



Project Level Data Validation Report

**N.W. Mauthe Superfund Site
Appleton, Wisconsin**

February 2024

**BRRTS #02-45-000127
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Prepared For:

U.S. Environmental Protection Agency
Region 5

and

Wisconsin Department of Natural
Resources

Prepared By:

TRC
999 Fourier Dr., Suite 101
Madison, Wisconsin 53717

A handwritten signature in black ink that reads "Ted O'Connell".

Ted O'Connell
Project Manager

A handwritten signature in black ink that reads "Kristen Morin".

Kristen Morin
Quality Assurance Chemist

Project-Level Data Validation Report

| I. Project Information | |
|-------------------------------|---|
| Site | N.W. Mauthe Superfund Site, Appleton, Wisconsin |
| Laboratory | ALS Environmental Laboratory, Holland, MI |
| SDG No. | 23080465 |
| 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 | |
|---|---|
| 21 Groundwater Samples | MW-101-230801, MW-102-230802, MW-103-230802, MW-104-230802, MW-105-230801, MW-106-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-6-230802, PZ-7-230802, PZ-8-230802, W-2-230801, W-8-230801, W-15-23082, DUP-01-230802 ¹ , DUP-02-230802 ² |
| 1 Equipment Blank | EB-01-230802 |
| 2 Field Blanks | FB-01-230802, FB-02-230802 |

Notes:

The above-listed samples were collected on August 1 and 2, 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 MW-111-230802
- ² Field duplicate of MW-102-230802

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.
- PFAS Groundwater Investigation at N.W. Mauthe Superfund Site Quality Assurance Project Plan (QAPP), Revision 1, February 2023.

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 (MSDs)
- Laboratory Fortified Blanks (LFBs)
- QAPP Compliance

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

- Page 2 of 32 of the ICF-ESAT data validation report mistakenly indicated that samples were collected between 1/1/2023-8/2/2023.
- Page 3 of 32 of the ICF-ESAT data validation report discussed sample containers for samples that are not applicable to this data set.
- Section 4 of the ICF-ESAT data validation report incorrectly stated that the project LOQ was 5.0 ng/L when the LOQ for select PFAS was 2.0 ng/L.
- 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 for samples that were not applicable to this data set. As discussed in Section VII of this report, this evaluation is not required; no further action was required.
- 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.
- The ICF-ESAT data validation report did not indicate that the laboratory reported three additional PFAS:10:2 FTS, PFHxDA and PFODA. 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.
- The ICF-ESAT data validation report did not evaluate the MS/MSD analyses performed on the samples in this data set. Instead, Section 6 of ICF-ESAT's data validation report discussed MS/MSD nonconformances and issues for samples that are not applicable to this data set. The MS/MSD results were evaluated during this project-level validation and are summarized in Section VII.

- 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.
- Section 11 of the ICF-ESAT data validation report summarizing field blank contamination incorrectly cited sample MW-101-230801 as MW-01-230801. In the same section of the ICF-ESAT data validation report, validation qualifiers for the samples impacted by field blank contamination were not applied by ICF-ESAT. In addition, a discrepancy was noted with the samples listed as being less than 10x the field blank concentrations; the ICF-ESAT data validation report did not indicate that the results for PFOA in samples MW-107-230802 and MW-110-230802 were less than 10x the field blank contamination. The field sample and field blank results were further evaluated and qualified as needed during this project-level validation and are summarized in Section VII.
- 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 did not include a "QCS/CCV Standards Recovery Summary" form for the continuing calibration verification (CCV) results associated with the analyses performed on 8/10/23 (associated with sample W-15-23082). Further, the ICF-ESAT data validation report did not include CCV nonconformances for one of the CCVs analyzed on 8/9/23 associated with samples W-2-230801, W-8-230801, DUP-01-230802, DUP-02-230802, and EB-01-230802. These CCV results were evaluated during this project-level validation and are summarized in Section VII.
- The ICF-ESAT data validation report noted that low-level CCVs were analyzed by the laboratory and were missing from the level IV data package; only bracketing mid-level CCVs were provided within the level IV data package. It was assumed that the data validation report incorrectly noted that the missing low-level CCV files were provided by the laboratory to ICF-ESAT since these missing files were not included as an appendix or supplement to the ICF-ESAT data validation report. Based on the available information, ICF-ESAT only utilized the mid-level CCVs provided by the laboratory in the level IV data package in their validation.

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 PZ-5; this sample could not be collected as planned due to the lack of tubing in the well. Prior to sampling, it was determined by EPA that a performance evaluation (PE) sample was not required with this data set since a PE sample was previously submitted for another site with acceptable results. Field completeness for the August 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 August 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 electronic data deliverables (EDDs) 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 blanks 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(s) | Analyte | Qualifier | Reason for Qualification |
|---|----------|-----------------------------------|---|
| MW-107-230802, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802 | 4:2 FTS | UJ | High EIS percent recoveries (%Rs) |
| MW-107-230802 | 6:2 FTS* | J- | High EIS %R |
| MW-105-230801, MW-106-230802, PZ-7-230802, W-2-230801, W-8-230801 | PFOA | UJ at the reported concentrations | Field blank contamination and detection < the LOQ |
| MW-101-230801, MW-102-230802, MW-104-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-8-230802, W-15-23082, DUP-01-230802, DUP-02-230802 | PFOA | U at the reported concentrations | Field blank contamination and detection > the LOQ |

Notes:

* Note that this result was also qualified as estimated (J) by the laboratory due to detection < the LOQ.

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.

- CCV Standards
 - A low-level CCV was not reported with each analytical sequence. There is no impact on the data usability due to this issue since an initial calibration was performed within 24 hours of the affected analyses and the lowest initial calibration standard was at or below the LOQ.
 - As previously stated, ICF-ESAT did not provide a summary of the results for the CCVs associated with the analysis of sample W-15-23082 in the data validation report. These CCVs were reviewed during this project-level validation and were within the QAPP acceptance limits.
 - The ICF-ESAT data validation report did not discuss the nonconformance for 10:2 FTS (23.96 %R) in the low-level CCV analyzed on 8/9/23 (LLCCV1-230809-WI, data file 23080907) that was associated with samples W-2-230801, W-8-230801, DUP-01-230802, DUP-02-230802, and EB-01-230802. There is no adverse impact on the data usability due to this issue since 10:2 FTS is not a required target analyte per the QAPP for this site.
- EISs
 - The following samples had EIS %Rs for 13C2-FTS 4:2 above the QAPP acceptance limits: MW-107-230802, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, and MW-113-230802. According to ICF-ESAT, non-detect results for 4:2 FTS in these samples were qualified as “UJ”. This is summarized in Table 1.
 - Sample MW-107-230802 had an EIS %R for 13C2-FTS 6:2 above the QAPP acceptance limit. According to ICF-ESAT, the positive result for 6:2 FTS in this sample was qualified as “J-”. This is summarized in Table 1.
- Injection Internal Standards
 - An evaluation of the injection internal standard, 13C7-PFUnDA, as required in the QAPP, was not provided by ICF-ESAT.
 - Upon review of ICF-ESAT’s Isotope Performance Standard (IPS) Summary provided within the data validation report, it was noted that the EIS area (not injection internal standard area) was evaluated by ICF-ESAT and compared to the injection internal standard criteria. The EIS area associated with 4:2 FTS in sample MW-107-230802 was above the acceptance limits used by ICF-ESAT. It was determined during project-level validation that no new qualifiers would have been assigned to any field sample results based on this evaluation. 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 the MS/MSD analyses performed on samples MW-109-230801 and MW-112-230802. Therefore, the MS/MSD results were reviewed by TRC during project-level validation. Select %Rs were noted by the laboratory as being outside of the acceptance limits. However, the %Rs and relative percent differences (RPDs) for target PFAS were within the QAPP acceptance limits (50-150% and 30%, respectively) with one exception. The %R for 10:2 FTS in the MSD performed on sample MW-112-230802 (152%) was above the QAPP acceptance limits. No validation actions would have been required on this basis, if reviewed by ICF-ESAT, since 10:2 FTS was not detected in the parent sample.
- 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. All criteria were met and no validation actions were required on this basis.
- Field Blanks
 - PFOA was detected in both field blanks at concentrations > ½ the LOQ: FB-01-230802 at 1.7 J ng/L and FB-02-230802 at 1.1 J ng/L. ICF-ESAT noted select sample results which were less than 10x the field blank contamination; however, as previously stated above, no validation qualifiers were applied by ICF-ESAT and samples MW-107-230802 and MW-110-230802 were not listed as impacted by the field blank contamination in the ICF-ESAT data validation report but should have been. Results were qualified by TRC as follows:
 - The positive results for PFOA in samples MW-105-230801, MW-106-230802, PZ-7-230802, W-2-230801, and W-8-230801 were qualified as estimated nondetects (UJ) at the reported concentrations since the results were < the LOQ.
 - The positive results for PFOA in samples MW-101-230801, MW-102-230802, MW-104-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-8-230802, W-15-23082, DUP-01-230802, and DUP-02-230802 were qualified as nondetects (U) at the reported concentration since the results were > the LOQ and were <10x the maximum field blank concentration.
 - No validation actions were required for samples MW-103-230802 and PZ-6-230802 since PFOA was either detected >10x the field blank concentration or was not detected.
- 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 did not indicate any issues with ion transition ratios for the samples in this data set.
- 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 limitation.

- Nondetect results for PFOA in samples in samples MW-101-230801, MW-102-230802, MW-104-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-8-230802, W-15-23082, DUP-01-230802, and DUP-02-230802 may not be usable to verify the achievement of project action levels as the nondetect results for PFOA in these samples are above the Wisconsin Department of Health Services (DHS), cycle 10 and 11, Recommended Preventive Action Limit (PAL) for groundwater due to qualification as nondetects at the reported concentrations as a result of field blank contamination. It should be noted that the detected results for PFOA prior to validation of these samples exceeded the Wisconsin DHS, cycle 10 and 11, Recommended PAL for groundwater.

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 | Analyte Affected | Reason for High Bias | Reason Data Usability or Decision-making Process Not Affected |
|---|------------------|---|--|
| MW-112-230802 | 10:2 FTS | High MSD %R | 10:2 FTS not detected in associated sample. |
| MW-101-230801, MW-102-230802, MW-104-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-8-230802, W-15-23082, DUP-01-230802, DUP-02-230802 | PFOA | Field blank contamination | See beginning of Section VIII for potential effect on decision-making process. |
| MW-105-230801, MW-106-230802, PZ-7-230802, W-2-230801, W-8-230801 | PFOA | Detection < the LOQ and field blank contamination | Detected results for PFOA, prior to validation, below project action limits. |

Low Biased Results

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

| Associated Samples | Analyte Affected | Reason for Low Bias | Reason Data Usability or Decision-making Process Not Affected |
|--|------------------|---------------------|---|
| MW-107-230802, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802 | 4:2 FTS | High EIS %Rs | No project action limits exist for 4:2 FTS. |
| W-2-230801, W-8-230801, DUP-01-230802, DUP-02-230802, EB-01-230802 | 10:2 FTS | Low %R in CCV | 10:2 FTS is not a contaminant of concern at the site. |

B. Evaluation of Precision

Field Duplicate Evaluation

Samples MW-111-230802/Dup-01-230802 and MW-102-230802/Dup-02-230802 were submitted as the field duplicate pairs with this sample set. The following tables summarize the RPDs and absolute differences (AbsDs), as applicable, of the detected results; all criteria were met.

| Analyte | LOQs (ng/L) | MW-111-230802 (ng/L) | Dup-01-230802 (ng/L) | AbsD (ng/L) | Validation Action |
|---------|-------------|----------------------|----------------------|-------------|------------------------------|
| PFBS | 4.9/5.1 | 1.8 J | 1.6 J | 0.2 | None; all criteria were met. |
| PFBA | 4.9/5.1 | 7.8 | 7.5 | 0.3 | |
| PFHxS | 4.9/5.1 | 1.3 J | 1.1 J | 0.2 | |
| PFHxA | 4.9/5.1 | 1.6 J | 1.6 J | 0 | |
| PFOS | 2.0/2.0 | 8.4 | 7.4 | 1 | |
| PFOA* | 2.0/2.0 | 3.3 | 3.1 | 0.2 | |

| Analyte | LOQs (ng/L) | MW-102-230802 (ng/L) | Dup-02-230802 (ng/L) | RPD (%) or AbsD (ng/L) | Validation Action |
|---------|-------------|----------------------|----------------------|------------------------|------------------------------|
| PFBS | 5.1/5.2 | 34 | 37 | RPD: 8.5 | None; all criteria were met. |
| PFBA | 5.1/5.2 | 4.6 J | 4.4 J | AbsD: 0.2 | |
| PFHpA | 5.1/5.2 | 1.9 J | 2.1 J | AbsD: 0.2 | |
| PFHxS | 5.1/5.2 | 3.5 J | 3.9 J | AbsD: 0.4 | |
| PFHxA | 5.1/5.2 | 4.2 J | 4.6 J | AbsD: 0.4 | |
| PFOS | 2.1/2.1 | 7.1 | 7.3 | AbsD: 0.2 | |
| PFOA* | 2.12.1 | 3.8 | 5.0 | AbsD: 1.2 | |
| PFPeS | 5.1/5.2 | 0.73 J | ND | AbsD: 4.47 | |
| PFPeA | 5.1/5.2 | 3.8 J | 4.3 J | AbsD: 0.5 | |

Notes:

ND: Nondetect; LOQ used in calculation of AbsD.

* The original results reported by the laboratory are listed for PFOA; these results were later qualified as nondetect (U) at the reported concentrations due to field blank contamination.

QAPP Criteria:

- RPD \leq 30 when positive results for one or both samples are \geq 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-107-230802 | 6:2 FTS | High EIS %R and detection < the LOQ | No project action limits exist for 6:2 FTS. |

C. Sensitivity

Prior to the application of validation qualifiers, 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 Enforcement Standard for groundwater). After validation, the nondetect results for PFOA (range: 2.4-16 ng/L) in samples MW-101-230801, MW-102-230802, MW-104-230802, MW-107-230802, MW-108-230801, MW-109-230801, MW-110-230802, MW-111-230802, MW-112-230802, MW-113-230802, PZ-8-230802, W-15-23082, DUP-01-230802, and DUP-02-230802 were above the Wisconsin DHS, cycle 10 and 11, Recommended PAL (2.0 ng/L) for groundwater due to qualification as nondetects at the reported concentrations due to field blank contamination.

IX. Achievement of Data Quality Objectives Defined in the QAPP

All data are usable for the project objective: To investigate the presence of PFAS in groundwater at the site in a second round of sampling following the detection of PFAS in groundwater samples collected in December 2020.