Quality Assessment Report for Water Quality Monitoring

July – September 2020

Submitted to the
Technical Oversight Committee
December 17, 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 July 1, 2020, through September 30, 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 October 29, 2020. 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 field sampling procedures, respectively, followed in field sample collection from July 1 to September 30, 2020. 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_jul_sep_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 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 13 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 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project [a]	Date Collected
P118350	76647	PIN	07/06/2020
P117155	76060	EVPA	07/07/2020
P118205	76571	PIE	07/07/2020
P118306	76625	PIE	07/07/2020
P118462	76706	EVPA	07/08/2020
P118361	76656	PIN	07/13/2020
P118219	76584	PIE	07/14/2020
P118284	76617	PIE	07/17/2020
P118359	76655	PIN	07/20/2020
P118307	76626	PIE	07/21/2020
P118207	76573	PIE	07/21/2020
P118368	76657	PIN	07/27/2020
P118320	76633	PIE	07/28/2020
P118208	76574	PIE	07/28/2020
P118352	76649	PIN	08/03/2020
P117156	76061	EVPA	08/04/2020
P118209	76575	PIE	08/04/2020
P118308	76627	PIE	08/04/2020
P118463	76707	EVPA	08/05/2020
P118369	76658	PIN	08/10/2020
P118210	76576	PIE	08/11/2020
P118321	76634	PIE	08/11/2020
P118353	76650	PIN	08/17/2020
P118211	76577	PIE	08/18/2020
P118309	76628	PIE	08/18/2020
P118370	76659	PIN	08/24/2020
P118212	76578	PIE	08/25/2020
P118322	76635	PIE	08/25/2020
P118354	76651	PIN	08/31/2020
P118310	76629	PIE	09/01/2020
P117627	76307	EVPA	09/01/2020
P118213	76579	PIE	09/01/2020
P117637	76310	EVPA	09/02/2020
P118371	76660	PIN	09/08/2020
P118323	76636	PIE	09/09/2020
P118214	76580	PIE	09/10/2020
P118355	76652	PIN	09/14/2020
P118215	76581	PIE	09/15/2020
P118311	76630	PIE	09/15/2020
P118372	76661	PIN	09/21/2020
P118324	76637	PIE	09/22/2020
P118216	76582	PIE	09/22/2020
P118356	76653	PIN	09/28/2020
P118217	76583	PIE	09/29/2020
P118312	76631	PIE	09/29/2020

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
76647013	PIN	P118350	S355B	07/06/2020	Gates closed. No flow.
76647015	PIN	P118350	S355A	07/06/2020	Gates closed. No flow.
76647031	PIN	P118350	S12B	07/06/2020	Gates closed. No flow.
76060004	EVPA	P117155	LOX10	07/07/2020	Too shallow to sample.
76060009	EVPA	P117155	LOX4	07/07/2020	Too shallow to sample.
76656030	PIN	P118361	S12B	07/13/2020	Gates closed. No flow.
76617004	PIE	P118284	BERMB3	07/16/2020	Too shallow to sample.
76650013	PIN	P118353	S355B	08/17/2020	Gates closed. No flow.
76650015	PIN	P118353	S355A	08/17/2020	Gates closed. No flow.
76651013	PIN	P118354	S355B	08/31/2020	Gates closed. No flow.
76651015	PIN	P118354	S355A	08/31/2020	Gates closed. No flow.
76652013	PIN	P118355	S355B	09/14/2020	Gates closed. No flow.
76652015	PIN	P118355	S355A	09/14/2020	Gates closed. 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 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 27 field quality control blanks and four 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 quality assurance process-related qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

FIELD AUDITS

SFWMD conducted one field audit on the EVPA project during the period specified in this report. One process improvement (PI) was noted concerning the reviewed chain of custody and the marsh surface water field sheet that had tests/parameters crossed-off. However, there were no date and initials for the cross-offs. After a comprehensive quality assurance/quality control (QA/QC) review of this deficiency, it was determined that the deficiency 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 Analytical Services Chemistry Laboratory staff conducted a total of 407 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 407 TP results, 177 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 407 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 177 TP results from samples collected from projects/locations listed in the *Introduction*, no qualifiers were added as a result of laboratory QC 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 117 TP results reported, no result was below the MDL and 14 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:

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

where:
$U(x)$ is the combined standard uncertainty in the result x at the 95% confidence interval (CI).
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.
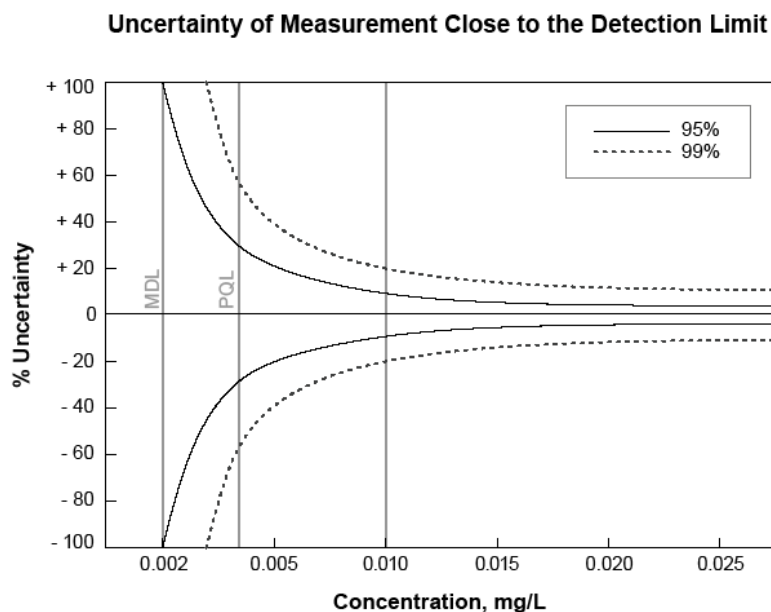

Figure 1. Estimated uncertainties at the 95% and 99% CIs
relative to the MDL and PQL of the TP measurement process.

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 third quarter of 2020, the laboratory did not participate in any studies and received no results.

LABORATORY AUDITS

During this reporting period one external laboratory assessment was conducted for the SFWMD Analytical Services Chemistry Laboratory. An American National Standards Institute (ANSI) National Accreditation Board (ANAB) contractor conducted a biannual external laboratory audit as required by the Florida Department of Health (FDOH). One deficiency was found for the laboratory's TP analytical procedure. The recording of the unique identifier for the pipette used in the sample preparation process was not properly recorded. This finding has been corrected and necessary information is documented.

PROCEDURE UPDATES

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

REFERENCES

Eurachem/CITAC. 2012. *Quantifying Uncertainty in Analytical Measurement, Third Edition*. Guide CG4, Eurachem/CITAC, Austria. ISBN 0-948926-15-5.

Ingersoll, W.S. 2001. *Environmental Analytical Measurement Uncertainty Estimation. Nested Hierarchical Approach*. ADA396946, Defense Technical Information Center, Fort Belvoir, VA.

FDEP. 2018. *Quality Assurance*. Chapter 62-160, Florida Administrative Code. Florida Department of Environmental Protection, Tallahassee, FL. Effective April 16, 2018.

JCGM. 1993. *International Vocabulary of Basic and General Standard Terms in Metrology*. Joint Committee on Guides for Metrology, Geneva, Switzerland. ISBN 92-67-10175-1.

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