

Quality Assessment Report for Water Quality Monitoring

October – December 2023



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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 October 1, 2023, through December 31, 2023. The analysis reflects the status of the data at the time of download and does not account for changes made to the data after February 23, 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 followed in field sample collection, respectively, from October 1 to December 31, 2023. 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_oct_dec_2023_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 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 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
P146699	89408	PIN	10/02/2023
P146749	89433	PIE	10/03/2023
P146797	89461	PIE	10/04/2023
P144395	88252	EVPA	10/04/2023
P144401	88255	EVPA	10/05/2023
P146703	89410	PIN	10/09/2023
P144346	88228	PIE	10/10/2023
P144318	88213	PIE	10/10/2023
P144290	88197	PIN	10/16/2023
P144332	88220	PIE	10/17/2023
P144356	88232	PIE	10/17/2023
P144276	88192	PIN	10/23/2023
P146834	89462	PIE	10/24/2023
P146789	89450	PIE	10/24/2023
P146711	89411	PIN	10/30/2023
P146758	89434	PIE	10/31/2023
P146847	89471	PIE	10/31/2023
P146736	89418	PIN	11/07/2023
P146835	89463	PIE	11/07/2023
P146790	89451	PIE	11/07/2023
P146712	89412	PIN	11/13/2023
P147355	89709	EVPA	11/14/2023
P146848	89472	PIE	11/14/2023
P146759	89435	PIE	11/15/2023
P147357	89710	EVPA	11/15/2023
P146737	89419	PIN	11/21/2023
P146836	89464	PIE	11/21/2023
P146791	89452	PIE	11/21/2023
P146849	89473	PIE	11/28/2023
P146760	89436	PIE	11/28/2023
P146713	89413	PIN	11/28/2023
P147699	89880	EVPA	12/05/2023
P146837	89465	PIE	12/05/2023
P146738	89420	PIN	12/05/2023
P146792	89453	PIE	12/05/2023
P147701	89881	EVPA	12/06/2023
P146714	89414	PIN	12/12/2023
P146761	89437	PIE	12/12/2023
P146850	89474	PIE	12/12/2023
P146838	89466	PIE	12/19/2023
P146793	89454	PIE	12/19/2023
P146739	89421	PIN	12/20/2023
P146715	89415	PIN	12/28/2023
P146762	89438	PIE	12/28/2023
P146851	89475	PIE	12/28/2023

- 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 twelve grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to bad weather or the site being no flow. 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
87378013	PIN	P144276-13	S355B	10/23/2023	No flow during site visited.
87378015	PIN	P144276-15	S355A	10/23/2023	No flow during site visited.
87436004	PIN	P146737-13	S355B	11/20/2023	No flow during site visited.
87430025	PIN	P146737-15	S355A	11/20/2023	Gates closed. No flow.
88222004	EVPA	P147567-2	LOX6	11/21/2023	Bad weather
88215028	EVPA	P147567-3	LOX11	11/21/2023	Bad weather
88187013	EVPA	P147567-5	LOX13	11/21/2023	Bad weather
88187015	EVPA	P147567-6	LOX14	11/21/2023	Bad weather
88216025	EVPA	P147567-7	LOX16	11/21/2023	Bad weather
88189013	EVPA	P147567-8	LOX15	11/21/2023	Bad weather
88189015	PIN	P146739-13	S355B	12/19/2023	Gates closed. No flow.
88191013	PIN	P146739-15	S355A	12/19/2023	Gates closed. No flow.

a. EVPA – Everglades Protection Area; 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 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, 23 field quality control blanks (one EB, seven FBs, 15 FCEBs) and four RSs were collected. Only one of the 23 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. Eleven “G” qualifiers, however, were assigned to 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 (0.002 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 for the 45 sample events listed in Table 2.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
89420003	PIN	P146738-3	S356-334	12/05/2023	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.
89420013	PIN	P146738-13	S355B	12/05/2023	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.
89420015	PIN	P146738-15	S355A	12/05/2023	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.
89420017	PIN	P146738-17	S333N	12/05/2023	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.
89420027	PIN	P146738-27	S333	12/05/2023	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.
89420037	PIN	P146738-37	S12D	12/05/2023	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.
89420038	PIN	P146738-38	S12C	12/05/2023	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.
89420040	PIN	P146738-40	S12B	12/05/2023	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.

89420042	PIN	P146738-42	S12A	12/05/2023	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.
89438004	PIE	P146762-4	G737	12/28/2023	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.
89438008	PIE	P146762-8	S18C	12/28/2023	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; PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects in the fourth 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 355 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 355 TP results, 179 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 355 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 179 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 179 TP results reported, no results were below the MDL and 19 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.

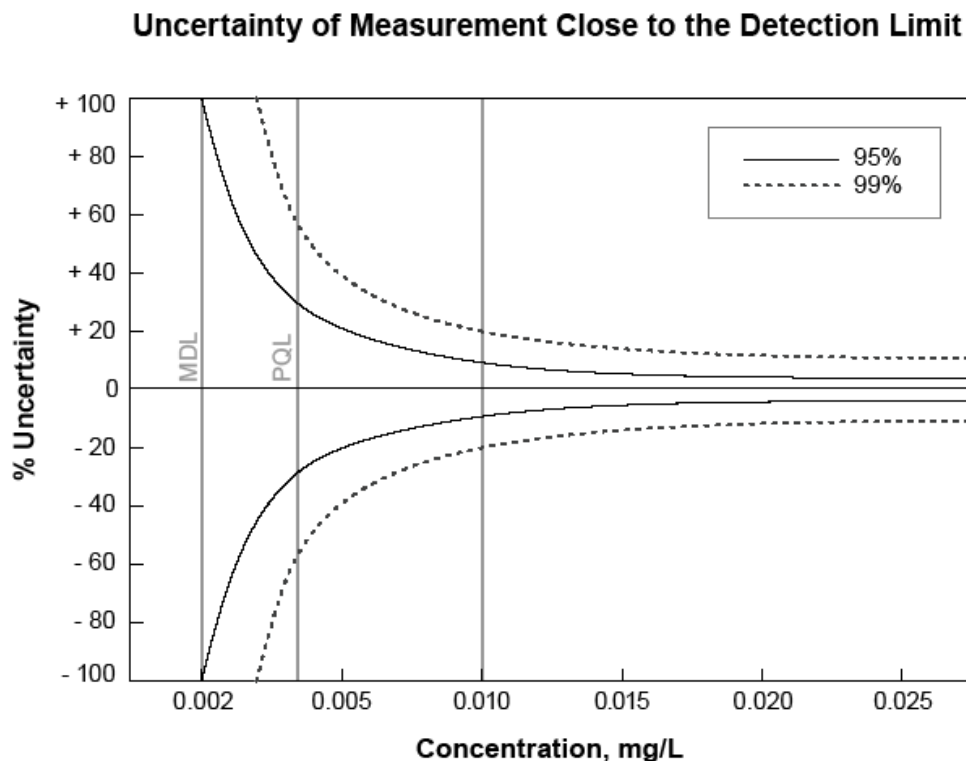


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 fourth quarter of 2023, the laboratory received TP results from one performance evaluation study, Phenova #WP0423. The reported result was evaluated as "acceptable" with a calculated Z-score of 0.083.

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. However, further method development on the FIALab resulted in determination that a calculated weighting of $1/\sqrt{\text{response}}$ produced superior analytical results throughout the entirety of the analytical curve.

REFERENCES

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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).