9	69.4	89.6	77.2	9	68.4	75.9	73.1	9	94.7	119.7	109.5
8	103.8	152.5	118.9	9	45.2	79.1	63.9	9	67.8	80.4	73.7	9	90.7	112.3	101.1
8	110.2	117.9	113.2	9	48.4	101.5	85.1	9	67	84.4	75.0	9	95.8	106.2	101.4
0	--	--	--	9	51	134	87.5	9	72.5	87.5	81.7	9	106.5	123.5	112.6
8	120.6	130.3	125.2	9	52.6	118.4	87.3	9	91.8	106.7	97.3	9	105	126.1	119.2
8	109.5	122.8	117.8	9	81.8	103.2	90.0	9	87.5	92.5	89.7	9	103.2	128	120.0
8	108	118.5	113.2	9	84.2	93.2	89.6	9	85	95	88.9	0	--	--	--
8	107.5	115.3	111.6	9	80	108.7	93.2	9	82.5	97.5	89.2	0	--	--	--
8	106.2	119.2	114.0	9	78	108	88.0	9	67.5	82.5	75.0	9	108	122.2	116.3
8	117	123.8	120.3	9	86.2	107	93.9	9	70	82.5	72.8	9	106.2	121.8	116.3
8	111	130	117.5	9	77.3	108	91.8	9	81	91	84.3	9	105	123	117.1
8	97.8	121	110.4	9	83.1	105	89.8	9	87	97	91.0	9	106	124	116.7
8	107.2	138.2	119.4	9	47.5	98.8	80.2	9	90	97.5	94.2	9	94.2	118.8	110.4
8	95	130.8	114.2	9	83	128	96.8	9	90	100	95.6	9	97.8	118	111.9
8	114.5	140	126.5	9	63.5	176.2	104.3	9	92.5	100	95.3	9	92.5	109.7	100.9
8	88.2	117	106.7	9	75.5	101.2	92.7	9	80	87.5	84.7	9	81	104	93.7
8	111.1	150.5	131.6	9	78.8	111.6	95.0	9	85.9	90.9	87.6	9	106.8	122.2	116.0
8	97.5	128.4	116.3	9	73.6	101.7	92.4	9	79.8	99.8	91.7	9	98	123.7	111.8
8	60.2	143.8	110.7	9	73.1	133.3	102.2	9	89.6	102	97.0	9	97	121.1	110.3
8	64.1	149.2	114.3	9	69.7	104.3	88.4	9	68.2	80.8	75.2	9	87.9	117.9	100.6
8	64.2	96	84.1	9	58.2	76.2	68.2	9	30	62.5	45.8	9	47	87.5	71.2
8	72.5	110	90.2	9	60	95	77.8	9	34	61.5	49.0	9	55.5	111	86.6
8	49.5	95	73.7	9	59.5	93.5	75.3	9	39	64.5	54.2	9	53	109.5	84.2

Table C-2. Summary of Soil Spike Percent Recoveries in Low-Spiked Samples.

Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike % recovery			
n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
8	91	97.8	94.0	9	88.2	111.5	101.0	86	80	164.7	100.0
9	88.5	94.2	91.1	9	83.2	111.2	96.0	89	83.2	144	101.1
9	89.2	94.2	91.7	9	90.4	116.6	105.4	89	80.2	116.8	98.0
9	85.5	94.8	90.0	9	89.5	116.5	101.2	89	76.8	118.3	97.2
9	80.8	90.8	87.1	9	85.5	106.4	93.8	89	76.6	130.8	96.9
9	78.2	97.5	89.4	9	83.2	109.2	98.1	89	73	140.2	96.8
9	79.8	98.2	91.5	9	80.8	110.8	97.0	89	79.8	134.2	99.9
9	70	93	86.1	9	88.2	115	100.1	89	70	137	97.8
9	69.5	96.5	86.2	9	82	107.7	97.2	89	69.5	145	100.7
9	72	99.1	89.8	9	88.5	109.9	100.3	89	65.5	133.8	97.8
9	69.5	97.5	87.0	9	84.8	107.7	97.8	88	63.7	145	97.1
9	79.8	95.8	89.7	9	71.2	108.7	88.3	89	71.2	118.3	95.3
9	80.2	92.6	87.8	9	84.7	107.4	97.0	89	70.5	142.3	96.9
9	80.8	95.8	89.5	9	90.5	101.2	95.7	89	76.1	121.7	98.5
9	77.6	99.8	88.2	9	92	117.2	101.5	89	76.3	158.4	99.6
9	88.8	129	101.9	9	88.8	104.1	96.5	89	71.8	129	97.7
9	75.7	97	89.2	9	82.2	101.7	90.1	89	72.3	128.5	95.5
9	71.6	99.2	88.6	9	81.8	103	92.4	89	43.5	130.1	91.1
9	66.1	94.5	83.8	9	77.4	99.2	83.7	89	23.8	152.5	86.1
9	92.1	97.3	94.6	9	49.4	98	74.4	89	48.4	117.9	91.7
9	89.2	98.2	94.3	9	76	121.8	99.7	81	51	134	96.2
9	83.6	103	95.6	9	83.1	137.5	109.8	89	52.6	137.5	105.9
9	76.5	98.2	88.0	9	83.2	110.2	96.7	89	76.5	128	99.0
9	71	98	88.5	9	86.2	105.4	97.1	79	71	118.5	96.5
9	73.2	99.8	90.6	9	90.8	110	100.0	77	73.2	128.8	98.5
9	68.2	96.2	85.1	9	77.2	96.5	87.6	89	67.5	122.2	95.3
9	71	95.8	87.0	9	90	124.8	113.6	89	70	124.8	99.0
9	63.9	95.1	84.3	9	80.8	101	92.4	89	63.9	130	95.9
9	66.5	98.6	86.1	9	82.4	102.1	93.5	88	66.5	124	97.5
9	21.1	93.8	64.6	9	76.2	105	92.5	89	21.1	138.2	92.0
9	91	132.2	101.3	9	81.2	105.5	93.1	89	81.2	132.2	100.0
9	87	96.2	89.9	9	79.5	110.8	95.1	89	63.5	176.2	97.7
9	86	95.5	91.3	9	99.5	147.5	110.0	89	75.5	147.5	97.5
9	91.2	100	94.7	9	97.7	147.7	118.2	89	78.8	150.5	103.5
9	79.6	98.8	90.9	9	83.3	114.7	97.0	89	66.8	128.4	96.1
9	79.1	107.2	98.3	9	103.2	149	123.0	89	17.6	149	103.3
9	75.5	108.6	98.2	9	99.2	136.9	110.5	88	39.9	149.2	95.2
9	37.2	82	60.0	9	55.2	84.8	72.4	89	30	96	68.0
9	61	88.5	78.7	9	64.5	97	82.4	89	34	112.5	76.2
9	66.5	93	76.9	9	64	110	88.3	89	38	133	77.2

Table C-3. Summary of Soil Spike Percent Recoveries in High Spike Samples for each Laboratory.

Analyte	Lab 1 spike % recovery				Lab 2 spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	90.4	97.8	94.6	9	98.6	104.6	101.9	8	93.6	108.8	103.9	9	106.2	116.4	110.3
PFPeA	9	86.2	94.8	90.3	9	98.2	105.8	102.7	9	92.8	120.2	104.0	9	95.8	105.4	101.1
PFHxA	9	82.8	92.9	87.8	9	99.2	106.8	103.7	9	80.8	104	95.8	9	94.4	107.2	100.0
PFHpA	9	82.8	94	88.4	9	101.2	107.2	104.4	9	85.6	101.2	94.1	9	97.6	104	100.9
PFOA	9	86.5	98.1	90.8	9	102.5	113.3	107.3	9	97.6	112	105.5	9	93.6	110.9	101.8
PFNA	9	78	96.1	85.9	9	98	107.2	102.0	9	86.4	112.4	98.8	9	96.8	106	101.8
PFDA	9	82.8	105.6	93.6	9	101.6	110.8	105.3	9	92	116.8	101.6	9	92.8	102.1	97.7
PFUnA	9	79.6	95.6	88.6	9	98	109.2	102.8	9	93.2	114	100.7	9	88.8	107.2	100.0
PFDoA	9	76.4	101.2	84.6	9	101.6	111.6	106.2	9	92	112.8	101.5	9	92	107.6	97.7
PFTrDA	9	76.8	94.4	85.3	9	72.8	108.8	99.0	9	97.6	109.6	102.7	9	87.2	105.4	95.6
PFTeDA	9	79.6	91.6	85.9	8	94	104.4	100.6	9	70.8	95.6	84.0	9	92.8	108	100.0
PFBS	9	80.8	91.6	84.2	9	96.4	105.2	102.0	9	96	111.2	103.0	9	101.6	117.2	110.0
PFPeS	9	82	96.8	85.9	9	103.6	136.8	109.8	9	91.2	108	100.8	9	97.2	116.8	105.2
PFHxS	9	78.4	104	86.8	9	98.4	106.4	103.0	9	91.2	104.4	99.0	9	106	116.8	110.3
PFHpS	9	80	96.8	88.7	9	99.6	147.2	111.5	9	98	115.2	104.8	9	88.4	110.8	99.6
PFOS	9	86.6	99.8	93.1	9	100	112	104.8	9	91.3	102.8	97.2	9	90.8	105	99.8
PFNS	9	83.2	96.4	88.8	9	62	108.4	95.7	9	96.4	112.4	102.8	9	88.8	106.4	101.2
PFDS	9	68.1	84.9	78.7	9	33.6	101.6	87.0	9	94.8	107.6	100.9	9	84.9	106	99.3
PFDoS	9	54.4	76	67.6	9	14.1	100.4	80.2	9	104	118.4	109.0	9	87.2	104.8	96.4
4:2FTS	9	81.2	108	89.9	9	86.8	103.2	94.8	9	90.8	105.6	98.1	9	95.2	107.6	103.0
6:2FTS	9	86.3	98.4	94.3	9	102.4	113.3	107.2	9	90.8	107.6	100.7	9	91.2	116.1	101.0
8:2FTS	9	87.6	110.8	97.3	9	108.4	122.8	114.8	9	103.6	118.8	111.4	9	98.8	119.2	108.0
PFOSA	9	85.2	100	93.0	9	95.6	104.4	101.4	9	99.2	107.6	103.0	9	95.6	109.6	101.7
NMeFOSA	9	84	94	88.1	9	87.6	105.6	99.4	9	85.6	109.2	101.4	9	85.6	112.8	101.2
NEtFOSA	9	84.4	99.6	92.5	9	88.8	97.6	93.3	9	93.2	121.6	110.5	8	103.6	122	111.7
NMeFOSAA	9	81.4	96.5	87.0	9	94	106.2	102.0	9	100.4	123.8	112.4	9	87.1	107.6	101.6
NEtFOSAA	9	83.6	93.2	87.4	9	93.2	102.9	97.5	9	86.4	112.2	100.4	9	96.4	112.8	105.3
NMeFOSE	9	84.8	92	88.3	9	87.4	99	95.8	9	86	113.8	99.2	9	96.8	109	103.8
NEtFOSE	9	84	98.4	90.5	8	91	102.8	96.6	9	87	119.4	106.0	9	96.4	108.4	102.0
PFMPA	9	67.8	106.2	98.4	9	57.6	105.2	93.3	9	31.6	96.2	72.2	9	65.8	108.2	96.3
PFMBA	9	84.6	95.2	89.2	9	98	111.8	104.5	9	91.6	122.8	101.5	9	101	111.6	106.0
NFDHA	9	66.9	101.2	80.5	9	98.8	108.1	105.1	9	75.6	110	90.5	9	86.9	133.1	116.7
HFPO-DA	9	90.8	108.8	97.2	9	89.6	113.2	105.7	9	82	100.4	93.2	9	99.6	120.8	111.2
ADONA	9	83.9	99.6	92.5	9	95.6	111.2	102.4	9	91.2	129.7	103.8	9	95.6	119.7	106.9
PFEESA	9	80.7	96.9	85.6	9	90.7	108.1	101.6	9	73.3	100	89.7	9	100.6	110.6	105.7
9Cl-PF3ONS	9	84	108.8	100.8	9	18.1	112	91.3	9	70.4	150.4	99.1	9	102.4	122.8	113.8
11Cl-PF3OUdS	9	66.3	92	82.3	9	4.9	102.8	80.2	9	71.5	144.6	99.7	9	95.6	124.1	111.0
3:3FTCA	9	53.2	77.2	66.6	9	62	89.6	75.8	9	43.6	107.6	83.6	9	67.6	80.4	74.6
5:3FTCA	9	52.9	71.9	62.8	9	66.7	93.2	83.5	9	83.1	125.6	103.4	9	70.6	91.2	81.7
7:3FTCA	9	54.7	82.5	65.0	9	62.4	87.7	75.0	9	117.5	166.2	136.6	9	71.9	91.9	82.2

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Table C-3. Summary of Soil Spike Percent Recoveries in High Spike Samples for each Laboratory.

Lab 5 spike % recovery				Lab 6 spike % recovery				Lab 7 spike % recovery				Lab 8 spike % recovery			
n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
9	111.8	116.8	115.2	9	84.8	92.6	88.6	9	66.8	104.6	92.9	9	110.2	126.6	120.9
9	99.9	123	113.6	9	76.6	91.4	85.5	9	74.6	115.6	104.0	9	109.2	118.4	113.7
9	88.8	125.2	107.7	9	77.6	88.4	83.9	9	73.6	108	98.8	9	110.8	644	176.9
9	108	129.6	116.8	9	72.4	89.2	81.5	9	66.8	106.8	95.3	9	101.6	688	181.0
9	101.6	118.8	110.1	9	73.3	97.3	84.4	9	72.8	110.8	99.3	9	97.2	122.8	111.2
9	102	146	126.6	9	68.8	101.8	88.5	9	76.1	113.2	101.7	9	98.8	129.8	116.7
9	90	156.4	115.9	9	78	94	84.8	9	84.6	119.6	106.3	9	94.4	130	116.2
9	100.4	158	124.2	9	78.8	93.2	85.8	9	87.8	109.2	97.7	9	105.2	132.8	121.5
9	102.8	129.2	116.0	9	58	122.8	90.4	9	72	108.8	99.3	9	106	129.2	119.2
9	108.4	133.6	119.7	9	76.8	144.8	100.4	9	58	96.4	87.4	9	118	142.4	127.3
9	102.8	128.4	111.4	9	63.2	99.6	81.9	9	79.6	112.4	101.8	9	100.8	121.6	113.5
9	105.6	113.6	109.1	9	62.4	108	86.3	9	78.8	124.8	107.3	9	109.2	127.6	118.6
9	115.6	123.6	118.2	9	75.2	107.2	85.7	9	71.6	119.6	100.1	9	111.6	133.2	122.8
9	112	120	114.4	9	75.6	107.2	85.9	9	74	133.2	112.0	9	109.2	126.4	118.8
9	119.6	127.2	123.9	9	74	109.2	91.2	9	80.4	114.4	105.6	9	112.4	133.6	120.1
9	110.4	119.7	115.2	9	75.8	107.5	87.8	9	75.1	116.9	105.1	9	98.4	126.8	112.5
9	108	118.8	113.8	9	68	100.8	81.5	9	81.2	118	108.5	9	92.4	129.2	112.3
9	115.9	130.3	123.5	9	62.9	85.7	75.8	9	74.1	95.2	88.5	9	76.1	123.1	103.2
9	117.6	130.8	123.3	9	51.6	85.2	68.8	9	50.8	103.6	88.1	9	62	111.6	92.8
9	112	122.8	117.4	9	60.4	109.6	89.2	9	66	97.2	88.1	9	97.2	114.4	104.7
0	--	--	--	9	58	123.7	84.4	9	74.7	106	96.0	9	102.8	125.3	116.9
9	123.2	136	129.9	9	61.2	107.2	78.8	9	92	125.2	113.0	9	101.2	121.2	113.7
9	117.6	122.8	120.0	9	78	94.8	84.4	9	82.8	113.6	102.1	9	106	620	172.8
9	110.8	116.4	114.3	9	80	96	85.5	9	81.6	110.4	99.6	0	--	--	--
9	108	114	111.4	9	82	105.2	93.1	9	76	114.4	102.3	0	--	--	--
9	115.1	126.2	121.6	9	75.2	90.4	84.2	9	28.7	90	76.8	9	108.6	124.6	118.7
9	118.4	131.6	124.3	9	74.4	107.2	90.1	9	32.4	94.8	80.9	9	106.8	122.8	115.6
9	106.6	122.6	116.9	9	77.4	96.6	88.5	9	80.6	105.8	94.7	9	104.8	123.8	118.1
9	91.2	113.6	100.3	9	71.6	99.4	87.9	9	77.2	113	98.2	9	103	123.8	115.4
9	105.2	130	120.8	9	33.2	95.6	68.9	9	74.8	120.2	107.1	9	112	129.2	122.0
9	103.8	134.8	118.1	9	86.2	126.4	101.2	9	71.6	117.6	104.7	9	113	123.4	118.7
9	106.9	128.8	118.0	9	74.4	150	97.7	9	73.8	110	101.2	9	88.1	101.2	93.8
9	100.8	134.4	114.4	9	81.6	106	92.6	9	76	106.4	96.1	9	82	108.4	97.3
9	129.7	161.4	143.5	9	77.9	91.2	84.8	9	64.7	101.2	91.0	9	102.4	119.7	111.8
9	110.6	132.3	124.5	9	77	95.7	87.0	9	80.1	116.8	103.8	9	116.1	128.6	123.3
9	121.6	146	132.6	9	70.8	101.6	87.4	9	66.4	106.8	95.0	9	92	124.8	109.7
9	125.3	162.2	142.4	9	68.7	88.4	80.6	9	67.9	91.6	82.0	9	76.3	121.3	100.7
9	86.4	114.4	100.6	9	53.2	82.8	68.5	9	16.4	69.6	50.9	9	60.8	101.2	81.2
9	81.9	114.4	95.0	9	62.5	83.8	72.6	9	20.9	71.2	54.5	9	64.4	118.8	92.0
9	75	103.8	84.7	9	47.6	82.5	69.8	9	26.1	79.4	61.4	9	62.1	121.2	87.7

Table C-3. Summary of Soil Spike Percent Recoveries in High Spike Samples for each Laboratory.

Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike % recovery			
n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
7	93.3	97.7	95.4	9	83.6	112.8	101.5	87	66.8	126.6	102.7
9	93.6	100.4	96.2	9	73.2	121.2	98.1	90	73.2	123	100.9
9	91.6	99.6	94.8	9	82.4	114.5	104.0	90	73.6	644	105.3
9	90.4	98	93.3	9	68	120.2	100.3	90	66.8	688	105.6
9	86.4	98.8	93.4	9	72.1	116.1	100.1	90	72.1	122.8	100.4
9	85.2	99.6	95.0	9	60.4	124.9	91.4	90	60.4	146	100.8
9	85.2	104	96.6	9	67.6	115.2	100.4	90	67.6	156.4	101.8
9	80.8	100.9	94.2	9	76.8	117.4	101.5	90	76.8	158	101.7
9	77.2	98.8	93.6	9	72.4	120.4	98.6	90	58	129.2	100.7
9	80.4	103.4	97.4	9	71.2	117.4	101.9	90	58	144.8	101.7
9	76	99.6	92.8	9	66.8	109.2	94.2	89	63.2	128.4	96.6
9	90.4	98	94.7	9	73.6	105.2	91.6	90	62.4	127.6	100.7
9	90.8	97.6	93.9	9	75.6	113.2	100.6	90	71.6	136.8	102.3
9	86.4	98	94.0	9	76.4	118.8	96.1	90	74	133.2	102.0
9	86	96.8	92.9	9	72	114.4	99.8	90	72	147.2	103.8
9	92.6	116.4	99.8	9	73.5	110.3	96.6	90	73.5	126.8	101.2
9	82	98.8	94.9	9	68.4	98.4	89.9	90	62	129.2	98.9
9	82.1	100.4	95.6	9	70.5	98.8	89.7	90	33.6	130.3	94.2
9	74	98	92.0	9	61.6	94	83.2	90	14.1	130.8	90.1
9	94	101.6	96.4	9	74.8	125.2	97.3	90	60.4	125.2	97.9
9	92.8	102.8	97.8	9	85.5	168.3	117.6	81	58	168.3	101.8
9	91.2	108	101.1	9	72	152.4	116.4	90	61.2	152.4	108.5
9	81.6	95.2	89.5	9	59.2	110.7	97.8	90	59.2	620	106.6
9	78.4	100.8	94.0	9	69.6	111	98.6	81	69.6	116.4	98.0
9	81.2	102.4	97.1	9	69.2	114	102.1	80	69.2	122	101.4
9	80.4	96.2	92.0	9	63.6	122.2	96.1	90	28.7	126.2	99.2
9	80.4	100.8	95.0	9	82.4	136.8	112.9	90	32.4	136.8	100.9
9	71	95.6	88.7	9	69.4	104.8	96.1	90	69.4	123.8	99.0
9	75.6	96.4	90.8	9	64.4	106.8	96.4	89	64.4	123.8	98.4
9	20.4	99.8	66.8	9	73.8	116.2	93.4	90	20.4	130	93.9
9	96.8	148.6	110.0	9	81	121.8	94.3	90	71.6	148.6	104.8
9	98.1	105	101.2	9	71.2	108.1	95.1	90	66.9	150	100.0
9	91.6	100.4	94.8	9	86	131.6	109.7	90	76	134.4	101.2
9	98	108	103.6	9	82.7	134.9	114.2	90	64.7	161.4	105.4
9	98.8	105.6	102.4	9	77.6	123	105.0	90	73.3	132.3	102.9
9	96	112.8	106.8	9	87.2	132.4	118.4	90	18.1	150.4	105.5
9	91.6	115.3	108.9	9	79.9	123.3	108.8	90	4.9	162.2	99.7
9	31	92.8	66.3	9	55.6	117.6	80.3	90	16.4	117.6	74.9
9	68.8	98.1	86.9	9	61.6	106.9	80.7	90	20.9	125.6	81.3
9	73.1	103.1	89.5	9	64.4	114.4	88.7	90	26.1	166.2	84.1

Table C-4. Summary of Soil EIS Percent Recovery for each Laboratory.

EIS Compound	Lab 1 % recovery				Lab 2 % recovery				Lab 3 % recovery				Lab 4 % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
$^{13}C_4$-PFBA	21	28.9	89.1	77.1	21	89.2	98.1	94	21	8	92	54.4	21	23.5	92.3	81.2
$^{13}C_5$-PFPeA	21	75.2	91.8	83.6	21	86.5	99.7	93.6	21	27	89	64.4	21	82.2	95.9	88.1
$^{13}C_5$-PFHxA	21	79.4	95.2	85.2	21	84.7	99.2	93.3	21	62	100	85	28	79.5	97.4	88.5
$^{13}C_4$-PFHpA	21	71.9	85.9	79.4	21	74	97.5	90.2	21	81	105	92.9	21	77.5	95.4	86.5
$^{13}C_8$-PFOA	21	76.5	90.6	82.6	21	58.3	96.1	85.1	21	80	102	90	21	82	98.2	88.7
$^{13}C_9$-PFNA	21	69.1	90.2	81.2	21	53.2	101	89.7	21	79	109	94	21	79.2	95	88.5
$^{13}C_6$-PFDA	21	67.5	87.5	77.1	21	34	102	84.1	21	74	106	92.4	21	78.9	97.4	87
$^{13}C_7$-PFUnA	21	56.7	81.8	72	21	26.1	101	83.2	21	87	125	106.8	21	79.5	114	92.1
$^{13}C_2$-PFDoA	21	39.5	75.3	64.7	21	15	94.4	76	21	90	129	107	21	78.4	91.1	84.7
$^{13}C_2$-PFTeDA	21	43.3	77.6	61.8	21	7.38	97.3	73.2	21	90	144	111.3	21	71.7	93.3	79.2
$^{13}C_3$-PFBS	21	70.8	83.2	77.5	21	66.6	100	90.7	21	62	101	85.8	21	77.5	92.2	84.3
$^{13}C_3$-PFHxS	21	76.4	92	83.9	21	39.7	97.7	85.8	21	86	104	92.7	21	77.7	93.2	85.6
$^{13}C_8$-PFOS	21	74.9	93	81.6	21	20.3	95.8	79.8	21	79	102	91	21	82.5	104	91.8
$^{13}C_2$-4:2FTS	21	83	98.8	89.6	21	89	144	122.1	21	69	253	142.4	21	90.4	111	98.7
$^{13}C_2$-6:2FTS	21	85.7	113	96.4	21	60.3	108	93.7	21	89	193	124.1	21	84.6	125	106.6
$^{13}C_2$-8:2FTS	21	111	146	123.8	21	31.7	160	113.6	21	111	295	187.5	21	86.1	125	108.8
$^{13}C_8$-PFOSA	21	40.7	86.1	71.4	21	28.7	109	85.9	21	54	108	91.8	21	70.5	85	77.5
D_3-NMeFOSA	21	27.2	77.2	64.8	21	25.5	87.4	70	21	58	90	80.2	21	8.7	40.7	21.2
D_5-NEtFOSA	21	31.1	74.8	62.3	21	22.5	77.4	62.4	21	60	90	75.5	21	7.2	32	17.9
D_3-NMeFOSAA	21	45.6	75.3	63.2	21	26.8	118	94.3	21	94	184	133	21	72.2	102	86.9
D_5-NEtFOSAA	21	40.3	74.3	63.4	21	20.3	134	97.4	21	87	154	117.3	21	79.5	94.4	87.9
D_7-NMeFOSE	21	31.8	70.8	58.4	21	12	91.4	72.7	21	66	115	100.2	21	24.6	61.2	42
D_9-NEtFOSE	21	33.4	73.1	62.1	21	8.71	97	74.5	21	65	105	85.4	21	23.9	57.9	41.1
$^{13}C_3$-HFPO-DA	21	70.3	89.5	82.5	21	80.1	100	91.5	21	64	102	86	21	68.7	96.1	86.4

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-- : X-flagged results

Table C-4. Summary of Soil EIS Percent Recovery for each Laboratory.

Lab 5 % recovery				Lab 6 % recovery				Lab 7 % recovery				Lab 8 % recovery			
n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
20	39.1	100	77.2	21	10.2	93.2	54.4	21	65	87	72.8	21	99	114	109.6
20	35.8	122	78.5	21	45	93	70.6	21	54	80	63.2	21	88.3	117	103.1
20	34.3	121	83.6	21	63	94	78.1	21	60	84	68.7	21	89.5	120	104.6
20	30	113	79.9	21	63.5	96.5	79.3	21	60	84	68.1	21	80.5	119	102.7
20	26.1	107	75	21	61.5	94	78.6	21	60	82	71.1	21	93.5	115	105.5
20	20.2	93.6	69.5	21	62.4	92.9	77.6	21	58	84	66.5	21	82.6	115	103.6
20	18.3	106	70	21	57.6	100	77.2	21	59	76	67.1	21	86.3	112	101.5
20	13.2	114	74.7	21	56.8	92.1	75.3	21	61	83	70.5	21	74.4	117	101.8
20	12.1	106	67.7	21	49.6	113	70.5	21	53	89	60.9	21	62.2	109	95.5
20	14.4	100	68.8	21	40	77.1	57.5	21	49	67	57	21	34	101	83.2
20	33	100	78.8	21	60.2	109	78.2	21	64	82	70.1	21	101	127	113
20	25.9	97.9	75.2	21	59	93.2	76.2	21	61	83	69	21	89.5	119	105.9
20	17.9	104	75.5	21	57.3	96.4	80.1	21	57	84	67	21	97.4	115	105.5
20	41.2	98.5	74.1	21	62.1	114	85.2	21	58	80	69.6	21	114	205	162.3
20	35.5	104	77.2	21	55.5	148	87.2	21	55	75	64.2	21	111	169	146
20	27.5	119	84.8	21	65.9	145	102.6	21	48	68	59	21	97.7	170	140.9
20	19.4	108	78.3	21	52.5	77	65.6	21	46	72	58.5	21	77	117	98.1
20	10.9	94.8	52.5	21	42.1	63	54.4	21	27	46	38.3	0	--	--	--
20	10.4	83.6	50.1	21	37.3	63	50.5	21	22	43	35.6	0	--	--	--
20	20.6	126	82.3	21	52.5	80.2	66	21	53	95	63.9	21	67.8	107	91
20	20	124	82.3	21	50.8	81.5	67.6	21	63	106	73.5	21	65.3	107	90.9
20	13.8	95.6	62.7	21	43.2	72	56.2	21	24	37	32.2	21	67.5	86	78.5
20	15.6	98.4	62.9	21	39.4	74.5	56.3	21	24	42	33.9	21	64	79.5	72.1
20	28.6	94.7	71.1	21	65	97.6	80.4	21	63	96	72.2	21	98.3	126	113.5

Table C-4. Summary of Soil EIS Percent Recovery for each Laboratory.

Lab 9 % recovery				Lab 10 % recovery				All Labs % recovery			
n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
21	5	96	56.9	21	90.1	116	97.4	209	5	116	77.5
21	42	98	79.9	21	78.9	119	99.5	209	27	122	82.5
21	78	101	88.1	21	84.6	104	94	216	34.3	121	87
21	76	98	87.7	21	74.5	121	96.8	209	30	121	86.4
21	71	97	87.3	21	82.3	109	94.2	209	26.1	115	85.9
21	72	97	86	21	75.9	102	91.8	209	20.2	115	84.9
21	69	96	86.3	21	81.5	103	92	209	18.3	112	83.5
21	73	98	90.1	21	77.1	109	88.1	209	13.2	125	85.5
21	71	99	90	21	79.5	103	88.5	209	12.1	129	80.6
21	73	102	91.1	21	69.4	93.7	78.2	209	7.38	144	76.2
21	73	93	84	21	85.4	111	94.4	209	33	127	85.7
21	69	97	86.2	21	81.2	107	93.7	209	25.9	119	85.5
21	70	94	85.5	21	87.9	112	100	209	17.9	115	85.8
21	87	129	102.9	21	80.6	145	106.1	209	41.2	253	105.5
21	90	127	105.8	21	64.6	135	104	209	35.5	193	100.6
21	94	150	115	21	68.4	138	91.4	209	27.5	295	112.9
21	66	98	84.4	21	67.6	105	84.5	209	19.4	117	79.6
21	62	82	72.8	21	34.5	68.7	54.7	188	8.7	94.8	56.6
21	42	68	51.5	21	30.1	68.7	52.5	188	7.2	90	50.9
21	64	93	80.6	21	78.3	122	94.6	209	20.6	184	85.6
21	67	95	81.8	21	70.4	117	91.2	209	20	154	85.3
21	64	93	76.6	21	64.5	89.9	73.6	209	12	115	65.3
21	63	97	73.1	21	62.9	85.6	71.7	209	8.71	105	63.3
21	78	102	89.8	21	72.9	106	90.7	209	28.6	126	86.5

Appendix D

Sediment Supporting Tables

Table D-1. Target Analytes Detected in Unspiked Sediment Samples by Laboratory (ug/kg).

Analyte	Number of Labs	SDAA1		SDY1		SDZ1	
		Min	Max	Min	Max	Min	Max
PFBA	9	0.05 U	0.31 U	0.0514 U	0.31 U	0.05 U	0.31 U
PFPeA	9	0.039 U	0.133 U	0.039 U	0.133 U	0.039 U	0.15 J
PFHxA	9	0.0375 U	0.185 J	0.0375 U	0.297 J+B	0.0375 U	0.204
PFHpA	9	0.023 U	0.112 U	0.03 U	0.112 U	0.023 U	0.156 J
PFOA	9	0.0315 U	0.215	0.0315 U	0.0896 J+B	0.0315 U	0.172 J
PFNA	9	0.044 U	0.565 U	0.044 U	0.565 U	0.044 U	0.565 U
PFDA	9	0.036 U	0.128 U	0.036 U	0.128 U	0.036 U	0.128 U
PFUnA	9	0.024 U	0.457 U	0.024 U	0.457 U	0.024 U	0.457 U
PFDoA	9	0.038 U	0.11 U	0.038 U	0.11 U	0.038 U	0.11 U
PFTrDA	9	0.022 U	0.192 U	0.022 U	0.192 U	0.022 U	0.192 U
PFTeDA	9	0.03 U	0.106 U	0.03 U	0.106 U	0.03 U	0.106 U
PFBS	9	0.027 U	0.088 U	0.027 U	0.088 U	0.027 U	0.088 U
PFPeS	9	0.023 U	0.16 U	0.0149 U	0.16 U	0.023 U	0.16 U
PFHxS	9	0.015 U	0.16 U	0.015 U	0.16 U	0.0159 J	0.16 U
PFHpS	9	0.025 U	0.15 U	0.025 U	0.15 U	0.025 U	0.15 U
PFOS	9	0.0414 U	0.132 U	0.176 J	0.367	0.0426 U	0.132 U
PFNS	9	0.0344 J	0.18 U	0.0213 U	0.18 U	0.038 U	0.18 U
PFDS	9	0.027 U	0.176 U	0.027 U	0.176 U	0.027 U	0.176 U
PFDoS	9	0.027 U	0.15 U	0.027 U	0.15 U	0.027 U	0.15 U
4:2FTS	9	0.081 U	0.513 J	0.081 U	0.397 U	0.081 U	0.492 J
6:2FTS	8	0.139 U	3.53 J	0.139 U	4.21 J	0.139 U	3.58 J
8:2FTS	9	0.102 U	0.61 U	0.102 U	0.61 U	0.102 U	0.61 U
PFOSA	9	0.014 U	0.127 U	0.014 U	0.127 U	0.014 U	0.127 U
NMeFOSA	8	0.029 U	0.14 U	0.029 U	0.14 U	0.029 U	0.14 U
NEtFOSA	8	0.017 U	0.128 U	0.017 U	0.128 U	0.017 U	0.128 U
NMeFOSAA	9	0.0304 U	0.16 U	0.0318 U	0.16 U	0.0318 U	0.16 U
NEtFOSAA	9	0.026 U	0.2 U	0.026 U	0.2 U	0.026 U	0.2 U
NMeFOSE	9	0.151 U	1 U	0.151 U	1 U	0.151 U	1 U
NEtFOSE	9	0.063 U	0.83 U	0.063 U	0.83 U	0.063 U	0.83 U
PFMPA	9	0.041 U	0.133 U	0.041 U	0.133 U	0.041 U	0.133 U
PFMBA	9	0.031 U	0.133 U	0.031 U	0.133 U	0.031 U	0.133 U
NFDHA	9	0.06 U	0.282 U	0.06 U	0.282 U	0.06 U	0.282 U
HFPO-DA	9	0.051 U	0.432 U	0.051 U	0.432 U	0.051 U	0.432 U
ADONA	9	0.079 U	0.34 U	0.079 U	0.34 U	0.079 U	0.34 U
PFEESA	9	0.034 U	0.136 U	0.034 U	0.136 U	0.034 U	0.136 U
9Cl-PF3ONS	9	0.081 U	0.44 U	0.081 U	0.44 U	0.081 U	0.44 U
11Cl-PF3OUdS	9	0.088 U	0.36 U	0.088 U	0.36 U	0.088 U	0.36 U
3:3FTCA	9	0.103 U	0.51 U	0.103 U	0.51 U	0.103 U	0.51 U
5:3FTCA	9	0.133 U	1.31 U	0.133 U	1.31 U	0.133 U	1.31 U
7:3FTCA	9	0.563 U	1.76 U	0.563 U	1.76 U	0.563 U	1.76 U

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Table D-2. Summary of Sediment Spike Percent Recoveries in Low Spike Samples for each Laboratory.

Analyte	Lab 1 spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	59	75	68.0	9	98.7	130	103.7	9	65.5	95	83.5
PFPeA	9	60.5	76.2	69.5	9	96.2	128.2	103.7	9	78	96	87.4
PFHxA	9	58	73	66.5	9	91.1	109.4	97.3	9	73.5	93.5	84.1
PFHpA	9	55.5	68.8	63.0	9	91.5	104.5	97.0	9	73.8	93	82.5
PFOA	9	49.1	69.5	60.0	9	91.4	117.6	99.6	9	68.6	98.8	82.2
PFNA	9	48	69.5	55.3	9	87	106.3	96.6	9	66.2	96.8	80.4
PFDA	9	39.8	82	61.2	9	93.5	123.5	102.3	9	52	90.2	72.4
PFUnA	9	35	70.8	54.1	9	85.5	99	94.1	9	46.2	92	71.0
PFDoA	9	31.2	73	51.2	9	101.8	115.8	107.3	9	49.5	93.2	71.9
PFTrDA	9	31	68.2	49.5	9	93	117.8	104.0	9	41	89.5	67.4
PFTeDA	9	27.5	61.3	46.5	9	71.2	104.2	89.3	9	42.8	91.8	68.0
PFBS	9	52	71.2	63.8	9	99.8	114.5	103.6	9	78.5	112	92.9
PFPeS	9	52.5	68.3	63.0	9	96.5	110.9	102.2	9	77.7	103	90.1
PFHxS	9	54.9	68.2	61.5	9	88.8	100.5	96.4	9	79.3	105.7	89.8
PFHpS	9	49.6	67.6	59.3	9	100.2	122.9	107.7	9	67.3	96.3	81.2
PFOS	9	49	64.9	58.0	9	92.5	115.1	99.4	9	66.5	92.6	76.3
PFNS	9	37.9	60.1	51.2	9	93.6	120.3	101.4	9	56.9	95	74.2
PFDS	9	30.4	69.6	46.6	9	92.4	119.7	100.2	9	50.1	94.2	70.7
PFDoS	9	23.5	39.7	33.1	9	93.2	129.8	106.2	9	41.2	78.1	61.5
4:2FTS	9	56.8	79.9	67.5	9	90.1	111.7	98.5	9	72.2	98.3	84.7
6:2FTS	9	53.3	76.8	63.6	9	89.6	116	97.4	9	71.5	100.8	86.8
8:2FTS	9	40.2	69.2	58.1	9	97.8	125.1	108.9	9	65.8	106.9	86.6
PFOSA	9	49	69.5	58.9	9	91	114.8	96.4	9	64.8	94	76.4
NMeFOSA	9	39.8	63.2	53.0	9	99	122.8	104.7	9	63	98.2	79.1
NEtFOSA	9	39.8	65.2	54.2	9	100	127.5	109.9	9	58.2	99	81.8
NMeFOSAA	9	37.8	61.5	50.9	9	90	123.5	109.0	9	55	90.5	71.4
NEtFOSAA	9	37.5	69	53.4	9	93.8	110.8	103.5	9	58	92	75.0
NMeFOSE	9	35.9	62.8	50.7	9	83.8	116	101.8	9	55.3	93.5	72.8
NEtFOSE	9	32.7	62	46.8	9	99.4	124	107.0	9	52.1	91.4	72.4
PFMPA	9	61.5	82.8	72.9	9	81.2	110.5	88.4	9	63.2	98	80.9
PFMBA	9	56.8	72.2	66.2	9	83.5	115	91.7	9	78.2	103.8	90.0
NFDHA	9	48	66.2	59.7	9	86.5	123	99.9	9	71.8	102.8	88.5
HFPO-DA	9	57.2	73.8	66.5	9	87	106.2	94.2	9	74.8	107.5	91.0
ADONA	9	62.4	77.8	68.1	9	82.3	108.6	90.6	9	76.5	105.3	87.1
PFEESA	9	57.9	76.6	69.4	9	72.3	81.3	77.4	9	75.3	96	86.0
9Cl-PF3ONS	9	47.5	70.6	63.9	9	75.6	92.5	83.3	9	71.6	106.7	87.3
11Cl-PF3OUdS	9	29	63.9	48.1	9	75.5	95.5	81.0	9	49.2	98.5	75.7
3:3FTCA	9	43	74.2	61.1	9	65.5	92.5	82.8	9	63.2	90	75.6
5:3FTCA	9	39.6	58.5	48.6	9	66	88	76.2	9	56	92	74.7
7:3FTCA	9	29.2	54	45.1	9	85	103.5	94.6	9	57	90.5	70.4

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Table D-2. Summary of Sediment Spike Percent Recoveries in Low Spike Samples for each Laboratory.

Analyte	Lab 6 spike % recovery				Lab 7 spike % recovery				Lab 8 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	6	84	93.8	88.3	9	80	90	85.8	9	114.8	120.8	117.4
PFPeA	9	84	106	95.1	9	97.5	112.5	104.7	9	92	120	108.4
PFHxA	9	75.5	100.5	88.7	9	92.5	100	96.4	9	109.2	143.2	123.5
PFHpA	9	70.2	88	81.8	9	90	97.5	94.4	9	98.2	120.8	111.6
PFOA	9	72.2	100	88.0	9	92.5	100	96.1	9	99.2	125	115.3
PFNA	9	76	92.5	82.0	9	92.5	102.5	97.2	9	112.2	121.5	117.9
PFDA	9	61.3	100.5	86.1	9	92.5	110	102.2	9	118	129.2	124.1
PFUnA	9	74.8	113.8	91.7	9	92.5	100	97.2	9	115	127.5	121.4
PFDoA	9	71.8	98.2	85.9	9	95	105	100.3	9	117.5	129.5	123.8
PFTrDA	9	78.8	131.5	105.6	9	75	92.5	85.3	9	129.2	153.5	141.9
PFTeDA	9	66	112.5	98.6	9	105	120	112.8	9	112.8	123	117.5
PFBS	9	81	104.5	91.8	9	97.5	110	102.2	9	103	111	106.7
PFPeS	9	65.8	93.1	84.2	9	89.1	99	93.8	9	112.6	130	120.1
PFHxS	9	76.8	104.2	89.7	9	99.8	122.2	108.9	9	109	122.4	113.9
PFHpS	9	76.1	106.7	85.3	9	84.8	94.8	90.1	9	111.7	122.4	115.8
PFOS	9	70.3	83	79.0	9	88.5	101	95.3	9	107.2	117	112.3
PFNS	9	53.7	97.8	79.4	9	99	116.3	107.0	9	108.7	118.1	114.6
PFDS	9	54.4	101.8	78.9	9	73.4	91.1	81.6	9	90.4	114.4	105.8
PFDoS	9	46.7	81.4	65.7	9	70.4	100.5	84.6	9	53.5	93.5	76.8
4:2FTS	9	62.5	112.2	92.5	9	72	96.8	86.0	9	89.8	121.8	109.5
6:2FTS	9	73.2	122.2	102.4	9	80	95	87.5	6	34.5	101.3	56.4
8:2FTS	9	64.3	128.8	85.4	9	96.8	111.7	103.9	9	121.8	134	126.3
PFOSA	9	73.2	93	87.3	9	87.5	97.5	92.5	9	101	119.8	113.8
NMeFOSA	9	65.5	99	87.6	9	85	92.5	90.0	0	--	--	--
NEtFOSA	7	88.8	99.2	92.4	9	82.5	95	89.2	0	--	--	--
NMeFOSAA	9	74.5	91.2	83.8	9	87.5	102.5	97.8	9	112.7	121	116.7
NEtFOSAA	9	78.5	105	93.2	9	85	97.5	90.0	9	115.8	126	119.5
NMeFOSE	9	77.9	110	88.5	9	78	88	84.3	9	116	124	119.4
NEtFOSE	9	70.9	107	88.3	9	88	97	93.3	9	110	122	117.3
PFMPA	9	33.8	98	62.7	9	97.5	112.5	106.1	9	113.2	128.8	121.9
PFMBA	9	84.2	124.2	105.2	9	97.5	112.5	106.1	9	99.2	126.2	114.8
NFDHA	9	56	137.5	101.2	9	80	100	91.7	9	74.2	113.2	93.9
HFPO-DA	9	67.8	96.5	85.3	9	85	100	89.4	9	113.8	124	118.9
ADONA	9	62.1	100.5	84.1	9	88.4	108.6	98.8	9	109.8	123.5	117.1
PFEESA	9	75.1	103.5	90.9	9	94.8	104.7	98.9	9	111.7	133.7	120.8
9Cl-PF3ONS	9	52.5	108.7	83.7	9	97	119.4	106.1	9	110.4	128.4	118.7
11Cl-PF3OUdS	9	41.4	103	76.6	9	75.8	101	88.7	9	80.8	116.4	102.0
3:3FTCA	9	51.2	88.2	70.6	9	70	95	82.8	9	96	123.2	110.7
5:3FTCA	9	70.5	100.5	80.6	9	68.5	89.5	78.2	9	95.5	166	121.5
7:3FTCA	9	66.5	93	81.2	9	81.5	105.5	92.1	9	80.5	158.5	112.2

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Table D-2. Summary of Sediment Spike Percent Recoveries in Low Spike Samples for each Laboratory.

Analyte	Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	86.8	94.2	90.2	9	64	87.5	80.1	69	59	130	89.7
PFPeA	9	83	94	87.6	9	53	82.2	73.9	72	53	128.2	91.3
PFHxA	9	80.5	92	86.4	9	65.3	100.3	83.7	72	58	143.2	90.8
PFHpA	9	82.2	91.2	85.7	9	56.5	93.5	78.3	72	55.5	120.8	86.8
PFOA	9	81.5	90.2	84.9	9	55	103	72.9	72	49.1	125	87.4
PFNA	9	84	90	86.8	9	52.8	79.5	66.7	72	48	121.5	85.4
PFDA	9	82.8	97.2	88.6	9	39.2	89.3	64.5	72	39.2	129.2	87.7
PFUnA	9	82	93.2	86.1	9	38.5	95.2	65.1	72	35	127.5	85.1
PFDoA	9	83.5	92.5	86.8	9	34.8	78	57.2	72	31.2	129.5	85.6
PFTrDA	9	84.5	96.2	90.3	9	32.2	68.8	52.9	72	31	153.5	87.1
PFTeDA	9	85.2	93.2	88.8	9	29	74	54.9	72	27.5	123	84.5
PFBS	9	84.8	92.5	88.5	9	65.8	86	74.2	72	52	114.5	90.5
PFPeS	9	86.4	92.3	89.0	9	64.9	86.4	76.0	72	52.5	130	89.8
PFHxS	9	80.9	93.5	85.5	9	67.8	95.3	80.1	72	54.9	122.4	90.7
PFHpS	9	85.5	92.8	88.2	9	55.6	95.3	74.2	72	49.6	122.9	87.7
PFOS	9	81.6	89.8	85.6	9	47.5	86.3	69.4	72	47.5	117	84.4
PFNS	9	85.6	94.1	90.0	9	34.4	74.8	57.3	72	34.4	120.3	84.4
PFDS	9	86.3	96.2	89.8	9	30.4	66.6	48.4	72	30.4	119.7	77.7
PFDoS	9	62.3	94	79.9	9	22.8	51.8	33.6	72	22.8	129.8	67.7
4:2FTS	9	85.1	93.1	88.4	9	45.4	76.7	62.5	72	45.4	121.8	86.2
6:2FTS	9	79.8	93.2	86.6	9	51	111	78.9	69	34.5	122.2	83.6
8:2FTS	9	85.1	97.5	92.1	9	39.5	96	68.7	72	39.5	134	91.3
PFOSA	9	74.5	94.2	79.4	9	51	79.2	65.9	72	49	119.8	83.8
NMeFOSA	9	83.5	91.8	86.5	9	31.8	82	61.0	63	31.8	122.8	80.3
NEtFOSA	9	83.8	92.8	88.2	8	33.8	81.2	59.2	60	33.8	127.5	82.2
NMeFOSAA	9	81.2	92.8	85.1	9	31.5	70.8	54.4	72	31.5	123.5	83.6
NEtFOSAA	9	84.8	94.8	88.3	9	40.8	92	67.1	72	37.5	126	86.2
NMeFOSE	9	75.3	91.6	82.9	9	33.5	74.8	57.5	72	33.5	124	82.3
NEtFOSE	9	82.6	92.3	87.0	9	31.3	78.2	57.6	72	31.3	124	83.7
PFMPA	9	81.2	94	87.8	9	49.5	86.8	74.9	72	33.8	128.8	86.9
PFMBA	9	85	95.2	88.8	9	54.2	88.5	73.8	72	54.2	126.2	92.1
NFDHA	9	78.2	93.5	87.9	9	54.2	85.2	73.3	72	48	137.5	87.0
HFPO-DA	9	81.8	92.8	87.1	9	63.5	98	82.5	72	57.2	124	89.4
ADONA	9	89.9	97	93.0	9	68.2	107.1	85.1	72	62.1	123.5	90.5
PFEESA	9	84.8	97	90.6	9	61.8	96	77.5	72	57.9	133.7	88.9
9Cl-PF3ONS	9	90.8	107.7	97.1	9	60	94.5	79.0	72	47.5	128.4	89.9
11Cl-PF3OUdS	9	94.2	108.6	97.7	9	39.1	72.2	52.5	72	29	116.4	77.8
3:3FTCA	9	57.8	82.5	72.1	9	50.7	75.5	68.9	72	43	123.2	78.1
5:3FTCA	9	62.5	87	77.6	9	54.5	82	69.9	72	39.6	166	78.4
7:3FTCA	9	68	117	91.9	9	58	78	67.1	72	29.2	158.5	81.8

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Table D-3. Summary of Sediment Spike Percent Recoveries in High-Spiked Samples for each Laboratory.

Analyte	Lab 1 spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	65.2	83	72.9	9	96.1	113.6	101.4	9	83.2	105.4	96.5
PFPeA	9	61.6	79.2	70.4	9	95.6	113.4	101.7	9	76.4	93	88.0
PFHxA	9	57.6	74.8	67.9	9	88.6	103.6	95.1	9	74.8	93.6	84.3
PFHpA	9	56.4	72.4	66.5	9	87	106.8	95.2	9	74.8	89.2	83.6
PFOA	9	59.1	69.7	64.2	9	95.6	106	100.7	9	74	95.6	84.3
PFNA	9	51.2	64.8	56.9	9	91.2	112.8	98.1	9	61.6	92.4	78.6
PFDA	9	45.6	76.4	63.6	9	90	133.6	106.9	9	45.2	85.2	71.0
PFUnA	9	39.6	66.8	56.3	9	84.7	119.2	98.0	9	43.2	90.8	66.7
PFDoA	9	29.1	65.2	50.4	9	91.2	113.2	102.6	9	41.6	84.4	64.8
PFTrDA	9	32.5	66.8	51.5	9	84.2	107.6	98.9	9	36.5	82.4	62.2
PFTeDA	9	32.5	59.6	47.6	9	78.8	101.2	87.6	9	35.2	83.6	62.4
PFBS	9	58	76.8	66.7	9	96.4	114	101.3	9	80	106	92.8
PFPeS	9	59.6	74.8	68.4	9	99.6	116	103.2	9	80.8	97.6	89.5
PFHxS	9	59.2	70.3	66.1	9	94	110	99.5	9	79.2	96	89.2
PFHpS	9	57.2	72	64.6	9	99.6	120.8	104.6	9	76.8	92.8	85.0
PFOS	9	54.2	70.4	63.8	9	89.2	111.6	96.7	9	66.7	91.1	77.5
PFNS	9	40.8	67.6	57.7	9	95.6	113.6	101.4	9	52.8	90.8	71.7
PFDS	9	33.3	64.5	51.5	9	91.2	113.1	98.5	9	45.8	88	66.8
PFDoS	9	26.6	48	38.2	9	94	122	103.9	9	42.8	71.2	57.1
4:2FTS	9	60.4	77.6	67.8	9	88	113.6	94.8	9	74.4	96.4	86.0
6:2FTS	9	60.4	75.1	67.9	9	95.6	114.9	100.5	9	72.3	94.8	86.3
8:2FTS	9	43.6	72	61.2	9	100.4	113.6	106.1	9	53.2	94.4	76.3
PFOSA	9	52.4	73.6	62.8	9	92.8	108.4	99.3	9	52.4	88.8	72.0
NMeFOSA	9	38.5	62.8	52.8	9	93.2	112.8	100.6	8	48.4	91.6	69.2
NEtFOSA	9	39.6	67.6	55.3	9	104	127.6	110.1	8	46.4	84.4	71.5
NMeFOSAA	9	40.4	67.6	53.6	9	99	122.5	112.6	9	47.4	82.1	67.9
NEtFOSAA	9	33.2	66.8	53.5	9	89.2	116	101.5	9	45.6	87.6	69.0
NMeFOSE	9	36.6	64	51.7	9	91.8	132	105.2	9	41	88.8	66.0
NEtFOSE	9	35.4	64.7	49.3	9	96	119.2	106.2	9	39.4	85.8	64.9
PFMPA	9	64.4	85.4	75.2	9	86	100.2	90.3	9	39.2	95.4	74.3
PFMBA	9	61.8	73.8	68.2	9	82.4	94.8	87.4	9	81.2	100.6	91.7
NFDHA	9	55.8	81.9	66.6	9	93.1	143.1	108.1	9	58	112.5	83.0
HFPO-DA	9	63.6	77.2	72.3	9	89.2	104.8	93.6	9	72	110.8	92.7
ADONA	9	65.1	76.3	71.7	9	83.5	100.4	91.1	9	75.5	99.6	90.1
PFEESA	9	60.5	75.8	70.4	9	78.9	93.8	84.5	9	78.9	93.8	87.7
9Cl-PF3ONS	9	61.2	84.8	73.0	9	76.4	92.8	81.6	9	56	102	85.8
11Cl-PF3OUdS	9	36.4	72.3	56.1	9	73.1	91.2	81.0	9	39.8	93.6	73.3
3:3FTCA	9	52.8	84.8	67.2	9	75.2	111.6	95.4	9	66.4	90.4	80.5
5:3FTCA	9	46.6	68.1	55.8	9	70.6	103.8	84.5	9	68.8	90	79.6
7:3FTCA	9	46.8	57.4	52.2	9	90.6	123.8	104.1	9	54.2	90	71.1

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Table D-3. Summary of Sediment Spike Percent Recoveries in High-Spiked Samples for each Laboratory.

Analyte	Lab 6 spike % recovery				Lab 7 spike % recovery				Lab 8 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	5	83.8	88.2	85.9	9	77.2	107	101.2	6	117.4	123.4	119.3
PFPeA	9	75.2	96	84.6	9	84	125.2	114.1	6	106.2	114.2	111.1
PFHxA	9	74.4	88.4	81.7	9	80.8	112	103.4	6	113.6	125.6	118.4
PFHpA	9	71.2	92	81.4	9	74.4	106.8	100.7	6	114.8	125.6	120.7
PFOA	9	77.2	98.8	84.8	9	80.8	112	104.3	6	104.4	129.2	114.9
PFNA	9	67.2	86	77.1	9	81.6	115.2	105.9	6	113.2	126	117.7
PFDA	9	73.6	91.2	82.0	9	87.6	125.2	113.7	6	115.2	124.4	121.0
PFUnA	9	69.6	93.2	79.5	9	95.2	113.2	106.6	6	120	134.8	126.5
PFDoA	9	51.6	91.6	80.7	9	80.4	110.8	104.9	6	119.6	130.4	123.9
PFTrDA	9	77.6	166	108.8	9	75.6	98	86.8	6	119.6	162.8	135.6
PFTeDA	9	69.2	103.6	90.6	9	87.2	124.8	116.1	6	110	118.4	113.6
PFBS	9	56.8	98.8	80.4	9	78.8	124.4	115.2	6	113.6	128	121.8
PFPeS	9	60.8	98.8	85.3	9	82	114.8	106.7	6	112.8	131.2	120.2
PFHxS	9	70.8	94.4	83.7	9	82	134.8	123.5	6	113.2	121.6	118.3
PFHpS	9	69.2	97.6	85.7	9	90.8	120	108.6	6	114.8	125.6	120.2
PFOS	9	63.3	92.8	77.6	9	80.1	122.1	109.6	6	110.4	116.9	114.1
PFNS	9	66.8	90	79.3	9	87.2	132.4	118.2	6	112.4	121.6	116.8
PFDS	9	61	86.5	75.5	9	83.3	101.6	93.6	6	101.6	116.3	108.4
PFDoS	9	31	76.4	64.2	9	77.2	114	90.5	6	68.4	116	84.2
4:2FTS	9	84.4	118.4	103.0	9	74	103.6	93.3	6	101.6	109.6	105.2
6:2FTS	9	80.3	165.5	107.4	9	81.1	112.4	102.4	6	105.1	155.3	119.1
8:2FTS	9	68.8	132	92.5	9	100.4	137.2	122.5	6	122.4	128.8	125.2
PFOSA	9	74	92.4	83.4	9	76.8	111.2	103.4	6	106	119.6	112.1
NMeFOSA	9	80.4	91.6	85.6	9	77.6	104.8	100.0	0	--	--	--
NEtFOSA	9	84.8	99.2	91.1	9	76.8	113.2	103.2	0	--	--	--
NMeFOSAA	9	79	98	87.7	9	67.5	111.2	102.1	6	116.9	126.2	123.1
NEtFOSAA	9	79.2	98.4	88.8	9	62.8	108.4	100.1	6	115.2	122.4	117.5
NMeFOSE	9	73.2	107.2	87.2	9	74	103.2	95.9	6	116.8	127	121.4
NEtFOSE	9	61	104.8	82.8	9	68.4	107.8	101.2	6	116.6	123	119.7
PFMPA	9	31.4	97.8	57.6	9	83.8	132	118.5	6	91.4	125.8	115.1
PFMBA	9	81	116.4	94.2	9	78.6	128.6	114.9	6	115.2	126.6	119.3
NFDHA	9	77.5	123.1	99.5	9	83.8	108.7	100.4	6	93.8	108.1	101.2
HFPO-DA	9	71.2	107.6	87.5	9	78.8	106.4	99.0	6	115.6	126	120.7
ADONA	9	58.2	88	75.5	9	71.5	113.3	101.0	6	113.7	123.7	116.9
PFEESA	9	80.7	98.8	88.1	9	81.4	114.9	107.7	6	118	136	126.2
9Cl-PF3ONS	9	56	94.8	79.0	9	62.8	116.8	100.9	6	110.8	120.8	116.7
11Cl-PF3OUdS	9	56.2	96.8	78.6	9	70.3	102	87.6	6	97.2	120.9	107.5
3:3FTCA	9	55.6	96	74.0	9	45.6	121.2	100.7	6	108.4	121.6	116.6
5:3FTCA	9	69.4	91.9	77.0	9	51.8	103.8	90.0	6	113.1	133.1	119.6
7:3FTCA	9	72.5	90	80.9	9	64.4	119.4	103.2	6	103.8	130.6	118.5

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Table D-3. Summary of Sediment Spike Percent Recoveries in High-Spiked Samples for each Laboratory.

Analyte	Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	8	86.2	97	93.2	9	70.6	92	82.5	64	65.2	123.4	93.4
PFPeA	8	87	97.2	94.0	9	65	82	73.6	68	61.6	125.2	91.3
PFHxA	8	87.2	96.4	92.2	9	70.1	112.4	84.7	68	57.6	125.6	89.7
PFHpA	8	88	97.6	91.6	9	69.2	99.6	82.8	68	56.4	125.6	89.0
PFOA	8	82.4	94.4	90.1	9	65.2	102	75.8	68	59.1	129.2	88.8
PFNA	8	87.2	98	92.7	9	46.4	94.4	63.9	68	46.4	126	84.9
PFDA	8	88.8	98.4	93.3	9	40.8	85	60.2	68	40.8	133.6	87.5
PFUnA	8	89.2	94.8	92.8	9	40	86	59.3	68	39.6	134.8	83.8
PFDoA	8	90.4	98.4	92.6	9	34.9	81.6	53.4	68	29.1	130.4	82.3
PFTrDA	8	89.6	104.8	95.9	9	34.2	74	49.3	68	32.5	166	83.8
PFTeDA	8	88.4	100.8	92.3	9	29.7	86	52.1	68	29.7	124.8	81.3
PFBS	8	86.8	99.2	94.1	9	57.2	88.4	71.6	68	56.8	128	91.7
PFPeS	8	88.4	99.6	93.8	9	73.2	101.2	85.5	68	59.6	131.2	92.9
PFHxS	8	85.2	96.1	90.6	9	70.4	96.4	81.7	68	59.2	134.8	93.1
PFHpS	8	86.4	93.6	90.6	9	67.2	94.4	77.0	68	57.2	125.6	90.8
PFOS	8	86.7	95.6	90.8	9	52.6	86.1	68.5	68	52.6	122.1	86.1
PFNS	8	88.8	95.6	92.7	9	41.2	71.2	54.5	68	40.8	132.4	85.1
PFDS	8	88.4	97.6	93.2	9	31.8	57.8	46.7	68	31.8	116.3	77.8
PFDoS	8	66.4	98.5	84.0	9	18	44.4	34.7	68	18	122	68.7
4:2FTS	8	87.2	99.2	95.0	9	41.6	96.8	67.8	68	41.6	118.4	88.3
6:2FTS	8	85.9	106	92.0	9	54.2	97.2	69.7	68	54.2	165.5	92.0
8:2FTS	8	90.4	101.6	96.9	9	43.2	96.8	70.1	68	43.2	137.2	92.4
PFOSA	8	78.8	92.4	83.0	9	50	89.2	61.0	68	50	119.6	83.5
NMeFOSA	8	84.4	96.8	90.3	8	44.4	95.2	57.3	60	38.5	112.8	79.7
NEtFOSA	8	86	96.4	92.4	8	42	96.8	57.0	60	39.6	127.6	83.4
NMeFOSAA	8	88.8	93.8	90.5	9	29.2	84.4	53.3	68	29.2	126.2	84.7
NEtFOSAA	8	90	95.6	93.5	9	44.8	102.4	63.6	68	33.2	122.4	84.4
NMeFOSE	8	76	92	84.9	9	36.2	83.2	51.9	68	36.2	132	81.3
NEtFOSE	8	83.6	93.4	88.2	9	35.4	83.2	52.1	68	35.4	123	81.4
PFMPA	8	63.4	99.2	86.0	9	64	81.2	73.8	68	31.4	132	85.1
PFMBA	8	86.8	101.6	97.0	9	67	97.6	78.6	68	61.8	128.6	92.8
NFDHA	8	92.5	104.4	98.4	9	61.5	86.2	71.3	68	55.8	143.1	90.5
HFPO-DA	8	83.6	96.4	91.2	9	80.8	101.2	90.9	68	63.6	126	92.3
ADONA	8	96.4	110.4	103.4	9	79.9	111.2	93.4	68	58.2	123.7	91.7
PFEESA	8	96.3	107.5	101.7	9	59.8	95	78.2	68	59.8	136	91.5
9Cl-PF3ONS	8	100.4	111.6	106.6	9	68.8	101.2	81.1	68	56	120.8	89.2
11Cl-PF3OUdS	8	102.4	121.7	108.6	9	38.4	66.7	55.0	68	36.4	121.7	79.4
3:3FTCA	8	67.2	98.4	83.5	9	65.6	88.4	77.4	68	45.6	121.6	85.6
5:3FTCA	8	79.4	108.1	96.6	9	54.3	101.2	77.2	68	46.6	133.1	83.3
7:3FTCA	8	83.1	139.4	111.3	9	52.5	80.6	64.8	68	46.8	139.4	86.6

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Table D-4. Summary of Sediment EIS Percent Recovery for each Laboratory

EIS Compound	**Lab 1 % Recovery**				**Lab 3 % Recovery**				**Lab 4 % Recovery**			
	n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
$^{13}C_4$-PFBA	21	72.5	90.1	82.6	21	59	98	88.4	21	15.7	93.1	60.3
$^{13}C_5$-PFPeA	21	71.5	94	85.1	21	54	93	82.9	21	84.7	99	90
$^{13}C_5$-PFHxA	21	77.1	94.6	83.5	21	60	100	90	28	87.3	99.7	91.8
$^{13}C_4$-PFHpA	21	71.4	94	80.1	21	62	107	92	21	82	100	88.9
$^{13}C_8$-PFOA	21	71.8	91.1	81.6	21	60	102	91.4	21	81.7	97.2	88.5
$^{13}C_9$-PFNA	21	72.3	92.4	80.7	21	62	103	90	21	82.8	99.3	90.2
$^{13}C_6$-PFDA	21	67	88.8	78.8	21	58	115	88	21	77.6	99.6	87.2
$^{13}C_7$-PFUnA	21	57.8	94.4	77.9	21	62	129	101.9	21	78.9	97.8	86.7
$^{13}C_2$-PFDoA	21	41.1	88.5	67.9	21	62	132	100.3	21	72.2	95.2	85
$^{13}C_2$-PFTeDA	21	46.4	68	60	21	64	132	102.4	21	67.7	87.2	77.3
$^{13}C_3$-PFBS	21	72.8	91.5	79.2	21	64	105	93.4	21	75.7	99.1	89
$^{13}C_3$-PFHxS	21	78.8	91.1	84.5	21	61	103	91	21	80.6	95	88
$^{13}C_8$-PFOS	21	76.7	88.2	82.3	21	58	101	89	21	77.7	108	87.3
$^{13}C_2$-4:2FTS	21	83.6	108	96.3	21	83	234	153.2	21	82.6	123	99.2
$^{13}C_2$-6:2FTS	21	91	141	108.1	21	70	138	111.8	21	80.8	120	97.5
$^{13}C_2$-8:2FTS	21	107	189	138.8	21	127	265	195.7	21	80.6	146	106.2
$^{13}C_8$-PFOSA	21	40.7	81.1	69.5	21	60	114	95.7	21	64.5	91.8	78.8
D_3-NMeFOSA	21	30.8	71.4	60.1	21	54	101	83.1	21	6.7	45.3	27.4
D_5-NEtFOSA	21	31.9	70.8	56	21	35	90	73.9	21	6.6	40.4	25.1
D_3-NMeFOSAA	21	51.7	87.6	72.8	21	79	169	130.4	21	75.7	101	84.8
D_5-NEtFOSAA	21	46.9	89.8	72.3	21	77	158	122.2	21	76.8	98.6	84.6
D_7-NMeFOSE	21	35.5	90.2	61.6	21	75	133	116.1	21	32.9	69.6	52.3
D_9-NEtFOSE	21	39.4	78.7	58.9	21	69	122	105.6	21	22.2	71.9	46.7
$^{13}C_3$-HFPO-DA	21	66.6	87	80.4	21	60	107	89.2	21	77.5	96.3	87.6

Version: Summary_tables_Exa_CH7_10312023.xlsx and/or Appendix_Sediment 11152023.xlsx

-- : X-flagged results

Table D-4. Summary of Sediment EIS Percent Recovery for each Laboratory

EIS Compound	Lab 6 % Recovery				Lab 7 % Recovery				Lab 8 % Recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
$^{13}C_4$-PFBA	21	8.09	87.5	36.6	21	61	87	74.3	18	68.6	116	108.1
$^{13}C_5$-PFPeA	21	32.2	82	58.9	21	47	84	58.3	18	90.8	131	108
$^{13}C_5$-PFHxA	21	45.3	99.5	75.7	21	54	87	65.9	18	94	128	109.1
$^{13}C_4$-PFHpA	21	44.4	89.5	75.2	21	55	86	67.4	18	84	126	106.3
$^{13}C_8$-PFOA	21	51	98	70.6	21	61	85	73.2	16	80	126	107.3
$^{13}C_9$-PFNA	21	54.9	98.3	79.2	21	53	86	65	18	90.5	128	109
$^{13}C_6$-PFDA	21	53.3	88.5	76	21	54	76	65.3	18	88.5	114	104
$^{13}C_7$-PFUnA	21	35	90.9	77.2	21	56	82	67.8	18	84.7	122	102.7
$^{13}C_2$-PFDoA	21	35	93.1	74.9	21	55	99	64.6	18	71.3	111	92.5
$^{13}C_2$-PFTeDA	21	24.9	75.1	57.3	21	43	65	49.8	18	48.3	99.3	65.3
$^{13}C_3$-PFBS	21	61.8	138	80.5	21	55	87	67.7	18	98.4	145	121.2
$^{13}C_3$-PFHxS	21	45.4	105	78.2	21	52	83	66.9	18	85.3	128	110.5
$^{13}C_8$-PFOS	21	56.8	102	82.2	21	55	88	64.3	18	104	120	112.9
$^{13}C_2$-4:2FTS	21	68.8	120	90.3	21	45	91	66	18	140	272	189.8
$^{13}C_2$-6:2FTS	21	56	235	104.8	21	51	108	66.4	18	132	279	175.8
$^{13}C_2$-8:2FTS	21	57.8	260	119.5	21	50	91	65.6	18	124	276	171.9
$^{13}C_8$-PFOSA	21	44.6	107	71.1	21	46	94	59.6	18	49.1	122	89.9
D_3-NMeFOSA	21	11.2	68.5	53.6	21	25	38	31.8	0	--	--	--
D_5-NEtFOSA	21	8.65	62	47.9	21	22	35	26.9	0	--	--	--
D_3-NMeFOSAA	21	54	109	80.9	21	64	132	75	18	98.3	182	124.2
D_5-NEtFOSAA	21	51.8	125	83.7	21	71	148	85.6	18	86	184	115.6
D_7-NMeFOSE	21	24.6	70.5	53.8	21	16	33	24.9	18	32.5	64	51.6
D_9-NEtFOSE	21	24.2	76	56.6	21	16	38	26	18	30.4	58	45.4
$^{13}C_3$-HFPO-DA	21	61.1	117	79.6	21	49	99	66.7	18	106	138	116.5

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Table D-4. Summary of Sediment EIS Percent Recovery for each Laboratory

EIS Compound	Lab 9 % Recovery				Lab 10 % Recovery				All Labs			
	n	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**	**n**	**Min**	**Max**	**Avg**
$^{13}C_4$-PFBA	20	10	97	75.8	21	93	110	101.7	164	8.09	116	77.9
$^{13}C_5$-PFPeA	20	35	100	87.4	21	87.6	135	107.9	164	32.2	135	84.4
$^{13}C_5$-PFHxA	20	83	99	92.2	21	85.2	115	101.1	171	45.3	128	88.4
$^{13}C_4$-PFHpA	20	80	100	91.2	21	82.3	122	100.2	164	44.4	126	87.3
$^{13}C_8$-PFOA	20	82	99	91.4	21	75.6	120	95.3	162	51	126	86.8
$^{13}C_9$-PFNA	20	82	99	91.3	21	80.7	109	95.7	164	53	128	87.2
$^{13}C_6$-PFDA	20	80	100	91.8	21	69.1	110	93.2	164	53.3	115	85.2
$^{13}C_7$-PFUnA	20	85	102	93.6	21	41.8	105	78.6	164	35	129	85.4
$^{13}C_2$-PFDoA	20	82	101	92.8	21	40.3	101	73.7	164	35	132	81.2
$^{13}C_2$-PFTeDA	20	68	107	89	21	20.4	90.8	58.2	164	20.4	132	69.9
$^{13}C_3$-PFBS	20	81	101	91.7	21	85.2	137	103	164	55	145	90.2
$^{13}C_3$-PFHxS	20	80	100	92.4	21	80	113	97.9	164	45.4	128	88.2
$^{13}C_8$-PFOS	20	81	99	91.1	21	86.8	114	101.5	164	55	120	88.4
$^{13}C_2$-4:2FTS	20	94	173	124	21	95	165	117.5	164	45	272	115.7
$^{13}C_2$-6:2FTS	20	97	214	144	21	97.8	198	130.4	164	51	279	116.1
$^{13}C_2$-8:2FTS	20	116	255	166.2	21	75	204	106.4	164	50	276	132.9
$^{13}C_8$-PFOSA	20	79	121	99.8	21	48.7	99.7	81.6	164	40.7	122	80.5
D_3-NMeFOSA	20	29	90	64.6	21	11.1	67.6	44.3	146	6.7	101	52.0
D_5-NEtFOSA	20	15	70	44.9	21	9.78	60.6	40.7	146	6.6	90	45.1
D_3-NMeFOSAA	20	77	117	100.7	21	49.5	121	88	164	49.5	182	94.0
D_5-NEtFOSAA	20	79	122	104.7	21	36.7	109	79.8	164	36.7	184	93.1
D_7-NMeFOSE	20	39	91	65.8	21	37	85.6	67.8	164	16	133	61.9
D_9-NEtFOSE	20	31	86	63	21	31.2	82.6	63.1	164	16	122	58.4
$^{13}C_3$-HFPO-DA	20	80	101	91.9	21	75.1	115	94.3	164	49	138	87.7

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