Quality Assessment Report for Water Quality Monitoring

April – June 2019

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INTRODUCTION

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, 2019, through June 30, 2019. The analysis contained in this document reflects the status of the data at the time the data were downloaded and does not account for changes made to the data after August 27, 2019.

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

The SFWMD's *Field Sampling Quality Manual* (SFWMD 2017) provides the requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2019) 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_2019_data.xlsx" was created and contains all TP results and any no sample collected (NOB) records obtained from DBHYDRO, the SFWMD corporate environmental database, for all sampling events that include grab samples collected for the projects/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 that were completed during the period specified in this report.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

A total of 45 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, the project codes, and the dates the samples were collected.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project [a]	Date Collected
P105198	70759	PIN	04/01/2019
P105090	70729	EVPA	04/02/2019
P104827	70634	PIE	04/02/2019
P104811	70620	PIE	04/02/2019
P101540	69212	EVPA	04/03/2019
P105219	70769	PIN	04/08/2019
P103535	70070	PIE	04/09/2019
P103392	70010	PIE	04/09/2019
P105223	70780	PIN	04/15/2019
P104813	70622	PIE	04/16/2019
P104828	70635	PIE	04/16/2019
P105258	70782	PIN	04/22/2019
P104847	70642	PIE	04/23/2019
P104814	70623	PIE	04/23/2019
P105282	70794	PIN	04/29/2019
P104835	70636	PIE	04/30/2019
P104815	70624	PIE	04/30/2019
P105259	70783	PIN	05/06/2019
P105091	70730	EVPA	05/07/2019
P104848	70643	PIE	05/07/2019
P104816	70625	PIE	05/07/2019
P106040	71146	EVPA	05/08/2019
P105283	70795	PIN	05/13/2019
P104836	70637	PIE	05/14/2019
P104817	70626	PIE	05/14/2019
P105260	70784	PIN	05/20/2019
P104818	70627	PIE	05/21/2019
P104849	70644	PIE	05/21/2019
P104837	70638	PIE	05/28/2019
P104819	70628	PIE	05/28/2019
P105284	70796	PIN	05/28/2019
P105261	70785	PIN	06/03/2019
P104850	70645	PIE	06/04/2019
P104820	70629	PIE	06/04/2019
P103994	70300	EVPA	06/10/2019
P105285	70797	PIN	06/10/2019
P104001	70304	EVPA	06/11/2019
P104821	70630	PIE	06/11/2019
P104838	70639	PIE	06/11/2019
P105262	70786	PIN	06/17/2019
P104851	70646	PIE	06/18/2019
P104822	70631	PIE	06/18/2019
P105286	70798	PIN	06/24/2019
P104839	70640	PIE	06/25/2019
P104823	70632	PIE	06/25/2019

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

During the 45 sampling events described above, a total of 72 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected, typically due to low water levels or no flow conditions. The list of grab sample identifiers and reasons these samples were not collected is shown in **Table 2**.

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

Work Identifier	Project [a]	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P105198	PIN	P105198-29	S12D	04/01/2019	Gates closed. No flow.
P105198	PIN	P105198-30	S12C	04/01/2019	Gates closed. No flow.
P105198	PIN	P105198-31	S12B	04/01/2019	Gates closed. No flow.
P105090	EVPA	P105090-2	LOX3	04/02/2019	Too shallow to sample.
P104827	PIE	P104827-5	G737	04/02/2019	No flow.
P105090	EVPA	P105090-9	LOX4	04/02/2019	Too shallow to sample.
P105219	PIN	P105219-28	S12D	04/08/2019	Gates closed. No flow.
P105219	PIN	P105219-29	S12C	04/08/2019	Gates closed. No flow.
P105219	PIN	P105219-30	S12B	04/08/2019	Gates closed. No flow.
P103535	PIE	P103535-4	BERMB3	04/09/2019	No flow.
P103535	PIE	P103535-6	G737	04/09/2019	No flow.
P105223	PIN	P105223-16	S355B	04/15/2019	Gates closed. No flow.
P105223	PIN	P105223-18	S355A	04/15/2019	Gates closed. No flow.
P105223	PIN	P105223-32	S12D	04/15/2019	Gates closed. No flow.
P105223	PIN	P105223-33	S12C	04/15/2019	Gates closed. No flow.
P105223	PIN	P105223-34	S12B	04/15/2019	Gates closed. No flow.
P104828	PIE	P104828-5	G737	04/16/2019	No flow.
P105258	PIN	P105258-25	S12D	04/22/2019	Gates closed. No flow.
P105258	PIN	P105258-26	S12C	04/22/2019	Gates closed. No flow.
P105258	PIN	P105258-27	S12B	04/22/2019	Gates closed. No flow.
P104847	PIE	P104847-4	BERMB3	04/23/2019	No flow.
P104847	PIE	P104847-6	G737	04/23/2019	No flow.
P105282	PIN	P105282-29	S12D	04/29/2019	Gates closed. No flow.
P105282	PIN	P105282-30	S12C	04/29/2019	Gates closed. No flow.
P105282	PIN	P105282-31	S12B	04/29/2019	Gates closed. No flow.
P104835	PIE	P104835-5	G737	04/30/2019	No flow.
P105259	PIN	P105259-25	S12D	05/06/2019	Gates closed. No flow.
P105259	PIN	P105259-26	S12C	05/06/2019	Gates closed. No flow.
P105259	PIN	P105259-27	S12B	05/06/2019	Gates closed. No flow.
P104848	PIE	P104848-4	BERMB3	05/07/2019	No flow.
P105091	EVPA	P105091-5	LOX9	05/07/2019	Too shallow to sample.
P105091	EVPA	P105091-4	LOX10	05/07/2019	Too shallow to sample.
P104848	PIE	P104848-6	G737	05/07/2019	No flow.
P105091	EVPA	P105091-3	LOX5	05/07/2019	Too shallow to sample.
P105091	EVPA	P105091-2	LOX3	05/07/2019	Too shallow to sample.
P105283	PIN	P105283-13	S355B	05/13/2019	Gates closed. No flow.
P105283	PIN	P105283-15	S355A	05/13/2019	Gates closed. No flow.
P105283	PIN	P105283-29	S12D	05/13/2019	Gates closed. No flow.
P105283	PIN	P105283-30	S12C	05/13/2019	Gates closed. No flow.
P105283	PIN	P105283-31	S12B	05/13/2019	Gates closed. No flow.

Table 2. Continued.

Work Identifier	Project [a]	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P104836	PIE	P104836-5	G737	05/14/2019	Too shallow to sample.
P105260	PIN	P105260-25	S12D	05/20/2019	Gates closed. No flow.
P105260	PIN	P105260-26	S12C	05/20/2019	Gates closed. No flow.
P105260	PIN	P105260-27	S12B	05/20/2019	Gates closed. No flow.
P104849	PIE	P104849-4	BERMB3	05/21/2019	No flow.
P104849	PIE	P104849-5	G737	05/21/2019	No flow.
P104837	PIE	P104837-5	G737	05/28/2019	No flow.
P105284	PIN	P105284-29	S12D	05/28/2019	Gates closed. No flow.
P105284	PIN	P105284-30	S12C	05/28/2019	Gates closed. No flow.
P105284	PIN	P105284-31	S12B	05/28/2019	Gates closed. No flow.
P105261	PIN	P105261-25	S12D	06/03/2019	Gates closed. No flow.
P105261	PIN	P105261-26	S12C	06/03/2019	Gates closed. No flow.
P105261	PIN	P105261-27	S12B	06/03/2019	Gates closed. No flow.
P104850	PIE	P104850-4	BERMB3	06/04/2019	No flow.
P104850	PIE	P104850-6	G737	06/04/2019	No flow.
P103994	EVPA	P103994-8	LOX9	06/10/2019	No representative contiguous water body due to dry condition
P103994	EVPA	P103994-7	LOX10	06/10/2019	No representative contiguous water body due to dry condition
P103994	EVPA	P103994-6	LOX5	06/10/2019	No representative contiguous water body due to dry condition
P103994	EVPA	P103994-5	LOX3	06/10/2019	No representative contiguous water body due to dry condition
P103994	EVPA	P103994-12	LOX4	06/10/2019	Too shallow to sample.
P105285	PIN	P105285-13	S355B	06/10/2019	No flow.
P105285	PIN	P105285-15	S355A	06/10/2019	No flow.
P105285	PIN	P105285-29	S12D	06/10/2019	Gates closed. No flow.
P105285	PIN	P105285-30	S12C	06/10/2019	Gates closed. No flow.
P105285	PIN	P105285-31	S12B	06/10/2019	Gates closed. No flow.
P105262	PIN	P105262-25	S12D	06/17/2019	Gates closed. No flow.
P105262	PIN	P105262-26	S12C	06/17/2019	Gates closed. No flow.
P105262	PIN	P105262-27	S12B	06/17/2019	Gates closed. No flow.
P104851	PIE	P104851-4	BERMB3	06/18/2019	No flow.
P105286	PIN	P105286-29	S12D	06/24/2019	Gates closed. No flow.
P105286	PIN	P105286-30	S12C	06/24/2019	Gates closed. No flow.
P105286	PIN	P105286-31	S12B	06/24/2019	Gates closed. No flow.

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 and as required by the *Field Sampling Quality Manual* (SFWMD 2017), 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 event (or a related sampling event) 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.]; FDEP 2018),

qualifiers will be added to all of the associated sample results. The types of field quality control samples that are collected may include replicate samples (RSs), and field blank controls (FBCs) 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 45 sampling events described above, a total of 24 FBCs and six RSs were collected. None of the FBCs had a concentration at 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 or remark codes on sample results based on project specific requirements, historical results for a given location, issues related to site conditions, or problems encountered by samplers 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 PMRs were assigned by project managers and nine J qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). These qualifiers are detailed in **Table 3**.

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

Work Identifier	Project [a]	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
P104811	PIE	P104811-31	S328	04/02/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P103392	PIE	P103392-34	S328	04/09/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104813	PIE	P104813-31	S328	04/16/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104814	PIE	P104814-31	S328	04/23/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104815	PIE	P104815-31	S328	04/30/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104816	PIE	P104816-31	S328	05/07/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104817	PIE	P104817-31	S328	05/14/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104818	PIE	P104818-31	S328	05/21/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P104819	PIE	P104819-31	S328	05/28/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the second quarter of 2019.

FIELD PROCEDURE UPDATES

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

LABORATORY ANALYSIS QUALITY ASSESSMENT

SAMPLE ANALYSES

The SFWMD Analytical Services Chemistry Laboratory conducted a total of 309 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 309 TP results, 118 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 309 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* (SFWMD 2019). 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* (SFWMD 2019). 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 118 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 isn't a 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 below the MDL (0.002 mg/L) are assigned a "U" qualifier, indicating 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 the results are at concentrations that cannot be accurately quantified. Of the 118 TP results reported, no result was below the MDL and one sample had a concentration between the MDL and 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:

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

where:
U(x) is the combined standard uncertainty in the result x at the 95% confidence interval (CI).
$\mathbf{S_0}$ is a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.
$\mathbf{S_1}$ is a proportionality constant derived from nested hierarchical methodology by Ingersoll (2001).

During this reporting period, the uncertainty constants are $\mathbf{S_0}$ = 0.002 and $\mathbf{S_1}$ = 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** is presented to show estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process. As can be seen from the graph, the percent measurement uncertainty (95% CI) is 100% at the MDL, nearly 30% at the PQL, and remains relatively constant at higher concentrations.

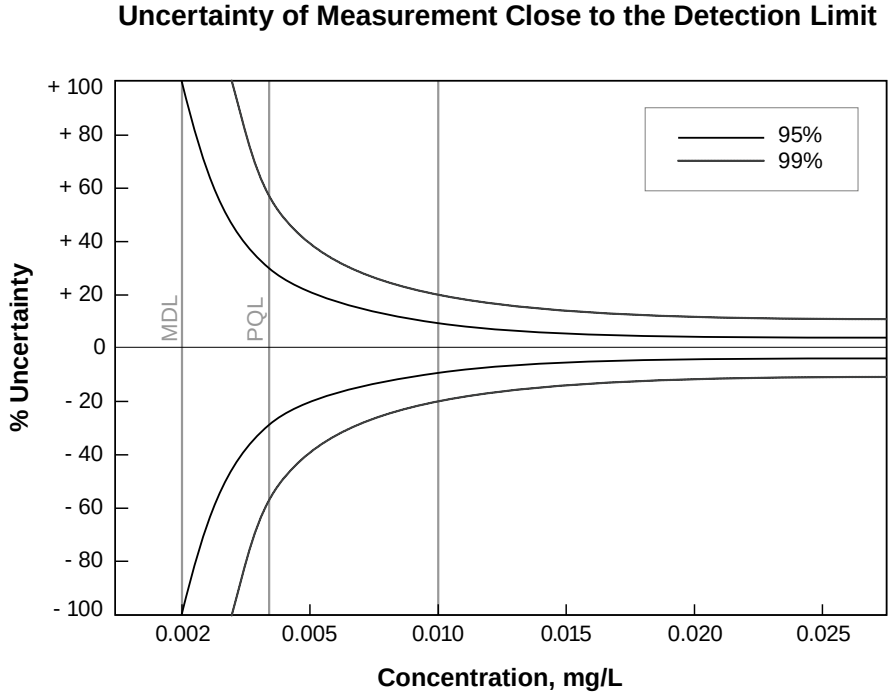

Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

PROFICIENCY TESTING AND EVALUATION

The SFWMD Analytical Services Chemistry Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During this reporting period, results from one performance evaluation study (Environment Canada #113; April 2019) and one proficiency testing sample (ERA Waters Study #290; ERA April 2019) were received for TP analysis. TP results from the Environment Canada performance evaluation were rated as "Ideal" with no Z-score greater than 1σ. TP results from the ERA performance test were rated as "acceptable" with a Z-score of -0.0515σ. The laboratory received a "Certificate of Excellence" for achieving 100% acceptable data in performance testing study, which included 981 participating laboratories. This achievement is a demonstration of the superior quality of the SFWMD Analytical Services Chemistry Laboratory in evaluation of the analytes including TP during this reporting period.

LABORATORY AUDITS

There was no laboratory audit conducted during this reporting period.

PROCEDURE UPDATES

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

REFERENCES

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.

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.

FDEP. 2018. *Quality Assurance*. Chapter 62-160, Florida Administrative Code. Florida Department of Environmental Protection, Tallahassee, FL. Effective April 16, 2018.

SFWMD. 2017. *Field Sampling Quality Manual*. SFWMD-FIELD-QM-001-09.0, South Florida Water Management District, West Palm Beach, FL. Effective June 29, 2017.

SFWMD. 2019. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-2019-001, South Florida Water Management District, West Palm Beach, FL. Effective January 5, 2019.

GLOSSARY

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 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.

Split Sample (SS): A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory 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 (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi - X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2012).