SERDP

TECHNICAL REPORT

Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 (Volume III): Landfill Leachates and Biosolids

Janice Willey
Naval Sea Systems Command, U.S. Navy

Adrian Hanley
U.S. Environmental Protection Agency, Office of Water

Richard Anderson
Air Force Civil Engineering Center

Andrea Leeson
SERDP and ESTCP

Timothy Thompson
Science and Engineering for the Environment, LLC

January 2024

SERDP Project ER19-1409

Principal Authors

Willey, Janice	Naval Sea Systems Command, U.S. Navy
Hanley, Adrian	U.S. Environmental Protection Agency, Office of Water.
Anderson, Richard	Air Force Civil Engineering Center
Leeson, Andrea	SERDP & ESTCP
Thompson, Tim	Science and Engineering for the Environment, LLC

Other Contributing Authors

PFAS Multi-Laboratory Validation Study Data Compilation Report

Buytendyk, Allyson	Institute for Defense Analyses
Smorong, Dawn	Exa Data and Mapping Services, Inc.
McCarty, Harry	General Dynamics Information Technology, Inc.
Alpizar, Mirna	General Dynamics Information Technology, Inc.
Rivers, Denise	HydroGeoLogic, Inc.

This report should be cited as

Willey, J., A. Hanley, R. Anderson, A. Leeson, and T. Thompson. 2024. Report on the Multi-Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS. Volume III. Landfill Leachates and Biosolids. Strategic Environmental Research and Development Program (SERDP) Project ER19-1409.

Acknowledgments

This report was prepared under contract to the Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP). The helpful leadership, guidance and contributions by the Program Directors, Dr. Andrea Leeson, and Dr. Kim Spangler are gratefully acknowledged.

This study has been a joint effort between the DoD at SERDP and the U.S. Environmental Protection Agency (EPA). The assistance of Troy Strock, EPA Office of Land and Emergency Management, Brian D'Amico, EPA Office of Water (OW), Office of Science and Technology, Engineering and Analysis Division, and Robert Wood, EPA OW, Office of Science and Technology, Engineering and Analysis Division, is also acknowledged.

This report was a team effort. Special thanks go to the following individuals.

U.S. Army Corps of Engineers
Melinda McClellan, Huntsville Environmental and Munitions Center of Expertise
Mike Malone, Huntsville Engineering and Support Center

HydroGeoLogic, Inc
Joe Skibinski
Denise Rivers
Andrea Fletcher

Exa Data and Mapping, LLC
Dawn Smorong
Peggy Myre
Michael Tweiten

Institute for Defense Analyses, Inc
Sara Runkel

Jacobs Engineering Group, Inc
Maggie Radford
Jeremy Bishop

Pyron Environmental, Inc
Mingta Lin

Noblis, Inc.
Cara Patton
Stephen Levitas

Abstract

This report is the third in a series presenting the results of a multi-laboratory validation study (MLVS or "the Study") undertaken 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). The Study was undertaken through the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP).

This report addresses the multi-laboratory study results for the landfill leachate and biosolids. The final report for tissues will be published separately at a later date. The overall 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).

The detailed methods and project information is provided in the first two documents in this MLVS series. 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* provides the detailed project information for the characterization of aqueous media. The same processes and operating procedures were applied to PFAS-spiked landfill leachates samples. The second report, *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume II: Soil and Sediment Matrices* provides additional information and methods specific for solid media and were applied for the evaluation of PFAS-spiked biosolid samples.

The objective of the study was to demonstrate the efficacy of the method using PFAS-spiked environmental samples. The aqueous matrices, including landfill leachates, are prepared via solid-phase extraction (SPE) and carbon clean-up processes. Solid matrices, including biosolids, are prepared via solvent extraction and SPE, followed by carbon clean-up processes. The method utilizes 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. . The method includes 40 target analytes, 24 extracted internal standard (EIS) compounds, and 7 non-extracted internal standards (NIS) compounds. The isotope dilution and EIS compound quantification schemes correct the analyte results for the measured recovery. All PFAS analytes were quantified and reported as their acid form.

Eight laboratories participated in the evaluation of PFAS-spiked landfill leachate and biosolids samples. While 10 laboratories contributed to *Volume I* and *Volume II* of the study, one commercial and one state laboratory opted out of the remaining matrices. All laboratories had previously demonstrated their initial calibrations (ICAL) and completed an initial demonstration of capabilities study for aqueous and solid media. Unspiked, and PFAS-spiked landfill leachate and biosolid samples were sent to each of the laboratories. Three landfill leachate and three biosolid sample series were analyzed. Each series consisted of an unspiked sample, three replicate low spiked samples, and three replicate high spiked samples. For each laboratory there were 21 landfill leachate and 21 biosolid samples.

For the eight laboratories that received PFAS-spiked landfill leachates and biosolids, 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).

The data from Laboratories 5 and 8 were rejected completely from the statistical evaluation of landfill leachate data and the data from Laboratories 1 and 5 were rejected completely from the statistical evaluation of biosolids data due errors identified during review and validation of the data packages submitted by these laboratories.

No specific criteria for matrix spike recoveries were established *a priori* in the Study; a goal of the study was to evaluate what criteria might be appropriately applied. The efficacy of the matrix spike recovery was evaluated in two ways; (1) mean matrix spike recovery of 70–130% of the spike concentration as was done for the Single-Laboratory Validation Study, and (2) the target recoveries in the Method for Ongoing Precision and Recovery, and for the Low-level Ongoing Precision and Recovery of 40 – 150%.

For the landfill leachate PFAS-spiked samples, the results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world samples. The pooled (low spike/high-spiked samples) average percent recoveries were between 64.3–114%. For the three biosolid sample series, over the six laboratories, the pooled spiked target PFAS percent recovery results ranged from 48.9% (PFDoS) to 116% (4:2FTS). Pooled percent recoveries were between 70 – 130% for 38 of the 40 target compounds; the exceptions were PFNS (67.3%) and PFDoS (48.9). Variability was relatively high in the recoveries between the individual laboratories and specifically for PFTrDA, PFHpS, PFDoS, PFMPA, and for the three FTCA compounds.

The suitability of EPA Method 1633 to detect and quantify the 40 target analytes in landfill leachate and biosolids 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 OPR and LLOPR recoveries and the EIS and NIS compound recoveries associated with study samples were used to confirm these matrices should be considered for inclusion in the finalized method. The landfill leachate data collected in this study indicated the IPR and OPR/LLOPR acceptance criteria for aqueous media derived from the analysis of wastewater, surface water, and groundwater samples during the MLVS (*Volume I*) are suitable for leachate samples. Further, the biosolids data in this study demonstrated that the IPR and OPR/LLOPR acceptance criteria for solid media derived from the analysis of soil and sediment samples during the MLVS (*Volume II*) are suitable for biosolid samples.

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world landfill leachate and biosolids samples. However, the mean % recovery of PFDoS (48.9%) in spiked biosolid samples across all six laboratories indicated recovery of this analyte in biosolids samples may be biased low. OPR and LLOPR data associated with biosolids sample results for PFDoS should be considered when determining the usability of biosolids sample data for PFDoS.

EXECUTIVE SUMMARY

E.S.1 INTRODUCTION

This report is the third 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 was undertaken through the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP). The MLVS was undertaken cooperatively by 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.

This report addresses the multi-laboratory study results for the landfill leachate and biosolids. Previous reports in this series included the *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633: Volume I Wastewater, Surface Water, and Groundwater Matrices* and a second report, *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume II: Soil and Sediment Matrices.* The final report for tissues will be published separately at a later date.

E.S.2 OBJECTIVES

The overall 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).

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 this MLVS were to:

- Obtain data from matrices that are representative of the method's intended use.
- Obtain data from laboratories that are representative of those likely to use the method, but that were not directly involved in its development.
- Obtain feedback from laboratory users on the specifics of the draft method.
- Use study data to characterize performance of the method.
- Develop statistically derived QC acceptance criteria that will reflect method performance capabilities in real-world situations.

The Study was then formulated to provide the data and results necessary to update and finalize the draft EPA Method 1633.

E.S.3 METHOD DESCRIPTION

The Study Plan used for the MLVS is provided in Appendix A to *Volume I*. The Study Plan 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 for 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). Study elements specific to the evaluation of solid matrices were included with *Volume II.* The important differences from the methods from *Volume I* and *Volume II* is that for landfill leachate the spiked (and QC) sample volume is 100 mL[1], and the spiked mass for biosolids is 0.5 g[1]. Aside from the sample volume, the extraction and analysis procedure is the same for leachate and other aqueous matrices; and the same for biosolids and soil/sediment. The lower sample size reduces the amount of matrix interference that is more common with leachate and biosolids.

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 study objectives and technical approach 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.*

Eight laboratories participated in the evaluation of PFAS-spiked landfill leachate and biosolids samples. While 10 laboratories contributed to *Volume I* and *Volume II* of the Study, one commercial and one state laboratory opted out of the remaining matrices. All laboratories had previously demonstrated their initial calibrations (ICAL) and completed an initial demonstration of capabilities study for aqueous and solid media. Unspiked, and PFAS-spiked landfill leachate and biosolids samples were sent to each of the laboratories. Three landfill leachate and three biosolid sample series were analyzed. Each series consisted of an unspiked sample, three replicate low spiked samples, and three replicate high spiked samples. For each laboratory there were 21 landfill leachate and 21 biosolid samples.

For the eight laboratories that received PFAS-spiked landfill leachate and biosolids, 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).

Quality control errors associated with the data packages for three laboratories resulted in the complete rejection of data from the statistical evaluation. For one laboratory, all data for both the landfill leachate and biosolids analyses were rejected due to both calculation errors and omissions

[1] The volume used for wastewater, groundwater, and surface water samples in *Volume I* was 500 mL The spiked mass used for soil and sediment in *Volume II* was 5.0 g.

of information needed to correct the calculation errors. For a second laboratory the biosolid data were rejected due to the laboratory failing to follow the Method-required preparation guidelines. For a third laboratory, the landfill leachate data were rejected due in part to numerous calculation errors, EIS failures and reporting omissions, method blank errors in the data package and other errors that were not being resolved between the validator and the laboratory. That same laboratory had data rejected due to failures during the aqueous IDC portion of the Study (see *Volume I*, Sections 4.2 and 5). This then resulted in having 6 complete laboratory packages for the landfill leachate and biosolid statistical evaluations.

E.S.5 ICAL AND IDOC FINDINGS

Initial Calibration and Initial Demonstration of Capabilities

ICALs and IDOCs for aqueous samples were presented in *Volume I;* for solid samples in *Volume II.*

Method Detection Limits

As part of Phase 3 of the MLVS, each laboratory determined the MDLs for all 40 PFAS target analytes. *Volumes I* and *II*, Sections 5.1 provide information on the requirements for as well as how these studies were performed. The range of MDL values determined by the laboratories is presented relative to the initial sample volume of 500 mL for aqueous samples and 5.0 g for solid samples. Per the method, a smaller volume (100 mL) and mass (0.5 g) is used for landfill leachates and biosolids samples, respectively, due to the typically high concentrations of PFAS and complexity of these media types. MDL average concentrations from the pooled laboratory data for landfill leachates were higher by approximately five times that reported for the aqueous media in *Volume I*. The MDLs for biosolids were also elevated by approximately 10 times relative to that reported in *Volume II* for soils and sediment.

Initial Precision and Recovery

IPR studies performed in aqueous and solid matrices are discussed in *Volumes I* and *II*, Sections 5.2

Limits of Quantitation Verification Analyses

Since an 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 during Phase 3. LOQVER sample results are discussed in *Volumes I* and *II*, Sections 5.3.

The LOQs reported for landfill leachates and biosolids are different than that of other aqueous (wastewater, groundwater, surface water) and solid (soil and sediment) samples due to the difference in the volume/mass of sample extracted (100 mL versus 500 mL and 0.5 g versus 5.0 g). The LOQs for landfill leachates ranged approximately 2.5 to 5 times higher than the LOQs reported for the other aqueous media in *Volume I* and the LOQs for biosolids ranged approximately 2 to 10 times higher than the LOQs reported for soil and sediment in *Volume II*.

E.S. 6 LEACHATE PERFORMANCE EVALUATION

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world landfill leachate samples. The pooled (low spike/high-spiked samples) average percent recoveries were between 64.3–114%. For the low-spiked samples, 27 of the 40 spiked PFAS wererecovered between 40 – 150% of the spiked concentration. Those exceeding this range were PFDoA, PFTrDA, PFTeDA, PFDS, PFDoS, NEtFOSA, NMeFOSE, NEtFOSE, PFMPA, NFDHA, 11Cl-PF3OUdS, 3:3FTCA, and 5:3FTCA. With the exception of the NFDHA, 3:3FTCA, and 5:3FTCA, which exceeded the 150% criteria, all of these analytes reported recoveries of less than 40%. Excluding these analytes, most recoveries fell between the 70 – 130% range. For the high-spiked samples the results were the same: 27 of the 40 spiked PFAS were recovered between 40 – 150% of the spiked concentration. Those exceeding this range were PFDoA, PFTrDA, PFTeDA, PFDS, PFDoS, NEtFOSA, NMeFOSE, NEtFOSE, PFMPA, and 11Cl-PF3OUdS, 4:2FTS, 6:2FTS, and 8:2FTS. With the exception of the FTSs, which exceeded the 150% criteria, all of these analytes reported recoveries of less than 40%.

Mean individual laboratory EIS percent recoveries were compared to the acceptance limits for EIS compounds that EPA determined for all aqueous 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 with the exception of the average recovery of $^{13}C_4$-PFBA for one laboratory.

E.S. 7 BIOSOLID PERFORMANCE EVALUATION

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world biosolid samples for most, but not all compounds. Overall, the pooled laboratory mean % recoveries were greater than 90% for 38 of the 40 PFAS compounds. For the three biosolid sample series, over the six laboratories, the pooled spiked target PFAS percent recovery results ranged from 48.9% (PFDoS) to 116% (4:2FTS). Pooled percent recoveries were between 70 – 130% for 38 of the 40 target compounds; the exceptions were PFNS (67.3%) and PFDoS (48.9). Variability in the recoveries between the individual laboratories and specifically for PFTrDA, PFHpS, PFDoS, PFMPA, and for the three FTCA compounds.

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% shows that for both the low- and high-spiked samples the recoveries in particular for the perfluoroalkyl sulfonic acids, had overall lower recoveries. All laboratories consistently had lower percent recoveries for the FTCAs.

Mean individual laboratory EIS percent recoveries relative to the acceptance limits for EIS compounds that EPA determined for all solid matrices and QC samples in *Volume II*. All average EIS percent recoveries for all compounds and all laboratories were solidly within the acceptance criteria range.

E.S.10 CONCLUSION

The suitability of EPA Method 1633 to detect and quantify the 40 target analytes in landfill leachate and biosolids 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 OPR and LLOPR recoveries and the EIS and NIS compound recoveries associated with study samples were used to confirm these matrices should be considered for inclusion in the finalized method. The landfill leachate data collected in this study indicated the IPR and OPR/LLOPR acceptance criteria for aqueous media derived from the analysis of wastewater, surface water, and groundwater samples during the MLVS (*Volume I*) are suitable for leachate samples. Further, the biosolids data in this study demonstrated that the IPR and OPR/LLOPR acceptance criteria for solid media derived from the analysis of soil and sediment samples during the MLVS (*Volume II*) are suitable for biosolid samples.

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world landfill leachate and biosolids samples. However, the mean % recovery of PFDoS (48.9%) in spiked biosolid samples across all six laboratories indicated recovery of this analyte in biosolids samples may be biased low. OPR and LLOPR data associated with biosolids sample results for PFDoS should be considered when determining the usability of biosolids sample data for PFDoS.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ACRONYMS AND ABBREVIATIONS

AFCEC	Air Force Civil Engineer Center
AFFF	aqueous film-forming foam
ANOVA	analysis of variance
ATP	alternate test procedure
BS	biosolids
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	landfill leachate
LC-MS/MS	liquid chromatography–tandem mass spectrometry
LCS	laboratory control sample
LHA	lifetime health advisory
LL	landfill leachate
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
mg/L	milligram per liter
MLVS	Multi-Laboratory Validation Study
MRM	multiple reaction monitoring
MS	matrix spike
MSD	matrix spike duplicate
NAVSEA	Naval Sea Systems Command
ng/g	nanogram per gram
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
ppt	parts per trillion
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
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
SOP	standard operating procedure
SOW	statement of work
SPE	solid-phase extraction
SW	surface water
TDS	total dissolved solids
TSS	total suspended solids
USACE	U.S. Army Corps of Engineers
Waters ERA	ERA – A Waters Company
Wellington	Wellington Laboratories, LLC

1 INTRODUCTION

This report is the third in a series presenting the results of a multi-laboratory validation study (MLVS or "the Study") undertaken 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). The Study 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) level 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.

This report addresses the multi-laboratory study results for the landfill leachate and biosolids. The final report for tissues will be published separately at a later date. The methods for conducting the Study are presented in the following documents and are incorporated herein by reference.

- *Single-Laboratory Validation Study of PFAS by Isotope Dilution LC-MS/MS*
- *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume I: Wastewater, Surface Water, and Groundwater Matrices* (*Volume I*)
- *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume II: Soil and Sediment Matrices* (*Volume II*)
- 4th Draft Method 1633 (EPA 2023)

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 all subsequent reports. *Volume I* provides the project background, the overall project management structure, data validation, and data management procedures. It describes the processes for laboratory selection, selection of study sample sources, and study sample creation and instructions to each laboratory with sample delivery. *Volume I* includes results from evaluation of the overall EPA Method 1633 capabilities of each laboratory for aqueous media. This included the evaluation of each laboratory's Standard Operating Procedure (SOP) and documentation of Initial Calibrations (ICAL), the Initial Demonstration of Capabilities (IDOC), method detection limit (MDL) determination, and verification of their sample limit of quantitation (LOQ) for aqueous matrices. The second report, *Multi-Laboratory Validation Study for Analysis of PFAS by EPA Draft Method 1633 Volume II: Soil and Sediment Matrices* provides additional information and methods specific for solid media. The processes, evaluation, and procedures of the previous reports are incorporated herein by reference and are not repeated herein.

1.1 BACKGROUND

The background supporting the undertaking of the Study is presented in *Volumes I and II*. Briefly, the Study was undertaken as a joint effort that included SERDP&ESTCP, EPA, the US Navy, US Air Force, and the US Army Corps of Engineers. The necessity and importance of validating 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).

1.2 METHOD SUMMARY

The Study Plan used for the MLVS is provided in Appendix A to the *Volume I*. The Study Plan 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 for 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).

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, including landfill leachates, are prepared via solid-phase extraction (SPE) and carbon clean-up processes. Soil, sediment, biosolids, and tissue matrices are prepared via solvent extraction and SPE, followed by carbon clean-up processes. The method utilizes 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.

The important differences from the methods from *Volume I* and *Volume II* are that for landfill leachate the spiked (and QC) sample volume is 100 mL[2] and the spiked mass for biosolids is 0.5 g.

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

[2] The volume used for wastewater, groundwater, and surface water samples in *Volume I* was 500 mL The spiked mass used for soil and sediment in *Volume II* was 5 g.

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
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
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	

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
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:
[1] 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.*

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) initially agreed to participate in the Study. The initial ten laboratories participating are listed in Table 2-1. For the MLVS 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 overall MLVS objectives and design are detailed in Section 2 of the *Volume I* and *Volume II* report. For this report the study design involved:

- Eight laboratories, with a goal of complete landfill leachate and biosolid sample data sets from at least six of those laboratories
- Three landfill leachate samples of varying physical/chemical characteristics including alkalinity, pH, conductivity, total dissolved solids and total suspended solids.
- Three biosolid from different sources and different pH.
- Multi-point calibration of the target analytes by each laboratory
- Initial Demonstration of Capabilities (IDOC) in solid media by each laboratory
- Determination of MDLs by each laboratory
- Analyses of matrix spike samples prepared from each of the landfill leachate and biosolid samples.

The calibration, IDOC, and MDL studies of water and solids were previously conducted by each laboratory; those results are presented for aqueous samples in *Volume I,* Section 4, and for solid samples in *Volume II,* Section 4.

2.2 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 landfill leachate and biosolids 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.

The MLVS was designed so that for each sample there would be a pre-spike characterization sample, an unspiked (or "native") sample, three replicates at a low spike concentration, and three replicates at a high spike concentration (Table 2-3). Each sample was assigned a matrix code: landfill leachates LC and biosolids BS. 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 spike replicates 2–4, and the high spike replicates 5–7.

EPA provided three individual landfill leachate samples collected as part of other on-going EPA site investigations. Three biosolids samples were used: two were provided by EPA, collected as part of other on-going EPA efforts. A third biosolids sample was collected by SEE from a wastewater treatment facility in Washington state. All samples were sent to Waters ERA in Colorado.

2.3 SELECTION OF SPIKING LEVELS AND SOLID MEDIA

All of the landfill leachate and biosolids were screened for baseline PFAS levels. Waters ERA 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) for conventional physical and chemical analyses.

Results of the baseline target PFAS for biosolids are presented in Table 2-4, and for landfill leachates in Table 2-5. PFAS in biosolids were less than 10 µg/kg for all compounds, with the exceptions of 5:3 and 7:3FTCA in all three samples. Biosolids were only evaluated for pH; the three measures were between 7.4 and 8.1., For landfill leachate, PFAS were elevated in all three samples, and particularly in sample LCAE0. Levels of PFBA, PFPEA, PFHxA, and PFBS exceeded 1,000 ng/L, and 3:3 FTCA was measured at 31,600 ng/L. ERA was directed to dilute sample LCAE0 by 10 times prior to spiking. The native PFAS results were used to set the calibration range and spiking concentrations (Table 2-5). The targeted and final spiking concentrations are given in Table 2-5.

2.4 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 landfill leachate and biosolids followed by Waters ERA are provided in *Volume II*, Appendix A.

Low and high spiking levels were set by the Study Quality Assurance (QA) Manager and EPA based upon review of the baseline (background) PFAS concentrations for the landfill leachate samples (Table 2-4) and biosolids (Table 2-5).

The spiking of landfill leachates was done similarly to the previously described for other aqueous matrices in *Volume I*, with the exception that 100 mL of landfill leachate was spiked, vs. 500 mL in the wastewater, surface water and groundwater matrices.

For the biosolids, study samples of 0.5 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 spike samples (high and low). An example certificate is shown in Figure 2-1. Certificates of Spiking for all matrices and concentrations are maintained with the project record.

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 spike level, and three bottles spiked at a high spike 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 below.

Landfill Leachates

- The laboratories were instructed to not measure the volume of the sample in the container as required by Section 11.2.2 of the MLV Study Method, but instead, to record 100 mL as the volume of sample prepared, and to use that volume when calculating PFAS concentrations in each sample.

Biosolids

- Instead of homogenizing the sample and weighing out an aliquot of the sample, as required in the Section 11.3 of Method 1633, the laboratories were instructed to transfer the entire contents (0.500 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 0.500 g dry weight of each sample.
- The laboratories were instructed to record 0.500 g as the mass of sample prepared and 0% 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 Method 1633.

2.4.1 Landfill Leachate Samples

The landfill leachate samples prepared and shipped by Waters ERA are listed in Table 2-3. The three parent landfill leachate matrices were each prepared as one unspiked, three replicates at the low spike level, and three replicate at the high spike level. This resulted in 21 individual landfill leachate samples at each laboratory for analysis. Only eight laboratories participated in the landfill leachate analyses. Laboratories 2 and 7 had opted out.

Landfill leachate samples were spiked on 1 September 2022, frozen at -20° C over the weekend, and shipped on 5 September under chain-of-custody, and 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 landfill leachate sample preparation guidelines accompanied each shipment to the laboratory (Figure 2-2).

Additional sets of samples had to be sent to Laboratories 4 and 8. Laboratory 4 experienced issues with low recoveries (<10%) on their FTCA analytes for the leachate samples. The issues affected landfill leachate samples LCAF4 through LCAF7 and LCAG1 through LCAG7. Replacement samples were sent on 9 November and received on 10 November 2022.

Laboratory 8 requested a replacement set for sample LCAG, due to low percent EIS recoveries. This was sent out on 3 November and received on 4 November 2022.

2.4.2 Biosolids Samples

The biosolids samples prepared and shipped by Waters ERA are listed in Table 2-3. The three parent biosolids were each prepared as one unspiked, three replicates at the low spike level, and three replicates at the high spike level. This resulted in 21 individual biosolids samples at each laboratory for analysis. Only eight laboratories participated in the biosolid analyses. Laboratories 2 and 7 opted out of the biosolids.

Biosolids samples were spiked on 11 August 2022, frozen at -20° C, shipped under chain-of-custody, and arrived within one day 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. A set of biosolid sample preparation guidelines accompanied each shipment to the laboratory (Figure 2-3).

Laboratory 8 experienced quality control problems during sample preparation. The laboratory reported that an incorrect solution was used to rinse the SPE cartridge prior to sample elution, causing extremely low EIS compound and target analytes recoveries (<10 %). Additional aliquots for samples BSAI4 through BSAI7, and BSAJ1 through BSAJ7 were sent on 4 October and received on 5 October 2022. Laboratory 8 subsequently requested a third group of replacement biosolid samples (BSAH, BSAI, and BSAJ only) as they reported extremely low percent recoveries for the EIS compounds. These were sent out 3 November and received on 4 November 2022.

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		**Role**
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:
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	Waste water	Surface Water	Ground water	Landfill Leachate	Soil	Sediment	Biosolids	Fish	Shellfish
1	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
2	✓	✓	✓	×	✓	✓	✓	×	✓	×	×	×	×
3	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
4	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
5	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
7	✓	✓	✓	×	✓	✓	✓	×	✓	✓	×	×	×
8	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
9	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
10	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Source file: Chapter 2 Tables 01082024.xlsx

Notes:
✓ indicates participated in specific media/matrices.
× indicates did not participate in specific media/matrices.

Table 2-3. Landfill leachate and biosolids Samples Used for the Low/High PFAS 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	
Landfill Leachate												
MSW LF Leachate Sample	MSW LF Leachate	LC	AE	LCAE0	LCAE1	LCAE2	LCAE3	LCAE4	LCAE5	LCAE6	LCAE7	1-Sep-22
CDD Landfill	CDD	LC	AF	LCAF0	LCAF1	LCAF2	LCAF3	LCAF4	LCAF5	LCAF6	LCAF7	1-Sep-22
Ash leachate	Ash leachate	LC	AG	LCAG0	LCAG1	LCAG2	LCAG3	LCAG4	LCAG5	LCAG6	LCAG7	1-Sep-22
Biosolids												
Southern CA WWTP	Wet cake	BS	AH	BSAH0	BSAH1	BSAH2	BSAH3	BSAH4	BSAH5	BSAH6	BSAH7	11-Aug-22
Mid-Atlantic WWTP	Biosolids #1 East	BS	AI	BSAI0	BSAI1	BSAI2	BSAI3	BSAI4	BSAI5	BSAI6	BSAI7	11-Aug-22
Pacific NW WWTP	WWTP Biosolid	BS	AJ	BSAJ0	BSAJ1	BSAJ2	BSAJ3	BSAJ4	BSAJ5	BSAJ6	BSAJ7	11-Aug-22

Table 2-4. Target Low/High PFAS Spike Concentrations and Calibration Range based on Native PFAS Analyses in Landfill Leachate Samples

Target PFAS	Target Calibration (100 mL sample size)		Target PFAS Spike Concentrations		Final PFAS Spike Concentrations		PFAS Target Compound Analytical Results (ng/L)		
	Low Cal [1]	High Cal [1]	Low Spike[1]	High Spike[1]	Low Spike[1]	High Spike[1]	LCAE0 [2]	LCAF0	LCAG0
PFBA	32	10000	200	1000	200	1000	1351	98.86	34.34
PFPeA	16	5000	200	1000	200	1000	1087	559.9	33.21
PFHxA	8	2500	200	1000	200	1000	2247	281	70.34
PFHpA	8	2500	200	1000	200	1000	376.6	76.96	4.471
PFOA	8	2500	200	1000	200	1000	732.7	81.38	5.442
PFNA	8	2500	50	500	50	500	23.56	3.625	< 1.476
PFDA	8	2500	50	500	50	500	10	< 1.596	< 1.476
PFUnA	8	2500	50	500	50	500	1.768	< 1.596	< 1.476
PFDoA	8	2500	50	500	50	500	2.508	< 1.596	< 1.476
PFTrDA	8	2500	50	500	50	500	< 1.702	< 1.596	< 1.476
PFTeDA	8	2500	50	500	50	500	< 2.403	< 1.596	< 1.476
PFBS	8	2500	100	1000	99.5	1003.4	1385	34.56	40.78
PFPeS	8	2500	50	500	50.8	498.2	34.61	2.794	< 1.483
PFHxS	8	2500	50	500	49.2	501.6	359.2	19.45	2.145
PFHpS	8	2500	50	500	49.6	496.1	3.626	< 1.596	< 1.476
PFOS	8	2500	50	500	50.2	502.2	47.16	14.04	1.664
PFNS	8	2500	50	500	50	500.2	< 1.584	< 1.596	< 1.476
PFDS	8	2500	50	500	50.1	501.3	< 1.584	< 1.596	< 1.476
PFDoS	8	2500	50	500	50.4	504.4	< 1.584	< 1.596	< 1.476
4:2FTS	32	2000	100	1000	99.4	994.3	7.329	< 6.383	< 5.903
6:2FTS	32	2000	100	1000	100.9	990.1	220	10.3	< 5.320
8:2FTS	32	2000	100	1000	99.8	998.4	8.421	< 6.383	< 5.903
PFOSA	20	2500	50	500	50	500	2.326	< 1.596	< 1.476
NMeFOSA	20	2500	50	500	50	500	< 1.821	< 1.835	< 1.697
NEtFOSA	20	2500	50	500	50	500	< 3.959	< 3.989	< 3.689
NMeFOSAA	20	500	50	500	50	500	126.4	< 1.596	< 1.476
NEtFOSAA	8	2500	50	500	50	500	14.27	< 1.596	< 1.476
NMeFOSE	80	5000	200	2000	200	2000	55.79	< 15.96	< 14.76
NEtFOSE	80	5000	200	2000	200	2000	20.6	< 11.94	< 11.04

Table 2-4. Target Low/High PFAS Spike Concentrations and Calibration Range based on Native PFAS Analyses in Landfill Leachate Samples (Continued)

Target PFAS	Target Calibration (100 mL sample size)		Target PFAS Spike Concentrations		Final PFAS Spike Concentrations		PFAS Target Compound Analytical Results (ng/L)		
	Low Cal [1]	High Cal [1]	Low Spike[1]	High Spike[1]	Low Spike[1]	High Spike[1]	LCAE0 [2]	LCAF0	LCAG0
HFPO-DA	32	2000	100	500	100	500	55.52	< 6.064	< 5.608
ADONA	32	2000	100	500	100.1	500.3	< 6.334	< 6.383	< 5.903
9Cl-PF3ONS	32	2000	100	500	100.9	504.4	< 6.350	< 6.399	< 5.918
11Cl-PF3OUdS	32	2000	100	500	100.1	500.3	< 6.342	< 6.391	< 5.911
3:3FTCA	40	2496	100	1000	100	1000	140.7	< 6.383	< 5.903
5:3FTCA	200	12480	500	5000	500	5000	31600	80.46	< 36.89
7:3FTCA	200	12480	500	5000	500	5000	226.7	< 39.89	< 36.89
PFEESA	16	1000	50	500	50	499.5	< 1.584	< 1.596	< 1.476
PFMPA	16	5000	50	500	50	500	< 3.167	< 3.191	< 2.952
PFMBA	16	5000	50	500	50	500	< 1.584	< 1.596	< 1.476
NFDHA	40	1000	100	500	100	500	3.352	< 3.191	< 2.952

Source file: Chapter 2 Tables 01082024.xlsx

Notes:
[1] All spike concentrations are presented as acid concentrations; as final concentration in sample in ng/L.
[2] Sample LCAE0 was diluted by 10:1 prior to spiking.

Table 2-5. Target Low/High PFAS Spike Concentrations and Calibration Range based on Native PFAS Analyses in Biosolid Samples

Target PFAS	Target Calibration (0.5 g sample size)		Target PFAS Spike Concentrations		Final PFAS Spike Concentrations		PFAS Target Compound Analytical Results (µg/kg)		
	Low Cal [1]	High Cal [1]	Low Spike[1]	High Spike[1]	Low Spike[1]	High Spike[1]	BSAH0	BSAI0	BSAJ0
PFBA	6.4	2000	40	400	40	400	< 1.749	1.923	< 1.405
PFPeA	3.2	1000	20	400	20	400	< 0.8745	1.626	< 0.7023
PFHxA	1.6	500	10	100	10	100	3.575	9.411	1.165
PFHpA	1.6	500	10	100	10	100	< 0.4373	0.5381	< 0.3511
PFOA	1.6	500	10	100	10	100	2.069	2.687	0.8285
PFNA	1.6	500	10	100	10	100	1.08	0.8099	2.021
PFDA	1.6	500	10	100	10	100	5.19	5.677	2.957
PFUnA	1.6	500	10	100	10	100	1.412	1.109	1.192
PFDoA	1.6	500	10	100	10	100	5.096	2.405	2.231
PFTrDA	1.6	500	10	100	10	100	1.065	0.7794	0.9899
PFTeDA	1.6	500	10	100	10	100	1.152	< 0.5509	1.447
PFBS	1.6	500	10	100	9.95	99.5	0.01555	0.7888	0.05019
PFPeS	1.6	500	10	100	10.2	99.6	< 0.5600	< 0.4230	< 0.3529
PFHxS	1.6	500	10	100	9.85	100.3	4.56	1.049	0.5255
PFHpS	1.6	500	10	100	9.92	99.2	25.36	< 0.4209	3.924
PFOS	1.6	500	10	100	10	100.4	10.35	24.34	13.24
PFNS	1.6	500	10	100	10	100	0.682	< 0.4209	< 0.3511
PFDS	1.6	500	10	100	10	100.3	1.077	0.4775	1.259
PFDoS	1.6	500	10	100	10.1	100.9	< 0.4373	< 0.4209	< 0.3511
4:2FTS	6.4	400	40	240	39.4	240.1	< 1.749	< 1.684	< 1.405
6:2FTS	6.4	400	40	240	40	239.9	< 1.576	3.442	< 1.266
8:2FTS	6.4	400	40	240	40.3	238.1	< 1.749	2.515	< 1.405
PFOSA	1.6	500	10	100	10	100	1.365	0.841	1.515
NMeFOSA	4	500	20	100	20	100	< 0.5028	< 0.4840	< 0.4038
NEtFOSA	4	500	20	100	20	100	< 1.093	< 1.052	< 0.8778
NMeFOSAA	4	100	20	100	20	100	6.831	12.58	15.64
NEtFOSAA	1.6	500	10	100	10	100	5.156	4.391	8.468
NMeFOSE	16	1000	100	600	100	600	10.68	< 4.209	14.02
NEtFOSE	16	1000	100	600	100	600	5.404	< 3.148	6.856
HFPO-DA	6.4	400	40	320	40	320	< 1.662	< 1.599	< 1.334

Table 2-5. Target Low/High PFAS Spike Concentrations and Calibration Range based on Native PFAS Analyses in Biosolid Samples (Continued)

Target PFAS	Target Calibration (0.5 g sample size)		Target PFAS Spike Concentrations		Final PFAS Spike Concentrations		PFAS Target Compound Analytical Results (µg/kg)		
	Low Cal [1]	High Cal [1]	Low Spike[1]	High Spike[1]	Low Spike[1]	High Spike[1]	BSAH0	BSAI0	BSAJ0
ADONA	6.4	400	40	320	39.6	321	< 1.749	< 1.684	< 1.405
9Cl-PF3ONS	6.4	400	40	320	39.2	321.3	< 1.753	< 1.688	< 1.408
11Cl-PF3OUdS	6.4	400	40	320	39.6	321	< 1.751	< 1.686	< 1.406
3:3 FTCA	8	400	40	320	40	320	< 1.749	< 1.684	< 1.405
5:3 FTCA	40	2500	500	2000	500	2000	184.5	84.67	250.7
7:3 FTCA	40	2500	500	2000	500	2000	84.42	17.37	26.44
PFEESA	3.2	200	20	160	20	160.6	< 0.4373	< 0.4209	< 0.3511
PFMPA	3.2	1000	20	200	20	200	< 0.8745	< 0.8418	< 0.7023
PFMBA	3.2	1000	20	200	20	200	< 0.4373	< 0.4209	< 0.3511
NFDHA	8	200	40	160	40	160	< 0.8745	< 0.8418	< 0.7023

Source file: Chapter 2 Tables 01082024.xlsx

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

Table 2-6. Conventional Analytical Results for Landfill Leachate and Biosolids

Analyte	Units	Landfill Leachate						Biosolids					
		LCAG0		LCAF0		LCAE0		BSAHO		BSAI0		BSAJ0	
		Result	Flag	Result	Flag	Result	Flag	Result	Flag	Result	Flag	Result	Flag
HEM (Oil and Grease)	mg/L	4	U	4	U	6	U	---		---		---	
SGT-HEM (Total Petroleum Hydrocarbons)	mg/L	6	U	6	U	8	U	---		---		---	
Ammonia as N	mg/L	19		260		1,200		---		---		---	
Calcium	mg/L	6,500		270		110		---		---		---	
Sodium	mg/L	5,600		110		1,600		---		---		---	
pH adj. to 25 deg C	SU	7		8		8		8		7.4		8.1	
Specific Conductance	umhos/cm	56,000		2,200		15,000		---		---		---	
Chloride	mg/L	21,000		180		1,900		---		---		---	
Sulfate	mg/L	78		440		84		---		---		---	
Total Alkalinity as CaCO3	mg/L	130		480		5,500		---		---		---	
Bicarbonate Alkalinity as CaCO3	mg/L	130		480		5,300		---		---		---	
Carbonate Alkalinity as CaCO3	mg/L	6	U	6	U	190		---		---		---	
Total Dissolved Solids (TDS)	mg/L	40,000		1,500		6,500		---		---		---	
Total Suspended Solids	mg/L	3	U	4	J	9		---		---		---	

Source file: Chapter 2 Tables 01082024.xlsx

ERA
A Waters Company

▪ Certificate of Spiking ▪

Hydrogeologic MLV Study Samples

ERA Project Number: 11252101

Matrix Type: Biosolids
Spike Level: High Level
Certificate Issue Date: 22-Aug-2022
Revision Number: 1.0

CERTIFICATION

Compound	Spiked Concentration[1] ng/g
PFBA	400.0
PFPEA	400.0
PFHXA	100.0
PFHPA	100.0
PFOA	100.0
PFNA	100.0
PFDA	100.0
PFUNA	100.0
PFDOA	100.0
PFTRDA	100.0
PFTEDA	100.0
PFBS	99.5
PFPES	99.6
PFHXS	100.3
PFHPS	99.2
PFOS	100.4
PFNS	100.0
PFDS	100.3
PFDOS	100.9
4:2FTS	240.1
6:2FTS	239.9
8:2FTS	238.1
PFOSA	100.0
NMeFOSA	100.0
NEtFOSA	100.0
NMeFOSAA	100.0
NEtFOSAA	100.0
NMeFOSE	600.0
NEtFOSE	600.0
HFPO-DA	320.0
ADONA	321.0
9CL-PF3ONS	321.3
11CL-PF3OUDS	321.0
3:3FTCA	320.0
5:3FTCA	2000.0
7:3FTCA	2000.0
PFEESA	160.6
PFMPA	200.0
PFMBA	200.0
NFDHA	160.0

SAMPLE-MATRIX TABLE

Lot Number:	Matrix Name:	Sampling Date[2]:	Sampling Time[2]:
BSAH5 BSAH6 BSAH7	Playa Del Ray, CA	11-Aug-2022	10:00 AM
BSAI5 BSAI6 BSAI7	Biosolids #1 East	11-Aug-2022	10:00 AM
BSAJ5 BSAJ6 BSAJ7	South Plant Biosolids	11-Aug-2022	10:00 AM

Figure 2-1. Example Biosolids Certificate of Spiking

PFAS Method Validation Study:

Landfill Leachate Sample Preparation Guidelines

Shipment Contents

- (1) 18"x14"x15" Styrofoam box cooler
- (3) Leachate Lots – packaged in (21) 125 mL amber HDPE bottles
- Temperature blank
- Ice Packs
- Sample Preparation Guidelines
- Sample Chain of Custody (COC)

Sample Description

- Samples are packaged in a 125 mL amber HDPE bottles containing approximately 100 mL of spiked sample.
- Samples will 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 prepared and analyzed as soon as possible.

Sample Instructions

1. The sample preparation procedure found in the MLV Study Method is to be followed, with one exception. Do not measure the volume of the sample in the container as required by Section 11.2.2 of the MLV Study Method. Instead, record 100 mL as the volume of sample prepared. This is the volume to be used when calculating PFAS concentrations in each sample. The container is to be rinsed as required by the MLV Study Method.

2. Report your results as ng/L 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).

Figure 2-2. Landfill Leachate Sample Preparation Guideline Form

PFAS Method Validation Study:

Biosolids Sample Preparation Guidelines

Shipment Contents

- (1) 18"x14"x15" Styrofoam box cooler
- (3) Biosolids 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 0.500 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 analyze 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 0.500 g dry weight of each sample has been sent for each sample. Record 0.500 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

Figure 2-3. Biosolids Sample Preparation Guideline Form

PFAS Method Validation Study:

Biosolids Sample Preparation Guidelines

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).

Figure 2-3. Biosolid 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, in the Study Plan (*Volume I, Appendix A*), and in *Volume II,* Section 3.

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 of the eight laboratories that received landfill leachate and biosolids PFAS-spiked matrices 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 A (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. Details of the EDD checking procedures and overall data management are included in *Volume I,* Appendix C.

3.2 DATA VALIDATION

For the eight laboratories that received PFAS-spiked landfill leachate and biosolids, 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). A data validation report (DVR) and an amended electronic data deliverable (EDD) with the addition of data qualifiers as appropriate was submitted for each laboratory and matrix. These were subsequently reviewed by NAVSEA and EPA's contractor GDIT. If/where necessary, additional information was required from the laboratories, and the DVRs and EDDs were amended. The final validated study results comprise the documents listed in the General List of Documents and are maintained in the Project record.

For most laboratories, the data validation process improved as compared to the review of the matrices in *Volume I* (aqueous) and *Volume II* (soil and sediment). For some of the laboratories the data package problems identified in *Volume II* Section 3.2 persisted and required multiple iterations. 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, and,
- Incorrect manual integration of peaks from chromatographs with an inability to confirm the laboratories' calculations.

Errors associated with the data packages for three laboratories resulted in the complete rejection of data from the statistical evaluation. For Laboratory 5, all data for both the landfill leachate and biosolids analyses were rejected due to both calculation errors and omissions of information needed to correct the calculation errors. As part of the data validation, 10 percent of the raw data were examined and re-calculation performed on reported values for instrument calibration, calibration verification, EIS, NIS, and sample results. It was found during the verification process, the raw data included in these data packages were not correct and/or not correlated with the reported results. When the laboratory was contacted to provide corrections, they either would not or could not provide that information. As a result, the data could not be verified and was rejected. This same issue resulted in the omission of Laboratory 5 sediment data in *Volume II*.

Laboratory 1 biosolids data were rejected due to the laboratory failing to follow the Waters ERA preparation guidelines. The guidelines (Figure 2-3) required the extraction of the entire 0.5 g of biosolids sent; Laboratory 1 extracted only 0.3 g of material. While the submitted data otherwise conformed to the Study quality assurance requirements, the Study Team determined that the statistical comparisons needed to be made between the laboratories data that extracted an equivalent mass (i.e., 0.5 g).

3.3 DATA USED IN THE STATISTICAL ANALYSES

The IDA Statistical Data Analysis Report for landfill leachate and biosolids media are Appendix A to this volume. Statistical analyses of the laboratory data were previously detailed in *Volume I* and *Volume II.* 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 8.4 (AFCEC) and 8.6 (GDIT).

Of the eight laboratories receiving spiked samples, only six laboratories' data were carried forward for statistical analysis. Table 3-1 present a summary of the total type and number of analyses reviewed for the landfill leachate and biosolids study. A total of 27,202 individual results were submitted by the six laboratories, and of those data, 23,800 data points passed all quality assurance reviews and were advanced for statistical analyses.

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 were presented in *Volume I,* Section 3.4, and *Volume II,* Section 3.4. 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.

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
Landfill Leachate							
Unspiked Samples	6	1,491	18	719	432	128	1,279
Low-Level Spike	6	4,331	54	2,156	1,296	382	3,834
High-Level Spike	6	4,331	54	2,155	1,296	383	3,834
Low-Level Ongoing Precision and Recovery	6	994	14	560	336	98	994
Method Blanks	6	994	14	560	336	98	994
Ongoing Precision and Recovery	6	1,065	14	560	336	99	995
Biosolids							
Unspiked Samples	6	1,568	18	708	426	134	1,268
Low-Level Spike	6	4,704	54	2,130	1,278	402	3,810
High-Level Spike	6	4,730	54	2,129	1,291	408	3,828
Low-Level Ongoing Precision and Recovery	6	998	14	554	332	102	988
Method Blanks	6	998	14	554	332	102	988
Ongoing Precision and Recovery	6	998	14	554	332	102	988
Total Number of Results		**27,202**	**336**	**13,339**	**8,023**	**2,438**	**23,800**

Source File: Summary_tables_LCBS_Exa_CH5_11292023.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.

4 CALIBRATION AND QUANTIFICATION: LANDFILL LEACHATE AND BIOSOLID MEDIA

The process for evaluating the calibration and quantitation schemes used for sample analysis are described in *Volume I,* Section 4. This section pertains solely to the processes specific to the valuation of landfill leachate and biosolids.

4.1 MASS CALIBRATION AND MASS CALIBRATION VERIFICATION

Please see *Volume I* for additional details on the mass calibration and mass calibration verification.

4.2 MULTI-POINT INITIAL CALIBRATION

This section provides an overview of the multi-point initial calibrations evaluated in Phase 3 of the MLVS. A more detailed discussion is provided 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 biosolids samples were spiked correctly. Therefore, data from Laboratory 8 was included in the statistical analysis of data for the biosolids samples and excluded for landfill leachate samples.

4.3 QUALITATIVE STANDARDS

Please see *Volume I,* Section 4.3 for 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 criteria for CVs associated with sample results that were reported.

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 concentrations of the ISCs associated with sample analysis were at 0.25 times their LOQ. 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 three exceptions. There were two instances of ISC standards failing to meet this criterion that affected the biosolid data that was reported by Laboratory 3 (Table 4-1). One of these failures (NFDHA) was associated with one sample only while the other failures (PFOS and/or NMeFOSAA) affected all biosolids samples (21 samples total). There was only one instance of ISC standards failing to meet this criterion that affected landfill leachate data. This failure, reported by Laboratory 4 (Table 4-1),

for PFTeDA, affected 11 samples. 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 are routinely achievable. It is also worth noting that all of the data points in Table 4-1 are less than 10% outside the ±30% criteria. If the criteria had been ±40% there would have been no failures.

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

Laboratory ID	Sample ID	Analyte	% Recovery	Data Qualifier Applied
Landfill Leachates				
4	LCAF4	PFTeDA	130.5	J+
4	LCAF5	PFTeDA	130.5	J+
4	LCAF6	PFTeDA	130.5	J+
4	LCAF7	PFTeDA	130.5	J+
4	LCAG1	PFTeDA	130.5	UJ
4	LCAG2	PFTeDA	130.5	J+
4	LCAG3	PFTeDA	130.5	J+
4	LCAG4	PFTeDA	130.5	J+
4	LCAG5	PFTeDA	130.5	J+
4	LCAG6	PFTeDA	130.5	J+
4	LCAG7	PFTeDA	130.5	J+
Biosolids				
3	BSAH5	NFDHA	65.5	J-
3	BSAH1	PFOS	138.2	J+
3	BSAH1	NMeFOSAA	139.8	J+
3	BSAH2	PFOS	138.2	J+
3	BSAH2	NMeFOSAA	139.8	J+
3	BSAH3	PFOS	138.2	J+
3	BSAH3	NMeFOSAA	139.8	J+
3	BSAH4	PFOS	138.2	J+
3	BSAH4	NMeFOSAA	139.8	J+
3	BSAH5	PFOS	158.7	J+
3	BSAH6	PFOS	138.2	J+
3	BSAH6	NMeFOSAA	139.8	J+
3	BSAH7	PFOS	138.2	J+
3	BSAH7	NMeFOSAA	139.8	J+
3	BSAI1	PFOS	138.2	J+
3	BSAI1	NMeFOSAA	139.8	J+
3	BSAI2	PFOS	138.2	J+
3	BSAI2	NMeFOSAA	139.8	J+
3	BSAI3	PFOS	138.2	J+
3	BSAI3	NMeFOSAA	139.8	J+
3	BSAI4	PFOS	138.2	J+

Table 4-1. Summary of Instances of ISC Recoveries Outside of MLVS Acceptance Criteria Range (Continued)

Laboratory ID	Sample ID	Analyte	% Recovery	Data Qualifier Applied
Biosolids (continued)				
3	BSAI4	NMeFOSAA	139.8	J+
3	BSAI5	PFOS	138.2	J+
3	BSAI5	NMeFOSAA	139.8	J+
3	BSAI6	PFOS	138.2	J+
3	BSAI6	NMeFOSAA	139.8	J+
3	BSAI7	PFOS	138.2	J+
3	BSAI7	NMeFOSAA	139.8	J+
3	BSAJ1	PFOS	138.2	J+
3	BSAJ1	NMeFOSAA	139.8	J+
3	BSAJ2	PFOS	138.2	J+
3	BSAJ2	NMeFOSAA	139.8	J+
3	BSAJ3	PFOS	138.2	J+
3	BSAJ3	NMeFOSAA	139.8	J+
3	BSAJ4	PFOS	138.2	J+
3	BSAJ4	NMeFOSAA	139.8	J+
3	BSAJ5	PFOS	138.2	J+
3	BSAJ5	NMeFOSAA	139.8	J+
3	BSAJ6	PFOS	138.2	J+
3	BSAJ6	NMeFOSAA	139.8	J+
3	BSAJ7	PFOS	138.2	J+
3	BSAJ7	NMeFOSAA	139.8	J+

Source Files: Chapter 4 Tables 01082024

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 MDL determination, the initial precision and recovery (IPR) study, 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 determined the MDLs for all 40 PFAS target analytes. *Volumes I* and *II*, Sections 5.1 provide information on the requirements for as well as how these studies were performed. The range of MDL values determined by the laboratories is presented relative to the initial sample volume of 500 mL for aqueous samples and 5.0 g for solid samples. Per the method, a smaller volume (100 mL) and mass (0.5 g) is used for landfill leachates and biosolids samples, respectively, due to the typically high concentrations of PFAS and complexity of these media types. Tables 5-1 and 5-2 provide MDLs for landfill leachates and biosolids adjusted for sample sizes. Since Laboratories 2 and 7 opted out of the landfill leachate and biosolids phase of the study, these tables do not include MDL data from these laboratories. In addition, Laboratory 5 was omitted from the statistical analysis of landfill leachate and biosolids samples due to the inability to validate the reported results using the raw data reported by the laboratory, therefore, they also are not included.

During the validation of solids MDL studies, 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 from this laboratory were eliminated from the biosolid statistical analyses.

5.2 INITIAL PRECISION AND RECOVERY (IPR) RESULTS

IPR studies performed in aqueous and solid matrices are discussed in *Volumes I* and *II*, Section 5.2 in each of the respective volumes.

5.3 SOLIDS LIMIT OF QUANTITATION VERIFICATION ANALYSES

Since an 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 during Phase 3. LOQVER sample results are discussed in *Volumes I* and *II*, Sections 5.3.

The LOQs reported for landfill leachates and biosolids are different than that of other aqueous and solid samples due to the difference in the volume/mass of sample extracted (100 mL versus 500 mL and 0.5 g versus 5.0 g). Tables 5-3 and 5-4 provide the range of LOQs the laboratories used to report landfill leachate and biosolids samples in this study. LOQs that were elevated due to extract dilutions prior to analysis were omitted from the summary.

Table 5-1. Summary of Verified MDLs for Landfill Leachates

Target Analyte	Number of Laboratories	MDL Minimum Concentration (ng/L) [1]	MDL Maximum Concentration (ng/L) [2]
PFBA	6	2.73	5.25
PFPeA	6	1.23	3.84
PFHxA	6	0.59	2.27
PFHpA	6	0.79	2.6
PFOA	6	0.786	3.4
PFNA	6	0.832	3.29
PFDA	6	0.906	4.05
PFUnA	6	0.908	3.32
PFDoA	6	0.846	3.76
PFTrDA	6	0.98	3.04
PFTeDA	6	0.838	2.77
PFBS	6	0.521	2.64
PFPeS	6	0.582	2.34
PFHxS	6	0.857	3.16
PFHpS	6	0.561	2.53
PFOS	6	1.24	6.8
PFNS	6	1.09	3.62
PFDS	6	0.767	3.44
PFDoS	6	0.9	4.44
4:2FTS	6	3.16	8.53
6:2FTS	6	4.73	14.1
8:2FTS	6	2.72	14.3
PFOSA	6	0.77	2.26
NMeFOSA	6	0.765	4.83
NEtFOSA	6	0.499	3.64
NMeFOSAA	6	0.93	5.79
NEtFOSAA	6	1.42	4.28
NMeFOSE	6	7.58	18.8
NEtFOSE	6	7.25	14.7
PFMPA	6	1.6	3.14
PFMBA	6	1.48	3.04
NFDHA	6	2.46	9.25
HFPO-DA	6	1.72	11.6
ADONA	6	2.86	8.35
PFEESA	6	1.06	3.65
9Cl-PF3ONS	6	3.5	9.3
11Cl-PF3OUdS	6	4.09	9.77
3:3FTCA	6	4.3	13.2
5:3FTCA	6	9.4	46.8
7:3FTCA	6	12.8	45.4

Source: Chapter 5 Tables 02082024

Notes:
[1] Minimum reported concentration based on initial sample volume of 100 mL
[2] Maximum reported concentration based on initial sample volume of 100 mL

Table 5-2. Summary of Verified MDLs for Biosolids

Target Analyte	Number of Laboratories	MDL Minimum Concentration (µg/kg) [1]	MDL Maximum Concentration (µg/kg) [2]
PFBA	6	0.504	2.67
PFPeA	6	0.39	1.33
PFHxA	6	0.375	1.09
PFHpA	6	0.232	0.886
PFOA	6	0.315	0.667
PFNA	6	0.441	0.784
PFDA	6	0.384	0.752
PFUnA	6	0.24	1.15
PFDoA	6	0.378	0.769
PFTrDA	6	0.22	0.667
PFTeDA	6	0.303	1.06
PFBS	6	0.269	0.624
PFPeS	6	0.23	0.69
PFHxS	6	0.328	1.3
PFHpS	6	0.249	0.959
PFOS	6	0.426	1.32
PFNS	5	0.38	0.64
PFDS	6	0.27	1.76
PFDoS	6	0.27	0.976
4:2FTS	6	0.808	3.97
6:2FTS	6	1.39	3.05
8:2FTS	6	1.02	5.18
PFOSA	6	0.14	0.667
NMeFOSA	5	0.29	1
NEtFOSA	5	0.17	1.28
NMeFOSAA	6	0.318	1.2
NEtFOSAA	6	0.262	0.824
NMeFOSE	6	1.51	6.67
NEtFOSE	6	0.63	6.67
PFMPA	6	0.408	1.33
PFMBA	6	0.312	1.33
NFDHA	6	0.597	2.82
HFPO-DA	6	0.51	4.32
ADONA	6	0.79	2.83
PFEESA	6	0.34	1.19
9Cl-PF3ONS	6	0.814	2.77
11Cl-PF3OUdS	6	0.88	2.52
3:3FTCA	6	1.03	2.67
5:3FTCA	6	1.33	13.1
7:3FTCA	6	5.63	17.6

Source: Chapter 5 Tables 01082024

Notes:
[1] Minimum reported concentration based on initial sample mass of 0.5 g.
[2] Maximum reported concentration based on initial sample mass of 0.5 g.

Table 5-3. Summary of Verified LOQs in Landfill Leachates

Target Analyte	Number of Laboratories	LOQ Minimum Concentration (ng/L) [1]	LOQ Maximum Concentration (ng/L) [2]
PFBA	6	20	40
PFPeA	6	10	20
PFHxA	6	5	10
PFHpA	6	5	10
PFOA	6	5	10
PFNA	6	5	10
PFDA	6	5	10
PFUnA	6	5	10
PFDoA	6	5	10
PFTrDA	6	5	10
PFTeDA	6	5	10
PFBS	6	5	10
PFPeS	6	5	10
PFHxS	6	5	10
PFHpS	6	5	10
PFOS	6	5	10
PFNS	6	5	10
PFDS	6	5	10
PFDoS	6	5	10
4:2FTS	6	20	40
6:2FTS	6	20	40
8:2FTS	6	20	40
PFOSA	6	5	10
NMeFOSA	6	5	10
NEtFOSA	6	5	10
NMeFOSAA	6	5	10
NEtFOSAA	6	5	10
NMeFOSE	6	50	100
NEtFOSE	6	50	100
PFMPA	6	10	20
PFMBA	6	10	20
NFDHA	6	10	20
HFPO-DA	6	20	40
ADONA	6	20	40
PFEESA	6	10	20
9Cl-PF3ONS	6	20	40
11Cl-PF3OUdS	6	20	40
3:3FTCA	6	25	50
5:3FTCA	6	125	250
7:3FTCA	6	125	250

Version: Summary_tables_LCBS_Exa_12132023

Notes:
[1] Minimum concentration reported based on an initial sample volume of 100 mL
[2] Minimum concentration reported based on an initial sample volume of 100 mL

Table 5-4. Summary of Verified LOQs for Biosolids

Target Analyte	Number of Laboratories	LOQ Minimum Concentration (µg/kg) [1]	LOQ Maximum Concentration (µg/kg) [2]
PFBA	6	6.4	8.01
PFPeA	6	3.2	4
PFHxA	6	1.6	2
PFHpA	6	1.6	2
PFOA	6	1.6	2
PFNA	6	1.6	2
PFDA	6	1.6	2
PFUnA	6	1.6	2
PFDoA	6	1.6	2
PFTrDA	6	1.6	2
PFTeDA	6	1.6	2
PFBS	6	1.6	2
PFPeS	6	1.6	2
PFHxS	6	1.6	2
PFHpS	6	1.6	2
PFOS	6	1.6	2
PFNS	5	1.6	2
PFDS	6	1.6	2
PFDoS	6	1.6	2
4:2FTS	6	6.4	8
6:2FTS	6	6.4	8
8:2FTS	6	6.4	8
PFOSA	6	1.6	2
NMeFOSA	5	1.6	2
NEtFOSA	5	1.6	2
NMeFOSAA	6	1.6	2
NEtFOSAA	6	1.6	2
NMeFOSE	6	16	20
NEtFOSE	6	16	20
PFMPA	6	3.2	4
PFMBA	6	3.2	4
NFDHA	6	3.2	4
HFPO-DA	6	6.4	8.35
ADONA	6	6.4	8
PFEESA	6	3.2	4
9Cl-PF3ONS	6	6.4	8
11Cl-PF3OUdS	6	6.4	8
3:3FTCA	6	8	10
5:3FTCA	6	40	50
7:3FTCA	6	40	50

Source: Chapter 5 Tables 01082024

Notes:
1 Minimum concentration based on initial sample mass of 0.5 g.
[2] Maximum concentration reported based on an initial sample mass of 0.5g.

6 LANDFILL LEACHATE

A total of 21 study 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 landfill leachate 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 5.2, Laboratories 2 and 7 did not participate in the landfill leachate analyses. Laboratories 5 and 8 data were rejected and were not included in the statistical analysis of landfill leachates.

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

6.1 PFAS CONCENTRATIONS IN UNSPIKED LANDFILL LEACHATES

Each laboratory received and analyzed a single sample unspiked aliquot of each landfill leachate 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 spike concentrations (Table 2-4). The total number of PFAS target analytes detected by at least one laboratory is given in Table 6-2. PFBA, PFPeA, PFHxA, PFHpA, PFOA, and PFBS were detected by every laboratory in every sample. A summary of the minimum and maximum reported values across all laboratories is found in Appendix B, Table B-1.

Of the 40 PFAS target analytes in the draft EPA Method 1633, 24 were not detected in any of the three landfill leachate samples by any of the 6 laboratories included in the statistical analysis of the landfill leachate portion of the validation study, nor by the reconnaissance laboratory. Table 6-1 also shows that the detections of PFAS reported from the three landfill leachate samples across the six laboratories ranged from 27 (Laboratories 6) to 36 (Laboratory 9); the reconnaissance laboratory reported 33 detected PFAS.

6.2 LANDFILL LEACHATE MATRIX SPIKE RESULTS

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

For the low-spiked landfill leachate samples (Table 6-3), the pooled mean % recovery was 95% across all 40 PFAS analyzed, with a range of 63.2% (PFDoS) and 125% (5:3FTCA). The inter- and intra-laboratory variability was low with only a few exceptions. The pooled between-laboratory standard deviation (s_b) for all PFAS were less than 20% with the exception of NEtFOSE (21.7%), PFTeDA (23.8%) and 5:3FTCA (39.1%). All others ranged from 8.69% (PFOSA) to 18.3% (11Cl-PF2OUdS). The pooled within-laboratory standard deviation (s_w) for all PFAS were

less than 20% with the exception of 5:3FTCA (54.7%). All others ranged from 4.79% (PFOSA) to 19% (NEtFOSAA).

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

- For 5:3FTCA, the pooled average percent recovery was 125%, while Laboratory 6 had three samples with recoveries that far exceeded this range for the low-spiked samples of in the LCAE series (356%, 382%, and 358%). Those anomalous reported values skewed the higher pooled mean percent recoveries and standard deviations for the three compounds (Table 6-2).
- For NFDHA and 3:3FTCA the pooled average percent recoveries were 96.9% and 112%, respectively. Laboratory 6's overall average for the measured landfill leachate samples were slightly higher than the pooled percent recovery, with two low-spiked samples in the LCAF series reporting recoveries greater than 140% (149%, 181% for NFDHA and 165% and 176% for 3:3FTCA).
- For PFDS, the pooled average percent recoveries was 78.9%. With the exception of two recoveries (81.2% and 93.0%), all low-spiked sample recoveries reported by Laboratory 6 were less than the pooled average, ranging from 46.1% to 69.9%.
- For PFDoA, PFTrDA, PFTeDA, PFDS, NEtFOSA, NMeFOSE, and NEtFOSE, the pooled average percent recoveries were 96.1%, 87.4%, 88.6%, 78.9%, 83.7%, 84.8%, and 80.3%, respectively. All of the recoveries reported by Laboratory 10 for the LCAG series low-spiked samples <40%.

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 65.3 (PFDoS) to 108% (3:3FTCA), averaging 93.3% across all 40 PFAS analyzed. The inter- and intra-laboratory variability was low with only a few exceptions. The pooled between-laboratory standard deviation (s_b) for all PFAS were less than 20% with the exception of NEtFOSE (23.4%) and PFTeDA (21.9%). All others ranged from 6.64% (PFOSA) to 18.8% (PFDoS). The pooled within-laboratory standard deviation (s_w) for all PFAS were less than 20%, ranging from 3.20% (PFBA) to 16.8% (3:3FTCA).

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

- For PFDS, the pooled average percent recoveries was 87.4%. With the exception of one recovery (89.6%), all high-spiked sample recoveries reported by Laboratory 6 were less than the pooled average, ranging from 37.9% to 70.8%.
- For PFDoA, PFTrDA, PFDS, NEtFOSA, NMeFOSE, and NEtFOSE, the pooled average percent recoveries were 90.8%, 84.5%, 79.6%, 84.2%, 81.7%, and 80.7%, respectively. All of the recoveries reported by Laboratory 10 for the LCAG series high-spiked samples <40%.

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 64.3% (PFDoS) and 114% (5:3FTCA).

With the exception of PFDoS, all mean percent recoveries were within the targeted recovery range (70–130%). With the exception of PFDS, PFDoS, and 11Cl-PF3OUdS, the remaining pooled recoveries were greater than 80%.

Results comparing the three different landfill leachate 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 landfill leachate samples.

6.3 LANDFILL LEACHATE 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 B, Table B-4. For the 6 laboratories the pooled average EIS percent recovery ranged between 56.5% ($^{13}C_2$-PFTeDA) and 123.4% ($^{13}C_2$-4:2FTS). Table 6-7 presents the pooled EIS percent recovery; all mean percent recoveries were within the MLVS method-specified target recovery.

Figures 6-4 show that the highest variabilities in EIS compound recoveries for all laboratories were for $^{13}C_4$-PFBA, D_7-NMeFOSE, D_9-NEtFOSE, $^{13}C_2$-4:2FTS, $^{13}C_2$-6:2FTS, and $^{13}C_2$-8:2FTS. Laboratory 4 had overall poor recovery and high variability for $^{13}C_4$-PFBA, ranging from 4.0% to 92.9%. Laboratory 6 had overall poor recovery and high variability for D_7-NMeFOSE, D_9-NEtFOSE, with results ranging from 10.0% to 69.0% and 2.46% to 67.2%, respectively. Laboratory 3 had high variability and recoveries for $^{13}C_2$-4:2FTS, ranging from 101% to 220%. Laboratory 6 had high recoveries for $^{13}C_2$-6:2FTS, ranging from 75.5% to 182%, while Laboratory 9 had high variability with recoveries from 38.0% to 177%.

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

Table 6-1. Summary of Target Analytes Detected in Unspiked Landfill Leachate Samples in ng/L

Analyte	Number of Labs	Lab 1		Lab 3		Lab 4		Lab 6		Lab 9		Lab 10		SGS-AXYS Baseline	
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual [1]
LCAE1 - MSW LF Leachate Sample															
PFBA	5	133		166		--	X	128		121		153		1351	
PFPeA	6	108		154		126		123		97.5		152		1087	
PFHxA	6	201		271		259		225		206		276		2247	
PFHpA	6	32.5		37.6		37.3		44.3		28.1		41		376.6	
PFOA	6	68		84		74.4		82.9		58.6		81.7		732.7	
PFNA	6	3.29	U	3.2	JI	2.11	J	2.79	J	1.61	J	2.48	J	23.56	
PFBS	6	152		200		187		125		140		205		1385	
PFPeS	6	3.3	J	4	J	4.53	JI	0.645	U	2.88	J	3.59	J	34.61	
PFHxS	6	34		40		37.3		32.9		28.4		48		359.2	
PFOS	6	3.49	J	8.4		6.8	U	3.42	J	3.39	J	4.92	J	47.16	
6:2FTS	6	24.8	J	26	J	24.6	J	16.2	J	19.4	J	20.3	J	220	
NMeFOSAA	6	9.89	J	12.8		8.02		3.28	U	7.37		9.38	J	126.4	
HFPO-DA	6	9.25	U	6	J	11.6	U	3.74	U	5.19	J	1.72	U	55.52	
3:3FTCA	6	4.3	U	30	J	25.4	J	8.35	U	29.6		31.9	J	140.7	
5:3FTCA	6	1030		1340		1640		22.3	U	1280		1540		31600	
LCAF1 - CDD Landfill															
PFBA	6	110		104		79.6		123		86.2		127		98.86	
PFPeA	6	615		726		663		658		562		672		559.9	
PFHxA	6	340		397	J	412		328		341		462		281	
PFHpA	6	76.8		94		98.3		85.4		73		107		76.96	
PFOA	6	99.2		114		98.4		79.7		82.5		121		81.38	
PFNA	6	3.44	J	6	J	5.03	J	5.34	J	4.13	J	6.98	JI	3.625	
PFBS	6	32.7		38.4		41.7		25.5		30.5		48.7		34.56	
PFPeS	6	2.44	J	3.6	J	2.55	J	0.645	U	2.9	J	3.31	J	2.794	
PFHxS	6	22		25.2		24.2		21		19.8		28.9		19.45	
PFHpS	6	1.98	U	2.44	U	2.53	U	1.02	U	0.683	JI	1.72	U	1.596	U
PFOS	6	7.85	J	16		14.1		16.3		14.6		19.8		14.04	
NMeFOSAA	6	3.68	U	4.28	U	3.03	U	3.28	U	1.12	J	5.79	U	1.596	U
9Cl-PF3ONS	6	4.63	J	6.44	U	9.3	U	3.5	U	3.67	U	3.8	U	6.399	U
3:3FTCA	6	4.3	U	13.2	U	8.73	J	8.35	U	11.2	J	6.57	U	6.383	U
LCAG1 - Ash leachate															
PFBA	6	44.2		46.8		45.3		41.6		38		59		34.34	
PFPeA	6	43.9		48.4		43.3		41.3		35.9		53.8		33.21	
PFHxA	6	72.8		86.4		71.9		96.7		67.4		93.6		70.34	
PFHpA	6	7.62	JI	5.6	J	5.27	JI	4.42	J	4.08	J	5.15	J	4.471	
PFOA	6	8.51	J	6.4	J	8.41		7.05	J	5.44		6.16	J	5.442	
PFBS	6	61		67.6		67.6		47		55.3		87.8		40.78	
PFHxS	6	3.42	J	2.8	J	3.16	U	2.37	J	2.26	J	3.82	J	2.145	
PFOS	6	2.22	J	2.96	U	6.8	U	2.21	J	1.92	J	2.66	J	1.664	
9Cl-PF3ONS	6	4.63	J	6.44	U	9.3	U	3.5	U	3.67	U	3.8	U	5.918	U
Total # Analytes Reported Across All Samples		32		32		29		27		36		32		33	

Version: Summary_tables_LCBS_Exa_CH6_11292023.xlsx

Notes:
'—" = X-qualified results; Data not used
J = Concentration falls between the MDL and LOQ; Qualitative value
I = Ion abundance ratio failed to meet acceptance criteria
U = analyte not detected at a concentration above the MDL

Table 6-2. Numbers of Detected Analytes by Landfill Leachate Sample

Unspiked Landfill Leachate Sample	Total Number of Analytes Detected by at least One Laboratory
LCAE1 - MSW LF Leachate Sample	15
LCAF1 - CDD Landfill	14
LCAG1 - Ash leachate	9

Source File: Summary_tables_LCBS_Exa_CH6_11292023.xlsx

Table 6-3. Pooled Laboratory PFAS-Spiked Landfill Leachate 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	6	51	97.8	9.47	6.48	6.63	51	96.9	8.36	3.20	3.31	102	97.4	8.88	5.02	5.15
PFPeA	6	36	98.2	13.6	6.21	6.33	54	98.0	11.7	4.65	4.75	90	98.1	12.3	5.48	5.59
PFHxA	6	18	96.7	12.8	8.83	9.13	54	94.5	8.11	5.88	6.22	72	95.1	9.19	6.76	7.11
PFHpA	6	54	95.8	11.0	6.62	6.91	54	94.8	7.91	4.75	5.02	108	95.3	9.42	5.83	6.12
PFOA	6	54	97.1	10.9	6.33	6.51	54	95.7	10.4	5.72	5.97	108	96.4	10.1	6.62	6.86
PFNA	6	54	100	11.7	7.41	7.42	54	97.6	8.15	7.39	7.57	108	98.8	9.91	7.5	7.59
PFDA	6	54	98.3	13.0	9.76	9.93	54	95.1	9.36	9.79	10.3	108	96.7	11.1	9.87	10.2
PFUnA	6	54	95.2	9.69	14.8	15.5	54	92.5	9.73	13.2	14.3	108	93.9	9.52	13.8	14.7
PFDoA	6	54	96.1	13.5	16.5	17.1	54	90.8	11.2	16.0	17.6	108	93.5	12.1	16.2	17.3
PFTrDA	6	54	87.4	15.6	15.0	17.1	54	84.5	12.6	14.8	17.5	108	86.0	13.6	15.0	17.4
PFTeDA	6	54	88.6	23.8	13.5	15.2	54	87.7	21.9	11.8	13.5	108	88.1	22.7	12.6	14.3
PFBS	6	36	102	15.2	6.42	6.26	54	101	14.0	7.46	7.40	90	101	14.4	7.16	7.05
PFPeS	6	54	98.0	11.6	7.01	7.15	54	96.8	11.3	6.88	7.11	108	97.4	11.2	7.11	7.3
PFHxS	6	54	98.8	15.6	8.51	8.61	54	98.0	13.6	6.84	6.98	108	98.4	14.4	7.82	7.95
PFHpS	6	54	104	15.3	7.83	7.53	54	103	14.5	7.25	7.06	108	103	14.6	7.81	7.56
PFOS	6	54	95.2	13.6	10.2	10.7	54	93.0	10.0	6.87	7.39	108	94.1	11.8	8.73	9.28
PFNS	6	54	88.5	9.63	11.8	13.4	54	89.4	9.80	13.1	14.6	108	88.9	9.65	12.1	13.6
PFDS	6	54	78.9	10.2	14.2	18	54	79.6	11.8	14.7	18.5	108	79.3	11.0	14.1	17.8
PFDoS	6	54	63.2	17.7	13.1	20.6	54	65.3	18.8	14.7	22.5	108	64.3	18.2	13.6	21.1
4:2FTS	6	53	97.5	11.1	11.4	11.7	54	95.1	7.26	14.8	15.5	107	96.3	8.93	13.1	13.6
6:2FTS	6	54	102	10.6	11.8	11.5	54	99.5	10.6	12.1	12.1	108	101	10.3	11.9	11.8
8:2FTS	6	54	104	10.7	14.4	13.8	54	103	8.79	13.2	12.8	108	104	9.33	13.7	13.2
PFOSA	6	54	96.4	8.69	4.79	4.97	54	96.0	6.64	6.61	6.89	108	96.2	7.63	5.72	5.95
NMeFOSA	6	54	92.9	12.4	15.4	16.6	54	91.3	10.2	12.7	13.9	108	92.1	11.1	13.9	15.1
NEtFOSA	6	54	83.7	17.0	13.8	16.5	54	84.2	18.1	12.8	15.2	108	83.9	17.5	13	15.5

Table 6-3. Pooled Laboratory PFAS-Spiked Landfill Leachate 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)
NMeFOSAA	6	54	99.6	10.9	13.4	13.5	54	95.3	11.8	13.8	14.5	108	97.5	10.8	13.8	14.2
NEtFOSAA	6	54	94.0	12.4	19.0	20.3	54	91.7	13.6	15.7	17.1	108	92.9	12.8	17.1	18.4
NMeFOSE	6	54	84.8	15.1	14.2	16.8	54	81.7	17.8	12.1	14.8	108	83.2	16.2	13.2	15.8
NEtFOSE	6	53	80.3	21.7	12.2	15.1	52	80.7	23.4	9.53	11.8	105	80.5	22.5	10.8	13.4
PFMPA	6	54	86.8	14.3	13.8	15.8	54	85.6	12.4	13.8	16.2	108	86.2	13.2	13.6	15.8
PFMBA	6	54	99.1	9.53	5.31	5.35	54	98.6	9.51	6.29	6.38	108	98.9	9.38	5.86	5.92
NFDHA	6	54	96.9	16.7	16.6	17.1	54	93.6	9.56	16.2	17.3	108	95.2	12.7	16.6	17.5
HFPO-DA	6	54	98.1	10.9	9.67	9.86	54	96.2	10.0	5.55	5.76	108	97.2	10.4	7.83	8.06
ADONA	6	54	101	10.3	6.61	6.57	54	99.7	12.7	7.79	7.81	108	100	11.2	7.48	7.47
PFEESA	6	54	102	11.3	8.33	8.13	54	102	9.55	5.74	5.63	108	102	10.2	7.26	7.1
9Cl-PF3ONS	6	54	91.8	10.9	13.9	15.1	54	92.0	13.9	12.6	13.7	108	91.9	12.2	13.1	14.2
11Cl-PF3OUdS	6	54	72.1	18.3	15.2	21	54	74.2	17.8	15.4	20.7	108	73.2	18.0	14.9	20.3
3:3FTCA	6	54	112	15.8	18.8	16.8	54	108	13.0	16.8	15.6	108	110	13.6	18.1	16.4
5:3FTCA	6	39	125	39.1	54.7	43.9	54	106	13.0	13.7	12.8	93	114	22.4	42.6	37.4
7:3FTCA	6	54	101	9.63	14.3	14.2	54	104	9.51	13.0	12.6	108	102	9.00	13.7	13.4

Source file: LC_Matrix_compiled_results_V0_231122_163114.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 spike concentration (indicated in Row 1) that do not have a U flag.
Mean % Recovery - The mean percent recovery for spiked samples across all laboratories.
s_b - The pooled between-laboratory standard deviation of the percent recovery for spiked samples (low, high, or combined as applicable). Equation from EPA 821-B-18-001 page G-25.
s_w - The pooled within-laboratory standard deviation of the percent recovery for spiked samples (low, high, or Combined as applicable). Equation from EPA 821-B-18-001 page G-25.
RSD - The pooled within-laboratory relative standard deviation for spiked samples (RSD = s_w / (mean % recovery) *100).

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

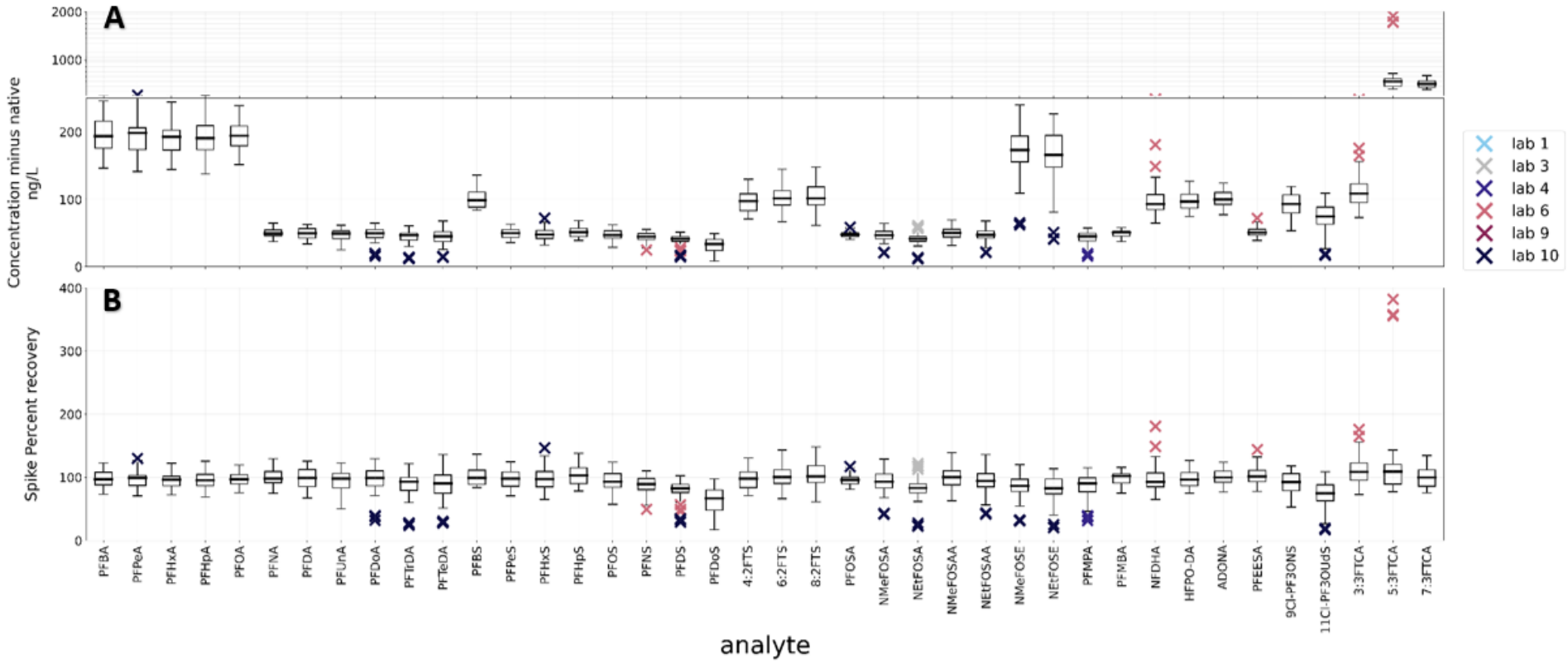
Analyte	LCAE					LCAF					LCAG				
	Number of Labs	Number of Results	Mean % Recovery	Min % Recovery	Max % Recovery	Number of Labs	Number of Results	Mean % Recovery	Min % Recovery	Max % Recovery	Number of Labs	Number of Results	Mean % Recovery	Min % Recovery	Max % Recovery
PFBA	5	30	96.4	83.5	123	6	36	97.9	73.2	114	6	36	97.6	83.5	113
PFPeA	6	36	97.4	70.5	130	6	18	97.6	73.2	122	6	36	99.0	81.6	127
PFHxA	6	18	94.4	80.5	111	6	18	95.2	79.2	114	6	36	95.4	72.2	122
PFHpA	6	36	95.6	69.8	116	6	36	95.2	68.8	126	6	36	95.0	82.0	110
PFOA	6	36	97.1	66.0	117	6	36	97.1	77.2	120	6	36	95.1	78.8	117
PFNA	6	36	101	82.4	122	6	36	98.6	74.7	122	6	36	96.9	76.4	130
PFDA	6	36	101	76.8	124	6	36	98.3	72.2	126	6	36	91.2	67.6	120
PFUnA	6	36	98.2	75.4	118	6	36	99.3	65.4	123	6	36	84.2	50.0	116
PFDoA	6	36	96.8	66.4	130	6	36	101	78.4	122	6	36	82.3	32.0	124
PFTrDA	6	36	88.6	58.8	116	6	36	91.3	79.2	103	6	36	78.0	23.8	125
PFTeDA	6	36	94.0	46.0	136	6	36	90.8	61.2	121	6	36	79.6	27.8	124
PFBS	6	18	103	85.5	136	6	36	99.9	60.2	133	6	36	102	83.1	137
PFPeS	6	36	97.0	66.4	124	6	36	97.3	61.6	117	6	36	98.0	70.5	122
PFHxS	6	36	96.6	65.2	134	6	36	98.7	63.4	134	6	36	99.9	78.7	147
PFHpS	6	36	103	78.2	128	6	36	102	69.7	129	6	36	106	71.4	138
PFOS	6	36	94.5	66.0	119	6	36	96.4	57.6	124	6	36	91.3	64.5	124
PFNS	6	36	93.3	65.6	115	6	36	94.4	67.4	117	6	36	79.1	46.8	103
PFDS	6	36	81.0	55.1	107	6	36	87.4	66.1	111	6	36	69.4	29.1	103
PFDoS	6	36	52.9	35.5	87	6	36	74.9	47.0	101	6	36	65.0	17.0	97.6
4:2FTS	6	36	96.8	71.1	131	6	35	99.6	80.5	159	6	36	92.5	58.3	124
6:2FTS	6	36	103	64.6	143	6	36	101	72.2	150	6	36	98.8	66.0	140
8:2FTS	6	36	107	82.3	148	6	36	107	61.4	154	6	36	96.8	75.7	123
PFOSA	6	36	97.5	80.8	117	6	36	97.1	82.8	119	6	36	94.0	82.0	104
NMeFOSA	6	36	96.6	72.4	129	6	36	97.7	80.0	122	6	36	82.0	41.4	118
NEtFOSA	6	36	88.3	65.8	122	6	36	89.9	74.6	120	6	36	73.5	22.6	117

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

Analyte	LCAE					LCAF					LCAG				
	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
NMeFOSAA	6	36	99.3	75.2	130	6	36	106	82.2	139	6	36	87.2	55.4	125
NEtFOSAA	6	36	99.2	70.0	131	6	36	98.6	74.4	130	6	36	80.8	41.0	136
NMeFOSE	6	36	81.6	41.6	108	6	36	91.3	73.5	108	6	36	76.9	27.6	120
NEtFOSE	6	34	79.7	33.2	111	6	36	86.9	60.5	113	6	35	74.6	20.4	114
PFMPA	6	36	78.9	25.4	108	6	36	86.3	39.2	115	6	36	93.4	73.0	113
PFMBA	6	36	100	74.6	122	6	36	99.7	71.6	112	6	36	96.6	80.2	113
NFDHA	6	36	92.9	56.6	133	6	36	93.3	64.9	181	6	36	99.6	77.5	134
HFPO-DA	6	36	101	79.8	127	6	36	95.0	74.8	120	6	36	95.3	76.5	122
ADONA	6	36	101	73.8	123	6	36	103	65.4	126	6	36	96.6	81.4	119
PFEESA	6	36	101	76.9	123	6	36	105	85.6	144	6	36	101	80.8	132
9Cl-PF3ONS	6	36	98.1	68.0	119	6	36	99.8	64.4	124	6	36	77.9	53.0	102
11Cl-PF3OUdS	6	36	75.4	39.9	113	6	36	84.0	56.2	112	6	36	60.2	17.0	92.5
3:3FTCA	6	36	111	73.0	156	6	36	124	98.3	176	6	36	94.2	74.0	114
5:3FTCA	6	21	148	84.6	382	6	36	115	82.2	143	6	36	94.0	77.4	119
7:3FTCA	6	36	107	81.6	120	6	36	112	83.4	138	6	36	88.0	75.4	102

Source file: LL_Matrix_sample_results_V0_231122_163114.csv

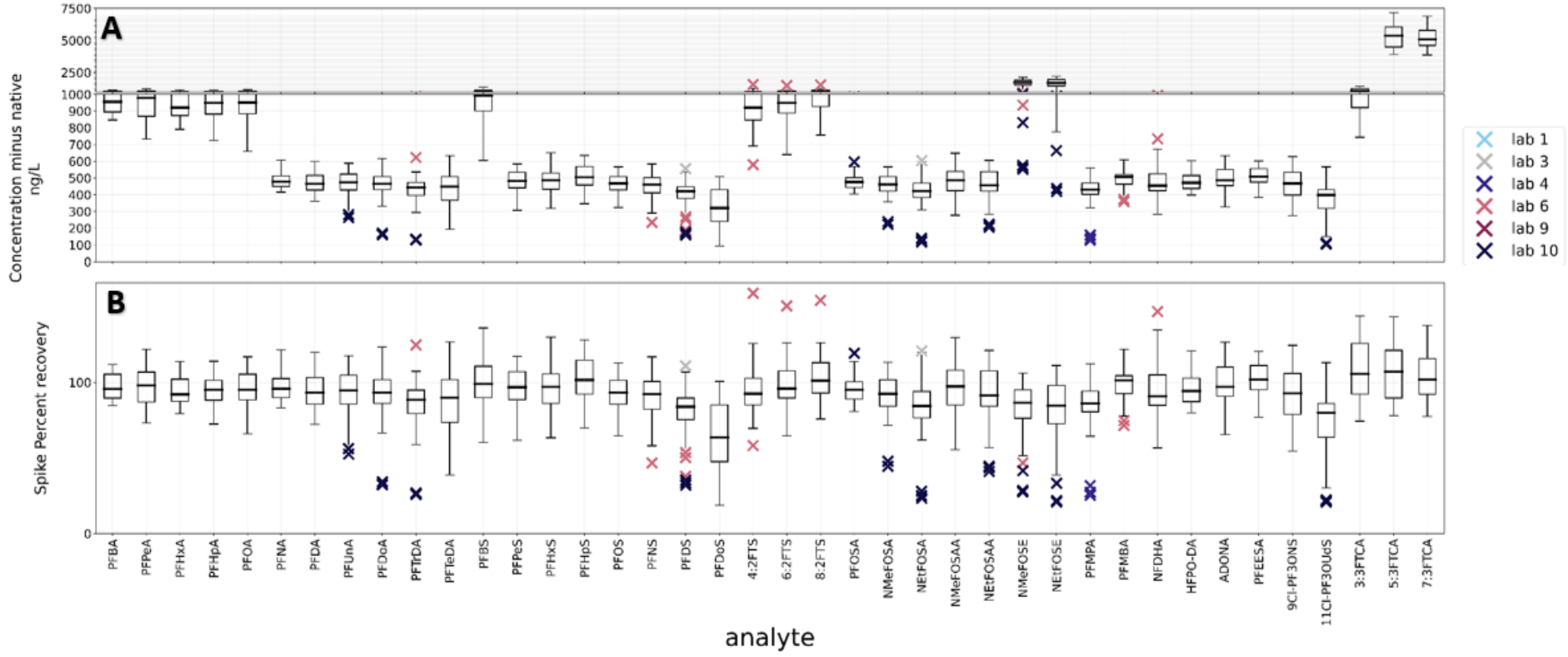
Notes:
Number of Labs - The number of laboratories reporting matrix spiked sample results.
Number of Results - The total number of matrix sample results categorized as low spike concentration (indicated in Row 1) that do not have a U flag.
Mean % Recovery - The mean percent recovery for spiked samples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



Source file: LC_LowSpike_Boxplot_V1_231220.csv

Figure 6-1. Landfill Leachate low matrix spike results by analyte by laboratory

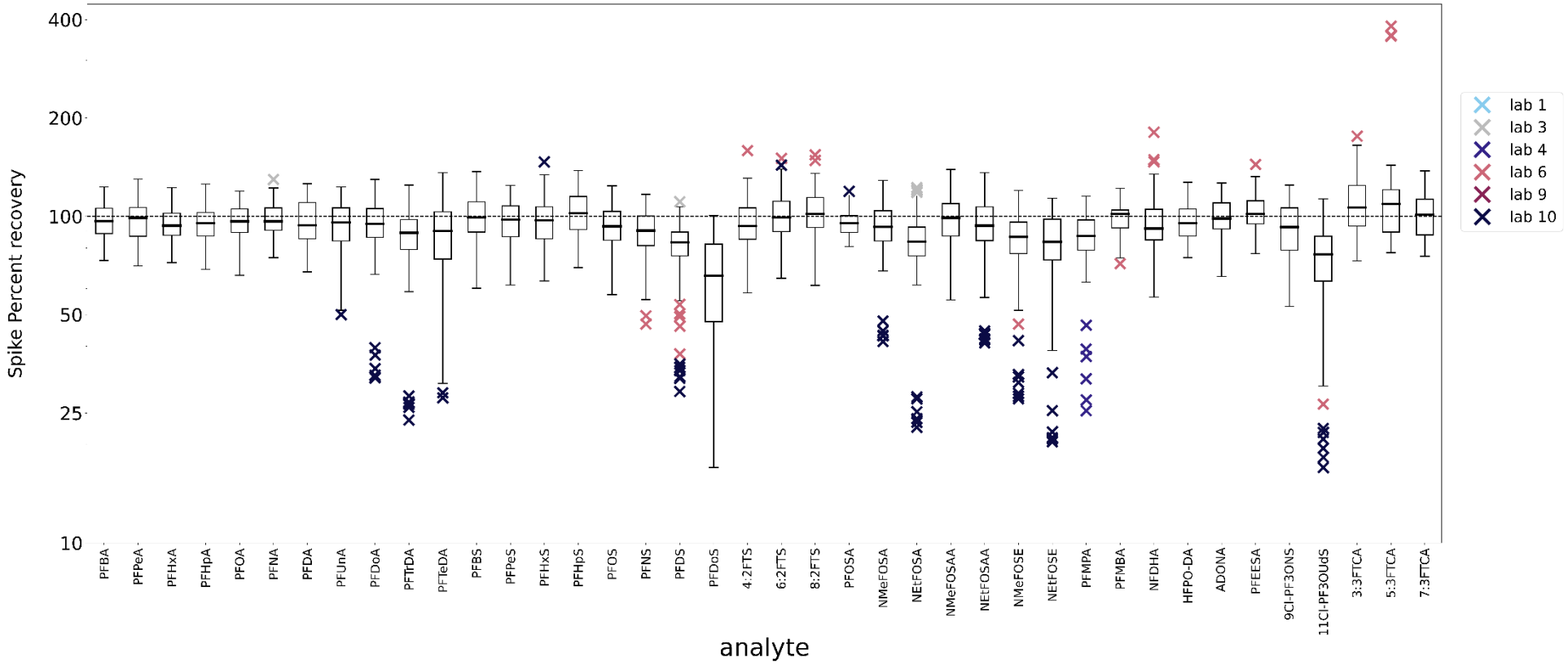
(A) Spiked concentration minus the laboratory-reported native concentration. (B) Low spike percent recovery.



Source File: LC_HighSpike_Boxplot_V1_231220

Figure 6-2. Landfill leachate high matrix spike results by analyte by laboratory

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



Source file: LC_LowHighCombinedSpike_Boxplot_V1_231220

Figure 6-3. Pooled low- and high- spiked landfill leachate 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/L)	Maximum Concentration (µg/L)
$^{13}C_4$-PFBA	400	500
$^{13}C_5$-PFPeA	200	250
$^{13}C_5$-PFHxA	100	125
$^{13}C_4$-PFHpA	100	125
$^{13}C_8$-PFOA	100	125
$^{13}C_9$-PFNA	50	62.5
$^{13}C_6$-PFDA	50	62.5
$^{13}C_7$-PFUnA	50	62.5
$^{13}C_2$-PFDoA	50	62.5
$^{13}C_2$-PFTeDA	50	62.5
$^{13}C_3$-PFBS	93	125
$^{13}C_3$-PFHxS	94.8	125
$^{13}C_8$-PFOS	95.8	125
$^{13}C_2$-4:2FTS	188	250
$^{13}C_2$-6:2FTS	190	250
$^{13}C_2$-8:2FTS	192	250
$^{13}C_8$-PFOSA	100	125
D_3-NMeFOSA	100	125
D_5-NEtFOSA	100	125
D_3-NMeFOSAA	200	250
D_5-NEtFOSAA	200	250
D_7-NMeFOSE	1000	1250
D_9-NEtFOSE	1000	1250
$^{13}C_3$-HFPO-DA	400	500

Version: Summary_tables_Exa_CH6_12132023.xlsx

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

EIS Compound [1]	All Laboratories % recovery			
	n	Min	Max	Mean
$^{13}C_4$-PFBA	126	4.00	97.2	66.3
$^{13}C_5$-PFPeA	126	48.0	108	83.7
$^{13}C_5$-PFHxA	126	68.0	104	85.4
$^{13}C_4$-PFHpA	126	68.0	107	88.0
$^{13}C_8$-PFOA	126	61.9	105	85.3
$^{13}C_9$-PFNA	126	66.0	103	85.1
$^{13}C_6$-PFDA	126	56.8	107	80.5
$^{13}C_7$-PFUnA	126	48.2	98.6	75.8
$^{13}C_2$-PFDoA	126	36.0	88.1	68.2
$^{13}C_2$-PFTeDA	126	16.1	84.0	56.5
$^{13}C_3$-PFBS	126	67.0	122	86.8
$^{13}C_3$-PFHxS	126	71.4	103	85.7
$^{13}C_8$-PFOS	126	64.9	117	82.9
$^{13}C_2$-4:2FTS	126	38.0	220	123.4
$^{13}C_2$-6:2FTS	126	43.0	173	102.4
$^{13}C_2$-8:2FTS	126	41.5	144	86.7
$^{13}C_8$-PFOSA	126	56.3	96.8	79.5
D_3-NMeFOSA	126	39.4	86.2	63.4
D_5-NEtFOSA	126	33.6	84.5	60.1
D_3-NMeFOSAA	126	33.6	114	77.6
D_5-NEtFOSAA	126	27.8	98.0	73.0
D_7-NMeFOSE	126	10.0	98.0	65.6
D_9-NEtFOSE	126	2.46	95.0	62.6
$^{13}C_3$-HFPO-DA	126	68.9	130	89.9

Version: Summary_tables_LCBS_Exa_CH6_12132023.xlsx

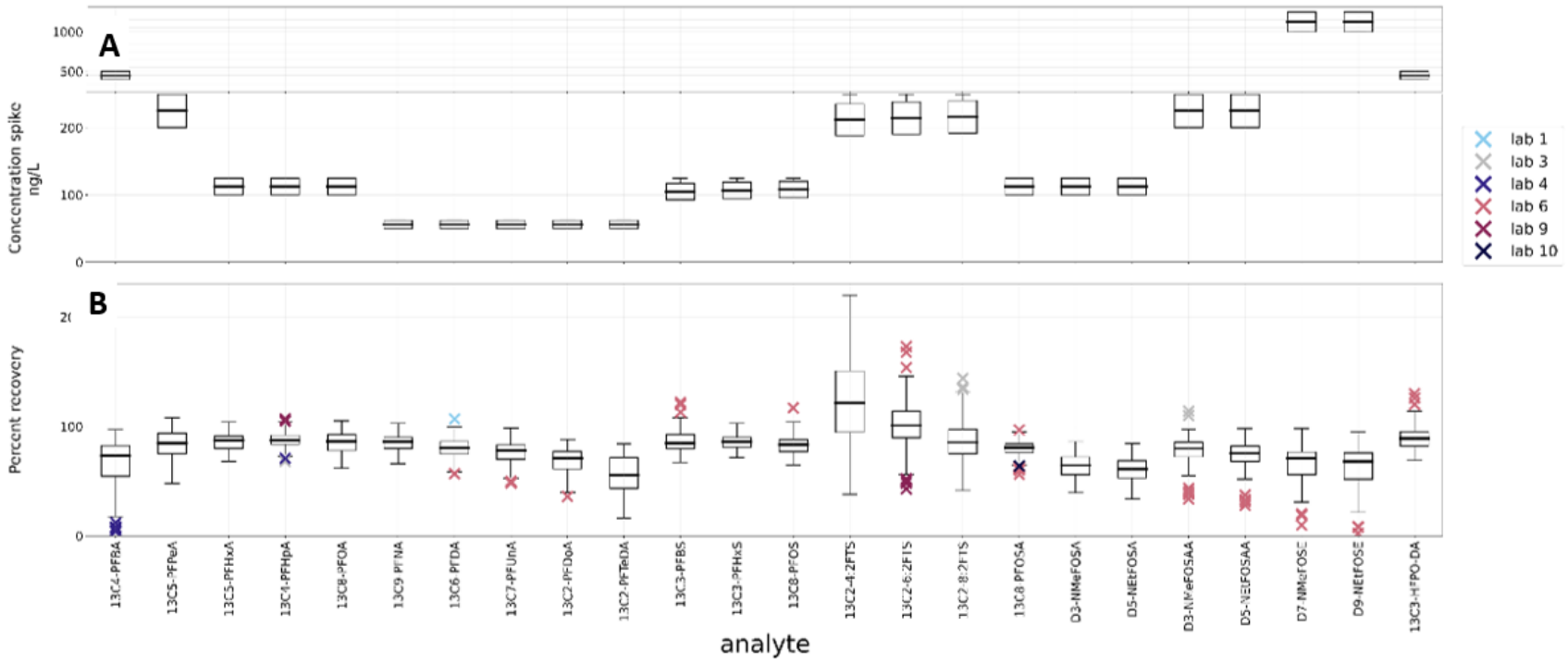
[1] Based on validated data. Does not include MB, OPR, LLOPR QC samples.

Table 6-7. Statistical Evaluation of EIS Compound Results Associated with Landfill Leachate 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	6	126	66.3	14.3	20.9	31.6
$^{13}C_5$-PFPeA	6	126	83.7	10.8	9.43	11.3
$^{13}C_5$-PFHxA	6	126	85.4	5.74	5.43	6.35
$^{13}C_4$-PFHpA	6	126	88.0	3.82	6.63	7.54
$^{13}C_8$-PFOA	6	126	85.2	6.93	6.33	7.42
$^{13}C_9$-PFNA	6	126	85.1	4.56	5.55	6.52
$^{13}C_6$-PFDA	6	126	80.5	6.79	7.45	9.26
$^{13}C_7$-PFUnA	6	126	75.8	7.05	8.59	11.3
$^{13}C_2$-PFDoA	6	126	68.3	9.65	8.81	12.9
$^{13}C_2$-PFTeDA	6	126	56.5	10.3	12.9	22.9
$^{13}C_3$-PFBS	6	126	86.8	8.15	6.92	7.97
$^{13}C_3$-PFHxS	6	126	85.7	4.45	5.26	6.14
$^{13}C_8$-PFOS	6	126	82.9	5.90	7.16	8.64
$^{13}C_2$-4:2FTS	6	126	123	20.0	35.9	29.1
$^{13}C_2$-6:2FTS	6	126	102	11.8	21.3	20.8
$^{13}C_2$-8:2FTS	6	126	86.6	14.4	17.6	20.3
$^{13}C_8$-PFOSA	6	126	79.5	4.50	6.70	8.42
D_3-NMeFOSA	6	126	63.4	9.54	5.83	9.21
D_5-NEtFOSA	6	126	60.1	10.1	5.72	9.52
D_3-NMeFOSAA	6	126	77.6	7.23	11.4	14.7
D_5-NEtFOSAA	6	126	73.0	7.04	11.5	15.8
D_7-NMeFOSE	6	126	65.6	14.3	9.12	13.9
D_9-NEtFOSE	6	126	62.6	16.3	10.2	16.3
$^{13}C_3$-HFPO-DA	6	126	89.9	11.4	6.85	7.62

Source file: LC_EIS_results_V0_231122_163114.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: LC_EIS_Boxplot_V0_231122_163114

Figure 6-4. Landfill Leachate EIS Compound Results by Compound by Laboratory

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

6.4 LANDFILL LEACHATE SUMMARY

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world landfill leachate samples. The pooled (low-spiked/high-spiked samples) average percent recoveries as shown in Table 6-3 were between 64.3–114%.

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, 27 of the 40 spiked PFAS were recovered between 40 – 150% of the spiked concentration (Table 6-8). Those outside this range were PFDoA, PFTrDA, PFTeDA, PFDS, PFDoS, NEtFOSA, NMeFOSE, NEtFOSE, PFMPA, NFDHA, 11Cl-PF3OUdS, 3:3FTCA, and 5:3FTCA. With the exception of the NFDHA, 3:3FTCA, and 5:3FTCA, which exceeded the 150% criteria, all of these analytes reported recoveries of less than 40%. Excluding these analytes, most recoveries fell between the 70 – 130% range. For the high-spiked samples the results were the same: 27 of the 40 spiked PFAS were recovered between 40 – 150% of the spiked concentration (Table 6-9). Those outside this range were PFDoA, PFTrDA, PFTeDA, PFDS, PFDoS, NEtFOSA, NMeFOSE, NEtFOSE, PFMPA, and 11Cl-PF3OUdS, 4:2FTS, 6:2FTS, and 8:2FTS. With the exception of the FTSs, which exceeded the 150% criterion, all of these analytes reported recoveries of less than 40%.

Table 6-10 provides a summary of the relative proportions of the pooled EIS compound 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 is approximately 60%. All results exceeding the 20% criteria were associated with $^{13}C_4$-PFBA (Laboratory 3) and $^{13}C_2$-PFTeDA (Laboratory 6), D_7-NMeFOSE (Laboratory 6), and D_9-NEtFOSE (Laboratory 6). All results exceeding the 150% criteria were associated with $^{13}C_2$-4:2FTS and $^{13}C_2$-6:2FTS.

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 aqueous 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 with the exception of the average recovery of $^{13}C_4$-PFBA for Laboratory 4.

Table 6-8. Proportion of Landfill Leachate Matrix Spike 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	51	0	0	100	0	0	0
PFPeA	36	0	0	97.2	2.8	0	0
PFHxA	18	0	0	100	0	0	0
PFHpA	54	0	3.7	96.3	0	0	0
PFOA	54	0	0	100	0	0	0
PFNA	54	0	0	100	0	0	0
PFDA	54	0	1.9	98.1	0	0	0
PFUnA	54	0	7.4	92.6	0	0	0
PFDoA	54	5.6	0	94.4	0	0	0
PFTrDA	54	5.6	7.4	87	0	0	0
PFTeDA	54	5.6	14.8	77.8	1.9	0	0
PFBS	36	0	0	91.7	8.3	0	0
PFPeS	54	0	0	100	0	0	0
PFHxS	54	0	1.9	92.6	5.6	0	0
PFHpS	54	0	0	94.4	5.6	0	0
PFOS	54	0	7.4	92.6	0	0	0
PFNS	54	0	11.1	88.9	0	0	0
PFDS	54	5.6	13	81.5	0	0	0
PFDoS	54	14.8	38.9	46.3	0	0	0
4:2FTS	53	0	0	96.2	3.8	0	0
6:2FTS	54	0	1.9	94.4	3.7	0	0
8:2FTS	54	0	1.9	90.7	7.4	0	0
PFOSA	54	0	0	100	0	0	0
NMeFOSA	54	0	7.4	92.6	0	0	0
NEtFOSA	54	5.6	7.4	87	0	0	0
NMeFOSAA	54	0	5.6	92.6	1.9	0	0
NEtFOSAA	54	0	11.1	85.2	3.7	0	0
NMeFOSE	54	5.6	13	81.5	0	0	0
NEtFOSE	53	5.7	13.2	81.1	0	0	0
PFMPA	54	5.6	5.6	88.9	0	0	0
PFMBA	54	0	0	100	0	0	0
NFDHA	54	0	7.4	85.2	5.6	1.9	0
HFPO-DA	54	0	0	100	0	0	0
ADONA	54	0	0	100	0	0	0
PFEESA	54	0	0	96.3	3.7	0	0
9Cl-PF3ONS	54	0	11.1	88.9	0	0	0
11Cl-PF3OUdS	54	9.3	29.6	61.1	0	0	0
3:3FTCA	54	0	0	79.6	9.3	11.1	0
5:3FTCA	39	0	0	87.2	5.1	0	7.7
7:3FTCA	54	0	0	92.6	7.4	0	0

Version: Summary_tables_LCBS_Exa_CH56_12132023.xlsx

[1] Does not include MB, OPR, LLOPR QC samples.

Table 6-9. Proportion of Landfill Leachate Matrix Spike 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	51	0	0	100	0	0	0
PFPeA	54	0	0	100	0	0	0
PFHxA	54	0	0	100	0	0	0
PFHpA	54	0	0	100	0	0	0
PFOA	54	0	1.9	98.1	0	0	0
PFNA	54	0	0	100	0	0	0
PFDA	54	0	0	100	0	0	0
PFUnA	54	0	11.1	88.9	0	0	0
PFDoA	54	5.6	1.9	92.6	0	0	0
PFTrDA	54	5.6	7.4	87	0	0	0
PFTeDA	54	1.9	18.5	79.6	0	0	0
PFBS	54	0	1.9	96.3	1.9	0	0
PFPeS	54	0	3.7	96.3	0	0	0
PFHxS	54	0	1.9	98.1	0	0	0
PFHpS	54	0	1.9	98.1	0	0	0
PFOS	54	0	3.7	96.3	0	0	0
PFNS	54	0	14.8	85.2	0	0	0
PFDS	54	7.4	11.1	81.5	0	0	0
PFDoS	54	14.8	38.9	46.3	0	0	0
4:2FTS	54	0	3.7	94.4	0	1.9	0
6:2FTS	54	0	1.9	96.3	0	1.9	0
8:2FTS	54	0	0	98.1	0	1.9	0
PFOSA	54	0	0	100	0	0	0
NMeFOSA	54	0	5.6	94.4	0	0	0
NEtFOSA	54	5.6	11.1	83.3	0	0	0
NMeFOSAA	54	0	9.3	90.7	0	0	0
NEtFOSAA	54	0	11.1	88.9	0	0	0
NMeFOSE	54	5.6	14.8	79.6	0	0	0
NEtFOSE	52	11.5	11.5	76.9	0	0	0
PFMPA	54	5.6	3.7	90.7	0	0	0
PFMBA	54	0	0	100	0	0	0
NFDHA	54	0	5.6	88.9	5.6	0	0
HFPO-DA	54	0	0	100	0	0	0
ADONA	54	0	3.7	96.3	0	0	0
PFEESA	54	0	0	100	0	0	0
9Cl-PF3ONS	54	0	13	87	0	0	0
11Cl-PF3OUdS	54	7.4	29.6	63.0	0	0	0
3:3FTCA	54	0	0	81.5	18.5	0	0
5:3FTCA	54	0	0	85.2	14.8	0	0
7:3FTCA	54	0	0	98.1	1.9	0	0

Version: Summary_tables_LCBS_Exa_CH6_12132023.xlsx

[1] Does not include MB, OPR, LLOPR QC samples.

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

Analyte	All Labs Proportion % Recovery					
	n	<10%	≥10% to <20%	≥20% to <150%	≥150% to <200%	≥200%
$^{13}C_4$-PFBA	126	5.6	1.6	92.9	0	0
$^{13}C_5$-PFPeA	126	0	0	100	0	0
$^{13}C_5$-PFHxA	126	0	0	100	0	0
$^{13}C_4$-PFHpA	126	0	0	100	0	0
$^{13}C_8$-PFOA	126	0	0	100	0	0
$^{13}C_9$-PFNA	126	0	0	100	0	0
$^{13}C_6$-PFDA	126	0	0	100	0	0
$^{13}C_7$-PFUnA	126	0	0	100	0	0
$^{13}C_2$-PFDoA	126	0	0	100	0	0
$^{13}C_2$-PFTeDA	126	0	0.8	99.2	0	0
$^{13}C_3$-PFBS	126	0	0	100	0	0
$^{13}C_3$-PFHxS	126	0	0	100	0	0
$^{13}C_8$-PFOS	126	0	0	100	0	0
$^{13}C_2$-4:2FTS	126	0	0	70.6	25.4	4
$^{13}C_2$-6:2FTS	126	0	0	96.8	3.2	0
$^{13}C_2$-8:2FTS	126	0	0	100	0	0
$^{13}C_8$-PFOSA	126	0	0	100	0	0
D_3-NMeFOSA	126	0	0	100	0	0
D_5-NEtFOSA	126	0	0	100	0	0
D_3-NMeFOSAA	126	0	0	100	0	0
D_5-NEtFOSAA	126	0	0	100	0	0
D_7-NMeFOSE	126	0	1.6	98.4	0	0
D_9-NEtFOSE	126	2.4	0	97.6	0	0
$^{13}C_3$-HFPO-DA	126	0	0	100	0	0

Version: Summary_tables_LCBS_Exa_CH6_12132023.xlsx

[1] Does not include MB, OPR, LLOPR QC samples.

Table 6-11. Summary of EIS Compound Percent Recovery in Landfill Leachates Samples for All Laboratories

EIS Compound	Final EIS Compound Acceptance Limits Applicable to All Aqueous Sample Types [1]		Individual and Pooled Laboratory Average % Recovery						
			Lab 1	Lab 3	Lab 4	Lab 6	Lab 9	Lab 10	Pooled Labs
$^{13}C_4$-PFBA	5	130	76.8	74.1	42.6	75.4	54.3	74.8	66.3
$^{13}C_5$-PFPeA	40	130	96.9	65.4	83.4	91.5	81.1	83.8	83.7
$^{13}C_5$-PFHxA	40	130	92.4	76.4	86.3	82.5	90.5	84.5	85.4
$^{13}C_4$-PFHpA	40	130	89.5	85.0	85.7	88.3	94.7	84.7	88.0
$^{13}C_8$-PFOA	40	130	92.5	78.7	85.5	76.5	93.5	85.0	85.3
$^{13}C_9$-PFNA	40	130	90.6	78.0	87.5	83.6	88.2	82.8	85.1
$^{13}C_6$-PFDA	40	130	89.2	71.1	81.8	80.1	86.0	74.6	80.5
$^{13}C_7$-PFUnA	40	130	80.9	70.5	80.7	73.9	83.4	65.5	75.8
$^{13}C_2$-PFDoA	10	130	77.8	61.0	75.3	58.4	77.8	59.1	68.2
$^{13}C_2$-PFTeDA	10	130	61.8	49.0	64.5	54.2	68.3	41.1	56.5
$^{13}C_3$-PFBS	40	135	94.7	77.2	84.3	98.5	83.0	83.2	86.8
$^{13}C_3$-PFHxS	40	130	89.5	78.7	85.6	89.3	88.5	82.5	85.7
$^{13}C_8$-PFOS	40	130	87.2	73.2	87.3	86.6	85.7	77.7	82.9
$^{13}C_2$-4:2FTS	40	200	125.3	158.0	102.5	129.3	120.0	105.3	123.4
$^{13}C_2$-6:2FTS	40	200	100.8	111.5	90.8	120.6	91.4	98.9	102.4
$^{13}C_2$-8:2FTS	40	300	92.9	112.4	84.4	73.8	81.0	75.4	86.7
$^{13}C_8$-PFOSA	40	130	84.2	75.0	81.2	78.2	84.4	73.9	79.5
D_3-NMeFOSA	10	130	72.7	67.7	57.5	58.5	74.0	50.0	63.4
D_5-NEtFOSA	10	130	69.8	62.9	58.0	54.6	71.0	44.3	60.1
D_3-NMeFOSAA	40	170	77.2	89.0	82.6	69.4	71.7	75.5	77.6
D_5-NEtFOSAA	25	135	80.2	74.7	80.9	62.7	70.3	68.9	73.0
D_7-NMeFOSE	10	130	71.5	80.9	72.3	46.1	73.9	49.1	65.6
D_9-NEtFOSE	10	130	68.2	79.3	73.2	40.3	70.5	43.9	62.6
$^{13}C_3$-HFPO-DA	40	130	89.7	76.4	82.6	109.9	92.5	88.6	89.9

Version: Summary_tables_LCBS_Exa_CH6_12132023.xlsx

[1] Criteria from 4th Draft EPA Method 1633, Table 6

7 BIOSOLIDS

A total of 21 study samples were shipped to each participating laboratory and analyzed according to the EPA Method 1633, as described in Section 2 of this report. This included a single unspiked sample, triplicate low- and triplicate high-spiked samples, in three biosolid matrices. As stated in Section 2, only eight laboratories participated in the biosolid analyses. Laboratories 2 and 7 did not participate in the landfill leachate analyses. As discussed in Section 3, data were rejected for Laboratories 1 and 5 and were not included in the statistical analysis of the biosolid data. All 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 BIOSOLIDS

The background native concentrations first measured prior to setting the spiking concentrations were done by SGS AXYS (Table 2-4). Each laboratory received and analyzed a single unspiked aliquot of each biosolid sample. The concentrations measured by the individual laboratories are given in Table 7-1, which also includes the original background concentration measured by SGS AXYS for comparison. Table 7-2 summarizes the number of detected analytes in the unspiked biosolid samples. The concentrations detected in this sample were considered the background or "native" concentration for each of the environmental matrices for each laboratory.

Of the 40 PFAS target analytes in the draft EPA Method 1633, all PFAS were detected by at least one laboratory. PFAS compounds PFHxS, PFOSA, NEtFOSE, and PFDS were not detected by five laboratories, and but were detected by Laboratory 10 and by SGS AXYS. 5:3FTCA and 7:3FTCAs had the highest reported concentrations across the three biosolid samples (Table 7-1).

A summary of the minimum and maximum reported values across all laboratories is found in Appendix C Table C-1.

7.2 BIOSOLID MATRIX SPIKE RESULTS

The compiled PFAS-spiked biosolid sample results from the six laboratories are given in Table 7 -3. Overall, the pooled laboratory mean % recoveries were greater than 90% for 31 of the 40 PFAS compounds. Graphic presentations of both the low- and high-spiked samples is given in (Figures 7-1 and 7-2). Supporting individual laboratory spike recovery data are given in Appendix C, Tables C-1 (low-spiked) and C-2 (high-spiked).

For the low-spiked biosolid samples (Table 7-3), the pooled mean % recovery was 93% across all 40 PFAS analyzed, with a range of 50.5% (PFDoS) and 130% (6:2FTS). For the high-spiked samples, the mean pooled recovery across the 40 PFAS analyzed was 89.9%, with a range of 47.3 (PFDoS) and 104% (PFTrDA).

The inter- and intra-laboratory variabilities were higher than previously observed for soils and sediments.[3] The pooled between-laboratory standard deviation (s_b) for the 40 PFAS ranged between 27.4–48.2%, with an average of median of 20.7%. The pooled within-laboratory standard deviation (s_w) was also relatively broad: 5.6–112%, with an average of 17.1%. The RSD on the s_w was approximately 18.7%.

Figure 7-1 shows that there are differences in reported recoveries by individual laboratories and specific compounds in the low-spiked samples (data in Appendix C, Table C-2). From Figure 7-1 the following can be observed.

- Laboratory 9 had spike recoveries well below the pooled-laboratory median for 21 of the 40 target PFAS, and specifically for the perfluoroalkyl carboxylic acids, the fluorotelomer sulfonic acids, the perfluorooctane sulfonamides perfluorooctane sulfonamidoacetic acids, the perfluorooctane sulfonamide ethanols, and PFMBA and HFPO-DA. Percent recoveries in these PFAS were predominately below 40% (Appendix C, Table C-2). Laboratory 9 also had the poorest percent recoveries for 3:3, 5:3, and 7:3FTCA.
- For the low-spiked samples, higher variability was observed for PFTrDA, PFHpS, PFDOS, and PFMPA. This observation is consistent with what was observed for these same compounds in soils and sediments.

For the pooled high-spiked samples (Table 7-3), the pooled recoveries were similar to that observed in the low-spiked samples. The pooled mean % recovery ranged between 48.9% (PFDoS) to 107% (6:2FTS), averaging 91.4% across all 40 PFAS analyzed. The pooled between-laboratory standard deviation (s_b) for the 40 PFAS ranged between 20.7-48.2%, with an average of 27.4%. The pooled within-laboratory standard deviation (s_w) was also broad: 5.6–112%, with an average of 17.1%. The RSD of the s_w is similar at 18.7%.

Figure 7-2 shows the notable differences for individual laboratories and specific target analytes for the high-spiked samples (data in Appendix C, Table C-3). The trends observed in the figure and Appendix C, Table C-3 include:

- Laboratory 3 had poor recoveries for the perfluoroalkyl sulfonic acids, and specifically for PFHpS, PFOS, PFNS, PFDS, and PFDoS.
- Laboratory 8 recoveries for most PFAS were above the median and higher than all the other laboratories.
- Laboratory 9 consistently reported recoveries below the median and below all the other 5 laboratories for the same PFAS. Recoveries for the high-spiked samples were between 40 – 60%.
- The variability of the percent recovery was again greater for PFTrDA, PFHpS, PFDOS, and PFMPA. Variability among all laboratories was also higher for the FTCA compounds.

[3] For soils, 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%.

The combined low/high-spiked sample statistical results are given in Table 7-3 and shown on Figure 7-3. The mean percent recoveries were between 48.9% (PFDoS) and 116% (4:2FTS). With the exception of the following compounds, PFAS pooled recoveries for the biosolid samples were between 70 – 130%: PFNS (67.3%) and PFDoS (48.9).

Results comparing the three different biosolid samples using the pooled laboratory results are given in Table 7-4. Generally, the mean percent recoveries were similar for all target PFAS across the three samples, with the exception of the three FTCAs where the pooled mean percent recoveries for biosolid sample BSAI were lower than those measured for BSAH and BSAJ.

7.3 BIOSOLID EXTRACTED INTERNAL STANDARD RESULTS

The range of the EIS compound concentrations used by the laboratories is presented in Table 7-5. 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%.

The combined results for the minimum, maximum, and average percent recovery are given in Table 7-6. Supporting individual laboratory results are provided in Appendix C, Table C-4. For the 6 laboratories, the pooled average EIS percent recovery ranged between 2.4% ($^{13}C_4$-PFBA) and 379% ($^{13}C_2$-6:2FTS). Table 7-7 presents the pooled biosolid EIS percent recovery. With the following exceptions, all of mean EIS percent recoveries were within the MLVS method-specified target recovery: $^{13}C_2$-4:2FTS $^{13}C_2$-6:2FTS $^{13}C_2$-8:2FTS.

Figures 7-4 show that the highest variability in EIS compound recoveries for all laboratories were for $^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_8$-PFOSA, D_3-NMeFOSA, D_5-NEtFOSA, D_7-NMeFOSE and D_9-NEtFOSE. All laboratories had high EIS recoveries for the three FTS PFAS (Appendix C, Table C-4). Three laboratories showed overall lower EIS recovery.

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

Analyte	Number of Labs	Lab 3		Lab 4		Lab 6		Lab 8		Lab 9		Lab 10		SGS-AXYS Baseline	
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual [1]
BSAH1															
PFBA	5	0.504	U	0.514	U	--	X	2.67	U	1.44	U	0.83	U	1.749	U
PFPeA	6	0.88	J	0.857	U	0.842	U	1.33	U	0.616	U	0.39	U	0.8745	U
PFHxA	6	3.1		2.61		0.375	U	4.37		1.44	J	3.01		3.575	
PFHpA	6	0.256	JI	0.886	U	0.675	U	0.667	U	0.296	U	0.44	U	0.4373	U
PFOA	6	1.51	J	1.35	J	1.56	J	1.63	J	0.71	J	1.39	J	2.069	
PFNA	6	0.784	U	0.444	U	1.4	J	0.667	U	0.441	U	0.5	U	1.08	
PFDA	6	3.43		3.23		2.03		3.31		1.36	J	2.32		5.19	
PFUnA	6	0.872	J	1.15	U	0.56	J	0.667	U	0.364	J	0.537	J	1.412	
PFDoA	6	2.7		2.1		1.19	J	1.92	J	0.971	J	1.88	J	5.096	
PFTrDA	6	1.19	J	0.344	JI	0.344	J	0.667	U	0.314	U	0.22	U	1.065	
PFTeDA	6	1.06	U	0.59	JI	0.498	J	0.667	U	0.36	J	0.31	U	1.152	
PFPeS	6	0.232	U	31.5	I	0.69	U	0.627	U	1.03	JI	0.23	U	0.56	U
PFHxS	6	4.46	I	1.3	U	0.363	U	0.609	U	0.878	JI	0.36	U	4.56	
PFHpS	6	0.368	U	0.959	U	11.9	I	0.635	U	0.742	JI	0.46	U	25.36	
PFOS	6	3.62	J+I	7.91		6.36		8.3		4.39		7.49		10.35	
PFNS	5	0.424	U	--	X	0.495	U	0.64	U	0.396	U	0.38	U	0.682	
PFDS	6	0.32	U	1.76	U	0.597	U	0.643	U	0.587	JI	0.27	U	1.077	
PFOSA	6	1.13	JI	0.587	JI	0.273	U	0.86	J	0.471	U	0.608	J	1.365	
NMeFOSA	5	1	U	1	U	0.468	U	--	X	0.341	U	0.29	U	0.5028	U
NEtFOSA	5	1.12	U	1.28	U	0.417	U	--	X	0.588	U	0.17	U	1.093	U
NMeFOSAA	6	4.66	J+	3.08		3.09		4.52		1.48	J	2.83		6.831	
NEtFOSAA	6	3.24		2.77		2.27		3.52		1.38	J	3.29		5.156	
NMeFOSE	6	17.5	J	16.5	J	6.52	J	6.67	U	3.96	U	4.41	J	10.68	
NEtFOSE	6	6.47	J	4.44	U	3.09	U	6.67	U	4.42	U	2.09	J	5.404	
5:3FTCA	6	80.8		82.6		99.1		145		64.1		133		184.5	
7:3FTCA	6	39.8	J	42.2	J	46.6		66.1		45.1	J	29.3	J	84.42	
BSAI1															
PFBA	6	0.504	U	4.86	J	0.872	U	2.67	U	4.91	J+B	0.83	U	1.923	
PFPeA	6	1.55	J	1.36	J	2.35	J	1.33	U	0.822	J	1.83	J	1.626	
PFHxA	6	10.5		9.88		11.8		6.4		4.8		9.77		9.411	

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

Analyte	Number of Labs	Lab 3		Lab 4		Lab 6		Lab 8		Lab 9		Lab 10		SGS-AXYS Baseline	
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual [1]
PFHpA	6	0.4	J	0.886	U	0.675	U	0.667	U	0.296	U	0.44	U	0.5381	
PFOA	6	3.3		3.51		2.92		2.04		1.67	J	3.38		2.687	
PFDA	6	2.57		2.46		1.76		1.24	J	1.09	J	2.68		5.677	
PFDoA	6	1.02	J	0.917	J	0.648	U	0.667	U	0.43	J	0.41	U	2.405	
PFBS	6	0.432	U	0.462	U	0.624	U	0.591	U	0.322	J	0.537	J	0.7888	
PFHxS	6	0.592	U	1.3	U	0.363	U	0.609	U	0.328	U	0.419	J	1.049	
PFOS	6	9.06	J+	8.1		6.24		4.54		4.51		9.59		24.34	
PFNS	5	0.424	U	--	X	0.495	U	0.64	U	0.396	U	0.38	U	0.4209	U
6:2FTS	6	6.31	J+B	5.35	J	8.33		3.48	J+B	2.98	J	6.24	J	3.442	
PFOSA	6	0.432	U	0.305	U	0.273	U	0.667	U	0.471	U	0.392	J	0.841	
NMeFOSA	5	1	U	1	U	0.468	U	--	X	0.341	U	0.29	U	0.484	U
NEtFOSA	5	1.12	U	1.28	U	0.417	U	--	X	0.588	U	0.17	U	1.052	U
NMeFOSAA	6	6.67	J+	4.44		4.53		2.67		2.11		5.45		12.58	
NEtFOSAA	6	2.11		1.67	J	2.18		1.01	J	0.798	J	1.45	J	4.391	
NMeFOSE	6	3.62	J	4.97	U	2.9	U	6.67	U	3.96	U	1.51	U	4.209	U
NEtFOSE	6	5.1	U	4.44	U	3.09	U	6.67	U	4.42	U	0.811	J	3.148	U
5:3FTCA	6	6.81	J	13.1	U	6.45	U	1.33	U	11.1	U	4.43	U	84.67	
BSAJ1															
PFBA	5	0.504	U	--	X	0.872	U	2.67	U	1.44	U	0.83	U	1.405	U
PFPeA	6	0.56	U	0.857	U	2.89	J	1.33	U	0.616	U	0.39	U	0.7023	U
PFHxA	6	0.464	U	1.09	U	0.375	U	1.67	J	0.775	U	0.59	U	1.165	
PFOA	6	0.728	J	0.539	J	0.315	U	0.873	J	0.362	U	0.744	J	0.8285	
PFDA	6	2		1.21	J	0.618	U	1.86	J	0.669	J	1.46	J	2.957	
PFUnA	6	0.512	U	1.15	U	0.24	U	0.667	U	0.338	J	0.602	J	1.192	
PFDoA	6	1.54	J	1.33	J	0.648	U	1.41	J	0.622	J	1.48	J	2.231	
PFTrDA	6	0.704	J	0.323	U	0.339	U	1.04	J	0.314	U	0.22	U	0.9899	
PFTeDA	6	1.06	U	0.573	U	0.408	U	0.667	U	0.345	J	0.31	U	1.447	
PFBS	6	0.432	U	0.462	U	0.624	U	0.591	U	0.866	JI	0.4	U	0.05019	
PFHxS	6	2.58	I	1.3	U	0.363	U	0.609	U	0.489	J	0.36	U	0.5255	
PFOS	6	2.94	J+	7.4		6.29		9.21		4.08		7.55		13.24	
PFNS	5	0.424	U	--	X	0.495	U	0.64	U	0.396	U	0.38	U	0.3511	U

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

Analyte	Number of Labs	Lab 3		Lab 4		Lab 6		Lab 8		Lab 9		Lab 10		SGS-AXYS Baseline	
		Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual	Conc	Qual [1]
PFDS	6	0.32	U	1.76	U	0.597	U	0.643	U	0.333	U	0.414	J	1.259	
6:2FTS	6	2.8	U	1.87	U	1.93	U	48.1	JB	1.39	U	30.5	UD	1.266	U
PFOSA	6	0.72	JI	0.305	U	0.273	U	0.667	U	0.471	U	0.885	J	1.515	
NMeFOSA	5	1	U	1	U	0.468	U	--	X	0.341	U	0.29	U	0.4038	U
NEtFOSA	4	--	X	1.28	U	0.417	U	--	X	0.588	U	0.17	U	0.8778	U
NMeFOSAA	6	9.25	J+	6.23		6.45		8.84		3.16		6.93		15.64	
NEtFOSAA	6	3.71		4.21		3.29		5.81		2.01		4.86		8.468	
NMeFOSE	6	13.7	J	8.05	J	10.6	J	6.67	U	4.57	J	6.86	J	14.02	
NEtFOSE	6	5.1	U	4.44	U	6.05	J	6.67	U	4.42	U	3.52	J	6.856	
5:3FTCA	6	74.8		82.8		6.45	U	164		47.9	J	95.7		250.7	
7:3FTCA	6	17.6	U	9.92	J	7.41	U	16.8	J	9.98	U	9.25	J	26.44	
Total # Analytes Reported Across All Samples		40		33		28		28		37		38		53	

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

Notes:
[1] Axys-SGS reported non-detects as < the MDL. For this table those compounds were given a "U".
-- : X-flagged results

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

Unspiked Biosolid Sample	Total Number of Analytes Detected by at least One Laboratory
BSAH1	26
BSAI1	20
BSAJ1	24

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

Table 7-3. Pooled Laboratory PFAS-Spiked Biosolid 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	6	51	94	25.7	5.55	5.91	51	94.7	27.4	7.14	7.54	102	94.3	26.5	6.36	6.74
PFPeA	6	54	94.5	25.5	10.9	11.6	54	94.6	29.5	11.1	11.7	108	94.5	27.3	11.2	11.9
PFHxA	6	48	107	37.4	17.8	16.7	54	98.6	36.9	10.4	10.5	102	102	36.8	15.3	14.9
PFHpA	6	54	96.6	24.0	10.3	10.7	54	90.6	23.8	7.27	8.02	108	93.6	23.5	10.2	10.9
PFOA	6	54	94.9	26.9	9.93	10.5	54	90.9	27.5	7.91	8.7	108	92.9	26.8	9.79	10.5
PFNA	6	54	98.5	25.3	9.97	10.1	54	91.0	23.7	10.6	11.6	108	94.7	23.9	11.9	12.5
PFDA	6	54	92.5	25.8	8.98	9.71	54	94.6	29.3	10.2	10.8	108	93.5	27.2	10.4	11.1
PFUnA	6	54	95.5	25.2	9.10	9.53	54	89.1	24.1	10.2	11.4	108	92.3	24.5	10.4	11.3
PFDoA	6	54	92	24.4	11.5	12.5	54	90.9	24.7	9.08	9.99	108	91.4	24.5	10.2	11.2
PFTrDA	6	54	111	48.2	30.9	27.8	53	104	48.5	27.0	25.9	107	108	48.2	28.6	26.6
PFTeDA	6	54	93.8	27.2	12.1	12.9	54	89.4	26.5	11.0	12.3	108	91.6	26.3	12.4	13.6
PFBS	6	54	107	33.4	17.5	16.4	54	95.1	26.5	8.73	9.18	108	101	29.2	16.4	16.2
PFPeS	6	51	105	31.0	36.3	34.7	54	95.6	29.4	13.6	14.2	105	100	28.1	28.9	28.9
PFHxS	6	54	103	34.4	16.9	16.4	54	95.3	29.3	8.66	9.09	108	99.2	31.6	14.3	14.4
PFHpS	6	51	98.2	24.3	26.2	26.7	54	91.6	27.1	17.3	18.9	105	94.8	24.6	22.3	23.5
PFOS	6	54	89.6	28.9	19.1	21.3	54	85.6	26.9	16.2	19.0	108	87.6	27.7	17.6	20.1
PFNS	5	45	67.2	20.1	20.6	30.6	45	67.4	21.8	21.9	32.6	90	67.3	20.8	20.8	30.9
PFDS	6	54	73	24.5	20.3	27.8	54	70.6	22.6	20.1	28.5	108	71.8	23.3	19.9	27.8
PFDoS	6	54	50.5	26.1	23.1	45.7	54	47.3	20.5	19.9	42.2	108	48.9	23.2	21.3	43.5
4:2FTS	6	54	94.3	24.9	11.0	11.7	54	91.0	27.9	12.8	14.0	108	92.7	26.0	12.5	13.5
6:2FTS	6	51	132	75.8	152	115	54	101	34.1	19.3	19.1	105	116	45.3	112	96.6
8:2FTS	6	54	106	30.0	13.1	12.4	54	104	30.5	12.6	12.1	108	105	30.1	12.8	12.2
PFOSA	6	54	94.8	23.7	9.01	9.51	54	96.2	27.1	7.77	8.08	108	95.5	25.3	8.51	8.91
NMeFOSA	5	45	93.3	26.1	6.07	6.5	45	91.1	26	5.09	5.59	90	92.2	26.1	5.56	6.03
NEtFOSA	5	45	93.0	27.3	7.23	7.78	45	92	28.3	5.68	6.17	90	92.5	27.8	6.34	6.86
NMeFOSAA	6	54	91.5	27.2	11.2	12.2	54	93.8	28.4	9.08	9.68	108	92.7	27.8	9.98	10.8

Table 7-3. Pooled Laboratory PFAS-Spiked Biosolid 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)
NEtFOSAA	6	54	96.4	26.2	13.9	14.4	54	98.7	28.9	9.11	9.23	108	97.5	27.5	11.8	12
NMeFOSE	6	54	93.4	27.5	10.2	10.9	54	94.3	29.2	7.87	8.35	108	93.9	28.3	8.97	9.55
NEtFOSE	6	54	92.8	25.5	7.05	7.59	54	92.6	27.3	8.32	8.98	108	92.7	26.3	7.73	8.34
PFMPA	6	54	70.9	29.1	21.5	30.3	54	75.0	31.8	22.3	29.8	108	73	30.4	21.5	29.4
PFMBA	6	54	96.6	26.7	12.5	13.0	54	99.5	28.5	15.0	15.1	108	98.1	27.5	13.6	13.9
NFDHA	6	54	74.0	21.6	11.1	15.0	54	74.4	19.9	12.6	16.9	108	74.2	20.7	11.6	15.7
HFPO-DA	6	54	95.7	26.4	10.8	11.3	54	94.3	27.7	8.71	9.23	108	95	26.8	10.1	10.6
ADONA	6	54	96.9	29.0	10.2	10.6	54	95.2	27.5	10.7	11.3	108	96.1	28.2	10.3	10.7
PFEESA	6	54	87.4	25.4	9.48	10.8	54	90.2	27.5	8.43	9.35	108	88.8	26.4	9.03	10.2
9Cl-PF3ONS	6	54	92.3	28.4	12.7	13.7	54	91.7	29.1	16.3	17.8	108	92	28.7	14.2	15.5
11Cl-PF3OUdS	6	54	81.3	22.5	9.89	12.2	54	81.9	24.6	12.3	15	108	81.6	23.5	11.0	13.4
3:3FTCA	6	54	72.6	20.6	16.0	22	54	75.3	22.3	17.6	23.4	108	73.9	21.4	16.4	22.2
5:3FTCA	6	54	96.8	30.1	38.0	39.2	54	90.5	23.6	30.7	34	108	93.6	26.5	34.1	36.4
7:3FTCA	6	54	101	24.9	43.0	42.6	54	96.3	19.8	36.7	38.1	108	98.6	21.9	39.1	39.7

Source file: BS_Matrix_compiled_results_v0_231204_113058

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 spike 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 Biosolid Sample

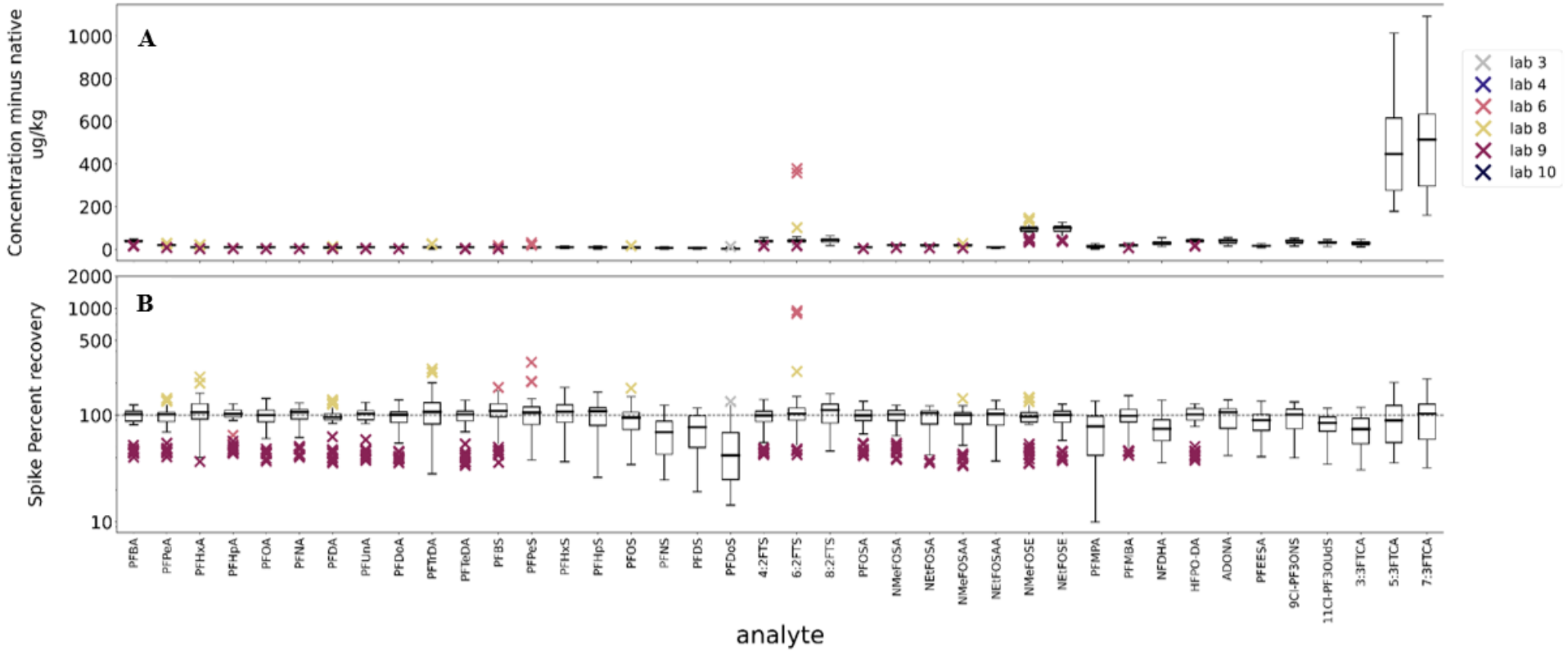
Analyte	BSAH				BSAI				BSAJ			
	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery	Number of Labs	Number of Results	Mean % Recovery	Range % Recovery
PFBA	6	35	94.5	43.8 - 118	6	36	94.9	40.5 - 126	6	31	93.6	43.8 - 163
PFPeA	6	36	93.9	45 - 130	6	36	91.8	40.7 - 144	6	36	97.9	44.2 - 182
PFHxA	6	36	98.5	44.2 - 159	6	30	104	36.8 - 228	6	36	105	44.1 - 204
PFHpA	6	36	92.3	45 - 123	6	36	95.3	41.2 - 128	6	36	93.1	42 - 134
PFOA	6	36	92.0	43.6 - 144	6	36	91.4	37.1 - 139	6	36	95.2	38.5 - 160
PFNA	6	36	90.4	44.8 - 124	6	36	96.3	40.4 - 130	6	36	97.5	42 - 132
PFDA	6	36	90.5	43.9 - 129	6	36	93.8	35.9 - 140	6	36	96.3	39.5 - 174
PFUnA	6	36	87.8	43.2 - 117	6	36	96.0	39.5 - 136	6	36	93.1	37.7 - 127
PFDoA	6	36	86.5	41.9 - 107	6	36	96.2	36 - 139	6	36	91.6	38.7 - 133
PFTrDA	6	36	114	36.5 - 193	6	36	98.3	28.3 - 195	6	35	111	27.4 - 271
PFTeDA	6	36	89.2	39.3 - 135	6	36	90.1	34.1 - 130	6	36	95.6	36.2 - 162
PFBS	6	36	106	42.5 - 182	6	36	98.2	42.3 - 139	6	36	98.8	36.1 - 148
PFPeS	6	33	108	40.7 - 314	6	36	94.7	38.1 - 142	6	36	98.1	43.6 - 194
PFHxS	6	36	98.3	36.7 - 182	6	36	97.7	38.4 - 143	6	36	102	36.6 - 164
PFHpS	6	33	99.8	58.7 - 131	6	36	94.7	41.3 - 132	6	36	90.4	24.8 - 164
PFOS	6	36	85.4	36.8 - 113	6	36	94.3	35.7 - 179	6	36	83.0	23.2 - 149
PFNS	5	30	60.8	26.3 - 94.2	5	30	86.0	37.7 - 125	5	30	55.0	22.5 - 92.7
PFDS	6	36	65.2	19.2 - 106	6	36	83.3	32.3 - 122	6	36	66.9	22.8 - 117
PFDoS	6	36	49.2	15.4 - 127	6	36	65.3	15.6 - 135	6	36	32.1	14.1 - 71.1
4:2FTS	6	36	90.8	44.4 - 138	6	36	94.0	42.9 - 150	6	36	93.2	40.9 - 157
6:2FTS	6	36	143	47.9 - 948	6	36	104	42.8 - 256	6	33	100	41.6 - 219
8:2FTS	6	36	107	50.8 - 143	6	36	99.4	45.4 - 145	6	36	108	44.5 - 178
PFOSA	6	36	94.8	46.7 - 122	6	36	93.8	41.7 - 130	6	36	97.8	42.9 - 163
NMeFOSA	5	30	93.3	45.7 - 116	5	30	91.2	38.6 - 124	5	30	92.2	44.5 - 124
NEtFOSA	5	30	95.1	42.8 - 118	5	30	89.6	35.9 - 122	5	30	92.8	43 - 120

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

Analyte	BSAH				BSAI				BSAJ			
	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	6	36	92.2	38.3 - 127	6	36	92.9	33.7 - 143	6	36	92.8	33.9 - 157
NEtFOSAA	6	36	96.2	48 - 137	6	36	97.5	37.3 - 138	6	36	98.9	38.3 - 169
NMeFOSE	6	36	92.3	41.3 - 134	6	36	92.3	39 - 128	6	36	96.9	35.3 - 172
NEtFOSE	6	36	92.0	39.7 - 114	6	36	90.8	38.7 - 122	6	36	95.2	37.5 - 156
PFMPA	6	36	70.5	14.3 - 126	6	36	83.0	37.4 - 140	6	36	65.4	10 - 164
PFMBA	6	36	94.6	45.4 - 118	6	36	95.3	42.2 - 147	6	36	104	45.2 - 180
NFDHA	6	36	70.1	37.8 - 138	6	36	79.9	36 - 107	6	36	72.6	39 - 108
HFPO-DA	6	36	90.9	41.6 - 120	6	36	96.4	38 - 130	6	36	97.6	40 - 157
ADONA	6	36	95.6	49.8 - 139	6	36	94.2	41.9 - 124	6	36	98.3	42.4 - 156
PFEESA	6	36	87.8	43.5 - 136	6	36	89.4	40.9 - 128	6	36	89.2	43.8 - 166
9Cl-PF3ONS	6	36	81.7	36.1 - 124	6	36	100	40.8 - 133	6	36	93.8	40.1 - 139
11Cl-PF3OUdS	6	36	76.5	38.9 - 112	6	36	86.4	34.8 - 127	6	36	81.9	36.6 - 128
3:3FTCA	6	36	88.3	33.2 - 130	6	36	61.5	30.8 - 85.6	6	36	72.0	32 - 118
5:3FTCA	6	36	123	64.8 - 203	6	36	53.8	35.4 - 86	6	36	104	43 - 179
7:3FTCA	6	36	132	80.7 - 219	6	36	52.9	31.8 - 78	6	36	111	46.2 - 173

Source File:BS_Matrix_sample_results_v0_231

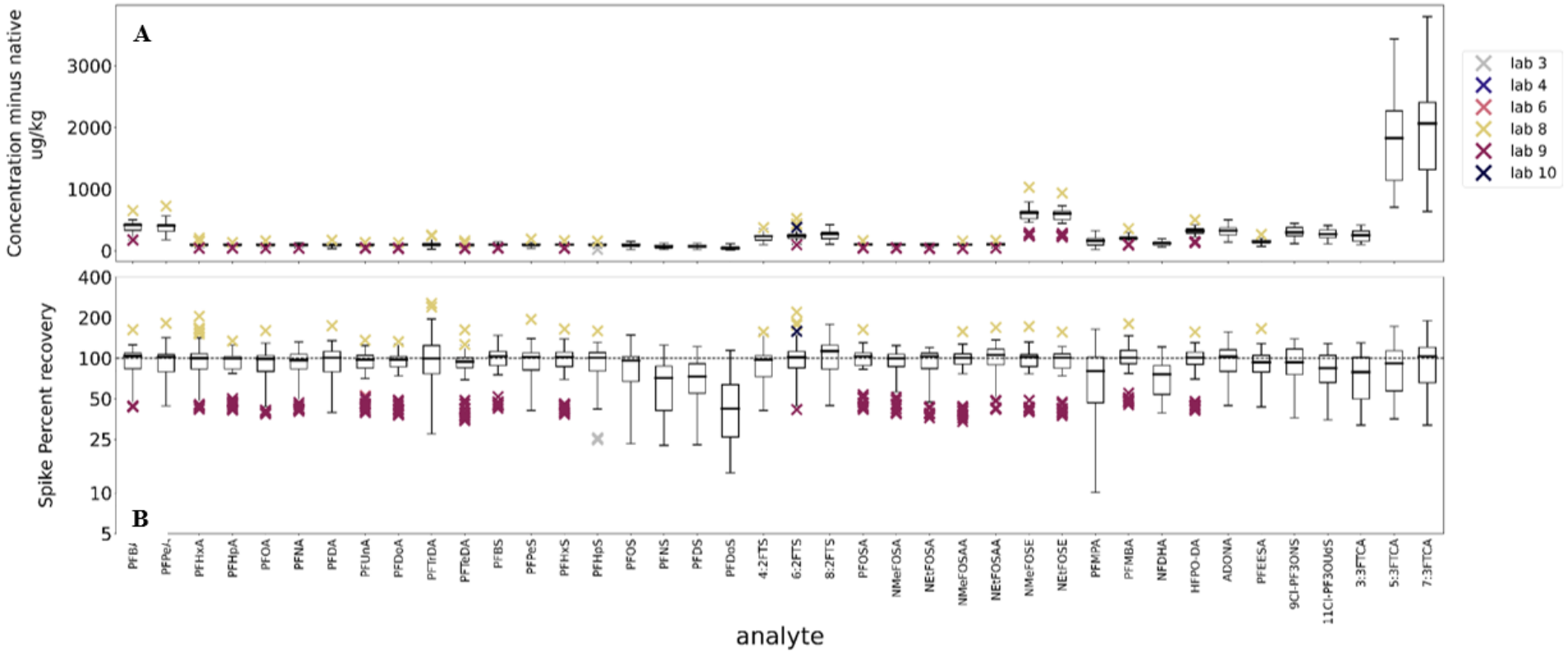
Notes:
Number of Labs - The number of laboratories reporting matrix spiked sample results.
Number of Results - The total number of results for the samples that do not have a U flag.
Mean % Recovery - The mean percent recovery for samples across all laboratories.
Range % Recovery - The minimum to maximum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



Source file: BS_LowSpike_Boxplot_v0_231204_113058

Figure 7-1. Biosolid Low Matrix Spiked Results by Analyte by Laboratory

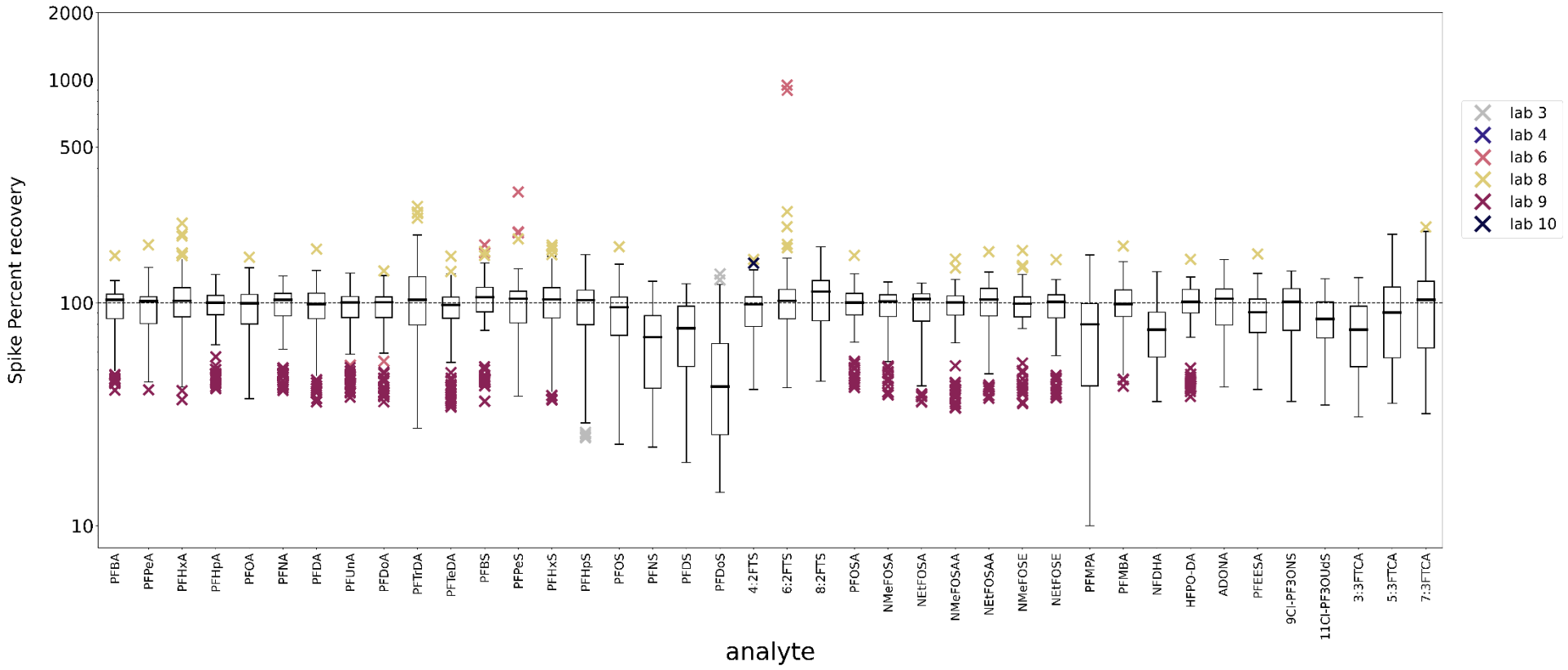
(A) Spiked concentration minus the laboratory-reported native concentration. (B) Low-spiked percent recovery



Source File: BS_HighSpike_Boxplot_v0_231204_113058

Figure 7-2. Biosolid High Matrix Spiked Results by Analyte by Laboratory

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



Source File: BS_LowHighCombinedSpike_Boxplot_v0_231204_113058

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

Table 7-5. Range of Concentrations of EIS Compounds Used by All Laboratories

EIS Compound	Minimum Concentration (ug/kg)	Maximum Concentration (ug/kg)
$^{13}C_4$-PFBA	80	100
$^{13}C_5$-PFPeA	40	50
$^{13}C_5$-PFHxA	20	25
$^{13}C_4$-PFHpA	20	25
$^{13}C_8$-PFOA	20	25
$^{13}C_9$-PFNA	10	12.5
$^{13}C_6$-PFDA	10	12.5
$^{13}C_7$-PFUnA	10	12.5
$^{13}C_2$-PFDoA	10	12.5
$^{13}C_2$-PFTeDA	10	12.5
$^{13}C_3$-PFBS	18.6	25
$^{13}C_3$-PFHxS	19	25
$^{13}C_8$-PFOS	19.2	25
$^{13}C_2$-4:2FTS	37.5	50
$^{13}C_2$-6:2FTS	38	50
$^{13}C_2$-8:2FTS	38.4	50
$^{13}C_8$-PFOSA	20	25
D_3-NMeFOSA	20	25
D_5-NEtFOSA	20	25
D_3-NMeFOSAA	40	50
D_5-NEtFOSAA	40	50
D_7-NMeFOSE	200	250
D_9-NEtFOSE	200	250
$^{13}C_3$-HFPO-DA	80	100

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

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

Table 7-6. Summary of EIS Compound Percent Recovery in Biosolids Samples for All Laboratories

EIS Compound	All Labs % Recovery			
	n	Min	Max	Mean
$^{13}C_4$-PFBA	127	2.4	117	64.9
$^{13}C_5$-PFPeA	132	10	117	81
$^{13}C_5$-PFHxA	130	13	111	89.9
$^{13}C_4$-PFHpA	126	68.8	130	94.5
$^{13}C_8$-PFOA	126	54	130	92.3
$^{13}C_9$-PFNA	126	71	144	99.8
$^{13}C_6$-PFDA	126	68	125	95.4
$^{13}C_7$-PFUnA	126	53.8	124	88.3
$^{13}C_2$-PFDoA	126	47.5	116	81.2
$^{13}C_2$-PFTeDA	126	12.7	166	59.9
$^{13}C_3$-PFBS	126	73	158	101.3
$^{13}C_3$-PFHxS	126	74	138	98.8
$^{13}C_8$-PFOS	126	63	127	94.7
$^{13}C_2$-4:2FTS	126	73.8	311	185.8
$^{13}C_2$-6:2FTS	126	57.9	379	166.3
$^{13}C_2$-8:2FTS	126	73.8	314	164.8
$^{13}C_8$-PFOSA	126	10	142	75.5
D_3-NMeFOSA	105	10	81.5	49.7
D_5-NEtFOSA	105	8	75.5	41.2
D_3-NMeFOSAA	126	12	150	93.1
D_5-NEtFOSAA	126	11	141	79.1
D_7-NMeFOSE	126	12	101	58.4
D_9-NEtFOSE	126	10	92	48.1
$^{13}C_3$-HFPO-DA	128	16	122	88.2

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

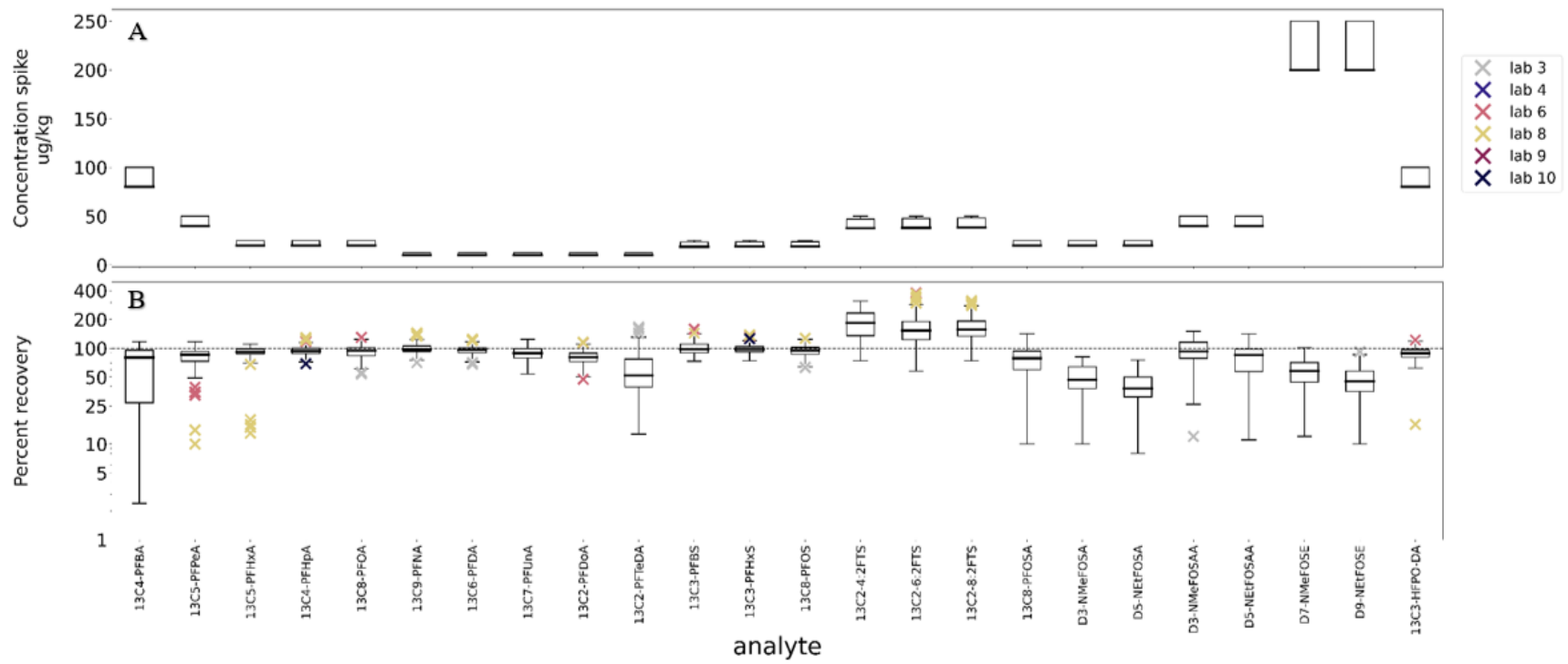
Note: Does not include MB, OPR, LLOPR QC samples.

Table 7-7. Statistical Evaluation of EIS Compound Results Associated with Biosolid 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)
13C4-PFBA	6	127	64.9	25.7	28.7	44.2
13C5-PFPeA	6	132	81	10.4	17.6	21.8
13C5-PFHxA	6	130	89.9	8.95	13.1	14.5
13C4-PFHpA	6	126	94.5	8.39	8.89	9.41
13C8-PFOA	6	126	92.3	12.4	10.7	11.6
13C9-PFNA	6	126	99.8	11.5	8.69	8.71
13C6-PFDA	6	126	95.4	8.81	7.55	7.91
13C7-PFUnA	6	126	88.3	10.8	11.8	13.3
13C2-PFDoA	6	126	81.2	8.1	13.5	16.6
13C2-PFTeDA	6	126	59.9	29.7	17.3	28.9
13C3-PFBS	6	126	101	11.9	11.9	11.7
13C3-PFHxS	6	126	98.7	9.03	9.04	9.15
13C8-PFOS	6	126	94.6	10.1	9.68	10.2
13C2-4:2FTS	6	126	186	49.4	36.3	19.5
13C2-6:2FTS	6	126	166	41	49.4	29.7
13C2-8:2FTS	6	126	165	34.7	33.4	20.3
13C8-PFOSA	6	126	75.5	22.3	18.9	25.1
D3-NMeFOSA	5	105	49.7	12.7	12.5	25.2
D5-NEtFOSA	5	105	41.2	11	12.5	30.2
D3-NMeFOSAA	6	126	93.1	20.6	23.8	25.6
D5-NEtFOSAA	6	126	79.1	14.1	27.1	34.3
D7-NMeFOSE	6	126	58.4	11.1	15.1	25.9
D9-NEtFOSE	6	126	48.2	5.83	16.4	34.1
13C3-HFPO-DA	6	128	88.2	9.55	13.1	14.9

Source file: BS_EIS_results_v0_231204_113058

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: BS_EIS_Boxplot_v0_231204_113058

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

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

7.4 BIOSOLID SUMMARY

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world biosolid samples for most target analytes. Select laboratories had significant bias with specific compounds. Overall, the pooled laboratory mean % recoveries were greater than 90% for 38 of the 40 PFAS compounds. PFDoS (48.9%) and PFNS (67%) were the exceptions in the pooled data.

Tables 7-8 and 7-9 provide summaries of the relative proportions of the spiked sample recoveries for all laboratories that fell within the target percent recovery acceptance criteria of 40–150% that was used to evaluate the OPR and LLOPR (40–150%). Table 7-8, compiled from the low-spiked samples data, shows that the recoveries in particular for the perfluoroalkyl sulfonic acids, had overall lower recoveries. This observation is consistent for the high-spiked samples (Table 7-9). As noted above, all laboratories consistently had lower percent recoveries for the FTCAs.

Table 7-10 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 pooled low- and high-spiked samples, the proportion of all values that were between 20–150% of the spiked concentrations was 100%.

Finally, Table 7-11 provides a comparison of the mean individual laboratory EIS percent recoveries relative to the acceptance limits for EIS compounds that EPA determined and is presented in the next chapter (Table 8-14). For that comparison, average EIS percent recoveries for all compounds and all laboratories were solidly within the acceptance criteria range.

Table 7-8. Proportion of Biosolids Matrix Spike 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	51	0	17.6	82.4	0	0	0
PFPeA	54	0	18.5	72.2	9.3	0	0
PFHxA	48	2.1	16.7	56.2	12.5	10.4	2.1
PFHpA	54	0	18.5	81.5	0	0	0
PFOA	54	3.7	13.0	77.8	5.6	0	0
PFNA	54	0	16.7	81.5	1.9	0	0
PFDA	54	5.6	11.1	77.8	5.6	0	0
PFUnA	54	3.7	13	81.5	1.9	0	0
PFDoA	54	7.4	11.1	79.6	1.9	0	0
PFTrDA	54	9.3	11.1	48.1	13	13	5.6
PFTeDA	54	7.4	9.3	74.1	9.3	0	0
PFBS	54	3.7	13	59.3	14.8	9.3	0
PFPeS	51	2	15.7	72.5	3.9	0	5.9
PFHxS	54	9.3	7.4	68.5	7.4	7.4	0
PFHpS	51	5.9	15.7	66.7	7.8	3.9	0
PFOS	54	14.8	9.3	68.5	5.6	1.9	0
PFNS	45	24.4	26.7	48.9	0	0	0
PFDS	54	22.2	18.5	59.3	0	0	0
PFDoS	54	46.3	29.6	22.2	1.9	0	0
4:2FTS	54	0	16.7	77.8	5.6	0	0
6:2FTS	51	0	19.6	64.7	9.8	0	5.9
8:2FTS	54	0	14.8	66.7	14.8	3.7	0
PFOSA	54	0	16.7	77.8	5.6	0	0
NMeFOSA	45	4.4	15.6	80	0	0	0
NEtFOSA	45	4.4	15.6	80	0	0	0
NMeFOSAA	54	9.3	11.1	77.8	1.9	0	0
NEtFOSAA	54	3.7	14.8	72.2	9.3	0	0
NMeFOSE	54	5.6	11.1	72.2	11.1	0	0
NEtFOSE	54	5.6	11.1	83.3	0	0	0
PFMPA	54	22.2	22.2	53.7	1.9	0	0
PFMBA	54	0	16.7	74.1	7.4	1.9	0
NFDHA	54	7.4	35.2	55.6	1.9	0	0
HFPO-DA	54	1.9	14.8	83.3	0	0	0
ADONA	54	0	22.2	68.5	9.3	0	0
PFEESA	54	0	18.5	77.8	3.7	0	0
9Cl-PF3ONS	54	1.9	20.4	72.2	5.6	0	0
11Cl-PF3OUdS	54	9.3	14.8	75.9	0	0	0
3:3FTCA	54	11.1	35.2	53.7	0	0	0
5:3FTCA	54	5.6	29.6	42.6	9.3	11.1	1.9
7:3FTCA	54	5.6	27.8	46.3	7.4	7.4	5.6

Version: Summary_tables_LCBS_Exa_CH6_12132023.xlsx

Table 7-9. Proportion of Biosolids Matrix Spike 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	51	0	17.6	80.4	0	2	0
PFPeA	54	0	18.5	70.4	9.3	1.9	0
PFHxA	54	0	18.5	64.8	5.6	9.3	1.9
PFHpA	54	0	16.7	81.5	1.9	0	0
PFOA	54	5.6	11.1	81.5	0	1.9	0
PFNA	54	0	16.7	81.5	1.9	0	0
PFDA	54	1.9	16.7	74.1	5.6	1.9	0
PFUnA	54	1.9	16.7	79.6	1.9	0	0
PFDoA	54	5.6	11.1	81.5	1.9	0	0
PFTrDA	53	13.2	9.4	54.7	5.7	13.2	3.8
PFTeDA	54	9.3	9.3	79.6	0	1.9	0
PFBS	54	0	16.7	81.5	1.9	0	0
PFPeS	54	0	20.4	68.5	9.3	1.9	0
PFHxS	54	3.7	14.8	75.9	3.7	1.9	0
PFHpS	54	5.6	18.5	72.2	1.9	1.9	0
PFOS	54	7.4	18.5	72.2	1.9	0	0
PFNS	45	24.4	24.4	51.1	0	0	0
PFDS	54	22.2	24.1	53.7	0	0	0
PFDoS	54	44.4	35.2	20.4	0	0	0
4:2FTS	54	0	22.2	70.4	3.7	3.7	0
6:2FTS	54	0	18.5	64.8	7.4	7.4	1.9
8:2FTS	54	0	18.5	64.8	14.8	1.9	0
PFOSA	54	0	16.7	79.6	1.9	1.9	0
NMeFOSA	45	4.4	15.6	80	0	0	0
NEtFOSA	45	6.7	13.3	80	0	0	0
NMeFOSAA	54	7.4	9.3	81.5	0	1.9	0
NEtFOSAA	54	0	18.5	75.9	3.7	1.9	0
NMeFOSE	54	0	16.7	77.8	3.7	1.9	0
NEtFOSE	54	7.4	9.3	81.5	0	1.9	0
PFMPA	54	24.1	22.2	48.1	3.7	1.9	0
PFMBA	54	0	16.7	68.5	13	1.9	0
NFDHA	54	7.4	25.9	66.7	0	0	0
HFPO-DA	54	0	16.7	79.6	1.9	1.9	0
ADONA	54	0	22.2	75.9	0	1.9	0
PFEESA	54	0	16.7	81.5	0	1.9	0
9Cl-PF3ONS	54	3.7	18.5	70.4	7.4	0	0
11Cl-PF3OUdS	54	9.3	20.4	70.4	0	0	0
3:3FTCA	54	9.3	35.2	55.6	0	0	0
5:3FTCA	54	5.6	33.3	48.1	7.4	5.6	0
7:3FTCA	54	5.6	25.9	51.9	11.1	5.6	0

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

Table 7-10. Proportion of Biosolids 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	127	6.3	15	78.7	0	0
$^{13}C_5$-PFPeA	132	0	3	97	0	0
$^{13}C_5$-PFHxA	130	0	3.1	96.9	0	0
$^{13}C_4$-PFHpA	126	0	0	100	0	0
$^{13}C_8$-PFOA	126	0	0	100	0	0
$^{13}C_9$-PFNA	126	0	0	100	0	0
$^{13}C_6$-PFDA	126	0	0	100	0	0
$^{13}C_7$-PFUnA	126	0	0	100	0	0
$^{13}C_2$-PFDoA	126	0	0	100	0	0
$^{13}C_2$-PFTeDA	126	0	8.7	89.7	1.6	0
$^{13}C_3$-PFBS	126	0	0	99.2	0.8	0
$^{13}C_3$-PFHxS	126	0	0	100	0	0
$^{13}C_8$-PFOS	126	0	0	100	0	0
$^{13}C_2$-4:2FTS	126	0	0	30.2	30.2	39.7
$^{13}C_2$-6:2FTS	126	0	0	46.8	33.3	19.8
$^{13}C_2$-8:2FTS	126	0	0	41.3	38.9	19.8
$^{13}C_8$-PFOSA	126	0	2.4	97.6	0	0
D_3-NMeFOSA	105	0	1	99	0	0
D_5-NEtFOSA	105	1	3.8	95.2	0	0
D_3-NMeFOSAA	126	0	0.8	98.4	0.8	0
D_5-NEtFOSAA	126	0	0.8	99.2	0	0
D_7-NMeFOSE	126	0	0.8	99.2	0	0
D_9-NEtFOSE	126	0	0.8	99.2	0	0
$^{13}C_3$-HFPO-DA	128	0	1.6	98.4	0	0

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

Does not include MB, OPR, LLOPR QC samples.

Table 7-11. Summary of EIS Compound Percent Recovery in Biosolids Samples for All Laboratories

EIS Compound	Final EIS Compound Acceptance Limits Applicable to All Solid Sample Types [1]		Individual and Pooled Laboratory Average % Recovery						
			Lab 3	Lab 4	Lab 6	Lab 8	Lab 9	Lab 10	Pooled Labs
$^{13}C_4$-PFBA	8	130	67.8	47.0	25.0	85.3	67.7	96.0	64.9
$^{13}C_5$-PFPeA	35	130	68.9	81.9	71.8	77.8	91.7	94.5	81.0
$^{13}C_5$-PFHxA	40	130	81.9	93.2	91.1	77.5	99.5	98.7	89.9
$^{13}C_4$-PFHpA	40	130	85.3	92.1	94.7	110.2	94.0	90.6	94.5
$^{13}C_8$-PFOA	40	130	68.2	95.8	91.5	101.6	100	96.7	92.3
$^{13}C_9$-PFNA	40	130	84.9	95.5	99.6	120.4	98.5	99.9	99.8
$^{13}C_6$-PFDA	40	130	82.3	98.3	95.6	107.2	100.3	88.6	95.4
$^{13}C_7$-PFUnA	40	130	76.5	89.4	82.7	107.2	81.7	92.2	88.3
$^{13}C_2$-PFDoA	40	130	87.3	79.2	84.2	90.2	79.1	67.3	81.2
$^{13}C_2$-PFTeDA	20	130	113	54.6	71.6	46.7	46.0	27.4	59.9
$^{13}C_3$-PFBS	40	135	86.7	98.4	110.9	118.9	92.2	100.9	101.3
$^{13}C_3$-PFHxS	40	130	84.9	95.8	103.2	112.1	100.1	96.7	98.8
$^{13}C_8$-PFOS	40	130	82.7	85.4	98.4	110.8	98.1	92.9	94.7
$^{13}C_2$-4:2FTS	40	165	229.9	151.3	186.1	241.3	196.8	109.5	185.8
$^{13}C_2$-6:2FTS	40	215	154.2	132.8	188.5	221.2	189.7	111.2	166.3
$^{13}C_2$-8:2FTS	40	275	177.5	144.2	169.1	212.9	175.2	109.7	164.8
$^{13}C_8$-PFOSA	40	130	44.3	78.1	69.0	98.0	102.9	60.6	75.5
D_3-NMeFOSA	10	130	47.4	39.7	68.2	--	56.2	37.0	49.7
D_5-NEtFOSA	10	130	44.3	33.3	59.2	--	35.6	33.5	41.2
D_3-NMeFOSAA	40	135**	70.9	77.6	79.5	118.9	96.0	115.9	93.1
D_5-NEtFOSAA	40	150	55.7	79.7	79	92.7	73.3	93.9	79.1
D_7-NMeFOSE	20	130	59.5	51.5	75.7	46.8	66.5	50.4	58.4
D_9-NEtFOSE	15	130	50.2	43.8	57.7	43.4	50.7	43.1	48.1
$^{13}C_3$-HFPO-DA	40	130	72.4	83.2	97.4	91.4	97.2	87.2	88.2

Version: Summary_tables_LCBS_Exa_CH7_12132023.xlsx

[1]Criteria from Table 8-23 this report
--- rejected EIS data

8 SUMMARY FOR LANDFILL LEACHATE AND BIOSOLIDS

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 in OPRs and LLOPRs was 40–150%, 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 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 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 100-mL aliquot of PFAS-free reagent water was used to prepare each method blank associated with landfill leachate samples and a 0.5-g aliquot of PFAS-free Ottawa or reagent-grade sand was used to prepare each method blank associated with biosolids samples. All were prepared in exactly the same manner as study samples. A total of 14 method blanks were included in the statistical analysis of each of these media types (14 for landfill leachates, 14 for biosolids).

Of these 14 method blanks associated with each of these media types, two method blanks associated with landfill leachate samples and three method blanks associated with biosolid samples included detections of target analytes concentrations above the laboratories' MDLs. One target analytes (PFHxA) was detected in two method blanks associated with landfill leachate samples while two target analytes (6:2FTS, PFBA) were detected in method blanks associated with biosolids samples. All of these reported concentrations were above the laboratories' MDL, but below the laboratories' LOQ, with the exception of a single detection of 6:2FTS in a method blank associated with biosolids. The low rate of detection in method blanks demonstrated by this study, 6 out of 1,114 target analytes reported (0.54%) 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. All of the method blanks associated with landfill leachate samples met this criteria, therefore, no landfill leachate results were B qualified. Four out of the 14 biosolids method blanks reported failed to meet the study criteria. Laboratories 3 and 9 failed to meet the study criteria in one biosolids method blank each, while Laboratory 8 failed to meet the criteria in two biosolids method blanks.

There were 11 valid sample results for 6:2FTS that were "B" qualified; 4 by Laboratory 3 and 7 by Laboratory 8. One result for PFBA reported by Laboratory 9 was also "B" qualified.

Table 8-1. Method Blank Detection Summary

Matrix of Associated Samples	Laboratory ID	Target Analyte	# of Occurrences	Concentrations (µg/kg for BS, ng/L for LC)
LC	9	PFHxA	2	0.902 J, 0.767 J
BS	3	6:2FTS	1	4.02 J
BS	8	6:2FTS	2	25.6, 6.03 J
BS	9	PFBA	1	2.86 J

Source Files: BS_DBExport_V0_20231120 and BS_LCExport_V0_20231120

Notes:
J = Analyte concentration >MDL but <LOQ; estimated value.

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 are 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.

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)
BSAH2	8	6:2FTS	47.9 J+B	25.6
BSAH3	8	6:2FTS	47.2 J+B	25.6
BSAH4	8	6:2FTS	56.6 J+B	25.6
BSAI1	3	6:2FTS	6.31 J+B	4.02 JB
BSAI1	8	6:2FTS	3.48 J+B	25.6 B
BSAI1	9	PFBA	4.91 J+B	2.86 JB
BSAI1	3	6:2FTS	47.9 B	4.02 JB
BSAI2	8	6:2FTS	57.2 J+B	25.6 B
BSAI3	3	6:2FTS	46.7 B	4.02 JB
BSAI3	8	6:2FTS	44.6 J+B	25.6 B
BSAI4	3	6:2FTS	45.6 B	4.02 JB
BSAJ1	8	6:2FTS	48.1 JB	6,03 JB

Source Files: BS_DBExport_V0_20231120 and BS_LCExport_V0_20231120

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.

Method blank contamination resulted in the "B" qualification of 11 results out of 554 biosolids sample results reported and the qualification of no landfill leachate samples. Thus, these measured

concentrations were only sufficient to warrant "B" flags for what ultimately represented <1.98% of the final biosolids data set. The method blanks demonstrate that any bias associated with background contamination introduced during sample preparation was negligible.

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 0.5-g aliquot of PFAS-free Ottawa or reagent-grade sand for biosolids and a 100 mL aliquot of reagent-grade water for landfill leachates 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. Each OPR was prepared and analyzed in exactly the same manner as study samples.

OPR target analyte recoveries across all landfill leachate and biosolids media for all laboratories were relatively tight, with all above 90% with narrow pooled between-laboratory standard deviation (s_b), within-laboratory standard deviation (s_w), and Relative Standard Deviation (RSD). (Tables 8-3 and 8-4, Figure 8-1B and 8-2B). The concentration at which the OPR was spiked by each laboratory did not vary greatly (Figure 8-1A and 8-2A).

A total of 14 OPRs were included in the statistical analysis for landfill leachates and biosolids each. All 28 OPRs met the study NIS criteria (>30% recovery). Of the 560 valid target analyte results reported from OPRs associated with landfill leachate samples, one failed to meet the target analyte criteria (40–150%), resulting in a failure rate of 0.179%. Laboratory 10 reported one target analyte exceedances in one OPR: NMeFOSA (176%). Of the 554 valid target analyte results reported from OPRs associated with biosolids samples, one failed to meet the target analyte criteria, resulting in a failure rate of 0.18%. Laboratory 6 reported one target analyte exceedances in one OPR: PFMPA (35.6%). All of the 336 valid EIS compound results reported from OPRs associated with landfill leachates met the EIS compound target acceptance criteria (20–150%). Of the 336 valid EIS compound results reported from OPRs associated with biosolids samples, one failed to meet the EIS compound target acceptance criteria, resulting in a failure rate of 0.30%. Laboratory 6 reported a single EIS compound exceedances in one OPR; $^{13}C_4$-PFBA (10.6%). Overall, for biosolids, 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 8-2B).

Following EPA guidance (EPA 821-B-18-001), lower and upper percent recovery limits OPRs for target analytes were generated for landfill leachates (Table 8-5) and biosolids (Table 8-6). 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 associated with landfill leachate and biosolids OPRs are greater than 70% with the exception of the lower limits for biosolids for PFMPA (65%) and 3:3FTCA (58%), are greater than 70%. All upper limits were less than or equal to 130% with the exception of 3 landfill leachate upper limits (PFDoA (131%), 8:2FTS (131%), and NMeFOSA (143%)) and 4 biosolids upper limits (6:2FTS (139%), NMeFOSAA (133%), PFMBA (134%), and 3:3FTCA (136%)).

8.1.3 Low-Level Ongoing Precision and Recovery Analyses

LLOPR samples, sometimes referred to as Low-Level Laboratory Control Samples (LLLCS), 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 100 mL of PFAS-free reagent-grade water (landfill leachates), or a 0.5-g aliquot of PFAS-free Ottawa or reagent-grade sand (biosolids), 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.

LLOPR target analyte recoveries across all landfill leachate and biosolids media for all laboratories were relatively tight, with all above 90%, a narrow pooled between-laboratory standard deviation (s_b), within-laboratory standard deviation (s_w), and Relative Standard Deviation (RSD). (Tables 8-7 and 8-8, Figure 8-3B and 8-4B). The concentration at which the OPR was spiked by each laboratory did not vary greatly (Figure 8-3A and 8-4A).

All of the 28 LLOPRs included in the statistical analysis met the study NIS compound recovery criteria (>30%) with the exception of one results, resulting in a failure rate of 0.98%. Laboratory 4 reported one NIS compound exceedance in one LLOPR; $^{13}C_4$-PFOS (36.0%). Of the 560 valid target analyte results reported from LLOPRs associated with landfill leachate samples, one failed to meet the target analyte criteria (40 – 150%), resulting in a failure rate of 0.18%. Laboratory 3 reported one target analyte exceedances in one LLOPR: PFHxA (222%). Of the 554 valid target analyte results reported from LLOPRs associated with biosolids samples, one failed to meet the target analyte criteria, resulting in a failure rate of 0.18%. Laboratory 8 reported one target analyte exceedances in one LLOPR: 8:2FTS (204%). This result was "B" qualified due to the detection of this target analyte in the associated method blank, indicating this failure most likely is due to contamination during the preparation or analysis steps. All of the 336 valid EIS compound results reported from LLOPRs associated with landfill leachates met the EIS compound target acceptance criteria (20–150%). Of the 332 valid EIS compound results reported from LLOPRs associated with biosolids samples, two failed to meet the EIS compound target acceptance criteria, resulting in a failure rate of 0.60%. Laboratory 6 reported one EIS compound exceedances in two LLOPR; $^{13}C_4$-PFBA (12.4% and 16.9%). 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 Tables 8-7 (landfill leachate) and 8-8 (biosolids). Overall, for biosolids, the recoveries of Laboratory 6 LLOPR recoveries trended lower than all other laboratories, while those of Laboratory 8 exhibited slightly higher LLOPR recoveries than most (Figure 8-4B). These trends are consistent with those observed for the biosolids OPRs.

Following EPA guidance (EPA 821-B-18-001), lower and upper percent recovery limits OPRs for target analytes were generated for landfill leachates (Table 8-9) and biosolids (Table 8-10). 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 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 PFHxA (162%) for landfill leachates and 6:2FTS (182%) for biosolids.

Table 8-3. Summary of Landfill Leachate 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)	Combined std. dev. (s_c)	RSD (s_w)
PFBA	6	14	107	11.8	5.78	13.5	5.39
PFPeA	6	14	109	11.8	7.35	13.9	6.75
PFHxA	6	14	105	8.45	9.41	11.6	8.96
PFHpA	6	14	108	13.0	7.93	15.3	7.36
PFOA	6	14	107	7.85	6.55	9.82	6.12
PFNA	6	14	106	13.5	10.1	16.5	9.55
PFDA	6	14	105	10.8	10.4	14.1	9.97
PFUnA	6	14	105	11.6	11.2	15.1	10.7
PFDoA	6	14	112	13.4	10.4	16.4	9.30
PFTrDA	6	14	107	15.1	7.03	17.1	6.57
PFTeDA	6	14	107	16.4	6.28	18.3	5.84
PFBS	6	14	110	16.5	9.28	19.1	8.42
PFPeS	6	14	104	13.3	6.31	15.2	6.09
PFHxS	6	14	103	20.3	7.47	22.6	7.29
PFHpS	6	14	106	15.5	8.08	17.8	7.63
PFOS	6	14	101	16.5	8.52	19	8.41
PFNS	6	14	102	15.3	7.36	17.4	7.19
PFDS	6	14	101	12.5	7.28	14.6	7.19
PFDoS	6	14	95.1	11.6	7.43	13.8	7.81
4:2FTS	6	14	105	17.0	9.53	19.7	9.04
6:2FTS	6	14	106	16.4	9.16	19.0	8.65
8:2FTS	6	14	116	16.8	8.58	19.3	7.40
PFOSA	6	14	108	12.4	9.62	15.3	8.88
NMeFOSA	6	14	120	22.4	14.0	26.4	11.7
NEtFOSA	6	14	111	21.3	9.52	24.1	8.59
NMeFOSAA	6	14	109	11.2	8.25	13.6	7.55
NEtFOSAA	6	14	101	15.0	10.6	18.1	10.4
NMeFOSE	6	14	110	16.9	7.18	19.1	6.55
NEtFOSE	6	14	112	17.0	9.46	19.7	8.46

Table 8-3. Summary of Landfill Leachate 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)	Combined std. dev. (s_c)	RSD (s_w)
PFMPA	6	14	104	14.9	6.07	16.7	5.83
PFMBA	6	14	106	14.6	6.59	16.6	6.23
NFDHA	6	14	104	13.4	10.0	16.4	9.64
HFPO-DA	6	14	109	15.1	4.28	16.6	3.94
ADONA	6	14	107	10.1	6.43	11.9	5.99
PFEESA	6	14	107	12.9	9.6	15.7	8.99
9Cl-PF3ONS	6	14	107	10.8	7.19	12.9	6.75
11Cl-PF3OUdS	6	14	100	8.33	6.23	10.2	6.2
3:3FTCA	6	14	109	14.8	7.56	16.9	6.94
5:3FTCA	6	14	102	9.24	11.9	13.4	11.6
7:3FTCA	6	14	96.8	11.9	10.8	15.2	11.1
$^{13}C_4$-PFBA	6	14	80.3	11.3	11.4	15.0	14.2
$^{13}C_5$-PFPeA	6	14	90.8	10.8	5.90	12.5	6.49
$^{13}C_5$-PFHxA	6	14	88.9	6.35	6.47	8.42	7.28
$^{13}C_4$-PFHpA	6	14	86.5	8.58	5.12	10	5.91
$^{13}C_8$-PFOA	6	14	84.2	7.31	4.77	8.68	5.67
$^{13}C_9$-PFNA	6	14	86.8	7.83	4.74	9.19	5.46
$^{13}C_6$-PFDA	6	14	84.7	2.83	5.45	5.12	6.43
$^{13}C_7$-PFUnA	6	14	85.3	6.63	7.24	9.02	8.48
$^{13}C_2$-PFDoA	6	14	76.6	6.30	4.55	7.62	5.93
$^{13}C_2$-PFTeDA	6	14	75.1	7.34	7.96	9.95	10.6
$^{13}C_3$-PFBS	6	14	87.1	6.91	3.9	8.03	4.47
$^{13}C_3$-PFHxS	6	14	87.5	7.82	7.46	10.2	8.52
$^{13}C_8$-PFOS	6	14	88.4	7.52	5.60	9.17	6.34
$^{13}C_2$-4:2FTS	6	14	94.1	5.35	9.73	9.36	10.3
$^{13}C_2$-6:2FTS	6	14	93.0	6.64	6.53	8.71	7.01
$^{13}C_2$-8:2FTS	6	14	87.3	6.56	6.26	8.52	7.17
$^{13}C_8$-PFOSA	6	14	79.9	4.66	6.94	7.27	8.69
D_3-NMeFOSA	6	14	56.5	14.1	6.08	15.9	10.8

Table 8-3. Summary of Landfill Leachate 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)	Combined std. dev. (s_c)	RSD (s_w)
D_5-NEtFOSA	6	14	55.5	13.3	4.57	14.8	8.23
D_3-NMeFOSAA	6	14	85.9	6.80	5.74	8.54	6.68
D_5-NEtFOSAA	6	14	86.0	6.35	5.11	7.87	5.94
D_7-NMeFOSE	6	14	77.8	8.45	6.12	10.2	7.86
D_9-NEtFOSE	6	14	77.0	6.46	6.18	8.40	8.03
$^{13}C_3$-HFPO-DA	6	14	86.5	9.86	7.34	12.0	8.48

Source IDA file: LC_EXPORT_V0_20231122_163114.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. Summary of Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
PFBA	6	14	109	6.78	6.2	8.7	5.69
PFPeA	6	14	107	8.96	5.94	10.7	5.57
PFHxA	6	14	104	9.62	9.46	12.6	9.11
PFHpA	6	14	111	8.27	6.4	10.2	5.77
PFOA	6	14	105	3.78	7.4	6.93	7.05
PFNA	6	14	111	10.4	8.82	13.1	7.98
PFDA	6	14	107	11.7	7.57	13.9	7.09
PFUnA	6	14	109	10.4	7.26	12.5	6.68
PFDoA	6	14	110	11	8.7	13.6	7.88
PFTrDA	6	14	111	10.9	4.57	12.2	4.11
PFTeDA	6	14	110	9.48	6.4	11.3	5.84
PFBS	6	14	111	13.1	2.9	14.3	2.6
PFPeS	6	14	109	11	10.4	14.3	9.54
PFHxS	6	14	108	9.13	4.39	10.4	4.06
PFHpS	6	14	109	11.6	4.94	13.1	4.54
PFOS	6	14	107	9.22	6.74	11.2	6.29
PFNS	5	12	108	11.4	6.26	13.3	5.79
PFDS	6	14	105	8.78	5.67	10.4	5.41
PFDoS	6	14	94.5	11.5	6.5	13.3	6.88
4:2FTS	6	14	113	10.4	9.79	13.5	8.67
6:2FTS	6	14	114	10.8	14	15.8	12.3
8:2FTS	6	14	115	11.3	12.9	15.6	11.2
PFOSA	6	14	110	8.23	5.9	9.95	5.37
NMeFOSA	5	12	104	4.7	13.2	11.3	12.7
NEtFOSA	5	12	106	8.75	3.61	9.97	3.42
NMeFOSAA	6	14	113	13.2	11.5	16.7	10.2
NEtFOSAA	6	14	108	11.7	8.92	14.3	8.28
NMeFOSE	6	14	108	9.33	4.7	10.7	4.35
NEtFOSE	6	14	107	7.81	4.03	8.97	3.78

Table 8-4. Summary of Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
PFMPA	6	14	97.6	20.7	15.7	25.3	16.1
PFMBA	6	14	109	12.0.	13.6	16.6	12.5
NFDHA	6	14	106	12.8	11.2	16.1	10.5
HFPO-DA	6	14	108	12	5.05	13.5	4.67
ADONA	6	14	107	12.3	5.28	13.9	4.93
PFEESA	6	14	105	9.49	7.2	11.6	6.83
9Cl-PF3ONS	6	14	112	11.4	6.23	13.2	5.57
11Cl-PF3OUdS	6	14	106	11.9	8.38	14.4	7.9
3:3FTCA	6	14	97.1	11.4	19	18.9	19.5
5:3FTCA	6	14	104	11.3	9.1	14	8.76
7:3FTCA	6	14	102	14.9	5.67	16.7	5.57
$^{13}C_4$-PFBA	6	14	82.7	24	17	28.9	20.5
$^{13}C_5$-PFPeA	6	14	90.8	13.3	10.1	16.3	11.2
$^{13}C_5$-PFHxA	6	14	96.5	10.7	3.12	11.8	3.23
$^{13}C_4$-PFHpA	6	14	93	11.3	8.66	13.8	9.31
$^{13}C_8$-PFOA	6	14	88.8	12.5	6.63	14.4	7.47
$^{13}C_9$-PFNA	6	14	96.7	7.45	6.56	9.45	6.79
$^{13}C_6$-PFDA	6	14	96.2	8.81	5.55	10.4	5.77
$^{13}C_7$-PFUnA	6	14	95.7	8.98	4.94	10.4	5.16
$^{13}C_2$-PFDoA	6	14	89.3	7.68	5.12	9.15	5.74
$^{13}C_2$-PFTeDA	6	14	81.1	13.3	5.41	14.9	6.68
$^{13}C_3$-PFBS	6	14	90.3	10.1	8.79	12.8	9.73
$^{13}C_3$-PFHxS	6	14	92.7	11.1	5.96	12.8	6.43
$^{13}C_8$-PFOS	6	14	93.2	11.4	3.72	12.6	3.99
$^{13}C_2$-4:2FTS	6	14	98.3	9.24	14.7	14.9	15
$^{13}C_2$-6:2FTS	6	14	100	10.8	14.1	15.8	14.1
$^{13}C_2$-8:2FTS	6	14	101	12.8	18.5	19.6	18.2
$^{13}C_8$-PFOSA	6	14	87.5	13.6	3.91	15	4.46
D_3-NMeFOSA	5	12	57.6	17.2	6.26	19.5	10.9

Table 8-4. Summary of Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
D_5-NEtFOSA	5	12	52	15	7.66	17.4	14.7
D_3-NMeFOSAA	6	14	94.2	16.2	8.75	18.7	9.29
D_5-NEtFOSAA	6	14	94.7	15.4	8.71	17.9	9.2
D_7-NMeFOSE	6	14	75.2	17.5	5.3	19.3	7.05
D_9-NEtFOSE	6	14	72	16.6	6.53	18.6	9.07
$^{13}C_3$-HFPO-DA	6	14	91.6	12.8	4.46	14.3	4.88

Source IDA file: BS_EXPORT_V0_20231122_163114..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 8-5. Statistically Derived Landfill Leachate OPR Acceptance Criteria

Analytes	Landfill Leachate Mean % Recovery	Landfill Leachate 2 x RSD[1]	Landfill Leachate LCL[2]	Landfill Leachate UCL[3]
PFBA	107	10.78	96	118
PFPeA	109	13.5	96	122
PFHxA	105	17.92	87	123
PFHpA	108	14.72	93	123
PFOA	107	12.24	95	119
PFNA	106	19.1	87	125
PFDA	105	19.94	85	125
PFUnA	105	21.4	84	126
PFDoA	112	18.6	93	131
PFTrDA	107	13.14	94	120
PFTeDA	107	11.68	95	119
PFBS	110	16.84	93	127
PFPeS	104	12.18	92	116
PFHxS	103	14.58	88	118
PFHpS	106	15.26	91	122
PFOS	101	16.82	84	118
PFNS	102	14.38	88	116
PFDS	101	14.38	87	115
PFDoS	95.1	15.62	79	111
4:2FTS	105	18.08	87	123
6:2FTS	106	17.3	89	123
8:2FTS	116	14.8	101	131
PFOSA	108	17.76	90	126
NMeFOSA	120	23.4	97	143
NEtFOSA	111	17.18	94	128
NMeFOSAA	109	15.1	94	124
NEtFOSAA	101	20.8	80	122
NMeFOSE	110	13.1	97	123
NEtFOSE	112	16.92	95	129
PFMPA	104	11.66	92	116
PFMBA	106	12.46	94	118
NFDHA	104	19.28	85	123
HFPO-DA	109	7.88	101	117
ADONA	107	11.98	95	119
PFEESA	107	17.98	89	125
9Cl-PF3ONS	107	13.5	94	121
11Cl-PF3OUdS	100	12.4	88	112
3:3FTCA	109	13.88	95	123
5:3FTCA	102	23.2	79	125
7:3FTCA	96.8	22.2	75	119

Source File: derived from DA file: LC_EXPORT_V0_20231122_163114.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 8-6. Statistically Derived Biosolids OPR Acceptance Criteria

Analytes	Biosolids Mean % Recovery	Biosolids 2 x RSD[1]	Biosolids LCL[2]	Biosolids UCL[3]
PFBA	109	11.38	98	120
PFPeA	107	11.14	96	118
PFHxA	104	18.22	86	122
PFHpA	111	11.54	99	123
PFOA	105	14.1	91	119
PFNA	111	15.96	95	127
PFDA	107	14.18	93	121
PFUnA	109	13.36	96	122
PFDoA	110	15.76	94	126
PFTrDA	111	8.22	103	119
PFTeDA	110	11.68	98	122
PFBS	111	5.2	106	116
PFPeS	109	19.08	90	128
PFHxS	108	8.12	100	116
PFHpS	109	9.08	100	118
PFOS	107	12.58	94	120
PFNS	108	11.58	96	120
PFDS	105	10.82	94	116
PFDoS	94.5	13.76	81	108
4:2FTS	113	17.34	96	130
6:2FTS	114	24.6	89	139
8:2FTS	115	22.4	93	137
PFOSA	110	10.74	99	121
NMeFOSA	104	25.4	79	129
NEtFOSA	106	6.84	99	113
NMeFOSAA	113	20.4	93	133
NEtFOSAA	108	16.56	91	125
NMeFOSE	108	8.7	99	117
NEtFOSE	107	7.56	99	115
PFMPA	97.6	32.2	65	130
PFMBA	109	25	84	134
NFDHA	106	21	85	127
HFPO-DA	108	9.34	99	117
ADONA	107	9.86	97	117
PFEESA	105	13.66	91	119
9Cl-PF3ONS	112	11.14	101	123
11Cl-PF3OUdS	106	15.8	90	122
3:3FTCA	97.1	39	58	136
5:3FTCA	104	17.52	86	122
7:3FTCA	102	11.14	91	113

Source IDA file: BS_EXPORT_V0_20231122_163114..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 8-7. Landfill Leachate LLOPR Results Summary

Analyte	Number of Labs	Number of Results	Min Concentration ng/L	Max Concentration ng/L	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	Combined std. dev. (s_c)	RSD (s_w)
PFBA	6	14	16.6	79.3	104	9.79	5.41	11.3	5.2
PFPeA	6	14	8.63	40.9	108	11.4	5.76	13.1	5.36
PFHxA	6	14	4.42	35.6	114	20.9	27.7	30.8	24.2
PFHpA	6	14	4.38	19.6	106	9.64	5.46	11.2	5.16
PFOA	6	14	4.36	19.8	108	11.3	5.27	12.9	4.89
PFNA	6	14	4.54	20.8	107	10.8	7.16	12.9	6.67
PFDA	6	14	4.24	20.3	104	12	7.78	14.2	7.47
PFUnA	6	14	3.97	23.5	107	18	10.2	20.9	9.52
PFDoA	6	14	4.16	19.6	104	10.2	5.62	11.8	5.4
PFTrDA	6	14	4.49	20.4	104	13.3	7.46	15.4	7.18
PFTeDA	6	14	4.59	22	105	17.8	5.84	19.8	5.57
PFBS	6	14	4.24	17.1	102	17.7	6.53	19.8	6.39
PFPeS	6	14	3.74	16.8	101	7.36	4.46	8.63	4.43
PFHxS	6	14	3.97	17.8	103	14.9	7.84	17.2	7.64
PFHpS	6	14	3.97	19.6	105	9.14	8.81	11.9	8.42
PFOS	6	14	4.09	18.8	107	9.52	6.51	11.4	6.06
PFNS	6	14	3.89	19.2	101	13	6.82	15	6.78
PFDS	6	14	3.63	17.8	98.3	11.5	5.15	13	5.24
PFDoS	6	14	3.34	18	92.2	10.6	5.92	12.3	6.42
4:2FTS	6	14	16.2	76.4	105	14.7	7.77	16.9	7.43
6:2FTS	6	14	16.1	70.4	102	10.8	8.91	13.5	8.7
8:2FTS	6	14	18.4	79.6	105	18.2	17.1	23.5	16.2
PFOSA	6	14	4.36	18.4	103	6.85	5.52	8.5	5.37
NMeFOSA	6	14	5.31	20.9	108	14.4	19.7	21.5	18.2
NEtFOSA	6	14	4.65	19.6	105	10.8	10.4	14.1	9.95
NMeFOSAA	6	14	4.18	21.2	104	14.8	9.84	17.6	9.47
NEtFOSAA	6	14	4.47	22	106	12.2	11.6	15.8	11
NMeFOSE	6	14	42.9	181	102	7.44	5.63	9.1	5.5

Table 8-7. Landfill Leachate LLOPR Results Summary (Continued)

Analyte	Number of Labs	Number of Results	Min Concentration ng/L	Max Concentration ng/L	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	Combined std. dev. (s_c)	RSD (s_w)
NEtFOSE	6	14	42.7	194	106	7.76	6.39	9.68	6.03
PFMPA	6	14	8.83	35.4	102	5.69	2.04	6.34	1.99
PFMBA	6	14	8.83	40.6	105	11.7	4.12	13	3.94
NFDHA	6	14	8.8	40.8	108	10.8	12.7	15.1	11.7
HFPO-DA	6	14	18	83.9	108	12.5	4.44	14	4.12
ADONA	6	14	15.8	75.5	110	9.99	6.6	11.9	6.02
PFEESA	6	14	8.54	39.5	112	14.7	5.67	16.5	5.07
9Cl-PF3ONS	6	14	15.4	69.2	105	3.52	7	6.52	6.69
11Cl-PF3OUdS	6	14	13.7	76.2	101	9.82	7.91	12.2	7.82
3:3FTCA	6	14	18.5	115	103	16.4	6.21	18.3	6.05
5:3FTCA	6	14	104	468	103	8.44	6.34	10.3	6.15
7:3FTCA	6	14	92.2	439	92.5	12.4	4.46	13.8	4.82
$^{13}C_4$-PFBA	6	14	88.8	481	82.1	9.35	9.18	12.3	11.2
$^{13}C_5$-PFPeA	6	14	42.5	250	88.6	8.47	4.97	9.89	5.62
$^{13}C_5$-PFHxA	6	14	21.3	118	84.9	5.03	4.27	6.33	5.03
$^{13}C_4$-PFHpA	6	14	21	118	83.6	6.49	4.9	7.93	5.87
$^{13}C_8$-PFOA	6	14	19.5	119	82.2	7.66	5.91	9.4	7.18
$^{13}C_9$-PFNA	6	14	10.6	57.8	85.8	6.41	4.66	7.77	5.43
$^{13}C_6$-PFDA	6	14	10.7	66.2	87.5	6.9	8.62	9.9	9.85
$^{13}C_7$-PFUnA	6	14	9.59	57.6	86.8	5.88	7.14	8.33	8.23
$^{13}C_2$-PFDoA	6	14	8.94	66.8	81.7	9.18	7.64	11.5	9.35
$^{13}C_2$-PFTeDA	6	14	7.96	64.7	77.1	12	8.22	14.3	10.7
$^{13}C_3$-PFBS	6	14	18.5	113	86.9	4.7	7.14	7.41	8.22
$^{13}C_3$-PFHxS	6	14	18.9	114	85.7	5.32	3.36	6.28	3.92
$^{13}C_8$-PFOS	6	14	19.5	114	85.4	6.41	7.09	8.76	8.3
$^{13}C_2$-4:2FTS	6	14	46.1	239	96.1	5.7	3.91	6.83	4.07
$^{13}C_2$-6:2FTS	6	14	37.4	243	93.9	6.6	7.42	9.07	7.91
$^{13}C_2$-8:2FTS	6	14	38	245	90.6	7.49	8.28	10.2	9.14

Table 8-7. Landfill Leachate LLOPR Results Summary (Continued)

Analyte	Number of Labs	Number of Results	Min Concentration ng/L	Max Concentration ng/L	Mean % Recovery	Pooled Between-Lab std. dev. (s_b)	Pooled Within-Lab std. dev. (s_w)	Combined std. dev. (s_c)	RSD (s_w)
$^{13}C_8$-PFOSA	6	14	18.4	115	80.1	9.28	7.27	11.4	9.07
D_3-NMeFOSA	6	14	11.5	90.7	53.3	14.7	3.91	16.1	7.33
D_5-NEtFOSA	6	14	12.4	93.3	53.7	14.3	3.84	15.7	7.16
D_3-NMeFOSAA	6	14	41.3	237	86.6	7.15	7.55	9.61	8.72
D_5-NEtFOSAA	6	14	35.9	242	81.4	7.09	7.97	9.74	9.79
D_7-NMeFOSE	6	14	178	1060	74.2	12.3	7.41	14.4	9.98
D_9-NEtFOSE	6	14	169	1040	74	11.5	5.4	13	7.31
$^{13}C_3$-HFPO-DA	6	14	91.8	469	85.1	6.57	3.8	7.66	4.47

Source File: IDA file: LC_LLOPR_results_V0_231122_.1631.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 8-8. Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
PFBA	6	14	7.38	17.8	98.3	12.5	6.34	14.3	6.46
PFPeA	6	14	3.06	9.32	99.7	13.6	7.92	15.8	7.94
PFHxA	6	14	1.84	4.22	94.6	7.91	6.34	9.8	6.7
PFHpA	6	14	1.77	4.43	98.7	11.6	4.89	13.1	4.95
PFOA	6	14	1.9	5.95	104	13	11.4	16.5	11
PFNA	6	14	1.87	4.54	97.5	8.64	6.96	10.7	7.14
PFDA	6	14	1.84	4.36	95.2	12.4	7.9	14.6	8.3
PFUnA	6	14	1.85	4.49	95.9	10.3	7.97	12.6	8.31
PFDoA	6	14	1.88	4.69	102	11.2	8.75	13.7	8.57
PFTrDA	6	14	1.77	4.28	97.1	7.92	7.95	10.5	8.2
PFTeDA	6	14	1.9	4.22	97.9	7.39	6.46	9.36	6.6
PFBS	6	14	1.63	4	99.6	8.2	9.27	11.3	9.3
PFPeS	6	14	1.67	4.27	94.9	10.2	8.64	12.8	9.1
PFHxS	6	14	1.73	4.07	98.9	11.5	4.23	12.9	4.28
PFHpS	6	14	1.55	4.62	97.5	15	10.8	18.1	11.1
PFOS	6	14	1.62	4.13	101	15.8	7.66	18.1	7.58
PFNS	5	12	1.7	4.52	100	14.2	9.53	17.2	9.53
PFDS	6	14	1.6	4.13	94.4	11.4	8.75	14	9.27
PFDoS	6	14	1.51	4.41	87.3	14.9	11.7	18.4	13.5
4:2FTS	6	14	6.89	18.7	96.4	11.4	15.9	17.2	16.4
6:2FTS	6	14	7.07	21.7	114	14.6	39	33.4	34.2
8:2FTS	6	14	7.48	16.1	96.7	8.55	6.96	10.6	7.2
PFOSA	6	14	2	5.2	103	12.8	5.74	14.4	5.55
NMeFOSA	5	12	1.96	4.51	98.8	9.02	7	11.2	7.08
NEtFOSA	5	12	1.94	4.59	98.6	6.52	11.1	11.1	11.2
NMeFOSAA	6	14	1.88	4.28	99.4	12.7	7.78	14.9	7.82
NEtFOSAA	6	14	1.85	5.03	98.9	15.8	10.2	18.8	10.3

Table 8-8. Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
NMeFOSE	6	14	19.5	42.9	98.5	8.25	3.19	9.23	3.24
NEtFOSE	6	14	18.8	42.6	96.5	9.03	6.13	10.8	6.35
PFMPA	6	14	3.33	8.55	85	20	6.58	22.2	7.74
PFMBA	6	14	3.75	11	102	13.1	11.9	16.8	11.7
NFDHA	6	14	3.87	9.64	99.6	12	9.44	14.8	9.48
HFPO-DA	6	14	7.55	18.7	98.9	11.9	8.17	14.3	8.26
ADONA	6	14	7.03	17.7	102	11.3	7.32	13.4	7.21
PFEESA	6	14	3.28	9.23	96.7	11.6	7.92	13.9	8.18
9Cl-PF3ONS	6	14	7.04	18.6	103	10.8	8.92	13.5	8.67
11Cl-PF3OUdS	6	14	6.41	18.2	97.8	11	9.49	13.9	9.7
3:3FTCA	6	14	4.16	21	86	21	7.99	23.5	9.29
5:3FTCA	6	14	32.7	100	91.4	11.9	5.49	13.5	6
7:3FTCA	6	14	35.8	102	88.4	13.3	8.75	15.8	9.9
$^{13}C_4$-PFBA	6	14	9.93	98.1	80.6	28.3	12.2	31.9	15.1
$^{13}C_5$-PFPeA	6	14	20	50.6	89.4	12.9	11.8	16.6	13.2
$^{13}C_5$-PFHxA	6	14	16.5	25.2	97	9.32	5.95	11	6.13
$^{13}C_4$-PFHpA	6	14	15.4	24.4	93.3	12.3	5.54	14	5.94
$^{13}C_8$-PFOA	6	14	11.9	28.2	92.2	16.1	8.6	18.6	9.33
$^{13}C_9$-PFNA	6	14	8.24	12.3	96	5.76	6.8	8.07	7.09
$^{13}C_6$-PFDA	6	14	8.32	12.5	93.6	8.89	5.55	10.5	5.93
$^{13}C_7$-PFUnA	6	14	8.09	12.5	94	6.56	5.88	8.36	6.26
$^{13}C_2$-PFDoA	6	14	6.46	11.9	86	8.54	8.42	11.2	9.79
$^{13}C_2$-PFTeDA	6	14	6.3	11.9	79	10.9	8.54	13.4	10.8
$^{13}C_3$-PFBS	6	14	15.1	23.5	90.9	6.7	7.23	9.07	7.95
$^{13}C_3$-PFHxS	6	14	16.2	25.3	94.2	8.19	4.59	9.5	4.87
$^{13}C_8$-PFOS	6	14	14.6	25.1	92.5	11.5	7.6	13.6	8.21
$^{13}C_2$-4:2FTS	6	14	26.5	58.1	101	9.27	19.1	17.6	18.9

Table 8-8. Biosolids 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)	Combined std. dev. (s_c)	RSD (s_w)
$^{13}C_2$-6:2FTS	6	14	33.8	54.1	101	11.2	10.8	14.6	10.7
$^{13}C_2$-8:2FTS	6	14	31	57	102	10.8	16.4	17	16
$^{13}C_8$-PFOSA	6	14	11.8	22.9	87.4	15.1	6.69	17.1	7.65
D_3-NMeFOSA	5	12	6.67	17.1	55.9	17.3	6.82	19.6	12.2
D_5-NEtFOSA	5	12	6.28	16.8	51.7	16	5.94	18.1	11.5
D_3-NMeFOSAA	6	14	29.2	52.6	96.8	15.6	8.17	17.9	8.43
D_5-NEtFOSAA	6	14	28.8	51.2	93.1	16.3	11.5	19.6	12.4
D_7-NMeFOSE	6	14	98.6	224	73.8	19.7	6.86	21.9	9.3
D_9-NEtFOSE	6	14	100	214	70.7	18.8	6.94	21	9.81
$^{13}C_3$-HFPO-DA	6	14	56.5	104	92.4	11.7	8.19	14.1	8.87

Source File: IDA file: BS_LLOPR_results_V0_231204_113058..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 8-9. Statistically Derived Landfill Leachate LLOPR Acceptance Criteria

Analytes	Landfill Leachate Mean % Recovery	Landfill Leachate 2 x RSD[1]	Landfill Leachate LCL[2]	Landfill Leachate UCL[3]
PFBA	104	10.4	94	114
PFPeA	108	10.72	97	119
PFHxA	114	48.4	66	162
PFHpA	106	10.32	96	116
PFOA	108	9.78	98	118
PFNA	107	13.34	94	120
PFDA	104	14.94	89	119
PFUnA	107	19.04	88	126
PFDoA	104	10.8	93	115
PFTrDA	104	14.36	90	118
PFTeDA	105	11.14	94	116
PFBS	102	12.78	89	115
PFPeS	101	8.86	92	110
PFHxS	103	15.28	88	118
PFHpS	105	16.84	88	122
PFOS	107	12.12	95	119
PFNS	101	13.56	87	115
PFDS	98.3	10.48	88	109
PFDoS	92.2	12.84	79	105
4:2FTS	105	14.86	90	120
6:2FTS	102	17.4	85	119
8:2FTS	105	32.4	73	137
PFOSA	103	10.74	92	114
NMeFOSA	108	36.4	72	144
NEtFOSA	105	19.9	85	125
NMeFOSAA	104	18.94	85	123
NEtFOSAA	106	22	84	128
NMeFOSE	102	11	91	113
NEtFOSE	106	12.06	94	118
PFMPA	102	3.98	98	106
PFMBA	105	7.88	97	113
NFDHA	108	23.4	85	131
HFPO-DA	108	8.24	100	116
ADONA	110	12.04	98	122
PFEESA	112	10.14	102	122
9Cl-PF3ONS	105	13.38	92	118
11Cl-PF3OUdS	101	15.64	85	117
3:3FTCA	103	12.1	91	115
5:3FTCA	103	12.3	91	115
7:3FTCA	92.5	9.64	83	102

Source Files: derived from IDA file: LC_LLOPR_results_V0_231122_.1631.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 8-10. Statistically Derived Biosolids LLOPR Acceptance Criteria

Analytes	Biosolids Mean % Recovery	Biosolids 2 x RSD[1]	Biosolids LCL[2]	Biosolids UCL[3]
PFBA	98.3	12.92	85	111
PFPeA	99.7	15.88	84	116
PFHxA	94.6	13.4	81	108
PFHpA	98.7	9.9	89	109
PFOA	104	22	82	126
PFNA	97.5	14.28	83	112
PFDA	95.2	16.6	79	111
PFUnA	95.9	16.62	79	113
PFDoA	102	17.14	85	119
PFTrDA	97.1	16.4	81	114
PFTeDA	97.9	13.2	85	111
PFBS	99.6	18.6	81	118
PFPeS	94.9	18.2	77	113
PFHxS	98.9	8.56	90	108
PFHpS	97.5	22.2	75	120
PFOS	101	15.16	86	116
PFNS	98.3	19.06	81	119
PFDS	99.7	18.54	76	113
PFDoS	94.6	27	60	114
4:2FTS	98.7	32.8	64	129
6:2FTS	104	68.4	46	182
8:2FTS	97.5	14.4	82	111
PFOSA	95.2	11.1	92	114
NMeFOSA	95.9	14.16	85	113
NEtFOSA	102	22.4	76	121
NMeFOSAA	97.1	15.64	84	115
NEtFOSAA	97.9	20.6	78	120
NMeFOSE	99.6	6.48	92	105
NEtFOSE	94.9	12.7	84	109
PFMPA	98.9	15.48	70	100
PFMBA	97.5	23.4	79	125
NFDHA	101	18.96	81	119
HFPO-DA	98.9	16.52	82	115
ADONA	102	14.42	88	116
PFEESA	96.7	16.36	80	113
9Cl-PF3ONS	103	17.34	86	120
11Cl-PF3OUdS	97.8	19.4	78	117
3:3FTCA	86	18.58	67	105
5:3FTCA	91.4	12	79	103
7:3FTCA	88.4	19.8	69	108

Source File: IDA file: BS_LLOPR_results_V0_231204_113058.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.

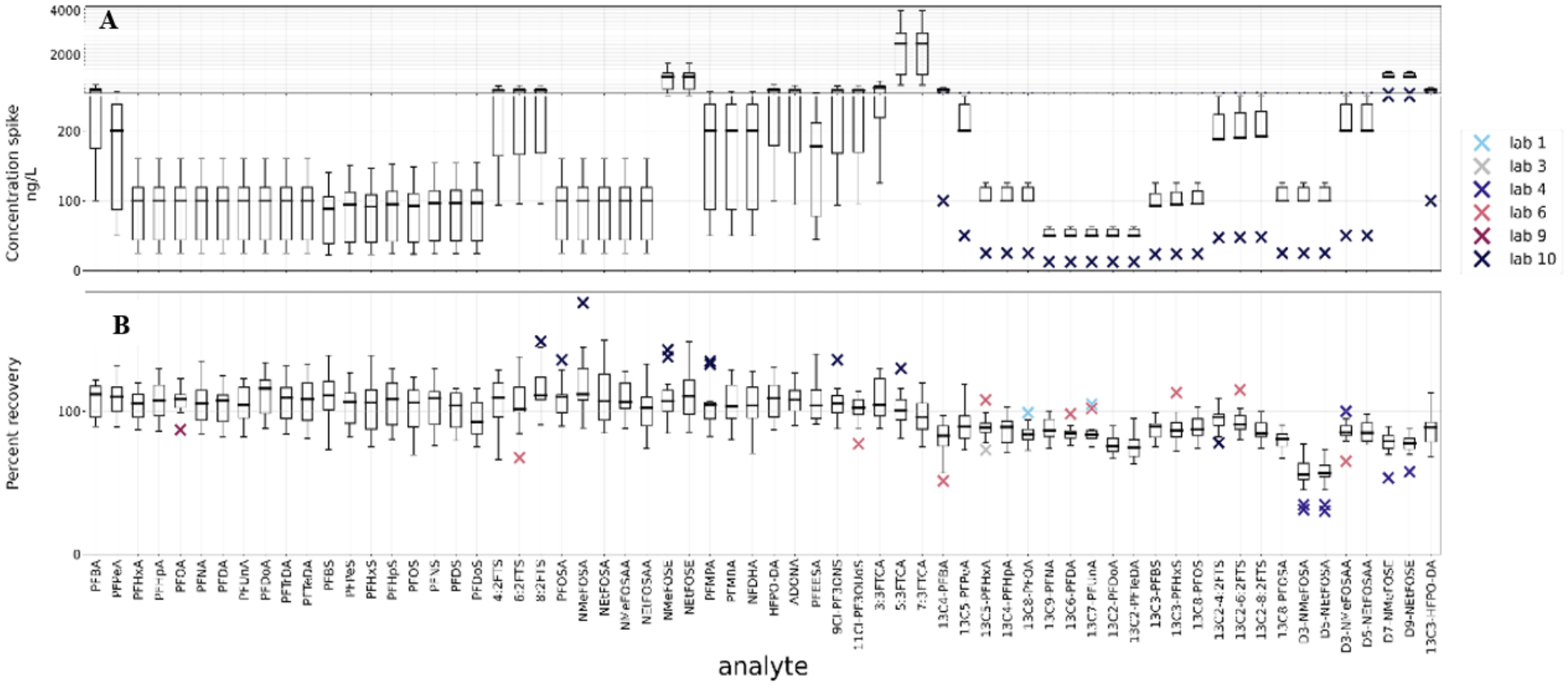


Figure 8-1. Landfill Leachate OPR results by compound by laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all OPR data batched with unspiked and spiked samples.

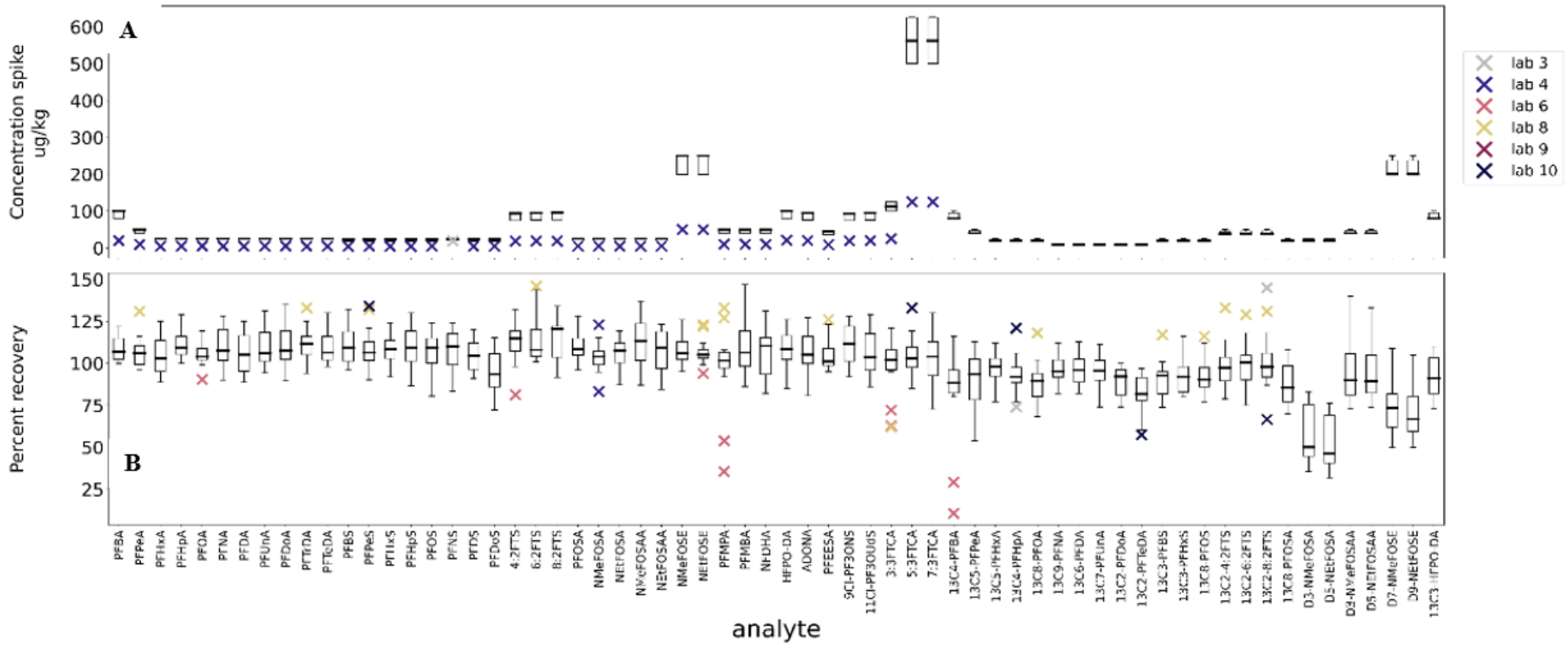


Figure 8-2. Biosolids LLOPR results by compound by laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all LLOPR data batched with unspiked and spiked samples.

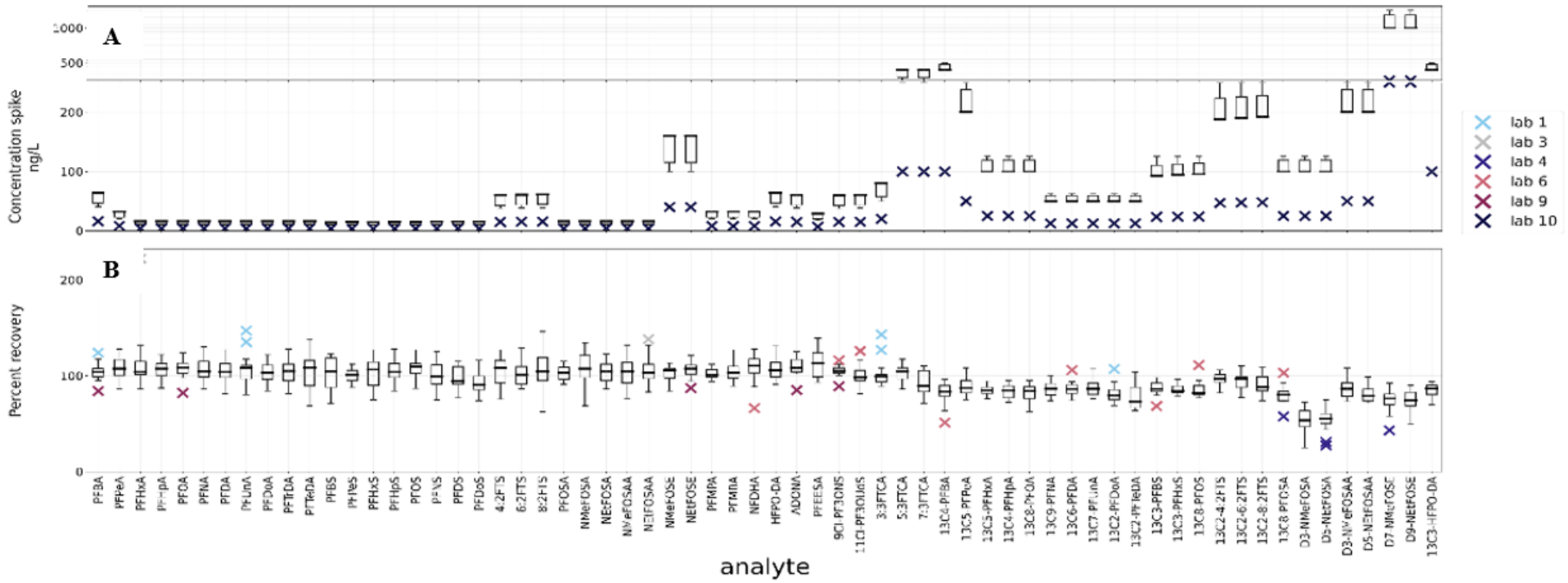


Figure 8-3. Landfill Leachate LLOPR results by compound by laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all LLOPR data batched with unspiked and spiked samples.

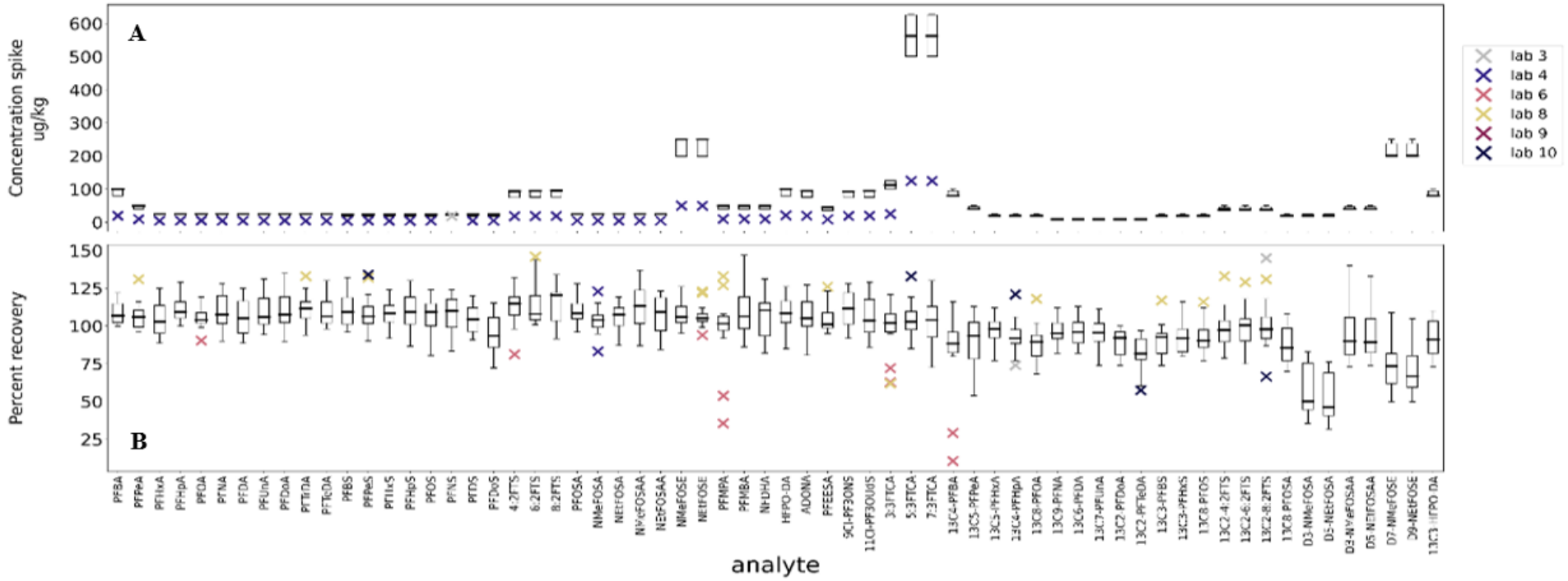


Figure 8-4. Biosolids LLOPR results by compound by laboratory

(A) Spiked Concentration. (B) Calculated percent recovery.
Figure includes all LLOPR data batched with unspiked and spiked samples.

8.2 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. For further discussion of the relationship 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.*

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 landfill leachate and biosolids samples were compiled and descriptive statistics for each NIS compound were generated across all landfill leachate and biosolid samples. Tables 8-11 (landfill leachates) and 8-12 (biosolids) summarize 893 (landfill leachates) and 944 (biosolids) NIS compound recoveries met the target recovery criteria (>30%). All landfill leachate NIS compound recoveries met not only the target recovery criteria of >30% but met the criteria for aqueous media for NIS recoveries (50-200%) stated in 4th Draft EPA 1633. All biosolid NIS compound recoveries met the target recovery criteria of >30%, and all met the NIS recoveries (50-200%) stated in 4th Draft EPA 1633 as well, with the exception of 7 NIS compound results from Laboratory 3. Laboratory 3 reported recoveries for $^{13}C_4$-PFOS that ranged from 269% to 675% for the BSAJ series of samples.

8.3 LANDFILL LEACHATE 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"), laboratories ("Lab"), and spike concentrations ("Spike Conc."). Because the final working dataset consisted of missing permutations of main effects (see Section 6 above), 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). All PFAS on average were observed with mean recoveries 70-130% of the target spike concentration with the exception for PFDoS (Figure 8-5). Spike Conc. and Lab main effects were also relatively consistent and close to the target spike concentration (i.e., 100% recovery) (Figure 8-6).

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 percent relative standard deviation (RSD) among replicate measures of the various spiked samples. Figure 8-7 illustrates the calculated accuracy and precision on a unit scale such that the results can be interpreted quantitively (i.e., a literal bullseye target, Figure 8-7). The method as validated by this multi-laboratory study can be summarized to result in less than 30% error for the landfill leachate matrix. Figure 8-8 provides a summary of the accuracy and precision for each aqueous matrix and Table 8-12 provides the percent probability of observing a result with <30% error for each aqueous matrix: groundwater (GW), surface water (SW), wastewater (WW), and landfill leachate (LC).

Table 8-11. Accuracy analysis: ANOVA results for the observed matrix spike recoveries

Effect	F Value	P Value
Laboratory	105.26	<0.0001
PFAS	33.02	<0.0001
Spike Concentration	10.78	<0.001

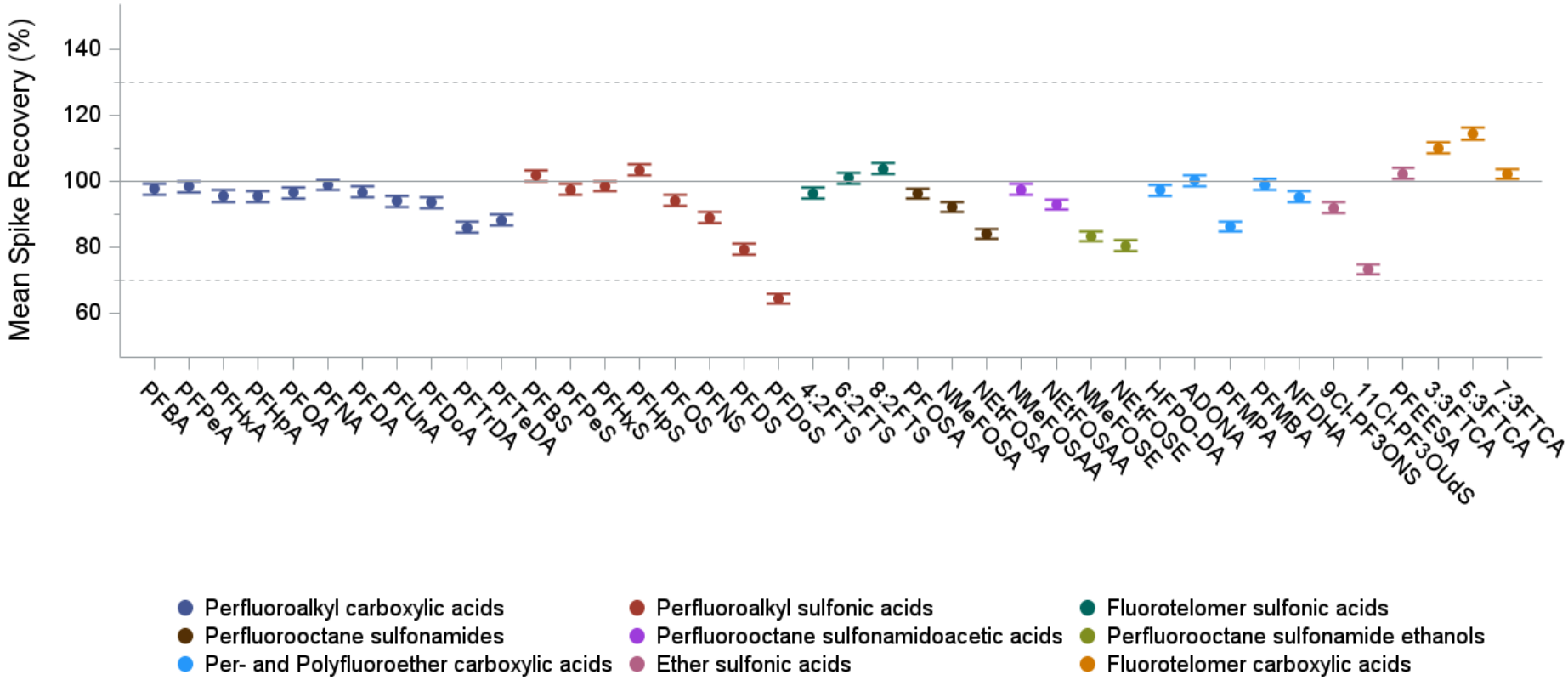


Figure 8-5. Mean spike recoveries summarized for each target analyte (i.e., the "PFAS" effect)

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

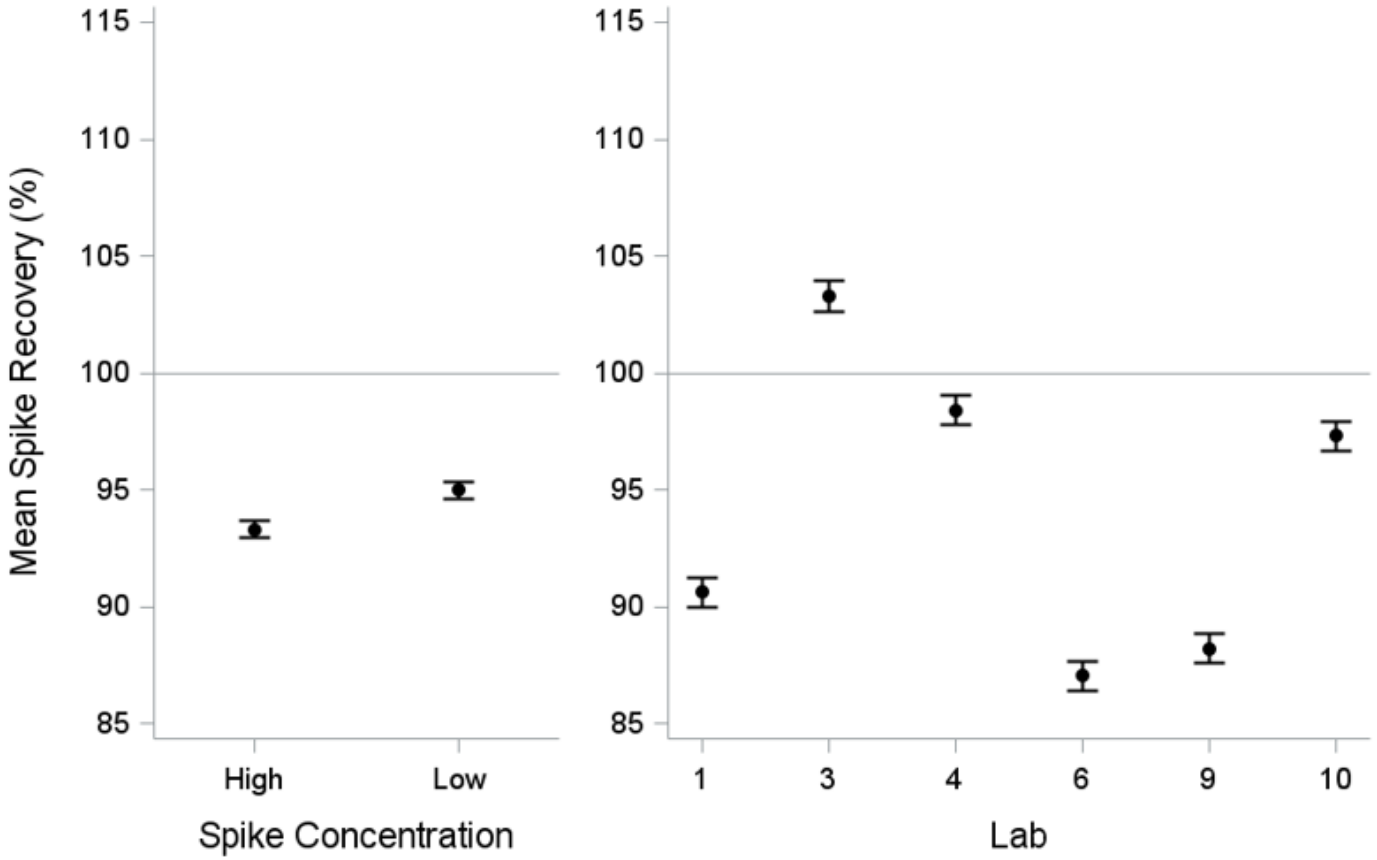


Figure 8-6. Mean spike recoveries summarized for each matrix, spike concentration, and laboratory (i.e., the "Matrix", "Spike Conc." and "Lab" effects)

Error bars reflect one standard error.

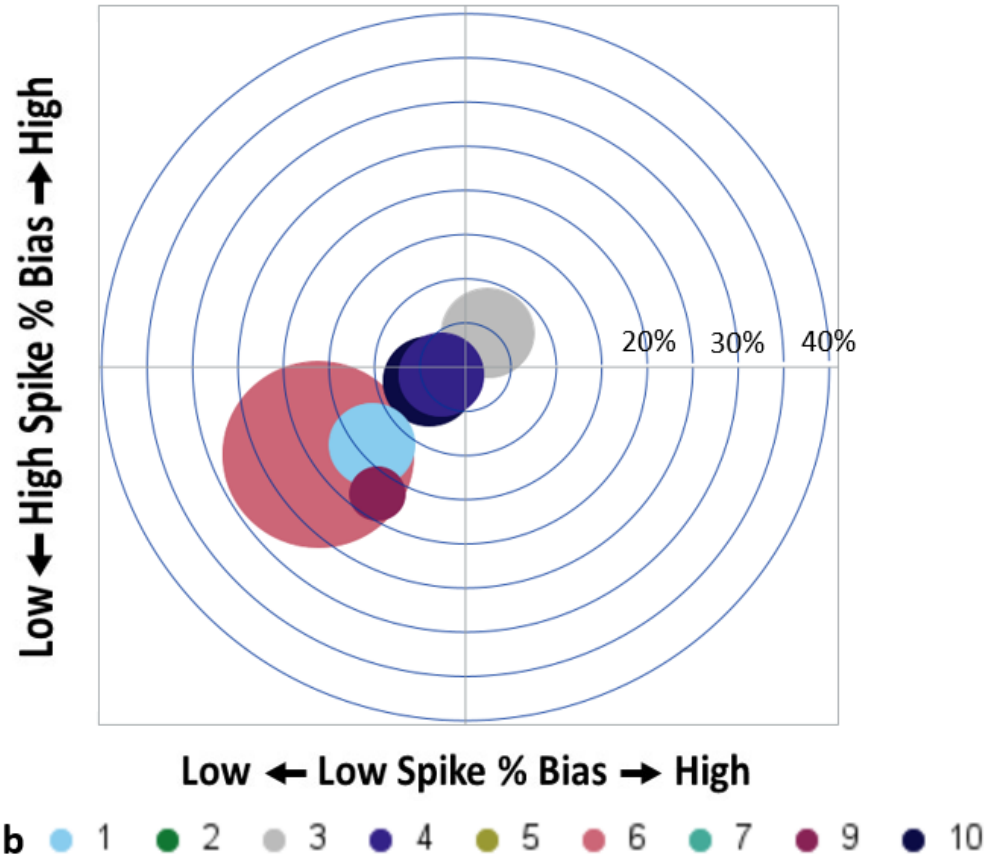


Figure 8-7. Summary illustration of the overall method accuracy and precision for Landfill Leachate

Bubble sizes reflect precision calculated as the intra-laboratory percent relative standard deviation (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.

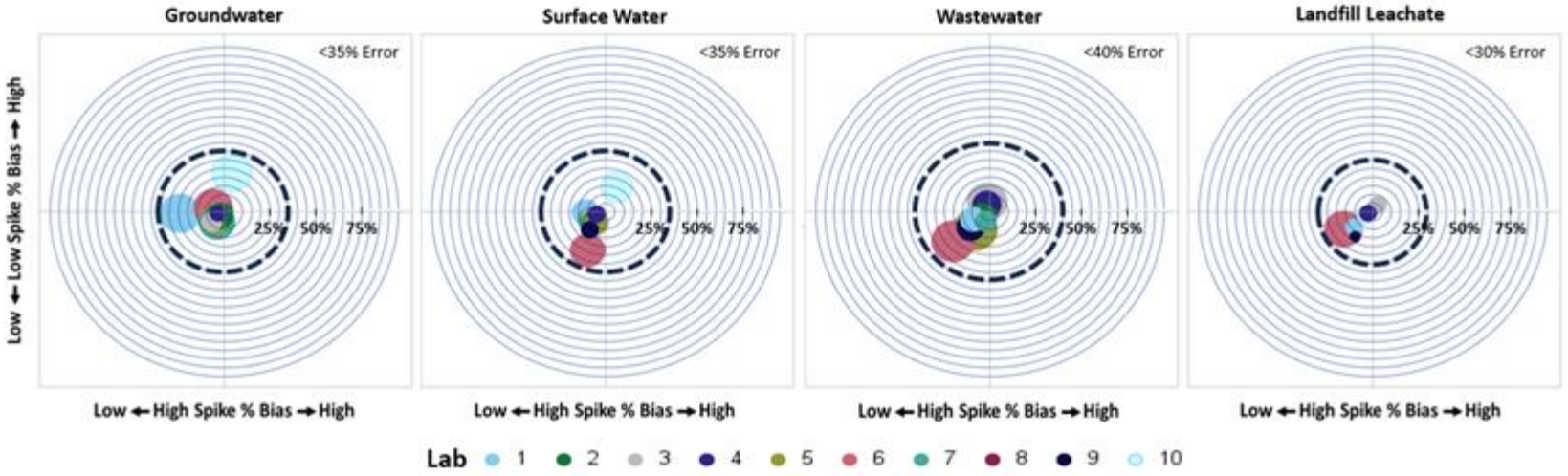


Figure 8-8. Summary illustration of a comparison of the overall method accuracy and precision for each aqueous media

Table 8-12. Probability (%) of observing a result with <30% error in aqueous media measured with EPA Method 1633

Analyte	GW Probability (%)	SW Probability (%)	WW Probability (%)	LC Probability (%)
PFBA	97.8	98.5	97.4	100
PFPeA	99.3	98.8	94.9	100
PFHxA	90.8	99.4	97.1	100
PFHpA	92	99.4	96.6	98.1
PFOA	90.2	98.1	95.1	99.1
PFNA	97.8	97.5	96.9	100
PFDA	94.7	97.5	96.2	99.1
PFUnA	95.7	96.2	96.2	90.7
PFDoA	95.5	93.7	89.8	93.5
PFTrDA	92.5	89.9	70.7	87
PFTeDA	90.9	94.9	85.8	78.7
PFBS	95.7	96.9	94.8	94.4
PFPeS	91.3	95.7	95.8	98.1
PFHxS	88	96.9	96.5	95.4
PFHpS	82.4	92.4	93.7	96.3
PFOS	76.8	93.8	96.2	94.4
PFNS	92.6	94.3	82.6	87
PFDS	86.6	75.6	57.1	81.5
PFDoS	58.2	30.4	22.3	46.3
4:2FTS	96.4	97.5	94.8	95.3
6:2FTS	85.7	92.5	93.4	95.4
8:2FTS	87	92.5	91.3	94.4
PFOSA	92.4	94.4	94.2	100
NMeFOSA	96.3	97.5	91.8	93.5
NEtFOSA	95.5	95	89.1	85.2
NMeFOSAA	70.1	64.4	64.3	91.7
NEtFOSAA	70.3	64.2	71.4	87
NMeFOSE	89.8	85.9	85.1	80.6
NEtFOSE	80.2	75	82.1	79
PFMPA	88.5	57.1	75.2	89.8
PFMBA	94.2	96.9	82.9	100
NFDHA	95	97.5	82.6	87
HFPO-DA	92.1	100	92.7	100
ADONA	88.4	95.7	81.5	98.1
PFEESA	96.4	99.4	94.1	98.1
9Cl-PF3ONS	83.2	88.7	75.3	88
11Cl-PF3OUdS	68.4	58.2	51.2	62
3:3FTCA	92.6	70.8	77.3	80.6
5:3FTCA	99.3	95.7	92	86
7:3FTCA	94.9	75.8	86.1	95.4

Source: AFCEC Calculations Chapter 8 Tables.xlsx

8.4 BIOSOLIDS 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"), and spike concentrations ("Spike Conc."). Because the final working dataset consisted of missing permutations of main effects (see Section 7 above), 1) no interaction effects were evaluated and 2) the Least Squares Means from the ANOVA predictions are reported to reflect mean differences more accurately (i.e., marginal means that control for other model parameters). All main effects were significant with greater than 99% confidence (Table 8-12). All PFAS on average were observed with mean recoveries of 70-130% of the target spike concentration with exception for PFDoS and PFNS (Figure 8-9). Matrix, Spike Conc., and Lab main effects were also relatively consistent and close to the target spike concentration (i.e., 100% recovery) (Figure 8-10).

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 percent relative standard deviation (RSD) among replicate measures of the various spiked samples. Figure 8-11 illustrates the calculated accuracy and precision on a unit scale such that the results can be interpreted quantitively (i.e., a literal bullseye target). Overall, the method as validated by this multi-laboratory study can be summarized to result in less than 90% error for biosolids matrix. Table 8-14 provides the percent probability of observing a result with <30% error for each solid matrix: soil, sediment, and biosolids.

Table 8-13. Accuracy analysis: ANOVA results for the observed matrix spike recoveries

Effect	F Value	P Value
Laboratory	632	<0.0001
PFAS	21.6	<0.0001
Spike Concentration	14.4	<0.0001

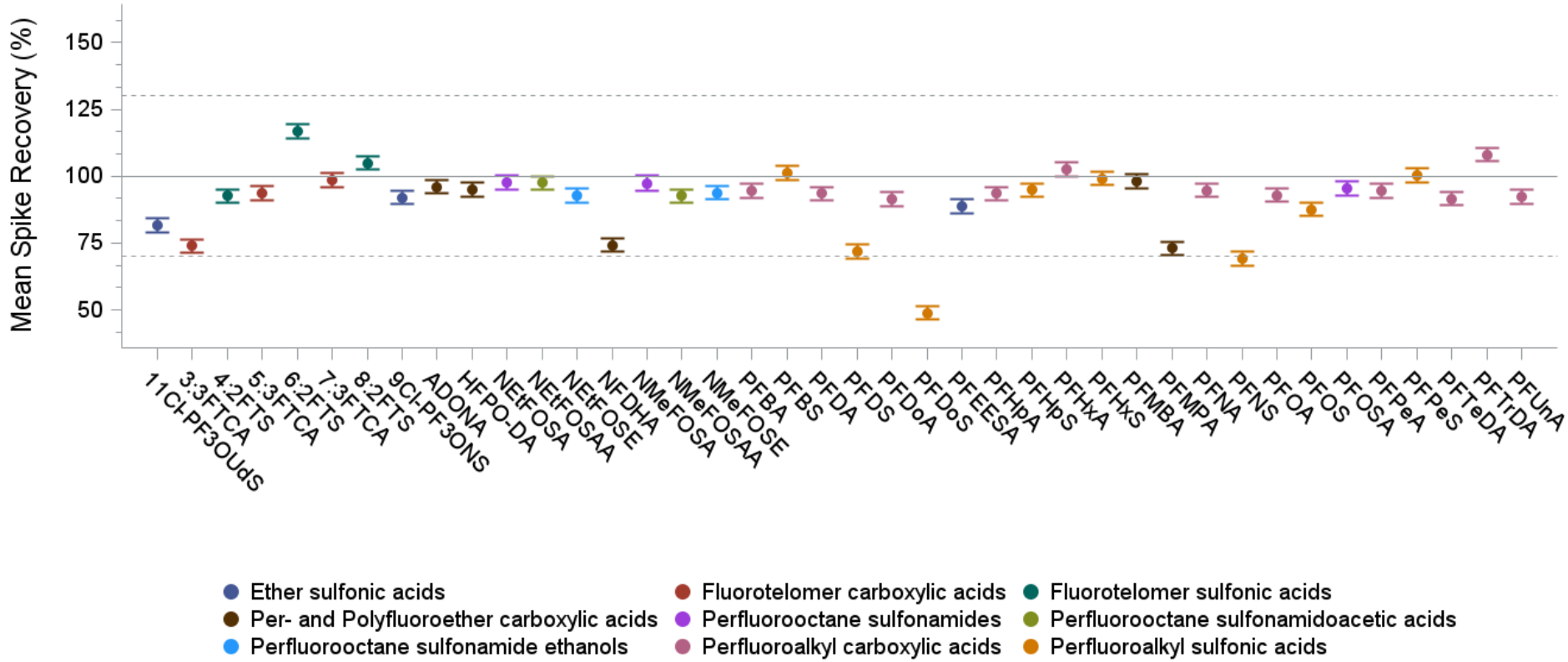


Figure 8-9. Mean spike recoveries summarized for each target analyte (i.e., the "PFAS" effect in Table 8-13)

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

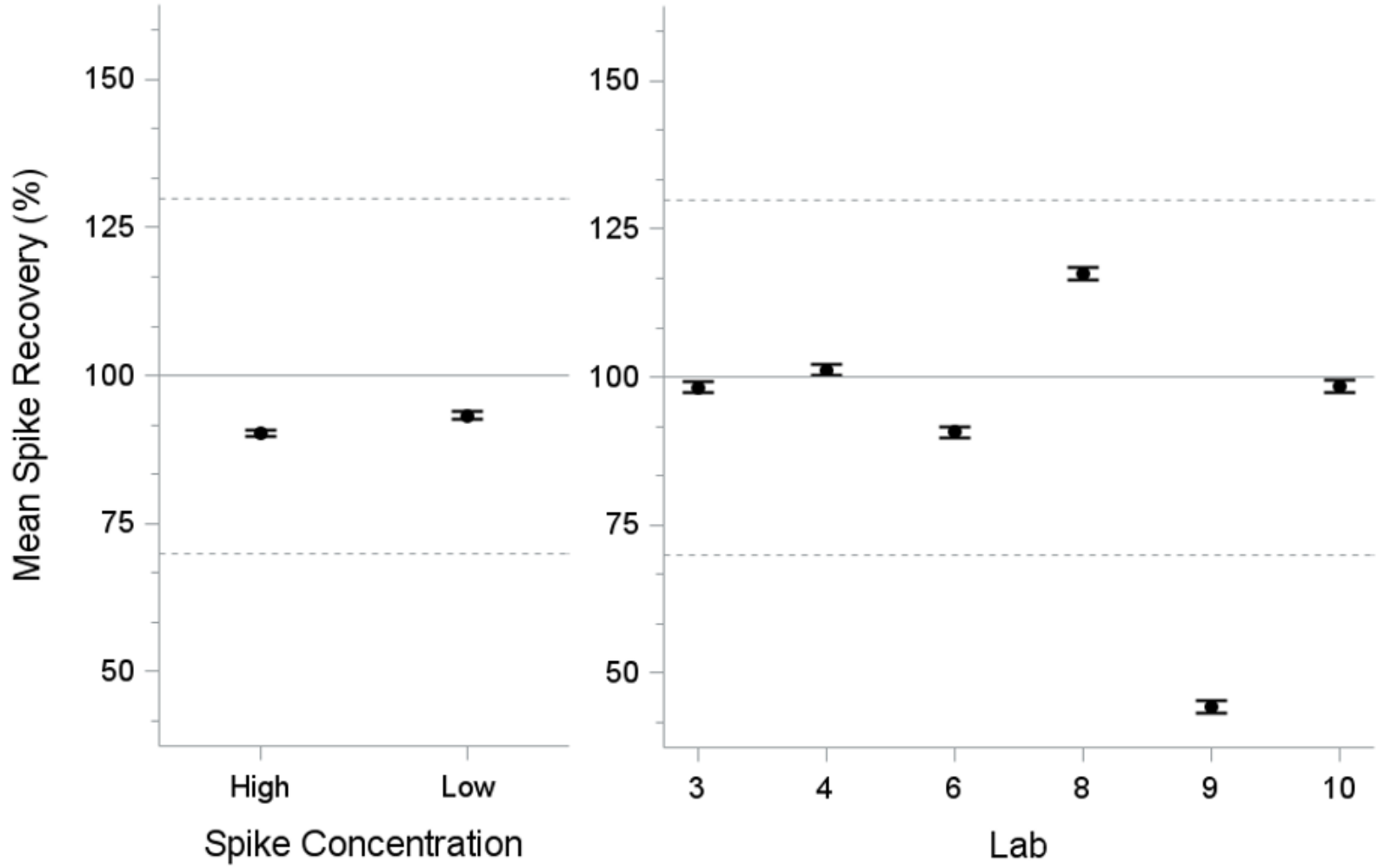


Figure 8-10. Mean spike recoveries summarized for each matrix, spike concentration, and laboratory (i.e., the "Matrix", "Spike Conc." and "Lab" effects in Table 8-13, respectively)

Error bars reflect one standard error.

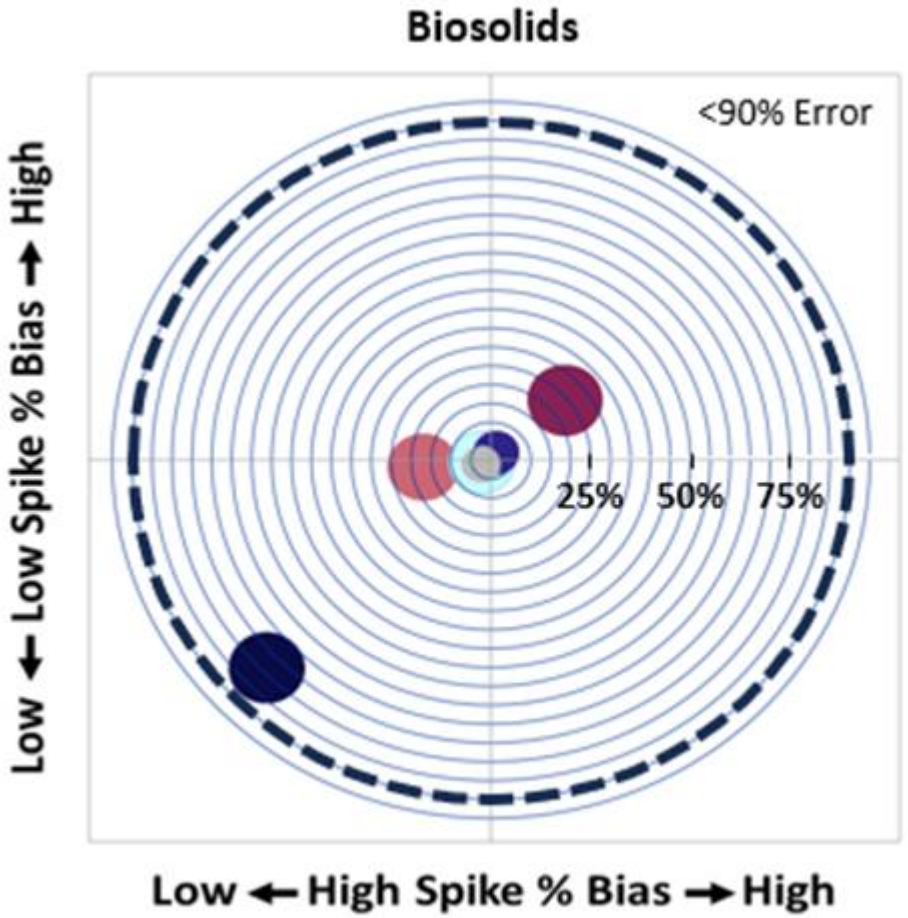


Figure 8-11. Summary illustration of the overall method accuracy and precision for the biosolids

Bubble sizes reflect precision calculated as the inter-laboratory percent relative standard deviation (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.

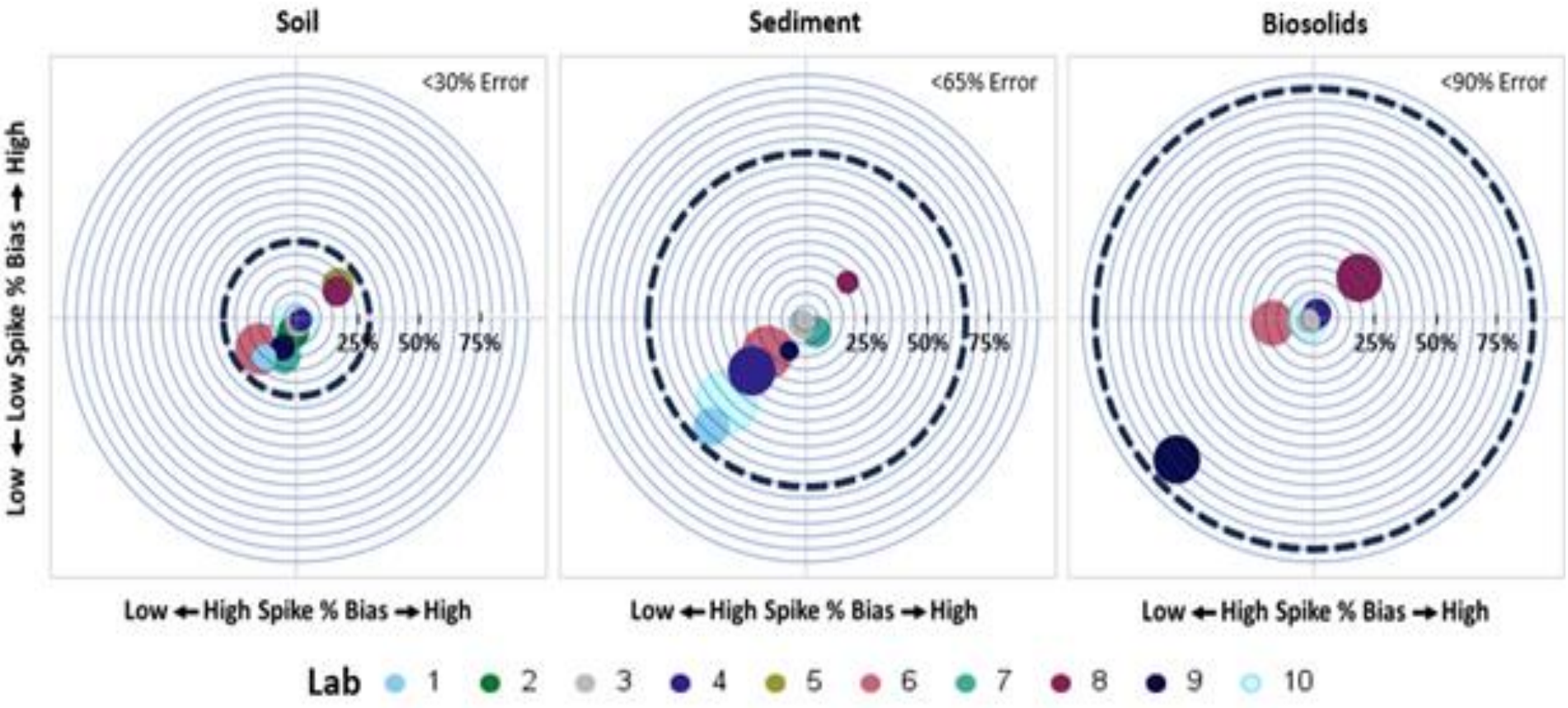


Figure 8-12. Summary illustration of a comparison of the overall method accuracy and precision for each solid media

Table 8-14. Probability (%) of observing a result with <30% error in solid media measured with EPA Method 1633

Analyte	Soil Probability (%)	Sediment Probability (%)	Biosolid Probability (%)
PFBA	98.8	92.5	81.4
PFPeA	96.6	91.4	72.2
PFHxA	99.4	89.3	62.7
PFHpA	98.3	87.9	81.5
PFOA	99.4	80	79.6
PFNA	95.5	75	82.4
PFDA	96.6	76.4	75.9
PFUnA	96.6	71.4	80.6
PFDoA	96.6	69.3	80.6
PFTrDA	94.4	57.9	52.3
PFTeDA	97.2	67.9	77.8
PFBS	99.4	84.3	70.4
PFPeS	98.3	86.4	70.5
PFHxS	99.4	84.3	72.2
PFHpS	95.5	83.6	70.5
PFOS	100	77.9	70.4
PFNS	98.3	67.9	50
PFDS	92.2	65	56.5
PFDoS	80.4	52.1	21.3
4:2FTS	95.5	82.9	74.1
6:2FTS	94.4	79.6	64.8
8:2FTS	90.5	73.6	65.7
PFOSA	98.9	75	80.6
NMeFOSA	99.4	69.1	80
NEtFOSA	99.4	69.2	80
NMeFOSAA	97.8	68.6	79.6
NEtFOSAA	97.8	72.9	74.1
NMeFOSE	98.3	69.3	75
NEtFOSE	98.9	67.9	82.4
PFMPA	85.5	80	51.9
PFMBA	97.8	91.4	71.3
NFDHA	94.4	82.1	61.1
HFPO-DA	97.8	92.1	81.5
ADONA	91.1	88.6	72.2
PFEESA	96.6	88.6	79.6
9Cl-PF3ONS	88.3	86.4	71.3
11Cl-PF3OUdS	88.2	67.1	73.1
3:3FTCA	52	73.6	54.6
5:3FTCA	66.5	72.1	45.4
7:3FTCA	62	64.3	50

Source: AFCEC Calculations Chapter 8 Tables.xlsx

8.5 DETERMINATION OF FINAL QC SPECIFICATIONS FOR LANDFILL LEACHATES FOR METHOD 1633

EPA and DoD used the same approach to determine the EIS and NIS QC acceptance criteria for the landfill leachate that they used for the results from the aqueous portion of the method validation study (see Section 9.5) with one exception. Because PFAS-free reagent water was used as the IPR reference matrix for the landfill leachates as well as for the groundwater, surface water, and wastewater in the aqueous portion of the study, DoD and EPA agreed that to reduce the burden on the laboratories and encourage more laboratories to participate in the landfill leachate portion of the study, t the same IPR data from the 9 laboratories in the aqueous portion of the study would be used in the landfill leachate portion. The OPR and LLOPR results generated during the landfill leachate portion was evaluated to determine leachate specific OPR and LLOPR criteria. The OPR and LLOPR results came from only 6 laboratories, while the IPR results were from 9 laboratories.

The only difference between the OPR and LLOPR landfill leachate samples and other aqueous matrices is that a smaller volume is used. Following completion of the statistical calculations, EPA and DoD examined the initial acceptance limits and agreed to take several additional steps that will allow EPA to establish the final QC specifications for Method 1633 for OPRs, LLOPRs, EIS compound, and NIS compound recoveries. Among those steps were:

- Additional analyses using statistical procedures previously applied to evaluate 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.
- Comparing the combined OPR and LLOPR data from the landfill leachate to the QC criteria that were generated for aqueous samples, since they use the same reference matrix reagent free water.
- 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

Because the IPR data were the same as that used for the aqueous portion of the study, the SAS calculation summary for the IPR data is not repeated here but is available in *Volume I*. Table 8-15 contains the initial SAS calculations of the OPR/LLOPR limits for the 40 target analytes using the entire leachate data set (all 6 laboratories), with the calculated recoveries, RSDs, minimum and maximum observed recoveries rounded to the nearest 1%.

Table 8-15. 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	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	Min. Obs. Rec.	Max. Obs. Rec.
PFBA	50	6	104	22	46	162	84	124
PFPeA	50	6	105	18	60	149	86	132
PFHxA	50	6	106	36	47	165	86	222
PFHpA	50	6	106	20	48	165	86	130
PFOA	50	6	108	19	47	169	82	124
PFNA	50	6	105	21	53	157	84	135
PFDA	50	6	103	21	55	150	81	127
PFUnA	50	6	105	30	49	161	80	147
PFDoA	50	6	105	21	62	148	84	134
PFTrDA	50	6	100	25	51	150	81	132
PFTeDA	50	6	104	22	47	161	69	138
PFBS	50	6	104	22	55	152	71	139
PFPeS	50	6	104	23	54	154	82	127
PFHxS	50	6	101	26	53	149	75	139
PFHpS	50	6	104	22	46	162	80	130
PFOS	50	6	104	26	55	153	70	127
PFNS	50	6	100	23	59	141	75	130
PFDS	50	6	99	26	58	141	77	116
PFDoS	50	6	93	27	47	138	74	116
4:2FTS	50	6	106	26	61	150	66	129
6:2FTS	50	6	103	26	50	155	68	138
8:2FTS	50	6	108	35	52	164	62	149
PFOSA	50	6	104	16	59	149	90	136
NMeFOSA	50	6	106	32	52	160	69	176
NEtFOSA	50	6	102	26	57	147	85	150
NMeFOSAA	50	6	104	24	60	148	76	132
NEtFOSAA	50	6	104	24	56	152	74	138
NMeFOSE	50	6	102	20	70	133	84	143
NEtFOSE	50	6	102	20	67	137	85	149
HFPO-DA	50	6	104	22	63	145	87	131
ADONA	50	6	105	22	70	141	85	127
9Cl-PF3ONS	50	6	104	22	67	140	88	136
11Cl-PF3OUdS	50	6	99	26	55	142	77	126
3:3FTCA	50	6	101	24	65	136	88	143
5:3FTCA	50	6	101	21	69	132	81	130
7:3FTCA	50	6	95	28	55	135	71	120
PFEESA	50	6	104	28	61	148	91	140
PFMPA	50	6	99	18	66	132	83	135
PFMBA	50	6	100	18	65	136	80	129
NFDHA	50	6	104	35	40	169	66	128

Source file: EPA_GDIT Chapter 8 Tables.xlsx

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

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:

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

As noted above, DoD and EPA decided to apply the IPR data from the aqueous portion of the study to the landfill leachate portion of the study. As a result, the same final IPR limits will be applied to landfill leachate analyses in Method 1633. Table 8-16 presents the IPR QC acceptance criteria that appear in Table 9-21 of *Volume I* for aqueous media.

Table 8-16. Final IPR Acceptance Limits

Analyte	IPR Max RSD	IPR Lower Limit (%)	IPR Upper Limit (%)
PFBA	21	70	135
PFPeA	23	70	135
PFHxA	24	70	135
PFHpA	28	70	135
PFOA	27	65	155
PFNA	28	70	140
PFDA	26	65	140
PFUnA	29	70	135
PFDoA	21	70	130
PFTrDA	29	60	145
PFTeDA	27	70	145
PFBS	23	70	140
PFPeS	25	70	135
PFHxS	27	70	135
PFHpS	30	70	140
PFOS	29	70	140
PFNS	29	70	135
PFDS	30	70	135
PFDoS	35	45	135
4:2FTS	27	70	135
6:2FTS	32	70	135
8:2FTS	33	70	140
PFOSA	22	70	135
NMeFOSA	30	70	135
NEtFOSA	26	70	130
NMeFOSAA	32	65	140
NEtFOSAA	28	70	135
NMeFOSE	29	70	135

Table 8-16. Final IPR Acceptance Limits (Continued)

Analyte	IPR Max RSD	IPR Lower Limit (%)	IPR Upper Limit (%)
NEtFOSE	21	70	130
HFPO-DA	23	70	135
ADONA	23	70	135
9Cl-PF3ONS	30	70	145
11Cl-PF3OUdS	35	50	150
3:3FTCA	23	70	130
5:3FTCA	24	70	130
7:3FTCA	34	55	130
PFEESA	25	70	135
PFMPA	23	60	140
PFMBA	27	65	145
NFDHA	37	65	140

Source file: EPA_GDIT Chapter 8 Tables.xlsx

The OPR statistically generated criteria shown in Table 8-15 are different from the criteria for the OPR and LLOPR data that was generated for the aqueous matrices, sometimes wider sometimes narrower. There were 28 OPR and LLOPR landfill leachate data samples run with the actual landfill leachates (1,120 data points). When the actual data were compared to the current aqueous criteria, only 7 data points were outside of the aqueous criteria (roughly 0.6%). Given that 99.4% of the landfill leachate LLOPRs and OPR data fit within the aqueous criteria, the aqueous criteria are deemed adequate for landfill leachate. Using the same criteria also simplifies the QC for the method.

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 aqueous sample portion of the study (Table 8-17).

Table 8-17. Final OPR/LLOPR Acceptance Limits for Landfill Leachate Samples

Analyte	Aqueous OPR/LLOPR Lower Limit (%)	Aqueous OPR/LLOPR Upper Limit (%)	# Landfill Leachate LLOPR/OPR Results Below Aqueous Limit	# Landfill Leachate LLOPR/OPR Results Above Aqueous Limit
PFBA	70	145		
PFPeA	65	135		
PFHxA	70	145		One data point: 222%
PFHpA	70	150		
PFOA	70	150		
PFNA	70	150		
PFDA	70	140		
PFUnA	70	145		One data point: 147%
PFDoA	70	140		

Table 8-17. Final OPR/LLOPR Acceptance Limits for Landfill Leachate Samples (Continued)

Analyte	Aqueous OPR/LLOPR Lower Limit (%)	Aqueous OPR/LLOPR Upper Limit (%)	# Landfill Leachate LLOPR/OPR Results Below Aqueous Limit	# Landfill Leachate LLOPR/OPR Results Above Aqueous Limit
PFTrDA	65	140		
PFTeDA	50	140		
PFBS	60	145		
PFPeS	65	140		
PFHxS	65	145		
PFHpS	70	150		
PFOS	55	150		
PFNS	65	145		
PFDS	60	145		
PFDoS	50	145		
4:2FTS	70	145	One data point: 66%	
6:2FTS	65	155		
8:2FTS	60	150		
PFOSA	70	145		
NMeFOSA	60	150		One data point: 176%
NEtFOSA	65	145		One data point: 150%
NMeFOSAA	50	140		
NEtFOSAA	70	145		
NMeFOSE	70	145		
NEtFOSE	70	135		One data point: 149%
HFPO-DA	70	140		
ADONA	65	145		
9Cl-PF3ONS	70	155		
11Cl-PF3OUdS	55	160		
3:3FTCA	65	130		One data point: 143%
5:3FTCA	70	135		
7:3FTCA	50	145		
PFEESA	70	140		
PFMPA	55	140		
PFMBA	60	150		
NFDHA	50	150		

Source file: EPA_GDIT Chapter 8 Tables.xlsx

Most of the acceptance criteria in Tables 8-15 and 8-16 are inclusive of the highest or lowest observed result from Table 8-15.

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.

The acceptance limits in Table 8-18 were developed from the entire study landfill leachate sample data set of 126 recoveries per EIS compound using both a non-parametric approach and professional judgement. 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.

Table 8-18. EIS Compound Acceptance Limits Applicable to Landfill Leachate Sample Types

EIS Compound	Lower Limit (%)	Upper Limit (%)	Notes
$^{13}C_4$-PFBA *	5	130	The five lowest recoveries were: 4, 4.1, 4.6, 5.5, 7.5, 8.1. The lowest recover that was not from Laboratory 4 is 25%.
$^{13}C_5$-PFPeA	40	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	35	130	
$^{13}C_2$-PFTeDA	25	130	The lowest recovery was 16%. The second lowest recovery was 25%. Over 99% of the data was 25% or greater.
$^{13}C_3$-PFBS	40	130	
$^{13}C_3$-PFHxS	40	130	
$^{13}C_8$-PFOS	40	130	
$^{13}C_2$-4:2FTS	40	220	The lowest recovery was 38%. The 7 lowest recoveries were from Laboratory 9 (38, 39, 43, 43, 45, 47, and 51). The lowest recover from a different laboratory was 63%.
$^{13}C_2$-6:2FTS	40	170	The highest recovery was 173%. The 8 highest recoveries were from Laboratory 6 (173, 168, 168, 154, 146, 145, 145, 140). Over 99% of the data was 170% or lower. The highest recovery not from Laboratory 6 was 140%.
$^{13}C_2$-8:2FTS	40	145	
$^{13}C_8$-PFOSA	40	130	
D_3-NMeFOSA	40	130	
D_5-NEtFOSA	35	130	
D_3-NMeFOSAA	35	130	The lowest recovery was 34%. The 6 lowest recoveries were from Laboratory 6 (34, 38, 39, 41, 41, and 44). Over 99% of the data was 35% or greater. The lowest recovery not from Laboratory 6 is 55.

Table 8-18. EIS Compound Acceptance Limits Applicable to Landfill Leachate Sample Types (Continued)

EIS Compound	Lower Limit (%)	Upper Limit (%)	Notes
D_5-NEtFOSAA	30	130	The lowest recovery was 28%. The lowest 6 recoveries were from Laboratory 6 (28, 31, 33, 33, 33, and 37). Over 99% of the data was 30% or greater. The lowest recovery that was not from Laboratory 6 was 52%.
D_7-NMeFOSE	20	130	The lowest recovery was 10%. The lowest 5 recoveries were from Laboratory 6 (10, 19, 20, 31, 34). The lowest recovery that was not from Laboratory 6 was 35%.
D_9-NEtFOSE	20	130	The lowest recovery was 2%. The lowest 6 recoveries were from Laboratory 6 (2, 8, 8, 21, 22, and 24%), the lowest recovery that was not from Laboratory 6 was 29%.
$^{13}C_3$-HFPO-DA	40	130	

Source File: Source file: EPA_GDIT Chapter 8 Tables.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.

The NIS compound data were compiled only using the study samples, which generated 126 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 8-19, all of the acceptance criteria were set at 50-200%, which is consistent with the approach used for the aqueous portion of the study. All 126 data points for every NIS compound were recovered between 50 and 200%.

Table 8-19. NIS Compound Acceptance Limits Applicable to All Sample Types

NIS Compound	n	p1	p99	Lower Limit (%)	Upper Limit (%)
$^{13}C_2$-PFDA	126	68	146	50	200
$^{13}C_2$-PFHxA	126	65	133	50	200
$^{13}C_3$-PFBA	126	68	130	50	200
$^{13}C_4$-PFOA	126	70	144	50	200
$^{13}C_4$-PFOS	126	66	125	50	200
$^{13}C_5$-PFNA	126	67	144	50	200
$^{18}O_2$-PFHxS	126	72	133	50	200

Source file: Source file: EPA_GDIT Chapter 8 Tables.xlsx

8.6 DETERMINATION OF FINAL QC SPECIFICATIONS FOR BIOSOLIDS FOR METHOD 1633

EPA and DoD used the same approach to determine the QC acceptance criteria for the biosolids that they used for the results from the other portions of the method validation study (see Section 9.5 of *Volume II*) with one exception. Because PFAS-free sand was used as the IPR reference

matrix for the biosolids as well as for the soils/sediments in the solid portion of the study, DoD and EPA agreed that to reduce the burden on the laboratories and encourage more laboratories to participate in the biosolids portion of the study, the same IPR data from the 10 laboratories in the solids portion of the study would be used in the biosolids portion. The OPR and LLOPR results generated during the biosolids portion of the study were used to generate OPR and LLOPR QC specifications. The impact is that the OPR and LLOPR results came from only 6 of the 10 laboratories, while the IPR results were from 10 laboratories. The only difference between the OPR and LLOPR biosolids samples and other solid matrices is that a smaller mass is used. Following completion of the statistical calculations, EPA and DoD examined the initial acceptance limits and agreed to take several additional steps that will allow EPA to establish the final QC specifications for Method 1633 for IPRs, OPRs, LLOPRs, EIS compound, and NIS compound recoveries. 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.
- Comparing the combined OPR and LLOPR data from the biosolid matrix to the QC criteria that were generated for solid samples, because they use the same reference matrix.
- 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%.

8.6.1 Initial SAS Calculations

Because the IPR data were the same as that used for the solids portion of the study, the SAS calculation summary for the IPR data is not repeated here but is available in *Volume II.* Table 8-20 contains the initial SAS calculations of the OPR/LLOPR limits for the 40 target analytes using the entire biosolid data set (e.g., the IPR data from the 10 laboratories in the soil-sediment portion of the study plus the OPR/LLOPR data from the 6 laboratories that also participated in the biosolids portion), with the calculated recoveries, and minimum and maximum observed recoveries rounded to the nearest 1%.

Table 8-20. Initial SAS Calculations of the OPR/LLOPR Limits for the 40 Target Analytes Using the Entire Data Set of Biosolid Sample Results

Analyte	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	Min. Obs. Rec.	Max. Obs. Rec.
PFBA	63	148	74	122
PFPeA	64	143	61	150
PFHxA	68	139	68	134
PFHpA	71	139	73	129
PFOA	72	139	77	149
PFNA	62	151	77	133
PFDA	56	151	73	150

Table 8-20. Initial SAS Calculations of the OPR/LLOPR Limits for the 40 Target Analytes Using the Entire Data Set of Biosolid Sample Results (Continued)

Analyte	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	Min. Obs. Rec.	Max. Obs. Rec.
PFUnA	59	148	76	133
PFDoA	61	151	76.2	140
PFTrDA	51	157	80	133
PFTeDA	64	147	74	130
PFBS	64	148	69	136
PFPeS	64	151	59	175
PFHxS	61	149	60.5	142
PFHpS	64	147	65	134
PFOS	66	147	70	171
PFNS	61	148	61	124
PFDS	63	139	38.5	121
PFDoS	52	133	31.5	123
4:2FTS	70	145	60	132
6:2FTS	67	157	61	204
8:2FTS	65	154	80	139
PFOSA	67	145	78	130
NMeFOSA	70	147	74.5	136
NEtFOSA	75	139	73	129
NMeFOSAA	56	155	78	150
NEtFOSAA	52	150	68	159
NMeFOSE	74	139	77	126
NEtFOSE	70	141	75	123
HFPO-DA	61	151	74	140
ADONA	53	165	74	152
9Cl-PF3ONS	65	150	75	143
11Cl-PF3OUdS	59	146	51.8	131
3:3FTCA	38	152	42	121
5:3FTCA	49	151	65	133
7:3FTCA	41	151	67	145
PFEESA	62	151	74	130
PFMPA	39	161	35.6	133
PFMBA	56	153	65	147
NFDHA	40	170	73.4	144

Source files: Biosolids IPR-OPR stat specs vs BPJ for solids with actual BioS Ranges 12-26-23rev1.xlsx and Biosolids OPR-LLOPR min and max values.xlsx

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

As was done for the solids 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:

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

As noted above, DoD and EPA decided to apply the IPR data from the solids portion of the study to the biosolids portion of the study. As a result, the same final IPR limits will be applied to biosolids analyses in Method 1633. Table 8-21 presents the IPR QC acceptance criteria that appear in *Volume II* (Table 8-14) for solids.

Table 8-21. IPR Acceptance Limits for Biosolids Samples

Analyte	IPR Max RSD	IPR Lower Limit (%)	IPR Upper Limit (%)
PFBA	17	70	140
PFPeA	26	70	140
PFHxA	23	70	135
PFHpA	21	70	140
PFOA	23	70	140
PFNA	24	65	145
PFDA	26	70	145
PFUnA	26	70	145
PFDoA	25	70	145
PFTrDA	26	55	160
PFTeDA	24	70	145
PFBS	25	60	145
PFPeS	29	65	140
PFHxS	28	65	145
PFHpS	27	70	140
PFOS	27	70	135
PFNS	27	70	140
PFDS	31	50	150
PFDoS	40	40	140
4:2FTS	27	70	135
6:2FTS	50	60	160
8:2FTS	27	70	140
PFOSA	19	70	140

Table 8-21. IPR Acceptance Limits for Biosolids Samples (Continued)

Analyte	IPR Max RSD	IPR Lower Limit (%)	IPR Upper Limit (%)
NMeFOSA	26	65	145
NEtFOSA	19	70	135
NMeFOSAA	31	65	145
NEtFOSAA	31	60	150
NMeFOSE	19	70	140
NEtFOSE	17	70	135
HFPO-DA	25	70	140
ADONA	26	70	155
9Cl-PF3ONS	23	65	135
11Cl-PF3OUdS	31	50	135
3:3FTCA	32	45	155
5:3FTCA	28	70	135
7:3FTCA	39	70	145
PFEESA	20	70	140
PFMPA	25	70	140
PFMBA	33	55	145
NFDHA	27	45	145

Source File: Volume II, Table 8-13

The statistically generated OPR/LLOPR criteria shown in Table 8-20 were compared to the corresponding final acceptance limits from the solids portion of the study in Table 8-21. When the actual data were compared to the current solids criteria (Table 8-22), only 3 data points were outside of those criteria (roughly 0.3%). Given that 99.7% of the biosolid LLOPRs and OPR data fit within the solids criteria, the solids criteria are deemed suitable for biosolids. Using the same criteria also simplifies the QC for the method.

Table 8-22. Comparison of Statistically Calculated Biosolids OPR/LLOPR Acceptance Limits with the Final Solid Sample Limits

Analyte	Calculated Biosolids Limits		Final Solid Sample Limits		# Biosolid LLOPR/OPR Results Below Solids Limit	# Biosolid LLOPR/OPR Results Above Solids Limit
	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)		
PFBA	63	148	70	140		
PFPeA	64	143	60	150		
PFHxA	68	139	65	140		
PFHpA	71	139	65	145		
PFOA	72	139	70	150		
PFNA	62	151	70	155		
PFDA	56	151	70	155		
PFUnA	59	148	70	155		

Table 8-22. Comparison of Statistically Calculated Biosolids OPR/LLOPR Acceptance Limits with the Final Solid Sample Limits (Continued)

Analyte	Calculated Biosolids Limits		Final Solid Sample Limits		# Biosolid LLOPR/OPR Results Below Solids Limit	# Biosolid LLOPR/OPR Results Above Solids Limit
	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)	OPR/LLOPR Lower Limit (%)	OPR/LLOPR Upper Limit (%)		
PFDoA	61	151	70	150		
PFTrDA	51	157	65	150		
PFTeDA	64	147	65	150		
PFBS	64	148	65	145		
PFPeS	64	151	55	160		
PFHxS	61	149	60	150		
PFHpS	64	147	65	155		
PFOS	66	147	65	160		
PFNS	61	148	55	140		
PFDS	63	139	40	155		
PFDoS	52	133	25	160		
4:2FTS	70	145	60	150		
6:2FTS	67	157	55	200		One result: 204%
8:2FTS	65	154	70	150		
PFOSA	67	145	70	140		
NMeFOSA	70	147	70	155		
NEtFOSA	75	139	70	140		
NMeFOSAA	56	155	65	155		
NEtFOSAA	52	150	65	165		
NMeFOSE	74	139	70	140		
NEtFOSE	70	141	70	135		
HFPO-DA	61	151	70	145		
ADONA	53	165	70	160		
9Cl-PF3ONS	65	150	70	150		
11Cl-PF3OUdS	59	146	45	160		
3:3FTCA	38	152	45	130	One result: 42%	
5:3FTCA	49	151	60	130		One result: 133%
7:3FTCA	41	151	60	150		
PFEESA	62	151	70	140		
PFMPA	39	161	30	140		
PFMBA	56	153	60	150		
NFDHA	40	170	60	155		

Source files: Biosolids IPR-OPR stat specs vs BPJ for solids with actual BioS Ranges 12-26-23rev1.xlsx

As was done for the aqueous and solids 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.

The acceptance limits in Table 8-23 were developed from the entire biosolids study sample data set of typically 126 recoveries per EIS compound using both a non-parametric approach and professional judgement. 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 biosolid sample portion of the study. The notes mention every case where the criteria does not include all 126 EIS data point for each EIS compound.

Table 8-23. Final EIS Compound Acceptance Limits Applicable to Biosolid Sample Types

EIS Compound	Lower Limit (%)	Upper Limit (%)	Notes
$^{13}C_4$-PFBA *	5	130	The five lowest recoveries were all from Laboratory 4 (2, 2, 3, 4, and 4%). The next lowest recovery is 8%.
$^{13}C_5$-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	145	
$^{13}C_6$-PFDA	40	130	
$^{13}C_7$-PFUnA	40	130	
$^{13}C_2$-PFDoA	40	130	
$^{13}C_2$-PFTeDA	10	160	
$^{13}C_3$-PFBS	40	150	
$^{13}C_3$-PFHxS	40	140	
$^{13}C_8$-PFOS	40	130	
$^{13}C_2$-4:2FTS	40	300	
$^{13}C_2$-6:2FTS	40	300	The highest recovery was 379%. There are 4 recoveries above 300% (330, 346, 370, and 379), three are from Laboratory 8 and one from Laboratory 6. Laboratory 8 has 7 of the 10 highest recoveries. The p99 value is 297 if the Laboratory 8 data is not used.
$^{13}C_2$-8:2FTS	40	300	
$^{13}C_8$-PFOSA	20	140	
D_3-NMeFOSA	20	130	
D_5-NEtFOSA	20	130	The lowest 6 recoveries are from Laboratory 3 (8, 18, 18, 19, 19 and 20). The lowest recovery not from Laboratory 3 is 20%.

Table 8-23. Final EIS Compound Acceptance Limits Applicable to Biosolid Sample Types (Continued)

EIS Compound	Lower Limit (%)	Upper Limit (%)	Notes
D_3-NMeFOSAA	30	150	The lowest 7 recoveries are from Laboratory 3 (12, 26, 29, 30, 31, 31, and 34). The lowest recovery not from Laboratory 3 is 43%.
D_5-NEtFOSAA	20	140	
D_7-NMeFOSE	25	130	
D_9-NEtFOSE	20	130	
$^{13}C_3$-HFPO-DA	40	130	The two lowest recoveries are 16%, and the third lowest is 62%. Both or the 16% recoveries are from Laboratory 8 and were diluted 5:1. The undiluted EIS recovery would have been about 80%, so these 2 data points should not be considered.

Source file: 1633 Biosolids EIS & NIS Specs 2023-11-22.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.

The NIS compound data were compiled only using the study samples, which generated 126 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 8-24, all the acceptance criteria were set at 50-200%, which is consistent with the approach used for the aqueous portion of the study. The recoveries for every NIS compound were between 50 and 200%, with the exception of one NIS compound. $^{13}C_4$-PFOS had 7 recoveries from Laboratory 3 above 200% (269, 284, 293, 303, 308, 314, and 675). The highest recovery that was not from Laboratory 3 was 155%. The upper acceptance limit was kept at 200%, because Laboratory 3 appeared to be a dramatic anomaly compared to all the other data.

Table 8-24. NIS Compound Acceptance Limits Applicable to All Sample Types

NIS Compound	n	p1	p99	Lower Limit (%)	Upper Limit (%)
$^{13}C_2$-PFDA	126	68	146	50	200
$^{13}C_2$-PFHxA	126	65	133	50	200
$^{13}C_3$-PFBA	126	68	130	50	200
$^{13}C_4$-PFOA	126	70	144	50	200
$^{13}C_4$-PFOS	126	66	125	50	200
$^{13}C_5$-PFNA	126	67	144	50	200
$^{18}O_2$-PFHxS	126	72	133	50	200

Source file: 1633 Biosolids EIS & NIS Specs 2023-11-22.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 Performance 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 landfill leachate and biosolids 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 OPR and LLOPR recoveries (Tables 8-3, 8-4, 8-7, and 8-8) and the EIS and NIS compound recoveries (Tables 6-6 and 7-6, and Section 8-2) associated with study samples were used to confirm these matrices should be considered for inclusion in the finalized method. The landfill leachate data collected in this study indicated the IPR and OPR/LLOPR acceptance criteria for aqueous media derived from the analysis of wastewater, surface water, and groundwater samples during the MLVS (*Volume I*) are suitable for leachate samples. Further, the biosolids data in this study demonstrated that the IPR and OPR/LLOPR acceptance criteria for solid media derived from the analysis of soil and sediment samples during the MLVS (*Volume II*) are suitable for biosolid samples.

The MLVS results demonstrate the ability of EPA Method 1633 to adequately measure PFAS concentrations in real-world landfill leachate and biosolids samples. However, the mean % recovery of PFDoS (48.9%) in spiked biosolid samples across all six laboratories (Table 7-3) indicated recovery of this analyte in biosolids samples may be biased low. OPR and LLOPR data associated with biosolids sample results for PFDoS should be considered when determining the usability of biosolids sample data for PFDoS.

10 REFERENCES

Anderson RH, Thompson T, Stroo HF, Leeson A. 2020. U.S. Department of Defense–funded fate and transport research on per- and polyfluoroalkyl substances at aqueous film-forming foam–impacted sites. Environ Toxicol Chem 40:37–43.

EPA, 2019. EPA Per- and Polyfluoroalkyl Substances (PFAS) Action Plan. US Environmental Protection Agency. EPA 823R18004. February 2019. Available on the web at https://www.epa.gov/sites/default/files/2019-02/documents/pfas_action_plan_021319_508compliant_1.pdf

EPA 2020. EPA PFAS Action Plan Program Update February 2020. US Environmental Protection Agency. Office of Water (MS-140) EPA 815-B-19-021. December 2019, Available on the web at https://www.epa.gov/sites/default/files/2020-01/documents/pfas_action_plan_feb2020.pdf#:~:text=The%20PFAS%20Action%20Plan%20outlines%20the%20tools%20EPA,PFAS%20scientific%20research%2C%20and%20exercise%20effective%20enforcement%20tools

ITRC. 2020. *Per- and Polyfluoroalkyl Substances (PFAS)*. The Interstate Technology and Regulatory Council (ITRC) Per-and Polyfluoroalkyl Substances (PFAS) Team. April 2020. https://pfas-1.itrcweb.org.

Leeson A, Thompson T, Stroo HF, Anderson RH, Speicher J, Mills MA, Willey J, Coyle C, Ghosh R, Lebrón C, Patton C. 2020. Identifying and managing aqueous film-forming foam-derived per- and polyfluoroalkyl substances in the environment. Environ Toxicol Chem 40:24-36.

U.S. Environmental Protection Agency (EPA). 2016a. Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA). USEPA, Office of Water, Health and Ecological Criteria Division, Washington, DC. EPA 822-R-16-005. 2016.

U.S. Environmental Protection Agency (EPA). 2016b. Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS). USEPA, Office of Water, Health and Ecological Criteria Division, Washington, DC. EPA 822-R-16-004. 2016.

U.S. Environmental Protection Agency (EPA). 2018. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC, 2018.

U.S. Environmental Protection Agency (EPA). 2018b. *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program*. U.S. Environmental Protection Agency. Office of Water, Engineering and Analysis Division. EPA 821-B-18-001. February. Available online at https://www.epa.gov/sites/default/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf.

U.S. Environmental Protection Agency (EPA). 2020. Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid

Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. USEPA Office of Water, Office of Groundwater and Drinking Water, Standards and Risk Management Division, Cincinnati, OH. EPA 815-B-19-020

U.S. Environmental Protection Agency (EPA). 2021. *Draft Method 1633, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS*. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division, Washington, DC 20460. EPA 821-D-21-001. August. Available online at https://www.epa.gov/newsreleases/epa-announces-first-validated-laboratory-method-test-pfas-wastewater-surface-water.

U.S. Department of Defense (DoD). 2021. *Department of Defense (DoD) and Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories. Based on ISO/IEC 17025:2005(E), ISO/IEC 17025:2017(E), and the NELAC Institute (TNI) Standards, Volume I, (September 2009)*. DoD Quality Systems Manual Version 53. October. https://www.denix.osd.mil/edqw/home/.

Willey, J., A. Hanley, R. Anderson, A. Leeson and T. Thompson. 2023. Report on the Multi-Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS. Volume I. Wastewater, Surface Water, and Groundwater. Strategic Environmental Research and Development Program (SERDP) Project ER19-1409.

Willey, J., A. Hanley, R. Anderson, A. Leeson and T. Thompson. 2024. Report on the Multi-Laboratory Validation of PFAS by Isotope Dilution LC-MS/MS. Volume II. Soils and Sediments. Strategic Environmental Research and Development Program (SERDP) Project ER19-1409.

Code of Federal Regulations. Appendix B to Title 40, Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 2. https://ecfr.io/Title-40/Part-136/Appendix-B#40:25.0.1.1.1.0.1.8.2

Appendix A

PFAS MLVS Institute for Defense Analyses Report

INTEROFFICE MEMORANDUM

IDA

SCIENCE & TECHNOLOGY
DIVISION

19 January 2024

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[2] and solids IDC and five environmental matrices: wastewater (WW), surface water (SW), ground water (GW), soils (SS) and sediments (SD) datasets provided by the sponsor.

---

[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 biosolids (BS) and landfill leachate (LC) environmental matrix datasets in the PFAS MLV 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 LC and BS 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.

---

[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]

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

where $\bar{X}_j$ = 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:

---

[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]

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

where m = the number of labs, $\overline{X}$ = 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]

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

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]

$$RSD = \frac{s_w}{\bar{X}} \cdot 100;$$

where s_w = the within lab standard deviation, $\bar{X}$= 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:

[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.

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

DATASETS & IDA GENERATED PRODUCTS FILE NAMES

IDA Generated Product	
Tables	**Figures**
Biosolids Matrix Dataset BS_DBexport_V0_20231120.xlsx	
BS_LLOPR_results_v0_231204_113058.csv BS_OPR_results_v0_231204_113058.csv BS_EIS_results_v0_231204_113058.csv BS_Matrix_sample_results_v0_231204_113058.csv BS_Matrix_compiled_results_v0_231204_113058.csv BS_MB_results_v0_231204_113058.csv BS_NIS_results_v0_231204_113058.csv	BS_LLOPR_Boxplot_v0_231204_113058.png BS_LLOPR_Horwitz_v0_231204_113058.png BS_OPR_Boxplot_v0_231204_113058.png BS_OPR_Horwitz_v0_231204_113058.png BS_HighSpike_Boxplot_v0_231204_113058.png BS_LowSpike_Boxplot_v0_231204_113058.png BS_LowHighCombinedSpike_Boxplot_v0_231204_113058.png BS_EIS_Boxplot_v0_231204_113058.png BS_NIS_Boxplot_v0_231204_113058.png
Landfill Leachate Matrix Dataset LC_DBexport_V0_20231110.xlsx	
LC_LLOPR_results_V0_231122_163114.csv LC_OPR_results_V0_231122_163114.csv LC_EIS_results_V0_231122_163114.csv LC_Matrix_sample_results_V0_231122_163114.csv LC_Matrix_compiled_results_V0_231122_163114.csv LC_MB_results_V0_231122_163114.csv LC_NIS_results_V0_231122_163114.csv	LC_LOPR_Boxplot_V1_231220.png LC_LLOPR_Horwitz_V1_231220.png LC_OPR_Boxplot_V1_231220.png LC_OPR_Horwitz_V1_231220.png LC_HighSpike_Boxplot_V1_231220.png LC_LowSpike_Boxplot_V1_231220.png LC_LowHighCombinedSpike_Boxplot_V1_231220.png LC_EIS_Boxplot_V1_231220.png LC_NIS_Boxplot_V1_231220.png

Appendix B

Landfill Leachate Supporting Tables

Table B-1. Range of Target Analytes in Unspiked Landfill Leachate Samples (ng/L).

Analyte	Number of Labs	LCAE1		LCAF1		LCAG1	
		Min	Max	Min	Max	Min	Max
PFBA	6[a]	121	166	79.6	127	38	59
PFPeA	6	97.5	154	562	726	35.9	53.8
PFHxA	6	201	276	328	462	67.4	96.7
PFHpA	6	28.1	44.3	73	107	4.08 J	7.62 JI
PFOA	6	58.6	84	79.7	121	5.44	8.51 J
PFNA	6	3.29 U	3.2 JI	3.44 J	6.98 JI	0.832 U	3.29 U
PFDA	6	0.906 U	4.05 U	0.906 U	4.05 U	0.906 U	4.05 U
PFUnA	6	0.908 U	3.32 U	0.908 U	3.32 U	0.908 U	3.32 U
PFDoA	6	0.846 U	3.76 U	0.846 U	3.76 U	0.846 U	3.76 U
PFTrDA	6	0.98 U	3.04 U	0.98 U	3.04 U	0.98 U	3.04 U
PFTeDA	6	0.838 U	2.77 U	0.838 U	2.77 U	0.838 U	2.77 U
PFBS	6	125	205	25.5	48.7	47	87.8
PFPeS	6	0.645 U	4.53 JI	0.645 U	3.6 J	0.582 U	2.34 U
PFHxS	6	28.4	48	19.8	28.9	3.16 U	3.82 J
PFHpS	6	0.561 U	2.53 U	1.02 U	0.683 JI	0.561 U	2.53 U
PFOS	6	6.8 U	8.4	7.85 J	19.8	2.96 U	2.66 J
PFNS	6	1.09 U	3.62 U	1.09 U	3.62 U	1.09 U	3.62 U
PFDS	6	0.767 U	3.44 U	0.767 U	3.44 U	0.767 U	3.44 U
PFDoS	6	0.9 U	4.44 U	0.9 U	4.44 U	0.9 U	4.44 U
4:2FTS	6	3.16 U	8.53 U	3.16 U	85.3 UD	3.16 U	8.53 U
6:2FTS	6	16.2 J	26 J	4.73 U	14.1 U	4.73 U	14.1 U
8:2FTS	6	2.72 U	14.3 U	2.72 U	14.3 U	2.72 U	14.3 U
PFOSA	6	0.77 U	2.26 U	0.77 U	2.26 U	0.77 U	2.26 U
NMeFOSA	6	0.765 U	4.83 U	0.765 U	4.83 U	0.765 U	4.83 U
NEtFOSA	6	0.499 U	3.64 U	0.499 U	3.64 U	0.499 U	3.64 U
NMeFOSAA	6	3.28 U	12.8	3.03 U	1.12 J	0.93 U	5.79 U
NEtFOSAA	6	1.42 U	4.28 U	1.42 U	4.28 U	1.42 U	4.28 U
NMeFOSE	6	7.58 U	18.8 U	7.58 U	18.8 U	7.58 U	18.8 U
NEtFOSE	6	7.25 U	14.7 U	7.25 U	14.7 U	7.25 U	14.7 U
PFMPA	6	1.6 U	3.14 U	1.6 U	3.14 U	1.6 U	3.14 U
PFMBA	6	1.48 U	3.04 U	1.48 U	3.04 U	1.48 U	3.04 U
NFDHA	6	2.46 U	9.25 U	2.46 U	9.25 U	2.46 U	9.25 U
HFPO-DA	6	1.72 U	6 J	1.72 U	11.6 U	1.72 U	11.6 U
ADONA	6	2.86 U	8.35 U	2.86 U	8.35 U	2.86 U	8.35 U
PFEESA	6	1.06 U	3.65 U	1.06 U	3.65 U	1.06 U	3.65 U
9Cl-PF3ONS	6	3.5 U	9.3 U	3.5 U	4.63 J	3.5 U	4.63 J
11Cl-PF3OUdS	6	4.09 U	9.77 U	4.09 U	9.77 U	4.09 U	9.77 U
3:3FTCA	6	4.3 U	31.9 J	4.3 U	11.2 J	4.3 U	13.2 U
5:3FTCA	6	22.3 U	1640	9.4 U	46.8 U	9.4 U	46.8 U
7:3FTCA	6	12.8 U	45.4 U	12.8 U	45.4 U	12.8 U	45.4 U

Version: Appendix B_LandFill Leachate 01182024.xlsx

[a] 5 labs for LCAE1

Table B-2. Summary of Landfill Leachate Spike Percent Recoveries in Low Spike Samples for each Laboratory.

Analyte	Lab 1 spike spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery				Lab 6 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	91.5	98	95.1	9	99.5	114.5	107.8	6	73.2	111.2	96.7	9	85.5	102	92.2
PFPeA	6	97	101.5	99.7	6	96	114.3	103.3	6	89	103	99.4	6	70.5	95.4	83.9
PFHxA	3	92.1	97.6	95.1	3	95.8	122.3	105.8	3	96	102	98.2	3	72.2	97.6	82.1
PFHpA	9	85.2	95.2	90.2	9	95	108	102.2	9	89.8	109.8	100.3	9	68.8	101.3	86.6
PFOA	9	88.7	104	94.8	9	93.8	113	102.9	9	89.8	104.3	96.6	9	82.6	115.6	96.8
PFNA	9	74.7	101.6	91.9	9	91.2	129.6	108.4	9	94.2	110.8	99.3	9	76.4	107.4	98.9
PFDA	9	87.8	112.2	96.2	9	108.8	116	113.7	9	100.2	118	106.2	9	67.6	95.4	81.2
PFUnA	9	83.2	117.6	102	9	96	113.6	105.2	9	94.4	112.2	102.7	9	69	97.8	85.2
PFDoA	9	88.6	110.6	98.1	9	109.6	129.6	117.3	9	100	119.2	105.6	9	71	113	87.5
PFTrDA	9	84.4	108	98.2	9	88	121.6	102	9	93.8	116	102.2	9	60.2	96	78.2
PFTeDA	9	78.8	124.8	102.4	9	98.4	136	111.6	9	99.2	128	109.6	9	54.2	77.2	67.3
PFBS	6	84.7	98.5	91.3	6	104.9	131.1	114.1	6	95.9	104.8	99.7	6	86.9	105	97.1
PFPeS	9	80.1	96.3	87.9	9	99.2	113.4	107.6	9	91.3	113.5	102.8	9	70.5	110.6	91
PFHxS	9	82.9	97.2	88.8	9	97.6	110.6	104.2	9	92.3	110.6	101.9	9	65.2	109.6	91.2
PFHpS	9	86.9	105.6	94.7	9	106.5	130.6	116.9	9	90.1	108.7	101.4	9	78.2	114.5	95.7
PFOS	9	82.6	116.4	95.8	9	89.2	123.5	106.8	9	84.7	119.3	98.7	9	57.6	97.6	75.8
PFNS	9	80.2	97.8	89.1	9	88.8	110.4	100.5	9	84.4	103.2	95	9	49.6	88.8	73.6
PFDS	9	70.5	89.8	81.6	9	70.3	100.6	88.5	9	82.2	102.8	90.4	9	46.1	93	65.2
PFDoS	9	47.2	80.4	64.1	9	47.6	97.6	76.7	9	74.6	93.1	83.2	9	32.5	66.7	47.5
4:2FTS	9	80.5	100.2	89	9	101.6	113.7	108.5	9	87.1	108.7	99.3	9	71.1	130.8	96.7
6:2FTS	9	87.4	101.1	95.5	9	102.1	118.9	111.9	9	90.2	116	103	9	66	122.7	99.9
8:2FTS	9	86.2	102.2	94.6	9	101.2	129.3	115.3	9	101.2	130.3	112.6	9	61.4	148.3	99.4
PFOSA	9	89.4	97.6	94.2	9	92	104	98	9	91.4	107.6	100.5	9	81	99.2	90.4
NMeFOSA	9	84.8	100	92	9	104.8	128.8	114.3	9	93.4	105.2	98.5	9	68	93.4	79
NEtFOSA	9	72	85.4	78.8	9	98.4	122.4	113.5	9	81.2	105	90.9	9	61.6	88.6	73.2
NMeFOSAA	9	86	106.6	96.5	9	96.8	139.2	117.7	9	95.2	117.8	103.1	9	85.6	110	97.1
NEtFOSAA	9	65	100.6	86.5	9	100.8	136	115.6	9	85.2	108	99.3	9	56.4	100	82.4
NMeFOSE	9	80	91.5	84.6	9	92	120	106	9	92.5	104	97.9	9	59	90.5	74.4
NEtFOSE	9	74	92.5	82.9	9	99	113.5	106.2	9	93	103	97.8	8	43.8	81.5	63
PFMPA	9	75.2	91.2	82.2	9	93.6	115.2	103.7	9	31.8	101.2	65.9	9	95	102.8	98
PFMBA	9	100.8	105.6	102.7	9	89.6	110.4	100.9	9	100.8	115.4	105.6	9	75	100.8	85.2
NFDHA	9	78	98.1	89.6	9	71.2	128	91.1	9	67.4	99.9	91.4	9	77.5	181	123.7
HFPO-DA	9	89.5	118	96.8	9	96	112	101.4	9	76.5	124	98.4	9	74.8	124	89.9
ADONA	9	85.4	100.9	94.7	9	88.3	110.9	102.3	9	100.9	115.9	106.7	9	76.8	99.4	90.3
PFEESA	9	98	104	100.8	9	77.6	92	85.1	9	98.4	112.6	103.9	9	92.4	144.2	114.6
9Cl-PF3ONS	9	76.8	105.1	86.4	9	76.9	101.1	87.7	9	94.6	117.9	107.1	9	53	94.8	75.8
11Cl-PF3OUdS	9	62.9	89.3	75	9	54.3	89.5	70.6	9	86.6	106.9	93.2	9	26.6	72.5	48.9
3:3FTCA	9	92.4	114	101.9	9	73	122	99.6	9	92.6	114.3	99.6	9	99.7	176	139.3
5:3FTCA	6	83.2	89	85.9	6	94	109.2	103.6	6	89.4	117	102.2	9	82.6	382	192.6
7:3FTCA	9	81.6	90.8	84.6	9	86.4	130.6	108	9	83.4	112.2	97.9	9	78.8	134.6	108.6

Version: Appendix B_LandFill Leachate 01182024.xlsx

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

Table B-2. Summary of Landfill Leachate Spike Percent Recoveries in Low Spike Samples for each Laboratory. (continued)

Analyte	Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	83.5	87.4	85	9	106	123	109.9	51	73.2	123	97.8
PFPeA	6	81.6	84.2	83.1	6	109.1	130	119.8	36	70.5	130	98.2
PFHxA	3	81.8	84.8	83.5	3	107.2	121.7	115.4	18	72.2	122.3	96.7
PFHpA	9	81	88.5	83.3	9	103.9	125.5	112.2	54	68.8	125.5	95.8
PFOA	9	75.7	82.8	79.3	9	104.2	119.5	112.4	54	75.7	119.5	97.1
PFNA	9	82.4	87.9	84.1	9	105.4	122.2	117.2	54	74.7	129.6	100
PFDA	9	83.2	88.2	85.2	9	77.8	125.8	107.5	54	67.6	125.8	98.3
PFUnA	9	76.6	85.4	82.4	9	50	123	93.6	54	50	123	95.2
PFDoA	9	79.2	90.4	85.3	9	32	122.4	83.1	54	32	129.6	96.1
PFTrDA	9	72.6	85.4	79.5	9	23.8	97.8	64.6	54	23.8	121.6	87.4
PFTeDA	9	77	94	86.8	9	27.8	83.6	53.8	54	27.8	136	88.6
PFBS	6	84.1	88.9	85.8	6	116.8	136.9	126.7	36	84.1	136.9	102.4
PFPeS	9	82.1	87	85.1	9	105.5	124.4	113.6	54	70.5	124.4	98
PFHxS	9	78.7	84.3	81.4	9	110.8	146.7	125.5	54	65.2	146.7	98.8
PFHpS	9	83.7	91.3	87.7	9	123.6	138.1	127.8	54	78.2	138.1	104
PFOS	9	79.9	86.7	82.8	9	95.7	124.1	111.1	54	57.6	124.1	95.2
PFNS	9	79.8	83.6	81.6	9	55.6	110.2	91.2	54	49.6	110.4	88.5
PFDS	9	76.8	82.8	78.7	9	29.1	93.2	68.8	54	29.1	102.8	78.9
PFDoS	9	56.7	79.6	70.7	9	17	54.8	37.1	54	17	97.6	63.2
4:2FTS	9	80	85	82.1	8	85	130.8	111	53	71.1	130.8	97.5
6:2FTS	9	83.8	89.6	87.3	9	85.3	143.4	116.3	54	66	143.4	102.3
8:2FTS	9	86.1	94.5	91.1	9	90.3	135.3	113.8	54	61.4	148.3	104.5
PFOSA	9	82	88.6	84.9	9	100.2	117	110	54	81	117	96.4
NMeFOSA	9	78.8	90.4	84.9	9	41.4	121.6	88.6	54	41.4	128.8	92.9
NEtFOSA	9	72	86.2	80.8	9	22.6	89.2	64.8	54	22.6	122.4	83.7
NMeFOSAA	9	76.4	90	84.3	9	62.8	125.2	98.8	54	62.8	139.2	99.6
NEtFOSAA	9	77.2	90.6	84.9	9	41.8	131	95.4	54	41.8	136	94
NMeFOSE	9	76	86.5	80.7	9	31	107.5	65.1	54	31	120	84.8
NEtFOSE	9	78	86.5	82.4	9	20.4	81	47.5	53	20.4	113.5	80.3
PFMPA	9	66.2	83.8	76.9	9	76.8	113.2	94.1	54	31.8	115.2	86.8
PFMBA	9	84.6	96.8	90.2	9	103.2	116	110.2	54	75	116	99.1
NFDHA	9	64.9	90.3	76.5	9	99.2	118	109.2	54	64.9	181	96.9
HFPO-DA	9	83.2	88	85.3	9	106	127	116.9	54	74.8	127	98.1
ADONA	9	82.5	100.9	92.5	9	109.9	123.9	117.3	54	76.8	123.9	100.6
PFEESA	9	91.4	103.8	96.1	9	106.2	119.8	114.4	54	77.6	144.2	102.5
9Cl-PF3ONS	9	77.6	115	98.2	9	59.7	114	95.4	54	53	117.9	91.8
11Cl-PF3OUdS	9	71.8	108.9	90.9	9	17	80.2	54.2	54	17	108.9	72.1
3:3FTCA	9	74	138.8	110.7	9	99.7	144	121.9	54	73	176	112.2
5:3FTCA	6	77.4	122.8	100.7	6	114.6	143.2	127.9	39	77.4	382	124.5
7:3FTCA	9	75.4	110.6	96.3	9	87.8	131	108.5	54	75.4	134.6	100.7

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

Table B-3. Summary of Landfill Leachate Spike Percent Recoveries in High Spike Samples for each Laboratory.

Analyte	Lab 1 spike spike % recovery				Lab 3 spike % recovery				Lab 4 spike % recovery				Lab 6 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	90.5	97	93.9	9	103.3	108.6	105.5	6	92.1	105	97.3	9	85.5	94.1	89.5
PFPeA	9	96.6	101.6	99.1	9	103.6	113.4	108.1	9	91.7	106.4	98.7	9	73.2	93.4	82.5
PFHxA	9	84	99	90.7	9	85.9	112.3	98.9	9	84.8	109.1	93.3	9	79.2	97.2	86.8
PFHpA	9	86.4	97.3	91.6	9	95.6	102.4	99.8	9	90	107.3	97.9	9	72.4	95.4	86.2
PFOA	9	94.1	99.1	96.1	9	98.1	112.6	104.8	9	88.7	110.6	95.3	9	66	94.8	83.7
PFNA	9	86	100.7	91.3	9	96	115.2	103	9	89.6	109.2	97.6	9	83.4	114.6	95.3
PFDA	9	80.6	102.6	90.8	9	93.6	120	108.2	9	87.8	112.8	97.5	9	72.2	98.6	84.1
PFUnA	9	87.6	108.4	96.6	9	87.6	117.6	104.1	9	94.2	108.2	100.1	9	61.4	95.2	77.7
PFDoA	9	77.2	108	93.6	9	98.8	123.4	107.2	9	90.4	105.4	97.4	9	66.4	92	78.7
PFTrDA	9	77.8	101.4	89.9	9	79.8	98.6	92.2	9	85.6	107.2	94	9	65.2	124.6	87.9
PFTeDA	9	74.2	126.6	94	9	102	124.8	113.9	9	89.2	124.8	103.1	9	59.2	87.8	71.3
PFBS	9	85.5	91.4	89.4	9	103.6	114.8	109.8	9	96.9	110.9	103.2	9	60.2	106.1	89.8
PFPeS	9	83.6	94.7	91	9	103.8	115.8	107.7	9	94.8	105.9	101.8	9	61.6	108.2	82
PFHxS	9	88.1	99.1	94.6	9	98.1	107.1	102.9	9	91.3	109	98.9	9	63.4	106.6	85
PFHpS	9	91.7	101	97	9	109.3	122.8	114.9	9	92.1	115.9	104.4	9	69.7	108.8	84.9
PFOS	9	90.8	98.7	94.3	9	90.9	108.3	100.9	9	84	106.5	97.6	9	64.5	91.5	76.6
PFNS	9	78.6	104	91.8	9	84.4	116.8	99.9	9	84.8	115.2	97.9	9	46.8	102.6	73
PFDS	9	69.4	91.8	82.7	9	66.2	110.9	90.1	9	81.2	106.9	92.3	9	37.9	89.6	62.5
PFDoS	9	46.8	77.7	63.8	9	41.2	100.7	78.3	9	79.5	95.2	87.4	9	18.8	85.1	51.1
4:2FTS	9	80.6	102.6	90.9	9	96.6	111.6	104.6	9	85	106.6	91.1	9	58.3	158.9	96.9
6:2FTS	9	86.9	100.7	91.8	9	102	111.1	106.6	9	89.2	123.8	102.3	9	64.6	150.5	89.6
8:2FTS	9	82.3	104.2	91.4	9	104.2	117.2	112.6	9	97.3	107.2	101.7	9	75.7	154.2	105.6
PFOSA	9	89.4	101	95.5	9	92	103.2	98	9	88.6	110	99.8	9	80.8	101.4	89.5
NMeFOSA	9	79.6	92.8	87.3	9	98.2	113.2	107.6	9	92.8	107.8	99.2	9	71.6	89.4	80.8
NEtFOSA	9	65.6	84	75	9	108.6	120.8	113.4	9	85.6	101.6	94	9	61.8	83.8	73.4
NMeFOSAA	9	82.8	102.4	95.6	9	96.8	129.6	112.6	9	97.2	111.2	104.1	9	62.8	101	79.7
NEtFOSAA	9	66.4	95	82.2	9	100.4	121	114.1	9	94	107.8	100.9	9	56.8	90	77
NMeFOSE	9	76	91.5	83.7	9	94.5	106	100.5	9	91	106	97.8	9	46.8	80	68.6
NEtFOSE	9	73.5	89	81.4	9	98	111	105.6	9	92.5	108	99.3	7	59.5	75	66.9
PFMPA	9	73	86	81.1	9	92	107.8	102.1	9	25.4	95.8	66.4	9	78.8	99.8	87.7
PFMBA	9	93	108.6	100.6	9	95.2	108.8	101.4	9	90.6	121.8	105.7	9	71.6	90	81.2
NFDHA	9	84.2	106.2	90.9	9	72.4	109.8	90.5	9	56.6	96.8	84.1	9	68.6	146.8	103.5
HFPO-DA	9	84.4	96.6	91.1	9	94.4	107.8	101.6	9	87.2	110	95.3	9	79.8	96.6	87.7
ADONA	9	89.1	101.3	93.8	9	91.5	115.1	104.2	9	96.3	120.3	105.9	9	65.4	89.9	79.4
PFEESA	9	91.9	102.7	97.9	9	76.9	93.3	86.1	9	93.7	113.3	100.7	9	92.3	120.5	110.3
9Cl-PF3ONS	9	70.3	100	85.9	9	79.7	100.7	90	9	92.6	118.6	104	9	54.5	78.5	68.3
11Cl-PF3OUdS	9	58.8	87.3	74.9	9	57	92.9	75.5	9	81	113.1	91.6	9	30.2	69	50.7
3:3FTCA	9	74.4	108	90.6	9	93.3	121	102.7	9	86.3	111.1	96.9	9	86.5	142	117.7
5:3FTCA	9	82.2	92	86	9	86.2	121.8	104.7	9	89.4	122.4	101.5	9	78	131.8	107.9
7:3FTCA	9	81.4	94	89	9	93.6	137.6	113.4	9	85	114.4	95.7	9	77.4	129.2	103.2

Version: Appendix B_LandFill Leachate 01182024.xlsx

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

Table B-3. Summary of Landfill Leachate Spike Percent Recoveries in High Spike Samples for each Laboratory. (continued)

Analyte	Lab 9 spike % recovery				Lab 10 spike % recovery				All Labs spike spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	84.7	96.2	87.3	9	102.1	111.7	107.8	51	84.7	111.7	96.9
PFPeA	9	84.5	93.6	86.9	9	103.6	121.8	112.6	54	73.2	121.8	98
PFHxA	9	85.8	97.3	88.8	9	102.8	113.8	108.7	54	79.2	113.8	94.5
PFHpA	9	84.5	94.2	86.8	9	99.9	113.9	106.2	54	72.4	113.9	94.8
PFOA	9	82.8	92.7	84.9	9	105.4	116.8	109.7	54	66	116.8	95.7
PFNA	9	83.1	95.8	87.9	9	95	121.3	110.5	54	83.1	121.3	97.6
PFDA	9	82.8	93	87.3	9	74.8	118.2	102.9	54	72.2	120	95.1
PFUnA	9	80.6	90.8	86	9	52.6	113.6	90.7	54	52.6	117.6	92.5
PFDoA	9	84.8	99.2	89.5	9	32.2	120	78.2	54	32.2	123.4	90.8
PFTrDA	9	73.6	95.8	82.9	9	26	99.2	60	54	26	124.6	84.5
PFTeDA	9	79.4	101	90.2	9	38.8	80	53.6	54	38.8	126.6	87.7
PFBS	9	86.7	97.1	89.3	9	116.8	136	123.4	54	60.2	136	100.8
PFPeS	9	85.1	95.7	88.4	9	105.9	117.2	109.9	54	61.6	117.2	96.8
PFHxS	9	81.8	94.2	85	9	113.3	129.8	121.4	54	63.4	129.8	98
PFHpS	9	86.7	102.4	91.6	9	115.7	128	123.3	54	69.7	128	102.7
PFOS	9	80.4	93.4	85.8	9	87.7	112.7	102.7	54	64.5	112.7	93
PFNS	9	80.2	92.6	84.6	9	58	108.2	89.2	54	46.8	116.8	89.4
PFDS	9	76.6	90	81.8	9	31.9	93.2	68.4	54	31.9	110.9	79.6
PFDoS	9	57.5	96	74.6	9	24.4	49.2	36.6	54	18.8	100.7	65.3
4:2FTS	9	81.5	94.1	85.4	9	76.1	123.7	101.6	54	58.3	158.9	95.1
6:2FTS	9	85.3	96.1	90.8	9	101	126.2	116	54	64.6	150.5	99.5
8:2FTS	9	92.3	97.2	94.3	9	77.3	126.2	111.6	54	75.7	154.2	102.9
PFOSA	9	85.2	95	87.9	9	89.4	119.2	105.6	54	80.8	119.2	96
NMeFOSA	9	83.2	95.4	88.8	9	44.6	110.8	84	54	44.6	113.2	91.3
NEtFOSA	9	79	92.6	87.1	9	23.4	93.4	62.3	54	23.4	120.8	84.2
NMeFOSAA	9	77.6	95.8	86.7	9	55.4	121.2	93.1	54	55.4	129.6	95.3
NEtFOSAA	9	83.8	95	88.3	9	41	119.8	87.6	54	41	121	91.7
NMeFOSE	9	80	95	85.8	9	27.6	96	53.7	54	27.6	106	81.7
NEtFOSE	9	79.5	95.5	86.6	9	21	74.5	41.2	52	21	111	80.7
PFMPA	9	69.4	91.4	81.3	9	82.6	112.2	94.9	54	25.4	112.2	85.6
PFMBA	9	89.4	102.2	95.3	9	102.6	113.8	107.4	54	71.6	121.8	98.6
NFDHA	9	70.2	105	85.2	9	103	116.2	107	54	56.6	146.8	93.6
HFPO-DA	9	84.8	100	88	9	102.2	120.8	113.7	54	79.8	120.8	96.2
ADONA	9	84.9	110.1	98.2	9	101.9	126.5	117	54	65.4	126.5	99.7
PFEESA	9	97.5	113.1	103.9	9	105.5	118.3	112.7	54	76.9	120.5	101.9
9Cl-PF3ONS	9	84.9	124.5	105.2	9	68.4	116.2	98.8	54	54.5	124.5	92
11Cl-PF3OUdS	9	79.8	111.9	95.2	9	20.8	83.9	57.5	54	20.8	113.1	74.2
3:3FTCA	9	77	143.9	116	9	106	139	123.4	54	74.4	143.9	107.9
5:3FTCA	9	90	133.8	113.8	9	112.8	143.2	124.9	54	78	143.2	106.5
7:3FTCA	9	89.6	125.2	109.6	9	93.8	124.8	110.3	54	77.4	137.6	103.5

Version: Appendix B_LandFill Leachate 01182024.xlsx

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

Table B-4. Summary of EIS Compound Percent Recovery in Landfill Leachate Samples for Each Laboratory

EIS Compound	Lab 1 % recovery				Lab 3 % recovery				Lab 4 % recovery				Lab 6 % recovery			
	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean
$^{13}C_4$-PFBA	21	50.8	97.2	76.8	21	70	79	74.1	21	4	92.9	42.6	21	59.2	91	75.4
$^{13}C_5$-PFPeA	21	88.4	108	96.9	21	48	89	65.4	21	65.6	99.3	83.4	21	73	107	91.5
$^{13}C_5$-PFHxA	21	86.3	104	92.4	21	68	88	76.4	21	74.4	97.4	86.3	21	72	98.8	82.5
$^{13}C_4$-PFHpA	21	84	100	89.5	21	68	96	85.0	21	70.9	97.6	85.7	21	75.8	101	88.3
$^{13}C_8$-PFOA	21	84.1	97.7	92.5	21	71	86	78.7	21	74.5	92.5	85.5	21	61.9	102	76.5
$^{13}C_9$-PFNA	21	77	103	90.6	21	66	90	78.0	21	75.3	94.1	87.5	21	70.8	96.8	83.6
$^{13}C_6$-PFDA	21	73.6	107	89.2	21	60	80	71.1	21	75	91.9	81.8	21	56.8	95.4	80.1
$^{13}C_7$-PFUnA	21	71.5	98.6	80.9	21	58	86	70.5	21	74.6	90.1	80.7	21	48.2	92.6	73.9
$^{13}C_2$-PFDoA	21	66.3	88.1	77.8	21	42	80	61.0	21	64.7	85.4	75.3	21	36	78.6	58.4
$^{13}C_2$-PFTeDA	21	36.7	79.6	61.8	21	25	74	49.0	21	46.9	79.3	64.5	21	16.1	78.8	54.2
$^{13}C_3$-PFBS	21	89.1	101	94.7	21	67	91	77.2	21	76.1	97.9	84.3	21	75.1	122	98.5
$^{13}C_3$-PFHxS	21	83.1	103	89.5	21	73	88	78.7	21	76.3	92.9	85.6	21	71.4	102	89.3
$^{13}C_8$-PFOS	21	80	98.9	87.2	21	66	80	73.2	21	73.8	101	87.3	21	64.9	117	86.6
$^{13}C_2$-4:2FTS	21	87	159	125.3	21	101	220	158.0	21	81.3	129	102.5	21	75.5	182	129.3
$^{13}C_2$-6:2FTS	21	88.1	117	100.8	21	86	140	111.5	21	83.4	105	90.8	21	62.6	173	120.6
$^{13}C_2$-8:2FTS	21	79.4	112	92.9	21	73	144	112.4	21	70.3	103	84.4	21	41.5	112	73.8
$^{13}C_8$-PFOSA	21	79.2	94.9	84.2	21	68	83	75.0	21	66.6	90.1	81.2	21	56.3	96.8	78.2
D_3-NMeFOSA	21	66.7	86.2	72.7	21	62	79	67.7	21	49.7	67.1	57.5	21	39.4	75.4	58.5
D_5-NEtFOSA	21	62.1	84.5	69.8	21	55	72	62.9	21	45.8	70.8	58.0	21	37.9	69.6	54.6
D_3-NMeFOSAA	21	68.8	92.4	77.2	21	75	114	89.0	21	73	90.8	82.6	21	33.6	97.5	69.4
D_5-NEtFOSAA	21	71.9	92.4	80.2	21	56	98	74.7	21	72	89.2	80.9	21	27.8	90.5	62.7
D_7-NMeFOSE	21	64.2	79.3	71.5	21	68	98	80.9	21	57.4	83.2	72.3	21	10	69	46.1
D_9-NEtFOSE	21	57.6	74.5	68.2	21	66	95	79.3	21	56.1	85	73.2	21	2.46	68.4	40.3
$^{13}C_3$-HFPO-DA	21	83.6	96.1	89.7	21	71	85	76.4	21	68.9	93.8	82.6	21	91.8	130	109.9

Table B-4. Summary of EIS Compound Percent Recovery in Landfill Leachate Samples for Each Laboratory (continued)

EIS Compound	Lab 9 % recovery				Lab 10 % recovery				All Labs % Recovery			
	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean
$^{13}C_4$-PFBA	21	25	94	54.3	21	58.2	92.4	74.8	126	4	97.2	66.3
$^{13}C_5$-PFPeA	21	68	95	81.1	21	70.3	93.5	83.8	126	48	108	83.7
$^{13}C_5$-PFHxA	21	85	95	90.5	21	76.4	91.8	84.5	126	68	104	85.4
$^{13}C_4$-PFHpA	21	84	107	94.7	21	72.3	93.8	84.7	126	68	107	88.0
$^{13}C_8$-PFOA	21	88	98	93.5	21	75.4	105	85.0	126	61.9	105	85.3
$^{13}C_9$-PFNA	21	82	96	88.2	21	75.4	90	82.8	126	66	103	85.1
$^{13}C_6$-PFDA	21	79	93	86.0	21	65.6	80.4	74.6	126	56.8	107	80.5
$^{13}C_7$-PFUnA	21	77	91	83.4	21	54.9	73.5	65.5	126	48.2	98.6	75.8
$^{13}C_2$-PFDoA	21	65	87	77.8	21	49.7	69.1	59.1	126	36	88.1	68.2
$^{13}C_2$-PFTeDA	21	50	84	68.3	21	28.3	51	41.1	126	16.1	84	56.5
$^{13}C_3$-PFBS	21	76	97	83.0	21	73.4	92.8	83.2	126	67	122	86.8
$^{13}C_3$-PFHxS	21	83	95	88.5	21	75.3	90.8	82.5	126	71.4	103	85.7
$^{13}C_8$-PFOS	21	78	95	85.7	21	70	83.2	77.7	126	64.9	117	82.9
$^{13}C_2$-4:2FTS	21	38	177	120.0	21	62.6	143	105.3	126	38	220	123.4
$^{13}C_2$-6:2FTS	21	43	124	91.4	21	79	119	98.9	126	43	173	102.4
$^{13}C_2$-8:2FTS	21	44	109	81.0	21	51.1	92.9	75.4	126	41.5	144	86.7
$^{13}C_8$-PFOSA	21	78	93	84.4	21	63.9	82.9	73.9	126	56.3	96.8	79.5
D_3-NMeFOSA	21	68	83	74.0	21	41	58.5	50.0	126	39.4	86.2	63.4
D_5-NEtFOSA	21	62	77	71.0	21	33.6	53.4	44.3	126	33.6	84.5	60.1
D_3-NMeFOSAA	21	55	88	71.7	21	58.5	89.4	75.5	126	33.6	114	77.6
D_5-NEtFOSAA	21	52	85	70.3	21	55.9	84.4	68.9	126	27.8	98	73.0
D_7-NMeFOSE	21	60	83	73.9	21	35.2	60.3	49.1	126	10	98	65.6
D_9-NEtFOSE	21	52	80	70.5	21	28.8	54.7	43.9	126	2.46	95	62.6
$^{13}C_3$-HFPO-DA	21	82	104	92.5	21	75.1	102	88.6	126	68.9	130	89.9

Version: Summary_tables_LCBS_Exa_CH5_12132023.xlsx

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

Appendix C

Biosolid Supporting Tables

Table C-1. Range of Target Analytes in Unspiked Biosolids Samples (µg/kg).

Analyte	Number of Labs	BSAH1		BSAI1		BSAJ1	
		Min	Max	Min	Max	Min	Max
PFBA	6[a]	0.504 U	2.67 U	0.504 U	4.91 J+B	0.504 U	2.67 U
PFPeA	6	0.39 U	0.88 J	1.33 U	2.35 J	0.39 U	2.89 J
PFHxA	6	0.375 U	4.37	4.8	11.8	0.375 U	1.67 J
PFHpA	6	0.296 U	0.256 JI	0.296 U	0.4 J	0.232 U	0.886 U
PFOA	6	0.71 J	1.63 J	1.67 J	3.51	0.315 U	0.873 J
PFNA	6	0.441 U	1.4 J	0.441 U	0.784 U	0.441 U	0.784 U
PFDA	6	1.36 J	3.43	1.09 J	2.68	0.618 U	2
PFUnA	6	0.667 U	0.872 J	0.24 U	1.15 U	0.24 U	0.602 J
PFDoA	6	0.971 J	2.7	0.41 U	1.02 J	0.648 U	1.54 J
PFTrDA	6	0.22 U	1.19 J	0.22 U	0.667 U	0.22 U	1.04 J
PFTeDA	6	0.31 U	0.59 JI	0.303 U	1.06 U	0.31 U	0.345 J
PFBS	6	0.269 U	0.624 U	0.432 U	0.537 J	0.4 U	0.866 JI
PFPeS	6	0.23 U	31.5 I	0.23 U	0.69 U	0.23 U	0.69 U
PFHxS	6	0.36 U	4.46 I	0.328 U	0.419 J	0.36 U	2.58 I
PFHpS	6	0.368 U	11.9 I	0.249 U	0.959 U	0.249 U	0.959 U
PFOS	6	3.62 J+I	8.3	4.51	9.59	2.94 J+	9.21
PFNS	5	0.38 U	0.64 U	0.38 U	0.64 U	0.38 U	0.64 U
PFDS	6	0.27 U	0.587 JI	0.27 U	1.76 U	0.32 U	0.414 U
PFDoS	6	0.27 U	0.976 U	0.27 U	0.976 U	0.27 U	0.976 U
4:2FTS	6	0.808 U	17 UD	0.808 U	3.97 U	0.808 U	3.97 U
6:2FTS	6	1.39 U	3.05 U	2.98 J	8.33	1.39 U	48.1 JB
8:2FTS	6	1.02 U	5.18 U	1.02 U	5.18 U	1.02 U	5.18 U
PFOSA	6	0.273 U	1.13 J	0.273 U	0.392 J	0.273 U	0.885 J
NMeFOSA	5	0.29 U	1 U	0.29 U	1 U	0.29 U	1 U
NEtFOSA	5[b]	0.17 U	1.28 U	0.17 U	1.28 U	0.17 U	1.28 U
NMeFOSAA	6	1.48 J	4.66 J+	2.11	6.67 J+	3.16	9.25 J+
NEtFOSAA	6	1.38 J	3.52	0.798 J	2.18	2.01	5.81
NMeFOSE	6	3.96 U	17.5 J	1.51 U	3.62 J	6.67 U	13.7 J
NEtFOSE	6	3.09 U	6.47 J	3.09 U	0.811 J	4.42 U	6.05 J
PFMPA	6	0.408 U	1.33 U	0.408 U	1.33 U	0.408 U	1.33 U
PFMBA	6	0.312 U	1.33 U	0.312 U	1.33 U	0.312 U	1.33 U
NFDHA	6	0.597 U	2.82 U	0.597 U	2.82 U	0.597 U	2.82 U
HFPO-DA	6	0.51 U	4.32 U	0.51 U	4.32 U	0.51 U	4.32 U
ADONA	6	0.79 U	2.83 U	0.79 U	2.83 U	0.79 U	2.83 U
PFEESA	6	0.34 U	1.19 U	0.34 U	1.19 U	0.34 U	1.19 U
9Cl-PF3ONS	6	0.814 U	2.77 U	0.814 U	2.77 U	0.814 U	2.77 U
11Cl-PF3OUdS	6	0.88 U	2.52 U	0.88 U	2.52 U	0.88 U	2.52 U
3:3FTCA	6	1.03 U	2.67 U	1.03 U	2.67 U	1.03 U	2.67 U
5:3FTCA	6	64.1	145	1.33 U	6.81 J	6.45 U	164
7:3FTCA	6	29.3 J	66.1	5.63 U	17.6 U	7.41 U	16.8 J

Version: Appendix C_Biosolids 01182024.xlsx

[a] 5 labs for BSAH1, BSAJ1

[b] 4 labs for BSAJ1

Table C-2. Summary of Biosolids Spike Percent Recoveries in Low Spike Samples for each Laboratory.

Analyte	Lab 3 spike % recovery				Lab 4 spike % recovery				Lab 6 spike % recovery				Lab 8 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	98.5	105.2	101.9	7	101.5	109.7	105.9	8	81.2	99	88.1	9	101.2	124.8	119.1
PFPeA	9	98.2	107.6	104.5	9	101	110.2	104.7	9	69.6	99	88.3	9	78	144	120.7
PFHxA	6	89	109	100.3	9	98.2	121.2	107.8	6	78.3	130	111.8	9	133	228	163.4
PFHpA	9	96.5	105.4	99.7	9	95.6	110	102.5	9	64.8	128	106.7	9	89.4	122	108
PFOA	9	102	116.7	109.5	9	92.9	111.9	100.7	9	72.4	115.8	98.6	9	93.6	143.7	124.5
PFNA	9	92.5	124	108.1	9	92.2	111	104.5	9	88	129	114.6	9	86.7	126	102.6
PFDA	9	86.7	113	97.9	9	90.7	103.4	96	9	83.7	102.4	94.5	9	92.6	139.6	122.4
PFUnA	9	93.3	128	111	9	105	117	110.7	9	83.3	111	95.7	9	86.7	132	104.2
PFDoA	9	90.8	109.8	103.2	9	102	116.8	108.9	9	54.7	114	92.5	9	86.7	139	103.3
PFTrDA	9	109	189.1	140.5	9	99.6	108	104.5	9	114	192.6	133	9	86	270.6	172.6
PFTeDA	9	73.3	102	88.8	9	97.1	108	104.1	9	92.2	135	113	9	70	138	112.4
PFBS	9	98.2	121.6	111.3	9	90.6	133.7	107.2	9	93	181.9	123.6	9	111.6	169.8	142.7
PFPeS	9	103.9	127.5	111.7	6	97.9	122.5	114.3	9	78.3	313.7	135.1	9	97.7	142.2	119.4
PFHxS	9	82.4	108.6	93.8	9	108.6	161.4	124.1	9	79.6	131	103.6	9	94.8	181.7	141.9
PFHpS	9	26.2	130	86.3	9	87.9	131	109.3	6	78.5	164.3	118.1	9	89.5	132.1	116.8
PFOS	9	34.4	110.4	75.1	9	83.9	149	111.4	9	69.4	95.6	84.6	9	105.6	178.6	122.2
PFNS	9	24.7	104	72.4	0	--	--	--	9	53.2	83.7	69.7	9	52.9	124	75.9
PFDS	9	25.1	110	77.7	9	91.5	115	100.9	9	67.6	104	84.3	9	48.7	117	81.2
PFDoS	9	30.3	134.7	92.6	9	42	83.3	57.3	9	33.8	77.7	59.9	9	24	68	43.8
4:2FTS	9	95.7	109.4	102.3	9	91.9	103.8	100.3	9	74.9	111.7	92.1	9	87.1	133	117.8
6:2FTS	9	97.5	114.8	104.1	9	92.5	113.2	102.6	9	64.7	947.5	273.9	6	102.8	256.3	145.5
8:2FTS	9	114.6	142.4	127.2	9	93.1	122.8	108.4	9	80.1	105.7	87.9	9	91.1	158.8	132.1
PFOSA	9	97.3	116.8	107.3	9	98.1	114	105.9	9	85.5	101	91.7	9	85.3	135	117.9
NMeFOSA	9	99.5	117.5	108.1	9	108	124	112.9	9	83	101.5	92.3	0	--	--	--
NEtFOSA	9	107.5	122.5	113.6	9	100	118.5	110.4	9	72.5	108.5	89.9	0	--	--	--
NMeFOSAA	9	94.3	122.7	105.6	9	92.1	106.3	100.6	9	66.1	104.7	87.3	9	95.2	143.2	116.5
NEtFOSAA	9	92.9	136.9	109	9	87.9	110.3	100.2	9	69.1	112.1	87.6	9	91.9	134.9	120.6
NMeFOSE	9	90.6	113.4	102.5	9	87.5	108	99.4	9	82.3	93.2	87.8	9	84.4	147	128
NEtFOSE	9	105	119	112.4	9	103	110	105.2	9	81.9	91.9	87.1	9	79.6	127	109.4
PFMPA	9	46.8	89	78.6	9	10	104	62.6	9	31.8	74.5	41.4	9	54	135.5	110.2
PFMBA	9	84	101	93.6	9	105.5	153	116.1	9	86.5	129	103.3	9	102.5	145	124
NFDHA	9	70	97.2	84.6	9	59	98	78.6	9	89.5	138	103.3	9	47.5	73	59.3
HFPO-DA	9	91.5	107	99.4	9	83.8	121.5	106.8	9	78.5	120.3	101.8	9	90	127.8	117.6
ADONA	9	98	127	109.8	9	103.3	119.7	110.8	9	56.8	90.7	75.2	9	89.1	139.4	125.9
PFEESA	9	69.5	73.5	72.1	9	90	102	97.7	9	78.5	119.5	90.9	9	91.5	135.5	120.2
9Cl-PF3ONS	9	77.8	93.1	84.7	9	107.9	132.7	119.3	9	45.4	113.5	79.6	9	90.6	122.4	110.5
11Cl-PF3OUdS	9	78.8	96.5	86.8	9	96	116.2	105.8	9	60.1	99.5	80	9	71	115.7	97.1
3:3FTCA	9	71	106	91.4	9	53.8	98.2	78.8	9	46	73.2	58.5	9	46.2	112	72.9
5:3FTCA	9	48.2	99.8	77.7	9	55.2	114.3	91.2	9	44	163.4	103.6	9	50.4	203	144.1
7:3FTCA	9	64.8	131.6	99.8	9	52.8	131.2	95.6	9	44.6	181.1	109.5	9	46.6	218.8	144.8

Version: Appendix C_Biosolids 01182024.xlsx

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

-- : X-flagged results

Table C-2. Summary of Biosolids 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	40.5	52.2	45.8	9	91.5	115.5	105.4	51	40.5	124.8	94
PFPeA	9	40.7	54.5	46.9	9	88.5	122	102.1	54	40.7	144	94.5
PFHxA	9	36.8	59.2	45.9	9	88.9	143.3	109.6	48	36.8	228	106.5
PFHpA	9	43.9	57.2	48.6	9	91.5	123	113.7	54	43.9	128	96.6
PFOA	9	37.1	60.6	45.3	9	77.9	100.6	90.4	54	37.1	143.7	94.9
PFNA	9	40.4	61.9	47.8	9	98.6	130	113.6	54	40.4	130	98.5
PFDA	9	35.9	62.8	44.3	9	90.2	112.4	99.7	54	35.9	139.6	92.5
PFUnA	9	37.7	58.8	45.3	9	93.7	126	106.4	54	37.7	132	95.5
PFDoA	9	36	59.4	43.4	9	87.2	112	100.5	54	36	139	92
PFTrDA	9	28.3	47.6	37.4	9	61	95.1	79	54	28.3	270.6	111.2
PFTeDA	9	34.1	54	41.2	9	93.4	109	103.5	54	34.1	138	93.8
PFBS	9	36.1	50.2	44.1	9	96.1	131.7	114.1	54	36.1	181.9	107.2
PFPeS	9	38.1	54.4	45.3	9	92.9	121.6	106.1	51	38.1	313.7	104.8
PFHxS	9	36.6	52.8	41.7	9	95	125.9	113.8	54	36.6	181.7	103.1
PFHpS	9	41.3	76.8	55.6	9	103.8	120	109.9	51	26.2	164.3	98.2
PFOS	9	35.7	57.7	42.3	9	88.1	111.5	101.9	54	34.4	178.6	89.6
PFNS	9	25.6	43.1	32.8	9	75.1	95.1	85.3	45	24.7	124	67.2
PFDS	9	19.2	39.1	29.1	9	48.2	82.3	64.8	54	19.2	117	73
PFDoS	9	14.4	19.1	17.1	9	15.9	52.1	32.2	54	14.4	134.7	50.5
4:2FTS	9	42.9	55.3	46.5	9	85.5	140.4	107	54	42.9	140.4	94.3
6:2FTS	9	42.8	62.8	50.5	9	83.6	149.9	122.1	51	42.8	947.5	132.4
8:2FTS	9	46.2	73.4	54.4	9	101.7	151.1	125	54	46.2	158.8	105.8
PFOSA	9	41.8	66.5	50.3	9	83.9	112.1	95.3	54	41.8	135	94.8
NMeFOSA	9	38.6	64	48.7	9	98.5	111	104.8	45	38.6	124	93.3
NEtFOSA	9	35.9	62	46.8	9	100.5	106.5	104.1	45	35.9	122.5	93
NMeFOSAA	9	33.7	52.2	39.4	9	82.4	120.3	99.4	54	33.7	143.2	91.5
NEtFOSAA	9	37.3	63.1	48.1	9	78.1	137.5	112.7	54	37.3	137.5	96.4
NMeFOSE	9	35.3	53.7	44.4	9	89.2	108.6	98.2	54	35.3	147	93.4
NEtFOSE	9	37.6	57.9	44.2	9	94.8	102.9	98.5	54	37.6	127	92.8
PFMPA	9	14.3	56.5	37.7	9	83.5	119	95.1	54	10	135.5	70.9
PFMBA	9	42.2	54.5	47.9	9	81	124.5	94.9	54	42.2	153	96.6
NFDHA	9	36	48	40.5	9	58	98.8	77.7	54	36	138	74
HFPO-DA	9	38	51	43.3	9	86.2	124.8	105.1	54	38	127.8	95.7
ADONA	9	41.9	57.8	48.6	9	96.2	121.2	111	54	41.9	139.4	96.9
PFEESA	9	40.9	54.5	46.1	9	78	117	97.3	54	40.9	135.5	87.4
9Cl-PF3ONS	9	39.8	62.5	44.8	9	101	133.4	114.6	54	39.8	133.4	92.3
11Cl-PF3OUdS	9	34.8	52.8	41	9	59.6	89.6	77	54	34.8	116.2	81.3
3:3FTCA	9	30.8	61.5	39.9	9	80.7	118.5	94	54	30.8	118.5	72.6
5:3FTCA	9	35.8	76.4	55.3	9	52.2	148.4	108.7	54	35.8	203	96.8
7:3FTCA	9	32.2	125.6	74.8	9	43.4	111.6	81	54	32.2	218.8	100.9

Version: Appendix C_Biosolids 01182024.xlsx

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

-- : X-flagged results

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

Analyte	Lab 3 spike % recovery				Lab 4 spike % recovery				Lab 6 spike % recovery				Lab 8 spike % recovery			
	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg	n	Min	Max	Avg
PFBA	9	101.2	106.5	103.8	7	100.2	113.8	109.3	8	80.8	88.5	84.5	9	109	162.8	123
PFPeA	9	101.2	109	104.6	9	99.8	107.5	103.5	9	64.4	90.5	78.6	9	107.7	181.8	134
PFHxA	9	91.5	105.9	98.8	9	96.1	111	105.2	9	61.5	97.2	82.1	9	136.6	204.3	158.5
PFHpA	9	91.3	107.6	100.1	9	97.5	105	100.8	9	77.1	94.1	83.2	9	95.9	134	108.9
PFOA	9	90.4	116.3	104.6	9	93.1	104.5	99.5	9	71.7	87.1	78.8	9	111	160.1	123.6
PFNA	9	87.6	107	99	9	99.6	112	105.7	9	74.5	97.3	87.1	9	81	132	105
PFDA	9	91.8	120.6	104.3	9	98.8	105.5	101.7	9	69.3	86.9	78.6	9	110.7	174.1	128.5
PFUnA	9	85	111	100.6	9	102	108	104.6	9	52.6	87.3	79.4	9	84.3	136	106
PFDoA	9	93.5	115	103.9	9	100.9	108.7	104.2	9	74	96.7	86.9	9	85.5	132.6	108.7
PFTrDA	9	101	173.8	133	9	94.3	104.7	99.5	9	92.8	174.7	113.4	8	116	255	176.8
PFTeDA	9	80.1	101	88.6	9	94.3	102	100.2	9	69.3	114.5	89	9	93.8	162	119
PFBS	9	102.5	120.6	112.6	9	101.5	114.6	106.6	9	75.2	114.6	89.6	9	101.5	147.7	119.7
PFPeS	9	102.4	109.4	105.6	9	92.9	112.4	103.1	9	66.9	111.4	84.5	9	108.4	193.8	133.1
PFHxS	9	93.3	103.2	99	9	100.7	113.7	107.8	9	69.7	102.7	87.3	9	117.6	164.5	129
PFHpS	9	24.8	109.9	75.2	9	96.9	107.9	101.6	9	69.6	90.8	84.4	9	112.9	159.3	126.9
PFOS	9	23.2	101.5	68.4	9	93.7	103.2	98.7	9	54.6	86.5	77.1	9	104.3	148.2	118
PFNS	9	22.5	103	66	0	--	--	--	9	45.3	84.1	67.3	9	51.4	125	83.5
PFDS	9	22.8	108.7	70	9	85.6	99.7	93.4	9	55.8	85	74.7	9	47.5	121.6	90.3
PFDoS	9	26.5	114	75.9	9	40.7	76.5	55.7	9	37.2	81.7	55.6	9	24.5	64.8	47.2
4:2FTS	9	95	104.5	100.3	9	91.6	113.7	99.7	9	56.2	78.3	70.3	9	97.5	156.6	121.3
6:2FTS	9	100.3	109.6	104.9	9	98	113.4	104.2	9	72.5	114.6	89.5	9	115.5	219.2	154.6
8:2FTS	9	110.9	125.6	121.1	9	100.8	137.8	116.3	9	68.5	111.7	85.4	9	115.9	178.1	134.1
PFOSA	9	104	121.9	111.6	9	97.6	109.4	104.9	9	82.9	91.6	87.4	9	109.1	163	125.5
NMeFOSA	9	98.2	113	106.9	9	102	124	109.8	9	86	97.2	90	0	--	--	--
NEtFOSA	9	108	120	113.3	9	106	116	109.7	9	76.7	103	89.6	0	--	--	--
NMeFOSAA	9	94.8	127.3	108.7	9	96.8	110.8	100.8	9	76.7	102.9	90.2	9	106.5	157.2	120
NEtFOSAA	9	94.8	107.9	102.6	9	99.8	116.2	108.2	9	68.9	97.8	88	9	119.5	169.2	128.2
NMeFOSE	9	94.7	111	104.8	9	102.2	107.3	104.6	9	76.7	90.8	85	9	115.8	171.7	129.5
NEtFOSE	9	100.8	113.2	108.1	9	102.3	109.3	106.2	9	74	92.5	83.2	9	96.5	156.2	115.8
PFMPA	9	55.5	96	87.9	9	10.1	106.5	65.5	9	30.6	66	42	9	61.5	164	120.8
PFMBA	9	92.5	114.5	98.1	9	103	142	117.4	9	80	139.5	104.4	9	103.5	179.5	132.9
NFDHA	9	71.9	95	84.6	9	48.1	105	79.1	9	73.8	121.2	97	9	49.9	76.2	61.9
HFPO-DA	9	90	102.5	96.7	9	95.9	115.6	105.9	9	70	98.8	87.7	9	106.2	156.6	124
ADONA	9	94.4	116.8	105.7	9	102.8	118.7	112.1	9	49.8	93.8	75.2	9	114	156.4	123.5
PFEESA	9	72.2	82.8	77.3	9	97.8	106.5	103	9	79.7	105.2	91.3	9	117.7	165.6	128.6
9Cl-PF3ONS	9	74.7	88.7	81.8	9	110.5	132.6	120.5	9	42	122.6	80.8	9	87.8	138.8	113.3
11Cl-PF3OUdS	9	81	91.9	86.8	9	104	117.1	108.2	9	51.4	105.6	79.4	9	73.5	128.3	103.8
3:3FTCA	9	80	111.2	99.7	9	53.8	101.2	82.7	9	43.8	89.1	60.4	9	45	110.9	75.3
5:3FTCA	9	53.2	112	81.5	9	54.5	119.9	95.3	9	44.6	120	86.6	9	69.5	171.8	121.4
7:3FTCA	9	65.5	133	104.5	9	53	138.9	101.4	9	43.8	143.2	94.9	9	68.5	189.7	126.4

Version: Appendix C_Biosolids 01182024.xlsx

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

-- : X-flagged results

Table C-3. Summary of Biosolids Spike Percent Recoveries in High 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	43.5	48.5	45.1	9	96.2	109.5	104.3	51	43.5	162.8	94.7
PFPeA	9	44.2	51.5	46.4	9	79.8	120	100.3	54	44.2	181.8	94.6
PFHxA	9	41.8	50.5	44.9	9	91.8	112.2	102.4	54	41.8	204.3	98.6
PFHpA	9	41.2	50.1	45.3	9	91.1	119	105.1	54	41.2	134	90.6
PFOA	9	38.5	48.8	43.3	9	84.9	104.3	95.6	54	38.5	160.1	90.9
PFNA	9	40.4	48.5	44.6	9	89.8	128	104.3	54	40.4	132	91
PFDA	9	39.6	52.4	44.6	9	99.5	122.3	109.7	54	39.6	174.1	94.6
PFUnA	9	39.5	51.2	44	9	92.2	111	99.9	54	39.5	136	89.1
PFDoA	9	37.9	48.9	42.9	9	95.7	102.1	98.7	54	37.9	132.6	90.9
PFTrDA	9	27.4	41.8	35	9	60.2	88.9	76.3	53	27.4	255	104.3
PFTeDA	9	34.4	48.6	40.3	9	89.7	114	99.4	54	34.4	162	89.4
PFBS	9	42.5	51.7	45.8	9	87.8	106.5	96.5	54	42.5	147.7	95.1
PFPeS	9	40.8	49.4	44.8	9	90.6	122.5	102.6	54	40.8	193.8	95.6
PFHxS	9	38.4	45.8	42.4	9	91.6	112.2	106	54	38.4	164.5	95.3
PFHpS	9	41.9	66.3	51	9	102.8	121	110.6	54	24.8	159.3	91.6
PFOS	9	38.7	52	45.4	9	97	117	105.9	54	23.2	148.2	85.6
PFNS	9	26.3	40.8	32.5	9	77.4	95.4	87.7	45	22.5	125	67.4
PFDS	9	25.4	36.3	30.7	9	54.7	73.9	64.5	54	22.8	121.6	70.6
PFDoS	9	14.1	20.4	17.1	9	17.7	44.9	31.9	54	14.1	114	47.3
4:2FTS	9	40.9	49.6	45.5	9	86.2	150.4	108.8	54	40.9	156.6	91
6:2FTS	9	41.6	54.2	48.2	9	62.1	158.3	102.7	54	41.6	219.2	100.7
8:2FTS	9	44.5	57.5	51	9	94.5	135.2	115.7	54	44.5	178.1	103.9
PFOSA	9	41.7	53.5	47.2	9	96	107.6	100.3	54	41.7	163	96.2
NMeFOSA	9	38.8	56.1	46.5	9	98	106	102.4	45	38.8	124	91.1
NEtFOSA	9	36.2	50.9	44	9	99.9	107	103.7	45	36.2	120	92
NMeFOSAA	9	34	44	39.4	9	91.6	120.2	104	54	34	157.2	93.8
NEtFOSAA	9	41.7	55.7	46.7	9	107.1	136.7	118.4	54	41.7	169.2	98.7
NMeFOSE	9	40	48.7	42.3	9	92.8	106	99.7	54	40	171.7	94.3
NEtFOSE	9	37.5	47.3	41.6	9	96.7	106.7	100.5	54	37.5	156.2	92.6
PFMPA	9	22	49	39.6	9	72.5	110	94.2	54	10.1	164	75
PFMBA	9	45.2	55	48.8	9	77	111.5	95.4	54	45.2	179.5	99.5
NFDHA	9	39.2	46.4	41	9	65	106.9	82.6	54	39.2	121.2	74.4
HFPO-DA	9	40.9	47.8	43.5	9	90.6	126.2	107.9	54	40.9	156.6	94.3
ADONA	9	44.5	55.5	49.6	9	84.4	118.1	105.4	54	44.5	156.4	95.2
PFEESA	9	43.5	51.9	46.1	9	81.6	113.9	94.7	54	43.5	165.6	90.2
9Cl-PF3ONS	9	36.1	48.2	43.1	9	94	130.1	110.6	54	36.1	138.8	91.7
11Cl-PF3OUdS	9	34.9	44.5	40.2	9	63.6	85	72.8	54	34.9	128.3	81.9
3:3FTCA	9	31.9	49.1	39.8	9	68.4	129.7	93.8	54	31.9	129.7	75.3
5:3FTCA	9	35.4	75.3	52.1	9	55	149.4	106	54	35.4	171.8	90.5
7:3FTCA	9	31.8	119.2	69	9	40.8	112.5	81.5	54	31.8	189.7	96.3

Version: Appendix C_Biosolids 01182024.xlsx

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

-- : X-flagged results

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

EIS Compound	Lab 3				Lab 4				Lab 6				Lab 8			
	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean
$^{13}C_4$-PFBA	21	19	95	67.8	21	2.4	93.2	47.0	21	7.58	70.8	25.0	22	17	117	85.3
$^{13}C_5$-PFPeA	21	49	90	68.9	21	56.7	98.9	81.9	21	32.5	106	71.8	27	10	109	77.8
$^{13}C_5$-PFHxA	21	70	102	81.9	21	83	105	93.2	21	76	105	91.1	25	13	103	77.5
$^{13}C_4$-PFHpA	21	70	108	85.3	21	82.2	107	92.1	21	76	118	94.7	21	90	130	110.2
$^{13}C_8$-PFOA	21	54	81	68.2	21	87.6	113	95.8	21	67.5	130	91.5	21	70	124	101.6
$^{13}C_9$-PFNA	21	71	96	84.9	21	88.8	109	95.5	21	87.7	111	99.6	21	91	144	120.4
$^{13}C_6$-PFDA	21	68	103	82.3	21	91.7	117	98.3	21	84.4	105	95.6	21	80	125	107.2
$^{13}C_7$-PFUnA	21	55	94	76.5	21	77.1	101	89.4	21	53.8	109	82.7	21	90	124	107.2
$^{13}C_2$-PFDoA	21	58	114	87.3	21	66.9	92.1	79.2	21	47.5	114	84.2	21	68	116	90.2
$^{13}C_2$-PFTeDA	21	74	166	113.0	21	35.9	78.4	54.6	21	48.7	93.3	71.6	21	14	96	46.7
$^{13}C_3$-PFBS	21	73	106	86.7	21	89.4	115	98.4	21	81.2	158	110.9	21	89	144	118.9
$^{13}C_3$-PFHxS	21	74	102	84.9	21	88.9	112	95.8	21	78.4	132	103.2	21	83	138	112.1
$^{13}C_8$-PFOS	21	63	116	82.7	21	70.2	95.7	85.4	21	82.8	124	98.4	21	86	127	110.8
$^{13}C_2$-4:2FTS	21	157	302	229.9	21	118	204	151.3	21	118	293	186.1	21	183	311	241.3
$^{13}C_2$-6:2FTS	21	102	208	154.2	21	109	175	132.8	21	99.2	379	188.5	21	135	371	221.2
$^{13}C_2$-8:2FTS	21	140	222	177.5	21	112	189	144.2	21	117	236	169.1	21	136	314	212.9
$^{13}C_8$-PFOSA	21	10	94	44.3	21	56.3	94.8	78.1	21	40.3	93.5	69.0	21	59	123	98.0
D_3-NMeFOSA	21	10	80	47.4	21	26.6	55.5	39.7	21	57	81.5	68.2	0	--	--	--
D_5-NEtFOSA	21	8	75	44.3	21	21.7	52.5	33.3	21	43.4	75.5	59.2	0	--	--	--
D_3-NMeFOSAA	21	12	140	70.9	21	58.8	92.4	77.6	21	43	97	79.5	21	102	137	118.9
D_5-NEtFOSAA	21	11	116	55.7	21	52.8	99.5	79.7	21	34	104	79.0	21	54	141	92.7
D_7-NMeFOSE	21	12	101	59.5	21	39.8	67.7	51.5	21	57.5	86.5	75.7	21	28	75	46.8
D_9-NEtFOSE	21	10	92	50.2	21	29.3	70.3	43.8	21	32.3	84	57.7	21	23	74	43.4
$^{13}C_3$-HFPO-DA	21	62	88	72.4	21	72.8	92	83.2	21	72.6	122	97.4	23	16	119	91.4

Table C-4. Summary of Biosolids EIS Percent Recovery for each Laboratory (continued).

EIS Compound	Lab 9				Lab 10				All Labs % Recovery			
	n	Min	Max	Mean	n	Min	Max	Mean	n	Min	Max	Mean
$^{13}C_4$-PFBA	21	14	100	67.7	21	85.5	107	96.0	127	2.4	117	64.9
$^{13}C_5$-PFPeA	21	81	98	91.7	21	72.1	117	94.5	132	10	117	81.0
$^{13}C_5$-PFHxA	21	96	104	99.5	21	89.3	111	98.7	130	13	111	89.9
$^{13}C_4$-PFHpA	21	90	103	94.0	21	68.8	109	90.6	126	68.8	130	94.5
$^{13}C_8$-PFOA	21	92	105	100.0	21	82.3	122	96.7	126	54	130	92.3
$^{13}C_9$-PFNA	21	94	107	98.5	21	83	113	99.9	126	71	144	99.8
$^{13}C_6$-PFDA	21	95	109	100.3	21	81.1	109	88.6	126	68	125	95.4
$^{13}C_7$-PFUnA	21	62	99	81.7	21	75.6	113	92.2	126	53.8	124	88.3
$^{13}C_2$-PFDoA	21	65	95	79.1	21	50.1	92.6	67.3	126	47.5	116	81.2
$^{13}C_2$-PFTeDA	21	36	57	46.0	21	12.7	47.9	27.4	126	12.7	166	59.9
$^{13}C_3$-PFBS	21	84	103	92.2	21	76.4	118	100.9	126	73	158	101.3
$^{13}C_3$-PFHxS	21	94	108	100.1	21	75.6	126	96.7	126	74	138	98.8
$^{13}C_8$-PFOS	21	92	102	98.1	21	81.5	102	92.9	126	63	127	94.7
$^{13}C_2$-4:2FTS	21	163	248	196.8	21	73.8	138	109.5	126	73.8	311	185.8
$^{13}C_2$-6:2FTS	21	136	272	189.7	21	57.9	148	111.2	126	57.9	379	166.3
$^{13}C_2$-8:2FTS	21	122	222	175.2	21	73.8	139	109.7	126	73.8	314	164.8
$^{13}C_8$-PFOSA	21	76	142	102.9	21	43.2	72.7	60.6	126	10	142	75.5
D_3-NMeFOSA	21	38	73	56.2	21	22.1	50.2	37.0	105	10	81.5	49.7
D_5-NEtFOSA	21	26	51	35.6	21	20.3	46	33.5	105	8	75.5	41.2
D_3-NMeFOSAA	21	85	105	96.0	21	75.9	150	115.9	126	12	150	93.1
D_5-NEtFOSAA	21	33	95	73.3	21	64.8	140	93.9	126	11	141	79.1
D_7-NMeFOSE	21	55	82	66.5	21	31.5	75	50.4	126	12	101	58.4
D_9-NEtFOSE	21	34	71	50.7	21	24.1	73.1	43.1	126	10	92	48.1
$^{13}C_3$-HFPO-DA	21	87	105	97.2	21	65.8	102	87.2	128	16	122	88.2

Version: Appendix C_Biosolids 01182024.xlsx

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