
Quality Assessment Report for Water Quality Monitoring

April – June 2023



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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD) field sampling and laboratory analysis for total phosphorus (TP), primarily for the following projects and their associated stations as shown in **Table 1** from April 1, 2023, through June 30, 2023. The analysis in this document reflects the status of the data at the time of download and does not account for changes made to the data after October 6, 2023.

Table 1. Projects and associated stations.

Project Name	Project ID	Stations
Everglades National Park Inflows North	PIN	S12A, S12B, S12C, S12D, S333, S333N, S355A, S355B, and S356-334
Everglades National Park Inflows East	PIE	G737, S332DX, S18C, S328, and BERMB3
Everglades Protection Area	EVPA	LOX3, LOX4, LOX5, LOX6, LOX7, LOX8, LOX9, LOX10, LOX11, LOX12, LOX13, LOX14, LOX15, and LOX16

The Water Quality Monitoring Section (WQM) *Field Quality Manual* (SFWMD-FIELD-QM-001) and *Field Sampling Manual* (SFWMD-FIELD-FSM-001) provided the quality system requirements and the field sampling procedures followed in field sample collection, respectively, from April 1 to June 30, 2023. The Analytical Services Section’s *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001) 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.

To prepare this report, a Microsoft Excel workbook named “qa_report_apr_jun_2023_data.xlsx” was created, containing all TP results obtained from DBHYDRO, SFWMD’s corporate environmental database, for all sampling events. This includes grab samples collected for the projects/stations listed above during the period specified in this report. The Excel workbook will be referred to as the Reference Data Set (RDS) throughout this report and both the documents are available for reference on the Everglades Technical Oversight Committee (TOC) website (<https://www.sfwmd.gov/our-work/toc>). All sample analyses for TP were completed at the SFWMD Analytical Services Chemistry Laboratory (Department of Health Identification # E46077).

If available, 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 completed during the period specified in this report will also be included.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

All samples were collected by WQM staff. A total of 45 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 2**. The table details the work order identifiers, work order numbers, project codes, sample collection dates, and number of samples collected.

Table 2. Sampling events for the reporting period.

Work Order Identifier	Work Order	Project ^a	Date Collected
P142421	87405	PIN	04/03/2023
P140799	86827	EVPA	04/04/2023
P142656	87498	PIE	04/04/2023
P142658	87499	PIE	04/05/2023
P140805	86830	EVPA	04/05/2023
P142309	87379	PIN	04/10/2023
P139484	86309	PIE	04/11/2023
P142443	87413	PIE	04/12/2023
P142429	87406	PIN	04/17/2023
P137507	85350	PIE	04/18/2023
P137519	85362	PIE	04/19/2023
P142282	87373	PIN	04/24/2023
P139477	86302	PIE	04/25/2023
P142444	87414	PIE	04/26/2023
P142430	87407	PIN	05/01/2023
P140800	86828	EVPA	05/02/2023
P142466	87425	PIE	05/02/2023
P142492	87431	PIE	05/03/2023
P140806	86831	EVPA	05/03/2023
P142283	87374	PIN	05/09/2023
P142445	87415	PIE	05/09/2023
P142455	87420	PIE	05/10/2023
P142431	87408	PIN	05/15/2023
P142467	87426	PIE	05/16/2023
P142493	87432	PIE	05/16/2023
P142284	87375	PIN	05/22/2023
P142446	87416	PIE	05/23/2023
P142456	87421	PIE	05/23/2023
P142468	87427	PIE	05/30/2023
P142432	87409	PIN	05/30/2023
P142494	87433	PIE	05/30/2023
P142285	87376	PIN	06/06/2023
P138929	86053	EVPA	06/06/2023
P142457	87422	PIE	06/06/2023
P142447	87417	PIE	06/06/2023
P143795	87959	EVPA	06/07/2023
P142433	87410	PIN	06/13/2023
P142495	87434	PIE	06/13/2023
P142469	87428	PIE	06/13/2023
P142286	87377	PIN	06/19/2023
P142458	87423	PIE	06/20/2023
P142448	87418	PIE	06/20/2023
P142434	87411	PIN	06/26/2023
P142470	87429	PIE	06/27/2023
P142496	87435	PIE	06/27/2023

- a. EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.

During the 45 sampling events described in **Table 2**, a total of 30 grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to the site being dry, or not representative, no flow, or water too shallow. The grab sample identifiers and reasons these samples were rejected or not collected are shown in **Table 3**.

Table 3. Grab samples rejected or not collected during the reporting period.

Work Order Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Rejected or Not Collected ^b
86827004	EVPA	P140799-4	LOX10	04/04/2023	Too shallow to sample.
86827003	EVPA	P140799-3	LOX5	04/04/2023	Too shallow to sample.
86827002	EVPA	P140799-2	LOX3	04/04/2023	Site dry.
86827009	EVPA	P140799-9	LOX4	04/04/2023	Too shallow to sample.
87499004	PIE	P142658-4	G737	04/04/2023	Gates closed. No flow.
87498028	PIE	P142656-28	BERMB3	04/04/2023	No flow during site visited.
87413004	PIE	P142443-4	G737	04/11/2023	Gates closed. No flow.
85362004	PIE	P137519-4	G737	04/18/2023	Gates closed. No flow.
85350025	PIE	P137507-25	BERMB3	04/18/2023	No flow during site visited.
87373013	PIN	P142282-13	S355B	04/24/2023	Gates closed. No flow.
87373015	PIN	P142282-15	S355A	04/24/2023	Gates closed. No flow.
87414004	PIE	P142444-4	G737	04/25/2023	Gates closed. No flow.
87431004	PIE	P142492-4	G737	05/02/2023	Gates closed. No flow.
87425024	PIE	P142466-24	S328	05/02/2023	Site being not representative.
87374013	PIN	P142283-13	S355B	05/08/2023	Gates closed. No flow.
87374015	PIN	P142283-15	S355A	05/08/2023	Gates closed. No flow.
87415004	PIE	P142445-4	G737	05/09/2023	Gates closed. No flow.
87432004	PIE	P142493-4	G737	05/16/2023	Gates closed. No flow.
87426024	PIE	P142467-24	S328	05/16/2023	Site being not representative.
87426025	PIE	P142467-25	BERMB3	05/16/2023	No flow during site visited.
87416004	PIE	P142446-4	G737	05/23/2023	Gates closed. No flow.
87433004	PIE	P142494-4	G737	05/30/2023	Gates closed. No flow.
87427025	PIE	P142468-25	BERMB3	05/30/2023	No flow during site visited.
87417004	PIE	P142447-4	G737	06/06/2023	Gates closed. No flow.
87434004	PIE	P142495-4	G737	06/13/2023	Gates closed. No flow.
87377013	PIN	P142286-13	S355B	06/19/2023	Gates closed. No flow.
87377015	PIN	P142286-15	S355A	06/19/2023	Gates closed. No flow.
87418004	PIE	P142448-4	G737	06/20/2023	Gates closed. No flow.
87435004	PIE	P142496-4	G737	06/27/2023	Gates closed. No flow.
87429025	PIE	P142470-25	BERMB3	06/27/2023	No flow during site visited.

- EVPA – Everglades Protection Area; PIE – Everglades National Park Inflows East; and PIN – Everglades National Park Inflows North.
- These abbreviated notes don't necessarily convey all the detail from the sample comments that can be seen in DBHYDRO.

FIELD QUALITY CONTROL

Field quality control samples are collected at sampling locations during each sampling event to assess the quality of the sample collection process as required by the *Field Sampling Manual*. The results from these quality control samples are associated with all samples collected during the sampling trip (day).

Suppose a specific field quality control sample fails to meet the requirements outlined in the Florida Department of Environmental Protection (FDEP) *Quality Assurance Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]). In that case, qualifiers will be added to the appropriate sample results. The types of field quality control samples that are collected may include replicate samples (RSs) and field quality control blanks, which have field generated equipment blanks (EBs), field-cleaned equipment blanks (FCEBs), and field blanks (FBs). The sampling events listed in **Table 2** may include field quality control samples collected at locations other than those listed in the *Introduction*.

For the 45 sampling events described above, 22 field quality control blanks (one EB, six FBs, 15 FCEBs) and four RSs were collected. One of the 22 field quality control blanks (P142421-51) had a concentration (0.017 mg/L) 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), an SFWMD-derived and -applied remark code indicating a potential quality issue not otherwise defined by the qualifiers specified 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. Nine “G” qualifiers, however, were assigned to two RSs and seven samples due to analyte was detected at or above the method detection limit (0.002 mg/L) in both the sample and the associated FCEB, and the blank value (0.017 mg/L) was greater than 10% of the associated sample value (**Table 4**) as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

Table 4. Results with qualifiers and remark codes during the reporting period.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
87405003	PIN	P142421-3 ^b	S356-334	04/03/2023	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.
87405004	PIN	P142421-4 ^b	S356-334	04/03/2023	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.
87405006	PIN	P142421-6	S356-334	04/03/2023	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.
87405016	PIN	P142421-16	S333N	04/03/2023	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.

87405026	PIN	P142421-26	S333	04/03/2023	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.
87405036	PIN	P142421-36	S12D	04/03/2023	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.
87405037	PIN	P142421-37	S12C	04/03/2023	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.
87405040	PIN	P142421-40	S12B	04/03/2023	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.
87405042	PIN	P142421-42	S12A	04/03/2023	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.

- a. PIN – Everglades National Park Inflows North.
- b. RS (replicate sample).

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the second quarter of 2023.

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

SFWMD Analytical Services Chemistry Laboratory staff conducted 314 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 314 TP results, 167 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 314 grab TP results can be found in the RDS described in the *Introduction* 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*. The results of these laboratory quality control samples are associated with all the analyses conducted in each batch, and qualifiers are added to the data as required by the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.) which is 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 (laboratory control samples), matrix spikes, precision checks (duplicates or matrix spike duplicates), and method blanks. No laboratory operation related qualifiers were added for the 167 TP results of samples collected from projects/locations listed in the *Introduction* because the laboratory exhibited no 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 not any universally accepted (or required) method for determining 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 an “I” qualifier, indicating that the results are at concentrations that cannot be accurately quantified. Of the 167 TP results reported, no results were below the MDL and two samples had concentrations between the MDL (0.002 mg/L) and the PQL (0.004 mg/L).

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

All measurements are subject to uncertainty and a measured value is only complete if a statement of the associated uncertainty accompanies it. 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:

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

$U(x)$ 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** presents estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

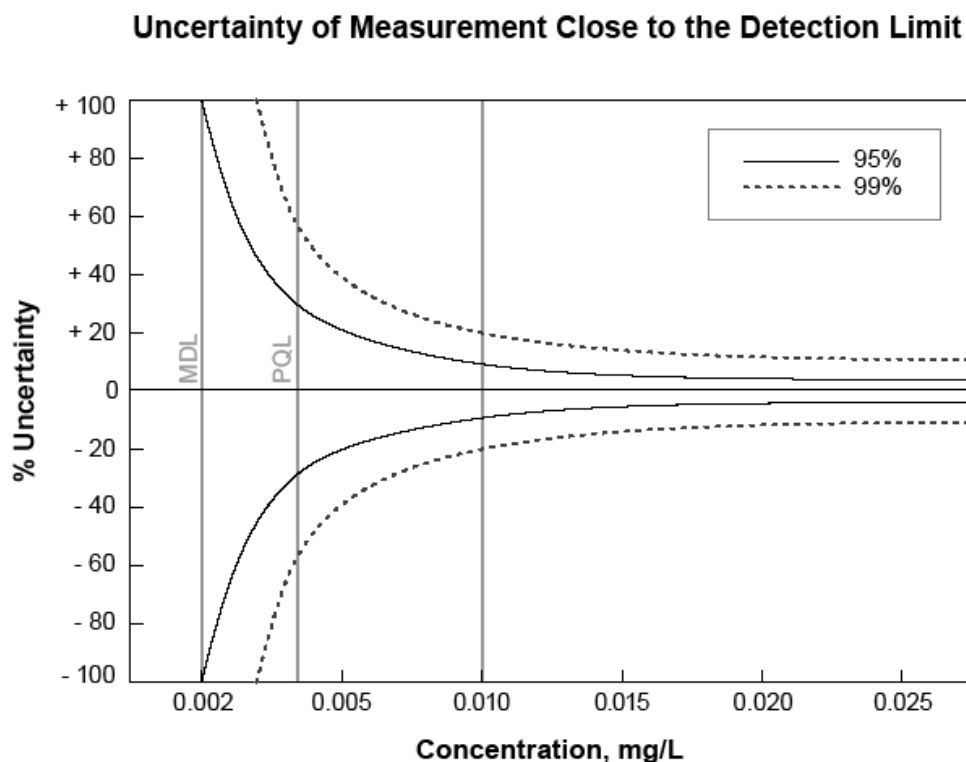


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

As seen in **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 PERFORMANCE EVALUATION

The SFWMD Analytical Services Chemistry Laboratory participates in a variety of studies to evaluate the proficiency of the laboratory's quality system. During the second quarter of 2023, the laboratory received TP results for the Phenova #WP0423 proficiency testing study. The reported result was evaluated as "acceptable" with a calculated Z-score of 0.0833. The laboratory also participated in the Environmental and Climate Change Canada performance evaluation study but had not received the results of the study.

LABORATORY AUDITS

During this reporting period no quality system laboratory audits were conducted.

PROCEDURE UPDATES

The TP sample preparation (Standard Method 4500 P-B 5, Persulfate Digestion Method) and analytical procedures (Standard Methods 4500 P-F, Automated Ascorbic Acid Reduction Method) did not change during this reporting period.

REFERENCES

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- SFWMD. *Field Sampling Manual*. SFWMD-FIELD-FSM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. *Standard Operating Procedure for the Determination of Total and Dissolved Phosphorus*. SFWMD-LAB-SOP-3100, most current, effective version. 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, 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 a 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).