Quality Assessment Report for Water Quality Monitoring

October – December 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, 2019, through December 31, 2019. 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 October 1 to December 31, 2019, respectively. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD 2019c) 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_oct_dec_2019_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 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.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project [a]	Date Collected
P108455	72081	PIE	10/01/2019
P108438	72073	PIE	10/01/2019
P108356	72043	PIN	10/07/2019
P109094	72323	EVPA	10/08/2019
P110419	73011	PIE	10/08/2019
P108442	72075	PIE	10/09/2019
P110835	73166	EVPA	10/09/2019
P110190	72890	PIN	10/14/2019
P108456	72082	PIE	10/15/2019
P110399	72998	PIE	10/15/2019
P110198	72893	PIN	10/21/2019
P110400	72999	PIE	10/22/2019
P108576	72088	PIE	10/22/2019
P108368	72049	PIN	10/28/2019
P110401	73000	PIE	10/29/2019
P110410	73005	PIE	10/29/2019
P110199	72894	PIN	11/04/2019
P109095	72324	EVPA	11/05/2019
P110402	73001	PIE	11/05/2019
P110417	73009	PIE	11/05/2019
P110834	73165	EVPA	11/06/2019
P110317	72955	PIN	11/12/2019
P110411	73006	PIE	11/12/2019
P110403	73002	PIE	11/12/2019
P110200	72895	PIN	11/19/2019
P110418	73010	PIE	11/19/2019
P110404	73003	PIE	11/19/2019
P110318	72956	PIN	11/25/2019
P110412	73007	PIE	11/26/2019
P110405	73004	PIE	11/26/2019
P110201	72896	PIN	12/02/2019
P113313	74180	PIE	12/03/2019
P113306	74175	PIE	12/03/2019
P113468	74257	EVPA	12/09/2019
P110319	72957	PIN	12/09/2019
P113472	74259	EVPA	12/10/2019
P113298	74172	PIE	12/10/2019
P113307	74176	PIE	12/10/2019
P111710	73570	PIN	12/16/2019
P113314	74181	PIE	12/17/2019
P113308	74177	PIE	12/17/2019
P113309	74178	PIE	12/26/2019
P113299	74173	PIE	12/26/2019
P110320	72958	PIN	12/27/2019
P111711	73571	PIN	12/30/2019

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

During the 45 sampling events described above, a total of 33 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
72893027	PIN	P110198-27	S12B	10/21/2019	Gates closed. No flow.
72049031	PIN	P108368-31	S12B	10/28/2019	Gates closed. No flow.
72894026	PIN	P110199-26	S12C	11/04/2019	Gates closed. No flow.
72894027	PIN	P110199-27	S12B	11/04/2019	Gates closed. No flow.
72955030	PIN	P110317-30	S12C	11/12/2019	Gates closed. No flow.
72955031	PIN	P110317-31	S12B	11/12/2019	Gates closed. No flow.
72895025	PIN	P110200-25	S12D	11/18/2019	Gates closed. No flow.
72895026	PIN	P110200-26	S12C	11/18/2019	Gates closed. No flow.
72895027	PIN	P110200-27	S12B	11/18/2019	Gates closed. No flow.
72956013	PIN	P110318-13	S355B	11/25/2019	Gates closed. No flow.
72956015	PIN	P110318-15	S355A	11/25/2019	Gates closed. No flow.
72956030	PIN	P110318-30	S12C	11/25/2019	Gates closed. No flow.
72956031	PIN	P110318-31	S12B	11/25/2019	Gates closed. No flow.
72896026	PIN	P110201-26	S12C	12/02/2019	Gates closed. No flow.
72896027	PIN	P110201-27	S12B	12/02/2019	Gates closed. No flow.
74180004	PIE	P113313-4	BERMB3	12/03/2019	Too shallow to sample.
72957029	PIN	P110319-29	S12D	12/09/2019	Gates closed. No flow.
72957030	PIN	P110319-30	S12C	12/09/2019	Gates closed. No flow.
72957031	PIN	P110319-31	S12B	12/09/2019	Gates closed. No flow.
73570025	PIN	P111710-25	S12D	12/16/2019	Gates closed. No flow.
73570026	PIN	P111710-26	S12C	12/16/2019	Gates closed. No flow.
73570027	PIN	P111710-27	S12B	12/16/2019	Gates closed. No flow.
74181004	PIE	P113314-4	BERMB3	12/17/2019	Too shallow to sample.
72958013	PIN	P110320-13	S355B	12/26/2019	Gates closed. No flow.
72958015	PIN	P110320-15	S355A	12/26/2019	Gates closed. No flow.
72958029	PIN	P110320-29	S12D	12/26/2019	Gates closed. No flow.
72958030	PIN	P110320-30	S12C	12/26/2019	Gates closed. No flow.
72958031	PIN	P110320-31	S12B	12/26/2019	Gates closed. No flow.
73571025	PIN	P111711-25	S12D	12/30/2019	Gates closed. No flow.
73571026	PIN	P111711-26	S12C	12/30/2019	Gates closed. No flow.
73571027	PIN	P111711-27	S12B	12/30/2019	Gates closed. No flow.
72893027	PIN	P110198-27	S12B	10/21/2019	Gates closed. No flow.
72049031	PIN	P108368-31	S12B	10/28/2019	Gates closed. No flow.

a. 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 26 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 no quality assurance process-related qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

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 381 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 381 TP results, 155 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 381 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 2019c). 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 2019c). 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 155 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 155 TP results reported, no result was below the MDL and 13 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:

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

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** presents estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

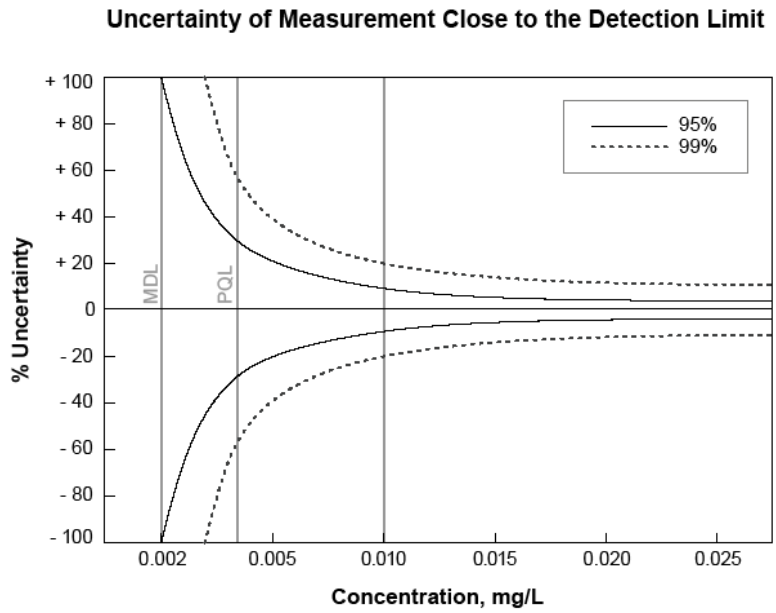

Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 fourth quarter of 2019, no results were received from any performance evaluation or proficient testing studies.

LABORATORY AUDITS

During this reporting period no laboratory assessment was conducted for the District's Analytical Services Chemistry 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. 2019c. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-2019-001, South Florida Water Management District, West Palm Beach, FL. Effective January 5, 2019.

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