

Quality Assessment Report for Water Quality Monitoring

April – June 2024



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Technical Oversight Committee

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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) in surface water, primarily for the projects and their associated stations as shown in **Table 1** from April 1, 2024, through June 30, 2024. The analysis reflects the status of the data at the time of download and does not account for changes made to the data after August 27, 2024.

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, and S328
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 were followed in field sample collection from April 1 to June 30, 2024. The Analytical Services Section’s *Chemistry Laboratory Quality Manual* (SFWMD-LAB-QM-001) provides the guidance and 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 surface water samples collected from the locations and timeframe described above.

To prepare this report, a Microsoft Excel workbook named “qa_report_apr_jun_2024_data.xlsx” was also 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 of the documents are available for reference on the Everglades Technical Oversight Committee (TOC) website (<https://www.sfwmd.gov/our-work/toc>). TP analyses were completed at the SFWMD Analytical Services Chemistry Laboratory (Florida Department of Health Identification # E46077).

If available, TP sample results for biannual laboratory proficiency testing as required by 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 42 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, and sample collection dates.

Table 2. Sampling events for the reporting period.

Work Order Identifier	Work Order	Project ^a	Date Collected
P150174	91083	PIN	04/02/2024
P150026	91011	PIE	04/02/2024
P150028	91012	PIE	04/03/2024
P150184	91088	EVPA	04/09/2024
P148059	90060	PIE	04/09/2024
P150176	91084	PIN	04/09/2024
P148210	90135	PIE	04/09/2024
P150186	91089	EVPA	04/10/2024
P149490	90768	PIE	04/16/2024
P148946	90487	PIN	04/16/2024
P149001	90509	PIE	04/16/2024
P150049	91020	PIE	04/23/2024
P148985	90499	PIE	04/23/2024
P148935	90482	PIN	04/24/2024
P149491	90769	PIE	04/30/2024
P149002	90510	PIE	04/30/2024
P148947	90488	PIN	04/30/2024
P150875	91442	PIE	05/07/2024
P150901	91455	PIE	05/07/2024
P150436	91214	PIN	05/08/2024
P150813	91412	EVPA	05/08/2024
P150819	91415	EVPA	05/09/2024
P150913	91461	PIE	05/14/2024
P150887	91448	PIE	05/14/2024
P150446	91220	PIN	05/14/2024
P150902	91456	PIE	05/21/2024
P150876	91443	PIE	05/21/2024
P150437	91215	PIN	05/21/2024
P150914	91462	PIE	05/28/2024
P150447	91221	PIN	05/28/2024
P150903	91457	PIE	06/04/2024
P150877	91444	PIE	06/04/2024
P150438	91216	PIN	06/04/2024
P150448	91222	PIN	06/11/2024
P150915	91463	PIE	06/11/2024
P150889	91450	PIE	06/11/2024
P150439	91217	PIN	06/18/2024
P150904	91458	PIE	06/18/2024
P150878	91445	PIE	06/18/2024
P150890	91451	PIE	06/25/2024
P150916	91464	PIE	06/25/2024
P150449	91223	PIN	06/26/2024

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

During the 42 sampling events described in **Table 2**, a total of 37 grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to dry conditions, gates closed, and/or the site being no flow or too shallow to collect. 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
91012004	PIE	P150028-4	G737	04/02/2024	Gates closed. No flow.
91088003	EVPA	P150184-3	LOX5	04/09/2024	Too shallow to sample.
91088002	EVPA	P150184-2	LOX3	04/09/2024	Dry conditions, Helicopter didn't land.
90060004	PIE	P148059-4	G737	04/09/2024	No flow. No samples.
90768004	PIE	P149490-4	G737	04/16/2024	Gates closed. No flow.
91020004	PIE	P150049-4	G737	04/23/2024	Gates closed. No flow.
90482013	PIN	P148935-13	S355B	04/23/2024	Gates closed. No flow.
90482015	PIN	P148935-15	S355A	04/23/2024	Gates closed. No flow.
90769004	PIE	P149491-4	G737	04/30/2024	Gates closed. No flow.
91442005	PIE	P150875-5	G737	05/07/2024	Gates closed. No flow.
91412009	EVPA	P150813-9	LOX4	05/08/2024	Dry conditions, Helicopter didn't land.
91412007	EVPA	P150813-7	LOX7	05/08/2024	Too shallow to sample.
91412005	EVPA	P150813-5	LOX9	05/08/2024	Dry conditions, Helicopter didn't land.
91412004	EVPA	P150813-4	LOX10	05/08/2024	Dry conditions, Helicopter didn't land.
91412003	EVPA	P150813-3	LOX5	05/08/2024	Dry conditions, Helicopter didn't land.
91412002	EVPA	P150813-2	LOX3	05/08/2024	Dry conditions, Helicopter didn't land.
91415005	EVPA	P150819-5	LOX13	05/09/2024	Too shallow to sample.
91415002	EVPA	P150819-2	LOX6	05/09/2024	Too shallow to sample.
91448005	PIE	P150887-5	G737	05/14/2024	Gates closed. No flow.
91443005	PIE	P150876-5	G737	05/21/2024	Gates closed. No flow.
91449009	PIE	P150888-9	S18C	05/28/2024	No flow. Site not visited.
91449005	PIE	P150888-5	G737	05/28/2024	Site dry. No samples.
91444005	PIE	P150877-5	G737	06/04/2024	Gates closed. No flow.
91779012	EVPA	P151539-12	LOX4	06/05/2024	Dry conditions, Helicopter didn't land.
91779010	EVPA	P151539-10	LOX7	06/05/2024	Dry conditions, Helicopter didn't land.
91779009	EVPA	P151539-9	LOX8	06/05/2024	Dry conditions, Helicopter didn't land.
91779008	EVPA	P151539-8	LOX9	06/05/2024	Dry conditions, Helicopter didn't land.
91779007	EVPA	P151539-7	LOX10	06/05/2024	Dry conditions, Helicopter didn't land.
91779006	EVPA	P151539-6	LOX5	06/05/2024	Dry conditions, Helicopter didn't land.
91779005	EVPA	P151539-5	LOX3	06/05/2024	Dry conditions, Helicopter didn't land.
91780005	EVPA	P151541-5	LOX6	06/06/2024	Dry conditions, Helicopter didn't land.
91780006	EVPA	P151541-6	LOX11	06/06/2024	Dry conditions, Helicopter didn't land.
91780008	EVPA	P151541-8	LOX13	06/06/2024	Dry conditions, Helicopter didn't land.
91780009	EVPA	P151541-9	LOX14	06/06/2024	Dry conditions, Helicopter didn't land.
91780010	EVPA	P151541-10	LOX16	06/06/2024	Dry conditions, Helicopter didn't land.
91780011	EVPA	P151541-11	LOX15	06/06/2024	Dry conditions, Helicopter didn't land.
91780012	EVPA	P151541-12	LOX12	06/06/2024	Too shallow to sample.

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

b. These abbreviated notes do not necessarily convey all the details from the sample comments that can be seen in DBHYDRO.

FIELD QUALITY CONTROL

Field quality control samples were 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 were associated with all samples collected during the sampling trip (day). If a specific field quality control sample failed 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.]), qualifiers were added to the appropriate sample results. The types of field quality control samples could include replicate samples (RSs) and field quality control blanks, along with 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 **Table 1**.

For the 42 sampling events described above, 28 field quality control blanks (one EB, seven FBs, 20 FCEBs) and two RSs were collected. None of the 28 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 **Table 1**, no PMR was assigned by project managers. Two “J” and one “Y” qualifiers, however, were assigned to samples (**Table 4**) due to estimated values or the laboratory analysis was from an improperly preserved sample 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 for the 42 sample events listed in Table 2.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
91456003	PIE	P150902-3	S332DX	05/21/2024	Y: Analysis was from an improperly preserved sample. Pumps were running during sample collection. Visible flow was observed.
91461007	PIE	P150913-7	S328	05/14/2024	J: Estimated value. Gates closed. Sample was taken from a disconnected pool and was not representative of the surrounding wetland.
91462007	PIE	P150914-7	S328	05/28/2024	J: Estimated value. Gates closed. Sample was taken from a disconnected pool and was not representative of the surrounding wetland.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD conducted one field audit of the Everglades Protection Area (EVPA) project in the second quarter of 2024. There was one Process Improvement (PI - a notation on the audit report indicating a deficiency that does not result in the qualification of data and is not suspected to directly affect the quality

of a sample and/or field data) noted for EVPA. The PI was for the sampling reference documents requiring updates.

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 281 TP analyses for the grab samples collected during the 42 sampling events listed in **Table 2** and detailed in RDS. Of those 281 TP results, 152 were for grab samples collected from projects/locations listed in **Table 1** (excluding field quality control samples). For reference, a complete set of all 281 grab TP results can be found in the RDS described in **Table 1** 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-LAB-QM-001). The results of these laboratory quality control samples are associated with 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* (SFWMD-LAB-QM-001). 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. Since the laboratory exhibited no quality control failures, none of the laboratory operation related qualifiers were added for the 152 TP results of samples collected from projects/locations listed in **Table 1**.

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 152 TP results reported, no results were below the MDL and no 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:

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

$U(x)$ 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.

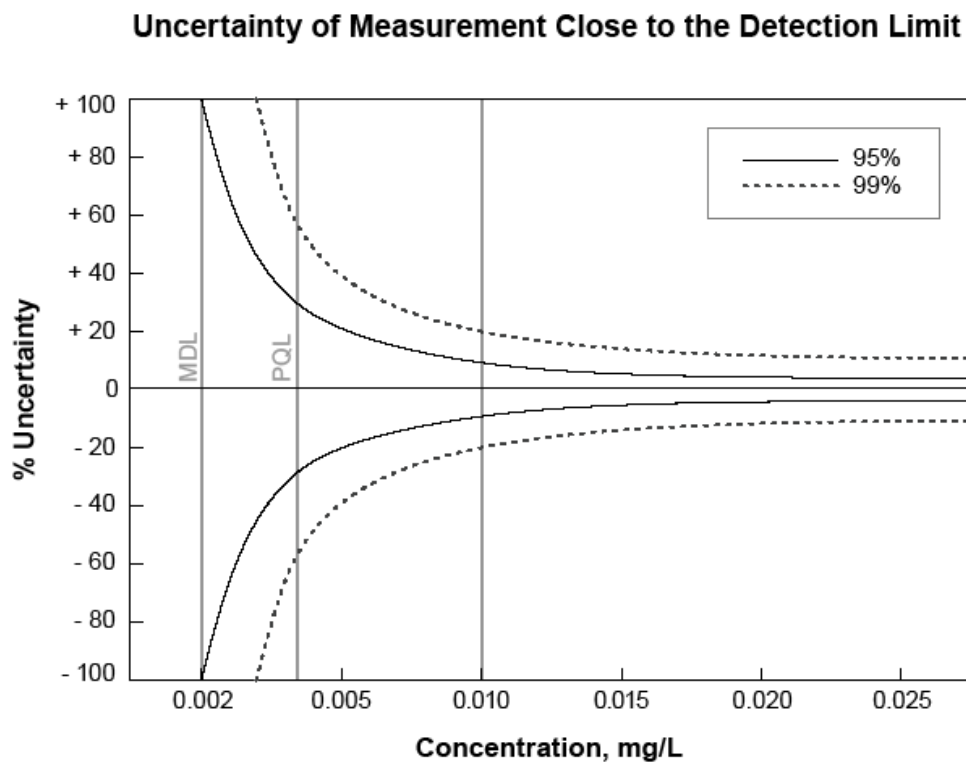


Figure 1. Estimated uncertainties at 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

As seen in **Figure 1**, the percentage measurement uncertainty (95% CI) is 100% at MDL, nearly 30% at 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 2024, the laboratory received TP results for the Phenova #WP0424 proficiency testing study. The reported results were evaluated as "acceptable" with a calculated Z-score of 0.0957. The laboratory also participated in the Environmental and Climate Change Canada performance evaluation study but had not received the results of the study I when the report was written

LABORATORY AUDITS

During this reporting period the laboratory was inspected on-site to verify compliance with Florida Department of State *Certification of Environmental Testing Laboratories Rule* (Chapter 64E-1, F. A. C.), which incorporates by reference the 2016 Environmental Laboratory standards adopted at The NELAC Institute. The American National Standards Institute National Accreditation Board contractor conducted a biennial external laboratory audit as required by the Florida Department of Health. During the audit there were seven deficiencies identified. The findings have been entered into the laboratory's corrective action log and have been addressed. Only one deficiency was relevant to the laboratory's TP analytical procedure. Standard Methods 3000 and 4000 must include QC criteria for calibration standard error evaluations to evaluate each point of the calibration curve. The laboratory previously evaluated only two as required by The NELAC Institute for most methods. In response to the audit findings, the laboratory is now evaluating each point on the calibration curve. This deficiency, however, did not affect the quality of the reported TP sample data.

PROCEDURE UPDATES

The TP sample preparation (Standard Method 4500-P B (5)-2011, Persulfate Digestion Method) and analytical procedures (Standard Method 4500-P F-2011, 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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- 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-3140, 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 in 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 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).