Quality Assessment Report for Water Quality Monitoring

January – March 2025

Prepared for the Technical Oversight Committee

August 7, 2025

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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 January 1, 2025, through March 31, 2025. The analysis reflects the status of the data at the time of download and does not account for changes made to the data after May 15, 2025.

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 January 1, 2025, to March 31, 2025. 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_jan_mar_2025_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 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 Water Quality Monitoring (WQM) staff. A total of 43 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
P153848	92942	PIN	01/02/2025
P153916	92979	PIE	01/03/2025
P153880	92961	PIE	01/03/2025
P155751	93878	PIN	01/07/2025
P155860	93927	PIE	01/07/2025
P155912	93953	PIE	01/08/2025
P155937	93968	EVPA	01/13/2025
P155935	93967	EVPA	01/14/2025
P155900	93947	PIE	01/14/2025
P155764	93885	PIN	01/15/2025
P155848	93921	PIE	01/15/2025
P155827	93912	PIE	01/21/2025
P155891	93944	PIE	01/21/2025
P153860	92948	PIN	01/22/2025
P155785	93894	PIN	01/28/2025
P155901	93948	PIE	01/28/2025
P155849	93922	PIE	01/29/2025
P155861	93928	PIE	02/04/2025
P155913	93954	PIE	02/04/2025
P155773	93888	PIN	02/04/2025
P156325	94170	EVPA	02/05/2025
P156327	94171	EVPA	02/06/2025
P155902	93949	PIE	02/11/2025
P155786	93895	PIN	02/11/2025
P155850	93923	PIE	02/11/2025
P155914	93955	PIE	02/18/2025
P155774	93889	PIN	02/18/2025
P155862	93929	PIE	02/18/2025
P155903	93950	PIE	02/25/2025
P155851	93924	PIE	02/25/2025
P155787	93896	PIN	02/25/2025
P155915	93956	PIE	03/04/2025
P155775	93890	PIN	03/04/2025
P157101	94549	EVPA	03/04/2025
P155863	93930	PIE	03/04/2025
P157103	94550	EVPA	03/05/2025
P155852	93925	PIE	03/11/2025
P155904	93951	PIE	03/11/2025
P155788	93897	PIN	03/11/2025
P155916	93957	PIE	03/18/2025
P155776	93891	PIN	03/19/2025
P155905	93952	PIE	03/25/2025
P155789	93898	PIN	03/26/2025

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

During the 43 sampling events described in **Table 2**, a total of eight grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to gates closed and/or being 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]
94171005	EVPA	P156327-5	LOX3	02/06/2025	Too shallow to collect.
94549002	EVPA	P157101-2	LOX5	03/04/2025	Too shallow to collect.
94550005	EVPA	P157103-5	LOX3	03/05/2025	Too shallow to collect.
93925009	PIE	P155852-9	S18C	03/11/2025	Gates closed. No flow.
93931005	PIE	P155864-5	G737	03/18/2025	Gates closed. No flow.
93931009	PIE	P155864-9	S18C	03/18/2025	Gates closed. No flow.
93926004	PIE	P155853-4	G737	03/25/2025	Gates closed. No flow.
93926009	PIE	P155853-9	S18C	03/25/2025	Gates closed. No flow.

a. EVPA – Everglades Protection Area; and PIE – Everglades National Park Inflows East.
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 43 sampling events described above, 28 field quality control blanks (one EB, eight FBs, 19 FCEBs) and two RSs were collected. One of the 19 FCEBs, which was collected from S-12C (Sample ID: P155786-44), 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.). No PMR was assigned to field quality control replicate samples that had a concentration equal to or greater than the TP MDL of 0.002 mg/L.

Qualifiers were assigned to samples (**Table 4**): Nine “G” qualifiers due to analyte detection at or above the method detection limit (0.002 mg/L) where the associated FCEB value, 0.003 mg/L, was greater than 10 percent (1/10) of the sample value, and three “J” qualifiers because the laboratory analysis was from an improper field protocol 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 43 sample events listed in Table 2.

Work Identifier	Project [a]	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
93954007	PIE	P155913-7	S328	02/04/2025	J: Estimated value because of improper laboratory or field protocols.
93895003	PIN	P155786-3	S356-334	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895005	PIN	P155786-5	S355B	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895007	PIN	P155786-7	S355A	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895010	PIN	P155786-10	S333N	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895020	PIN	P155786-20	S333	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895029	PIN	P155786-29	S12D	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895030	PIN	P155786-30	S12C	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895033	PIN	P155786-33	S12B	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93895035	PIN	P155786-35	S12A	02/11/2025	G: Field quality control blank detection greater than 10 percent of sample value for blank.
93956007	PIE	P155915-7	S328	03/04/2025	J: Estimated value because of improper laboratory or field protocols.
93957007	PIE	P155916-7	S328	03/18/2025	J: Estimated value because of improper laboratory or field protocols.

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

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the first quarter of 2025.

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 329 TP analyses for the grab samples collected during the 43 sampling events listed in **Table 2** and detailed in RDS. Of those 329 TP results, 169 were for grab samples collected from projects/locations listed in **Table 1** (excluding field quality control samples). For reference, a complete set of all 329 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 for batches associated with the RDS, none of the laboratory operation related qualifiers were added for the 169 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 169 TP results reported, no results were below the MDL, and four 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:

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

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. 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 first quarter of 2025, the laboratory received results from the QUASIMEME saline / brackish waters performance evaluation study. All seven reported results were identified as "acceptable" with no Z-score exceeding ±1.5.

LABORATORY AUDITS

During this reporting period the laboratory performed its annual internal audit. At the time of drafting this report, the audit findings have not been finalized.

PROCEDURE UPDATES

The TP sample preparation (Standard Method 4500-P B (5)-2011, Persulfate Digestion Method) and analytical procedure (Standard Method 4500-P H-2011, Automated Ascorbic Acid Reduction Method) did not change during this reporting period.

REFERENCES

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FDEP. 2018. *Quality Assurance*. Chapter 62-160, Florida Administrative Code. Florida Department of Environmental Protection, Tallahassee, FL. Effective April 16, 2018.

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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-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 (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi - X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2012).