

# Quality Assessment Report for Water Quality Monitoring

January – March 2017



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## INTRODUCTION

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This report is an assessment of the South Florida Water Management District (SFWMD) laboratory analysis and field sampling for total phosphorus (TP) monitoring, primarily for the following projects and their associated stations from January 1, 2017, through March 31, 2017. 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 May 19, 2017.

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356-334
- Everglades National Park Inflow East (PIE): S332DX, S18C, S328, and BERMB3
- Everglades Protection Area (EVPA): LOX3 through LOX16

The SFWMD's *Field Sampling Quality Manual* (SFWMD 2015) provides the requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2017) 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\_010117\_to\_033117.xlsx" was created and contains all TP results and 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 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.

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## FIELD SAMPLING QUALITY ASSESSMENT

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### SAMPLE COLLECTION

A total of 46 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 Laboratory Information Management System (LIMS) for the 46 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 46 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 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.

<b>Work Identifier</b>	<b>Work Order</b>	<b>Project <sup>a</sup></b>	<b>Date Collected</b>
P87383	59146	PIN	01/03/2017
P87545	59304	PIE/S357P	01/03/2017
P87154	58988	PIE	01/04/2017
P87598	59355	EVPA	01/04/2017
P87600	59357	EVPA	01/05/2017
P87386	59149	PIN	01/09/2017
P87552	59311	PIE/S357P	01/09/2017
P87576	59332	PIE	01/10/2017
P87384	59147	PIN	01/17/2017
P87546	59305	PIE/S357P	01/17/2017
P87566	59325	PIE	01/18/2017
P87387	59150	PIN	01/23/2017
P87553	59312	PIE/S357P	01/23/2017
P87577	59333	PIE	01/24/2017
P87385	59148	PIN	01/30/2017
P87547	59306	PIE/S357P	01/30/2017
P87573	59329	PIE/BBCW	01/31/2017
P87599	59356	EVPA	02/01/2017
P87870	59629	PIN	02/01/2017
P87601	59358	EVPA	02/02/2017
P87554	59313	PIE/S357P	02/06/2017
P87662	59415	PIN	02/06/2017
P87578	59334	PIE	02/07/2017
P87559	59318	PIE/S357P	02/13/2017
P87664	59421	PIN	02/13/2017
P87572	59328	PIE	02/14/2017
P87555	59314	PIE/S357P	02/20/2017
P87667	59422	PIN	02/20/2017
P87579	59335	PIE	02/21/2017
P87549	59308	PIE/S357P	02/27/2017
P87574	59330	PIE/BBCW	02/28/2017
P88049	59778	PIN/NECP	02/28/2017
P87556	59315	PIE/S357P	03/06/2017
P88155	59844	PIN	03/06/2017
P87580	59336	PIE	03/07/2017
P88143	59832	EVPA	03/08/2017
P88144	59833	EVPA	03/09/2017
P87550	59309	PIE/S357P	03/13/2017
P87876	59635	PIN	03/13/2017
P87570	59326	PIE	03/14/2017
P87557	59316	PIE/S357P	03/20/2017
P88156	59845	PIN	03/20/2017
P87581	59337	PIE	03/21/2017
P87551	59310	PIE/S357P	03/27/2017
P88157	59846	PIN	03/27/2017
P87575	59331	PIE/BBCW	03/28/2017

a. 357P – 357 Pump Station; BBCW – Biscayne Bay Coastal Wetlands; EVPA – Everglades Protection Area; NECP – Non-Everglades Construction Project; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.

**Table 2.** Grab samples not collected during the reporting period.

<b>Work Identifier</b>	<b>Project</b>	<b>Sample Identifier</b>	<b>Station</b>	<b>Date Collected</b>	<b>Reason Sample Was Not Collected</b>
P87383	PIN	P87383-12	S12B	1/3/2017	No flow
P87383	PIN	P87383-13	S12C	1/3/2017	No flow
P87383	PIN	P87383-14	S12D	1/3/2017	No flow
P87598	EVPA	P87598-2	LOX5	1/4/2017	Too shallow to sample
P87154	PIE	P87154-9	BERMB3	1/4/2017	Too shallow to sample
P87386	PIN	P87386-11	S12B	1/9/2017	No flow
P87386	PIN	P87386-12	S12C	1/9/2017	No flow
P87386	PIN	P87386-13	S12D	1/9/2017	No flow
P87384	PIN	P87384-12	S12B	1/17/2017	No flow
P87384	PIN	P87384-13	S12C	1/17/2017	No flow
P87566	PIE	P87566-9	BERMB3	1/18/2017	No flow
P87387	PIN	P87387-11	S12B	1/23/2017	No flow
P87387	PIN	P87387-12	S12C	1/23/2017	No flow
P87387	PIN	P87387-25	S355A	1/23/2017	No flow
P87387	PIN	P87387-27	S355B	1/23/2017	No flow
P87385	PIN	P87385-12	S12B	1/30/2017	No flow
P87385	PIN	P87385-13	S12C	1/30/2017	No flow
P87573	PIE	P87573-10	BERMB3	1/31/2017	No flow
P87599	EVPA	P87599-2	LOX5	2/1/2017	Too shallow to sample
P87662	PIN	P87662-11	S12B	2/6/2017	No flow
P87662	PIN	P87662-12	S12C	2/6/2017	No flow
P87662	PIN	P87662-13	S12D	2/6/2017	No flow
P87664	PIN	P87664-12	S12B	2/13/2017	No flow
P87664	PIN	P87664-13	S12C	2/13/2017	No flow
P87572	PIE	P87572-10	BERMB3	2/14/2017	No flow
P87667	PIN	P87667-11	S12B	2/20/2017	No flow
P87667	PIN	P87667-12	S12C	2/20/2017	No flow
P87667	PIN	P87667-13	S12D	2/20/2017	No flow
P87667	PIN	P87667-23	S355A	2/20/2017	No flow
P87667	PIN	P87667-25	S355B	2/20/2017	No flow
P87574	PIE	P87574-10	BERMB3	2/28/2017	No flow
P88049	PIN	P88049-13	S12B	2/28/2017	No flow
P88049	PIN	P88049-14	S12C	2/28/2017	No flow
P88049	PIN	P88049-15	S12D	2/28/2017	No flow
P88155	PIN	P88155-12	S12B	3/6/2017	No flow
P88155	PIN	P88155-13	S12C	3/6/2017	No flow
P88155	PIN	P88155-14	S12D	3/6/2017	No flow
P88155	PIN	P88155-25	S355A	3/6/2017	No flow
P88155	PIN	P88155-27	S355B	3/6/2017	No flow
P88143	EVPA	P88143-4	LOX3	3/8/2017	Too shallow to sample
P88143	EVPA	P88143-5	LOX5	3/8/2017	Too shallow to sample
P87876	PIN	P87876-12	S12B	3/13/2017	No flow
P87876	PIN	P87876-13	S12C	3/13/2017	No flow
P87876	PIN	P87876-14	S12D	3/13/2017	No flow
P87570	PIE	P87570-9	BERMB3	3/14/2017	No flow
P88156	PIN	P88156-12	S12B	3/20/2017	No flow
P88156	PIN	P88156-13	S12C	3/20/2017	No flow
P88156	PIN	P88156-14	S12D	3/20/2017	No flow
P88157	PIN	P88157-12	S12B	3/27/2017	No flow
P88157	PIN	P88157-13	S12C	3/27/2017	No flow
P88157	PIN	P88157-14	S12D	3/27/2017	No flow
P87575	PIE	P87575-10	BERMB3	3/28/2017	No flow

## FIELD QUALITY CONTROL

To assess the quality of the sample collection process and as required by the *Field Sampling Quality Manual* (SFWMD 2015), 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 *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 field generated equipment blanks (EB), field-cleaned equipment blanks (FCEB), field blanks (FB), and replicate samples (RS). It should be noted that 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 46 sampling events described above, a total of 67 FBs and ten RSs were collected. All 67 FBs had concentrations below the TP method detection limit (MDL) of 0.002 milligrams per liter (mg/L) and it was not necessary to add any qualifiers to associated samples as a result of blank contamination. The replicate samples were evaluated according to the specifications described in the *Field Sampling Quality Manual* (SFWMD 2015) and none of the TP sample results collected for the project/locations described in the *Introduction* were qualified as a result of insufficient precision in replicate sampling. The results of all field quality control samples can be found in the RDS.

## FIELD PROJECT MANAGEMENT

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.

For grab samples collected at locations described in the *Introduction*, five remark codes were added by field project managers to TP sample results as shown in **Table 3**. These remark codes include any assigned as per the Florida Department of Environmental Protection (FDEP) *Quality Assessment Rule* (Chapter 62-160, F.A.C.) and/or 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 *Quality Assessment Rule*.

**Table 3.** Results with Remark Codes by field project managers during the reporting period.

Work Identifier	Project	Sample Identifier	Station	Collection Date	Remark Code(s)/Reason <sup>a</sup>
P87598	EVPA	P87598-1	LOX3	01/04/2017	PMR / TD between 0.10 and 0.20m. Partial sample. TPO4 only.
P87598	EVPA	P87598-3	LOX10	01/04/2017	PMR / TD between 0.10 and 0.20m. Partial sample. TPO4 only.
P87598	EVPA	P87598-4	LOX9	01/04/2017	PMR / Returned to PBIA to wait out storm before continuing to this site. TD between 0.10 and 0.20m. Partial sample. TPO4 only.
P87598	EVPA	P87598-6	LOX7	01/04/2017	PMR / TD between 0.10 and 0.20m. Partial sample. TPO4 only.
P87598	EVPA	P87598-8	LOX4	01/04/2017	PMR / Staff Gauge Reading 17.00. TD between 0.10 and 0.20m. Partial sample. TPO4 only.

a. Definitions of abbreviations: m – meter; PBIA – Palm Beach International Airport; PMR – project manager remark; TD – total depth; and TPO4 – total phosphorus.

## FIELD AUDITS

SFWMD did not conduct any field audits on Everglades Technical Oversight Committee (TOC)-related projects during the first quarter of 2017.

## FIELD PROCEDURE UPDATES

No major procedural updates related to TP sample collection were made during the period specified in this report.

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# LABORATORY ANALYSIS QUALITY ASSESSMENT

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## SAMPLE ANALYSES

The SFWMD Laboratory conducted a total of 300 TP analyses for the grab samples collected during the 46 sampling events listed in **Table 1**. Of those 300 results, 155 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 300 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 laboratory in analytical batches of approximately 100 samples. In order 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 2017). The results of these laboratory quality control samples are associated with some or all of 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 (LCS), matrix spikes (MS), precision checks (DUP or MSD), and method blanks (MB).

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 no universally accepted (or required) method for determination of the PQL. In the case of TP analyses, the SFWMD 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 114 results reported, no results were below the MDL and seven samples had a concentration between the MDL and PQL and were therefore qualified with an “I”.

## 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 Laboratory provides uncertainty estimates using the nested hierarchical methodology by Ingersoll (2001) in combination with a mathematical model found in Eurachem/CITAC (2000). 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:

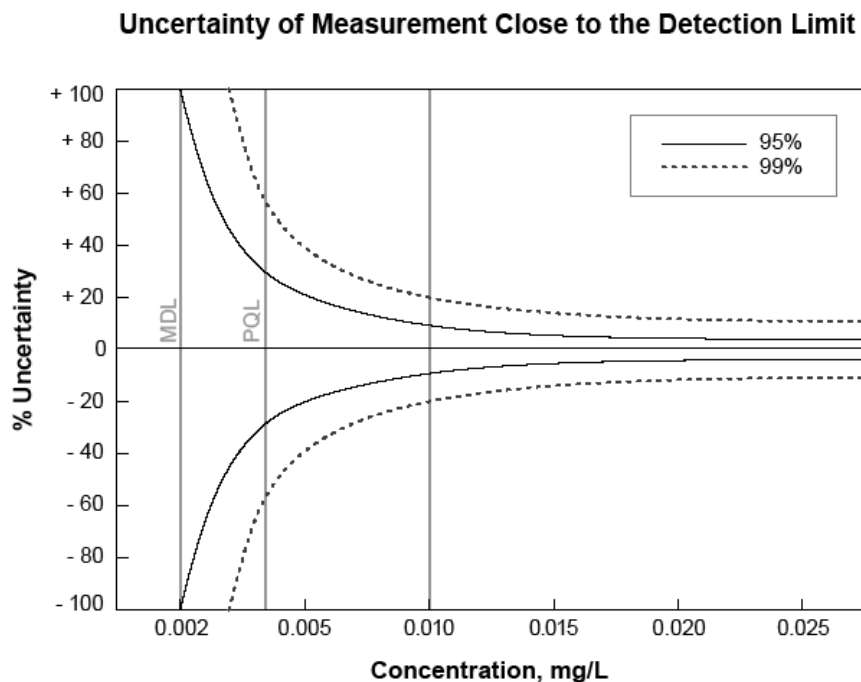
**U(x)** is the combined standard uncertainty in the result x at the 95% confidence interval (CI).

**S<sub>0</sub>** – a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.

**S<sub>1</sub>** – proportionality constant derived from nested hierarchical methodology by Ingersoll (2001).

During this reporting period, the uncertainty constants are **S<sub>0</sub>** = 0.002 and **S<sub>1</sub>** = 0.068. Estimated uncertainties are calculated automatically by LIMS using the equation and constants shown above and are provided with all of the 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 laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During this reporting period, no proficiency testing samples for TP analysis were completed. During this reporting period, no performance evaluation samples for TP analysis were completed.

## LABORATORY AUDITS

There were no laboratory audits conducted during this reporting period.

## PROCEDURE UPDATES

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



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## REFERENCES

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## GLOSSARY

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**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, the 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, the 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 percent 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.

**Relative Percent Difference (RPD):** A measure of precision, used when comparing two values. It is calculated as  $\%RPD = [Value1 - Value2]/Mean \times 100$ .

**Relative Standard Deviation (RSD):** A measurement of precision, used when comparing more than two results. It is calculated as  $\%RSD = [Standard\ Deviation/Mean] \times 100$ .

**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 ( $X_i$ ) from the assigned value ( $X$ ) for that determinant (calculated as  $z = (X_i - X)/s$ , where  $s$  is a standard deviation) (Eurachem/CITAC 2000).