Massachusetts Department of Environmental Protection

Review of Per- and Polyfluoroalkyl Substances (PFAS) data collected for the Massachusetts Department of Environmental Protection (MassDEP) Biosolids and Residuals Program, 2020-2021

Data Summary and Quality Control Report

May 19, 2023

Summary Report: Final

TETRA TECH

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PRESENTED TO

Massachusetts Department of Environmental Protection
MassDEP NPDES and Residuals Program

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EXECUTIVE SUMMARY

Overview

Per- and polyfluoroalkyl substances (PFAS) have been widely used in industry and consumer products since the 1950s. PFAS are extremely stable and therefore persist in the environment and human body and have been associated with increased human health risks, including cancers and infertility. The U.S. Environmental Protection Agency (USEPA) issued drinking water health advisories for PFOA and PFOS in 2016 and continues to consider regulations for PFAS relative to exposure. The Massachusetts Department of Environmental Protection (MassDEP) has developed cleanup standards for PFAS in soil and groundwater and has issued a drinking water quality standard (maximum contaminant level) for the sum of six PFAS compounds.

MassDEP required entities that hold an Approval of Suitability (AOS) to sell or distribute organic waste residuals for land application in Massachusetts to perform quarterly PFAS monitoring in 2020-2022. No EPA-approved methods for testing residuals for PFAS were available in 2020–2022. Laboratories used a modified EPA Method 533 approved by MassDEP for determination of PFAS in drinking water to analyze residual samples.

In this report, an evaluation of the analytical results was performed for PFAS residuals samples collected during the third quarter of 2020 through the first quarter of 2022. Five laboratories provided PFAS analysis for 35 facilities over seven sampling quarters (September 2020 through March 2022). The facilities were characterized by residual treatment type. In this report we include summaries and analyses for PFAS6 and PFAS_16, the sum of all 16 PFAS compounds tested for residuals. The analyses focus on characterizing data quality and reliability through comparison of replicated measurements and compilation of laboratory qualifier flags. Analytical results in this report allow differentiation of PFAS concentrations and reliability of measures across duplicate measurements, over time, among facilities, and among laboratories.

Key Conclusions

There were no overall trends in PFAS levels over time. Compost Type I residuals had the highest PFAS concentrations, with four compost facilities averaging above 50 ng/g PFAS_16. There were no distinct differences in PFAS_16 levels by AOS type, CFR 503 designation, or Industrial Pretreatment Program status.

Of the most common PFAS compounds by percent, three are components of PFAS6 (PFOS, PFOA, and PFDA), while two are not components of PFAS6 (PFHxA and PFBA). Trends in PFAS compounds by percentage of total PFAS_16 were found for some treatment types: paper sludge showed high percentages of long-chain carboxylic PFAS, compost showed relatively higher percentages of short-chain PFAS compounds. The other treatment types showed a high percentage of PFOS.

When comparing primary and duplicate measurements for the two labs analyzing the most samples (lab A and lab B), both showed similar levels of precision. Variability of PFAS measurements between quarters was greater than variability between primary-duplicate pairs, suggesting a temporal effect, but without a temporal pattern in PFAS levels. Eight sampling events included a pseudo-split sample, where an additional sample was analyzed at a different lab than the primary sample. PFAS levels in primary-pseudo-split pairs were more variable than primary-duplicate pairs, suggesting a lab effect, but not a lab bias. No lab showed evidence of PFAS results biased higher or lower than other labs.

The most common qualifier flag for all PFAS compounds was the “R” flag, denoting that the method reporting limit (MRL) was above 1 ng/g. High MRLs precluded enumeration of flags assigned to analytes

due to low internal standard percent recovery. If percent recovery is low, then there might be more of a particular analyte in the sample than being detected. R flag frequency generally decreased over time, independent of total solids content. Lab A and B had similar occurrences of R flags, and a similar occurrence of flags overall. Lab C, which analyzed data from two facilities, had uncharacteristically high MRLs given the percent solids concentrations. A third of samples from Lab C did not follow the required step of analyzing the Matrix Spike Duplicate (MSD) along with the sample batch.

Key Recommendations

Based on the summary of PFAS data and review of laboratory reporting, there are several recommendations for improving sampling and reporting efficiency and quality. Considering the variability across sampling events and among laboratories and even among primary and duplicate samples, it is recommended that facilities should continue sampling quarterly. However, if duplicate samples are collected and analyzed for the main purpose of refining the understanding of sample concentration variability, they could be collected at a reduced frequency in the future. Because the magnitude of variability in concentrations would be captured by the quarterly sampling results, additional variability from duplicates would not change the variability observed over time in facilities. Splits do not need to be required in the sampling schedule.

The greatest concerns with the PFAS analysis were the high MRLs and the low % recovery of internal standards. Besides increasing the frequency of non-detect results, high MRLs decrease the ability to identify if results are biased low based on internal standard percent recovery. It can be expected that the new EPA Method 1633 with additional extraction steps (3-stage versus single stage extraction) and additional cleanup step with activated carbon might allow for lower MRLs while at the same time improving internal standard percent recovery. No more than speculation about the new method performance in comparison to modified Method 533 can be made until adoption of the method, application to the sample analysis, and evaluation of results.

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ACRONYMS/ABBREVIATIONS

Acronyms/Abbreviations	Definition
ANOVA	Analysis of Variance
AOS	Approval of Suitability
ATSDR	Agency for Toxic Substances and Disease Registry
CALM	Consolidated Assessment and Listing Manual
CASN	Chemical Abstract Serial Number
CV	Coefficient of Variability
EPA	Environmental Protection Agency
IPP	Industrial Pretreatment Program
LC-MS/MS	liquid chromatography-tandem mass spectrometry
LCS	Laboratory Control Sample
MassDEP	Massachusetts Department of Environmental Protection
MGL	Massachusetts General Laws
MMCL	Massachusetts Maximum Contamination Level
MRL	method reporting limit
MRM	Multiple Reaction Monitoring
MS/MSD	matrix spike and matrix spike duplicate
ng/g	nanograms per gram
ng/L	nanograms per liter
PCA	Principal Components Analysis
PFAS	Per- and polyfluoroalkyl Substances
PFAS6	Sum of PFOA, PFOS, PFNA, PFHxS, PFHpA, and PFDA
PFAS_16	Sum of 16 required PFAS components
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid

PFUnA	Perfluoroundecanoic acid
PFDoA	Perfluorododecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFBS	Perfluorobutanesulfonic acid
PFPeS	Perfluoropentanesulfonic acid
PFHxS	Perfluorohexanesulfonic acid
PFOS	Perfluorooctanesulfonic acid
PFNS	Perfluorononanesulfonic acid
PFDS	Perfluorodecanesulfonic acid
ppt	parts per trillion
QA	Quality Assurance
QC	Quality Control
RMSE	Root Mean Square Error
RPD	Relative percent difference
SIU	significant industrial user
SOP	standard operating procedures
SPE	solid phase extraction
USGS	U.S. Geological Survey

ACKNOWLEDGEMENTS

This project and report were produced through collaboration of the Massachusetts Department of Environmental Protection (MassDEP), the University of Massachusetts Donahue Institute (UMDI), and Tetra Tech. The agreement was to initiate a PFAS quality control review procedure, execute that procedure during reviews of data packages submitted by permitted facilities, and to summarize the project data and findings in this final report. The contractual agreement between these entities was in effect from July 1, 2020 to December 31, 2022.

The primary participants and contributors from MassDEP included Jennifer Wood, Nicole Galambos, and Lealdon Langley, who provided technical and administrative leadership throughout the project. This included coordination of the data packages for review (including file management, data compilation, and data qualification), oversight of all QC review reports, guidance and editing of the project summary report, and tracking of project objectives and deliverables. Susannah King, Kathleen Baskin, Dr. C. Mark Smith, and Dr. Oscar Pancorbo from MassDEP provided technical and administrative advice as needed.

Dana Henry, Alyssa Flemati, and Kathryn Swaim made up the contract team from UMDI. They were the primary contract administrators, who organized project communications, schedules, and deliverables so that expectations were met for all project members.

The Tetra Tech team included Ben Jessup, Kelly Jones, and Sue Lanberg as the key administrative, technical, and QC staff. Ben managed the project, Kelly reviewed all data packages, and Sue provided the final layer of QC on all products. They were the primary authors of the analyses and report. Theresa Lopez and John O'Donnell of Tetra Tech contributed technical advice on PFAS policy and laboratory topics.

1.0 INTRODUCTION

1.1 PROJECT BACKGROUND

Per- and polyfluoroalkyl Substances (PFAS) are a class of man-made compounds that have been widely used in industry and consumer products since the 1950s. Although some long-chain PFAS, including perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are no longer produced in the United States (Buck et al. 2011), PFAS are extremely stable and therefore persist in the environment and human body for extended periods of time. PFAS have been associated with increased human health risks, including cancers and infertility (ATSDR 2021).

The U.S. Environmental Protection Agency (EPA) issued drinking water health advisories for PFOA and PFOS in 2016 (USEPA 2016a, b). On June 15, 2022, EPA issued interim updated drinking water health advisories for PFOA and PFOS that replace those EPA issued in 2016 (USEPA 2022a, b, c). These updated advisory levels are based on new science and consider lifetime exposure. The updated advisory levels indicate that some negative health effects may occur with concentrations of PFOA or PFOS in water that are near zero. EPA has indicated that these interim health advisories will remain in place until EPA establishes a National Primary Drinking Water Regulation. EPA also issued final drinking water health advisories for hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt (referred to as "GenX chemicals"); and perfluorobutane sulfonic acid and its potassium salt (PFBS) (USEPA 2022d, e). The Agency for Toxic Substances and Disease Registry (ATSDR) released its final toxicological profile for perfluoroalkyls in May 2021, which included oral minimum risk levels for PFOA, PFOS, perfluorononanoic acid (PFNA), and perfluorohexanesulfonic acid (PFHxS) (ATSDR 2021). EPA published Regulatory Determinations for Contaminants on the Fourth Contaminant Candidate List in March 2021, which included a final determination to regulate PFOA and PFOS in drinking water. EPA will develop a proposed national PFAS National Primary Drinking Water Regulation by the end of 2022 and EPA anticipates developing a final regulation by the end of 2023 (USEPA, 2022f). EPA is currently conducting a biosolids risk assessment for PFOA and PFOS in biosolids. EPA anticipates completing the risk assessments for PFOA and PFOS in biosolids by December 2024 (USEPA 2022g).

In 2019, the Massachusetts Department of Environmental Protection (MassDEP) updated the Massachusetts Contingency Plan which includes cleanup standards in soil and groundwater for PFAS (MassDEP 2019a). In addition, on October 2, 2020, MassDEP published its PFAS public drinking water standard, called a Massachusetts Maximum Contamination Level (MMCL), of 20 nanograms per liter (ng/L) (or parts per trillion (ppt)) – individually or for the sum of the concentrations of six specific PFAS[1]. The six compounds in PFAS6 include PFOS; PFOA; PFHxS; PFNA; perfluoroheptanoic acid (PFHpA), and perfluorodecanoic acid (PFDA). The development of minimum risk levels, health advisories, and drinking water regulations for PFAS indicates that PFAS can pose health risks at low concentrations through the ingestion route. There are currently no Massachusetts or federal standards for PFAS in surface waters, residuals, or fish tissue. There are also no threshold values for PFAS currently listed in the MassDEP Consolidated Assessment and Listing Manual (CALM).

[1] 310 CMR 22: The Massachusetts Drinking Water Regulations | Mass.gov

In 2020, MassDEP jointly funded a U.S. Geological Survey (USGS) water quality study to evaluate the presence of PFAS in selected Massachusetts' rivers and streams. PFAS were detected in all the 27 rivers sampled (Savoie and Argue 2022). Multiple sources, including municipal/industrial wastewater discharges and non-point pollution, may contribute to riverine PFAS concentrations.

MassDEP required entities that hold an Approval of Suitability (AOS) to sell or distribute residuals[2] for land application in Massachusetts to perform quarterly PFAS monitoring beginning in 2020[3]. The quarterly monitoring of 16 PFAS analytes (i.e., PFBS, perfluorobutanoic acid (PFBA), perfluorodecanesulfonic acid (PFDS), PFDA, perfluoroundecanoic acid (PFDoA), PFHpA, PFHxS, perfluorohexanoic acid (PFHxA), PFNA, perfluorododecanoic acid (PFTrDA), PFOA, PFOS, perfluoropentanoic acid (PFPeA), perfluoroundecanoic acid (PFUnA), perfluoropentanesulfonic acid (PFPeS), and perfluorononanesulfonic acid (PFNS)) in residuals provides MassDEP with a baseline of information on PFAS content, a basis for regulating residuals distribution, an indication of the issues that analytical laboratories are encountering during analysis of residuals, and qualification of the data to enable end users to interpret the results. The permits and approvals are intended to protect public health, safety, and the environment by comprehensively regulating the land application of sludge, sludge products (such as compost and pellets), and septage. Statutory authority is provided in Massachusetts General Laws (MGL) Chapter 21, s. 27(9), 27(12), and 43; Chapter 21A s. 2(28); and Chapter 111, s. 160. Regulatory authority is stated in 310 CMR 32.00.

In 2020–2021, no EPA-approved methods were available for testing residuals for PFAS. EPA Draft Method 1633 is a method for analyzing PFAS in residuals and other media, but it is not yet multi-lab validated. It is currently single lab validated. (U.S. EPA 2021). Laboratories used "modified" EPA 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) to analyze samples. The modified EPA 533 method targets PFAS compounds generally with 12 or fewer carbon molecules, including perfluorinated acids, sulfonates, fluorotelomers, and poly/perfluorinated ether carboxylic acids. Method 533 is applicable for measuring 25 PFAS compounds. Laboratories also referenced "modified method 537" as their user-defined isotope dilution method. The laboratory standard operating procedures (SOPs) were reviewed and approved by the MassDEP before they were used to analyze the residuals samples. In addition, a standardized data quality evaluation checklist was developed and used to consistently perform reviews of the quality of results reported in laboratory data packages. Implementing these steps allowed for evaluation of whether the analytical results met the quality requirements outlined in EPA Method 533 (USEPA 2019), as well as the overall analytical quality requirements in 40 CFR Part 136.7 (Guidelines Establishing Test Procedures for the Analysis of Pollutants, Quality Assurance and Quality Control).

In 2021-2022, an evaluation of the analytical results was performed for quarterly residuals samples collected during the last quarter of 2020 through the first quarter of 2022. The method quality objectives (e.g., holding times, minimum reporting limits, relative percent difference (RPD) for laboratory or field duplicates) were evaluated and documented for each sample using a standardized data quality evaluation checklist (**Appendix A**). Additional issues that the laboratories encountered during analysis were also documented in these checklists. Results from these standard evaluations qualified the data to enable end users to interpret the quality of results.

[2] "Residuals" are organic (carbon-based) "wastes" used for beneficial uses. They are comprised of sludge from wastewater, drinking water, industrial, and paper manufacturing.

[3] 310 CMR 32.00: Land Application of Sludge and Septage, which states "any additional substance for which sampling and analysis is required by the Department, before or after the sludge or septage is approved by the Department pursuant to 310 CMR 32.11." Also, see URL: https://www.mass.gov/doc/required-laboratory-procedures-for-testing-pfas-in-residuals/download

1.2 REPORT PURPOSE

This report of the findings after the first year of residual sampling for PFAS and the associated QC of laboratory results is intended to support MassDEP in advancing the review and analysis process, including:

- Characterizing PFAS primary and duplicate concentrations across all samples, by residual treatment type, facility, laboratory, and sampling quarter
- Summarizing PFAS compounds individually, PFAS6, and the sum of all PFAS compounds tested for residuals (PFAS_16). Statistics include number of results > reporting limits (RL), % results > RL, % with estimated values (J values) above detection limits (DL) but below RL) (median, mean, max statistics, ranges (>RL), with J values etc.)
- Characterizing data quality and reliability
- Characterizing QC trends, improvements, and variability
- Recommending improvements in monitoring and assessment
- Evaluating and justifying sample frequency

The QA/QC analysis and review process adds confidence in interpretation of PFAS monitoring results. Understanding and reporting of data quality provides support for programmatic and management decisions regarding regulation of residuals. This report is not intended to interpret exceedances of PFAS relative to a threshold or standard.

2.0 METHODS AND APPLICATION ASSUMPTIONS

2.1 ANALYTICAL METHOD DESCRIPTION

Entities that sold or distributed residuals for land application in Massachusetts in 2020-2021 collected samples of their residuals quarterly. The samples were delivered to approved analytical laboratories **(Table 1**) for analysis of 16 required PFAS compounds (**Table 2**). The laboratories provided data packages to MassDEP. Tetra Tech was contracted to review the laboratory packages for compliance with data quality and reporting objectives.

Table 1. Laboratories participating in the 2020-2022 PFAS data package review process.

Alpha Analytical, Inc.	https://alpha-analytical.com/
Bureau Veritas Laboratories	https://www.bvna.com/
Enthalpy Analytical	https://enthalpy.com/
Eurofins Lancaster	https://www.eurofinsus.com/locations/eurofins-lancaster-laboratories/
Eurofins Test America	https://www.eurofinsus.com/environment-testing/

The drinking water analytical method (Method 533; USEPA 2019) was modified by laboratories for analysis of PFAS in solids. PFAS concentrations were reported in nanograms per gram (ng/g) dry weight,

which is equal to micrograms per kilogram (µg/kg) dry weight. Method 533 is a solid phase extraction (SPE) liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for the determination of select PFAS in drinking water. The method requires the use of MS/MS in Multiple Reaction Monitoring (MRM) mode to enhance selectivity. This method is intended for use by analysts skilled in the performance of solid phase extractions, the operation of LC-MS/MS instrumentation, and the interpretation of the associated data.

Table 2. PFAS compounds analyzed in residuals samples, showing Chemical Abstract Serial Number (CASN), Sulfonic or carboxylic acid type, and carbon chain length. "Long" and "Short" labels are according to ITRC (2022). Compounds with an asterisk (*) are components of PFAS6.

PFAS Code	PFAS Compound	CASN	Sulfonic or Carboxylic	Chain Length
PFBA	Perfluorobutanoic acid	375-22-4	Carboxylic	C4, Short
PFPeA	Perfluoropentanoic acid	2706-90-3	Carboxylic	C5, Short
PFHxA	Perfluorohexanoic acid	307-24-4	Carboxylic	C6, Short
PFHpA	Perfluoroheptanoic acid*	375-85-9	Carboxylic	C7, Short
PFOA	Perfluorooctanoic acid*	335-67-1	Carboxylic	C8, Long
PFNA	Perfluorononanoic acid*	375-95-1	Carboxylic	C9, Long
PFDA	Perfluorodecanoic acid*	335-76-2	Carboxylic	C10, Long
PFUnA	Perfluoroundecanoic acid	2058-94-8	Carboxylic	C11, Long
PFDoA	Perfluorododecanoic acid	307-55-1	Carboxylic	C12, Long
PFTrDA	Perfluorotridecanoic acid	72629-94-8	Carboxylic	C13, Long
PFBS	Perfluorobutanesulfonic acid	375-73-5	Sulfonic	C4, Short
PFPeS	Perfluoropentanesulfonic acid	2706-91-4	Sulfonic	C5, Short
PFHxS	Perfluorohexanesulfonic acid*	355-46-4	Sulfonic	C6, Long
PFOS	Perfluorooctanesulfonic acid*	1763-23-1	Sulfonic	C8, Long
PFNS	Perfluorononanesulfonic acid	68259-12-1	Sulfonic	C9, Long
PFDS	Perfluorodecanesulfonic acid	39108-34-4	Sulfonic	C10, Long

The published Method 533 (U.S. EPA 2019) summary is as follows:

> "A 100–250 mL sample is fortified with isotopically labeled analogues of the method analytes that function as isotope dilution standards. The sample is passed through an SPE cartridge containing polystyrene divinylbenzene with a positively charged diamino ligand to extract the method analytes and isotope dilution analogues. The cartridge is rinsed with sequential washes of aqueous ammonium acetate followed by methanol, then the compounds are eluted from the solid phase sorbent with methanol containing ammonium hydroxide. The extract is concentrated to dryness with nitrogen in a heated water bath. The extract volume is adjusted to 1.0 mL with 20% water in methanol (v/v), and three isotopically labeled isotope performance standards are added. Extracts are analyzed by LC-MS/MS in the MRM detection mode. The concentration of each analyte is calculated using the isotope dilution technique. For QC purposes, the percent recoveries of the isotope dilution analogues are calculated using the integrated peak areas of isotope performance standards, which are added to the final extract and function as traditional internal standards, exclusively applied to the isotope dilution analogues."

The method includes QC requirements, including each QC parameter, its required frequency, and the performance criteria that must be met to satisfy method objectives. Laboratory modifications of this method for drinking water as applied to residuals were approved by MassDEP through review of laboratory SOPs. These modifications were necessary, considering that no approved method is available for any matrix other than drinking water.

2.2 PFAS DATA REVIEW CHECKLIST

SOPs for laboratories under contract to MassDEP for analysis of PFAS in residuals and wastewater were reviewed and approved by MassDEP. The SOP and method 533 QC requirements provided a sampling and analysis framework for the facilities holding an AOS and for the analytical laboratories. In cooperation with MassDEP, Tetra Tech developed a QC checklist to standardize reviews of the laboratory data packages (**Appendix A**). Tetra Tech reported on sample adherence to QC requirements, but did not evaluate sample validity relative to QC results.

Measures included in the QC checklist included, but were not limited to the following:

- Percent recovery of isotope dilution analogues that were added to samples prior to extraction
- RPD of the primary and duplicate samples
- RPD of the matrix spike and matrix spike duplicate (MS/MSD)
- Percent recovery of isotope dilution analogues that were added prior to extraction for MS/MSD
- Percent recovery of isotope dilution analogues that were added prior to extraction for Laboratory Control Sample (LCSs)
- RPD of the LCS and LCS duplicate samples
- Lab and field blank concentrations in comparison to the method reporting limit (MRL)

3.0 SUMMARY OF SAMPLES REVIEWED

Samples were analyzed for PFAS for 35 AOS facilities, distinguished by treatment type, AOS type (I or II), and part 503 designation (**Table 3**). Treatments were distinguished as Water Treatment Plant (WTP) sludge, industrial sludge, heat drying, compost, and pasteurized or alkaline stabilized (PAS). WTP sludge is typically dried in lagoons. Industrial sludge is from the industrial processing of cranberries, cotton, and gelatin. WTP and industrial residuals are not stabilized, therefore MassDEP requires occasional bacteriological sampling. The three other treatment types (heat drying, compost, and PAS) are applied to residuals containing wastewater treatment plant sludge. These treatment types are defined in the MA regulations pertaining to residuals, 310 CMR 32.00. Specifically, 310 CMR 32.80 and 310 CMR 32.81. The products from these three treatment types meet the Federal designation for a Class A Biosolid according to 40 CFR Part 503.

Type I biosolids meet high quality standards and may be used as commercial fertilizers and soil conditioners. Type II biosolids meet a lower standard for use than Type I and require additional permitting for land application. Facilities may have an Industrial Pretreatment Program (IPP) if their inputs include wastewater treatment plant sludge and over 2 to 3 significant industrial users (SIUs). Facilities processing wastewater treatment plant sludge were designated by whether they have an IPP.

Table 3. Facilities contributing PFAS data for analysis. Shorthand facility identifiers are used in the tables and figures. See text for descriptions of treatments, AOS type, 503 designation, and IPP status.

AOS Facility Name	Identifier	Treatment and AOS Type	503 Desg	IPP
Amesbury Water	AW	Sludge- WTP_Type I	NA	NA
Barnhardt	BRNH	Sludge_Type II	NA	NA
Braintree Water	BW	Sludge- WTP_Type I	NA	NA
Bridgewater WWTF	BRDG	Compost_Type I	A	No
Bristol, RI Compost Facility	BRST	Compost_Type I	A	NA
Cascades Tissue Group	CTG	Sludge_Paper_Type I	NA	NA
Concord, NH WWTF	CONC	Sludge_PAS_Type I	A	Yes
Dartmouth WWTF	DRTM	Compost_Type I	A	No
Erseco, Inc. (Erving POTW #2)	ERSC	Sludge_Type II	B	NA
Greater Lawrence Sanitary District	GLSD	Heat Drying_Type I	A	Yes
Hawk Ridge	HR	Compost_Type I	A	Yes
Hoosac Water Quality District	HWQD	Compost_Type I	A	Yes
Ipswich Compost Facility	IPSW	Compost_Type I	A	Yes
Merrimack, NH WWTF	MRMK	Compost_Type I	A	Yes
Milorganite, Milwaukee Metro Sewerage District (MMSD)	MMSD	Heat Drying_Type I	A	Yes
Montague Water Pollution Control Facility	MONT	Compost_Type I	A	Yes
MWRA - NE Fertilizer Co	MWRA	Heat Drying_Type I	A	Yes
Nashua, NH WWTF	NASH	Sludge_Type II	B	Yes
Newburyport Water	NWBP	Sludge- WTP_Type I	NA	NA
North Chelmsford Water	NCW	Sludge- WTP_Type I	NA	NA
Ocean Spray WWTF, Carver	OSC	Sludge_Industrial_Type I	NA	NA
Ocean Spray WWTF, Middleborough	OSM	Sludge_Industrial_Type I	NA	NA
Resource Management Facility	RMF	Sludge_PAS_Type I	A	NA
Rockport Water Department	RWD	Sludge- WTP_Type I	NA	NA
Rousselot, Dissolved Air Floatation Waste	RDAF	Sludge_Industrial_Type I	NA	NA
Rousselot, Lime Slurry Waste	RLSW	Sludge_Industrial_Type I	NA	NA
Rousselot, WWTP Waste Activated Sludge	RWAS	Sludge_Industrial_Type I	NA	NA
Salem-Beverly Water Department	SLBV	Sludge- WTP_Type I	NA	NA
Somerset WWTF	SMRS	Compost_Type I	A	No
Soundview VT Holdings	SVH	Sludge_Paper_Type I	NA	NA
Southbridge WWTF	STHB	Compost_Type I	A	Yes
Taunton Water Division	TNTN	Sludge- WTP_Type I	NA	NA
Tewksbury Water Department	TWKS	Sludge- WTP_Type I	NA	NA
Waste Options Nantucket, LLC	WON	Compost_Type I	NA	No
Weymouth Water Dept.	WWD	Sludge- WTP_Type I	NA	NA

From the 35 facilities, there were 131 primary samples, 106 duplicate samples, and 8 pseudo-split samples analyzed (**Appendix B**). Samples were collected between March 2020 and March 2022, with only 4 samples from 3 facilities collected after September 2021. Facilities collected 2-5 primary samples each during that time. For four facilities (Salem-Beverly, Taunton, Tewksbury, and Weymouth), sample results from multiple on-site locations were averaged and counted as one sample per sampling event in this report. Minimum, mean, and maximum PFAS_16 and PFAS6 concentrations per facility are tabulated in **Appendix B**.

There were five laboratories conducting PFAS analyses in 2020 – 2022. Two laboratories conducted most of the analyses. (**Table 4**). There were eight samples from two facilities that were analyzed by more than one laboratory. These are designated as pseudo-splits, because they were not derived from one homogenized sample. Rather, two samples were collected at each facility during each sampling event and one sample was sent to one laboratory as the other sample was sent to the other laboratory. Therefore, these pseudo-splits represent variability attributed to the laboratories and to the overall sampling procedure. Results from the two laboratories were compared and the sampling variability was described.

Table 4. Facilities and samples analyzed by five approved laboratories.

Laboratory	# Facilities	# Primary Samples	# Duplicate Samples	# Pseudo-split Samples
A	23	67	56	4
B	14	52	47	0
C	2	5	0	0
D	1	4	0	4
E	1	3	3	0

4.0 DATA DISTRIBUTIONS AND TRENDS BY FACILITY AND ANALYTE

4.1 SAMPLE VARIABILITY OVER TIME AND BY TREATMENT TYPE

Samples were collected over seven calendar quarters from September 2020 through March 2022. Distributions of PFAS_16 concentrations (ng/g dry weight) were plotted to interpret general changes in PFAS throughout the years. As the sum of the 16 PFAS compounds, changes in PFAS_16 might suggest seasonal patterns in PFAS content at the facilities. Visual interpretation of the distributions indicates that there are no systematic differences in the PFAS_16 concentrations among sampling quarters (**Figure 1**). The interquartile ranges of the distributions overlap substantially.

PFAS values were reviewed to identify potentially erroneous outliers (**Appendix C**). Though some values were high, there was no indication that these should be dismissed as erroneous. Therefore, no outlier values were removed from the analyses or displays. Non-detect values were analyzed as zero (0) ng/g concentrations. Plots are displayed as the log10 of the PFAS concentration plus 1. This transformation allows better distinction of low values while also allowing non-detects (0 values) to be log transformed.

A log10 transformed value of 1 represents an untransformed value of 9 ng/g. Unless specifically addressing sample variability, the following plots include only primary samples (not duplicates or pseudo-splits).

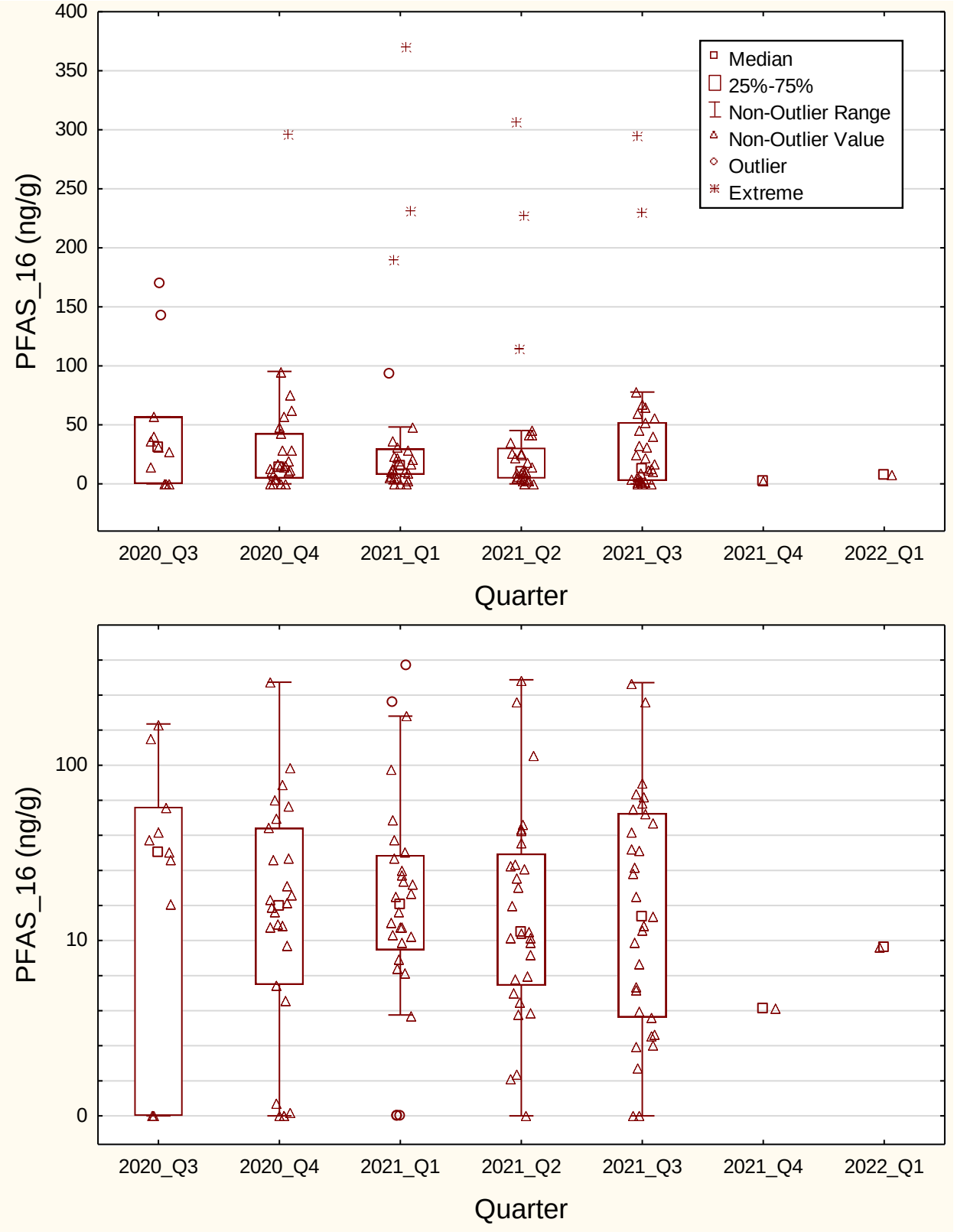

Figure 1. Distributions of PFAS_16 concentrations among sampling quarters, shown in both linear (top) and logorithmic (bottom) scales.

The distributions of PFAS_16 show greater variability among quarters when sub-setting by facility treatment type (**Figure 2**). However, the variability among treatment types is comparable to the variability among quarters and a systematic temporal pattern is not recognizable. PFAS_16 concentrations in Compost Type I facilities are consistently higher than concentrations in other facility treatment types for each quarter. When PFAS6 concentrations are combined over all quarters, Compost Type I facilities have significantly consistently higher concentrations than other facility treatment types (**Figure 3**). Based on analysis of variance (ANOVA) and the Tukey Honestly Significant Difference test, PFAS6 concentration raw values (untransformed by logarithms) were significantly ($p < 0.05$) higher in Compost Type I facilities than concentrations in most sludge treatments. Comparisons among treatment types do not imply that the treatment type is the reason for the PFAS concentrations. There are likely multiple other variables affecting concentrations. As with other distribution comparisons, the patterns observed for PFAS_16 were like those observed for PFAS6.

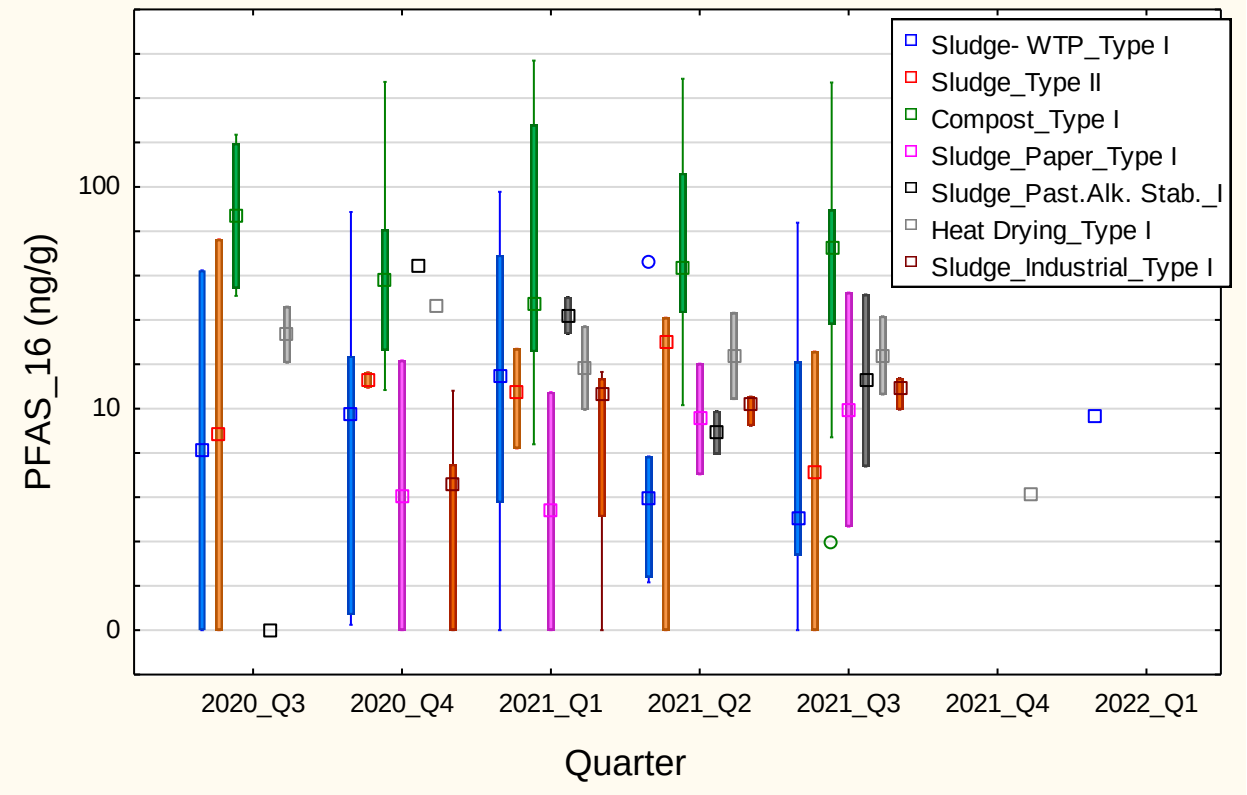

Figure 2. Distributions of PFAS_16 concentrations among sampling quarters and facility treatment types. Refer to Table 3 to associate treatment types with facilities.

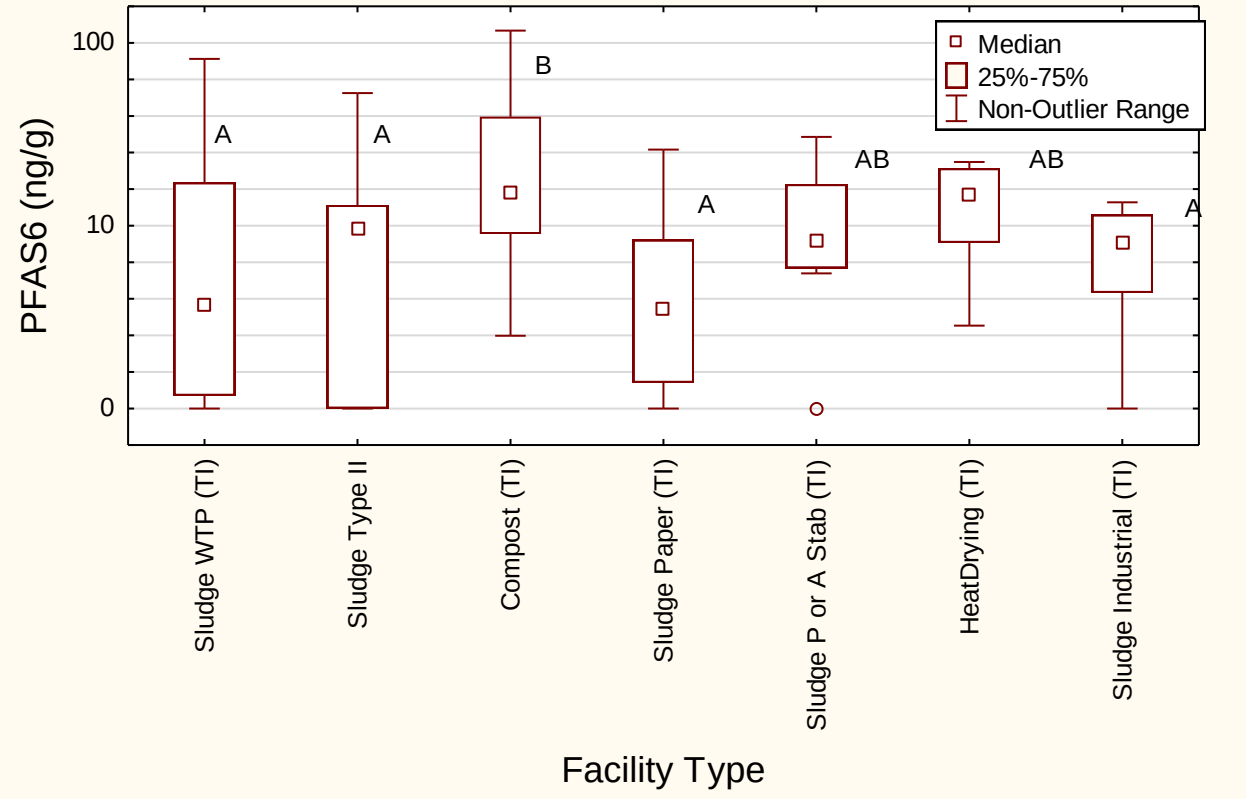

Figure 3. Distribution of PFAS6 for all facilities by facility type, showing statistically different groups A and B based on the ANOVA Tukey Honestly Significant Difference test. TI indicates Type I.

Most of the individual compost facilities had higher PFAS_16 than other facilities and facility treatments (**Figure 4**). Differences between PFAS_16 concentrations were indistinct (ANOVA p>0.10) when compared for AOS type (**Figure 5**), significant industrial user (SIU) status (**Figure 6**), or part 503 designation (**Figure 7**). Sites with missing designations were not included in statistical comparisons. Average percent solids in the samples were highest in the heat drying and compost facility treatments (**Figure 8**). Some sludge samples from waste treatment plants also had high (>50%) percent solids.

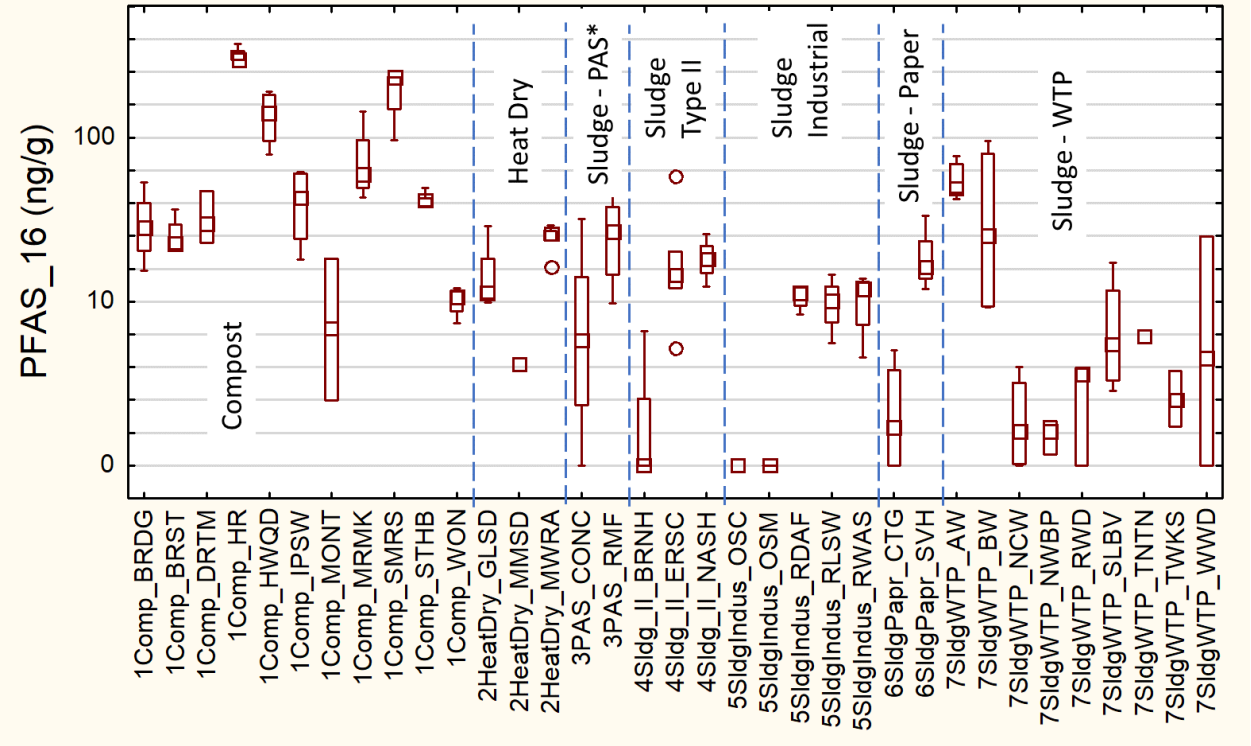

Figure 4. Distribution of PFAS_16 for all facilities by treatment and facility code (primary samples only). Facility designations on the x-axis include an abbreviation for the treatment and the facility code, as listed in Table 3. *PAS = Pasteurized or Alkaline Stabilized.

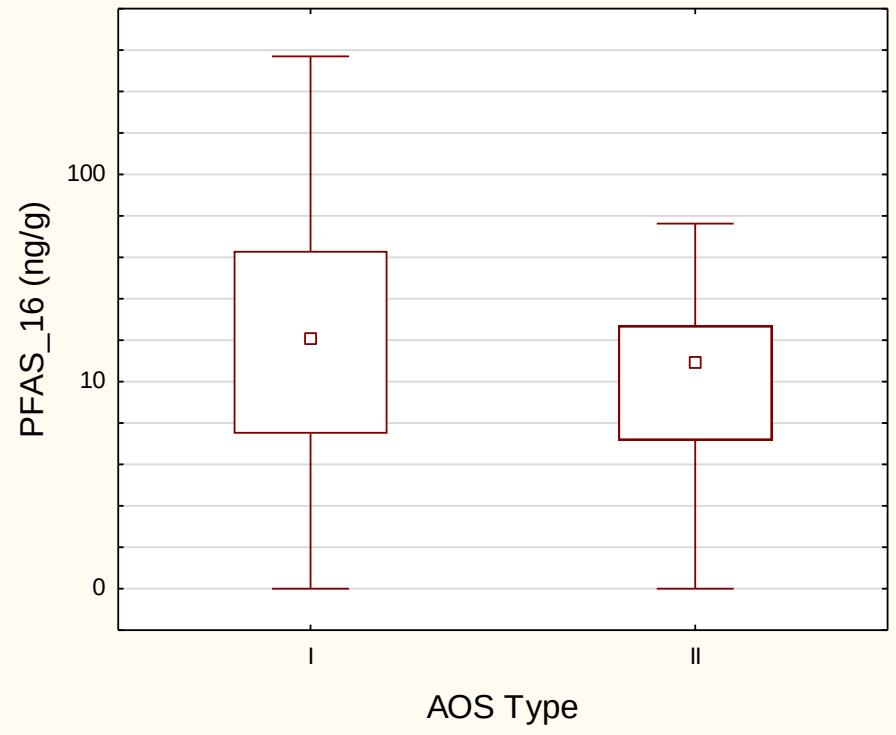

Figure 5. Distribution of PFAS_16 for all facilities by AOS facility type (I or II).

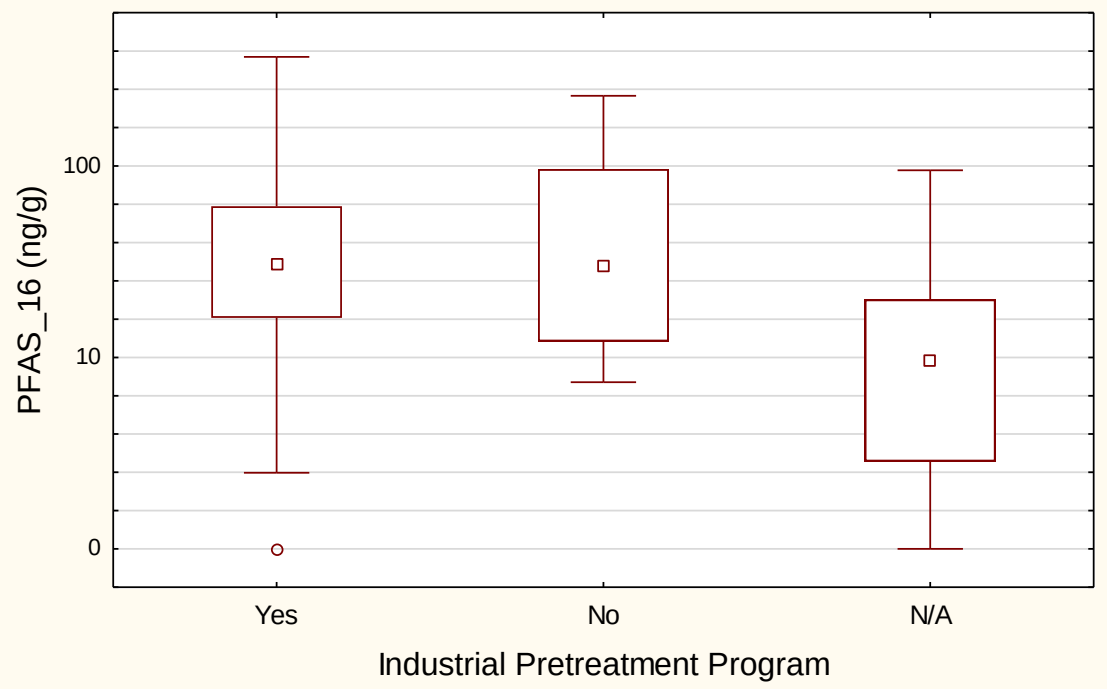

Figure 6. Distribution of PFAS_16 for all facilities by Industrial Pretreatment Program (IPP) status. Facilities marked N/A do not process wastewater treatment plant sludge.

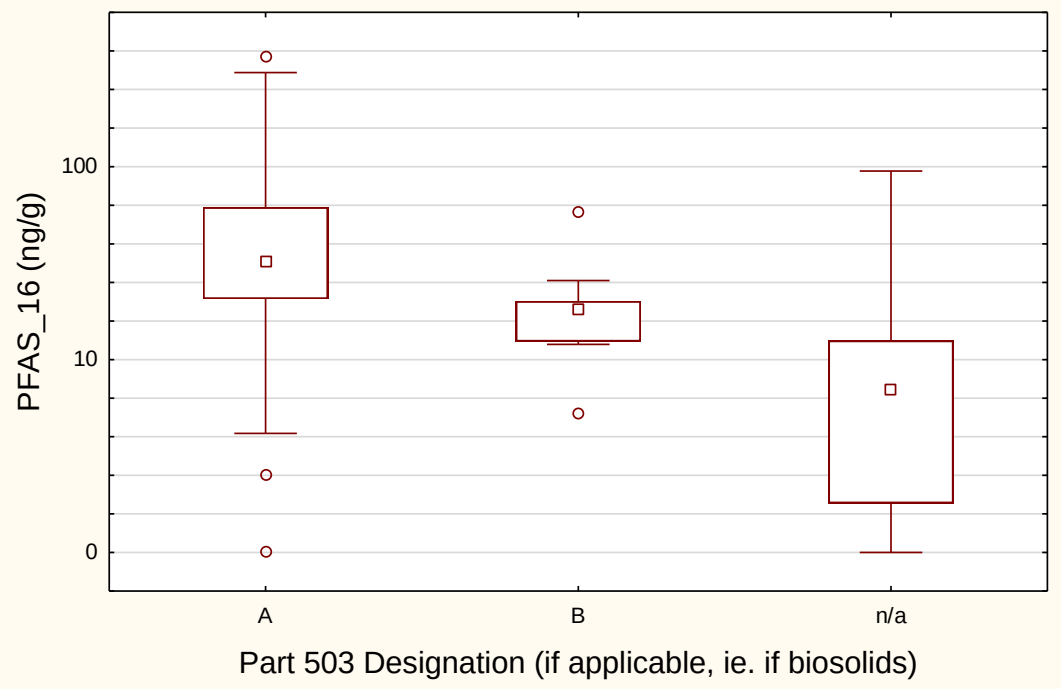

Figure 7. Distribution of PFAS_16 for all facilities by Part 503 designation (A, B, or not applicable [n/a]).

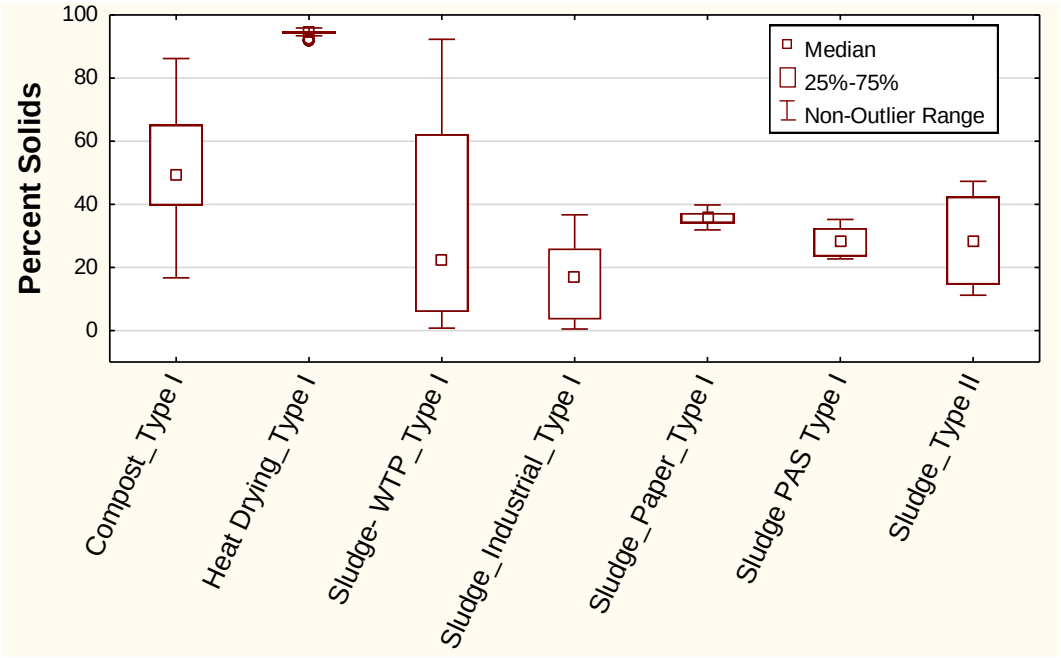

Figure 8. Percent solids for all samples, by facility treatment type. PAS = Pasteurized or Alkaline Stabilized.

4.2 PFAS COMPOSITION BY COMPOUND

Samples varied in the concentrations and composition of PFAS compounds. Variations in concentrations and composition per facility showed that five facilities had average PFAS_16 concentrations greater than 50 ng/g (**Figure 9**). The facilities included four Compost treatments (Hawk Ridge, Hoosac, Merrimack, Somerset), and one Sludge – WTP treatment (Amesbury). Of these, the PFAS compound composition was similar in all but Amesbury, which was predominantly composed of PFOS.

Other differences in composition between facilities can be discerned when comparing percent composition, regardless of concentration (**Figure 10**). The most common compounds by average percent composition in primary samples are PFOS (37%), PFHxA (15%), PFOA (10%), PFBA (7%), and PFDA (5%). Three of these common compounds (PFOS, PFOA, and PFDA) are components of PFAS6. PFHxA and PFBA are not components of PFAS6.

A Principal Components Analysis (PCA) of PFAS compound percent composition in the samples was conducted to determine how compound composition was related to the treatment types (Appendix D). Based on the PCA ordination arrangement of samples and associated percentages of PFAS compounds, it appears that the Sludge_Paper_I treatments (and one Sludge Type II sample) were distinct from other treatment types on the first principal axis. These samples had high percentages (80 – 100%) of long-chain carboxylic PFAS compounds such as PFNA, PFDoA, PFUnA, and PFTrDA. PFOA and PFDA are also long-chain carboxylic PFAS compounds, but they are common in other samples and do not show greater percentages in the Sludge_Paper_I treatments.

Samples with Compost_I treatments differed from other groups for the first two principal components. Short-chain PFAS compounds generally made up greater than 40% of the compounds in these samples.

Most of the short-chain compounds in these samples were carboxylic (PFHpA, PFHxA, and PFPeA), except for PFBS. The third distinct group of samples had a high composition of long-chain sulfonic compounds, mostly greater than 40% PFOS and lower percentages of most other compounds. There were several treatment types in this group of samples, so this composition signature did not isolate a single treatment class.

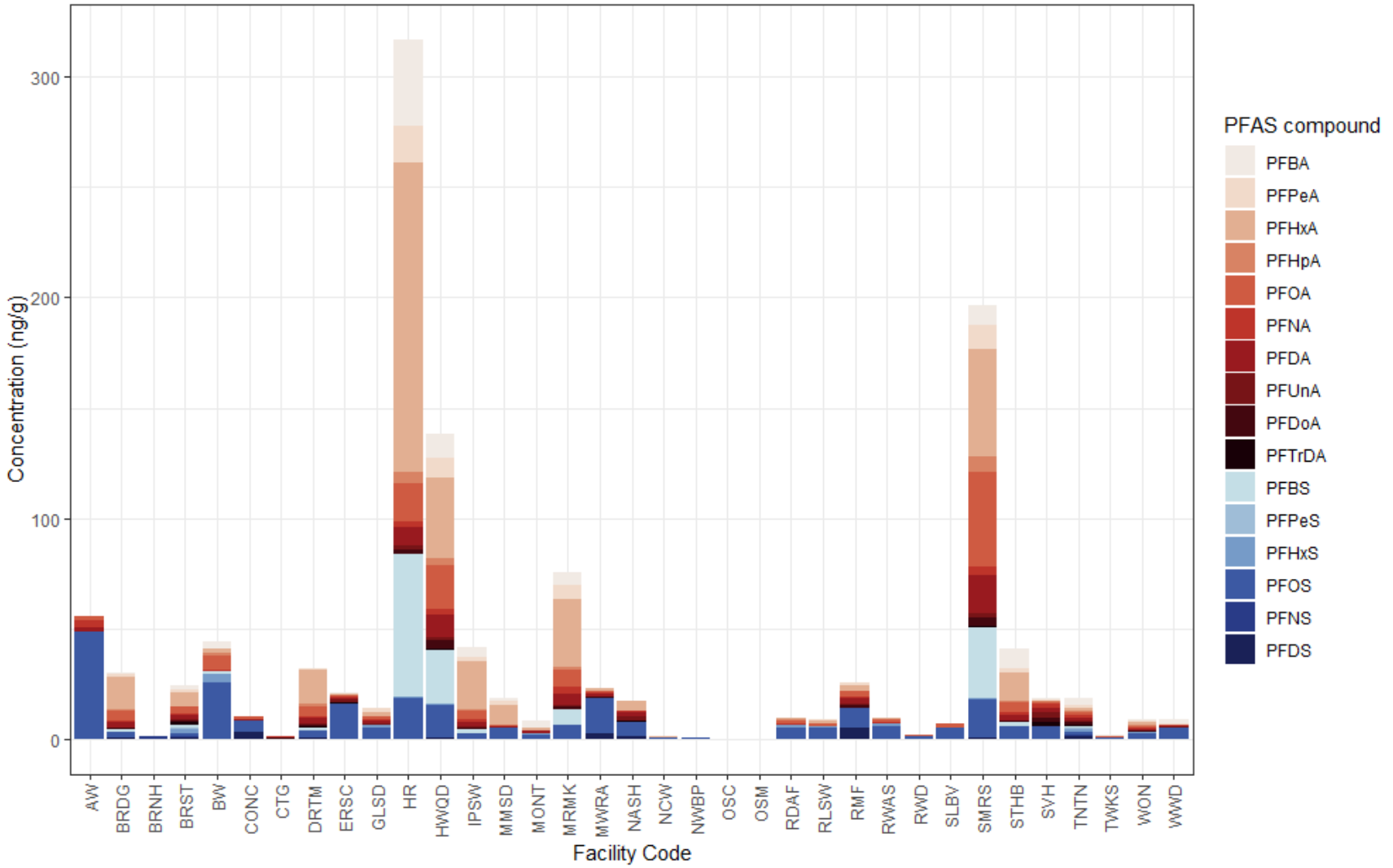

Figure 9. Concentration and composition of 16 PFAS compounds (ng/g), averaged over time per facility. Compounds are ordered by carbon acid type and chain length. Carboxylic PFAS are color-coded red, and sulfonic PFAS are blue. Darker colors indicate longer chain lengths. PFAS measured in ng/g were all non-detections in the OSC and OSM facilities.

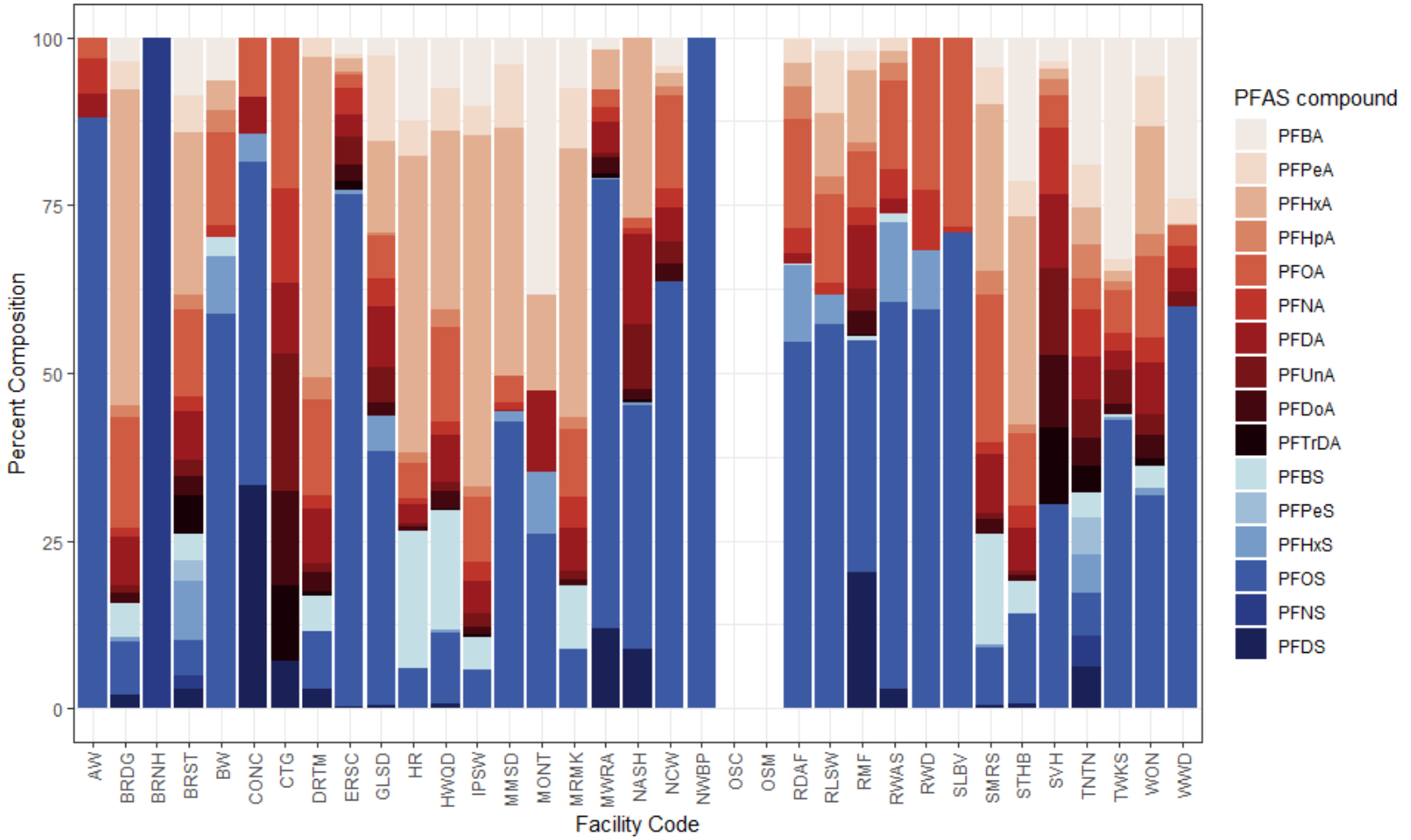

Figure 10. Percentage composition of 16 PFAS compounds, averaged over time per facility. Compounds are ordered by carbon acid type and chain length. Carboxylic PFAS are color-coded red, and sulfonic PFAS are blue. Darker colors indicate longer chain lengths. PFAS were all non-detections in the OSC and OSM facilities.

5.0 SAMPLE VARIABILITY

5.1 PRECISION OF DUPLICATE SAMPLES

In most sampling events, a duplicate sample was collected and analyzed. The primary and duplicate samples were compared to characterize the precision of the repeated measures. In the following figures and tables, statistics can be evaluated to compare precision among facilities, treatments, compounds, quarters, and laboratories (**Appendix E**). Variability between primary-duplicate pairs can be affected by multiple factors including matrix homogeneity, sampling method, and laboratory method. The difference between the primary and duplicate sample was calculated for each sampling event (|p-d|). To analyze precision, primary-duplicate pairs were grouped by facility, treatment, and laboratory. The average difference between the primary and duplicate samples was calculated for a given category (average |p-d|). The differences between primary and duplicate samples were used to calculate the Root mean Square Error (RMSE) for each category. RMSE was standardized to the mean PFAS concentration for the duplicate samples to calculate the coefficient of variability (CV). Lower average |p-d| and CV indicates greater precision. The magnitude of PFAS differences within duplicate sample sets was greater when the concentrations were greater (**Figure 11**), so both average |p-d| and CV are shown throughout this section.

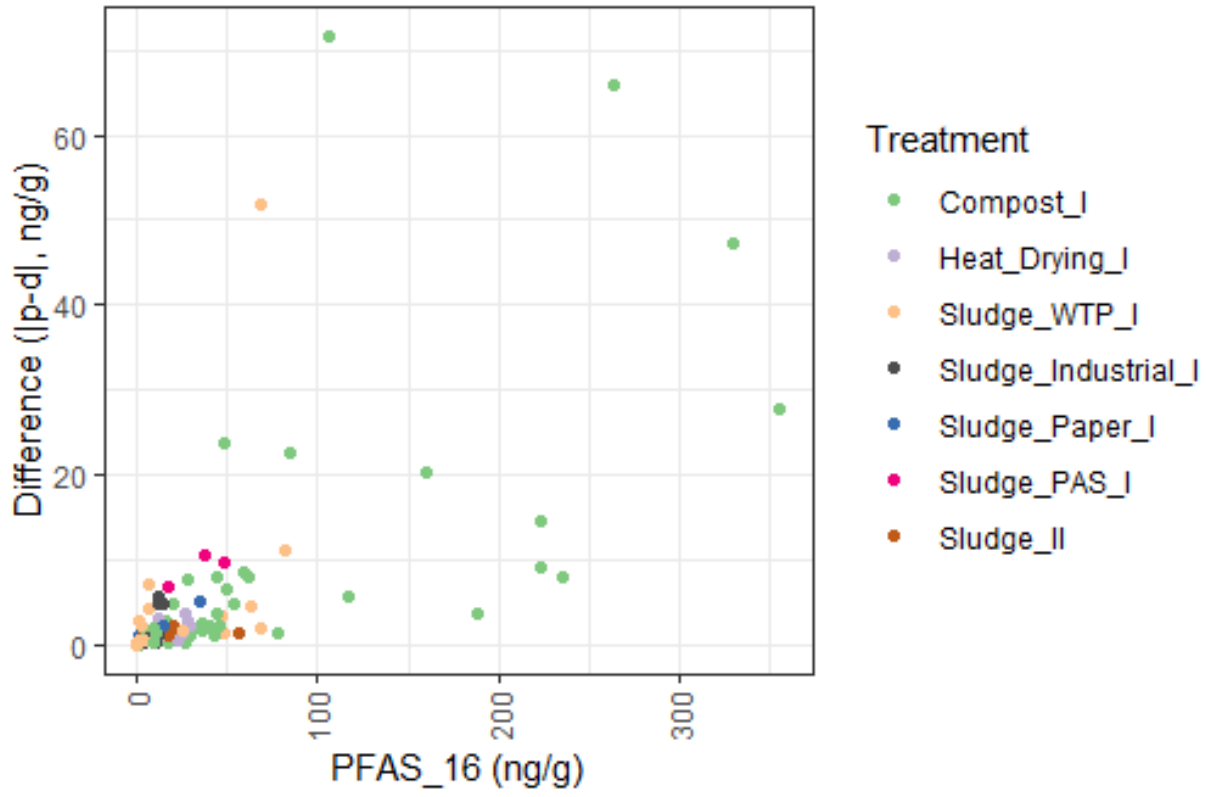

Figure 11. Average concentrations of PFAS_16 compared to the absolute difference in primary and duplicate samples, marked by facility treatment type.

Three laboratories provided enough duplicate data to allow for precision comparisons among laboratories. The PFAS_16 and PFAS6 statistics were similar (CVs of 18-26% for Labs A and B), although the laboratories were not analyzing the same samples and the mean concentrations of compounds were different among labs (**Table 5**). These comparative precision statistics do not suggest that one lab was more precise than the other. Precision results from Lab E are generally unreliable because of the small sample size (n = 3 pairs), though the low CV values suggest that precise measures might be found in a larger data set from Lab E.

CV was calculated for sampling quarters within facilities. The CV of for same-day duplicate PFAS_16 samples (23%, see Section 5.2) is lower than the CV calculated for samples collected over time within the same facilities (CV = 57%, see **Appendix F**), suggesting that the variability between quarters was greater than the variability of the duplicates on the same sample date.

Table 5. Precision statistics for duplicate PFAS samples analyzed by three laboratories. Average difference of the primary and duplicate sample (Avg |p-d|), mean, and Coefficient of Variability are shown.

	Lab A (n = 56 pairs)			Lab B (n = 47 pairs)			Lab E (n = 3 pairs)		
Compound	Avg |p-d| (ng/g)	Mean (ng/g)	CV (%)	Avg |p-d| (ng/g)	Mean (ng/g)	CV (%)	Avg |p-d| (ng/g)	Mean (ng/g)	CV (%)
PFAS_16	2.15	30.89	25	3.52	51.45	21	0.71	32.3	3.3
PFAS6	1.01	16.12	18	1.71	20.45	26	0.62	11.8	8.9

Variability of PFAS_16 and PFAS6 among duplicates by facility and quarter showed that most facilities had variable absolute differences among quarters for both PFAS_16 and PFAS6 (**Appendix F**). In most facilities, the average differences in PFAS_16 between primary and duplicate samples was less than 2 ng/g (**Figure 12**). Five of the seven facilities with greater average difference between primary and duplicate samples (>3.0 ng/g) were compost facilities with higher average concentrations of PFAS_16. The CV for these facilities shows that compost facilities have a moderate variability among treatment types after standardizing variability to mean concentrations. The high and low differences were not associated with percent solids in the samples (Pearson r = -0.07).

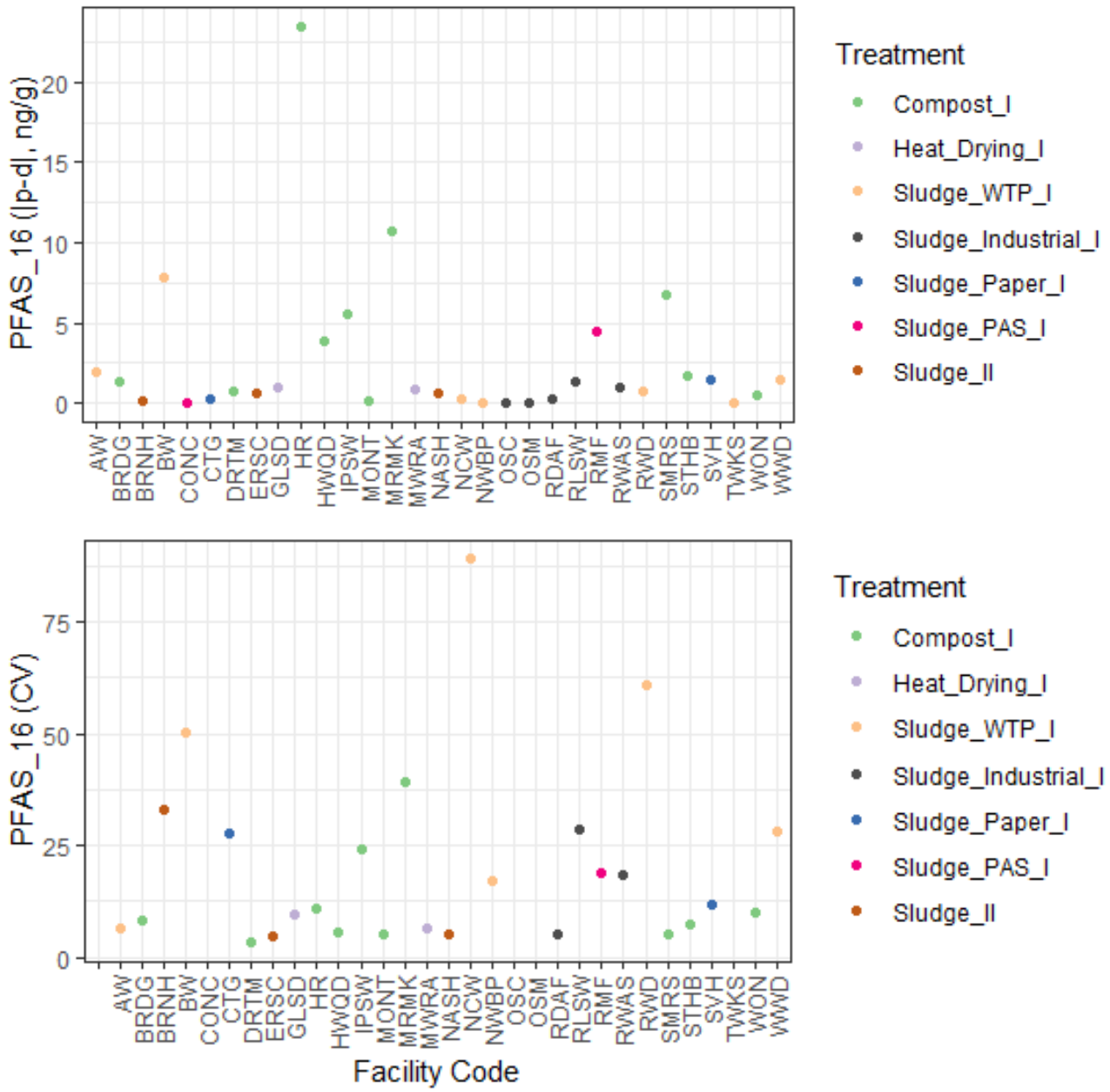

Figure 12. Average difference (top) and CV (bottom) in PFAS_16 for all duplicates by facility, showing treatment types.

When PFAS_16 and PFAS6 duplicate precision statistics are analyzed separately by facility treatment type, it is apparent that relative variability (CV) is highest in the Sludge-WTP_I treatment for both PFAS_16 and PFAS6 (**Table 6**). CV is lowest in the Sludge_II and Heat Drying Type I treatments. PFAS mean concentrations and absolute differences in primary and duplicate samples were highest in the Compost_I treatment. This treatment type was also represented by the most duplicate samples and moderate relative variability.

Table 6. Precision statistics for duplicate PFAS_16 and PFAS6 samples, analyzed separately by treatment type. "Avg. |p-d|" is the average absolute difference between primary and duplicate samples.

	PFAS_16			PFAS6		
Treatment	Avg. |p-d| (ng/g)	Mean (ng/g)	CV (%)	Avg. |p-d| (ng/g)	Mean (ng/g)	CV (%)
Sludge-WTP_I (n = 21)	2.18	21.7	38	1.96	20.5	33
Sludge_Paper_I (n = 7)	0.76	9.3	17	0.40	5.6	19
Sludge_Industrial_I (n = 15)	0.72	7.8	22	0.66	6.9	22
Sludge_PAS_Type I (n = 4)	3.37	25.5	22	1.70	13.2	23
Sludge_II (n = 12)	0.48	13.2	6	0.46	9.9	9
Compost_I (n = 37)	5.31	85.1	17	1.79	27.2	16
Heat Drying_Type I (n = 9)	0.90	19.7	7	0.53	14.3	7

5.2 PRECISION OF SPLIT SAMPLES

Precision statistics for duplicate and pseudo-split repeated PFAS measures indicate that the pseudo-split samples analyzed by different laboratories were more variable between labs (PFAS_16 CV = 102%) than the duplicate samples analyzed by the same laboratory (PFAS_16 CV = 23%). This is evident in the difference between primary and duplicate samples and CV statistics for both PFAS_16 and PFAS6 (**Table 7**). The absolute differences for pseudo-split samples are commonly higher than the absolute differences for duplicates for the same sampling events (**Figure 13**).

Table 7. Precision statistics for all duplicates and pseudo-split samples of PFAS aggregations and compounds. "|p-d|" is the average absolute difference between primary and duplicate samples.

	Duplicates (106 sample pairs)			Pseudo-splits (n = 8 pairs)		
Compound	|p -d| (ng/g)	Mean (ng/g)	CV (%)	|p -d| (ng/g)	Mean (ng/g)	CV (%)
PFAS_16	2.72	40.0	23	16.7	22.07	102
PFAS6	1.31	17.9	23	16.0	18.97	121

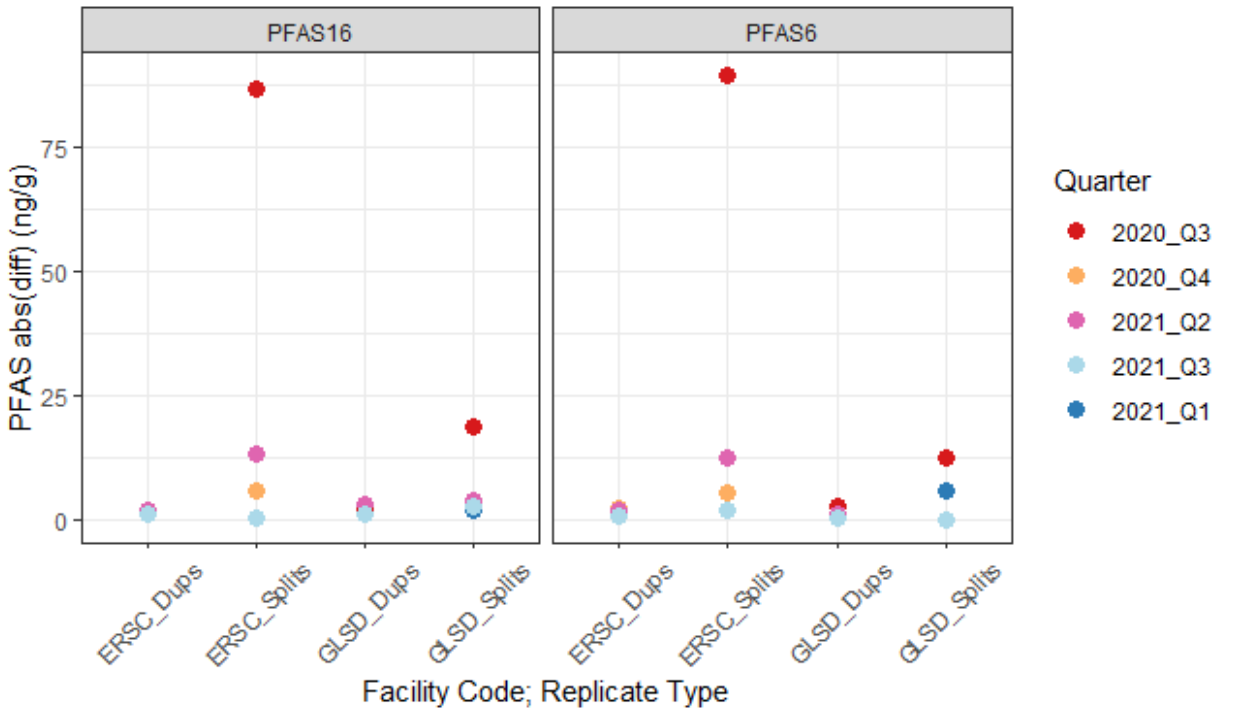

Figure 13. Absolute differences between primary samples and the corresponding duplicate or pseudo-split sample for PFAS_16 (left) and PFAS6 (right).

5.3 PFAS BIAS BY LAB

Replicate samples were compared at facilities that used more than one lab. In most cases, a second lab was used in separate sampling events. However, at two facilities Erseco (ERSC) and Greater Lawrence (GLSD) pseudo-split samples were analyzed (i.e., during the same sampling event, samples were analyzed by two laboratories). Sample results were compared among laboratories for the same facility regardless of the sampling event, showing that concentrations of PFAS_16 and PFAS6 did not appear to be biased by laboratory (**Figure 14**). A T-test comparing sample concentrations for the two most commonly used labs (Lab A n = 8, Lab B n = 32) did not show a statistical difference in concentrations for PFAS_16 (T = -0.61, p = 0.55) or PFAS6 (T = -0.98, p = 0.33). For one Erseco sampling event, the PFAS concentration in the pseudo-split sample was much higher than in the primary sample. However, this appears to be an isolated event, as the other Erseco pseudo-split samples did not show the same large difference. ANOVA by sample type for the samples with both duplicates and pseudo-splits did not show significant differences for PFAS_16 (F = 0.15, p = 0.86) or PFAS6 (F = 0.24, p = 0.79). This indicates that there was not a bias in measurement of PFAS among laboratories.

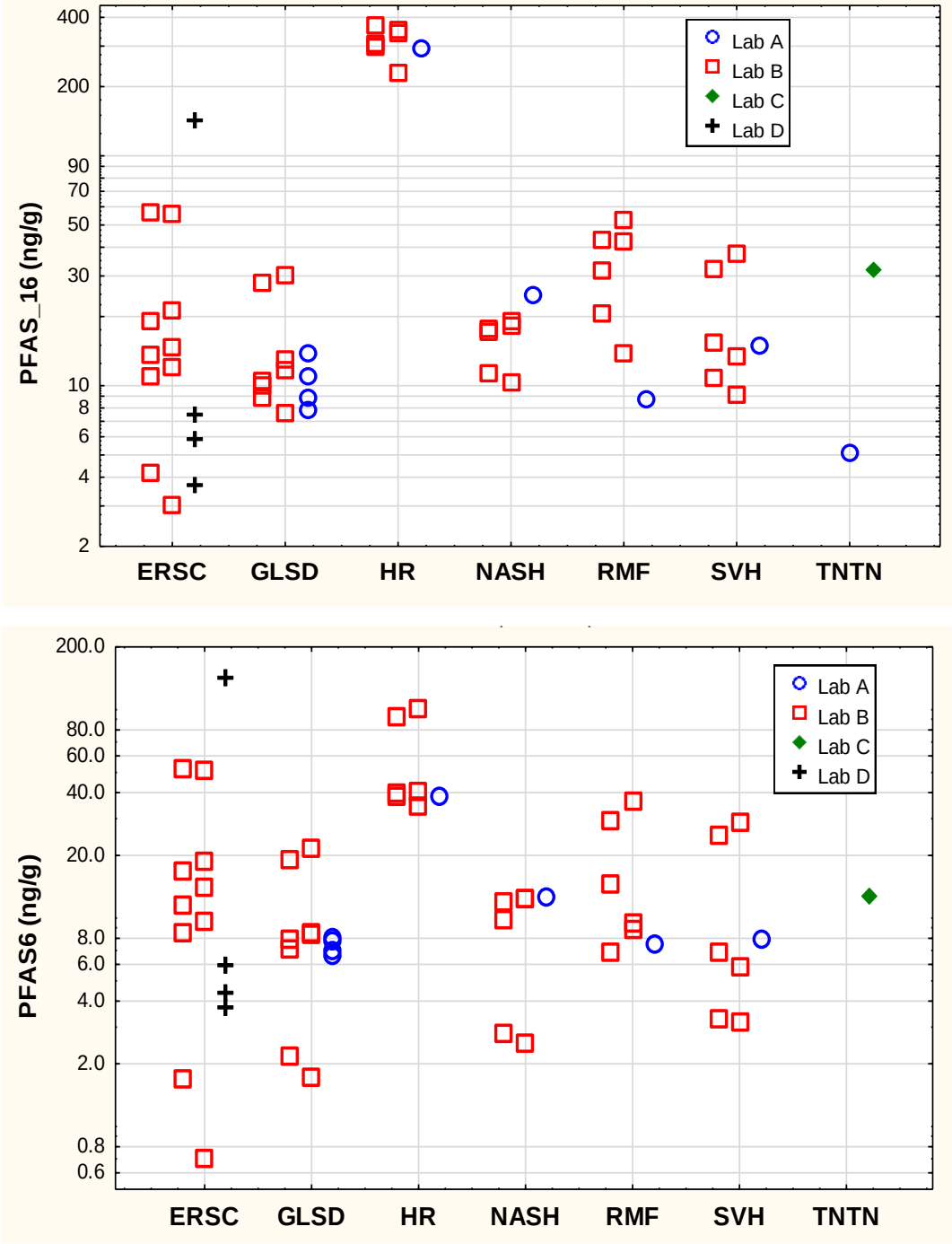

Figure 14. Concentrations of PFAS_16 (top) and PFAS6 (bottom) in facilities that used more than one laboratory (not necessarily for the same samples). Plots show primary and duplicate results for Lab B.

The PFAS6 primary value for facility TNTN was 0 (non-detect), which was not displayed on the log scale.

6.0 SUMMARY OF THE QUALIFIER FLAGS

6.1 FLAGS OCCURRING AMONG LABORATORIES, OVER TIME, AND ACROSS FACILITY TREATMENTS

The QC flags that were assigned by Tetra Tech upon receipt and review of the laboratory packages addressed multiple aspects of sample condition, laboratory processes, QC requirements, and analytical results. Description of flags are listed in **Table 8**. Application of the QC flags and other QC evaluations are illustrated in the QC checklist (**Appendix A**). Sample results from Lab D were not tallied in the analysis of the data package QC because they were only comprised of two locations at a single facility.

The most common flag assigned in all primary samples and all required PFAS compounds was "R", denoting that the reporting limit or MRL was greater than 1 ng/g (**Table 9**). The R flag (MRLs > 1 ng/g dry weight) was assigned in 46% of all samples, varying from 8% to 79% per lab. MRLs were highest when percent solids were lowest (Pearson r = -0.40). MRLs were consistently above 1 ng/g when percent solids were below 10% solids (**Figure 15**). With more than 50% solids, MRLs are commonly less than 10 ng/g. Lab A and Lab B have similar percentages of R qualifiers. Lab E with 8% R flags only tested Dartmouth with moderate percent solids (52%). Lab C, with 79% R flags, analyzed two different residuals: Bristol with 65% solids on average, and Taunton with 22% solids on average. Both had uncharacteristically high reporting limits for their percent solids levels.

The trend of decreasing dry weight MRLs with increasing percent solids can be explained by examining the lab procedure for sludges and solids. The procedure first yields a wet weight PFAS concentration and MRL, which is then divided by the percent solids to yield a dry weight concentration and MRL. **Figure 15** shows a reciprocal relationship between dry weight MRL and percent solids. Plotting the wet weight MRL in **Figure 15** confirms this relationship, showing no effect of percent solids on wet weight MRL. Compared with 46% of primary samples with an R flag for dry weight MRL greater than 1, only 18% of samples have wet weight MRL greater than 1. More investigation is needed to identify trends in wet weight MRLs.

The second most common QC flag was "J", which indicated that the reported value was between the method detection limit and the reporting limit. The "J" flag was not included in the calculation of flags per analysis because it does not have a negative QC connotation. Values between the detection limit and reporting limit are considered estimated, but reliable.

The three samples received at Lab E (98% of results) exceeded the holding temperature recommended for EPA Method 533 ("T" flag). This is a high percentage for the one lab, but the issue might be associated with how the facility (Dartmouth) chilled the samples for shipping, sampling protocols, or sample delivery instead of any lab functions. There were very few records affected by holding time exceedance ("H") or laboratory control sample (LCS) issues ("J2+"). Lab A had the most records (samples and compounds) and the fewest flags per analysis. Lab B had the second fewest flags per analysis.

When the flags are tallied over time, by sampling quarter, it becomes apparent that the most common flag ("R") decreased in frequency over time (**Table 10**). This is especially evident over those quarters with substantial numbers of records, from Q3 in 2020 to Q3 in 2021. It is unclear from this data whether R flag frequency decreased because of improved lab practices over time or due to other factors. The total number of flags per analysis (sample and compound) also decreased over time when discounting those quarters with few samples.

By facility treatment, the most flags per analysis were in the Compost Type I and Sludge Type II treatments, followed closely by the Heat Drying Type I treatment (**Table 11**). The fewest flags per analysis were in the Sludge WTP Type I facilities. The "R" flags were common in all treatment types, but least common in the Heat Drying Type I treatment. The Heat Drying treatment typically has high percent solids content.

Table 8. QC flags from review of laboratory data packages and their descriptions.

QC Flag	Description
B	A target PFAS was detected above the Reporting Limit (RL – equivalent to Minimum Reporting Level or MRL) in a blank (i.e., method blank or field reagent blank) as well as in the residual sample. Residual PFAS concentration is estimated (could be biased high) if the concentration is less than 10 times the concentration in the blank.
H	Residual sample was extracted and/or analyzed past the extraction and/or analysis holding times specified in EPA Method 533. Residual PFAS concentrations are estimated (could be biased low or high).
J	Estimated residual PFAS concentration greater than or equal to the Method Detection Limit (MDL) but less than the RL/MRL.
J1-	Isotopically labeled analogue recovery below the lower acceptance limit – Residual concentration is estimated (could be biased low) for the corresponding target PFAS.
J1+	Isotopically labeled analogue recovery above the upper acceptance limit – Residual concentration above the RL/MRL is estimated (could be biased high) for the corresponding target PFAS.
J2+	LCS recovery above the upper acceptance limit – Residual PFAS concentration above the RL/MRL is estimated (could be biased high).
J3-	Matrix spike (MS – equivalent to laboratory-fortified sample matrix or LFSM) recovery below the lower acceptance limit – Residual PFAS concentration is estimated (could be biased low).
J3+	MS recovery above the upper acceptance limit – Residual PFAS concentration above the RL/MRL is estimated (could be biased high).
J3±	MS was not analyzed with the residual extraction batch – Residual PFAS concentrations are estimated (could be biased high or low).
J5±	MSD, laboratory sample duplicate, or field sample duplicate RPD above the upper acceptance limit or not analyzed with the residual extraction batch – Residual PFAS concentrations above the RL/MRL are estimated (could be biased high or low).
J6+	The ratio of the quantifier ion response to qualifier ion response (i.e., primary mass transition) falls outside of the laboratory established criteria (i.e., outside ratio limits). Results are estimated maximum PFAS concentrations. Laboratories may use an F or I qualifier for this QC issue.

JO	Other QC criteria not met and other infrequent occurrences that require a qualifier. Description example: Concentrations were manually quantitated due to matrix interference in the primary mass transition and are estimated (could be biased low or high) for the corresponding target PFAS.
R	RL/MRL was reported as greater than 1 ng/g dry weight.
T	Residual sample temperature upon receipt at the laboratory exceeded the EPA Method 533 requirement of < 10°C (i.e., residual sample receipt temperature > 10°C). Residual sample PFAS concentrations are estimated (could be biased high or low).

Table 9. Primary records associated with QC flags including all samples and PFAS compounds, by laboratory. For the individual flags, the table shows the percentage of primary records with that flag.

	QC Flag	Lab A	Lab B	Lab C	Lab E	ALL
	Total Records	1067	798	80	48	2057
	Flags per Analysis*	0.6	0.8	1.1	1.2	0.7
	% results > RL	33	30	33	54	34
	RL > % results > DL	6	19	36	13	15
	Average TS%**	39	50	65	52	45
% of primary records with given flag	B	0.1	3.1	0	0	1.3
	H	0	0	0	2.1	0
	J	0	19.7	36.3	14.6	9.4
	J1-	7.2	2.0	1.3	6.3	4.7
	J1+	0	0.1	0	4.2	0.1
	J2+	0	0.1	0	0	0
	J3-	0.6	2.9	0	0	1.4
	J3+	0.7	2.9	0	0	1.5
	J3±	1.1	4.4	0	0	2.3
	J5±	5.3	7.0	33.8	2.1	6.9
	J6±	2.5	3.3	0	0	2.6
	JO	0.2	0.3	0	0	0.2
	R	46.4	49.2	78.8	8.3	46.4
	T	0	7.9	0	97.9	5.3

* The Flags per Analysis does not include the "J" flag.

** TS% = percent total solids

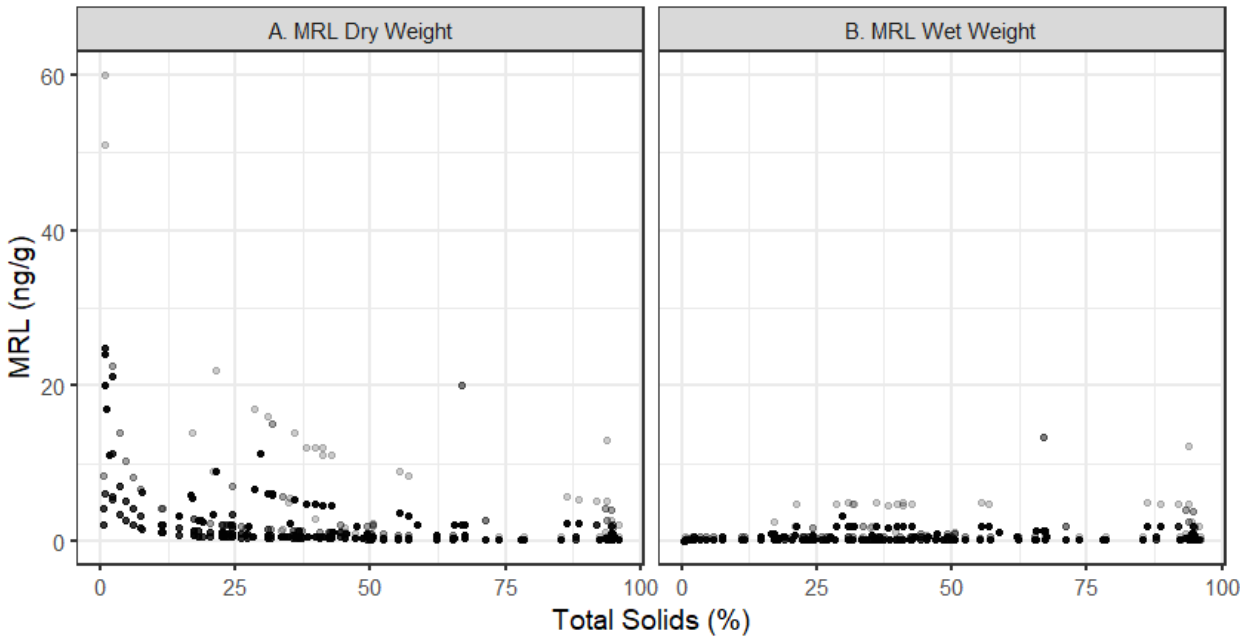

Figure 15. Method Reporting Limits (MRL) in relation to Percent solids in the samples, showing MRLs as both dry weight (A) and wet weight (B). MRLs for all 16 PFAS compounds are shown.

Table 10. Primary records associated with QC flags, by sampling quarter. For the individual flags, the table shows the percentage of primary records with that flag.

	QC Flag	2020 Q2	2020 Q3	2020 Q4	2021 Q1	2021 Q2	2021 Q3	2021 Q4	2022 Q1
	Total Records	9	176	416	448	451	512	29	16
	Flags per Analysis*	2.7	0.77	0.79	0.79	0.65	0.62	0.93	1.1
	Average TS%**	92	49	41	40	42	43	94	1.6
% of primary records with given flag	B	22.2	1.1	1.4	1.6	0	1.6	3.4	0
	H	0	0	0	0	0	0.2	0	0
	J	44.4	2.3	10.8	10.7	7.8	10	13.8	12.5
	J1-	0	5.7	2.9	6	3.3	6.1	6.9	0
	J1+	0	0.6	0	0	0	0.4	0	0
	J2+	0	0	0	0	0	0.2	0	0
	J3-	0	0.6	1.7	0.2	3.3	0.8	3.4	0
	J3+	0	2.8	0.7	0.7	0.9	0.6	0	0
	J3±	77.8	0	0	6.5	0.2	4.1	13.8	0
	J5±	77.8	7.4	1.9	5.8	10.6	6.3	20.7	6.3
	J6+	11.1	2.3	3.1	1.3	3.8	2	6.9	0
	JO	0	0	0.5	0.4	0	0	0	0
	R	77.8	56.8	59.1	53.1	39.7	30.9	37.9	100
	T	0	0	7.7	3.3	3.5	9.2	0	0

* The Flags per Analysis does not include the "J" flag.
** TS% = percent total solids

Table 11. Percentages of records associated with QC flags, by facility treatment. For the individual flags, the table shows the percentage of primary records with that flag.

QC Flag		Compost Type I	Heat Drying Type I	Sludge WTP Type I	Sludge Industrial Type I	Sludge Paper Type I	Sludge PAS* Type I	Sludge Type II
Total Records		688	174	480	251	128	128	208
Flags per Analysis**		0.90	0.78	0.47	0.73	0.60	0.70	0.83
Average TS%***		48	94	36	12	36	29	28
% of primary records with given flag	B	1.2	1.7	0.2	0	3.1	2.3	3.4
	H	0.1	0	0	0	0	0	0
	R	43.8	17.2	42.1	66.1	41.4	48.4	67.8
	T	16	0	0	0	0	0	0

* PAS = Pasteurized or Alkaline Stabilized

** The Flags per Analysis does not include the "J" flags.

*** TS% = percent total solids

6.2 SUMMARY OF QUALIFIER FLAGS

The most common flag assigned in all primary samples and all required PFAS compounds was "R", denoting that the reporting limit or MRL was greater than 1 ng/g dry weight. The R flag was more common in samples with low percent solids in the samples, though there was no threshold for percent solids associated with consistently high or low MRLs. Assessing whether the wet weight MRL is greater than 1 ng/g may be helpful in identifying issues such as inadequate sample size and sample interference. Flagging results based on dry weight MRLs is still appropriate, as PFAS limits for sludges and solids will likely be on a dry weight basis. High MRLs decrease the ability to determine if results are biased low based on internal standard percent recovery. High MRLs preclude enumeration of flags assigned to analytes due to low internal standard percent recovery, which indicate there might be more of a particular analyte in the sample than being detected.

In some cases, a lab would indicate that they diluted the sample to improve internal standard percent recoveries on a second run of the same sample. Needing additional dilutions in and of itself would cause the MRLs to be elevated. There were other reasons for high MRLs, given that high MRLs were also reported for samples that were not diluted.

The flags related to isotopic % recovery (J1- and J1+) were uncommon in the samples and comparisons among labs and quarters are not conclusive. These flags were variable over quarters but did not show a discernible pattern of increase or decrease.

Several flags were available to indicate issues with the matrix spike (MS) or matrix spike duplicate (MSD). Flags indicating that the MS recovery was below the lower acceptance limit (flag J3-), above the upper acceptance limit (flag J3+), or that the MS was not analyzed with the residual extraction batch (flag J3±) were infrequent. In Lab A and Lab B, the J3± was most common. The J5± flag, indicating that MSD, laboratory sample duplicate, or field sample duplicate RPD was above the upper acceptance limit or not analyzed with the residual extraction batch, was more common than any of the J3 flags. A third of the samples from Lab C were flagged with J5± due to an MSD not being analyzed with the sample batch, indicating that residual PFAS concentrations are estimated, and could be biased high or low.

A flag indicating temperature exceedance upon arrival at the lab (flag T) was associated with all three samples analyzed by Lab E. Issues with high PFAS detection in blank samples (flag B) were uncommon, but occurred most often in Lab B. Flags related to the ratio of the quantifier ion response to qualifier ion response (flag J6±) were relatively uncommon and occurred in similar percentages in Labs A and B. Other undefined QC issues (flag JO) only occurred infrequently in Labs A and B.

7.0 RECOMMENDATIONS FOR ONGOING LAB ANALYSIS AND QC REVIEWS

7.1 CONSIDERATIONS FOR FUTURE SAMPLING FREQUENCY

Residuals samples for PFAS testing are currently required to be collected quarterly. There is greater variability in concentrations of samples collected from the same facility during different sampling events (quarterly) than for concentrations of sample duplicates collected during the same sampling event, location, and time. The variability between sampling events necessarily includes variability in the composition of the sample collected. Quarterly sampling will show a fuller range of conditions than would less frequent sampling. An annual or semi-annual sample would not highlight the variability in sample concentrations that vary over quarters.

MassDEP currently requires a duplicate sample with each quarterly sampling event. An RMSE of ±9.2 ng/g PFAS_16 derived from duplicate measures in the data set indicates that an observed measurement of 40 ng/g PFAS_16 would have a true mean in the range of 30.8 – 49.2 ng/g for 68% (1 standard deviation) of repeated measures. The average of replicate measures would be closer to the true mean value than any single measurement, giving a more reliable indication of per sample PFAS concentrations. However, other MassDEP testing relies on only primary results. For example, testing requirements to obtain an AOS does not require duplicate testing, and testing requirements for PFAS in drinking water do not require duplicate sampling.

If duplicate samples are collected and analyzed for the main purpose of refining the understanding of sample concentration variability attributable to sampling error, then duplicate samples could be collected at a reduced frequency in the future. Collection of duplicate samples is not necessary at every sampling event if only the primary samples would be used to determine the PFAS sample concentration. Duplicates could be sampled and analyzed once every year or every two years for a program with quarterly sampling.

While not required, some AOS holders chose to submit a field blank for testing. Detections of PFAS in blanks were not common. The LCS and MS/MSD laboratory samples should not be reduced in frequency. These samples help to indicate possible interferences in residual samples with high solids.

Analysis of pseudo-split samples did not show a bias among labs, though there was higher variability compared to duplicates analyzed within the same lab. Split samples are not recommended to further qualify labs. If split samples are to be analyzed, then the sample to be split should be sufficiently homogenized to ensure that each laboratory is analyzing the same matrix.

7.2 OTHER RECOMMENDATIONS TO IMPROVE EFFICIENCY OR RELIABILITY

- Investigate laboratory methods to lower the MRL below 1 ng/g dry weight, especially for samples with lower percent solids and for Lab C.
- Assess MRLs on a wet weight basis to identify issues such as inadequate sample size and sample interference.
- Revisit other flag frequencies if MRLs are decreased. Because flags (other than “R” flags) are assigned when concentrations are detected above the MRL, if MRLs can be lowered for most samples in the future, the frequency of (non-“R”) flags assigned to results might increase.
- Refine laboratory methods to increase recovery as MRLs are lowered. The “J1-” flag (indicating that analogue recovery was low) would likely increase in frequency when the MRLs are lowered.

- Differentiate J5± flags for high RPDs from J5± flags for when the RPD was not analyzed. More specific J5 flags could be defined to help categorize the reason for assigning the flag without re-reviewing the laboratory reports.
- Continue laboratory data package review to characterize and communicate QC results.
- Ensure that the labs are aware of trends in the QC results. This will allow adaptive management to reduce the QC issues of greatest concern.
- Continue quarterly sampling to evaluate variability of concentrations, as well as any trends in concentrations, over time by residual treatment type, facility, or laboratory.
- If PFAS concentrations will be assessed based on the primary sample alone, then duplicate sampling can be reduced (not eliminated).
- Revisit MRLs and % recovery when testing with the new method 1633. The new method 1633 might allow for improved MRLs and % recovery, but this is not yet confirmed. No recommendations can be made about modifying sampling and analysis until adoption of the method, application to the samples, and evaluation of results.

8.0 REFERENCES CITED

ATSDR. 2021. *Toxicological Profile for Perfluoroalkyls*. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA. Accessed March 2022. https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf.

Buck, R.C., J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. de Voogt, A.A. Jensen, K. Kannan, S.A. Mabury, and S.P.J. van Leeuwen. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integrated Environmental Assessment and Management* 7(4):513-541.

ITRC (Interstate Technology & Regulatory Council). 2022. Per- and Polyfluoroalkyl Substances Technical and Regulatory Guidance. Prepared by The Interstate Technology & Regulatory Council PFAS Team. Accessed at: Front Page (itrcweb.org). https://pfas-1.itrcweb.org/

MassDEP. 2019a. *Final PFAS-Related Amendments, 310 CMR 40.0000*. Massachusetts Department of Environmental Protection, Boston, MA. Accessed March 2022. https://www.mass.gov/doc/final-pfas-related-changes-to-the-mcp-2019-12-13/download.

MassDEP. 2019b. *310 CMR 22.00: Drinking Water*. Massachusetts Department of Environmental Protection, Boston, MA. Accessed March 2022. https://www.mass.gov/doc/pfas-mcl-revisions-to-310-cmr-2200-clean-version-9-16-2020/download

McCune, B. and M. J. Mefford. 2018. PC-ORD. Multivariate Analysis of Ecological Data. Version 7.08. Wild Blueberry Media, Corvallis, Oregon, U.S.A.

Savoie, J.G., and D.M. Argue. 2022, Concentrations of per- and polyfluoroalkyl substances (PFAS) in selected rivers and streams in Massachusetts, 2020: U.S. Geological Survey Data Report 1160, 19 p., https://doi.org/10.3133/dr1160. Accessed August 2022: dr1160.pdf - Concentrations of Per- and Polyfluoroalkyl Substances (PFAS) in Selected Rivers and Streams in Massachusetts, 2020 (usgs.gov).

USEPA. 2016a. *Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)*. EPA 822-R-16-005. U.S. Environmental Protection Agency, Office of Water, Washington, DC. Accessed March 2022. https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final-plain.pdf.

USEPA. 2016b. *Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)*. EPA 822-R-16-004. U.S. Environmental Protection Agency, Office of Water, Washington, DC. Accessed March 2022. https://www.epa.gov/sites/default/files/2016-05/documents/pfos_health_advisory_final_508.pdf .

USEPA. 2019. 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. EPA 815-B-19-020. 2019. Cincinnati, OH: U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water.

USEPA. 2021. Draft Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. EPA 821-D-21-001. Washington D.C. Office of Science and Technology.

USEPA. 2022a. Interim Drinking Water Health Advisory: Perfluorooctanoic Acid (PFOA) CASRN 335-67-1. EPA/822/R-22/003. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/system/files/documents/2022-06/interim-pfoa-2022.pdf.

USEPA. 2022b. Interim Drinking Water Health Advisory: Perfluorooctane Sulfonic Acid (PFOS) CASRN 1763-23-1. EPA/822/R-22/004. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/system/files/documents/2022-06/interim-pfos-2022.pdf.

USEPA. 2022c. Drinking Water Health Advisories for PFOA and PFOS. 2022 Interim Updated PFOA and PFOS Health Advisories. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/sdwa/drinking-water-health-advisories-pfoa-and-pfos.

USEPA. 2022d. Drinking Water Health Advisory: Hexafluoropropylene Oxide (HFPO) Dimer Acid (CASRN 13252-13-6) and HFPO Dimer Acid Ammonium Salt (CASRN 62037-80-3), Also Known as "GenX Chemicals." EPA/822/R-22/005. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/system/files/documents/2022-06/drinking-water-genx-2022.pdf.

USEPA. 2022e. Drinking Water Health Advisory: Perfluorobutane Sulfonic Acid (CASRN 375-73-5) and Related Compound Potassium Perfluorobutane Sulfonate (CASRN 29420-49-3). EPA/822/R-22/006. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/system/files/documents/2022-06/drinking-water-pfbs-2022.pdf.

USEPA. 2022f. Per- and Polyfluoroalkyl Substances (PFAS). U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water, Washington, DC. Accessed November 2022. https://www.epa.gov/sdwa/forms/contact-us-about-safe-drinking-water-act.

USEPA. 2022g. Risk Assessment of Pollutants in Biosolids. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, DC. Accessed November 2022. https://www.epa.gov/biosolids/risk-assessment-pollutants-biosolids.

APPENDIX A: PFAS LABORATORY PACKAGE REVIEW CHECKLIST (TEMPLATE)

PFAS Laboratory Package Review Checklist

To:		**Date:**	
Cc:		**Memo No.:**	
From:		**File:**	
Subject:	Facility Name and Location: Laboratory Name and Location: Laboratory Job #:		
Sample Collection Date			

Overall Summary and Recommendations

Narrative:

Refer to the checklist below for detailed review findings.

<Insert narrative comments and results>

- **Recommend improvements in the next sampling cycle?**

Review Findings

Evaluation Questions	Requirements from Laboratory SOP or if Other, specify	Findings
Was Chain of Custody completed correctly?	Required to be completed	
Appropriate samples submitted and analyzed (i.e., field reagent blank, field duplicate, and when required by MassDEP, a QC volume for MS/MSD analysis) and numbers of containers for each	Per MassDEP instructions to facilities and laboratories	
Were proper sampling procedures followed?	NEBRA and MassDEP Field SOPs	
Is the Certificate of Analysis signed?	Required to be completed	
Was temperature acceptable upon arrival to lab?	<10°C	
Were samples received within the hold time?	14 days until extraction for water (leachate) samples; 28 days until extraction for soil (sludge) samples	

Evaluation Questions	Requirements from Laboratory SOP or if Other, specify	Findings
Were samples analyzed within the hold time?	28 days from extraction until analysis	
Were the samples received in good condition and in the proper containers?	Glass containers must not be used. Collect samples in a 50-mL or 250-mL plastic container (i.e., polypropylene bottles with polypropylene caps or HDPE bottles with polypropylene caps)	
Was sufficient volume of sample submitted to perform all QC?		
Were there any issues noted in the job narrative?		
Analytes Required to Be Tested	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFBS, PFPeS, PFHxS, PFOS, PFNS, and PFDS	
Extraction Method Used	Section 10.4 (Sample Prep and Extraction Protocol for Soils) of Alpha Analytical's SOP - methanol extraction with sonication/centrifugation	
Issues relevant to sample extraction?	Specify in Findings	
Analytical Method Used	SOP based on Method 537.1 (isotope dilution method closer to Method 533 than EPA Method 537.1)	
Percent solids	Specify in Findings	
Planned Minimum Reporting Limit (MRL or RL) Met	Per MassDEP, achieve MRL of ≤ 1 µg/kg (or ng/g) PFAS on a dry weight basis for residuals with a solids	

Evaluation Questions	Requirements from Laboratory SOP or if Other, specify	Findings
	content down to as low as 10%	
Internal standards are added to all standards and sample extracts, including QC samples.	Peak area counts for all ISs in all injections must be within ± 50% of the average peak area calculated during the initial calibration and 70-140% from the most recent CCC. If ISs do not meet this criterion, corresponding target results are invalid.	
One Laboratory Reagent Blank (LRB) included with each extraction batch	All method analytes are below one-third the MRL and possible interference from reagents and glassware do not prevent identification and quantitation of method analytes.	
One Laboratory Fortified Blank (LCS) using Ottawa sand included with each Extraction Batch	For analytes fortified at concentrations ≤2 x the MRL, the result must be within 50–150% of the true value; 70–130% of the true value if fortified at concentrations greater than 2x the MRL	
A Field Reagent Blank (FRB) may be analyzed if any analyte is detected in the associated field samples (not required by MassDEP for biosolid samples).	If an analyte detected in the field sample is present in the associated FRB at greater than one-third the MRL, the results for that analyte are invalid	
Isotope dilution analogues are added to all samples prior to extraction	50%–200% recovery for each analogue	
One Laboratory Fortified Sample Matrix (LFSM) included per Extraction Batch. Fortify the LFSM with method analytes at a concentration close to but greater than the native concentrations (if known).	In EPA Methods and Lab SOP: For analytes fortified at concentrations ≤2 x the MRL, the result must be within 50–150% of the true value; 70–130% of the true value if fortified at concentrations greater than 2 x the MRL.	

Evaluation Questions	Requirements from Laboratory SOP or if Other, specify	Findings
Laboratory Fortified Sample Matrix Duplicate (LFSMD) included with each sample extraction batch	In EPA Methods and Lab SOP: For LFSMDs, relative percent differences must be ≤30% (≤50% if analyte concentration ≤2 x the MRL).	
Field Duplicate included with each sample batch submitted to the laboratory by the facility.	In EPA Methods: RPDs for FDs should be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the MRL. At these concentrations, FDs should have RPDs that are ≤50%.	
Overall Evaluations		
Issues with sample results?		
Were there any qualifiers on the sample results? (*Refer to table of standard qualifiers following this checklist).		
Issues with isotope recovery?		

Table 1: PFAS Analytical Result for <Facility> Sludge Sample (11.6% solids). Determined by <Laboratory> with Applicable Qualifiers Assigned by DELS-WES

PFAS Analyte	Concentration (µg/Kg, dry wt)	RL[A] (µg/Kg)	MDL[B] (µg/Kg)	Qualifier(s) Assigned by Laboratory	Qualifier(s)[C] Assigned by DELS-WES
PFBS					
PFBA					
PFDS					
PFDA					
PFDoA					
PFHpA					
PFHxS					
PFHxA					
PFNA					

PFAS Analyte	Concentration (µg/Kg, dry wt)	RL[A] (µg/Kg)	MDL[B] (µg/Kg)	Qualifier(s) Assigned by Laboratory	Qualifier(s)[C] Assigned by DELS-WES
PFTrDA					
PFOA					
PFOS					
PFPeA					
PFUnA					
PFPeS					
PFNS					

[A] RL: Reporting Limit; equivalent to Minimum Reporting Level (MRL).
[B] MDL: Method Detection Limit – Determination of MDLs is not required for the analysis of PFAS in residuals or other matrices.
[C] Definitions of DELS-WES qualifiers:

- B: A target PFAS was detected above the Reporting Limit (RL – equivalent to Minimum Reporting Level or MRL) in a blank (i.e., method blank or field reagent blank) as well as in the residual sample. Residual PFAS concentration is estimated (could be biased high) if the concentration is less than 10 times the concentration in the blank.
- H: Residual sample was extracted and/or analyzed past the extraction and/or analysis holding times specified in EPA Method 533. Residual PFAS concentrations are estimated (could be biased low or high).
- J: Estimated residual PFAS concentration greater than or equal to the Method Detection Limit (MDL) but less than the RL/MRL.
- J1-: Isotopically labeled analogue recovery below the lower acceptance limit – Residual concentration is estimated (could be biased low) for the corresponding target PFAS.
- J1+: Isotopically labeled analogue recovery above the upper acceptance limit – Residual concentration above the RL/MRL is estimated (could be biased high) for the corresponding target PFAS.
- J2-: Laboratory control sample (LCS – equivalent to laboratory-fortified blank or LFB) recovery below the lower acceptance limit – Residual PFAS concentration is estimated (could be biased low).
- J2+: LCS recovery above the upper acceptance limit – Residual PFAS concentration above the RL/MRL is estimated (could be biased high).
- J3-: Matrix spike (MS – equivalent to laboratory-fortified sample matrix or LFSM) recovery below the lower acceptance limit – Residual PFAS concentration is estimated (could be biased low).
- J3+: MS recovery above the upper acceptance limit – Residual PFAS concentration above the RL/MRL is estimated (could be biased high).
- J3±: MS was not analyzed with the residual extraction batch – Residual PFAS concentrations are estimated (could be biased high or low).
- J4±: LCS duplicate (LCSD) relative percent difference (RPD) above the upper acceptance limit – Residual PFAS concentrations above the RL/MRL is estimated (could be biased high or low). Note that the LCSD is not a substitute for an MS duplicate (MSD), laboratory sample duplicate, or field sample duplicate.
- J5±: MSD, laboratory sample duplicate, or field sample duplicate RPD above the upper acceptance limit or not analyzed with the residual extraction batch – Residual PFAS concentrations above the RL/MRL are estimated (could be biased high or low).
- J6+: The ratio of the quantifier ion response to qualifier ion response (i.e., primary mass transition) falls outside of the laboratory established criteria (i.e., outside ratio limits). Results are estimated maximum PFAS concentrations. Laboratories may use an F or I qualifier for this QC issue.

- JO: Other QC criteria not met and other infrequent occurrences that require a qualifier. (see description)
- R: RL/MRL was reported as greater than 1 ng/g dry weight.
- T: Residual sample temperature upon receipt at the laboratory exceeded the EPA Method 533 requirement of < 10°C (i.e., residual sample receipt temperature was ≥ 10°C). Residual sample PFAS concentrations are estimated (could be biased high or low).

Table 2. Field Duplicate RPD Results

Relative Percent Difference on Duplicate Samples							
IDs: Sludge Grab and Sludge Grab Dup	**RDL**	**2x RL**	**Sample**	**Duplicate**	**RPD (%)**	**RPD Guidelines ≥2x MRL**	**RPD Guidelines ≤2x MRL**
PFBS							
PFBA							
PFDS							
PFDA							
PFDoA							
PFHpA							
PFHxS							
PFHxA							
PFNA							
PFTrDA							
PFOA							
PFOS							
PFPeA							
PFUnA							
PFPeS							
PFNS							
Total Solids							

Acronyms & Abbreviations

Acronyms/Abbreviations	Definition
COA	Certificate of Analysis
COC	Chain-of-Custody
CCV	Continuing Calibration Verification
°C	Degrees Celsius
DELS-WES	Division of Environmental Laboratory Services – Wall Experiment Station
DUP	Duplicate
EPA	Environmental Protection Agency
FD	Field Duplicate
FRB	Field Reagent Blank
g	gram
HDPE	High Density Polyethylene
ID	Identification
IS	Internal Standard
LCS	Laboratory Control Sample
LFSM	Lab Fortified Sample Matrix
LFSMD	Lab Fortified Sample Matrix Duplicate
LRB	Laboratory Reagent Blank
LC/MS/MS	Liquid chromatography/Mass Spectrometry/Mass Spectrometry
MassDEP	Massachusetts Department of Environmental Protection
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MB	Method Blank
MDL	Method Detection Limit
µg/kg	Microgram/kilogram
mL	Milliliter
MRL	Minimum Reporting Limit
ng/g	Nanogram/gram
NEBRA	North East Biosolids & Residuals Association

Acronyms/Abbreviations	Definition
ND	Not detected
oz	Ounce
ppb	Parts per billion
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFPeA	Perfluoropentanoic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnA	Perfluoroundecanoic acid
PFDoA	Perfluorododecanoic acid
PFTrDA	Perfluorotirdecanoic acid
PFBS	Perfluorobutanesulfonic acid
PFPeS	Perfluoropentanesulfonic acid
PFHxS	Perfluorohexanesulfonic acid
PFOS	Perfluorooctancesulfonic acid
PFNS	Perflurornonanesulfonic acid
PFDS	Perfluorodecanesulfonic acid
QA	Quality Assurance
QC	Quality Control
RPD	Relative Percent Difference
RDL	Reporting Detection Limit
RL	Reporting Limit
SIU	Significant Industrial User
SOP	Standard Operating Procedure
SPLP	Synthetic Precipitation Leaching Procedure

Limitations of report

Tetra Tech has prepared this QC report and its contents for the use of the Massachusetts Department of Environmental Protection (MassDEP), with the understanding that the QC Report may be shared with/utilized by MassDEP in conjunction with projects involving third parties. A portion of Tetra Tech's QC report, consisting of certain data, analysis and recommendations, has been provided to Tetra Tech by reports prepared by independent laboratories, and Tetra Tech assumes no responsibility for the accuracy of the information contained in these laboratory reports.

Closure

We trust this technical memo meets your present requirements. If you have any questions or comments, please contact the undersigned.

Respectfully submitted,

Prepared by:	Reviewed by:

APPENDIX B: SAMPLE COUNT AND PFAS CONCENTRATIONS BY FACILITY

Table B-1. Summary of the number of primary and duplicate (DUP) sample reviews conducted, tallied by reporting quarter and facility. Pseudo-Split samples were analyzed for samples marked with an asterisk (*). Refer to AOS facility codes and names as in Table 3. Continued on the following page.

AOS Facility Code	2020 Q2&3 Primary	2020 Q3 DUP	2020 Q4 Primary	2020 Q4 DUP	2021 Q1 Primary	2021 Q1 DUP	2021 Q2 Primary	2021 Q2 DUP	2021 Q3 Primary	2021 Q3 DUP	2021 Q4, 2022 Q1 Primary	2021 Q4, 2022 Q1 DUP	Total Primary Samples per Facility	Total DUP Samples per Facility
AW	1	1	1	1	1	1	1	1	1	1	--	--	5	5
BRNH	1	1	--	--	1	1	1	1	1	1	--	--	4	4
BW	--	--	1	1	1	1	--	--	1	1	1	1	4	4
BRDG	--	--	1	1	1	1	1	1	1	1	--	--	4	4
BRST	--	--	1	--	1	--	1	--	1	--	--	--	4	--
CTG	--	--	1	1	1	1	1	1	1	1	--	--	4	4
CONC	1	1	--	--	1	--	1	--	1	--	--	--	4	1
DRTM	--	--	1	1	--	--	1	1	1	1	--	--	3	3
ERSC	1*	1	1*	1	1	1	1*	1	1*	1	--	--	5	5
GLSD	1*	1	--	--	1*	1	1*	1	1*	1	--	--	4	4
HR	--	--	1	1	1	1	1	1	1	--	--	--	4	3
HWQD	1	1	--	--	1	1	1	1	1	1	--	--	4	4
IPSW	1	1	1	1	1	1	--	--	1	1	--	--	4	4
MRMK	1	1	1	1	--	--	1	1	1	1	--	--	4	4
MMSD	1	--	--	--	--	--	1	--	--	--	2	--	4	--
MONT	--	--	1	1	1	1	--	--	1	1	--	--	3	3
MWRA	1	1	1	1	1	1	1	1	1	1	--	--	5	5
NASH	--	--	1	1	1	1	1	--	1	1	--	--	4	3
NWBP	--	--	1	1	--	--	1	1	1	1	--	--	3	3

AOS Facility Code	2020 Q2&3 Primary	2020 Q3 DUP	2020 Q4 Primary	2020 Q4 DUP	2021 Q1 Primary	2021 Q1 DUP	2021 Q2 Primary	2021 Q2 DUP	2021 Q3 Primary	2021 Q3 DUP	2021 Q4, 2022 Q1 Primary	2021 Q4, 2022 Q1 DUP	Total Primary Samples per Facility	Total DUP Samples per Facility
NCW	--	--	1	1	1	1	--	--	2	2	--	--	4	4
OSC	--	--	1	1	--	--	--	--	--	--	1	--	2	1
OSM	--	--	1	1	1	1	--	--	--	--	--	--	2	2
RMF	--	--	1	1	1	1	1	--	1	1	--	--	4	3
RWD	1	1	--	--	--	--	1	1	1	--	--	--	3	2
RDAF	--	--	1	1	1	1	1	1	1	1	--	--	4	4
RLSW	--	--	1	1	1	1	1	1	1	1	--	--	4	4
RWAS	--	--	1	1	1	1	1	1	1	1	--	--	4	4
SLBV	--	--	1	--	1	--	1	--	1	--	--	--	4	--
SMRS	--	--	1	1	1	1	1	1	1	1	--	--	4	4
SVH	--	--	1	1	1	1	1	--	1	1	--	--	4	3
STHB	1	1	1	1	1	1	1	1	1	1	--	--	5	5
TNTN	--	--	--	--	--	--	1	--	1	--	--	--	2	--
TWKS	--	--	--	--	1	--	1	1	--	--	--	--	2	1
WON	--	--	1	1	1	1	1	1	1	--	--	--	4	3
WWD	--	--	--	--	1	1	1	1	1	1	--	--	3	3
Totals Per Quarter	12	**11**	**26**	**24**	**28**	**24**	**29**	**21**	**32**	**25**	**4**	**1**	**131**	**106**

Table B-2. PFAS _16 and PFAS6 statistics by facility, for all primary samples over all quarters.

AOS Facility Code	PFAS_16 Min	PFAS_16 Average	PFAS_16 Max	PFAS6 Min	PFAS6 Average	PFAS6 Max
AW	41.0	55.7	76.0	41.0	55.7	76.0
BRDG	14.5	30.4	52.3	3.9	10.7	16.1
BRNH	0.00	1.40	5.61	0.00	0.00	0.00
BRST	19.6	24.5	35.3	7.5	9.5	12.7
BW	8.2	44.0	93.9	0.0	37.9	80.8
CONC	0.0	10.1	30.8	0.0	6.8	17.3
CTG	0.0	1.5	4.0	0.0	0.7	1.9
DRTM	21.9	32.3	46.3	8.0	11.7	15.3
ERSC	4.2	21.0	56.9	1.7	18.2	52.2
GLSD	8.9	14.3	27.8	2.2	9.0	19.0
HR	294.8	316.8	370.0	38.3	52.4	92.9
HWQD	77.8	138.1	189.5	26.2	50.9	69.7
IPSW	17.0	41.6	60.6	4.2	10.3	16.8
MMSD	3.1	3.1	3.1	1.8	1.8	1.8
MONT	1.5	8.2	17.3	1.5	3.9	7.9
MRMK	42.1	75.8	142.4	13.9	24.2	42.5
MWRA	15.1	23.4	28.2	10.1	17.9	21.3
NASH	11.4	17.7	24.7	2.8	9.3	12.6
NCW	0.00	1.15	2.98	0.00	1.00	2.75
NWBP	0.17	0.56	0.87	0.17	0.56	0.87
OSC	0.00	0.00	0.00	0.00	0.00	0.00
OSM	0.00	0.00	0.00	0.00	0.00	0.00
RADF	7.4	9.8	11.3	6.4	9.1	10.5
RLSW	4.6	9.1	13.6	3.6	7.2	12.4
RMF	8.7	26.0	42.9	6.9	14.6	29.6
RWAS	3.6	9.6	12.7	3.3	8.8	12.1
RWD	0.0	1.9	2.9	0.0	1.9	2.9
SLBV	1.9	7.0	16.3	1.9	7.0	16.3
SMRS	95.3	196.2	231.5	42.1	88.2	115.8
STHB	36.8	41.0	48.5	10.5	14.5	18.1
SVH	10.9	18.4	32.4	3.3	10.8	25.1
TNTN	5.1	5.1	5.1	0.0	1.1	2.1
TWKS	0.7	1.7	2.8	0.0	0.6	1.2
WON	6.4	9.2	11.1	3.6	5.5	6.8
WWD	0.0	9.2	24.1	0.0	6.4	15.8

APPENDIX C: OUTLIER ANALYSIS

Outlier Analysis

The outlier analysis was intended to identify PFAS values that might be larger than expected or at the extremes of the distributions of values. Identifying outliers would give an opportunity to dismiss the values as erroneous or to dismiss them to avoid statistical bias in normal parametric analyses.

Data Set

The outlier analysis included all valid data, including dups and pseudo-splits, aggregated. This included data from 36 facilities and 8 calendar quarters. Overall there were 245 samples (with dups and pseudo-splits) and 4,138 records. The analysis addressed all 16 required residual PFAS compounds and the calculated PFAS6.

Analytical Approach

The analysis was intended to find extreme values of each distribution per PFAS compound, using all samples combined. The intra-quartile (IQ) ranges were used to estimate a common range of values. Outliers were defined in this first analysis as any values greater than the 75th percentile of the value distribution plus 1.5 times the IQ range. Extremes Outliers were defined as any values greater than the 75th percentile of the value distribution plus 2.0 times the IQ range. All values were first transformed by log10.

- Outliers > 75th percentile + 1.5 * IQ range
- Extremes > 75th percentile + 2 * IQ range
- First standardize to the Log10 scale

For compounds with many non-detect values, the IQ range can be small and low. This results in multiple outliers. When removing non-detects, the measurable range became apparent and fewer outliers were identified.

Results

For the analysis including using log-transformed values and non-detect values, the outlier and extreme counts and limits per PFAS compound are listed in Table C-1. The compounds with the most outliers and extremes included PFDS , PFHpA, PFDA, and PFHxS. The PFAS6 combination of compounds had a single outlier greater than 123.6 ng/g.

In the analysis with non-detect values removed and other values log-transformed, there were 46 outlier and extreme data points identified (Figure C-1). Only PFDS had extreme values after removing the non-detect values.

Table C-1. Outlier and extreme point counts and limits per PFAS compound.

Compound	# Outliers (Extremes)	Outlier Limit (ng/g)	Outlier Limit (Log10 ng/g +1)	Extreme Limit (ng/g)	Extreme Limit (Log10 ng/g +1)
PFAS6	1	123.6	2.10	224.6	2.35
PFOS*	1	85.3	1.94	155.3	2.19
PFDA*	9 (3)	12.5	1.13	19.2	1.31
PFNA*	3	6.4	0.87	9.3	1.01
PFOA*	4	41.7	1.63	79.3	1.90
PFUnA	0	4.8	0.76	6.5	0.88
PFNS	1	6.0	0.84	8.5	0.98
PFBA	0	108.0	2.04	254.9	2.41
PFHxA	0	511.9	2.71	1589.4	3.20
PFHxS*	5 (1)	4.6	0.75	6.6	0.88
PFBS	0	194.0	2.29	493.3	2.69
PFHpA*	9 (6)	4.9	0.77	6.8	0.89
PFDS	9 (7)	4.4	0.73	5.8	0.83
PFDoA	2	6.1	0.85	8.5	0.98
PFPeA	0	27.8	1.46	50.8	1.71
PFPeS	0	3.2	0.62	4.3	0.73
PFTrDA	2 (1)	2.4	0.53	3.2	0.62

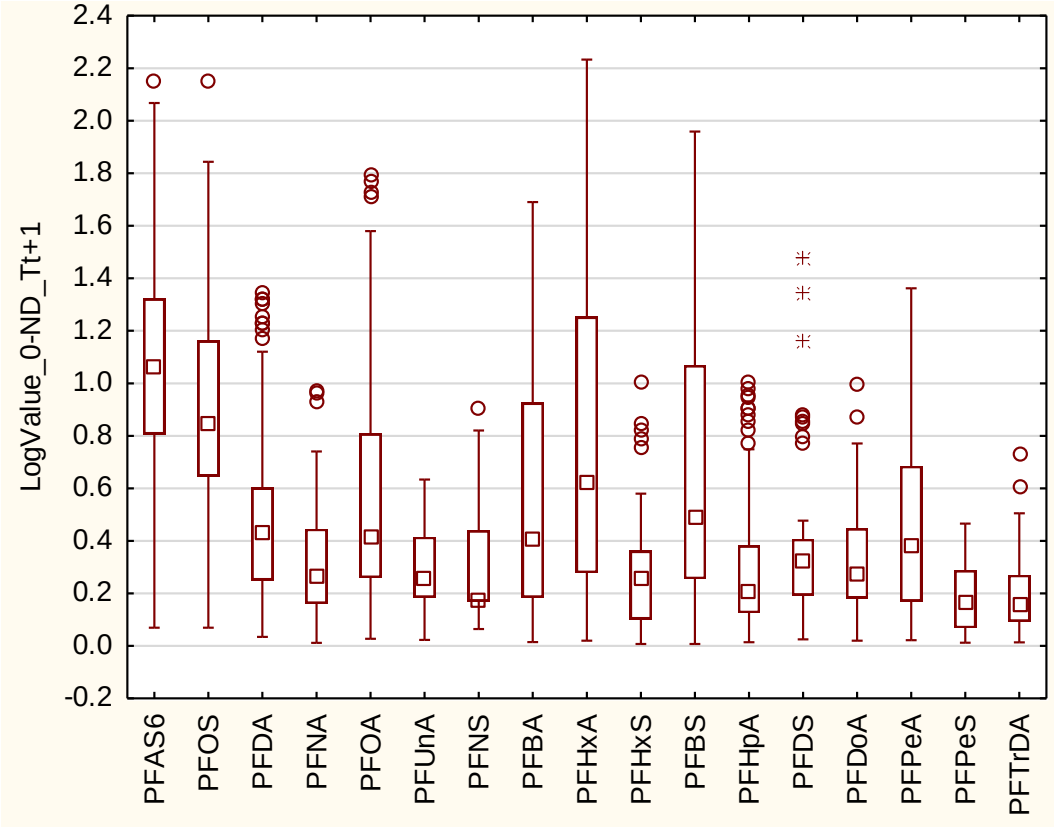

Figure C-1. Outlier and extreme values shown as circles and stars above PFAS compound distributions after removing non-detect values.

Conclusions

- All analytical results appear to be true measurements
  - Not transcription errors – this was checked during previous QC reviews
  - No justification for discounting records due to error
- Only a few values appear to be extremely high
  - Values labelled as extreme (n = 18)
- Outlier and extreme values can be de-emphasized in analysis
  - Log-transforming concentrations to approximate normal distributions
  - Using non-parametric analyses (e.g., Spearman rank correlation)
- Only 1 value was an outlier in the combined PFAS6 compounds
  - Removing outliers for individual compounds for any sample would prohibit calculation of PFAS6 or PFAS_16 for those samples
- Recommendation:
  - Retain all values unless obvious effects are noted during analyses (e.g., regression slopes that appear to be driven by outliers)

Table C-2. Outlier values by compound and sample.

Residuals Required Compounds	Value	LogValue +1	Outlier	Pct Solids	Residuals Facility Name	SampleID	Quarter	Lab	Sample Type
PFAS6	141.61	2.15	Outlier	42.1	Erseco, Inc. (Erving POTW #2)	410-14997-1	2020_Q3	Lab D	Pseudo-Split
PFOS	140	2.15	Outlier	42.1	Erseco, Inc. (Erving POTW #2)	410-14997-1	2020_Q3	Lab D	Pseudo-Split
PFDA	21	1.34	Extreme	71.2	Somerset WWTF	320-76524-1	2021_Q3	Lab B	Primary
PFDA	20	1.32	Extreme	54.1	Somerset WWTF	320-69131-3	2021_Q1	Lab B	Duplicate
PFDA	20	1.32	Extreme	56.9	Somerset WWTF	320-69131-1	2021_Q1	Lab B	Primary
PFDA	19	1.30	Outlier	41	Somerset WWTF	320-72958-1	2021_Q2	Lab B	Primary
PFDA	17	1.26	Outlier	32.9	Hawk Ridge	320-70746-2	2021_Q1	Lab B	Duplicate
PFDA	16	1.23	Outlier	53.9	Somerset WWTF	320-72958-2	2021_Q2	Lab B	Duplicate
PFDA	16	1.23	Outlier	66.4	Somerset WWTF	320-76524-2	2021_Q3	Lab B	Duplicate
PFDA	15	1.20	Outlier	30.9	Hawk Ridge	320-70746-1	2021_Q1	Lab B	Primary
PFDA	13.7	1.17	Outlier	43.1	Hoosac Water Quality District	L2038344-01	2020_Q3	Lab A	Primary
PFNA	8.44	0.97	Outlier	18	Amesbury Water	L2053716-02	2020_Q4	Lab A	Duplicate
PFNA	8.24	0.97	Outlier	27.4	Merrimack, NH WWTF	L2039564-01	2020_Q3	Lab A	Primary
PFNA	7.53	0.93	Outlier	18	Amesbury Water	L2053716-01	2020_Q4	Lab A	Primary
PFOA	61	1.79	Outlier	41	Somerset WWTF	320-72958-1	2021_Q2	Lab B	Primary
PFOA	58	1.77	Outlier	71.2	Somerset WWTF	320-76524-1	2021_Q3	Lab B	Primary
PFOA	52	1.72	Outlier	66.4	Somerset WWTF	320-76524-2	2021_Q3	Lab B	Duplicate
PFOA	50	1.71	Outlier	53.9	Somerset WWTF	320-72958-2	2021_Q2	Lab B	Duplicate
PFNS	7.09	0.91	Outlier	14.6	Barnhardt	L2114399-02	2021_Q1	Lab A	Duplicate
PFHxS	9.1	1.00	Extreme	0.8	Braintree Water	320-70901-1	2021_Q1	Lab B	Primary
PFHxS	6	0.85	Outlier	66.9	Bristol, RI Compost Facility	PVL419	2021_Q2	Lab C	Primary
PFHxS	5.7	0.83	Outlier	1.2	Braintree Water	320-79605-1	2021_Q3	Lab B	Primary
PFHxS	5.2	0.79	Outlier	1.3	Braintree Water	320-79605-2	2021_Q3	Lab B	Duplicate
PFHxS	4.7	0.76	Outlier	1.1	Braintree Water	320-70901-2	2021_Q1	Lab B	Duplicate
PFHpA	9.1	1.00	Extreme	41	Somerset WWTF	320-72958-1	2021_Q2	Lab B	Primary
PFHpA	8.5	0.98	Extreme	71.2	Somerset WWTF	320-76524-1	2021_Q3	Lab B	Primary

PFHpA	8.1	0.96	Extreme	66.4	Somerset WWTF	320-76524-2	2021_Q3	Lab B	Duplicate
PFHpA	7.8	0.94	Extreme	53.9	Somerset WWTF	320-72958-2	2021_Q2	Lab B	Duplicate
PFHpA	7.1	0.91	Extreme	30.9	Hawk Ridge	320-70746-1	2021_Q1	Lab B	Primary
PFHpA	7	0.90	Extreme	56.9	Somerset WWTF	320-69131-1	2021_Q1	Lab B	Primary
PFHpA	6.6	0.88	Outlier	54.1	Somerset WWTF	320-69131-3	2021_Q1	Lab B	Duplicate
PFHpA	6.1	0.85	Outlier	32.9	Hawk Ridge	320-70746-2	2021_Q1	Lab B	Duplicate
PFHpA	5.7	0.83	Outlier	0.8	Braintree Water	320-70901-1	2021_Q1	Lab B	Primary
PFDS	29	1.48	Extreme	34.4	Resource Management Facility	320-79651-4	2021_Q3	Lab B	Duplicate
PFDS	21	1.34	Extreme	34	Resource Management Facility	320-79651-3	2021_Q3	Lab B	Primary
PFDS	13.5	1.16	Extreme	23.3	Concord, NH WWTF	L2109952-01	2021_Q1	Lab A	Primary
PFDS	6.66	0.88	Extreme	95.5	MWRA	L2134462-02	2021_Q2	Lab A	Duplicate
PFDS	6.45	0.87	Extreme	94.6	MWRA	L2134462-01	2021_Q2	Lab A	Primary
PFDS	6.2	0.86	Extreme	24.3	Nashua, NH WWTF	L2222146-01	2021_Q2	Lab A	Primary
PFDS	6.02	0.85	Extreme	94.7	MWRA	L2057217-01	2020_Q4	Lab A	Primary
PFDS	5.23	0.79	Outlier	94.6	MWRA	L2057217-02	2020_Q4	Lab A	Duplicate
PFDS	4.93	0.77	Outlier	94.8	Greater Lawrence	L2132664-01	2021_Q2	Lab A	Pseudo-Split
PFDoA	8.9	1.00	Outlier	54.1	Somerset WWTF	320-69131-3	2021_Q1	Lab B	Duplicate
PFDoA	6.4	0.87	Outlier	56.9	Somerset WWTF	320-69131-1	2021_Q1	Lab B	Primary
PFTrDA	4.4	0.73	Extreme	66.9	Bristol, RI Compost Facility	PVL419	2021_Q2	Lab C	Primary
PFTrDA	3.05	0.61	Outlier	35.7	Soundview VT Holdings	L2125558-01	2021_Q2	Lab A	Primary

APPENDIX D: PRINCIPAL COMPONENTS ANALYSIS

A Principal Components Analysis (PCA) of PFAS compound percent composition in the samples was conducted to determine how the compound composition was related to the treatment types. The PCA was conducted with PC-Ord software (McCune and Mefford 2018) using percent composition of the 16 PFAS compounds in primary samples (131 samples). The PCA ordination was compared with facility, lab, treatment, dates, % solids and other variables that were available and suspected of influencing PFAS composition. The first three principal components accounted for 47% of the variability in PFAS composition.

As described in the report, the Sludge_Paper_I treatments (and one Sludge Type II sample) separate to the left of the diagram with high percentages of long-chain carboxylic PFAS compounds such as PFNA, PFDoA, PFUnA, and PFTrDA (**Figures D-1 and D-2**). The upper right of the diagram (high PC1 and PC2 values) was mostly Compost_I treatments with generally higher percentages of short-chain PFAS compounds. The lower right of the diagram had samples with high composition of long-chain sulfonic compounds, mostly greater than 40% PFOS and lower percentages of most other compounds. There were several treatment types in this quadrant of the diagram.

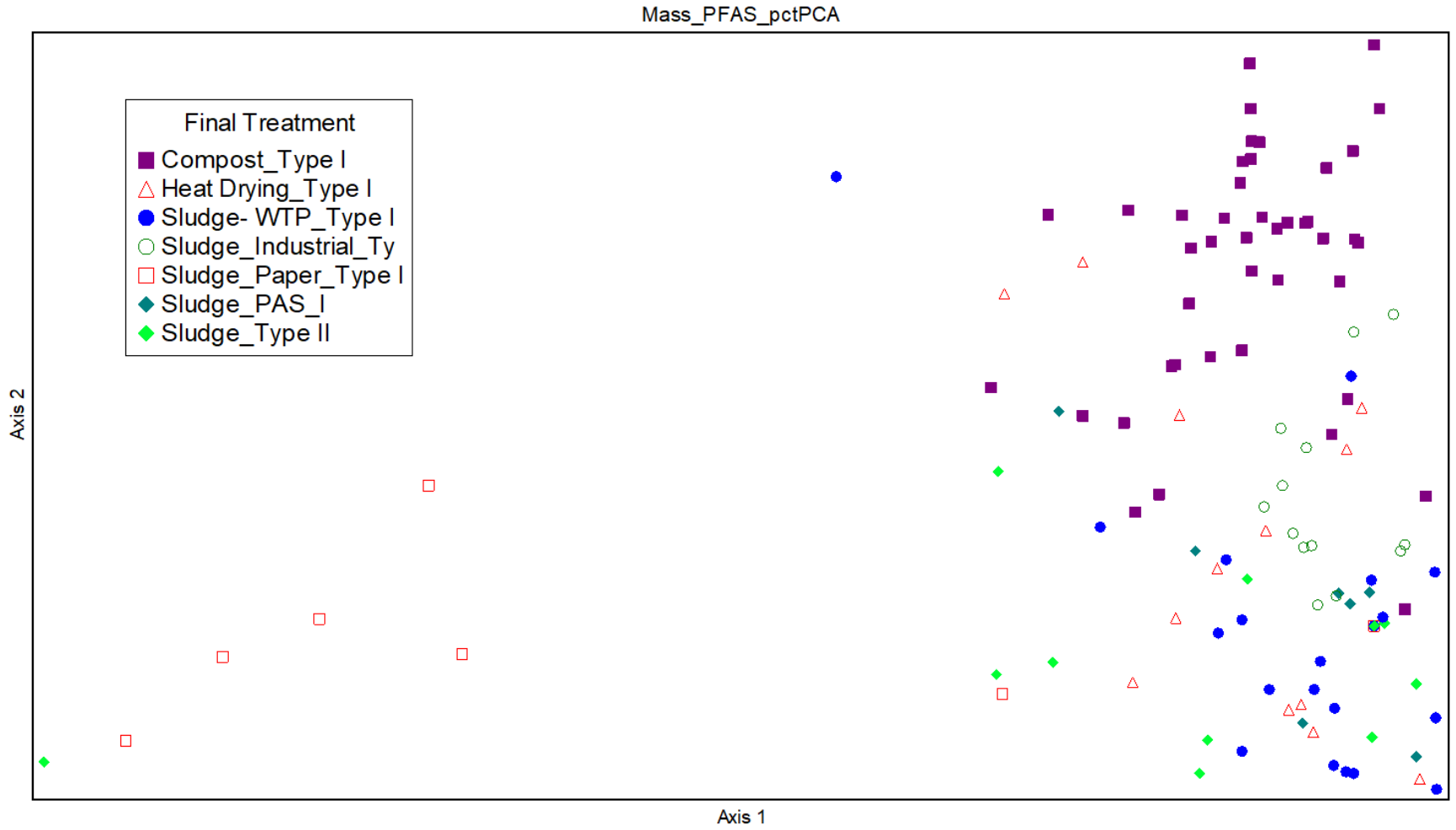

Figure D-1. PCA ordination of PFAS compounds (% composition), marked by treatment type.

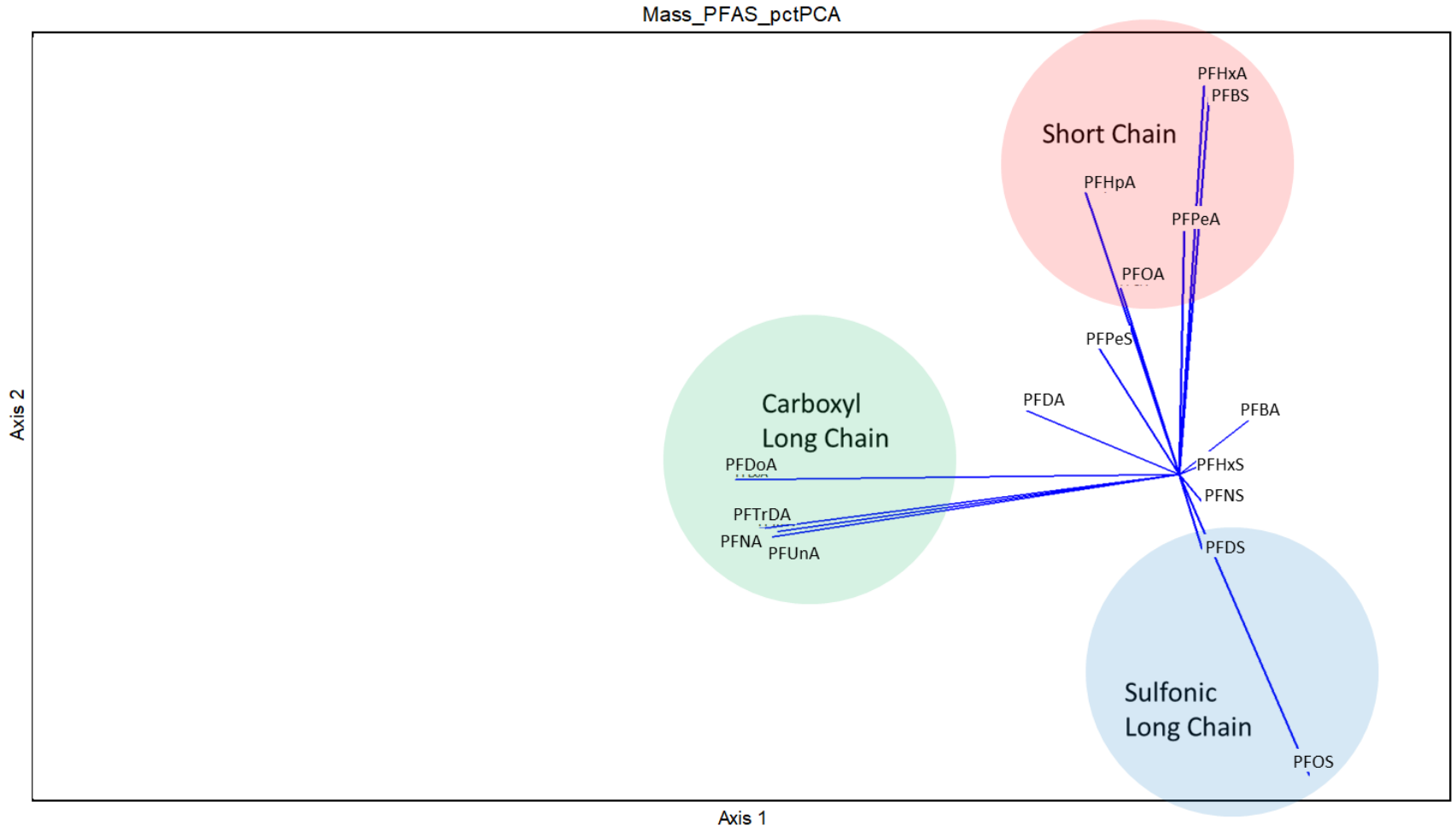

Figure D-2. PCA ordination of PFAS compounds (% composition), showing vectors of the PFAS compound percent composition.

APPENDIX E: DESCRIPTIONS OF STATISTICAL MEASURES

Table E-1. Statistical measures for interpreting precision of repeated measures.

Statistic Label	Statistic Name	Interpretation
% ND	Percent non-detect values	Statistics derived from a high percentage of non-detect values might be unreliable because there are few actual measurements for comparison. Non-detect values were assigned a zero (0) value for analysis. Zero values can prevent calculation of some statistics (e.g., zero values are not allowed in the denominator of calculations)
RMSE	Root Mean Square Error	RMSE is an estimate of the standard deviation of the compounds within replicate sets, averaged across sets. A low RMSE can result from precise repeated measures and from low concentrations.
Mean	Average of all values within an analysis	The mean is shown to help qualify the magnitude of the RMSE. The mean in the precision comparisons might be calculated from different samples and should not be interpreted as an indication of analytic results. For example, a high mean for one laboratory replicate set compared to the other laboratory replicate set should not be interpreted that the laboratory is biased, just that they analyzed different samples. In the case of pseudo-splits, the replicates are not completely homogenized before splitting and variability could still be attributed to the sample, not the laboratory.
CV	Coefficient of Variability	The CV standardizes the RMSE to the mean, so that comparisons of variability can be compared across replicate sets that have different means. Low CVs indicate good precision. High CVs can result from poor precision or from very low mean values. CVs cannot be calculated when all replicates have a mean of zero (0).
CI90	90% Confidence Interval	The CI90 is the range (+ and -) around the observed value that the true mean is expected to occur in 90 out of 100 measurements. A low CI90 indicates good precision. CI90 is scaled to the actual measurements, not standardized to the mean. This gives an estimate of the variability to be expected around single measurements, with 90% confidence.
RPD	Relative Percent Difference	The RPD is the difference between two measures divided by the average of those measures, as a percentage. RPD cannot be calculated when both values are zero (0). When one value is zero and the other is non-zero, the RPD is inflated to 200%.

APPENDIX F: PRECISION STATISTICS

Table F-1. Absolute differences between primary and duplicate samples (|p-d|) and relative percent difference (RPD) for all duplicates by facility, quarter, and laboratory, also showing average percent solids in the duplicates. Missing RPD values indicate that both duplicates had non-detect values. RPD of 200% indicate that one of the two duplicates was a non-detect and the other value was a detection. Table continued on following pages.

Facility Code	Treatment	Quarter	Lab	PFAS_16 |p-d|	PFAS6 |p-d|	PFAS_16 RPD	PFAS6 RPD	Avg % Solids
AW	Sludge- WTP_Type I	20Q3	Lab A	0.85	0.85	4%	4%	18.7
		20Q4	Lab A	5.46	5.46	13%	13%	18
		21Q1	Lab A	0.64	0.64	3%	3%	17.3
		21Q2	Lab A	1.64	1.64	7%	7%	20
		21Q3	Lab A	0.95	0.30	3%	1%	18.3
BRDG	Compost_Type I	20Q4	Lab B	1.30	0.69	17%	30%	54.9
		21Q1	Lab B	0.84	0.39	6%	9%	30.4
		21Q2	Lab B	0.14	0.27	1%	4%	42.4
		21Q3	Lab B	3.27	1.97	13%	22%	45.2
BRNH	Sludge_Type II	20Q3	Lab A	0.00	0.00	23%		14.6
		21Q1	Lab A	0.74	0.00			14.6
		21Q2	Lab A	0.00	0.00			10.9
		21Q3	Lab A	0.00	0.00			11.6
BW	Sludge- WTP_Type I	20Q4	Lab B	2.15	1.25	68%	200%	1.1
		21Q1	Lab B	25.85	21.30	76%	72%	1
		21Q3	Lab B	2.20	2.20	7%	7%	1.3
		22Q1	Lab B	0.90	2.25	20%	58%	1.6
CONC	Sludge_PAS_Type I	20Q3	Lab A	0.00	0.00			30.1
CTG	Sludge_Paper_Type I	20Q4	Lab B	0.45	0.00	200%		34.4
		21Q1	Lab B	0.00	0.00			35
		21Q2	Lab B	0.39	0.36	21%	46%	33.5
		21Q3	Lab B	0.01	0.02	1%	3%	34.7
DRTM	Compost_Type I	20Q4	Lab E	0.49	1.07	3%	17%	50.1
		21Q2	Lab E	0.59	0.71	5%	19%	42.8
		21Q3	Lab E	1.06	0.09	5%	1%	66.3
ERSC	Sludge_Type II	20Q3	Lab B	0.60	0.65	2%	3%	41.2
		20Q4	Lab B	0.56	1.18	8%	18%	42.3
		21Q1	Lab B	0.53	0.55	9%	12%	42.3
		21Q2	Lab B	1.02	0.94	10%	11%	41
		21Q3	Lab B	0.58	0.49	32%	82%	47.5
GLSD	Heat Drying_Type I	20Q3	Lab B	1.13	1.44	8%	14%	70
		21Q1	Lab B	0.62	0.23	15%	23%	94.3
		21Q2	Lab B	1.52	0.69	26%	18%	94.9
		21Q3	Lab B	0.53	0.31	10%	8%	95.7

Facility Code	Treatment	Quarter	Lab	PFAS_16 |p-d|	PFAS6 |p-d|	PFAS_16 RPD	PFAS6 RPD	Avg % Solids
HR	Compost_Type I	20Q4	Lab B	33.01	2.80	25%	15%	34.8
		21Q1	Lab B	13.92	3.74	8%	8%	31.9
		21Q2	Lab B	23.62	1.10	14%	6%	36.2
HWQD	Compost_Type I	20Q3	Lab A	10.19	5.12	13%	16%	45.4
		21Q1	Lab A	1.74	1.06	2%	3%	54.8
		21Q2	Lab A	2.82	1.33	5%	6%	56.5
		21Q3	Lab A	0.62	0.04	2%	0%	64.8
IPSW	Compost_Type I	20Q3	Lab A	3.82	0.88	28%	22%	63.7
		20Q4	Lab A	4.02	1.15	13%	18%	38.2
		21Q1	Lab A	2.41	0.97	25%	37%	50.7
		21Q3	Lab A	11.92	3.18	49%	47%	48
MONT	Compost_Type I	20Q4	Lab B	0.03	0.93	0%	27%	17.3
		21Q1	Lab B	0.53	0.15	20%	14%	21.4
		21Q3	Lab B	0.00	0.00	0%	0%	15.6
MRMK	Compost_Type I	20Q3	Lab A	35.79	11.09	67%	71%	41.1
		20Q4	Lab A	4.28	1.53	15%	17%	49.9
		21Q2	Lab A	0.55	0.52	3%	7%	44.4
		21Q3	Lab A	2.31	0.93	9%	10%	49.1
MWRA	Heat Drying_Type I	20Q3	Lab A	0.46	0.51	6%	10%	95.1
		20Q4	Lab A	1.75	0.79	13%	8%	94.6
		21Q1	Lab A	0.15	0.01	1%	0%	93.7
		21Q2	Lab A	1.32	0.24	10%	2%	95.1
		21Q3	Lab A	0.62	0.53	5%	5%	94.9
NASH	Sludge_Type II	20Q4	Lab B	0.50	0.15	9%	11%	21
		21Q1	Lab B	0.75	1.35	8%	24%	29.6
		21Q3	Lab B	0.52	0.23	6%	4%	28.3
NCW	Sludge- WTP_Type I	20Q4	Lab B	0.01	0.00	52%		92.5
		21Q1	Lab B	0.00	0.00			82.1
		21Q3a	Lab B	0.17	0.11	25%	19%	81.4
		21Q3b	Lab B	1.05	1.11	108%	135%	76.8
NWBP	Sludge- WTP_Type I	20Q4	Lab A	0.00	0.00	2%	2%	81.4
		21Q2	Lab A	0.06	0.06	17%	17%	32.2
		21Q3	Lab A	0.12	0.12	24%	24%	21.7
OSC	Sludge_Industrial_Type I	20Q4	Lab A	0.00	0.00			0.6
OSM	Sludge_Industrial_Type I	20Q4	Lab A	0.00	0.00			2.3
		21Q1	Lab A	0.00	0.00			0.6
RDAF	Sludge_Industrial_Type I	20Q4	Lab A	0.07	0.04	1%	1%	19

Facility Code	Treatment	Quarter	Lab	PFAS_16 |p-d|	PFAS6 |p-d|	PFAS_16 RPD	PFAS6 RPD	Avg % Solids
		21Q1	Lab A	0.24	0.20	5%	4%	22
		21Q2	Lab A	0.41	0.38	12%	13%	17.3
		21Q3	Lab A	0.55	0.56	9%	10%	24.4
RLSW	Sludge_Industrial_Type I	20Q4	Lab A	0.18	0.17	8%	9%	7.5
		21Q1	Lab A	2.42	2.37	43%	47%	7.4
		21Q2	Lab A	2.87	2.29	46%	49%	2.9
		21Q3	Lab A	0.13	0.02	3%	1%	4.5
RMF	Sludge_PAS_Type I	20Q4	Lab B	4.80	3.26	20%	20%	34.7
		21Q1	Lab B	3.40	2.56	39%	43%	28.3
		21Q3	Lab B	5.28	0.97	29%	25%	34.2
RWAS	Sludge_Industrial_Type I	20Q4	Lab A	0.10	0.10	5%	6%	36.6
		21Q1	Lab A	2.36	2.23	33%	33%	25.8
		21Q2	Lab A	0.56	0.56	10%	12%	30.7
		21Q3	Lab A	0.97	0.99	16%	18%	27.3
RWD	Sludge- WTP_Type I	20Q3	Lab A	1.32	1.32	200%	200%	29.3
		21Q2	Lab A	0.15	0.15	10%	10%	51.8
SMRS	Compost_Type I	20Q4	Lab B	11.22	3.65	27%	19%	89.1
		21Q1	Lab B	4.00	2.70	3%	6%	55.5
		21Q2	Lab B	4.50	10.10	4%	19%	47.5
		21Q3	Lab B	7.32	4.66	7%	9%	68.8
STHB	Compost_Type I	20Q3	Lab A	1.29	0.34	7%	6%	66.6
		20Q4	Lab A	3.93	0.43	18%	6%	47.3
		21Q1	Lab A	0.72	0.42	4%	6%	52
		21Q2	Lab A	1.76	0.77	8%	12%	42.2
		21Q3	Lab A	1.01	0.06	5%	1%	43.4
SVH	Sludge_Paper_Type I	20Q4	Lab B	1.09	0.51	15%	16%	36.6
		21Q1	Lab B	0.86	0.05	17%	3%	39.7
		21Q3	Lab B	2.54	1.90	15%	14%	36.5
TWKS	Sludge- WTP_Type I	21Q2	Lab A	0.01	0.38	3%	200%	42.8
WON	Compost_Type I	20Q4	Lab B	0.70	0.43	13%	14%	73.8
		21Q1	Lab B	0.91	0.70	20%	23%	64
		21Q2	Lab B	0.07	0.20	2%	9%	76.9
WWD	Sludge- WTP_Type I	21Q1	Lab A	0.79	0.36	6%	4%	
		21Q2	Lab A	3.56	3.56	101%	101%	4.6
		21Q3	Lab A	0.00	0.00			2.1

The smallest CV for repeated measures within facilities over time was calculated for PFAS_16, followed by another small CV for PFAS6 (**Table F-2**). A smaller CV for these composites of multiple compounds compared to the individual compounds was a common pattern. The largest CV's were calculated for individual compounds with low mean values, such as PFNS and PFPeS. These compounds also had a high percentage of non-detect values. An RMSE of 22.2 ng/g for PFAS_16 is an estimate of the standard deviation of primary PFAS_16 measurements within facilities, averaged across facilities.

Table F-2. Root Mean Square Error (RMSE) calculated from ANOVA, mean, and coefficient of variability (CV) of repeated measures (samples by quarter) within facilities (primary samples only) for PFAS aggregations and compounds.

Compounds	Chain Lngth	Acid Type	% ND[a]	RMSE (ng/g)	Mean (ng/g)	CV (%)
PFAS_16			9	22.2	38.8	57
PFAS6			13	13.3	16.4	81
PFDA	Long	Carb	31	1.6	2.1	77
PFDoA	Long	Carb	57	0.6	0.6	96
PFNA	Long	Carb	34	1.0	0.9	111
PFOA	Long	Carb	27	4.6	4.1	114
PFTrDA	Long	Carb	80	0.4	0.2	240
PFUnA	Long	Carb	54	0.5	0.5	90
PFDS	Long	Sulf	76	2.4	0.6	403
PFHxS	Long	Sulf	70	1.0	0.4	246
PFNS	Long	Sulf	96	0.5	0.1	715
PFOS	Long	Sulf	22	7.8	8.2	96
PFBA	Short	Carb	48	2.1	3.0	71
PFHpA	Short	Carb	54	0.9	0.7	118
PFHxA	Short	Carb	35	7.4	10.8	69
PFPeA	Short	Carb	50	1.8	1.8	100
PFBS	Short	Sulf	65	5.0	4.3	118
PFPeS	Short	Sulf	96	0.2	0.0	366

a: ND = non-detect

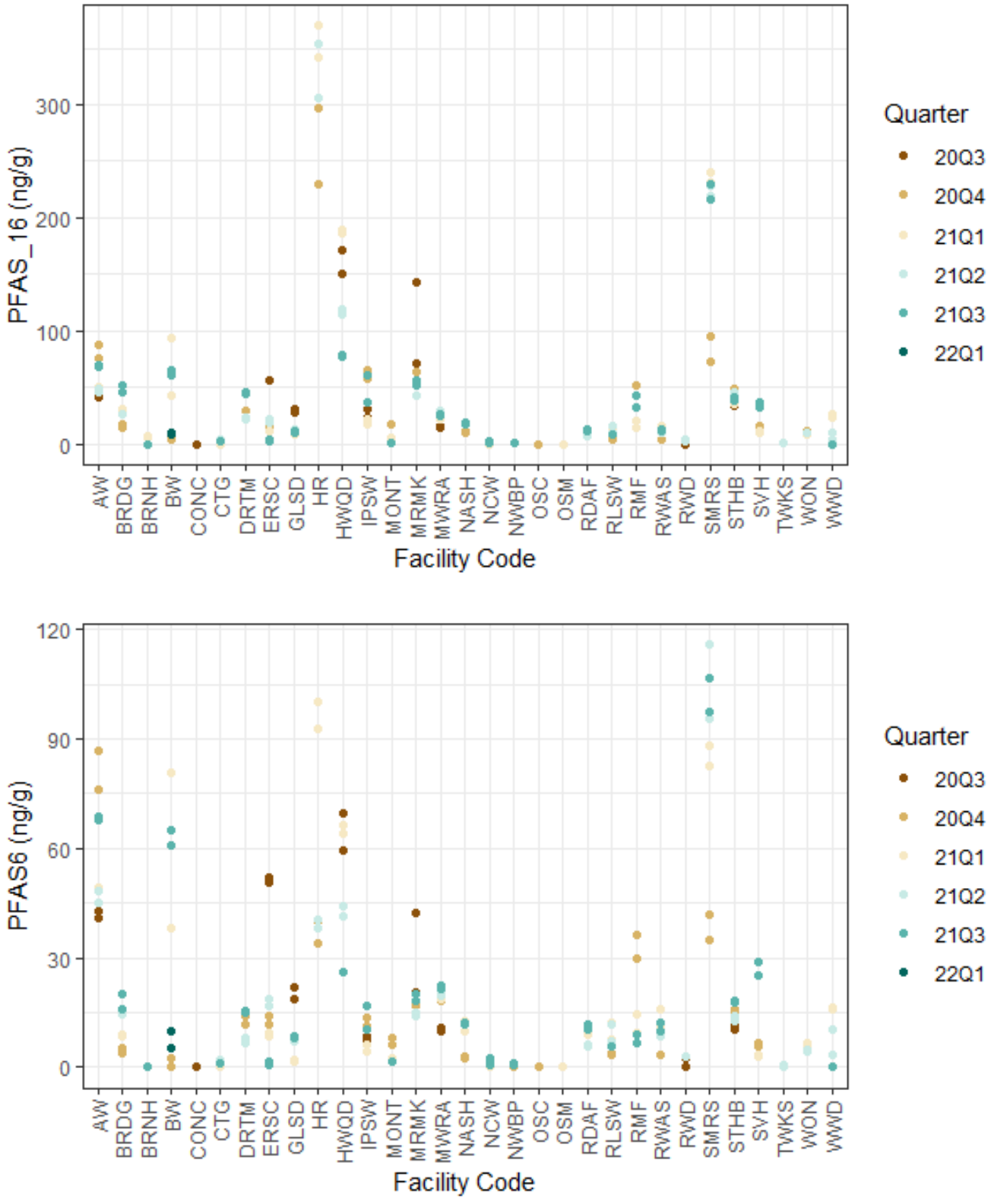

Figure F-1. Concentrations of PFAS_16 (top) and PFAS6 (bottom) in duplicate sample sets marked by facility and sampling quarter.