

Quality Assessment Report for Water Quality Monitoring

July – September 2017



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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 July 1, 2017, through September 30, 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 November 27, 2017.

- 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 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_070117_to_093017.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 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.

FIELD SAMPLING QUALITY ASSESSMENT

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 nine 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, excessive vegetation, 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.

Work Identifier	Work Order	Project ^a	Date Collected
P89662	61250	PIN	07/05/2017
P89798	61385	PIE/S357P	07/05/2017
P89823	61416	PIE	07/05/2017
P89656	61244	PIN	07/10/2017
P89813	61400	EVPA	07/10/2017
P89799	61386	PIE/S357P	07/11/2017
P89815	61402	EVPA	07/11/2017
P89836	61418	PIE	07/11/2017
P89663	61251	PIN	07/17/2017
P89805	61392	PIE/S357P	07/18/2017
P89824	61417	PIE	07/18/2017
P89657	61245	PIN	07/24/2017
P89800	61387	PIE/S357P	07/25/2017
P89842	61430	PIE/BBCW	07/25/2017
P89664	61252	PIN	08/01/2017
P89814	61401	EVPA	08/01/2017
P89831	61424	PIE	08/01/2017
P89920	61517	PIE/S357P	08/01/2017
P89816	61403	EVPA	08/02/2017
P89658	61246	PIN	08/07/2017
P89801	61388	PIE/S357P	08/08/2017
P89838	61420	PIE	08/08/2017
P89665	61253	PIN	08/14/2017
P89832	61425	PIE	08/15/2017
P89921	61518	PIE/S357P	08/15/2017
P89659	61247	PIN	08/21/2017
P89802	61389	PIE/S357P	08/22/2017
P89843	61431	PIE/BBCW	08/22/2017
P89666	61254	PIN	08/28/2017
P89833	61426	PIE	08/29/2017
P89922	61519	PIE/S357P	08/29/2017
P89660	61248	PIN	09/05/2017
P89803	61390	PIE/S357P	09/05/2017
P89840	61422	PIE	09/05/2017
P90469	62014	EVPA	09/06/2017
P89667	61255	PIN	09/13/2017
P89654	61242	PIN	09/14/2017
P89834	61427	PIE	09/14/2017
P89923	61520	PIE/S357P	09/14/2017
P90470	62015	EVPA	09/14/2017
P89661	61249	PIN	09/18/2017
P89804	61391	PIE/S357P	09/19/2017
P89844	61432	PIE/BBCW	09/19/2017
P89668	61256	PIN	09/25/2017
P89835	61428	PIE	09/26/2017
P89924	61521	PIE/S357P	09/26/2017

a. S357P – S357 Pump Station; BBCW – Biscayne Bay Coastal Wetlands; 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	Sample Identifier	Station	Date	Reason Sample Was Not Collected
61400005	EVPA	P89813-5	LOX8	7/10/2017	Too shallow to sample
61392029	PIE	P89805-29	BERMB3	7/18/2017	Too shallow to sample
61245025	PIN	P89657-25	S355A	7/24/2017	No flow
61424013	PIE	P89831-13	BERMB3	8/1/2017	Too shallow to sample
61425013	PIE	P89832-13	BERMB3	8/15/2017	Too shallow to sample
61247025	PIN	P89659-25	S355A	8/21/2017	No flow
61426013	PIE	P89833-13	BERMB3	8/29/2017	Too much vegetation to sample
61248025	PIN	P89660-25	S355A	9/5/2017	No flow
62014004	EVPA	P90469-4	LOX3	9/6/2017	Too shallow to sample

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 (EBs), field-cleaned equipment blanks (FCEBs), field blanks (FBs), and replicate samples (RSs). 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 63 FBs and six RSs were collected. No FBs had concentrations at or above the TP method detection limit (MDL) of 0.002 milligrams per liter (mg/L). For grab samples collected at locations described in the *Introduction*, no qualifiers were assigned as per the Florida Department of Environmental Protection (FDEP) *Quality Assessment Rule* (Chapter 62-160, F.A.C.).

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 *Quality Assessment Rule*. For grab samples collected at locations described in the *Introduction*, one remark code was added by the field project manager to TP sample result as shown in **Table 3**.

Table 3. Results with Remark Codes during the reporting period.

Work Identifier	Project	Sample Identifier	Station	Collection Date	Remark Code/Reason
61254025	PIN	P89666-25	S356-334	8/28/2017	PMR/ Depth not recorded on Chain of Custody

FIELD AUDITS

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

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 Environmental Services Laboratory conducted a total of 444 TP analyses for the grab samples collected during the 46 sampling events listed in **Table 1**. Of those 444 results, 213 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 444 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. 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 (LCSs), matrix spikes (MSs), precision checks (DUPs or MSDs), and method blanks (MBs). For the 213 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 Environmental Services 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 213 results reported, no results were below the MDL and no 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 Environmental Services 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_0 – a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.

S_1 – 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 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.

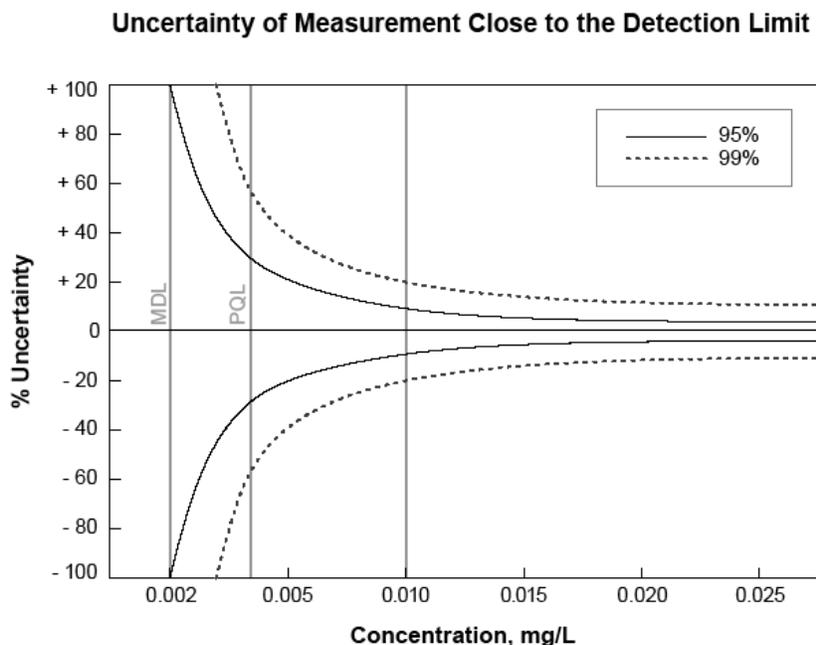


Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

PROFICIENCY TESTING AND EVALUATION

The SFWMD Environmental Services Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During this reporting period, performance evaluation samples for TP analysis were completed through Environment Canada (Environmental Canada 2017) Program #110. The results reported by the SFWMD Environmental Services Laboratory were rated as "ideal" with no Z score greater than 0.8. During this reporting period, no proficiency testing 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.

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, 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.

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).