Quality Assessment Report for Water Quality Monitoring

October – December 2016

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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 October 1, 2016, through December 31, 2016. 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 February 14, 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, DS4, and BERMB3
- Everglades Protection Area (EVPA): LOX3 through LOX16

The SFWMD's *Field Sampling Quality Manual* (SFWMD 2015b) provides the requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2015a) 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 Assessmen*t 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_100116_to_123116.xlxs" 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 bi-annual 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 45 sampling events were conducted that included collection of samples for the projects/locations and timeframe described in the *Introduction* section. A complete list of the laboratory work orders obtained from Laboratory Information Management System (LIMS) for the 45 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 45 sampling events described above, a total of 18 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
P85997	58103	PIN	10/03/2016
P86068	58160	PIE/S357P	10/03/2016
P84677	56917	EVPA	10/04/2016
P86098	58189	PIE	10/04/2016
P84673	56913	EVPA	10/10/2016
P86000	58106	PIN	10/10/2016
P86075	58159	PIE/S357P	10/10/2016
P86105	58198	PIE	10/11/2016
P85998	58104	PIN	10/17/2016
P86069	58161	PIE/S357P	10/17/2016
P86099	58190	PIE	10/18/2016
P86001	58107	PIN	10/24/2016
P86076	58168	PIE/S357P	10/24/2016
P86065	58156	PIE/BBCW	10/25/2016
P85999	58105	PIN	10/31/2016
P86070	58162	PIE/S357P	10/31/2016
P86100	58191	PIE	11/01/2016
P86077	58169	PIE/S357P	11/07/2016
P86635	58500	PIN	11/07/2016
P86107	58197	PIE	11/08/2016
P84676	56916	EVPA	11/14/2016
P86071	58163	PIE/S357P	11/14/2016
P86637	58502	PIN	11/14/2016
P84674	56914	EVPA	11/15/2016
P86103	58194	PIE	11/15/2016
P86078	58170	PIE/S357P	11/21/2016
P86636	58501	PIN	11/21/2016
P86067	58158	PIE/BBCW	11/22/2016
P86072	58164	PIE/S357P	11/28/2016
P86638	58503	PIN	11/28/2016
P86104	58195	PIE	11/29/2016
P86079	58171	PIE/S357P	12/05/2016
P87127	58961	PIN/NECP	12/05/2016
P86106	58196	PIE	12/06/2016
P87190	59023	EVPA	12/06/2016
P87191	59024	EVPA	12/07/2016
P86073	58165	PIE/S357P	12/12/2016
P87128	58962	PIN	12/12/2016
P86101	58192	PIE	12/13/2016
P86080	58172	PIE/S357P	12/19/2016
P87130	58964	PIN	12/19/2016
P86066	58157	PIE/BBCW	12/20/2016
P86074	58166	PIE/S357P	12/27/2016
P87129	58963	PIN	12/27/2016
P86102	58193	PIE	12/28/2016

a. BBCW – Biscayne Bay Coastal Wetlands; EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; PIN – Everglades National Park Inflows North; and S357P – S-357 Pump Station.

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

Work Identifier	Project	Sample Identifier	Station	Date & Time Collected	Reason Sample Was Not Collected
P85998	PIN	P85998-25	S355A	10/17/2016 11:20:00	No flow.
P85998	PIN	P85998-27	S355B	10/17/2016 11:21:00	No flow.
P85999	PIN	P85999-25	S355A	10/31/2016 11:21:00	No flow.
P85999	PIN	P85999-27	S355B	10/31/2016 11:22:00	No flow.
P86065	PIE	P86065-10	BERMB3	10/25/2016 09:14:00	Too shallow to sample.
P86066	PIE	P86066-10	BERMB3	12/20/2016 09:05:00	No flow.
P86106	PIE	P86106-9	BERMB3	12/06/2016 09:52:00	Too shallow to sample.
P86638	PIN	P86638-11	S12B	11/28/2016 10:08:00	No flow.
P86638	PIN	P86638-27	S355B	11/28/2016 11:57:00	No flow.
P87127	PIN	P87127-13	S12B	12/05/2016 11:23:00	No flow.
P87127	PIN	P87127-14	S12C	12/05/2016 11:29:00	No flow.
P87127	PIN	P87127-15	S12D	12/05/2016 11:34:00	No flow.
P87128	PIN	P87128-11	S12B	12/12/2016 09:36:00	No flow.
P87128	PIN	P87128-12	S12C	12/12/2016 09:43:00	No flow.
P87128	PIN	P87128-13	S12D	12/12/2016 09:50:00	No flow.
P87129	PIN	P87129-11	S12B	12/27/2016 09:28:00	No flow.
P87129	PIN	P87129-12	S12C	12/27/2016 09:35:00	No flow.
P87129	PIN	P87129-13	S12D	12/27/2016 09:41:00	No flow.

FIELD QUALITY CONTROL

In order to assess the quality of the sample collection process and as required by the *Field Sampling Quality Manual*, 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 particular 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* section.

For the 45 sampling events described above, a total of 74 blanks and 8 replicate samples were collected. All of the 74 field blank samples 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* 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* section, no qualifiers or remark codes were added by field project managers to TP sample results. These remark codes would 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*.

FIELD AUDITS

During the fourth quarter of 2016, one audit was conducted on the PIN project collected by District personnel. One quality improvement was issued due to a deficiency in sample processing procedure and one process improvement was issued as a result of a documentation deficiency. The responses to the quality improvement and process improvement from this audit are complete. After a review of the key deficiencies during this sampling trip, it was determined the deficiencies observed during the audit did not negatively affect the quality of the sample data for this event (SFWMD 2016).

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 Laboratory conducted a total of 447 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 447 results, 142 TP results were for grab samples collected from projects/locations listed in the *Introduction* section (excluding field quality control samples). For reference, a complete set of all 447 TP results can be found in the RDS described in the *Introduction* section 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*. 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 142 TP results from samples collected from projects/locations listed in the *Introduction* section, 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 142 results reported, no results were below the MDL and 7 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:

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

Where:

U(x) is the combined standard uncertainty in the result x at the 95% confidence interval (CI).
$\mathbf{S_0}$ – a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.
$\mathbf{S_1}$ – proportionality constant derived from nested hierarchical methodology by Ingersoll (2001).

During this reporting period, the uncertainty constants are $\mathbf{S_0}$ = 0.002 and $\mathbf{S_1}$ = 0.068. Estimated uncertainties are calculated automatically by LIMS using the equation and constants shown above and are provided with all the TP results.

Figure 1 is presented to show estimated uncertainties at the 95% and 99% CI 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.

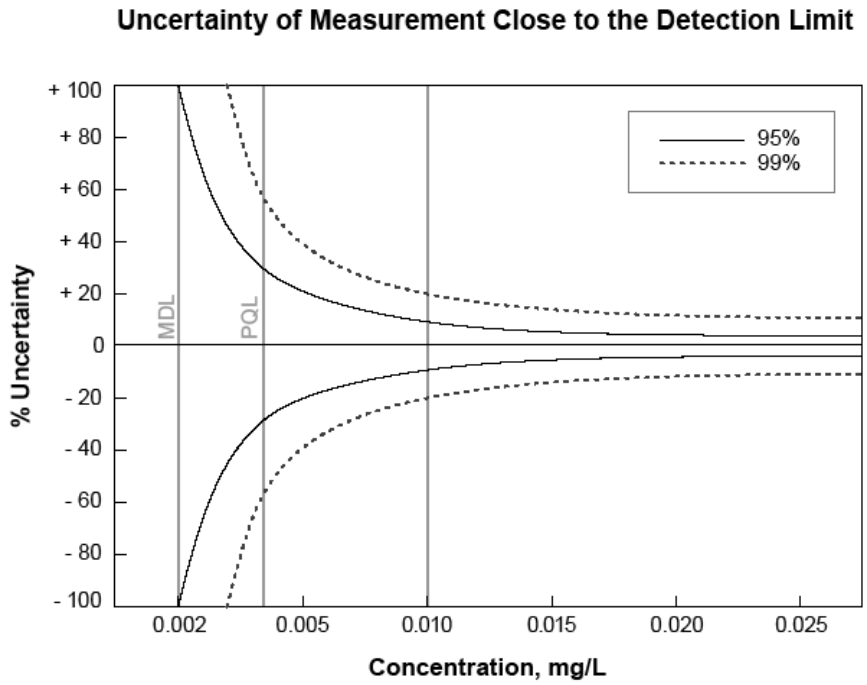

Figure 1. Estimated uncertainties at the 95% and 99% CI relative to the MDL and PQL of the TP measurement process.

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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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.

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

Relative Standard Deviation (RSD): A measurement of precision, used when comparing more than two results. It is calculated as %RSD = [Standard Deviation/Mean] x 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 (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi - X)/s$, where s is a standard deviation) (Eurachem/CITAC 2000).