

Quality Assessment Report for Water Quality Monitoring

January – March 2022



Submitted to the
Technical Oversight Committee
July 26, 2022

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), primarily for the following projects and their associated stations from January 1, 2022, through March 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 May 17, 2022. 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 January 1 to March 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_jan_mar_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 project/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 will be referred to as the Reference Data Set (RDS) in this report. All sample analyses for TP were completed at the SFWMD Analytical Services Chemistry Laboratory (Department of Health Identification # E46077).

If available, this report will also include 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 38 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 38 sampling events described in **Table 1**, a total of 57 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, water being too shallow, site under construction, platform being unsafe, or live insect in composite bucket. The grab sample identifiers and reasons these samples were not collected are shown in **Table 2**.

Table 1. Sampling events for the reporting period.

Work Identifier	Work Order	Project ^a	Date Collected
P129420	81582	PIN	01/03/2022
P130460	82083	EVPA	01/04/2022
P129534	81642	PIE	01/04/2022
P130468	82087	EVPA	01/05/2022
P129412	81578	PIN	01/10/2022
P129576	81663	PIE	01/11/2022
P129564	81657	PIE	01/11/2022
P131308	82504	PIN	01/18/2022
P131399	82534	PIE	01/18/2022
P131298	82499	PIN	01/24/2022
P131368	82541	PIE	01/25/2022
P131370	82542	PIE	01/25/2022
P131300	82500	PIN	02/01/2022
P130461	82084	EVPA	02/01/2022
P131400	82535	PIE	02/02/2022
P130469	82088	EVPA	02/02/2022
P131334	82515	PIN	02/07/2022
P131423	82549	PIE	02/08/2022
P131433	82554	PIE	02/09/2022
P131344	82520	PIN	02/14/2022
P131401	82536	PIE	02/16/2022
P131335	82516	PIN	02/21/2022
P131424	82550	PIE	02/22/2022
P131434	82555	PIE	02/22/2022
P131345	82521	PIN	02/28/2022
P133225	83323	EVPA	03/01/2022
P133164	83281	PIE	03/01/2022
P133231	83326	EVPA	03/02/2022
P131336	82517	PIN	03/07/2022
P131435	82556	PIE	03/08/2022
P131346	82522	PIN	03/14/2022
P133165	83282	PIE	03/15/2022
P131337	82518	PIN	03/21/2022
P131426	82552	PIE	03/23/2022
P131436	82557	PIE	03/23/2022
P131347	82523	PIN	03/28/2022
P133166	83283	PIE	03/29/2022
P133148	83292	PIE	03/29/2022

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 Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Rejected or Not Collected
81582013	PIN	P129420-13	S355B	01/03/2022	Gates closed. No flow.
81582015	PIN	P129420-15	S355A	01/03/2022	Gates closed. No flow.
81582027	PIN	P129420-27	S333	01/03/2022	Platform unsafe to sample.
81582038	PIN	P129420-38	S12C	01/03/2022	Gates closed. No flow.
81582039	PIN	P129420-39	S12B	01/03/2022	Gates closed. No flow.
81642026	PIE	P129534-26	G737	01/04/2022	Too shallow to sample.
81578023	PIN	P129412-23	S333	01/10/2022	Platform unsafe to sample.
81578034	PIN	P129412-34	S12C	01/10/2022	Gates closed. No flow.
81578035	PIN	P129412-35	S12B	01/10/2022	Gates closed. No flow.
81663004	PIE	P129576-4	G737	01/11/2022	Too shallow to sample.
82504027	PIN	P131308-27	S333	01/18/2022	Platform unsafe to sample.
82534026	PIE	P131399-26	G737	01/18/2022	Too shallow to sample.
82504038	PIN	P131308-38	S12C	01/18/2022	Gates closed. No flow.
82504039	PIN	P131308-39	S12B	01/18/2022	Gates closed. No flow.
82504040	PIN	P131308-40	S12A	01/18/2022	Gates closed. No flow.
82499027	PIN	P131298-27	S333	01/24/2022	Platform unsafe to sample.
82499026	PIN	P131298-26	S333	01/24/2022	Platform unsafe to sample.
82499037	PIN	P131298-37	S12C	01/24/2022	Gates closed. No flow.
82499038	PIN	P131298-38	S12B	01/24/2022	Gates closed. No flow.
82542004	PIE	P131370-4	G737	01/25/2022	Too shallow to sample.
82500030	PIN	P131300-30	S333	01/31/2022	Platform unsafe to sample.
82500041	PIN	P131300-41	S12C	01/31/2022	Gates closed. No flow.
82500042	PIN	P131300-42	S12B	01/31/2022	Gates closed. No flow.
82084002	EVPA	P130461-2	LOX3	02/01/2022	Live aquatic insect in composite bucket.
82535026	PIE	P131400-26	G737	02/01/2022	Too shallow to sample.
82515034	PIN	P131334-34	S12C	02/07/2022	Gates closed. No flow.
82515035	PIN	P131334-35	S12B	02/07/2022	Gates closed. No flow.
82520013	PIN	P131344-13	S355B	02/14/2022	Gates closed. No flow.
82520015	PIN	P131344-15	S355A	02/14/2022	Gates closed. No flow.
82520038	PIN	P131344-38	S12C	02/14/2022	Gates closed. No flow.
82520039	PIN	P131344-39	S12B	02/14/2022	Gates closed. No flow.
82516034	PIN	P131335-34	S12C	02/21/2022	Gates closed. No flow.
82516035	PIN	P131335-35	S12B	02/21/2022	Gates closed. No flow.
82550026	PIE	P131424-26	BERMB3	02/22/2022	Too shallow to sample.
82521038	PIN	P131345-38	S12C	02/28/2022	Gates closed. No flow.
82521039	PIN	P131345-39	S12B	02/28/2022	Gates closed. No flow.
83290014	PIE	P133146-14	S332DX	03/01/2022	Site under construction.
82517034	PIN	P131336-34	S12C	03/07/2022	Gates closed. No flow.
82517035	PIN	P131336-35	S12B	03/07/2022	Gates closed. No flow.
82517036	PIN	P131336-36	S12A	03/07/2022	Gates closed. No flow.
82551015	PIE	P131425-15	S332DX	03/08/2022	Site under construction.
82556004	PIE	P131435-4	G737	03/08/2022	Too shallow to sample.
82551025	PIE	P131425-25	S328	03/08/2022	Gates closed. No flow.
82551026	PIE	P131425-26	BERMB3	03/08/2022	Too shallow to sample.
82522013	PIN	P131346-13	S355B	03/14/2022	Gates closed. No flow.
82522015	PIN	P131346-15	S355A	03/14/2022	Gates closed. No flow.
82522038	PIN	P131346-38	S12C	03/14/2022	Gates closed. No flow.
82522039	PIN	P131346-39	S12B	03/14/2022	Gates closed. No flow.
83291014	PIE	P133147-14	S332DX	03/15/2022	Site under construction.
83282004	PIE	P133165-4	G737	03/15/2022	Too shallow to sample.

Work Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Rejected or Not Collected
82518034	PIN	P131337-34	S12C	03/21/2022	Gates closed. No flow.
82518035	PIN	P131337-35	S12B	03/21/2022	Gates closed. No flow.
82557004	PIE	P131436-4	G737	03/23/2022	Too shallow to sample.
82552026	PIE	P131426-26	BERMB3	03/23/2022	Too shallow to sample.
82523038	PIN	P131347-38	S12C	03/28/2022	Gates closed. No flow.
82523039	PIN	P131347-39	S12B	03/28/2022	Gates closed. No flow.
83283004	PIE	P133166-4	G737	03/29/2022	Too shallow to sample.

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 38 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 qualifiers were 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 period specified in this report.

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 297 TP analyses for the grab samples collected during the 38 sampling events listed in **Table 1**. Of those 297 TP results, 144 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 297 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 of the analyses conducted in a given 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 144 TP results from samples collected from projects/locations listed in the *Introduction*, no qualifiers were added as a result 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 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 144 TP results reported, no results were below the MDL and nine samples had concentrations between the MDL and the PQL.

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:

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

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.

Uncertainty of Measurement Close to the Detection Limit

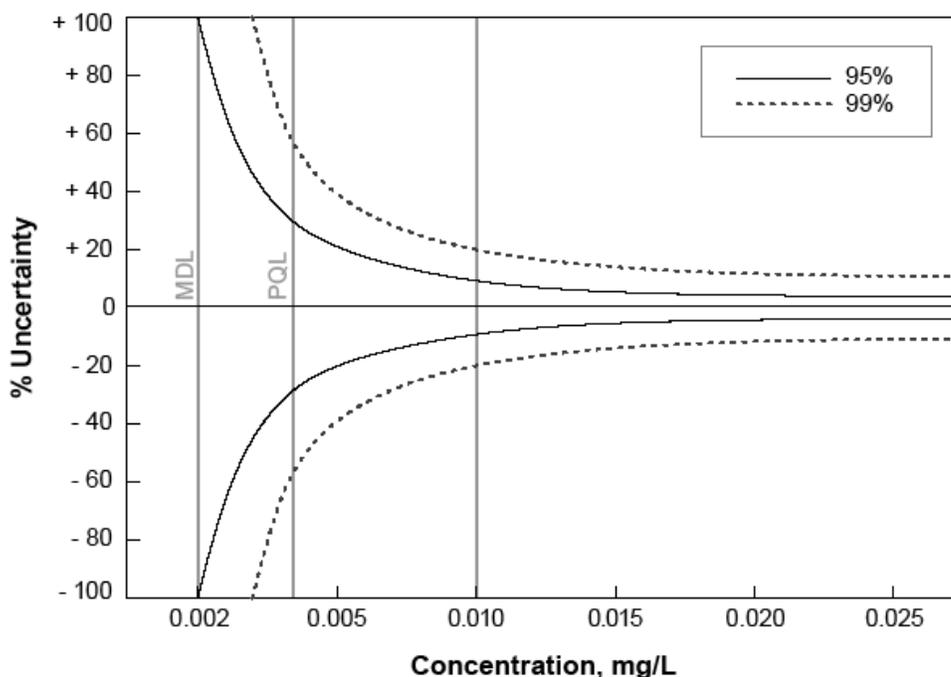


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 various studies to evaluate the proficiency of the laboratory's quality system. During the first quarter of 2022, the laboratory received results from the Environmental Canada surface water performance evaluation study. All ten results received a Z-score of less than 0.5, and the laboratory received a "very good" rating.

LABORATORY AUDITS

During this reporting period the laboratory performed its annual internal audit. There were five corrective actions, one observation, and two recommendations identified. These findings have been entered into the laboratory's corrective action log and in the process of being addressed.

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.
- 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-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 pre-cleaned 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 an 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).