

Quality Assessment Report for Water Quality Monitoring

April – June 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) monitoring, primarily for the following projects and their associated stations from April 1, 2017, through June 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 August 15, 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_040117_to_063017.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 40 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 40 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 40 sampling events described above, a total of 45 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.

Work Identifier	Work Order	Project ^a	Date Collected
P87558	59317	PIE/S357P	04/03/2017
P88463	60142	PIN	04/03/2017
P87582	59338	PIE	04/04/2017
P88608	60280	EVPA	04/05/2017
P88465	60147	PIN	04/10/2017
P88521	60200	PIE/S357P	04/10/2017
P88545	60223	PIE	04/11/2017
P88468	60148	PIN	04/17/2017
P88528	60201	PIE/S357P	04/17/2017
P88539	60212	PIE	04/18/2017
P88469	60146	PIN	04/24/2017
P88534	60207	PIE/S357P	04/24/2017
P88548	60220	PIE/BBCW	04/25/2017
P88529	60202	PIE/S357P	05/01/2017
P88809	60467	PIN	05/01/2017
P88540	60213	PIE	05/02/2017
P88535	60208	PIE/S357P	05/08/2017
P88812	60470	PIN	05/08/2017
P88546	60218	PIE	05/09/2017
P88611	60283	EVPA	05/09/2017
P88609	60281	EVPA	05/11/2017
P88530	60203	PIE/S357P	05/15/2017
P88810	60468	PIN	05/15/2017
P88541	60214	PIE	05/16/2017
P88536	60209	PIE/S357P	05/22/2017
P88813	60471	PIN	05/22/2017
P88549	60221	PIE/BBCW	05/23/2017
P88531	60204	PIE/S357P	05/30/2017
P88811	60469	PIN	05/30/2017
P88542	60215	PIE	05/31/2017
P89044	60682	PIN	06/05/2017
P89312	60945	PIE	06/06/2017
P89046	60684	PIN	06/12/2017
P89223	60869	EVPA	06/12/2017
P89224	60870	EVPA	06/13/2017
P89309	60942	PIE	06/13/2017
P89045	60683	PIN	06/19/2017
P89313	60946	PIE	06/20/2017
P89047	60685	PIN	06/26/2017
P89310	60943	PIE	06/27/2017

a. S357P – S-357 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
60142012	PIN	P88463-12	S12B	4/3/2017	No flow
60142013	PIN	P88463-13	S12C	4/3/2017	No flow
60142014	PIN	P88463-14	S12D	4/3/2017	No flow
60147012	PIN	P88465-12	S12B	4/10/2017	No flow
60147013	PIN	P88465-13	S12C	4/10/2017	No flow
60147014	PIN	P88465-14	S12D	4/10/2017	No flow
60223010	PIE	P88545-10	BERMB3	4/11/2017	No flow
60148011	PIN	P88468-11	S12B	4/17/2017	No flow
60148012	PIN	P88468-12	S12C	4/17/2017	No flow
60148013	PIN	P88468-13	S12D	4/17/2017	No flow
60146012	PIN	P88469-12	S12B	4/24/2017	No flow
60146013	PIN	P88469-13	S12C	4/24/2017	No flow
60146014	PIN	P88469-14	S12D	4/24/2017	No flow
60220010	PIE	P88548-10	BERMB3	4/25/2017	No flow
60467012	PIN	P88809-12	S12B	5/1/2017	No flow
60467013	PIN	P88809-13	S12C	5/1/2017	No flow
60467014	PIN	P88809-14	S12D	5/1/2017	No flow
60470012	PIN	P88812-12	S12B	5/8/2017	No flow
60470013	PIN	P88812-13	S12C	5/8/2017	No flow
60470014	PIN	P88812-14	S12D	5/8/2017	No flow
60283002	EVPA	P88611-2	LOX5	5/9/2017	Too shallow to sample
60218009	PIE	P88546-9	BERMB3	5/9/2017	No flow
60468012	PIN	P88810-12	S12B	5/15/2017	No flow
60468013	PIN	P88810-13	S12C	5/15/2017	No flow
60468014	PIN	P88810-14	S12D	5/15/2017	No flow
60468025	PIN	P88810-25	S355A	5/15/2017	No flow
60468027	PIN	P88810-27	S355B	5/15/2017	No flow
60471012	PIN	P88813-12	S12B	5/22/2017	No flow
60471013	PIN	P88813-13	S12C	5/22/2017	No flow
60471014	PIN	P88813-14	S12D	5/22/2017	No flow
60221010	PIE	P88549-10	BERMB3	5/23/2017	No flow
60469025	PIN	P88811-25	S355A	5/30/2017	No flow
60469027	PIN	P88811-27	S355B	5/30/2017	No flow
60469012	PIN	P88811-12	S12B	5/30/2017	No flow
60469013	PIN	P88811-13	S12C	5/30/2017	No flow
60469014	PIN	P88811-14	S12D	5/30/2017	No flow
60682012	PIN	P89044-12	S12B	6/5/2017	No flow
60682013	PIN	P89044-13	S12C	6/5/2017	No flow
60682014	PIN	P89044-14	S12D	6/5/2017	No flow
60945012	PIE	P89312-12	BERMB3	6/6/2017	No flow
60684012	PIN	P89046-12	S12B	6/12/2017	No flow
60683012	PIN	P89045-12	S12B	6/19/2017	No flow
60685025	PIN	P89047-25	S355A	6/26/2017	No flow
60685027	PIN	P89047-27	S355B	6/26/2017	No flow
60685012	PIN	P89047-12	S12B	6/26/2017	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 40 sampling events described above, a total of 55 FBs and six RSs were collected. Two FBs had concentrations at the TP method detection limit (MDL) of 0.002 milligrams per liter (mg/L) and 53 FBs had concentrations below the TP MDL. Qualifiers were added to two associated samples because of blank contamination (as shown in **Table 3**). 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 because of insufficient precision in replicate sampling. The results of all field quality control samples can be found in the RDS.

Table 3. Results with Qualifiers during the reporting period.

Work Identifier	Project	Sample Identifier	Station	Collection Date	Qualifier/Reason
60223003	PIE	P88545-3	S18C	4/11/2017	G/ Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.
60221003	PIE	P88549-3	S18C	5/23/2017	G/ Analyte was detected at or above the method detection limit in both the sample and the associated field blank, equipment blank, or trip blank, and the blank value was greater than 10% of the associated sample value.

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*, no qualifiers or remark codes were added by field project managers to TP sample results.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the second 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 239 TP analyses for the grab samples collected during the 40 sampling events listed in **Table 1**. Of those 239 results, 120 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 239 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 (LCS), matrix spikes (MS), precision checks (DUP or MSD), and method blanks (MB).

For the 120 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 120 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:

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

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.

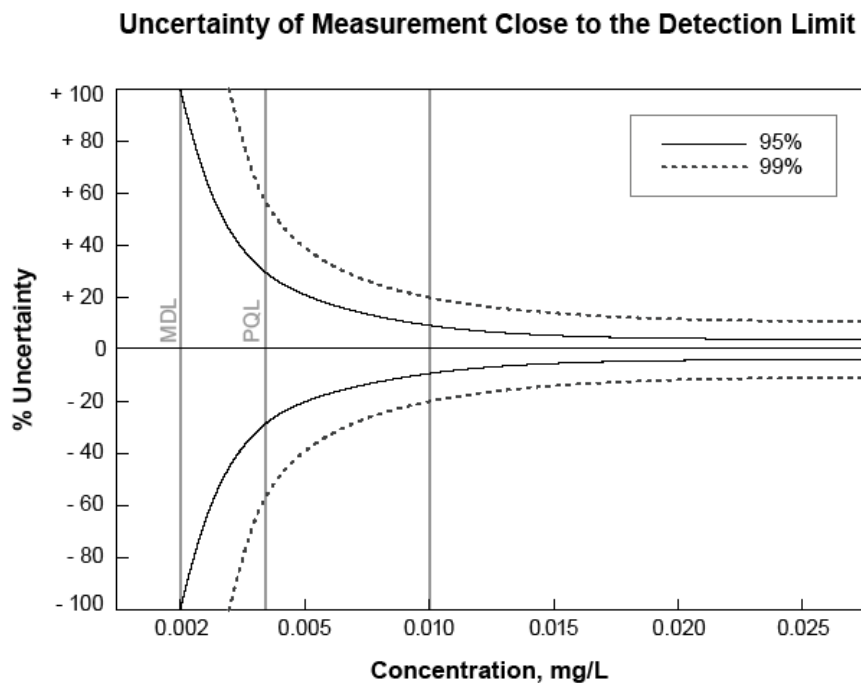


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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, proficiency testing samples for TP analysis were completed through ERA program WP-266. The TP result reported by SFWMD Environmental Services Laboratory for WP-266 was acceptable (ERA 2017). 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.

REFERENCES

- Eurachem/CITAC. 2000. *Quantifying Uncertainty in Analytical Measurement, Second Edition*. Guide CG4, Eurachem/CITAC, Austria. ISBN 0-948926-15-5.
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- JCGM. 1993. *International Vocabulary of Basic and General Standard Terms in Metrology*. Joint Committee on Guides for Metrology, Geneva, Switzerland. ISBN 92-67-10175-1.
- SFWMD. 2015. *Field Sampling Quality Manual*. SFWMD-FIELD-QM-001-08.2, South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 2017. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-2017, South Florida Water Management District, West Palm Beach, FL.

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).