Quality Assessment Report for Water Quality Monitoring

April – June 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 April 1, 2018, through June 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 August 24, 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 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_040118_to_063018.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 Environmental Services 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 code, and the date the samples were collected.

During the 45 sampling events described above, a total of 53 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected 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
P93226	64479	PIN	4/2/2018
P93715	64916	EVPA	4/3/2018
P93169	64422	PIE	4/3/2018
P93190	64443	PIE	4/3/2018
P93717	64918	EVPA	4/4/2018
P93234	64487	PIN	4/9/2018
P93204	64457	PIE	4/10/2018
P93170	64423	PIE	4/10/2018
P93233	64486	PIN	4/16/2018
P93191	64444	PIE	4/17/2018
P93171	64424	PIE	4/17/2018
P93240	64493	PIN	4/23/2018
P93182	64435	PIE	4/24/2018
P93203	64456	PIE	4/24/2018
P93228	64481	PIN	4/30/2018
P93716	64917	EVPA	5/1/2018
P93173	64426	PIE	5/1/2018
P93192	64445	PIE	5/1/2018
P93718	64919	EVPA	5/2/2018
P93236	64489	PIN	5/7/2018
P93205	64458	PIE	5/8/2018
P93174	64427	PIE	5/8/2018
P93229	64482	PIN	5/14/2018
P93175	64428	PIE	5/15/2018
P93193	64446	PIE	5/15/2018
P93237	64490	PIN	5/21/2018
P93176	64429	PIE	5/22/2018
P93200	64453	PIE	5/22/2018
P93230	64483	PIN	5/29/2018
P93194	64447	PIE	5/29/2018
P93177	64430	PIE	5/29/2018
P93238	64491	PIN	6/4/2018
P94347	65414	EVPA	6/5/2018
P93178	64431	PIE	6/5/2018
P93206	64459	PIE	6/5/2018
P94348	65415	EVPA	6/6/2018
P93231	64484	PIN	6/11/2018
P93179	64432	PIE	6/12/2018
P93195	64448	PIE	6/12/2018
P93239	64492	PIN	6/18/2018
P93202	64455	PIE	6/19/2018
P93180	64433	PIE	6/19/2018
P93232	64485	PIN	6/25/2018
P93196	64449	PIE	6/26/2018
P93181	64434	PIE	6/26/2018

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	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P93226	PIN	P93226-27	S355B	4/2/2018	Gate closed, no flow
P93226	PIN	P93226-25	S355A	4/2/2018	Gate closed, no flow
P93226	PIN	P93226-13	S12C	4/2/2018	Gate closed, no flow
P93226	PIN	P93226-12	S12B	4/2/2018	Gate closed, no flow
P93715	EVPA	P93715-1	LOX3	4/3/2018	Too shallow
P93715	EVPA	P93715-2	LOX5	4/3/2018	Too shallow
P93715	EVPA	P93715-3	LOX10	4/3/2018	Too shallow
P93715	EVPA	P93715-4	LOX9	4/3/2018	Too shallow
P93715	EVPA	P93715-8	LOX4	4/3/2018	Too shallow
P93169	PIE	P93169-26	S328	4/3/2018	Too shallow
P93190	PIE	P93190-3	G737	4/3/2018	Too shallow
P93234	PIN	P93234-13	S12C	4/9/2018	Gate closed, no flow
P93234	PIN	P93234-12	S12B	4/9/2018	Gate closed, no flow
P93204	PIE	P93204-18	BERMB3	4/10/2018	Too shallow
P93240	PIN	P93240-12	S12B	4/23/2018	Gate closed, no flow
P93240	PIN	P93240-13	S12C	4/23/2018	Gate closed, no flow
P93203	PIE	P93203-3	BERMB3	4/24/2018	Too shallow
P93203	PIE	P93203-5	G737	4/24/2018	Too shallow
P93228	PIN	P93228-12	S12B	4/30/2018	Gate closed, no flow
P93228	PIN	P93228-13	S12C	4/30/2018	Gate closed, no flow
P93716	EVPA	P93716-1	LOX3	5/1/2018	Too shallow
P93716	EVPA	P93716-2	LOX5	5/1/2018	Too shallow
P93716	EVPA	P93716-3	LOX10	5/1/2018	Too shallow
P93716	EVPA	P93716-4	LOX9	5/1/2018	Too shallow
P93716	EVPA	P93716-5	LOX8	5/1/2018	Too shallow
P93192	PIE	P93192-3	G737	5/1/2018	Too shallow
P93236	PIN	P93236-12	S12B	5/7/2018	Gate closed, no flow
P93236	PIN	P93236-13	S12C	5/7/2018	Gate closed, no flow
P93205	PIE	P93205-18	BERMB3	5/8/2018	Too shallow
P93205	PIE	P93205-16	G737	5/8/2018	Too shallow
P93229	PIN	P93229-12	S12B	5/14/2018	Gate closed, no flow
P93229	PIN	P93229-13	S12C	5/14/2018	Gate closed, no flow
P93193	PIE	P93193-3	G737	5/14/2018	Too shallow
P93237	PIN	P93237-12	S12B	5/21/2018	Gate closed, no flow
P93237	PIN	P93237-13	S12C	5/21/2018	Gate closed, no flow
P93200	PIE	P93200-3	BERMB3	5/22/2018	Too shallow
P93200	PIE	P93200-4	G737	5/22/2018	Too shallow
P93230	PIN	P93230-25	S355A	5/29/2018	Gate closed, no flow
P93230	PIN	P93230-27	S355B	5/29/2018	Gate closed, no flow
P93194	PIE	P93194-3	G737	5/29/2018	Too shallow
P93230	PIN	P93230-12	S12B	5/29/2018	Gate closed, no flow
P93238	PIN	P93238-12	S12B	6/4/2018	Gate closed, no flow
P93206	PIE	P93206-18	BERMB3	6/5/2018	Too shallow
P93206	PIE	P93206-16	G737	6/5/2018	Too shallow
P93231	PIN	P93231-12	S12B	6/11/2018	Gate closed, no flow
P93195	PIE	P93195-3	G737	6/12/2018	Too shallow
P93239	PIN	P93239-12	S12B	6/18/2018	Gate closed, no flow
P93202	PIE	P93202-3	BERMB3	6/19/2018	Too shallow
P93202	PIE	P93202-4	G737	6/19/2018	Too shallow
P93232	PIN	P93232-27	S355B	6/25/2018	Gate closed, no flow
P93232	PIN	P93232-25	S355A	6/25/2018	Gate closed, no flow
P93232	PIN	P93232-12	S12B	6/25/2018	Gate closed, no flow
P93196	PIE	P93196-3	G737	6/26/2018	Too shallow

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 61 FBCs and six RSs were collected. One FBC (FCEB collected on May 15, 2018) had a concentration above 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*.

For grab samples collected at locations described in the *Introduction*, one PMR and 14 qualifiers were assigned as per the FDEP *Quality Assessment Rule* (Chapter 62-160, F.A.C.). These qualifiers and the remark code are detailed in **Table 3**.

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

Work Identifier	Project	Sample Identifier	Station	Collection Date	Qualifier/Reason
P93173	PIE	P93173-26	S328	5/1/2018	Y/Analysis performed on un/improperly preserved sample
P93175	PIE	P93175-17	S332DX	5/15/2018	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
P93204	PIE	P93204-16	G737	4/10/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93170	PIE	P93170-26	S328	4/10/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93191	PIE	P93191-3	G737	4/17/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93171	PIE	P93171-26	S328	4/17/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93182	PIE	P93182-27	S328	4/24/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93173	PIE	P93173-26	S328	5/1/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93174	PIE	P93174-26	S328	5/8/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93175	PIE	P93175-26	S328	5/15/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93178	PIE	P93178-26	S328	6/5/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93179	PIE	P93179-26	S328	6/12/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93180	PIE	P93180-26	S328	6/19/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93181	PIE	P93181-26	S328	6/26/2018	J/The sample was collected from a disconnected pool and is not representative of the surrounding water body. The surrounding area is dry.
P93232	PIN	P93232-3	S12A	6/25/2018	PMR/No depth recorded on field documentation.

FIELD AUDITS

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

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 344 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 344 results, 191 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 344 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 191 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 Environmental Services 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 191 results reported, no results were below the MDL and no 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 Environmental Services 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.

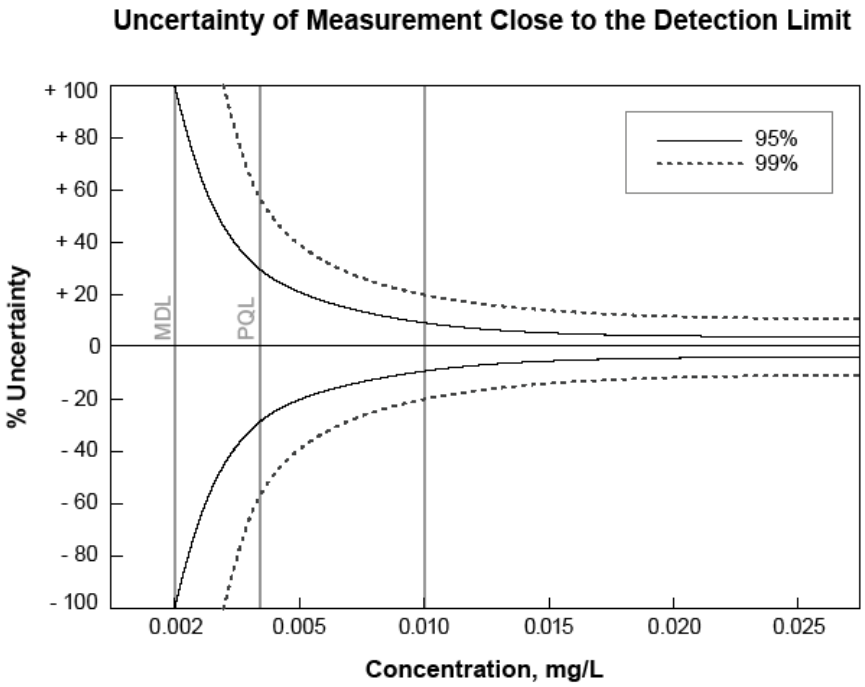

Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

PROFICIENCY TESTING AND EVALUATION

The SFWMD Environmental Services Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During this reporting period, performance testing samples for TP analysis were completed through Waters ERA (2018) Program Number 278. The results reported by the SFWMD Environmental Services Laboratory were rated as "acceptable" with a Z score of 0.0459. During this reporting period, no proficiency evaluation samples for TP analysis were completed.

LABORATORY AUDITS

The SFWMD Laboratory received its semiannual Department of Health audit on May 8 and 9, 2018. There were 18 findings in the final report which was received on June 1, 2018, none of which were directly related to TP analysis. A response to the final report was sent to the auditor (Paul Leblanc, Dade Moeller, Inc.) on June 29, 2018, with all the laboratories proposed corrections. The laboratory received approval of the proposed corrections on July 2, 2018.

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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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.

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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).