

# Quality Assessment Report for Water Quality Monitoring

April – June 2021



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## INTRODUCTION

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This report is an assessment of the South Florida Water Management District (SFWMD) laboratory analysis and field sampling for total phosphorus (TP), primarily for the following projects and their associated stations from April 1, 2021, through June 30, 2021. The analysis contained in this document reflects the status of the data at the time of download and does not account for changes made to the data after July 27, 2021. The projects and associated stations at which data are collected are as follows:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356-334
- Everglades National Park Inflow East (PIE): G737, S332DX, S18C, S328, and BERMB3
- Everglades Protection Area (EVPA): LOX3 through LOX16

The Water Quality Monitoring Section *Field Quality Manual* (SFWMD-FIELD-QM-001) and *Field Sampling Manual* (SFWMD-FIELD-FSM-001) provided the quality system requirements and the field sampling procedures followed in field sample collection, respectively, from April 1 to June 30, 2021. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001) provides the requirements for preparing and analyzing laboratory samples, as well as data verification and validation. The *Field Sampling Quality Assessment* and *Laboratory Analysis Quality Assessment* sections in this report provide a comprehensive evaluation and validation of the TP results for samples collected from the locations and timeframe described above.

For the purpose of preparing this report, a Microsoft Excel workbook named "qa\_report\_apr\_jun\_2021\_data.xlsx" was created and contains all TP results obtained from DBHYDRO, SFWMD's corporate environmental database, for all sampling events that include grab samples collected for the project/stations listed above during the period specified in this report. This Excel workbook is available for reference on the Everglades Technical Oversight Committee (TOC) website (<https://www.sfwmd.gov/our-work/toe>) along with this report and will be referred to as the Reference Data Set (RDS) in this report. All sample analyses for TP were completed at the SFWMD Analytical Services Chemistry Laboratory (Department of Health Identification E46077).

If available, this report will also include TP sample results for biannual laboratory proficiency testing as required for the National Environmental Laboratory Accreditation Program (NELAP) or results from other laboratory performance evaluation studies that were completed during the period specified in this report.

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## FIELD SAMPLING QUALITY ASSESSMENT

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### SAMPLE COLLECTION

All samples were collected by Water Quality Monitoring staff. A total of 44 sampling events were conducted that included collection of samples for the projects/locations and timeframe described in the *Introduction* to this report. A complete list of the laboratory work orders obtained from the Laboratory Information Management System (LIMS) for these sampling events is shown in **Table 1**. The table details the work identifiers, work order numbers, project codes, and dates the samples were collected.

During the 44 sampling events described in **Table 1**, a total of 66 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected, typically due to no flow or because it was too shallow to collect a sample. The grab sample identifiers and reasons these samples were not collected are shown in **Table 2**.

**Table 1.** Sampling events for the reporting period.

<b>Work Identifier</b>	<b>Work Order</b>	<b>Project <sup>a</sup></b>	<b>Date Collected</b>
P123134	78798	PIN	04/05/2021
P121785	78182	EVPA	04/06/2021
P123760	79093	PIE	04/06/2021
P123770	79088	PIE	04/06/2021
P121793	78186	EVPA	04/07/2021
P123144	78803	PIN	04/12/2021
P123248	78850	PIE	04/13/2021
P122904	78679	PIE	04/13/2021
P124771	79507	PIN	04/19/2021
P124818	79531	PIE	04/20/2021
P124816	79530	PIE	04/20/2021
P124775	79508	PIN	04/26/2021
P124857	79540	PIE	04/27/2021
P124845	79548	PIE	04/27/2021
P124782	79510	PIN	05/03/2021
P125770	79998	EVPA	05/04/2021
P124893	79558	PIE	05/04/2021
P124881	79566	PIE	05/04/2021
P125778	80002	EVPA	05/05/2021
P124793	79516	PIN	05/10/2021
P124858	79541	PIE	05/11/2021
P125822	80024	PIE	05/11/2021
P124783	79511	PIN	05/17/2021
P124894	79559	PIE	05/18/2021
P124882	79567	PIE	05/18/2021
P124794	79517	PIN	05/24/2021
P124859	79542	PIE	05/25/2021
P125823	80025	PIE	05/25/2021
P124784	79512	PIN	06/01/2021
P126173	80207	EVPA	06/02/2021
P124883	79568	PIE	06/02/2021
P124895	79560	PIE	06/02/2021
P124795	79518	PIN	06/08/2021
P125824	80026	PIE	06/08/2021
P124860	79543	PIE	06/08/2021
P124785	79513	PIN	06/14/2021
P124884	79569	PIE	06/15/2021
P124896	79561	PIE	06/15/2021
P124796	79519	PIN	06/21/2021
P125825	80027	PIE	06/22/2021
P124861	79544	PIE	06/22/2021
P124786	79514	PIN	06/28/2021
P124897	79562	PIE	06/29/2021
P124885	79570	PIE	06/30/2021

a. EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.

**Table 2.** Grab samples not collected during the reporting period.

<b>Work Identifier</b>	<b>Project<sup>a</sup></b>	<b>Sample Identifier</b>	<b>Station</b>	<b>Date</b>	<b>Reason Sample Was Not Collected</b>
78798034	PIN	P123134-34	S12C	04/05/2021	Gates closed. No flow.
78798035	PIN	P123134-35	S12B	04/05/2021	Gates closed. No flow.
78182004	EVPA	P121785-4	LOX10	04/06/2021	Too shallow to sample.
78182003	EVPA	P121785-3	LOX5	04/06/2021	Too shallow to sample.
78182002	EVPA	P121785-2	LOX3	04/06/2021	Too shallow to sample.
79088005	PIE	P123770-5	G737	04/06/2021	Too shallow to sample.
79093027	PIE	P123760-27	BERMB3	04/06/2021	Too shallow to sample.
78803013	PIN	P123144-13	S355B	04/12/2021	Gates closed. No flow.
78803015	PIN	P123144-15	S355A	04/12/2021	Gates closed. No flow.
78803038	PIN	P123144-38	S12C	04/12/2021	Gates closed. No flow.
78803039	PIN	P123144-39	S12B	04/12/2021	Gates closed. No flow.
78679005	PIE	P122904-5	G737	04/13/2021	Too shallow to sample.
79507037	PIN	P124771-37	S12C	04/19/2021	Gates closed. No flow.
79507038	PIN	P124771-38	S12B	04/19/2021	Gates closed. No flow.
79531005	PIE	P124818-5	G737	04/20/2021	Too shallow to sample.
79530031	PIE	P124816-31	BERMB3	04/20/2021	Too shallow to sample.
79508041	PIN	P124775-41	S12C	04/26/2021	Gates closed. No flow.
79508042	PIN	P124775-42	S12B	04/26/2021	Gates closed. No flow.
79540005	PIE	P124857-5	G737	04/27/2021	Too shallow to sample.
79510034	PIN	P124782-34	S12C	05/03/2021	Gates closed. No flow.
79510035	PIN	P124782-35	S12B	05/03/2021	Gates closed. No flow.
79998009	EVPA	P125770-9	LOX4	05/04/2021	Too shallow to sample.
79998005	EVPA	P125770-5	LOX9	05/04/2021	Too shallow to sample.
79998004	EVPA	P125770-4	LOX10	05/04/2021	Too shallow to sample.
79998003	EVPA	P125770-3	LOX5	05/04/2021	Too shallow to sample.
79998002	EVPA	P125770-2	LOX3	05/04/2021	Too shallow to sample.
79558005	PIE	P124893-5	G737	05/04/2021	Too shallow to sample.
79566027	PIE	P124881-27	BERMB3	05/04/2021	Too shallow to sample.
79516038	PIN	P124793-38	S12C	05/10/2021	Gates closed. No flow.
79516039	PIN	P124793-39	S12B	05/10/2021	Gates closed. No flow.
79541005	PIE	P124858-5	G737	05/11/2021	Too shallow to sample.
79511034	PIN	P124783-34	S12C	05/17/2021	Gates closed. No flow.
79511035	PIN	P124783-35	S12B	05/17/2021	Gates closed. No flow.
79559005	PIE	P124894-5	G737	05/18/2021	Too shallow to sample.
79567027	PIE	P124882-27	BERMB3	05/18/2021	Too shallow to sample.
79517037	PIN	P124794-37	S12D	05/24/2021	Gates closed. No flow.
79517039	PIN	P124794-39	S12B	05/24/2021	Gates closed. No flow.
79542005	PIE	P124859-5	G737	05/25/2021	Too shallow to sample.
80205010	EVPA	P126169-10	LOX7	06/01/2021	Too shallow to sample.
80205009	EVPA	P126169-9	LOX8	06/01/2021	Too shallow to sample.
80205008	EVPA	P126169-8	LOX9	06/01/2021	Too shallow to sample.
80205007	EVPA	P126169-7	LOX10	06/01/2021	Too shallow to sample.
80205006	EVPA	P126169-6	LOX5	06/01/2021	Too shallow to sample.
80205005	EVPA	P126169-5	LOX3	06/01/2021	Too shallow to sample.
80205012	EVPA	P126169-12	LOX4	06/01/2021	Too shallow to sample.
79512033	PIN	P124784-33	S12D	06/01/2021	Gates closed. No flow.
79512035	PIN	P124784-35	S12B	06/01/2021	Gates closed. No flow.
79560005	PIE	P124895-5	G737	06/02/2021	Too shallow to sample.
80207008	EVPA	P126173-8	LOX13	06/02/2021	Too shallow to sample.
80207005	EVPA	P126173-5	LOX6	06/02/2021	Too shallow to sample.

Work Identifier	Project <sup>a</sup>	Sample Identifier	Station	Date	Reason Sample Was Not Collected
79568027	PIE	P124883-27	BERMB3	06/02/2021	Too shallow to sample.
79518013	PIN	P124795-13	S355B	06/07/2021	Gates closed. No flow.
79518015	PIN	P124795-15	S355A	06/07/2021	Gates closed. No flow.
79518037	PIN	P124795-37	S12D	06/07/2021	Gates closed. No flow.
79518039	PIN	P124795-39	S12B	06/07/2021	Gates closed. No flow.
79543005	PIE	P124860-5	G737	06/08/2021	Too shallow to sample.
79513033	PIN	P124785-33	S12D	06/14/2021	Gates closed. No flow.
79513035	PIN	P124785-35	S12B	06/14/2021	Gates closed. No flow.
79569027	PIE	P124884-27	BERMB3	06/15/2021	Too shallow to sample.
79519037	PIN	P124796-37	S12D	06/21/2021	Gates closed. No flow.
79519039	PIN	P124796-39	S12B	06/21/2021	Too shallow to sample.
79544005	PIE	P124861-5	G737	06/22/2021	Too shallow to sample.
79514033	PIN	P124786-33	S12D	06/28/2021	Gates closed. No flow.
79514035	PIN	P124786-35	S12B	06/28/2021	Gates closed. No flow.
79570027	PIE	P124885-27	BERMB3	06/29/2021	Too shallow to sample.
79562005	PIE	P124897-5	G737	06/29/2021	Too shallow to sample.

a. EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.

## FIELD QUALITY CONTROL

To assess the quality of the sample collection process as required by the *Field Sampling Manual*, field quality control samples are collected at various sampling locations during each sampling event. The results from these quality control samples are associated with all samples collected during the sampling trip (day) and if a specific field quality control sample fails to meet the requirements set forth in the Florida Department of Environmental Protection (FDEP) *Quality Assurance Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]), qualifiers will be added to the appropriate sample results. The types of field quality control samples that are collected may include replicate samples (RSs), and field quality control blanks, which include field generated equipment blanks (EBs), field-cleaned equipment blanks (FCEBs), and field blanks (FBs). The sampling events listed in **Table 1** may include field quality control samples collected at locations other than those listed in the *Introduction* to this report.

For the 44 sampling events described above, a total of 21 field quality control blanks and four RSs were collected. None of the field quality control blanks had a concentration equal to or greater than the TP method detection limit (MDL) of 0.002 milligrams per liter (mg/L). Project managers responsible for directing the sampling activities may also place qualifiers and/or remark codes on sample results based on project specific requirements, historical results for a given location, issues related to site conditions, and/or problems encountered by technicians when the samples were collected. Remark codes include a project manager remark (PMR), which is a SFWMD-derived and -applied remark code indicating a potential quality issue not otherwise defined by the qualifiers in the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

For grab samples collected at locations described in the *Introduction*, no PMR was assigned by project managers and ten J qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). These quality assurance process-related qualifiers are detailed in **Table 3**.

**Table 3.** Results with qualifiers and remark codes during the reporting period.

Work Identifier	Project <sup>a</sup>	Sample Identifier	Station	Collection Date	Qualifier or Remark Code/Reason
79093025	PIE	P123760-25	S328	04/06/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79548025	PIE	P124845-25	S328	04/27/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79566025	PIE	P124881-25	S328	05/04/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
80024024	PIE	P125822-24	S328	05/11/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79567025	PIE	P124882-25	S328	05/18/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
80025024	PIE	P125823-24	S328	05/25/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79568025	PIE	P124883-25	S328	06/02/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
80026024	PIE	P125824-24	S328	06/08/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79569025	PIE	P124884-25	S328	06/15/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.
79570025	PIE	P124885-25	S328	06/29/2021	J: Sample was taken from an isolated pool and was not representative of the surrounding marsh.

a. PIE – Everglades National Park Inflows East.

## FIELD PROCEDURE UPDATES

No major procedural updates related to TP sample collection were made during the period specified in this report.

## FIELD AUDITS

SFWMD conducted one field audit on the PIE project during the period specified in this report. One quality improvement and one process improvement were noted for PIE. The quality improvement involved sample processing and the process improvement was a documentation error. After a review of these

deficiencies, it was determined that the deficiencies did not negatively affect the quality of the TP sample data for this event.

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## LABORATORY ANALYSIS QUALITY ASSESSMENT

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### SAMPLE ANALYSES

SFWMD Analytical Services Chemistry Laboratory staff conducted a total of 288 TP analyses for the grab samples collected during the 44 sampling events listed in **Table 1**. Of those 288 TP results, 125 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 288 grab TP results can be found in the RDS described in the *Introduction* of this report along with the sample identifiers, sampling locations, collection dates, etc.

### LABORATORY QUALITY CONTROL

TP analyses are routinely conducted in the SFWMD Analytical Services Chemistry Laboratory in analytical batches of approximately 100 samples. To assess the quality of the sample results produced during the analyses of these batches, various types of laboratory control samples are included according to the requirements described in the *Chemistry Laboratory Quality Manual*. The results of these laboratory quality control samples are associated with all of the analyses conducted in a given batch and qualifiers are added to the data as required by the *Quality Assurance Rule* (Chapter 62-160, F.A.C.) based on the specifications found in the *Chemistry Laboratory Quality Manual*. The types of laboratory quality control samples typically run in a batch include samples with certified concentrations (laboratory control samples), matrix spikes, precision checks (duplicates or matrix spike duplicates), and method blanks. For the 125 TP results from samples collected from projects/locations listed in the *Introduction*, no qualifiers were added as a result of laboratory quality control failures.

### METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined by the laboratory on an annual basis using the procedure described in the Code of Federal Regulations (CFR), 40 CFR 136, Appendix B. The practical quantitation limit (PQL) is the minimum concentration of an analyte that can be measured with a high degree of confidence that the analyte is present at or above that concentration. However, there is not any universally accepted (or required) method for determination of the PQL. In the case of TP analyses, the SFWMD Analytical Services Chemistry Laboratory PQL (0.004 mg/L) is set to the concentration of the lowest standard used for calibration, which is a typical approach among analytical laboratories. Any TP results that are below the MDL (0.002 mg/L) are assigned a “U” qualifier indicating that there is high confidence that the analyte is not present. The reported TP values between the MDL (0.002 mg/L) and the PQL (0.004 mg/L) are assigned an “I” qualifier, indicating that the results are at concentrations that cannot be accurately quantified. Of the 125 TP results reported, no result was below the MDL and no sample had concentrations between the MDL and the PQL.

### ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

All measurements are subject to uncertainty and a measured value is only complete if it is accompanied by a statement of the associated uncertainty. The definition of uncertainty (of measurement) can be found in the *International Vocabulary of Basic and General Standard Terms in Metrology*: “A parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand” (JCGM 1993). The uncertainty has a probabilistic basis and reflects incomplete knowledge of the quantity. The SFWMD Analytical Services Chemistry Laboratory

provides uncertainty estimates using the nested hierarchical methodology by Ingersoll (2001) in combination with a mathematical model found in Eurachem/CITAC (2012). This quality control-based nested approach uses the statistical quality control data attributed to laboratory measurement activities and does not include uncertainty attributed to field sampling activities. The estimated uncertainty is calculated using the following equation:

$$U(x) = \sqrt{S_0^2 + (S_1 x)^2}$$

where:

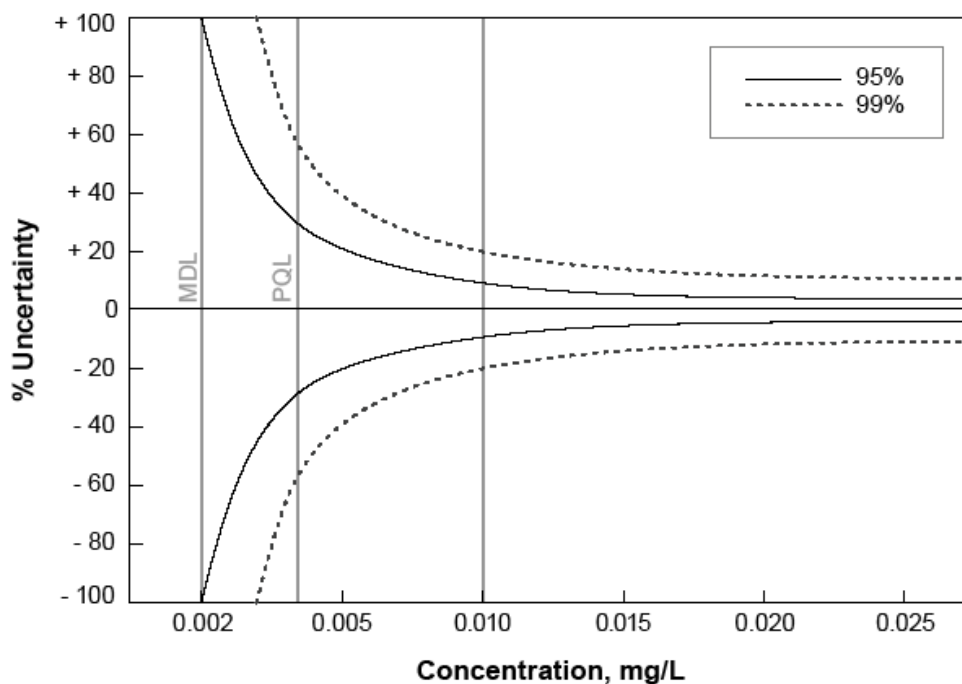
$U(x)$  is the combined standard uncertainty in the result  $x$  at the 95% confidence interval (CI).

$S_0$  is a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.

$S_1$  is a proportionality constant derived from nested hierarchical methodology by Ingersoll (2001).

During this reporting period, the uncertainty constants are  $S_0 = 0.002$  and  $S_1 = 0.068$ . Estimated uncertainties are calculated automatically by LIMS using the equation and constants shown above and are provided with all TP results. **Figure 1** presents estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

### Uncertainty of Measurement Close to the Detection Limit



**Figure 1.** Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

As can be seen from **Figure 1**, the percent measurement uncertainty (95% CI) is 100% at the MDL, nearly 30% at the PQL, and remains relatively constant at higher concentrations.



## PROFICIENCY TESTING AND PERFORMANCE EVALUATION

The SFWMD Analytical Services Chemistry Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During the second quarter of 2021, the laboratory received results from the Phenova WP0421 performance testing study. The reported result was identified as "acceptable" with a Z-score of 0.065.

## LABORATORY AUDITS

During this reporting period no quality system laboratory audits were conducted.

## PROCEDURE UPDATES

The TP analytical procedure (Standard Methods 4500 P-F, Automated Ascorbic Acid Reduction Method) did not change during this reporting period.

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## REFERENCES

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- Eurachem/CITAC. 2012. *Quantifying Uncertainty in Analytical Measurement, Third Edition*. Guide CG4, Eurachem/CITAC, Austria. ISBN 0-948926-15-5.
- Ingersoll, W.S. 2001. *Environmental Analytical Measurement Uncertainty Estimation. Nested Hierarchical Approach*. ADA396946, Defense Technical Information Center, Fort Belvoir, VA.
- FDEP. 2018. *Quality Assurance*. Chapter 62-160, Florida Administrative Code. Florida Department of Environmental Protection, Tallahassee, FL. Effective April 16, 2018.
- JCGM. 1993. *International Vocabulary of Basic and General Standard Terms in Metrology*. Joint Committee on Guides for Metrology, Geneva, Switzerland. ISBN 92-67-10175-1.
- SFWMD. *Field Quality Manual*. SFWMD-FIELD-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL. .
- SFWMD. *Field Sampling Manual*. SFWMD-FIELD-FSM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.

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## GLOSSARY

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**Accuracy:** The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.

**Confidence Interval (CI):** A range of values so defined that there is a specified probability that the value of a parameter lies within it.

**Equipment Blank (EB):** Field quality control sample prepared using sampling equipment that has been brought to the site or processing area precleaned and is collected before the equipment has been used. The results of these blanks are used to monitor the on-site sampling environment, sampling equipment decontamination, sample container cleaning, suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

**Field Blank (FB):** FBs are collected by pouring analyte-free water directly into the sample container, preserved, and kept open for the same approximate time and interval as required for collection and/or processing of the routine sample. The results of this blank are used to monitor the on-site sampling environment, sample container cleaning, the suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

**Field Cleaned Equipment Blank (FCEB):** Field quality control sample prepared using sampling equipment that has been cleaned in the field or at the processing area. The results of this blank are used to monitor the on-site sampling environment, sampling equipment field decontamination, sample container cleaning, suitability of sample preservatives and analyte-free water, sample transport and storage conditions, and laboratory process.

**Measurand:** Particular quantity subject to measurement.

**Method Detection Limit (MDL):** The smallest concentration of an analyte of interest that can be measured and reported with 99% confidence that the concentration is greater than zero. The MDLs are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in the Code of Federal Regulations (CFR) Section 40 CFR, Part 136, Appendix B, as established by the United States Environmental Protection Agency.

**Practical Quantitation Limit (PQL):** The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. The PQL is verified for each matrix, technology, and analyte. The validity of the PQL is verified by analysis of a quality control sample containing the analyte of concern.

**Precision:** The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical systems over a given time and field sampling period.

**Replicate Sample (RS):** An RS is collected by repeating (simultaneously or in rapid succession) the entire sample acquisition technique that was used to obtain the routine sample. A single RS set (e.g., one sample and two RSs) is collected per quarter, per project, at the same station, for the longest parameter list. RS data are compared to routine sample data to evaluate sampling precision.

**Uncertainty:** The range of values within which the true value is estimated to lie. It is a best estimate of possible inaccuracy due to both random and systematic error.

**Z-Score:** A measure of the deviation of the result ( $X_i$ ) from the assigned value ( $X$ ) for that determinant (calculated as  $z = (X_i - X)/\sigma$ , where  $\sigma$  is a standard deviation) (Eurachem/CITAC 2012).