

Quality Assessment Report for Water Quality Monitoring

July – September 2022



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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 from July 1, 2022, through September 30, 2022. 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 January 6, 2023. The projects and associated stations at which data are collected are as follows:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S333N, S355A, S355B, and S356-334.
- Everglades National Park Inflow East (PIE): G737, S332DX, S18C, S328, and BERMB3.
- Everglades Protection Area (EVPA): LOX3 through 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 July 1 to September 30, 2022. 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_jul_sep_2022_data.xlsx" was created and contains all TP results obtained from DBHYDRO, SFWMD's corporate environmental database, for all sampling events that include grab samples collected for the projects/stations listed above during the period specified in this report. This Excel workbook is available for reference on the Everglades Technical Oversight Committee (TOC) website (<https://www.sfwmd.gov/our-work/toc>) along with this report and is referred as the Reference Data Set (RDS). All sample analyses for TP were completed at the SFWMD Analytical Services Chemistry Laboratory (Department of Health Identification # E46077).

This report also includes 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.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

All samples were collected by WQM staff. A total of 45 grab 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 1**. The table details the work identifiers, work order numbers, project codes, and sample collection dates.

During the 45 sampling events described in **Table 1**, a total of 28 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected, typically because of no flow or water being too shallow to sample. The grab sample identifiers and reasons these samples were rejected or not collected are shown in **Table 2**.

Table 1. Sampling events for the reporting period.

Work Order Identifier	Work Order	Project ^a	Date Collected
P134006	83660	PIE	07/05/2022
P133986	83650	PIE	07/05/2022
P133482	83456	PIN	07/06/2022
P134426	83864	EVPA	07/06/2022
P134432	83867	EVPA	07/07/2022
P135173	84235	PIN	07/11/2022
P135755	84507	PIE	07/12/2022
P133807	83578	PIE	07/12/2022
P135187	84242	PIN	07/18/2022
P135715	84487	PIE	07/19/2022
P135773	84513	PIE	07/19/2022
P133466	83447	PIN	07/25/2022
P135781	84527	PIE	07/26/2022
P136346	84793	PIE	07/28/2022
P136344	84792	PIN	08/01/2022
P136206	84727	PIE	08/02/2022
P136258	84754	PIE	08/02/2022
P134427	83865	EVPA	08/03/2022
P134433	83868	EVPA	08/04/2022
P136397	84820	PIN	08/08/2022
P136245	84748	PIE	08/09/2022
P136195	84721	PIE	08/09/2022
P136352	84794	PIN	08/15/2022
P136230	84737	PIE	08/16/2022
P136264	84755	PIE	08/16/2022
P136402	84821	PIN	08/22/2022
P136200	84722	PIE	08/23/2022
P136253	84750	PIE	08/23/2022
P136353	84795	PIN	08/29/2022
P136231	84738	PIE	08/30/2022
P136265	84756	PIE	08/30/2022
P136403	84822	PIN	09/06/2022
P136254	84751	PIE	09/06/2022
P136201	84723	PIE	09/06/2022
P133227	83325	EVPA	09/07/2022
P136354	84796	PIN	09/12/2022
P136232	84739	PIE	09/13/2022
P136266	84757	PIE	09/13/2022
P133233	83328	EVPA	09/15/2022
P136404	84823	PIN	09/20/2022
P136255	84752	PIE	09/21/2022
P136202	84724	PIE	09/21/2022
P136355	84797	PIN	09/26/2022
P136233	84740	PIE	09/27/2022
P136267	84758	PIE	09/27/2022

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

Table 2. 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
83660004	PIE	P134006-4	G737	07/05/2022	No recorded flow. No sample.
83456013	PIN	P133482-13	S355B	07/05/2022	Gates closed. No flow.
83456015	PIN	P133482-15	S355A	07/05/2022	Gates closed. No flow.
83456028	PIN	P133482-28	S333	07/05/2022	Gates closed. No flow.
83456039	PIN	P133482-39	S12B	07/05/2022	Gates closed. No flow.
83864002	EVPA	P134426-2	LOX3	07/06/2022	Too shallow to sample.
83867003	EVPA	P134432-3	LOX11	07/07/2022	Too shallow to sample.
84235038	PIN	P135173-38	S12B	07/11/2022	Gates closed. No flow.
83578004	PIE	P133807-4	G737	07/12/2022	No recorded flow. No sample.
84513004	PIE	P135773-4	G737	07/19/2022	No recorded flow. No sample.
84792013	PIN	P136344-13	S355B	08/01/2022	Gates closed. No flow.
84792015	PIN	P136344-15	S355A	08/01/2022	Gates closed. No flow.
83865002	EVPA	P134427-2	LOX3	08/03/2022	Too shallow to sample.
84794039	PIN	P136352-39	S12B	08/15/2022	Gates closed. No flow.
84821035	PIN	P136402-35	S12B	08/22/2022	Gates closed. No flow.
84795013	PIN	P136353-13	S355B	08/29/2022	Gates closed. No flow.
84795015	PIN	P136353-15	S355A	08/29/2022	Gates closed. No flow.
84795038	PIN	P136353-38	S12C	08/29/2022	Gates closed. No flow.
84795039	PIN	P136353-39	S12B	08/29/2022	Gates closed. No flow.
84822034	PIN	P136403-34	S12C	09/06/2022	Gates closed. No flow.
84822035	PIN	P136403-35	S12B	09/06/2022	Gates closed. No flow.
83325008	EVPA	P133227-8	LOX9	09/07/2022	Too shallow to sample.
83325006	EVPA	P133227-6	LOX5	09/07/2022	Too shallow to sample.
83325005	EVPA	P133227-5	LOX3	09/07/2022	Too shallow to sample.
84796013	PIN	P136354-13	S355B	09/12/2022	Gates closed. No flow.
84796015	PIN	P136354-15	S355A	09/12/2022	Gates closed. No flow.
84796038	PIN	P136354-38	S12C	09/12/2022	Gates closed. No flow.
84823034	PIN	P136404-34	S12C	09/19/2022	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 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 1** may include field quality control samples collected at locations other than those listed in the *Introduction* to this report.

For the 45 sampling events described above, 29 field quality control blanks and four RSs were collected. None of the 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), a SFWMD-derived and -applied remark code indicating a potential quality issue not otherwise defined by the qualifiers 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 third quarter of 2022.

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 324 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 1**. Of those 324 TP results, 171 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 324 grab TP results can be found in the RDS described in the *Introduction* to this report along 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 *Quality Assurance Rule* (Chapter 62-160, F.A.C.) 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. For the 171 TP results from samples collected from projects/locations listed in the *Introduction*, no qualifiers were added because of laboratory 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 determination of the PQL. In the case of TP analyses, the SFWMD Analytical Services Chemistry Laboratory PQL (0.004 mg/L) is set at a level less than three times (typically two times) the analytically determined concentration.

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 171 TP results reported, no results were below the MDL and 15 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:

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

where:

$U(x)$ 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.

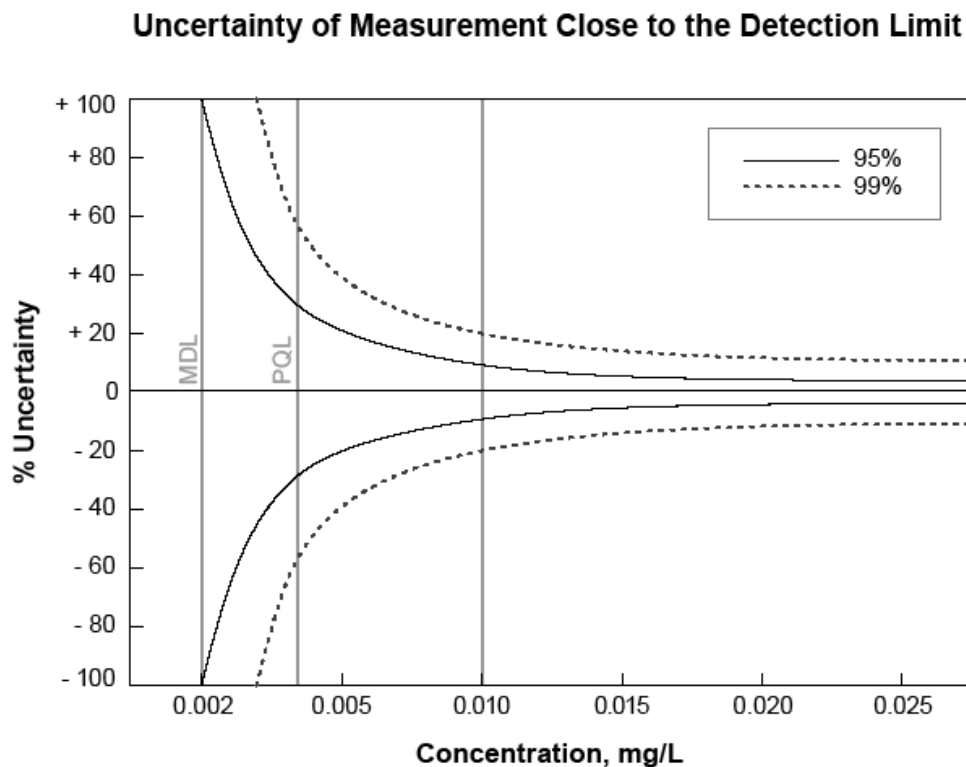


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

As can be seen from **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 third quarter of 2022, the laboratory received results from the Environment and Climate Change 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 "Fair".

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.

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. *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 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).