Quality Assessment Report for Water Quality Monitoring

July – September 2016

Submitted to the Technical Oversight Committee January 27, 2017

Michael Wright (mwright@sfwmd.gov)

Analytical Services
Water Quality Bureau
South Florida Water Management District
West Palm Beach, Florida

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 July 1, 2016, through September 30, 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 January 11, 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, an Microsoft Excel workbook named "RDS_for_TOC_QAR_070116_to_093016.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 44 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 44 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 44 sampling events described above, a total of 14 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample could not be collected due to low water levels or other sampling problems. The list of the grab sample identifiers and the reason for failure to collect these samples is shown in **Table 2**.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project	Date Collected
P83510	55935	PIN	07/05/2016
P84852	57091	PIE/S357P	07/05/2016
P83825	56240	EVPA	07/06/2016
P84837	57074	PIE/BBCW	07/06/2016
P83822	56237	EVPA	07/07/2016
P84862	57097	PIE/S357P	07/11/2016
P84957	57195	PIN	07/11/2016
P84845	57077	PIE	07/12/2016
P84778	57045	PIN	07/18/2016
P84861	57090	PIE/S357P	07/18/2016
P84841	57086	PIE	07/19/2016
P84863	57098	PIE/S357P	07/25/2016
P84960	57197	PIN	07/25/2016
P84846	57078	PIE	07/26/2016
P84854	57092	PIE/S357P	08/01/2016
P85237	57456	PIN	08/01/2016
P84838	57075	PIE/BBCW	08/02/2016
P84672	56912	EVPA	08/03/2016
P84864	57099	PIE/S357P	08/08/2016
P85240	57459	PIN	08/08/2016
P84847	57079	PIE	08/09/2016
P84855	57093	PIE/S357P	08/15/2016
P85238	57457	PIN	08/15/2016
P84842	57083	PIE	08/16/2016
P84865	57100	PIE/S357P	08/22/2016
P85241	57460	PIN	08/22/2016
P84848	57080	PIE	08/23/2016
P84856	57094	PIE/S357P	08/29/2016
P85239	57458	PIN	08/29/2016
P84843	57084	PIE	08/30/2016
P84866	57101	PIE/S357P	09/06/2016
P85501	57685	PIN	09/06/2016
P84849	57081	PIE	09/07/2016
P85625	57795	EVPA	09/08/2016
P85626	57796	EVPA	09/08/2016
P84857	57095	PIE/S357P	09/12/2016
P85503	57687	PIN	09/12/2016
P84839	57076	PIE/BBCW	09/13/2016
P84867	57102	PIE/S357P	09/19/2016
P85502	57686	PIN	09/19/2016
P84850	57082	PIE	09/20/2016
P84858	57096	PIE/S357P	09/26/2016
P85504	57688	PIN	09/26/2016
P86064	58155	PIE/BBCW	09/27/2016

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

Work Identifier	Project	Sample Identifier	Station	Date Collected	Reason Sample Was Not Collected
P83510	PIN	P83510-12	S12B	07/05/2016 10:14:00	No flow.
P83825	EVPA	P83825-6	LOX16	07/06/2016 09:16:00	Too shallow to sample.
P84672	EVPA	P84672-1	LOX6	08/03/2016 10:04:00	Too shallow to sample.
P84778	PIN	P84778-12	S12B	07/18/2016 10:37:00	No flow.
P84838	PIE	P84838-10	BERMB3	08/02/2016 11:55:00	No flow.
P84841	PIE	P84841-10	BERMB3	07/19/2016 10:49:00	Too shallow to sample.
P84957	PIN	P84957-11	S12B	07/11/2016 09:35:00	No flow.
P84960	PIN	P84960-11	S12B	07/25/2016 09:10:00	No flow.
P84960	PIN	P84960-25	S355A	07/25/2016 10:38:00	No flow.
P84960	PIN	P84960-27	S355B	07/25/2016 11:03:00	No flow.
P85237	PIN	P85237-12	S12B	08/01/2016 10:20:00	No flow.
P85240	PIN	P85240-11	S12B	08/08/2016 09:46:00	No flow.
P85502	PIN	P85502-25	S355A	09/19/2016 11:48:00	No flow.
P85502	PIN	P85502-27	S355B	09/19/2016 11:58:00	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* to this report.

For the 44 sampling events described above, a total of 74 blanks and eight 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 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,* two remark codes where 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 qualified by field project managers during the reporting period.

Work Identifier	Project	Sample Identifier	Station	Collection Date	Qualifier(s) / Reason
P85503	PIN	P85503-16	S333	09/12/2016 11:30:00	PMR / Structure gates were in closed position but began opening just after the sample was collected.
P85503	PIN	P85503-26	S356-334	09/12/2016 12:14:00	PMR / Structure gates were in closed position but began opening just after the sample was collected.

FIELD AUDITS

During the third quarter of 2016, one audit was completed by SFWMD Quality Assessment staff during a sampling event being conducted by Everglades National Park service personnel. One corrective action was required due to a deficiency in a sample processing procedure and four corrective actions were required as a result of documentation deficiencies. All of the required corrective actions from the audit were implemented, and after a review of the key deficiencies and the results for the blanks collected during this sampling event, it was determined that the deficiencies observed during the audit did not negatively affect the quality of the sample results, and therefore, no qualifiers were added to the sample data as a result of the audit findings.

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 362 TP analyses for the grab samples collected during the 44 sampling events listed in **Table 1**. Of those 362 results, 142 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 362 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*. 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*, 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 one sample had a concentration between the MDL and PQL and was 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).
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 $\mathbf{S_0}$ = 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 of 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.

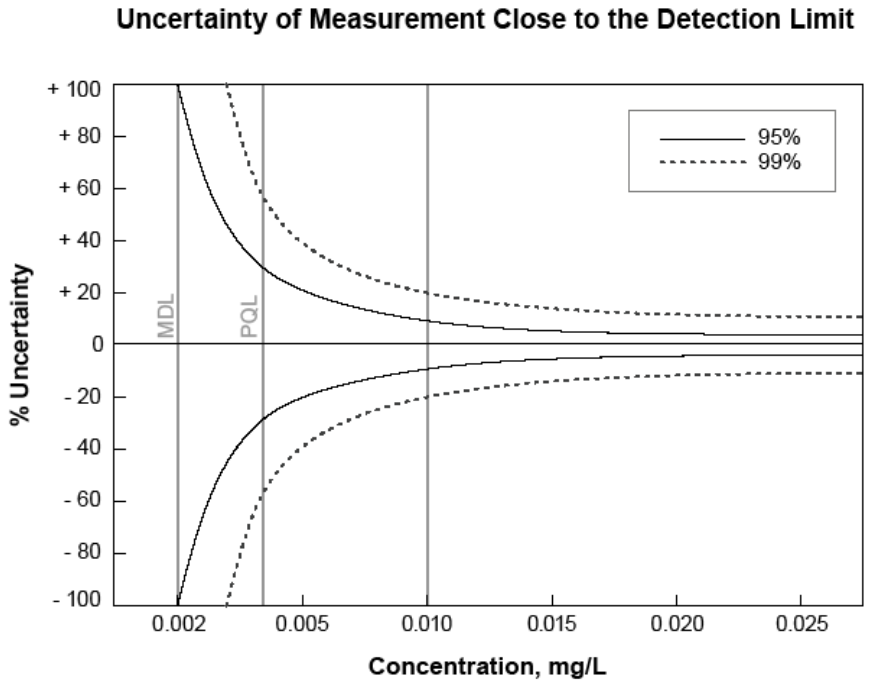

Figure 1. Estimated uncertainties at the 95% and 99% CI relative to the MDL and PQL of the TP measurement process.

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, one proficiency testing sample for TP analysis was completed and the results reported by the SFWMD laboratory are shown in **Table 4** along with the evaluation of the results by the study provider.

Table 4. Proficiency testing results for Study WP-260.

Assigned Value	2.81 mg/L
Study Mean	2.87 mg/L
SFWMD Reported Value	2.86 ± 0.2 mg/L
Z-Score	-0.09
Acceptance Limits	2.30 – 3.30 mg/L
Performance Evaluation	Acceptable

Notes:

- Assigned Value – This value is the concentration of the proficiency sample based upon the actual composition of the standard as it was prepared by the study provider.
- Study Mean – This is the mean concentration of the proficiency sample calculated from the results provided by study participants.
- SFWMD Reported Value – The test result reported by the SFWMD laboratory to the study provider.
- Z-Score - A measure of the deviation of the SFWMD reported value from the assigned value (calculated as $z = (\text{SFWMD Reported Value} - \text{Assigned Value})/\sigma$, where σ is the standard deviation calculated as proscribed in *Recommendation and Calculation of Acceptance Limits for Chemical, Radiochemical, and Microbiological Components of Proficiency Tests* (The NELAC Institute 2010).
- Acceptance Limits – this limit is given by the study provider and is calculated using equations promulgated in *Recommendation and Calculation of Acceptance Limits for Chemical, Radiochemical, and Microbiological Components of Proficiency Tests* (The NELAC Institute 2010).
- Performance Evaluation – The result reported by the SFWMD laboratory falls within the acceptance limits and has been reported as "Acceptable" by the study provider.

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.

Ingersoll, W.S. 2001. *Environmental Analytical Measurement Uncertainty Estimation. Nested Hierarchical Approach.* ADA396946, Defense Technical Information Center, Fort Belvoir, VA.

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.

The NELAC Institute. 2010. *Recommendation and Calculation of Acceptance Limits for Chemical, Radiochemical, and Microbiological Components of Proficiency Tests*. The National Environmental Laboratory Accreditation Conference Institute, Weatherford, TX.

SFWMD. 2015a. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-2015-01, South Florida Water Management District, West Palm Beach, FL.

SFWMD. 2015b. *Field Sampling Quality Manual*. SFWMD-FIELD-QM-001-08.2, 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.

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 $z = (Xi - X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2000).