



Project Level Data Validation Report

**Better Brite Plating Co., Chrome
and Zinc Shops Superfund Site
De Pere, Wisconsin**

February 2024

**BRRTS #02-05-000030 &
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Prepared For:

U.S. Environmental Protection Agency
Region 5

and

Wisconsin Department of Natural
Resources

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A handwritten signature in black ink, appearing to read "Ted O'Connell".

Ted O'Connell
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Kristen Morin
Quality Assurance Chemist

Project-Level Data Validation Report

I. Project Information	
Site	Better Brite Plating Co., Chrome and Zinc Shops Superfund Site, De Pere, Wisconsin
Laboratory	ALS Environmental Laboratory, Holland, MI
SDG No.	23041906
Parameter	Per- and Polyfluoroalkyl Substances (PFAS)
Report Prepared By	Kristen Morin/TRC
Peer Reviewer	Elizabeth Denly/TRC
Date	February 15, 2024

II. Samples Included in the Review	
33 Groundwater Samples	W-1-230418, W-1A-230418, MW-2-230418, MW-3R-230418, MW-5-230419, MW-5A-230420, MW-6-230418, MW-6A-230418, MW-7-230419, MW-7A-230419, MW-8-230420, MW-8A-230420, MW-9-230419, MW-10-230420, MW-11-230419, MW-12-230419, MW-106-230420, MW-106A-230420, MW-107-230419, MW-107A-230419, MW-108-230420, MW-108A-230420, MW-110-230420, MW-110A-230420, MW-112-230420, MW-113-230419, MW-115-230419, MW-115A-230419, MW-116-230419, SUMP-230418, DUP-01-230418 ¹ , DUP-02-230418 ² , DUP-03-230419 ³
1 Performance Evaluation Sample	MW-099-230420
1 Equipment Blank	EB-01-230420
2 Field Blanks	FB-01-230420, FB-02-230420

Notes:

The above-listed samples were collected on April 18-20, 2023 and were analyzed for PFAS (33 target analytes) based on EPA Method 537 (Modified) and using ALS Holland, MI's standard operating procedure (SOP) HN-LCMS-005-R02.

Footnotes:

- ¹ Field duplicate of SUMP-230418
- ² Field duplicate of W-1-230418
- ³ Field duplicate of MW-116-230419

III. Summary of Data Validation Performed

A third party, ICF-Environmental Services Assistance Team (ESAT), performed Stage 2B data validation [Stage_2B_Validation_Electronic_and_Manual (S2BVEM)] in accordance with the following guidance documents, modified for the methodology utilized:

- Data Review and Validation guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537 (EPA 910-R-18-001), November 2018.
- Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use, OSWER No. 9200.1-85 (EPA 540-R-08-005), January 2009.

- Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations, Version 12.16.2019, Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS.
- Better Brite Plating Co. Chrome and Zinc Shops Superfund Site Quality Assurance Project Plan (QAPP), Revision 1, October 2022.

The data were evaluated based on the following parameters during the Stage 2B validation:

- Holding Times and Sample Preservation
- Calibration
- Laboratory Blanks/Field Blanks
- Injection Internal Standards
- Extracted Internal Standards (EIS)
- Matrix Spike (MS)/MS Duplicates
- Laboratory Fortified Blanks (LFBs)
- QAPP Compliance

Note: ICF-ESAT did not evaluate field duplicate pairs or ion transition ratios during the Stage 2B validation. Field duplicates and ion transition ratios were evaluated by TRC in this report in Section VIII.

IV. Review of Data Validation Report for Completeness

The following issues were noted with ICF-ESAT's data validation report, in regard to completeness.

- ICF-ESAT did not evaluate or record continuing calibration results for three PFAS, 10:2 FTS, PFHxDA and PFODA, on the continuing calibration summary pages in the data validation report. Since these three PFAS were not required to be reported by the laboratory, per QAPP Worksheet 15, and since these three PFAS were not detected in any of the field samples, there is no adverse impact to the usability of data or achievement of project objectives due to the lack of evaluation.
- The validator mistakenly identified sample DUP-03-230419 as DUO-03-230419 on page 2 of 11 of ICF-ESAT's validation report. This sample ID was correct in the laboratory report and is referenced as DUP-03-230419 through this project-level validation report.
- Select associated samples were missing on the Laboratory Reagent Blank (LRB/MBLK) Summary and LCS Summary forms in the data validation report provided by ICF-ESAT for Batch ID 215053a. There is no adverse impact to the usability of data due to this issue.
- Section 5 of ICF-ESAT's data validation report included an evaluation of EIS areas compared to the average EIS responses from the initial calibration standards; an evaluation of the injection internal standard, 13C7-PFUnDA, was not provided by ICF-ESAT or the laboratory. Therefore, the injection internal standard results were not assessed during this project-level validation; refer to Section VII for further discussion.
- Field duplicate results were not evaluated in ICF-ESAT's data validation report since the parent sample IDs has not been provided. The field duplicate results were evaluated during this project-level validation and are summarized in Section VIII.

- The case narrative of the laboratory data package indicated that several ion transition ratios did not meet acceptance criteria due to matrix interference and/or the presence of branched isomers not represented in the calibration standards; however, these nonconformances were not discussed in ICF-ESAT's data validation report. The ion transition ratio results were evaluated during this project-level validation and are summarized in Sections VII and VIII.
- The ICF-ESAT data validation report did not note that the laboratory reported method reporting limits (MRLs) and method detection limits (MDLs) rather than LOQs and LODs per the QAPP. Since the terms LOQ and LOD are equivalent to MRLs and MDLs, respectively, there is no adverse impact to the usability of data or achievement of project objectives.
- The ICF-ESAT data validation report indicated that the electronic data deliverable (EDD) contained duplicate data values for the MS and MSD performed on sample MW-108-230420 and that the validator was unable to determine which MS/MSD results were applicable. However, upon review during project-level validation, it was determined that the appropriate MS/MSD summary forms were provided by the laboratory on pages 1535-1539 of 1544 of the Level IV data package. The MS/MSD analyses performed on sample MW-108-230420 were reviewed during project-level validation and are further discussed in Section VII. In order to report only one set of results for these MS/MSDs, the EDD was manually updated by TRC to indicate which set of MS/MSD results were used during the evaluation. The laboratory was not contacted to correct the EDD as suggested by ICF-ESAT.
- The ICF-ESAT validation report noted that several instrument raw data files were missing from the level IV data package. Since the missing files were provided by the laboratory to ICF-ESAT and were included in Appendix A of the ICF-ESAT data validation, the laboratory was not contacted to provide a revised Level IV data package as suggested by ICF-ESAT.

V. Data Completeness Percentage

Data completeness is a measurement of the amount of valid data obtained compared to the amount that is scheduled or expected to be obtained under normal conditions. All expected samples from QAPP Worksheet 18 were collected with the exception of sample MW-111 from the Chrome Shop; this sample could not be collected as planned due to the lack of a signed access agreement for the property. Field completeness for the April 2023 PFAS groundwater sampling event was calculated to be 97%, greater than the 95% program quality objective for completeness.

There were no data points rejected during the data validation process. Therefore, laboratory completeness for the April 2023 PFAS groundwater sampling event was calculated to be 100%.

VI. Application of Qualifiers for Global QC Issues

ICF-ESAT discussed qualifiers throughout the text of the data validation report; qualified EDD or analytical results pages were not provided by ICF-ESAT. Table 1 below summarizes qualifiers that were applied to the data in ICF-ESAT's data validation report, as interpreted by TRC; these include qualifications due to field duplicates as applied by TRC, the affected samples, and the reason for qualification. Qualifiers applied to the data during validation have been updated by TRC in the associated EDD.

All results are usable for project objectives. Qualifications applied to the field sample data because of sampling and/or analytical error are discussed below.

Table 1: Summary of Qualifiers in Samples

Sample ID	Analyte*	Qualifier	Reason for Qualification
MW-10-230420 (re-analysis)	4:2 FTS	UJ	High EIS %R
MW-2-230418	4:2 FTS	UJ	High EIS %R
MW-108-230420	PFTriA	UJ	CCV nonconformance
	PFTeA	UJ	CCV nonconformance
W-1_20230418	PFOS	J	Field duplicate variability
DUP-02-2304182	PFOS	J	Field duplicate variability

Notes:

* PFTrDA is another acronym for PFTriA and PFTeDA is another acronym for PFTeA. The acronyms used by ALS (PFTriA and PFTeA, respectively) have been used consistently throughout this report for these target compounds.

It should also be noted that select PFAS results were detected between the LOD and LOQ. These results were qualified as estimated (J) by the laboratory in the associated samples. These qualifications were not summarized in Table 1 above since they were not applied during data validation.

VII. Step IIb of Data Review Process

The sample results and quality control (QC) parameters were reviewed for compliance with QAPP Worksheets 12, 24, 25, and 28. Except as noted below, ICF-ESAT's data validation report documented measurement performance criteria in the QAPP that were not met. Measurement performance criteria which were not achieved are summarized below. Refer to ICF-ESAT's data validation report for complete details.

- Continuing Calibration Verification (CCV) Standards
 - As previously stated, ICF-ESAT did not evaluate CCV results for three PFAS, 10:2 FTS, PFHxDA and PFODA as these PFAS were not required to be reported for this program.
 - The recovery of 8:2 FTS was above the QAPP acceptance limit in the opening CCV associated with sample MW-7-230419 . No validation qualifiers were applied by ICF-ESAT since 8:2 FTS was not detected in this sample.
 - The recoveries of PFTriA and PFTeA were above the QAPP acceptance limit in bracketing CCVs associated with samples, MW-10-230420, MW-2-230418, MW-3R-230418, MW-5-230419, MW-5A-230420, MW-6-230418, MW-6A-230418, MW-7A-230419, MW-8-230420, and MW-8A-230420. No validation qualifiers were applied by ICF-ESAT since PFTriA and PFTeA were not detected in the associated samples.

- The recoveries of NMeFOSE, PFTriA, and PFTeA were above the QAPP acceptance limit in the initial calibration verification (ICV) standards associated with samples, MW-108A-230420, MW-110A-230420, MW-112-230420, MW-113-230419, MW-115-230419, MW-115A-230419, MW-116-230419, DUP-01-230418, DUP-02-230418, FB-01-230420, and FB-02-230420. Further, the recoveries of PFTriA and PFTeA were above the QAPP acceptance limit in the bracketing CCVs associated with these samples. No validation qualifiers were applied by ICF-ESAT since NMeFOSE, PFTriA, and PFTeA were not detected in the associated samples.
- The recoveries of PFTriA and PFTeA were below the QAPP acceptance limit in bracketing CCVs associated with sample MW-108-230420. Nondetect results for PFTriA and PFTeA in this sample were qualified as “UJ”. This is summarized in Table 1.
- EISs
 - The following samples had EIS %Rs for 13C2-FTS 4:2 above the QAPP acceptance limits: MW-2-230418 and MW-10-230420. According to ICF-ESAT, non-detect results for 4:2 FTS in these samples were qualified as “UJ”. This is summarized in Table 1.
 - ICF-ESAT’s data validation report indicated that the %R for the EIS 13C2-PFTeA was above the QAPP acceptance limits in the original analysis of sample MW-10-230420, indicating a potential low bias for the nondetect (UJ) result in this sample. However, the EIS %R for 13C2-PFTeA was within the QAPP acceptance limits in the re-analysis of this sample, which was the analysis reported by the laboratory for PFTeA in this sample. Therefore, no qualifier was applied by TRC to the result for PFTeA in sample MW-10-230420.
- Injection Internal Standards
 - An evaluation of the injection internal standard, 13C7-PFUnDA, as required in the QAPP, was not provided by ICF-ESAT. Select results were qualified by ICF-ESAT based on EIS areas (not injection internal standard areas) that were not within the injection internal standard criteria; it was determined during project-level validation that no new qualifiers would have been assigned to any field sample results based on this evaluation performed by ICF-ESAT. Therefore, as this EIS area evaluation is not warranted per the method or QAPP, it was not used to evaluate the usability of the data. It should be noted that only EIS %Rs were used by TRC for evaluating the usability of the data in accordance with the Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations, Version 12.16.2019.
- MS/MSD Results
 - The ICF-ESAT data validation report noted several instances where MS and/or MSD samples should be qualified based on various nonconformances. However, only field sample results were qualified by TRC during project-level validation.
 - ICF-ESAT did not evaluate nonconformances for the MS/MSD analyses performed on sample MW-108-230420. Only the MS/MSD analyses performed by the laboratory on 5/5/23 were evaluated by TRC as the other MS/MSD results reported by the laboratory were unusable. The %R for 10:2 FTS in the MS (216%) and the RPD for 10:2 FTS in MS/MSD (36.9%) were outside of the QAPP acceptance limits (50-150% and 30%, respectively). No validation actions were taken on this basis by TRC since 10:2 FTS was not detected in sample MW-108-230420.

- Field Duplicates
 - Field duplicate pairs were not evaluated in ICF-ESAT’s data validation report since the parent sample IDs were not provided. The field duplicate results were evaluated during this project-level validation and are summarized in Section VIII. The positive results for PFOS were qualified as estimated (J) in samples W-1-230418 and DUP-02-2304182 due to field duplicate variability. This is summarized in Table 1.
- Ion Transition Ratios
 - Ion transition ratios were not evaluated in ICF-ESAT’s data validation report. The laboratory case narrative was reviewed during this project-level validation and issues with ion transition ratios are summarized in Section VIII.
- LODs/LOQs
 - Laboratory LOQs met the QAPP-specified LOQs prior to adjustment for sample-specific volumes. Laboratory LODs varied slightly from the QAPP-specified LODs for select PFAS compounds.
- Field sampling data will be discussed in the Groundwater Investigation Report.

VIII. Step III of Data Review Process: Overall Usability Assessment

In general, data are usable for project decisions based on a review of accuracy, precision, and sensitivity of the data. The data are valid as reported and may be used for decision-making purposes with the following cautions.

- The results for PFOS in samples MW-7-230419, MW-107-230419, MW-110-230420, SUMP-230418, and W-1A-230418 are slightly above the Wisconsin Department of Health Services (DHS), cycle 10 and 11, Recommended Preventive Action Limit (PAL) for groundwater. There is potential uncertainty for the PFOS results in these samples due to ion transition ratios being outside of the acceptance limits; the results for PFOS in these samples may be lower and below the listed screening criteria due to this issue.
- The result for PFOS in sample MW-12-230419 is slightly above the Wisconsin DHS, cycle 10 and 11, Recommended Enforcement Standard (ES) for groundwater. There is potential uncertainty for the PFOS result in this samples due to the ion transition ratio being outside of the acceptance limits; the result for PFOS in this sample may be lower and below the listed screening criteria due to this issue.
- The results for PFOS in samples MW-8-230420 and MW-112-230420 are slightly below the Wisconsin DHS, cycle 10 and 11, Recommended PAL for groundwater. There is potential uncertainty for the PFOS results in these samples due to ion transition ratios being outside of the acceptance limits; the results for PFOS in these samples may be higher and above the listed screening criteria due to this issue.

Biases and uncertainties associated with the PFAS analyses of the groundwater samples are discussed below.

A. Evaluation of Accuracy

High Biased Results

Potential high bias exists for select results due to various QC nonconformances, as noted in the table below.

Associated Samples	Analytes Affected	Reason for High Bias	Reason Data Usability or Decision-making Process Not Affected
MW-7-230419	8:2 FTS	High CCV %Rs	Affected analytes not detected in associated samples.
MW-10-230420, MW-2-230418, MW-3R-230418, MW-5-230419, MW-5A-230420, MW-6-230418, MW-6A-230418, MW-7A-230419, MW-8-230420, MW-8A-230420	PFTriA, PFTeA		
MW-108A-230420, MW-110A-230420, MW-112-230420, MW-113-230419, MW-115-230419, MW-115A-230419, MW-116-230419, DUP-01-230418, DUP-02-230418, FB-01-230420, FB-02-230420	NMeFOSE, PFTriA, PFTeA		

Low Biased Results

Potential low bias exists for select results due to various QC nonconformances, as noted in the table below.

Associated Samples	Analytes Affected	Reason for Low Bias	Reason Data Usability or Decision-making Process Not Affected
MW-10-230420 (re-analysis), MW-2-230418	4:2 FTS	High EIS recoveries	No project action limits exist for 4:2 FTS.
MW-10-230420 (original analysis)	PFTeA, PFTriA		Affected analytes reported from a different analysis with acceptable EIS %Rs.

B. Evaluation of Precision

Field Duplicate Evaluation

Samples SUMP-230418/DUP-01-230418, W-1-230418/DUP-02-230418, and MW-116-230419/DUP-03-230419 were submitted as the field duplicate pairs with this sample set. The following tables summarize the absolute differences (AbsDs), as applicable, of the detected results; all criteria were met except as noted for PFOS in samples W-1_230418 and DUP-02-2304182.



Analyte	LOQs (ng/L)	SUMP-230418 (ng/L)	DUP-01-230418 (ng/L)	AbsD (ng/L)	Validation Action
PFBS	5.2/5.7	2.3 J	2.5 J	0.2	None; all criteria were met.
PFBA	5.2/5.7	10	10	0	
PFHxS	5.2/5.7	3.4 J	3.8 J	0.4	
PFHxA	5.2/5.7	5.1 J	5.1 J	0	
PFOS	2.1/2.3	3.0	4.2	1.2	
PFOA	2.1/2.3	7.2	7.9	0.7	
PFPeA	5.2/5.7	5.2 J	6.0	0.8	

Analyte	LOQs (ng/L)	W-1-230418 (ng/L)	DUP-02-230418 (ng/L)	AbsD (ng/L)	Validation Action
PFBS	4.9/5.0	2.2 J	1.5 J	0.7	None; all criteria were met.
PFBA	4.9/5.0	4.6 J	3.8 J	0.8	
PFHxS	4.9/5.0	1.2 J	ND	3.8	
PFHxA	4.9/5.0	1.8 J	2.5 J	0.7	None; all criteria were met.
PFOA	2.0/2.0	5.6	5.4	0.2	
PFPeA	4.9/5.0	ND	2.0 J	2.9	
PFOS	2.0/2.0	6.0	3.4	2.6	The positive results for PFOS were qualified as estimated (J) in samples W-1-230418 and DUP-02-2304182 since the AbsD was > the QL.

Notes:

ND: Nondetect; LOQ used in calculation of AbsD.

Analyte	LOQs (ng/L)	MW-116-230419 (ng/L)	DUP-03-230419 (ng/L)	AbsD (ng/L)	Validation Action
PFBS	5.3/5.3	1.1 J	1.2 J	0.1	None; all criteria were met.
PFBA	5.3/5.3	3.4 J	4.0 J	0.6	
PFHxS	5.3/5.3	2.3 J	2.6 J	0.3	
PFHxA	5.3/5.3	ND	1.5 J	3.8	
PFOS	2.1/2.1	9.3	8.7	0.6	
PFOA	2.1/2.1	5.7	5.4	0.3	
PFPeS	5.3/5.3	0.81 J	0.73 J	0.08	
PFPeA	5.3/5.3	2.2 J	1.7 J	0.5	

Notes:

ND: Nondetect; LOQ used in calculation of AbsD.

QAPP Criteria:

- RPD ≤30 when positive results for one or both samples are ≥5x LOQ
- AbsD < LOQ when positive results for both samples are <5x LOQ

Potential Uncertainty

Potential uncertainty exists for select results due to various QC nonconformances, as noted in the table below.

Associated Samples	Analytes Affected	Reason for Uncertainty	Reason Data Usability or Decision-making Process Not Affected
MW-7-230419, MW-8-230420, MW-12-230419, MW-107-230419, MW-110-230420, MW-112-230420, SUMP-230418, W-1A-230418	PFOS	Ion transition ratio outside criteria	See beginning of Section VIII for potential effect on decision-making process.
MW-2-230418, MW-6-230418, MW-9-230419, MW-11-230419, MW-113-230419, DUP-01-230418	PFOS	Ion transition ratio outside criteria	Results for affected analyte significantly above or below the project action levels in the associated samples.
W-1A-230418, MW-10-230420, MW-116-230419	PFPeS	Ion transition ratio outside criteria	No project action limits exist for PFPeS.
All samples in this data set	10:2 FTS, PFHxDA, PFODA	Lack of CCV evaluation in ICF-ESAT validation report	Affected analytes are not contaminants of concern at the site and were not detected in the affected samples.
MW-108-230420	PFTeA, PFTriA	Low CCV %Rs	Results for PFTeA significantly below the project action levels in the associated samples. No project action limits exist for PFTriA.
MW-108-230420	10:2 FTS	High MS recovery and M/MSD variability	10:2 FTS not detected in affected sample.
W-1-20230418, DUP-02-2304182	PFOS	Field duplicate variability	Results for PFOS significantly above or below the project action levels in both original and duplicate samples.

C. Sensitivity

Sensitivity was acceptable for the PFAS analyses of groundwater samples (i.e., the LODs for nondetect results were below the Wisconsin DHS, cycle 10 and 11, Recommended PALs and ESs for groundwater).

IX. Achievement of Data Quality Objectives Defined in the QAPP

All data are usable for the project objective: To independently evaluate the presence/absence of PFAS at the site.