

Quality Assessment Report for Water Quality Monitoring

April – June 2020



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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, 2020, through June 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 August 20, 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 the field sampling procedures followed in field sample collection from April 1 to June 30, 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_apr_jun_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 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 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 44 sampling events described in **Table 1**, a total of 77 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 or dry 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
P114357	74689	PIN	04/06/2020
P113683	74368	EVPA	04/07/2020
P114835	74935	PIE	04/07/2020
P114500	74755	PIE	04/07/2020
P114735	74882	EVPA	04/08/2020
P114347	74684	PIN	04/14/2020
P114811	74921	PIE	04/14/2020
P114490	74750	PIE	04/14/2020
P116436	75718	PIN	04/20/2020
P116198	75602	PIE	04/21/2020
P116222	75609	PIE	04/21/2020
P116424	75712	PIN	04/27/2020
P116210	75591	PIE	04/28/2020
P116229	75603	PIE	04/28/2020
P116442	75713	PIN	05/04/2020
P116211	75592	PIE	05/05/2020
P116241	75610	PIE	05/05/2020
P114736	74883	EVPA	05/06/2020
P116430	75707	PIN	05/11/2020
P116230	75604	PIE	05/12/2020
P116212	75593	PIE	05/12/2020
P116443	75714	PIN	05/18/2020
P116213	75594	PIE	05/19/2020
P116242	75611	PIE	05/19/2020
P116214	75595	PIE	05/26/2020
P116431	75708	PIN	05/26/2020
P116231	75605	PIE	05/26/2020
P116444	75715	PIN	06/01/2020
P117626	76306	EVPA	06/02/2020
P116215	75596	PIE	06/02/2020
P116243	75612	PIE	06/02/2020
P117636	76309	EVPA	06/04/2020
P116432	75709	PIN	06/08/2020
P116216	75597	PIE	06/09/2020
P116232	75606	PIE	06/09/2020
P116445	75716	PIN	06/15/2020
P116244	75613	PIE	06/16/2020
P116217	75598	PIE	06/16/2020
P116433	75710	PIN	06/22/2020
P116233	75607	PIE	06/23/2020
P116218	75599	PIE	06/23/2020
P116446	75717	PIN	06/29/2020
P116219	75600	PIE	06/30/2020
P116245	75614	PIE	06/30/2020

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
74689025	PIN	P114357-25	S12D	04/06/2020	Gates closed. No flow.
74689026	PIN	P114357-26	S12C	04/06/2020	Gates closed. No flow.
74689027	PIN	P114357-27	S12B	04/06/2020	Gates closed. No flow.
74368004	EVPA	P113683-4	LOX10	04/07/2020	Too shallow to sample.
74368003	EVPA	P113683-3	LOX5	04/07/2020	Too shallow to sample.
74368002	EVPA	P113683-2	LOX3	04/07/2020	Too shallow to sample.
74935006	PIE	P114835-6	G737	04/07/2020	Gates closed. No flow.
74935004	PIE	P114835-4	BERMB3	04/07/2020	Too shallow to sample.
74755031	PIE	P114500-31	S328	04/07/2020	Too shallow to sample.
74684013	PIN	P114347-13	S355B	04/13/2020	Gates closed. No flow.
74684015	PIN	P114347-15	S355A	04/13/2020	Gates closed. No flow.
74684029	PIN	P114347-29	S12D	04/13/2020	Gates closed. No flow.
74684030	PIN	P114347-30	S12C	04/13/2020	Gates closed. No flow.
74684031	PIN	P114347-31	S12B	04/13/2020	Gates closed. No flow.
74921005	PIE	P114811-5	G737	04/14/2020	Gates closed. No flow.
74750031	PIE	P114490-31	S328	04/14/2020	Gates closed. No flow.
75718028	PIN	P116436-28	S12D	04/20/2020	Gates closed. No flow.
75718029	PIN	P116436-29	S12C	04/20/2020	Gates closed. No flow.
75718030	PIN	P116436-30	S12B	04/20/2020	Gates closed. No flow.
75609004	PIE	P116222-4	BERMB3	04/21/2020	Too shallow to sample.
75609006	PIE	P116222-6	G737	04/21/2020	Gates closed. No flow.
75602034	PIE	P116198-34	S328	04/21/2020	Gates closed. No flow.
74920028	PIE	P114810-28	G760	04/23/2020	Too shallow to sample.
74920029	PIE	P114810-29	G761	04/24/2020	Too shallow to sample.
74920030	PIE	P114810-30	G762	04/25/2020	Too shallow to sample.
75712032	PIN	P116424-32	S12D	04/27/2020	Gates closed. No flow.
75712033	PIN	P116424-33	S12C	04/27/2020	Gates closed. No flow.
75712034	PIN	P116424-34	S12B	04/27/2020	Gates closed. No flow.
75603005	PIE	P116229-5	G737	04/28/2020	Gates closed. No flow.
75591031	PIE	P116210-31	S328	04/28/2020	Gates closed. No flow.
75713025	PIN	P116442-25	S12D	05/04/2020	Gates closed. No flow.
75713026	PIN	P116442-26	S12C	05/04/2020	Gates closed. No flow.
75713027	PIN	P116442-27	S12B	05/04/2020	Gates closed. No flow.
76059007	EVPA	P117154-7	LOX7	05/05/2020	Too shallow to sample.
76059006	EVPA	P117154-6	LOX8	05/05/2020	Too shallow to sample.
76059005	EVPA	P117154-5	LOX9	05/05/2020	Too shallow to sample.
76059004	EVPA	P117154-4	LOX10	05/05/2020	Too shallow to sample.
76059003	EVPA	P117154-3	LOX5	05/05/2020	Too shallow to sample.
76059002	EVPA	P117154-2	LOX3	05/05/2020	Too shallow to sample.
76059009	EVPA	P117154-9	LOX4	05/05/2020	Too shallow to sample.
75610004	PIE	P116241-4	BERMB3	05/05/2020	Too shallow to sample.
75610006	PIE	P116241-6	G737	05/05/2020	Gates closed. No flow.
75592031	PIE	P116211-31	S328	05/05/2020	Gates closed. No flow.

Table 2. Continued.

Work Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Not Collected
74883002	EVPA	P114736-2	LOX6	05/06/2020	Too shallow to sample.
75707013	PIN	P116430-13	S355B	05/11/2020	Gates closed. No flow.
75707015	PIN	P116430-15	S355A	05/11/2020	Gates closed. No flow.
75707029	PIN	P116430-29	S12D	05/11/2020	Gates closed. No flow.
75707031	PIN	P116430-31	S12B	05/11/2020	Gates closed. No flow.
75707030	PIN	P116430-30	S12C	05/11/2020	Gates closed. No flow.
75604005	PIE	P116230-5	G737	05/12/2020	Gates closed. No flow.
75593031	PIE	P116212-31	S328	05/12/2020	Gates closed. No flow.
75714025	PIN	P116443-25	S12D	05/18/2020	Gates closed. No flow.
75714026	PIN	P116443-26	S12C	05/18/2020	Gates closed. No flow.
75714027	PIN	P116443-27	S12B	05/18/2020	Gates closed. No flow.
75611004	PIE	P116242-4	BERMB3	05/19/2020	Too shallow to sample.
75611006	PIE	P116242-6	G737	05/19/2020	Gates closed. No flow.
75594031	PIE	P116213-31	S328	05/19/2020	Gates closed. No flow.
75708029	PIN	P116431-29	S12D	05/26/2020	Gates closed. No flow.
75708030	PIN	P116431-30	S12C	05/26/2020	Gates closed. No flow.
75708031	PIN	P116431-31	S12B	05/26/2020	Gates closed. No flow.
75715025	PIN	P116444-25	S12D	06/01/2020	Gates closed. No flow.
75715026	PIN	P116444-26	S12C	06/01/2020	Gates closed. No flow.
75715027	PIN	P116444-27	S12B	06/01/2020	Gates closed. No flow.
75612004	PIE	P116243-4	BERMB3	06/02/2020	Too shallow to sample.
75612006	PIE	P116243-6	G737	06/02/2020	Gates closed. No flow.
76306007	EVPA	P117626-7	LOX10	06/02/2020	Too shallow to sample.
76306006	EVPA	P117626-6	LOX5	06/02/2020	Too shallow to sample.
75709013	PIN	P116432-13	S355B	06/08/2020	Gates closed. No flow.
75709015	PIN	P116432-15	S355A	06/08/2020	Gates closed. No flow.
75709031	PIN	P116432-31	S12B	06/08/2020	Gates closed. No flow.
75606005	PIE	P116232-5	G737	06/09/2020	Gates closed. No flow.
75716027	PIN	P116445-27	S12B	06/15/2020	Gates closed. No flow.
75613006	PIE	P116244-6	G737	06/16/2020	Gates closed. No flow.
75710031	PIN	P116433-31	S12B	06/22/2020	Gates closed. No flow.
75607005	PIE	P116233-5	G737	06/23/2020	Gates closed. No flow.
75717027	PIN	P116446-27	S12B	06/29/2020	Gates closed. No flow.
75614006	PIE	P116245-6	G737	06/30/2020	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 44 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 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 304 TP analyses for the grab samples collected during the 44 sampling events listed in **Table 1**. Of those 304 TP results, 117 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 304 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 117 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 117 TP results reported, no result was below the MDL and one sample 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:

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

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.

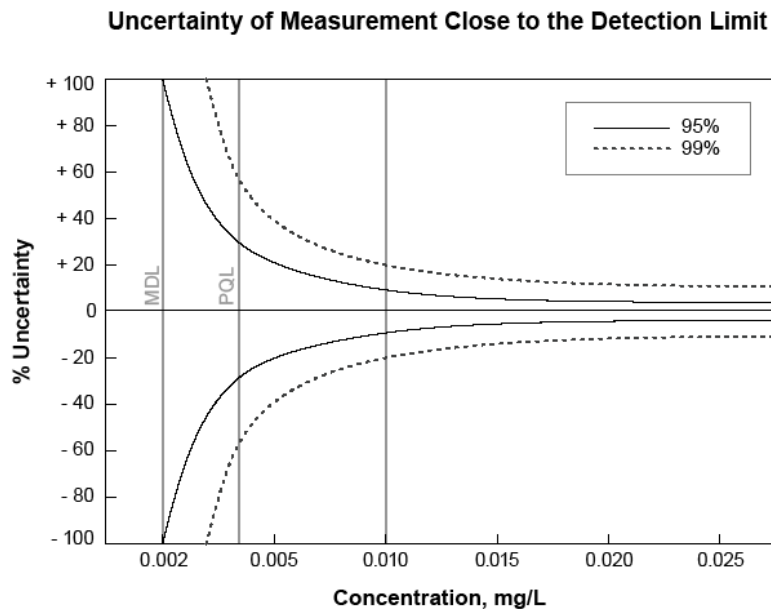


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 second quarter of 2020, the laboratory received TP results from one performance test study, Phenova #0420. The reported result was evaluated as "acceptable" with a calculated Z-score of 0.018.

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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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).