Quality Assessment Report for Water Quality Monitoring

January – March 2020

Submitted to the
Technical Oversight Committee
June 5, 2020

Prepared by:
Ming Chen (michen@sfwmd.gov)

Analytical Services
Water Quality Bureau
South Florida Water Management District
West Palm Beach, Florida

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, 2020, through March 31, 2020. 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 February 6, 2020.

- 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, 2020, respectively. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD 2020) 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_2020_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. A total of 47 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.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project [a]	Date Collected
P113310	74179	PIE	01/02/2020
P113318	74183	PIE	01/02/2020
P113615	74336	PIN	01/06/2020
P113681	74366	EVPA	01/07/2020
P114034	74529	PIE	01/07/2020
P114044	74535	PIE	01/07/2020
P110836	73167	EVPA	01/08/2020
P113621	74338	PIN	01/13/2020
P114040	74533	PIE	01/14/2020
P114035	74530	PIE	01/15/2020
P114036	74531	PIE	01/21/2020
P114045	74536	PIE	01/21/2020
P113642	74349	PIN	01/21/2020
P113622	74339	PIN	01/27/2020
P114037	74532	PIE	01/28/2020
P114041	74534	PIE	01/28/2020
P114342	74679	PIN	02/03/2020
P113682	74367	EVPA	02/04/2020
P114806	74916	PIE	02/04/2020
P114485	74745	PIE	02/04/2020
P114734	74881	EVPA	02/05/2020
P114353	74685	PIN	02/10/2020
P114828	74931	PIE	02/11/2020
P114496	74751	PIE	02/12/2020
P114343	74680	PIN	02/17/2020
P114807	74917	PIE	02/18/2020
P114486	74746	PIE	02/18/2020
P114354	74686	PIN	02/24/2020
P114502	74756	PIE	02/25/2020
P114815	74924	PIE	02/25/2020
P114344	74681	PIN	03/03/2020
P113469	74258	EVPA	03/03/2020
P114487	74747	PIE	03/03/2020
P114808	74918	PIE	03/03/2020
P113473	74260	EVPA	03/04/2020
P114355	74687	PIN	03/09/2020
P114833	74933	PIE	03/10/2020
P114498	74753	PIE	03/10/2020
P114345	74682	PIN	03/16/2020
P114488	74748	PIE	03/17/2020
P114809	74919	PIE	03/17/2020
P114356	74688	PIN	03/23/2020
P114834	74934	PIE	03/24/2020
P114499	74754	PIE	03/24/2020
P114346	74683	PIN	03/30/2020
P114810	74920	PIE	03/31/2020
P114489	74749	PIE	03/31/2020

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

During the 47 sampling events described above, a total of 52 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 are 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
74336032	PIN	P113615-32	S12D	01/06/2020	Gates closed. No flow.
74336033	PIN	P113615-33	S12C	01/06/2020	Gates closed. No flow.
74336034	PIN	P113615-34	S12B	01/06/2020	Gates closed. No flow.
74338025	PIN	P113621-25	S12D	01/13/2020	Gates closed. No flow.
74338026	PIN	P113621-26	S12C	01/13/2020	Gates closed. No flow.
74338027	PIN	P113621-27	S12B	01/13/2020	Gates closed. No flow.
74349013	PIN	P113642-13	S355B	01/21/2020	Gates closed. No flow.
74349015	PIN	P113642-15	S355A	01/21/2020	Gates closed. No flow.
74349029	PIN	P113642-29	S12D	01/21/2020	Too shallow to sample.
74349030	PIN	P113642-30	S12C	01/21/2020	Gates closed. No flow.
74349031	PIN	P113642-31	S12B	01/21/2020	Gates closed. No flow.
74339025	PIN	P113622-25	S12D	01/27/2020	Gates closed. No flow.
74339026	PIN	P113622-26	S12C	01/27/2020	Gates closed. No flow.
74339027	PIN	P113622-27	S12B	01/27/2020	Gates closed. No flow.
74679029	PIN	P114342-29	S12D	02/03/2020	Gates closed. No flow.
74679030	PIN	P114342-30	S12C	02/03/2020	Gates closed. No flow.
74679031	PIN	P114342-31	S12B	02/03/2020	Gates closed. No flow.
74685025	PIN	P114353-25	S12D	02/10/2020	Gates closed. No flow.
74685026	PIN	P114353-26	S12C	02/10/2020	Gates closed. No flow.
74685027	PIN	P114353-27	S12B	02/10/2020	Gates closed. No flow.
74931004	PIE	P114828-4	BERMB3	02/11/2020	Too shallow to sample.
74680029	PIN	P114343-29	S12D	02/17/2020	Gates closed. No flow.
74680030	PIN	P114343-30	S12C	02/17/2020	Gates closed. No flow.
74680031	PIN	P114343-31	S12B	02/17/2020	Gates closed. No flow.
74686025	PIN	P114354-25	S12D	02/24/2020	Gates closed. No flow.
74686026	PIN	P114354-26	S12C	02/24/2020	Gates closed. No flow.
74686027	PIN	P114354-27	S12B	02/24/2020	Gates closed. No flow.
74924004	PIE	P114815-4	BERMB3	02/25/2020	Too shallow to sample.
74681029	PIN	P114344-29	S12D	03/02/2020	Too shallow to sample.
74681030	PIN	P114344-30	S12C	03/02/2020	Too shallow to sample.
74681031	PIN	P114344-31	S12B	03/02/2020	Too shallow to sample.
74687025	PIN	P114355-25	S12D	03/09/2020	Gates closed. No flow.
74687026	PIN	P114355-26	S12C	03/09/2020	Gates closed. No flow.
74687027	PIN	P114355-27	S12B	03/09/2020	Gates closed. No flow.
74933004	PIE	P114833-4	BERMB3	03/10/2020	Too shallow to sample.
74682015	PIN	P114345-15	S355A	03/16/2020	Gates closed. No flow.
74682029	PIN	P114345-29	S12D	03/16/2020	Gates closed. No flow.
74682030	PIN	P114345-30	S12C	03/16/2020	Gates closed. No flow.

Table 2. Continued.

Work Identifier	Project [a]	Sample Identifier	Station	Date	Reason Sample Was Not Collected
74682031	PIN	P114345-31	S12B	03/16/2020	Gates closed. No flow.
75513009	PEST	P116041-9	S332DX	03/16/2020	Too shallow to sample.
74919005	PIE	P114809-5	G737	03/17/2020	Too shallow to sample.
74688025	PIN	P114356-25	S12D	03/23/2020	Gates closed. No flow.
74688026	PIN	P114356-26	S12C	03/23/2020	Too shallow to sample.
74688027	PIN	P114356-27	S12B	03/23/2020	Gates closed. No flow.
74934004	PIE	P114834-4	BERMB3	03/24/2020	Too shallow to sample.
74934006	PIE	P114834-6	G737	03/24/2020	Too shallow to sample.
74683013	PIN	P114346-13	S355B	03/30/2020	Gates closed. No flow.
74683015	PIN	P114346-15	S355A	03/30/2020	Gates closed. No flow.
74683029	PIN	P114346-29	S12D	03/30/2020	Gates closed. No flow.
74683030	PIN	P114346-30	S12C	03/30/2020	Gates closed. No flow.
74683031	PIN	P114346-31	S12B	03/30/2020	Gates closed. No flow.
74920005	PIE	P114810-5	G737	03/31/2020	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 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 47 sampling events described above, a total of 28 field quality control blanks and six RSs were collected. None 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 four J qualifiers and one Y qualifier 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 quality assurance process-related
qualifiers and remark codes during the reporting period.

Work Identifier	Project [a]	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
74183011	PIE	P113318-11	S18C	01/02/2020	J / Improper laboratory or field protocol. Precision or accuracy criteria not met.
74183015	PIE	P113318-15	S18C	01/02/2020	J / Improper laboratory or field protocol. Precision or accuracy criteria not met.
74751031	PIE	P114496-31	S328	02/11/2020	J / Improper laboratory or field protocol. Sample was collected from a disconnected pool and is non-representative of the surrounding water body.
74746031	PIE	P114486-31	S328	02/18/2020	Y / Analysis was performed from an improperly preserved sample.
74748031	PIE	P114488-31	S328	03/17/2020	J / Improper laboratory or field protocol. Sample was collected from a disconnected pool and is non-representative of the surrounding water body.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audit on the TOC-related projects during the period specified in this report.

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 364 TP analyses for the grab samples collected during the 47 sampling events listed in **Table 1**. Of those 364 TP results, 132 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 364 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 2020). 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 2020). 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 132 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 a "I" qualifier, indicating that the results are at concentrations that cannot be accurately quantified. Of the 132 TP results reported, no result was below the MDL and 11 samples had a concentration 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:

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

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.
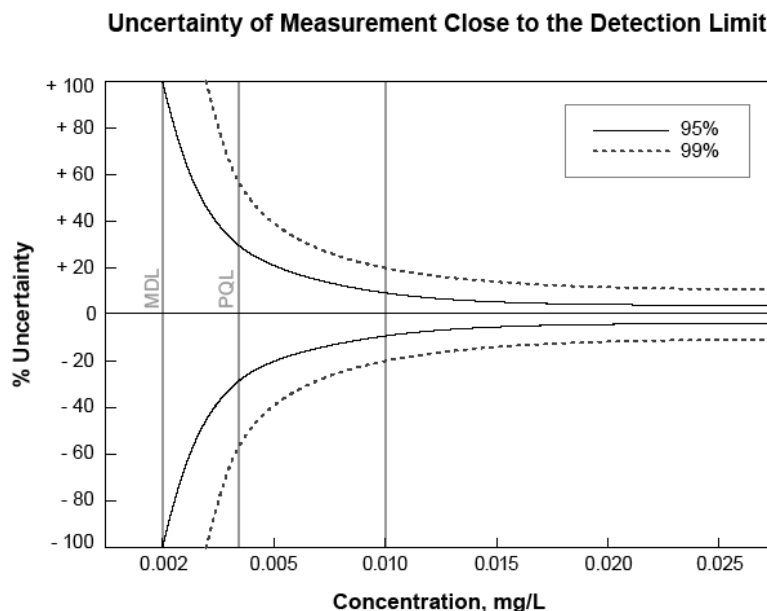
Uncertainty of Measurement Close to the Detection Limit

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 2020, the laboratory received TP results from one blind study, Environment and Climate Change Canada Performance Evaluation Study #115. Nine of the ten results were above detection limits and all reported results were acceptable. The laboratory received a "good" rating for TP analysis with this interlaboratory performance evaluation study.

LABORATORY AUDITS

During this reporting period the District's Analytical Services Chemistry Laboratory performed its annual quality systems internal audit. There were no findings with regards to TP analysis by the laboratory.

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. 2019a. *Field Quality Manual*. SFWMD-FIELD-QM-001-10, South Florida Water Management District, West Palm Beach, FL. Effective July 31, 2019.

SFWMD. 2019b. *Field Sampling Manual*. SFWMD-FIELD-FSM-001-10, Water Quality Monitoring Section, South Florida Water Management District, West Palm Beach, FL. Effective July 31, 2019.

SFWMD. 2020. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-2020-001, South Florida Water Management District, West Palm Beach, FL. Effective Feburary 5, 2020.

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.

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).