

# **Quality Assessment Report for Water Quality Monitoring**

**April – June 2022**



**Prepared for the  
Technical Oversight Committee  
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## INTRODUCTION

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This report is an assessment of the South Florida Water Management District (SFWMD) field sampling and laboratory analysis for total phosphorus (TP), primarily for the following projects and their associated stations from April 1, 2022, through June 30, 2022. The analysis 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 September 7, 2022. The projects and associated stations at which data are collected are as follows:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S333N, 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 (WQM) *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, 2022. 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.

To prepare this report, a Microsoft Excel workbook named “qa\_report\_apr\_jun\_2022\_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/toc>) 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 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 WQM 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 sample collection dates.

During the 44 sampling events described in **Table 1**, a total of 63 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected, typically because of no flow, water being too shallow, or site being not representative. The grab sample identifiers and reasons these samples were rejected or not collected are shown in **Table 2**.

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

<b>Work Order Identifier</b>	<b>Work Order</b>	<b>Project <sup>a</sup></b>	<b>Date Collected</b>
P131338	82519	PIN	04/04/2022
P130462	82085	EVPA	04/05/2022
P133724	83567	PIE	04/05/2022
P131437	82558	PIE	04/05/2022
P130470	82089	EVPA	04/06/2022
P131348	82524	PIN	04/11/2022
P133167	83284	PIE	04/12/2022
P133732	83568	PIE	04/12/2022
P133458	83445	PIN	04/19/2022
P133715	83563	PIE	04/19/2022
P133717	83564	PIE	04/19/2022
P133472	83457	PIN	04/25/2022
P133814	83571	PIE	04/26/2022
P133745	83570	PIE	04/26/2022
P133467	83448	PIN	05/02/2022
P134431	83866	EVPA	05/05/2022
P133802	83573	PIE	05/05/2022
P133790	83579	PIE	05/06/2022
P133478	83452	PIN	05/09/2022
P133982	83646	PIE	05/10/2022
P134002	83656	PIE	05/10/2022
P133468	83449	PIN	05/16/2022
P133791	83580	PIE	05/17/2022
P133803	83574	PIE	05/17/2022
P133479	83453	PIN	05/23/2022
P134003	83657	PIE	05/24/2022
P133983	83647	PIE	05/24/2022
P133469	83450	PIN	05/31/2022
P133804	83575	PIE	05/31/2022
P133792	83581	PIE	05/31/2022
P133480	83454	PIN	06/06/2022
P133226	83324	EVPA	06/07/2022
P134004	83658	PIE	06/07/2022
P133984	83648	PIE	06/08/2022
P133232	83327	EVPA	06/08/2022
P133470	83451	PIN	06/13/2022
P133805	83576	PIE	06/14/2022
P133793	83582	PIE	06/15/2022
P133481	83455	PIN	06/20/2022
P134005	83659	PIE	06/21/2022
P133985	83649	PIE	06/21/2022
P133465	83446	PIN	06/27/2022
P133806	83577	PIE	06/28/2022
P133794	83583	PIE	06/28/2022

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

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

<b>Work Order Identifier</b>	<b>Project <sup>a</sup></b>	<b>Sample Identifier</b>	<b>Station</b>	<b>Date</b>	<b>Reason Sample Was Rejected or Not Collected</b>
82519033	PIN	P131338-33	S12D	04/04/2022	Gates closed. No flow.
82519034	PIN	P131338-34	S12C	04/04/2022	Gates closed. No flow.
82519035	PIN	P131338-35	S12B	04/04/2022	Gates closed. No flow.
82558004	PIE	P131437-4	G737	04/05/2022	No recorded flow. No sample.
82085002	EVPA	P130462-2	LOX3	04/05/2022	Too shallow to sample.
83567024	PIE	P133724-24	S328	04/05/2022	Site being not representative.
83567025	PIE	P133724-25	BERMB3	04/05/2022	Too shallow to sample.
82524013	PIN	P131348-13	S355B	04/11/2022	Gates closed. No flow.
82524015	PIN	P131348-15	S355A	04/11/2022	Gates closed. No flow.
82524038	PIN	P131348-38	S12C	04/11/2022	Gates closed. No flow.
82524039	PIN	P131348-39	S12B	04/11/2022	Gates closed. No flow.
83284004	PIE	P133167-4	G737	04/12/2022	No recorded flow. No sample.
83445037	PIN	P133458-37	S12C	04/18/2022	Gates closed. No flow.
83445038	PIN	P133458-38	S12B	04/18/2022	Gates closed. No flow.
83445039	PIN	P133458-39	S12A	04/18/2022	Gates closed. No flow.
83564004	PIE	P133717-4	G737	04/19/2022	No recorded flow. No sample.
83563028	PIE	P133715-28	BERMB3	04/19/2022	Too shallow to sample.
83457041	PIN	P133472-41	S12C	04/25/2022	Gates closed. No flow.
83457042	PIN	P133472-42	S12B	04/25/2022	Gates closed. No flow.
83570004	PIE	P133745-4	G737	04/26/2022	No recorded flow. No sample.
83448034	PIN	P133467-34	S12C	05/02/2022	Gates closed. No flow.
83448035	PIN	P133467-35	S12B	05/02/2022	Gates closed. No flow.
83448036	PIN	P133467-36	S12A	05/02/2022	Gates closed. No flow.
83863009	EVPA	P134425-9	LOX4	05/04/2022	Too shallow to sample.
83863007	EVPA	P134425-7	LOX7	05/04/2022	Too shallow to sample.
83863006	EVPA	P134425-6	LOX8	05/04/2022	Too shallow to sample.
83863005	EVPA	P134425-5	LOX9	05/04/2022	Too shallow to sample.
83863004	EVPA	P134425-4	LOX10	05/04/2022	Too shallow to sample.
83863003	EVPA	P134425-3	LOX5	05/04/2022	Too shallow to sample.
83863002	EVPA	P134425-2	LOX3	05/04/2022	Too shallow to sample.
83573004	PIE	P133802-4	G737	05/04/2022	No recorded flow. No sample.
83579024	PIE	P133790-24	S328	05/05/2022	Gates closed. No flow.
83579025	PIE	P133790-25	BERMB3	05/05/2022	Too shallow to sample.
83452013	PIN	P133478-13	S355B	05/09/2022	Gates closed. No flow.
83452015	PIN	P133478-15	S355A	05/09/2022	Gates closed. No flow.
83452039	PIN	P133478-39	S12B	05/09/2022	Gates closed. No flow.
83656004	PIE	P134002-4	G737	05/10/2022	No recorded flow. No sample.
83449035	PIN	P133468-35	S12B	05/16/2022	Gates closed. No flow.
83574004	PIE	P133803-4	G737	05/17/2022	Too shallow to sample.
83580024	PIE	P133791-24	S328	05/17/2022	Gates closed. No flow.
83580025	PIE	P133791-25	BERMB3	05/17/2022	Too shallow to sample.
83453039	PIN	P133479-39	S12B	05/23/2022	Gates closed. No flow.
83657004	PIE	P134003-4	G737	05/24/2022	No recorded flow. No sample.
83575004	PIE	P133804-4	G737	05/31/2022	Too shallow to sample.
83450033	PIN	P133469-33	S12D	05/31/2022	Gates closed. No flow.
83450034	PIN	P133469-34	S12C	05/31/2022	Gates closed. No flow.
83450035	PIN	P133469-35	S12B	05/31/2022	Gates closed. No flow.
83450036	PIN	P133469-36	S12A	05/31/2022	Gates closed. No flow.

Work Order Identifier	Project <sup>a</sup>	Sample Identifier	Station	Date	Reason Sample Was Rejected or Not Collected
83581025	PIE	P133792-25	BERMB3	05/31/2022	Too shallow to sample.
83454013	PIN	P133480-13	S355B	06/06/2022	Gates closed. No flow.
83454015	PIN	P133480-15	S355A	06/06/2022	Gates closed. No flow.
83454039	PIN	P133480-39	S12B	06/06/2022	Gates closed. No flow.
83658004	PIE	P134004-4	G737	06/07/2022	No recorded flow. No sample.
83451034	PIN	P133470-34	S12C	06/13/2022	Gates closed. No flow.
83451035	PIN	P133470-35	S12B	06/13/2022	Gates closed. No flow.
83451033	PIN	P133470-33	S12D	06/13/2022	Gates closed. No flow.
83576004	PIE	P133805-4	G737	06/14/2022	No recorded flow. No sample.
83455037	PIN	P133481-37	S12D	06/20/2022	Gates closed. No flow.
83455038	PIN	P133481-38	S12C	06/20/2022	Gates closed. No flow.
83455039	PIN	P133481-39	S12B	06/20/2022	Gates closed. No flow.
83659004	PIE	P134005-4	G737	06/21/2022	No recorded flow. No sample.
83446035	PIN	P133465-35	S12B	06/27/2022	Gates closed. No flow.
83577004	PIE	P133806-4	G737	06/27/2022	No recorded flow. No sample.

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

## FIELD QUALITY CONTROL

Field quality control samples are collected at sampling locations during each sampling event to assess the quality of the sample collection process required by the Field Sampling Manual. The results from these quality control samples are associated with all samples collected during the sampling trip (day). Suppose a specific field quality control sample fails to meet the requirements outlined in the Florida Department of Environmental Protection (FDEP) Quality Assurance Rule (Chapter 62-160, Florida Administrative Code [F.A.C.]). In that case, 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 have 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, 30 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), 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 one “J” qualifier was assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). This quality assurance process-related qualifier is 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
83327012	EVPA	P133232-12	LOX12	06/08/2022	J: Improper laboratory or field protocol. Technician did not rinse bucket 3 times with site water from intermediate containers before processing station.

a. EVPA – Everglades Protection Area.

## FIELD AUDITS

SFWMD conducted an audit on the EVPA project in the second quarter. Two Quality Improvements (QI) were noted. The first QI involved sample processing and the second QI involved calibration of an instrument. The QI for sample processing resulted in a ‘J’ qualification of that sample for improper field or lab protocol.

## FIELD PROCEDURE UPDATES

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

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## LABORATORY ANALYSIS QUALITY ASSESSMENT

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### SAMPLE ANALYSES

SFWMD Analytical Services Chemistry Laboratory staff conducted 286 TP analyses for the grab samples collected during the 44 sampling events listed in **Table 1**. Of those 286 TP results, 138 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 286 grab TP results can be found in the RDS described in the *Introduction* to 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 the analyses conducted in each 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 138 TP results from samples collected from projects/locations listed in the *Introduction*, no qualifiers were added because 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 138 TP results reported, no results were below the MDL and no samples 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 a statement of the associated uncertainty accompanies it. 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:

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

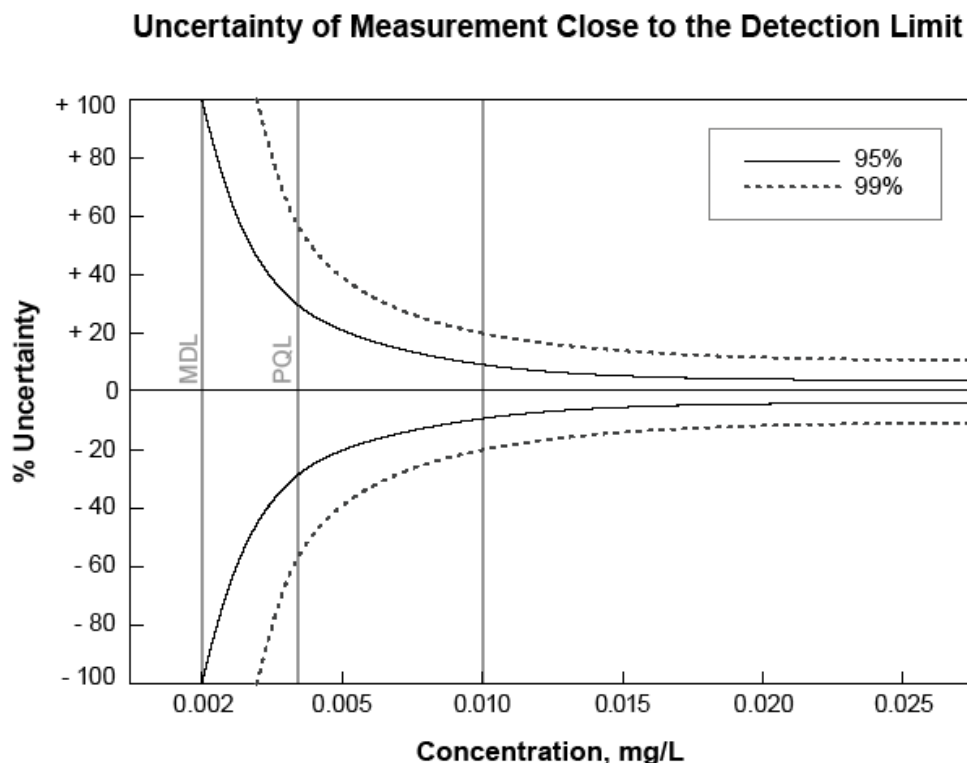
where:

$U(x)$  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.



**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 2022, the laboratory participated in an Environmental Canada surface water and sediment performance evaluation study but have not received the results of this study.

## LABORATORY AUDITS

During this reporting period, the laboratory was inspected on-site to verify compliance with F.A.C. Rule 64E-1, Certification of Environmental Testing Laboratories by referencing the 2016 Environmental Laboratory standards adopted at The NELAC Institute. The ANSI National Accreditation Board (ANAB) contractor conducted a biennial external laboratory audit as required by the Florida Department of Health. During the audit, there were six deficiencies identified, none directly related to the laboratory's TP analytical procedure. The findings have been entered into the laboratory's corrective action log and are in process of being addressed.

## PROCEDURE UPDATES

The TP sample preparation (Standard Method 4500 P-B 5, Persulfate Digestion Method) and analytical procedures (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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- 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. *Standard Operating Procedure for the Determination of Total and Dissolved Phosphorus*. SFWMD-LAB-SOP-3100, 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 pre-cleaned 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).