

Quality Assessment Report for Water Quality Monitoring

January – March 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 January 1, 2023, through March 31, 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 June 7, 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 January 1 to March 31, 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_jan_mar_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
P137482	85344	PIE	01/03/2023
P137426	85318	PIN	01/03/2023
P137470	85338	PIE	01/03/2023
P137757	85473	EVPA	01/04/2023
P137763	85476	EVPA	01/05/2023
P137401	85313	PIN	01/10/2023
P139510	86322	PIE	01/10/2023
P139512	86323	PIE	01/10/2023
P139366	86250	PIN	01/17/2023
P139478	86303	PIE	01/17/2023
P139503	86316	PIE	01/20/2023
P139338	86236	PIN	01/23/2023
P139527	86324	PIE	01/24/2023
P139491	86310	PIE	01/24/2023
P139336	86235	PIN	01/30/2023
P139479	86304	PIE	01/31/2023
P140798	86826	EVPA	02/01/2023
P140804	86829	EVPA	02/02/2023
P139372	86251	PIN	02/06/2023
P139528	86325	PIE	02/07/2023
P139492	86311	PIE	02/07/2023
P139362	86246	PIN	02/13/2023
P139505	86318	PIE	02/14/2023
P139480	86305	PIE	02/15/2023
P139373	86252	PIN	02/20/2023
P139493	86312	PIE	02/21/2023
P139529	86326	PIE	02/21/2023
P139363	86247	PIN	02/27/2023
P139506	86319	PIE	02/28/2023
P139481	86306	PIE	02/28/2023
P138928	86052	EVPA	03/01/2023
P138933	86055	EVPA	03/02/2023
P141625	87196	EVPA	03/06/2023
P139374	86253	PIN	03/06/2023
P139530	86327	PIE	03/08/2023
P139494	86313	PIE	03/08/2023
P139364	86248	PIN	03/13/2023
P139482	86307	PIE	03/14/2023
P139507	86320	PIE	03/15/2023
P139375	86254	PIN	03/20/2023
P139495	86314	PIE	03/21/2023
P139531	86328	PIE	03/21/2023
P142269	87369	PIN	03/28/2023
P139483	86308	PIE	03/28/2023
P139508	86321	PIE	03/28/2023

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 26 grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to site dry, no flow, or shallow water. 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
85318013	PIN	P137426-13	S355B	1/3/2023	Gates closed. No flow.
85318015	PIN	P137426-15	S355A	1/3/2023	Gates closed. No flow.
85344004	PIE	P137482-4	G737	1/3/2023	Gates closed. No flow.
85318039	PIN	P137426-39	S12B	1/3/2023	Gates closed. No flow.
85313035	PIN	P137401-35	S12B	1/9/2023	Gates closed. No flow.
86323004	PIE	P139512-4	G737	1/10/2023	Gates closed. No flow.
86322028	PIE	P139510-28	BERMB3	1/10/2023	No flow during site visited.
86250013	PIN	P139366-13	S355B	1/17/2023	Gates closed. No flow.
86250015	PIN	P139366-15	S355A	1/17/2023	Gates closed. No flow.
86316004	PIE	P139503-4	G737	1/17/2023	Gates closed. No flow.
86250039	PIN	P139366-39	S12B	1/17/2023	Gates closed. No flow.
86236038	PIN	P139338-38	S12B	1/23/2023	Gates closed. No flow.
86324004	PIE	P139527-4	G737	1/24/2023	Gates closed. No flow.
86310025	PIE	P139491-25	BERMB3	1/24/2023	No flow during site visited.
86235041	PIN	P139336-41	S12C	1/30/2023	Gates closed. No flow.
86235042	PIN	P139336-42	S12B	1/30/2023	Gates closed. No flow.
86317004	PIE	P139504-4	G737	1/31/2023	Gates closed. No flow.
86317008	PIE	P139504-8	S18C	1/31/2023	Gates closed. No flow.
86251034	PIN	P139372-34	S12C	2/6/2023	Gates closed. No flow.
86251035	PIN	P139372-35	S12B	2/6/2023	Gates closed. No flow.
86325004	PIE	P139528-4	G737	2/7/2023	Gates closed. No flow.
86311025	PIE	P139492-25	BERMB3	2/7/2023	No flow during site visited.
86246013	PIN	P139362-13	S355B	2/13/2023	Gates closed. No flow.
86246015	PIN	P139362-15	S355A	2/13/2023	Gates closed. No flow.
86246038	PIN	P139362-38	S12C	2/13/2023	Gates closed. No flow.
86246039	PIN	P139362-39	S12B	2/13/2023	Gates closed. No flow.
86318004	PIE	P139505-4	G737	2/14/2023	Gates closed. No flow.
86252034	PIN	P139373-34	S12C	2/20/2023	Gates closed. No flow.
86252035	PIN	P139373-35	S12B	2/20/2023	Gates closed. No flow.
86326004	PIE	P139529-4	G737	2/21/2023	Gates closed. No flow.
86312025	PIE	P139493-25	BERMB3	2/21/2023	Too shallow to sample.
86247038	PIN	P139363-38	S12C	2/27/2023	Gates closed. No flow.
86247039	PIN	P139363-39	S12B	2/27/2023	Gates closed. No flow.
86319004	PIE	P139506-4	G737	2/28/2023	Gates closed. No flow.
86052012	EVPA	P138928-12	LOX4	3/1/2023	Too shallow to sample.
86253035	PIN	P139374-35	S12B	3/6/2023	Gates closed. No flow.
86327004	PIE	P139530-4	G737	3/7/2023	Gates closed. No flow.
86313025	PIE	P139494-25	BERMB3	3/7/2023	Site dry.
86248013	PIN	P139364-13	S355B	3/13/2023	Gates closed. No flow.
86248015	PIN	P139364-15	S355A	3/13/2023	Gates closed. No flow.
86248039	PIN	P139364-39	S12B	3/13/2023	Gates closed. No flow.
86320004	PIE	P139507-4	G737	3/14/2023	Gates closed. No flow.

Work Order Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Rejected or Not Collected
86328004	PIE	P139531-4	G737	3/21/2023	Gates closed. No flow.
86314025	PIE	P139495-25	BERMB3	3/21/2023	No flow during site visited.
86321004	PIE	P139508-4	G737	3/28/2023	Gates closed. No flow.

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

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, 27 field quality control blanks (one EB, eight FBs, 18 FCEBs) and four RSs were collected. None of the 27 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), 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 and no qualifier was assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.).

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the first 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 308 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 308 TP results, 151 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 308 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 qualifiers were added for the 151 TP results from 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 151 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.

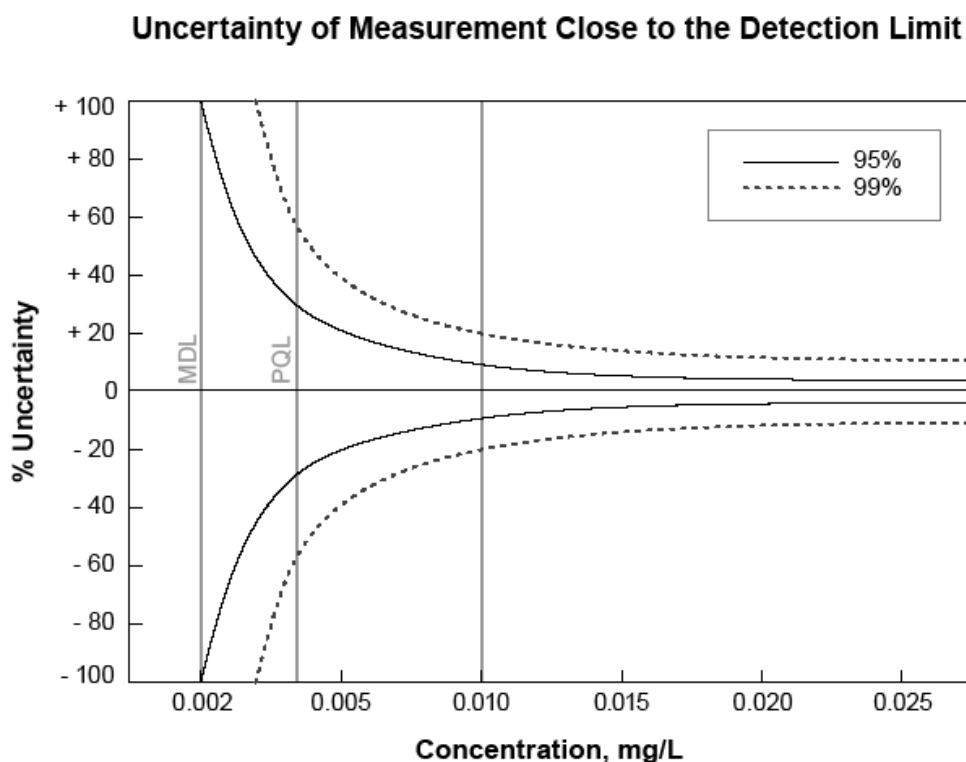


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 first quarter of 2023, the laboratory received results from the Environmental Canada surface water performance evaluation study. All ten results received a Z-score of less than 0.7 and the laboratory received a rating of "very good".

LABORATORY AUDITS

During this reporting period the laboratory performed its annual internal audit. There were five corrective actions, four observations and one recommendation identified. These findings have been entered into the laboratory's corrective action log and are in the process of being addressed. Only one deficiency was relevant to the laboratory's TP analytical procedure. Improper labeling was found on one of the reagent bottles. This deficiency, however, did not affect the quality of the TP sample data.

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

- Eurachem/CITAC. 2012. *Quantifying Uncertainty in Analytical Measurement, Third 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. *Chemistry Laboratory Quality Manual*. SFWMD-LAB-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. *Field Quality Manual*. SFWMD-FIELD-QM-001, most current, effective version. South Florida Water Management District, West Palm Beach, FL.
- 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 an 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 an 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 an 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).