

Quality Assessment Report for Water Quality Monitoring

October – December 2018



Submitted to the
Technical Oversight Committee
March 28, 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 October 1, 2018, through December 30, 2018. 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 March 7, 2019.

- 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 SFWMD's *Field Sampling Quality Manual* (SFWMD 2017) provides the requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2018) 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 "RDS_for_TOC_QAR_100118_to_123118.xlsx" was created and contains all TP results and any no sample collected (NOB) records 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

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 the 45 sampling events is shown in **Table 1**. The table shows the work order identifiers, the project codes, and the dates the samples were collected.

During the 45 sampling events described above, a total of 41 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 the grab sample identifiers and the reason these samples were not collected is shown in **Table 2**.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project ^a	Date Collected
P95833	66819	PIN	10/01/2018
P95793	66793	PIE	10/02/2018
P95810	66782	PIE	10/02/2018
P95955	66933	EVPA	10/08/2018
P96016	66993	PIN	10/08/2018
P95957	66935	EVPA	10/09/2018
P95809	66791	PIE	10/09/2018
P95817	66792	PIE	10/09/2018
P95999	66961	PIN	10/15/2018
P95811	66783	PIE	10/16/2018
P95795	66794	PIE	10/16/2018
P96017	66994	PIN	10/22/2018
P95818	66816	PIE	10/23/2018
P95796	66795	PIE	10/23/2018
P96011	66988	PIN	10/30/2018
P95797	66796	PIE	10/30/2018
P95812	66784	PIE	10/30/2018
P96018	66995	PIN	11/05/2018
P95956	66934	EVPA	11/06/2018
P95823	66806	PIE	11/06/2018
P95798	66797	PIE	11/06/2018
P95958	66936	EVPA	11/07/2018
P95813	66785	PIE	11/13/2018
P95799	66798	PIE	11/13/2018
P96012	66989	PIN	11/13/2018
P96019	66996	PIN	11/19/2018
P95800	66799	PIE	11/20/2018
P95819	66817	PIE	11/20/2018
P96013	66990	PIN	11/26/2018
P95814	66786	PIE	11/27/2018
P95801	66800	PIE	11/27/2018
P96020	66997	PIN	12/03/2018
P96508	67228	EVPA	12/04/2018
P95802	66801	PIE	12/04/2018
P95824	66807	PIE	12/04/2018
P96507	67227	EVPA	12/05/2018
P97451	68118	PIE	12/11/2018
P96537	67256	PIE	12/11/2018
P96672	67391	PIN	12/11/2018
P99083	68526	PIN	12/18/2018
P99237	68517	PIE	12/18/2018
P99731	68750	PIE	12/18/2018
P100618	68889	PIE	12/26/2018
P99715	68734	PIE	12/26/2018
P100555	68877	PIN	12/28/2018

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
P95833	PIN	P95833-12	S12B	10/01/2018	No flow.
P96016	PIN	P96016-11	S12B	10/08/2018	No flow.
P95999	PIN	P95999-24	S355A	10/15/2018	No flow.
P95999	PIN	P95999-11	S12B	10/15/2018	No flow.
P96017	PIN	P96017-11	S12B	10/22/2018	No flow.
P96011	PIN	P96011-27	S355B	10/30/2018	Too shallow to sample.
P96011	PIN	P96011-25	S355A	10/30/2018	Too shallow to sample.
P96011	PIN	P96011-13	S12D	10/30/2018	No flow.
P96011	PIN	P96011-12	S12C	10/30/2018	No flow.
P96011	PIN	P96011-11	S12B	10/30/2018	No flow.
P96018	PIN	P96018-13	S12D	11/05/2018	No flow.
P96018	PIN	P96018-12	S12C	11/05/2018	No flow.
P96018	PIN	P96018-11	S12B	11/05/2018	No flow.
P95956	EVPA	P95956-2	LOX5	11/06/2018	Too shallow to sample.
P95956	EVPA	P95956-1	LOX3	11/06/2018	Too shallow to sample.
P96012	PIN	P96012-13	S12D	11/13/2018	No flow.
P96012	PIN	P96012-12	S12C	11/13/2018	No flow.
P96012	PIN	P96012-11	S12B	11/13/2018	No flow.
P96019	PIN	P96019-13	S12D	11/19/2018	No flow.
P96019	PIN	P96019-12	S12C	11/19/2018	No flow.
P96019	PIN	P96019-11	S12B	11/19/2018	No flow.
P95819	PIE	P95819-18	BERMB3	11/20/2018	Too shallow to sample.
P96013	PIN	P96013-27	S355B	11/26/2018	No flow.
P96013	PIN	P96013-25	S355A	11/26/2018	No flow.
P96013	PIN	P96013-12	S12C	11/26/2018	No flow.
P96013	PIN	P96013-11	S12B	11/26/2018	No flow.
P95824	PIE	P95824-3	BERMB3	12/04/2018	Too shallow to sample.
P96508	EVPA	P96508-7	LOX9	12/04/2018	Too shallow to sample.
P96508	EVPA	P96508-5	LOX5	12/04/2018	Too shallow to sample.
P96508	EVPA	P96508-4	LOX3	12/04/2018	Too shallow to sample.
P96672	PIN	P96672-14	S12D	12/11/2018	No flow.
P96672	PIN	P96672-13	S12C	12/11/2018	No flow.
P96672	PIN	P96672-12	S12B	12/11/2018	No flow.
P99083	PIN	P99083-12	S12B	12/17/2018	No flow.
P99083	PIN	P99083-13	S12C	12/17/2018	No flow.
P99237	PIE	P99237-4	BERMB3	12/18/2018	Too shallow to sample.
P100555	PIN	P100555-33	S355B	12/27/2018	No flow.
P100555	PIN	P100555-31	S355A	12/27/2018	No flow.
P100555	PIN	P100555-16	S12D	12/27/2018	No flow.
P100555	PIN	P100555-15	S12C	12/27/2018	No flow.
P100555	PIN	P100555-14	S12B	12/27/2018	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 Assessment Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]), qualifiers will be added to some or all of the associated sample results. The types of field quality control samples that are collected may include replicate samples (RS), 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 39 FBCs and four RSs were collected. One 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 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 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 Assessment Rule* (Chapter 62-160, F.A.C.).

For grab samples collected at locations described in the *Introduction*, three PMRs were assigned by project managers and two qualifiers were assigned as per the FDEP *Quality Assessment Rule* (Chapter 62-160, F.A.C.). These qualifiers and the remark codes 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
P95957	EVPA	P95957-2	LOX11	10/09/2018	PMR / Partial sample taken due to total depth between 0.1 meter and 0.2 meter.
P95819	PIE	P95819-16	G737	11/20/2018	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.
P95819	PIE	P95819-3	S18C	11/20/2018	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.
P96013	PIN	P96013-29	S356-334	11/26/2018	PMR / Field notes state that "A 5th drop of Sulfuric Acid was added to the Grey Bottles at the FOC [Field Operations Center], since only 4 drops were added in the field and 5 drops are required".
P96013	PIN	P96013-15	S333	11/26/2018	PMR / Depth was not recorded. Field notes state that "A 5th drop of Sulfuric Acid was added to the Grey Bottles at the FOC, since only 4 drops were added in the field and 5 drops are required".

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

FIELD AUDITS

SFWMD conducted one field audit on the PIN project during the fourth quarter of 2018. Two “Quality Improvements” were issued concerning the filtration and preservation of the filtered samples, which did not impact the TP sample data. Two “Process Improvements” were issued. One concerned the setup of the autosampler and one concerned the documentation error. After a review of the key deficiencies during this sampling trip, it was determined the deficiencies observed during the audit did not negatively affect the quality of the 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

The SFWMD Environmental Services Laboratory conducted a total of 395 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 395 results, 151 TP results were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 395 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 Environmental Services 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 2018). The results of these laboratory quality control samples are associated with some or all the analyses conducted in a given batch and qualifiers are added to the data as required by the *Quality Assessment 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 151 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 no 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 the “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 less than PQL (0.004 mg/L) are assigned the “I” qualifier, indicating that the results are

at concentrations that cannot be accurately quantified. Of the 151 results reported, no result was below the MDL and nine samples 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:

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

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** 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.

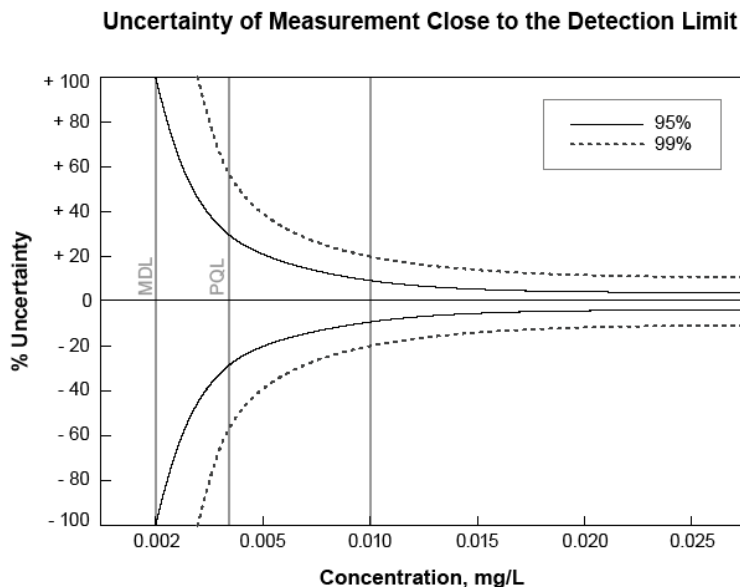


Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

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, no performance evaluation samples for TP analysis were completed and only one proficiency testing sample (ERA Waters Study #284; ERA 2018) for TP analysis was completed and reported. All results reported by the SFWMD Analytical Services Chemistry Laboratory were scored as "acceptable". The laboratory received a "Certificate of Excellence" for achieving 100% acceptable data in this study, which included 520 participating laboratories. This achievement is a demonstration of the superior quality of the SFWMD laboratory in evaluation of the analytes including TP during this reporting period.

LABORATORY AUDITS

There was one internal laboratory audit conducted during this reporting period. A total of 14 findings or observations of this audit were reported and followed-up by the auditor to confirm the recommended corrective action plan developed in response to this internal audit were completed within an agreed timescale.

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 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.

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 (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).