

Quality Assessment Report for Water Quality Monitoring

July – September 2019



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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, 2019, through September 30, 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 November 8, 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 Water Quality Monitoring Section (WQM) *Field Sampling Quality Manual* (SFWMD 2017) provided the requirements followed in field sample collection from July 1 to July 30, 2019. This document was revised, and the quality system elements were placed in the *WQM Field Quality Manual* (SFWMD 2019a) and the field sampling procedures were placed in the *Field Sampling Manual* (FSM) (SFWMD 2019b). Both documents were effective on July 31, 2019. The Analytical Services Section's *Chemistry Laboratory Quality Manual* (SFWMD 2019c) 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 "qa_report_jul_sep_data.xlsx" was created and contains all TP results 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.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

All samples were collected by WQM. 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 these sampling events is shown in **Table 1**. The table details the work identifiers, work order numbers, the project codes, and the dates the samples were collected.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project ^a	Date Collected
P105263	70787	PIN	07/01/2019
P104852	70647	PIE	07/02/2019
P104824	70633	PIE	07/02/2019
P105224	70781	PIN	07/09/2019
P101260	69070	EVPA	07/09/2019
P108426	72061	PIE	07/09/2019
P104840	70641	PIE	07/09/2019
P106042	71148	EVPA	07/09/2019
P105220	70770	PIN	07/15/2019
P108441	72074	PIE	07/16/2019
P108931	72239	PIE	07/17/2019
P105287	70799	PIN	07/22/2019
P108428	72063	PIE	07/23/2019
P108450	72076	PIE	07/23/2019
P108351	72038	PIN	07/29/2019
P108571	72083	PIE	07/30/2019
P108429	72064	PIE	07/30/2019
P108363	72044	PIN	08/05/2019
P106041	71147	EVPA	08/06/2019
P108451	72077	PIE	08/06/2019
P108430	72065	PIE	08/07/2019
P109093	72322	EVPA	08/07/2019
P108352	72039	PIN	08/12/2019
P108572	72084	PIE	08/13/2019
P108431	72066	PIE	08/13/2019
P108364	72045	PIN	08/19/2019
P108452	72078	PIE	08/20/2019
P108432	72067	PIE	08/20/2019
P108353	72040	PIN	08/26/2019
P108433	72068	PIE	08/27/2019
P108573	72085	PIE	08/27/2019
P108365	72046	PIN	09/04/2019
P108453	72079	PIE	09/04/2019
P108434	72069	PIE	09/05/2019
P103995	70301	EVPA	09/09/2019
P108354	72041	PIN	09/09/2019
P104002	70305	EVPA	09/10/2019
P108435	72070	PIE	09/10/2019
P108574	72086	PIE	09/10/2019
P108366	72047	PIN	09/16/2019
P108436	72071	PIE	09/17/2019
P108454	72080	PIE	09/17/2019
P108355	72042	PIN	09/23/2019
P108575	72087	PIE	09/24/2019
P108437	72072	PIE	09/25/2019
P108367	72048	PIN	09/30/2019

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 13 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 including where an area was impacted by vegetation. The list of the grab sample identifiers and the reason these samples were not collected are shown in **Table 2**.

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

Work Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Not Collected
P105263	PIN	P105263-27	S12B	07/01/2019	Gates closed. No flow.
P104852	PIE	P104852-4	BERMB3	07/02/2019	No flow
P105224	PIN	P105224-34	S12B	07/08/2019	No flow.
P105220	PIN	P105220-30	S12B	07/15/2019	Gates closed. No flow.
P108931	PIE	P108931-4	BERMB3	07/16/2019	Too shallow to sample.
P105287	PIN	P105287-13	S355B	07/22/2019	No flow.
P105287	PIN	P105287-15	S355A	07/22/2019	No flow.
P108571	PIE	P108571-4	BERMB3	07/30/2019	No flow. Nearby area is fully impacted by vegetation.
P108364	PIN	P108364-13	S355B	08/19/2019	Gates closed. No flow.
P108364	PIN	P108364-15	S355A	08/19/2019	Gates closed. No flow.
P108575	PIE	P108575-4	BERMB3	09/24/2019	No flow. Area is completely impacted by vegetation and algae.
P108367	PIN	P108367-13	S355B	09/30/2019	No flow.
P108367	PIN	P108367-15	S355A	09/30/2019	No flow.

a. 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 WQM *Field Sampling Quality Manual* (SFWMD 2017; 2019a) and *FSM* (SFWMD 2019b), 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 trip (day) and if a specific field quality control sample fails to meet the requirements set forth in the Florida Department of Environmental Protection (FDEP) *Quality Assurance Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]), qualifiers will be added to all of the associated sample results. The types of field quality control samples that are collected may include replicate samples (RSs), and field quality control blanks, 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 22 field quality control blanks and six RSs were collected. None of the field quality control blanks had a concentration equal to or greater than 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 technicians 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*, no PMR was assigned by project managers and no quality assurance process-related qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

FIELD AUDITS

SFWMD conducted one field audit on the EVPA project during the third quarter of 2019. Two Quality Improvements (QIs) were noted. One QI concerned placement of the sulfuric acid preserved samples into the cooler prior to acidification of the nitric acid preserved samples. The other QI concerned the rinsing of the sampling processing equipment. After a review of these deficiencies, it was determined that they did not negatively affect data quality of the samples collected for this event.

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 Analytical Services Chemistry Laboratory conducted a total of 425 TP analyses for the grab samples collected during the 46 sampling events listed in **Table 1**. Of those 425 TP results, 186 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 425 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 Analytical Services Chemistry 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 2019c). The results of these laboratory quality control samples are associated with all of 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* (SFWMD 2019c). 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 186 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 a “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 the PQL (0.004 mg/L) are assigned a “I” qualifier, indicating that the results are at concentrations that cannot be accurately quantified. Of the 186 TP results reported, no result was below the MDL and 17 samples had a concentration between the MDL and the 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.

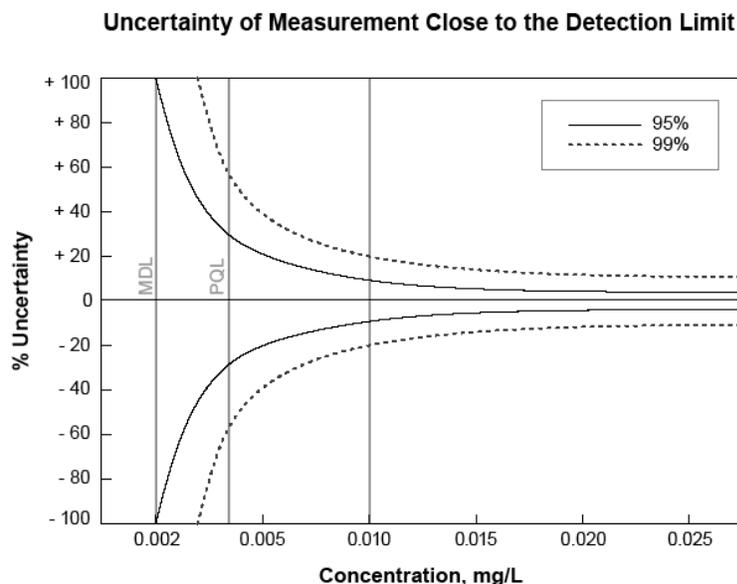


Figure 1. Estimated uncertainties at the 95 and 99% CIs relative to the MDL and PQL of the TP measurement process.

As can be seen from the graph (**Figure 1**), the percent measurement uncertainty (95% CI) is 100% at the MDL, nearly 30% at the PQL, and remains relatively constant at higher concentrations.

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, performance evaluation study samples from the Environment and Climate Change Canada (#114) were received for TP analysis in September 2019. TP results were rated as "Ideal" with no Z-score greater than 1.2σ being received for the nine results reported.

LABORATORY AUDITS

During the third quarter of 2019 one laboratory assessment was conducted by the United States Army Corps of Engineers on behalf of the Comprehensive Everglades Restoration Plan's Quality Assurance Oversight Team. No deficiencies were found for the laboratory's TP analytical procedure.

PROCEDURE UPDATES

The TP analytical procedure (Standard Methods 4500 P-F, Automated Ascorbic Acid Reduction Method) did not change during this reporting period. An addendum to the SFWMD Analytical Services Chemistry Laboratory standard operating procedure for TP analysis was approved and signed with an effective date on August 20, 2019 (SFWMD 2019d).

REFERENCES

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- SFWMD. 2019d. *SOP Addendums and Changes*. SFWMD-LAB-SOP-3100-013, South Florida Water Management District, West Palm Beach, FL. Effective August 20, 2019.

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, 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.

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 σ is a standard deviation) (Eurachem/CITAC 2012).