

Quality Assessment Report for Water Quality Monitoring

January – March 2021



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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 January 1, 2021, through March 31, 2021. 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 May 5, 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 (WQM) *Field Quality Manual* (SFWMD 2019a) and *Field Sampling Manual* (SFWMD 2019b) provided the quality system requirements and the field sampling procedures followed in field sample collection from January 1 to March 31, 2021, respectively. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD 2021) 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_jan_mar_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/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

All samples were collected by WQM staff. 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, project codes, and dates the samples were collected.

During the 45 sampling events described in **Table 1**, a total of 22 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 conditions. The grab sample identifiers and reasons these samples were not collected are shown in **Table 2**.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project ^a	Date Collected
P121145	77936	PIN	01/04/2021
P121783	78180	EVPA	01/05/2021
P122535	78509	PIE	01/05/2021
P121045	77892	PIE	01/05/2021
P121791	78184	EVPA	01/06/2021
P123110	78786	PIN	01/11/2021
P123207	78829	PIE	01/12/2021
P122962	78708	PIE	01/12/2021
P122860	78654	PIE	01/19/2021
P123112	78787	PIN	01/19/2021
P122898	78673	PIE	01/20/2021
P122964	78709	PIN	01/25/2021
P122529	78506	PIE	01/26/2021
P121070	77908	PIE	01/26/2021
P123124	78793	PIN	02/01/2021
P121784	78181	EVPA	02/02/2021
P122899	78674	PIE	02/02/2021
P123243	78845	PIE	02/02/2021
P121792	78185	EVPA	02/03/2021
P123130	78794	PIN	02/08/2021
P123766	79084	PIE	02/09/2021
P123756	79089	PIE	02/09/2021
P123140	78799	PIN	02/15/2021
P123244	78846	PIE	02/16/2021
P122900	78675	PIE	02/16/2021
P123131	78795	PIN	02/22/2021
P123757	79090	PIE	02/23/2021
P123767	79085	PIE	02/23/2021
P123141	78800	PIN	03/01/2021
P122235	78384	EVPA	03/02/2021
P122901	78676	PIE	03/02/2021
P123245	78847	PIE	03/02/2021
P122239	78386	EVPA	03/03/2021
P123132	78796	PIN	03/08/2021
P123758	79091	PIE	03/09/2021
P123768	79086	PIE	03/09/2021
P123142	78801	PIN	03/15/2021
P122902	78677	PIE	03/16/2021
P123246	78848	PIE	03/16/2021
P123133	78797	PIN	03/22/2021
P123769	79087	PIE	03/23/2021
P123759	79092	PIE	03/23/2021
P123143	78802	PIN	03/29/2021
P122903	78678	PIE	03/30/2021
P123247	78849	PIE	03/30/2021

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.

Work Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Not Collected
78787013	PIN	P123112-13	S355B	01/19/2021	Gates closed. No flow.
78787015	PIN	P123112-15	S355A	01/19/2021	Gates closed. No flow.
78793016	PIN	P123124-16	S355B	02/01/2021	Gates closed. No flow.
78793018	PIN	P123124-18	S355A	02/01/2021	Gates closed. No flow.
78793042	PIN	P123124-42	S12B	02/01/2021	Gates closed. No flow.
78794035	PIN	P123130-35	S12B	02/08/2021	Gates closed. No flow.
78799039	PIN	P123140-39	S12B	02/15/2021	Gates closed. No flow.
78795035	PIN	P123131-35	S12B	02/22/2021	Gates closed. No flow.
78800013	PIN	P123141-13	S355B	03/01/2021	Gates closed. No flow.
78800015	PIN	P123141-15	S355A	03/01/2021	Gates closed. No flow.
78800038	PIN	P123141-38	S12C	03/01/2021	Gates closed. No flow.
78800039	PIN	P123141-39	S12B	03/01/2021	Gates closed. No flow.
78796034	PIN	P123132-34	S12C	03/08/2021	Gates closed. No flow.
78796035	PIN	P123132-35	S12B	03/08/2021	Gates closed. No flow.
78801038	PIN	P123142-38	S12C	03/15/2021	Gates closed. No flow.
78801039	PIN	P123142-39	S12B	03/15/2021	Gates closed. No flow.
78797034	PIN	P123133-34	S12C	03/22/2021	Gates closed. No flow.
78797035	PIN	P123133-35	S12B	03/22/2021	Gates closed. No flow.
79087005	PIE	P123769-5	G737	03/23/2021	Too shallow to sample.
78802038	PIN	P123143-38	S12C	03/29/2021	Gates closed. No flow.
78802039	PIN	P123143-39	S12B	03/29/2021	Gates closed. No flow.
78678005	PIE	P122903-5	G737	03/30/2021	Too shallow to sample.

a. 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 *WQM Field Quality Manual* (SFWMD 2019a) and *Field Sampling Manual* (SFWMD 2019b), 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 all of the associated 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 45 sampling events described above, a total of 25 field quality control blanks and four RSs were collected. Only one 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 eight G 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 ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code/Reason
78709003	PIN	P122964-3	S356-334	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709004	PIN	P122964-4	S356-334	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709006	PIN	P122964-6	S356-334	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709026	PIN	P122964-26	S333	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709036	PIN	P122964-36	S12D	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709037	PIN	P122964-37	S12C	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709038	PIN	P122964-38	S12B	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
78709040	PIN	P122964-40	S12A	01/25/2021	G: Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.

a. PIN – Everglades National Park Inflows North.

FIELD AUDITS

SFWMD conducted one field audit on the EVPA project during the period specified in this report. Two quality improvements (QIs) were noted. One involved the sample processing and the other sample decontamination of the syringe used to process dissolved analytes. One process improvement (PI) was noted that involved technician training documentation. 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.

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

SFWMD Analytical Services Chemistry Laboratory staff conducted a total of 370 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 370 TP results, 168 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 370 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* (SFWMD 2021). 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 2021). 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 168 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 168 TP results reported, no result was below the MDL and 16 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 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.

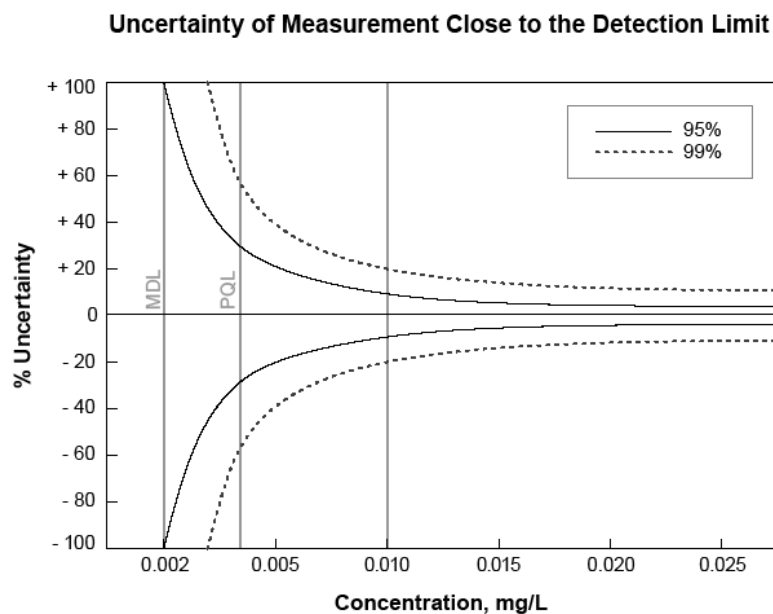


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 first quarter of 2021, the laboratory received results from the QUASIMEME saline/brackish waters performance evaluation study. All seven reported results were identified as "acceptable" with no Z-score exceeding ± 0.8 .

LABORATORY AUDITS

During this reporting period one quality system internal laboratory audit was conducted. One deficiency was found for implementing the laboratory's TP analytical procedure. The recording of the calibration standard expiration dates was entered into LIMS as 15 days from creation instead of 14 days as specified in the laboratory's standard operating procedure. This deficiency did not negatively affect the quality of the TP sample data. It has been addressed appropriately by the laboratory and documented in the laboratory's corrective action log.

PROCEDURE UPDATES

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

REFERENCES

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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 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 σ is a standard deviation) (Eurachem/CITAC 2012).