Quality Assessment Report for Water Quality Monitoring

July – September 2018

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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 July 1, 2018, through September 30, 2018.

- 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 analysis contained in this document reflects the status of the data at the time the data were downloaded on November 7, 2018, and does not account for changes made to the data after that date with the exception of the addition of a sample taken at LOX7 (P95526-15) on September 5, 2018, to make up for a missed sample the previous day. The sample was not taken on September 4, 2018, because of heavy rain.

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_070118_to_093018.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 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 the 44 sampling events is shown in **Table 1**. The table shows the work order identifiers, the project code, and the date the samples were collected.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project [a]	Date Collected
P94539	65597	PIN	7/2/2018
P94611	65671	PIE	7/2/2018
P94937	65968	EVPA	7/9/2018
P94560	65616	PIN	7/9/2018
P94939	65970	EVPA	7/10/2018
P94605	65654	PIE	7/10/2018
P94589	65635	PIE	7/10/2018
P94546	65615	PIN	7/16/2018
P94601	65633	PIE	7/17/2018
P94615	65676	PIE	7/17/2018
P94561	65610	PIN	7/23/2018
P94591	65636	PIE	7/24/2018
P94606	65655	PIE	7/24/2018
P94541	65598	PIN	7/30/2018
P94612	65672	PIE	7/31/2018
P94592	65637	PIE	7/31/2018
P94562	65611	PIN	8/6/2018
P94938	65969	EVPA	8/7/2018
P94593	65638	PIE	8/7/2018
P94607	65656	PIE	8/7/2018
P94940	65971	EVPA	8/8/2018
P94542	65599	PIN	8/13/2018
P94616	65662	PIE	8/14/2018
P94594	65639	PIE	8/14/2018
P94563	65612	PIN	8/20/2018
P94595	65640	PIE	8/21/2018
P94608	65657	PIE	8/21/2018
P94543	65600	PIN	8/27/2018
P94613	65673	PIE	8/28/2018
P94596	65641	PIE	8/28/2018
P95525	66522	EVPA	9/4/2018
P94597	65642	PIE	9/4/2018
P94609	65658	PIE	9/4/2018
P94564	65613	PIN	9/5/2018
P95526	66523	EVPA	9/5/2018
P94544	65601	PIN	9/10/2018
P94598	65643	PIE	9/11/2018
P94617	65663	PIE	9/11/2018
P94565	65614	PIN	9/17/2018
P94599	65644	PIE	9/18/2018
P94610	65659	PIE	9/18/2018
P94545	65602	PIN	9/24/2018
P94600	65645	PIE	9/25/2018
P94614	65674	PIE	9/25/2018

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

During the 44 sampling events described above, a total of 14 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 2. Grab samples not collected during the reporting period.

Work Identifier	Project [a]	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P94611	PIE	P94611-16	G737	7/2/2018	Too shallow to sample.
P94611	PIE	P94611-18	BERMB3	7/2/2018	Too shallow to sample.
P94539	PIN	P94539-12	S12B	7/2/2018	Gate closed, no flow.
P94937	EVPA	P94937-3	LOX10	7/9/2018	Too shallow to sample.
P94615	PIE	P94615-3	BERMB3	7/17/2018	Too shallow to sample.
P94561	PIN	P94561-27	S355B	7/23/2018	Gate closed, no flow.
P94561	PIN	P94561-25	S355A	7/23/2018	Gate closed, no flow.
P94612	PIE	P94612-18	BERMB3	7/31/2018	Too shallow to sample.
P94938	EVPA	P94938-3	LOX10	8/7/2018	Too shallow to sample.
P94938	EVPA	P94938-2	LOX5	8/7/2018	Too shallow to sample.
P94616	PIE	P94616-3	BERMB3	8/14/2018	Too shallow to sample.
P94563	PIN	P94563-14	S12D	8/20/2018	Sampling area inaccessible due to large floating mats of vegetation. No clear, representative area to collect sample.
P94563	PIN	P94563-25	S355A	8/20/2018	Gate closed, no flow.
P94613	PIE	P94613-18	BERMB3	8/28/2018	Too shallow to sample.

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

FIELD QUALITY CONTROL

To assess the quality of the sample collection process 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 44 sampling events described above, a total of 40 FBCs and 4 RSs were collected. One FBC (FB collected on August 27, 2018) had a concentration (0.004 milligrams per liter [mg/L]) above the TP method detection limit (MDL) of 0.002 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 11 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/Reason
P94588	PIE	P94588-26	S328	7/2/2018	J / Improper laboratory or field protocol. Gates closed. Sample was collected from disconnected pool and is not representative of surrounding area.
P94589	PIE	P94589-26	S328	7/10/2018	J / Improper laboratory or field protocol. Gates closed. Disconnected water body sampled as per FPM. J5 added to all test.
P94601	PIE	P94601-27	S328	7/17/2018	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P94561	PIN	P94561-2	S12A	7/23/2018	PMR / No depth recorded on field documentation.
P94592	PIE	P94592-26	S328	7/31/2018	J / Improper laboratory or field protocol. Gates closed. Sample was collected from a disconnected pool and is not representative of the surrounding water body.
P94593	PIE	P94593-26	S328	8/7/2018	J / Improper laboratory or field protocol. Gates closed. Disconnected pool, sample taken as per FPM.
P94543	PIN	P94543-25	S356-334	8/27/2018	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.
P94543	PIN	P94543-15	S333	8/27/2018	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.
P94543	PIN	P94543-14	S12D	8/27/2018	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.
P94543	PIN	P94543-13	S12C	8/27/2018	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.
P94543	PIN	P94543-12	S12B	8/27/2018	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.
P94543	PIN	P94543-2	S12A	8/27/2018	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.
P94597	PIE	P94597-26	S328	9/4/2018	PMR / Field notes state that 'all gates were open' at the time of sampling. However, the stage data shows that the gates did not open until 09/05/2018 and this discrepancy was verified by the Control Room notification.
P95526	EVPA	P95526-15	LOX7	9/5/2018	PMR / Sampling station LOX7 was not collected on previous day's sampling trip (P95525 on 9/4/2018) due to heavy rain, and as a result, this station was added to sampling trip P95526 on 9/5/2018.

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

LABORATORY ANALYSIS QUALITY ASSESSMENT

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the third quarter of 2018.

FIELD PROCEDURE UPDATES

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

SAMPLE ANALYSES

The SFWMD Environmental Services Laboratory conducted a total of 464 TP analyses for the grab samples collected during the 44 sampling events listed in **Table 1**. Of those 464 results, 174 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 464 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 174 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 174 results reported, no results were below the MDL and four 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:

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

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.

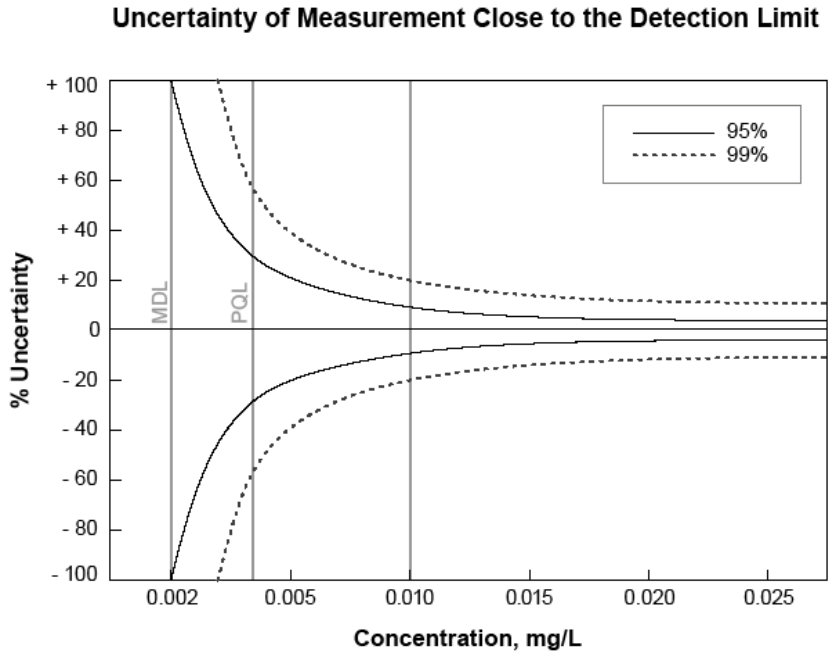

Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

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, performance evaluation samples for TP analysis were completed through Environment and Climate Change Canada (2018) Program Number 112. The results reported by the SFWMD Analytical Services Chemistry Laboratory were rated as "very good". Nine values were reported for this evaluation, which returned Z scores ranging from -0.15 to -0.71. During this reporting period, no proficiency testing samples for TP analysis were completed.

LABORATORY AUDITS

There were no laboratory audits 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

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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 (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi - X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2012).