

Quality Assessment Report for Water Quality Monitoring

October – December 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 as shown in **Table 1** from October 1, 2022, through December 31, 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 April 12, 2023.

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, S328, and BERMB3
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, 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_oct_dec_2022_data.xlsx” was 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 for 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
P137377	85299	PIN	10/03/2022
P137755	85471	EVPA	10/04/2022
P136895	85066	PIE	10/05/2022
P136241	84744	PIE	10/05/2022
P137761	85474	EVPA	10/05/2022
P137388	85305	PIN	10/10/2022
P136234	84741	PIE	10/11/2022
P136268	84759	PIE	10/11/2022
P136405	84824	PIN	10/18/2022
P136203	84725	PIE	10/18/2022
P136256	84753	PIE	10/19/2022
P136356	84798	PIN	10/24/2022
P137477	85339	PIE	10/26/2022
P137465	85333	PIE	10/26/2022
P137396	85308	PIN	10/31/2022
P137756	85472	EVPA	11/01/2022
P137502	85345	PIE	11/01/2022
P137514	85357	PIE	11/02/2022
P137762	85475	EVPA	11/02/2022
P137422	85314	PIN	11/07/2022
P137466	85334	PIE	11/08/2022
P137478	85340	PIE	11/08/2022
P137397	85309	PIN	11/15/2022
P137503	85346	PIE	11/16/2022
P137515	85358	PIE	11/16/2022
P137423	85315	PIN	11/22/2022
P137479	85341	PIE	11/22/2022
P137467	85335	PIE	11/22/2022
P137398	85310	PIN	11/28/2022
P137504	85347	PIE	11/29/2022
P137516	85359	PIE	11/30/2022
P137424	85316	PIN	12/05/2022
P138927	86051	EVPA	12/06/2022
P137480	85342	PIE	12/06/2022
P137468	85336	PIE	12/06/2022
P138932	86054	EVPA	12/07/2022
P137399	85311	PIN	12/12/2022
P137505	85348	PIE	12/13/2022
P137517	85360	PIE	12/13/2022
P137425	85317	PIN	12/20/2022
P137469	85337	PIE	12/20/2022
P137481	85343	PIE	12/21/2022
P137400	85312	PIN	12/27/2022
P137518	85361	PIE	12/27/2022
P137506	85349	PIE	12/28/2022

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 26 grab sample records for the projects/locations described in the *Introduction* indicate that a sample was not collected in most cases due to no flow or shallow water. 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
85305016	PIN	P137388-16	S355B	10/10/2022	Gates closed. No flow.
85305018	PIN	P137388-18	S355A	10/10/2022	Gates closed. No flow.
85308035	PIN	P137396-35	S12B	10/31/2022	Gates closed. No flow.
85345025	PIE	P137502-25	BERMB3	11/01/2022	Too shallow to sample.
85314013	PIN	P137422-13	S355B	11/07/2022	Gates closed. No flow.
85314015	PIN	P137422-15	S355A	11/07/2022	Gates closed. No flow.
85314039	PIN	P137422-39	S12B	11/07/2022	Gates closed. No flow.
85340004	PIE	P137478-4	G737	11/08/2022	Too shallow to sample.
85309035	PIN	P137397-35	S12B	11/14/2022	Gates closed. No flow.
85358004	PIE	P137515-4	G737	11/15/2022	No recorded flow. No sample.
85346025	PIE	P137503-25	BERMB3	11/15/2022	No flow during site visited.
85315039	PIN	P137423-39	S12B	11/21/2022	Gates closed. No flow.
85341004	PIE	P137479-4	G737	11/22/2022	No recorded flow. No sample.
85310035	PIN	P137398-35	S12B	11/28/2022	Gates closed. No flow.
85359004	PIE	P137516-4	G737	11/29/2022	No recorded flow. No sample.
85316013	PIN	P137424-13	S355B	12/05/2022	Gates closed. No flow.
85316015	PIN	P137424-15	S355A	12/05/2022	Gates closed. No flow.
85316039	PIN	P137424-39	S12B	12/05/2022	Gates closed. No flow.
85342004	PIE	P137480-4	G737	12/06/2022	No recorded flow. No sample.
85311035	PIN	P137399-35	S12B	12/12/2022	Gates closed. No flow.
85360004	PIE	P137517-4	G737	12/13/2022	No recorded flow. No sample.
85348025	PIE	P137505-25	BERMB3	12/13/2022	No flow during site visited.
85317039	PIN	P137425-39	S12B	12/19/2022	Gates closed. No flow.
85343004	PIE	P137481-4	G737	12/20/2022	No recorded flow. No sample.
85361004	PIE	P137518-4	G737	12/27/2022	No recorded flow. No sample.
85312035	PIN	P137400-35	S12B	12/27/2022	Gates closed. No flow.

a. 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 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, 29 field quality control blanks (one EB, six FBs, 22 FCEBs) and four RSs were collected. None of the 29 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*, one PMR was assigned by project managers and no qualifier was assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). This potential quality assurance process-related qualifier is detailed in **Table 4**.

Table 4. Results with qualifiers and remark codes during the reporting period.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code / Reason
85335012	PIE	P137467-12	S332DX	11/22/2022	PMR: No associated collection depth.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the fourth 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 325 TP analyses for the grab samples collected during the 45 sampling events listed in **Table 2** and detailed in RDS. Of those 325 TP results, 160 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 325 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 qualifiers were added for the 160 TP results from 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 160 TP results reported, two results were below the MDL and nine 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.

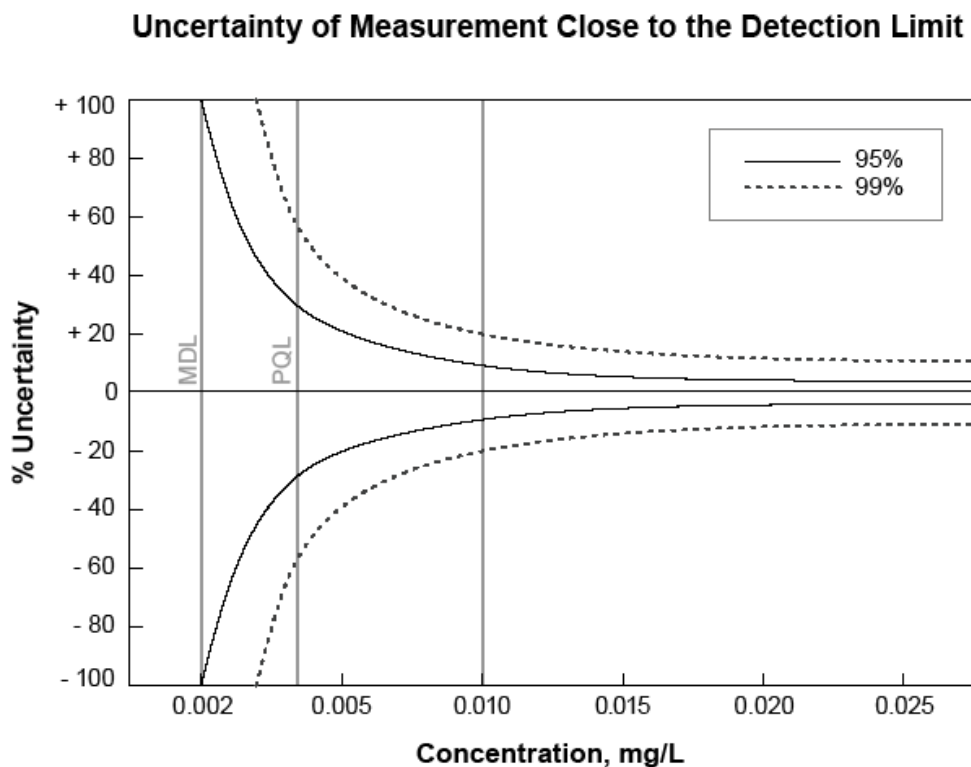


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 2022, the laboratory received TP results from one performance evaluation study, Phenova #WP1022. The reported result was evaluated as "acceptable" with a calculated Z-score of 0.112.

LABORATORY AUDITS

No quality system laboratory audits were conducted during this reporting period.

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.
- 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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- 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).