

Quality Assessment Report for Water Quality Monitoring

July – September 2024



Prepared for the
Technical Oversight Committee

January 15, 2025

Prepared by:
Ming Chen (michen@sfwmd.gov)

Analytical Services
Water Quality Bureau
South Florida Water Management District
West Palm Beach, Florida

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 July 1, 2024, through September 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 November 26, 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 July 1 to September 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_jul_sep_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 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, and sample collection dates.

Table 2. Sampling events for the reporting period.

Work Order Identifier	Work Order	Project ^a	Date Collected
P150879	91446	PIE	07/02/2024
P150905	91459	PIE	07/02/2024
P152081	92054	PIN	07/03/2024
P151988	92007	EVPA	07/09/2024
P152083	92055	PIN	07/09/2024
P152138	92082	PIE	07/09/2024
P152152	92089	PIE	07/09/2024
P151986	92006	EVPA	07/10/2024
P152092	92057	PIN	07/16/2024
P150880	91447	PIE	07/17/2024
P150906	91460	PIE	07/17/2024
P150891	91452	PIE	07/24/2024
P152106	92063	PIN	07/24/2024
P150917	91465	PIE	07/24/2024
P152159	92090	PIE	07/31/2024
P152093	92058	PIN	07/31/2024
P152145	92083	PIE	07/31/2024
P152634	92328	EVPA	08/06/2024
P152107	92064	PIN	08/06/2024
P150892	91453	PIE	08/07/2024
P150918	91466	PIE	08/07/2024
P152636	92329	EVPA	08/07/2024
P152160	92091	PIE	08/13/2024
P152146	92084	PIE	08/13/2024
P152094	92059	PIN	08/13/2024
P152108	92065	PIN	08/20/2024
P152536	92277	PIE	08/20/2024
P152524	92271	PIE	08/20/2024
P152161	92092	PIE	08/27/2024
P152095	92060	PIN	08/27/2024
P152147	92085	PIE	08/27/2024
P152537	92278	PIE	09/03/2024
P152109	92066	PIN	09/03/2024
P152525	92272	PIE	09/03/2024
P153159	92596	EVPA	09/10/2024
P152148	92086	PIE	09/10/2024
P152162	92093	PIE	09/10/2024
P152096	92061	PIN	09/10/2024
P153165	92603	EVPA	09/11/2024
P152110	92067	PIN	09/17/2024
P152526	92273	PIE	09/17/2024
P152538	92279	PIE	09/17/2024
P152163	92094	PIE	09/24/2024
P152097	92062	PIN	09/24/2024
P152149	92087	PIE	09/24/2024

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 only one grab sample record for the projects/locations described in the *Introduction* indicates that a sample was not collected due to the site being too shallow to collect. The grab sample identifier and reason the sample was 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
92328002	EVPA	P152634-2	LOX3	08/06/2024	Too shallow to sample.

a. EVPA – Everglades Protection Area.

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 45 sampling events described above, 27 field quality control blanks (three EBs, seven FBs, 17 FCEBs) and two RSs were collected. Two 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.). Two PMRs were assigned to field quality control replicate samples that had a concentration equal to or greater than the TP MDL of 0.002 mg/L.

For grab samples collected at locations described in **Table 1**, one PMR was assigned by project managers. Four “G” and one “Y” qualifiers, however, were assigned to samples (**Table 4**) due to field quality control blank detection greater than 10 percent (1/10) of sample value for blanks 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 45 sample events listed in Table 2.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
92089008	PIE	P152152-8	S332DX	07/09/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92089010	PIE	P152152-10	S328	07/09/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92083004	PIE	P152145-4	G737	07/30/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92083009	PIE	P152145-9	S18C	07/30/2024	G: Field quality control blank detection greater than 10 percent (1/10) of sample value for blank.
92067024	PIN	P152110-24	S12D	09/17/2024	Y: Analysis was from an improperly preserved sample. Pumps were running during sample collection. Visible flow was observed.

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 third quarter of 2024.

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 357 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 357 TP results, 175 were for grab samples collected from projects/locations listed in **Table 1** (excluding field quality control samples). For reference, a complete set of all 357 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 175 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 175 TP results reported, no results were below the MDL and ten 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.

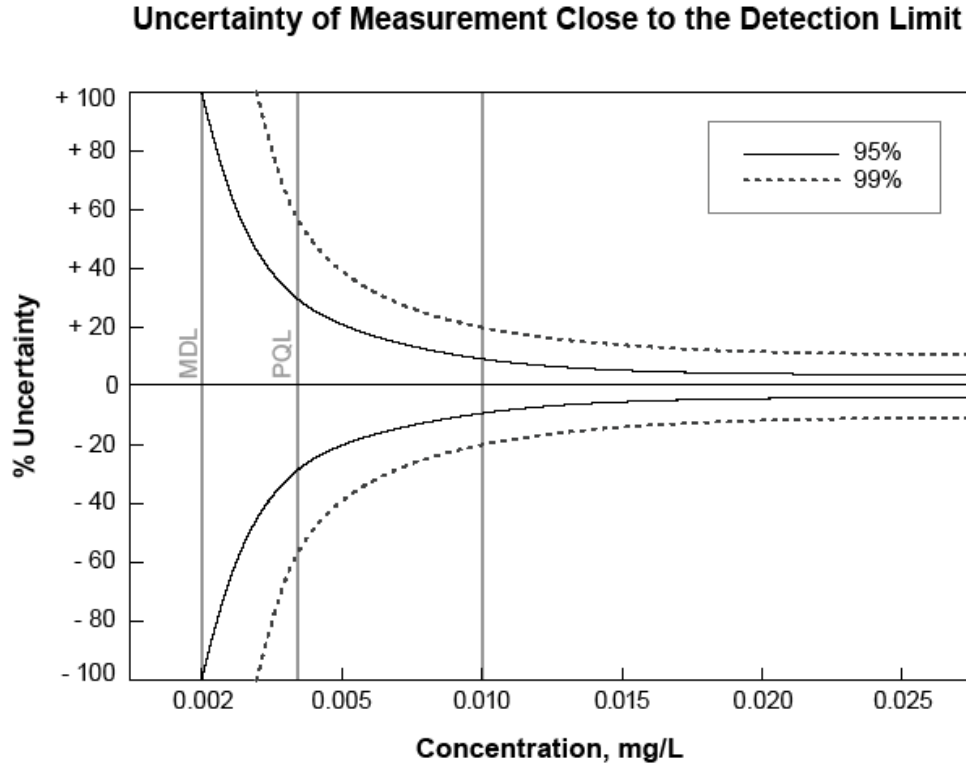


Figure 1. Estimated uncertainties at 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 third quarter of 2024, the laboratory received TP results from the Environment and Climate Change Canada surface water performance evaluation study. All ten results received a Z-score of less than 0.6 and the laboratory received a rating of "Very Good".

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)-2011, Persulfate Digestion Method) did not change during this reporting period. The analytical procedure (Standard Method 4500-P F-2011, Automated Ascorbic Acid Reduction Method) was changed to (Standard Method 4500-P H-2011, Automated Ascorbic Acid Reduction Method).

REFERENCES

- Eurachem/CITAC. 2012. *Quantifying Uncertainty in Analytical Measurement, Third Edition*. Guide CG4, Eurachem/CITAC, Austria. ISBN 0-948926-15-5.
- Florida Department of State. 2018. *Certification of Environmental Testing Laboratories*. Chapter 64E-1, Florida Administrative Code. Florida Department of State, Tallahassee, FL. Effective September 26, 2018.
- FDEP. 2018. *Quality Assurance*. Chapter 62-160, Florida Administrative Code. Florida Department of Environmental Protection, Tallahassee, FL. Effective April 16, 2018.
- Ingersoll, W.S. 2001. *Environmental Analytical Measurement Uncertainty Estimation. Nested Hierarchical Approach*. ADA396946, Defense Technical Information Center, Fort Belvoir, VA.
- 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 (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).