

# Quality Assessment Report for Water Quality Monitoring

January – March 2019



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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), primarily for the following projects and their associated stations from January 1, 2019, through March 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 May 9, 2019.

- 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 SFWMD's *Field Sampling Quality Manual* (SFWMD 2017) provides the requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2019) 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\_010119\_to\_033119.xlsx" was created and contains all TP results and any 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 (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.

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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 the Laboratory Information Management System (LIMS) for the 46 sampling events is shown in **Table 1**. The table details the work identifiers, work order numbers, project codes, and dates samples were collected.

**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>
P101017	69010	PIN	01/02/2019
P99238	68518	PIE	01/02/2019
P99716	68735	PIE	01/02/2019
P100607	68886	PIN	01/08/2019
P100619	68890	PIE	01/08/2019
P99717	68736	PIE	01/08/2019
P101258	69068	EVPA	01/09/2019
P101538	69210	EVPA	01/10/2019
P101018	69011	PIN	01/14/2019
P99239	68519	PIE	01/15/2019
P99718	68737	PIE	01/16/2019
P101811	69324	PIN	01/22/2019
P100620	68891	PIE	01/22/2019
P99719	68738	PIE	01/22/2019
P101019	69012	PIN	01/28/2019
P99240	68520	PIE	01/29/2019
P99720	68739	PIE	01/30/2019
P101812	69325	PIN	02/04/2019
P101259	69069	EVPA	02/05/2019
P99721	68740	PIE	02/05/2019
P100621	68892	PIE	02/05/2019
P101539	69211	EVPA	02/06/2019
P102783	69776	PIN	02/12/2019
P99724	68743	PIE	02/12/2019
P99242	68522	PIE	02/12/2019
P102801	69786	PIN	02/18/2019
P100622	68893	PIE	02/19/2019
P99723	68742	PIE	02/19/2019
P101021	69014	PIN	02/25/2019
P103391	70009	PIE	02/26/2019
P103534	70069	PIE	02/26/2019
P101814	69327	PIN	03/05/2019
P103993	70299	EVPA	03/05/2019
P100623	68894	PIE	03/05/2019
P99725	68744	PIE	03/05/2019
P104072	70331	PIN	03/05/2019
P104000	70303	EVPA	03/06/2019
P101022	69015	PIN	03/11/2019
P99243	68523	PIE	03/12/2019
P99726	68745	PIE	03/12/2019
P101815	69328	PIN	03/19/2019
P100624	68895	PIE	03/19/2019
P99727	68746	PIE	03/19/2019
P101023	69016	PIN	03/25/2019
P99244	68524	PIE	03/26/2019
P99728	68747	PIE	03/26/2019

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

During the 46 sampling events described above, a total of 59 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 is shown in **Table 2**.

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

<b>Work Identifier</b>	<b>Project<sup>a</sup></b>	<b>Sample Identifier</b>	<b>Station</b>	<b>Date</b>	<b>Reason Sample Was Not Collected</b>
P99238	PIE	P99238-4	BERMB3	01/02/2019	No flow.
P101017	PIN	P101017-14	S12D	01/02/2019	No flow.
P101017	PIN	P101017-13	S12C	01/02/2019	No flow.
P101017	PIN	P101017-12	S12B	01/02/2019	No flow.
P100607	PIN	P100607-14	S12B	01/07/2019	No flow.
P100607	PIN	P100607-15	S12C	01/07/2019	No flow.
P100607	PIN	P100607-16	S12D	01/07/2019	No flow.
P101258	EVPA	P101258-5	LOX9	01/09/2019	Too shallow to sample.
P101258	EVPA	P101258-4	LOX10	01/09/2019	Too shallow to sample.
P101258	EVPA	P101258-3	LOX5	01/09/2019	No flow.
P101258	EVPA	P101258-2	LOX3	01/09/2019	No flow.
P101018	PIN	P101018-14	S12D	01/14/2019	No flow.
P101018	PIN	P101018-13	S12C	01/14/2019	No flow.
P101018	PIN	P101018-12	S12B	01/14/2019	No flow.
P99239	PIE	P99239-4	BERMB3	01/15/2019	No flow.
P101811	PIN	P101811-29	S355B	01/22/2019	No flow.
P101811	PIN	P101811-27	S355A	01/22/2019	No flow.
P101811	PIN	P101811-12	S12B	01/22/2019	No flow.
P101811	PIN	P101811-13	S12C	01/22/2019	No flow.
P101811	PIN	P101811-14	S12D	01/22/2019	No flow.
P101019	PIN	P101019-14	S12D	01/28/2019	No flow.
P101019	PIN	P101019-13	S12C	01/28/2019	No flow.
P101019	PIN	P101019-12	S12B	01/28/2019	No flow.
P99240	PIE	P99240-4	BERMB3	01/29/2019	Too shallow to sample.
P101812	PIN	P101812-29	S355B	02/04/2019	No flow.
P101812	PIN	P101812-27	S355A	02/04/2019	No flow.
P101812	PIN	P101812-12	S12B	02/04/2019	No flow.
P101812	PIN	P101812-14	S12D	02/04/2019	No flow.
P101812	PIN	P101812-13	S12C	02/04/2019	No flow.
P99242	PIE	P99242-4	BERMB3	02/12/2019	No flow.
P102783	PIN	P102783-14	S12D	02/12/2019	No flow.
P102783	PIN	P102783-13	S12C	02/12/2019	No flow.
P102783	PIN	P102783-12	S12B	02/12/2019	No flow.
P102801	PIN	P102801-17	S12D	02/18/2019	No flow.
P102801	PIN	P102801-16	S12C	02/18/2019	No flow.
P102801	PIN	P102801-15	S12B	02/18/2019	No flow.

**Table 2.** Continued.

Work Identifier	Project <sup>a</sup>	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P101021	PIN	P101021-12	S12B	02/25/2019	No flow.
P101021	PIN	P101021-13	S12C	02/25/2019	No flow.
P101021	PIN	P101021-14	S12D	02/25/2019	No flow.
P103534	PIE	P103534-4	BERMB3	02/26/2019	Too shallow to sample.
P104072	PIN	P104072-27	S355A	03/05/2019	No flow.
P104072	PIN	P104072-29	S355B	03/05/2019	No flow.
P104072	PIN	P104072-12	S12B	03/05/2019	No flow.
P104072	PIN	P104072-13	S12C	03/05/2019	No flow.
P104072	PIN	P104072-14	S12D	03/05/2019	No flow.
P101022	PIN	P101022-12	S12B	03/11/2019	No flow.
P101022	PIN	P101022-13	S12C	03/11/2019	No flow.
P101022	PIN	P101022-14	S12D	03/11/2019	No flow.
P99243	PIE	P99243-4	BERMB3	03/12/2019	No flow.
P99243	PIE	P99243-6	G737	03/12/2019	No flow.
P101815	PIN	P101815-13	S12C	03/18/2019	No flow.
P101815	PIN	P101815-14	S12D	03/18/2019	No flow.
P101815	PIN	P101815-12	S12B	03/18/2019	No flow.
P100624	PIE	P100624-5	G737	03/19/2019	No flow.
P101023	PIN	P101023-14	S12D	03/25/2019	No flow.
P101023	PIN	P101023-13	S12C	03/25/2019	No flow.
P101023	PIN	P101023-12	S12B	03/25/2019	No flow.
P99244	PIE	P99244-4	BERMB3	03/26/2019	Too shallow to sample.
P99244	PIE	P99244-6	G737	03/26/2019	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 and as required by the *Field Sampling Quality Manual* (SFWMD 2017), 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 Florida Department of Environmental Protection's (FDEP's) *Quality Assurance 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 replicate samples (RS), and field blank controls (FBCs), 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 46 sampling events described above, a total of 26 FBCs and 6 RSs were collected. None of the FBCs had a concentration at 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 samplers 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*, 1 PMR was assigned by project managers and 8 J qualifiers were assigned as per FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). These qualifiers and the remark code are detailed in **Table 3**.

**Table 3.** Results with qualifiers and remark codes during the reporting period.

Work Identifier	Project <sup>a</sup>	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
P100620	PIE	P100620-4	G737	01/22/2019	PMR / Incorrect depth values were not modified as no verification is available. Depth (0.40 m) was recorded at twice the value of total depth (0.20 m). Suspect a data entry error and the values were switched. (Note: m – meters)
P99719	PIE	P99719-31	S328	01/22/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99720	PIE	P99720-31	S328	01/29/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99721	PIE	P99721-31	S328	02/05/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99724	PIE	P99724-31	S328	02/12/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99723	PIE	P99723-31	S328	02/19/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P103391	PIE	P103391-34	S328	02/26/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99725	PIE	P99725-31	S328	03/05/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.
P99726	PIE	P99726-31	S328	03/12/2019	J / Improper laboratory or field protocol. Sample collected from disconnected pool and is not representative of surrounding area.

a. PIE – Everglades National Park Inflows East.

## FIELD AUDITS

SFWMD conducted one field audit on the PIN project during the first quarter of 2019. One “Quality Improvement” was issued concerning storage of the nitric acid preserved samples, which did not impact the TP sample data. After a review of this deficiency during this sampling trip, it was determined the deficiency observed during the audit 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.

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## LABORATORY ANALYSIS QUALITY ASSESSMENT

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### SAMPLE ANALYSES

The SFWMD Environmental Services Laboratory conducted a total of 336 TP analyses for the grab samples collected during the 46 sampling events listed in **Table 1**. Of those 336 results, 134 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 336 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 Environmental Services 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 2019). The results of these laboratory quality control samples are associated with some or all 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*. 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 134 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 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 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 151 results reported, no result was below the MDL and nine samples had a concentration between the MDL and 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:

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

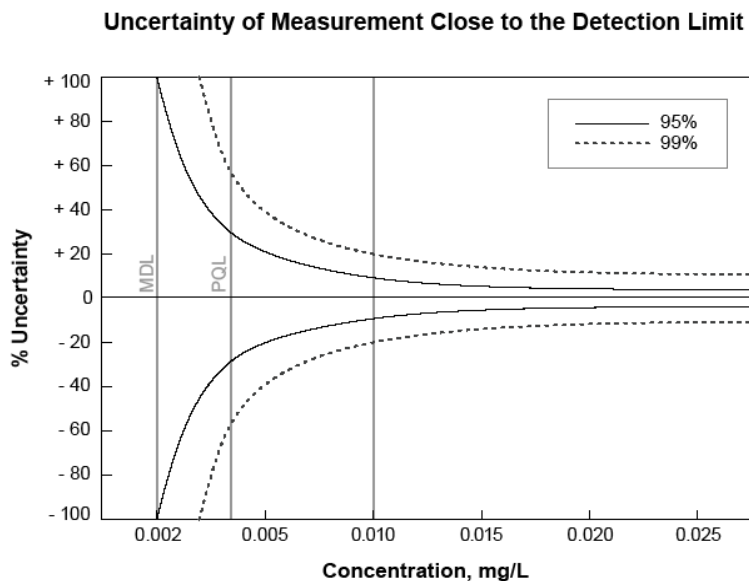
where:

$U(x)$  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** 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 Analytical Services Chemistry Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During this reporting period, no proficiency testing or performance evaluation samples were completed for TP analysis.

## LABORATORY AUDITS

There was one internal laboratory audit conducted during this reporting period. A total of 18 findings or observations of this audit were reported and followed-up by the auditor to confirm the recommended corrective action plan developed in response to this internal audit were completed within an agreed timeframe.



## PROCEDURE UPDATES

The SFWMD's *Chemistry Laboratory Quality Manual* was revised in January. 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, 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.

**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  $z = (X_i - X)/\sigma$ , where  $\sigma$  is a standard deviation) (Eurachem/CITAC 2012).