

Quality Assessment Report for Water Quality Monitoring

July – September 2021



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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD) laboratory analysis and field sampling for total phosphorus (TP), primarily for the following projects and their associated stations from July 1, 2021, through September 30, 2021. The analysis contained 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 November 9, 2021. 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, 2021. 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.

For the purpose of preparing this report, a Microsoft Excel workbook named "qa_report_jul_sep_2021_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 that were completed during the period specified in this report.

FIELD SAMPLING QUALITY ASSESSMENT

SAMPLE COLLECTION

All samples were collected by WQM staff. A total of 40 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 dates the samples were collected.

During the 40 sampling events described in **Table 1**, a total of 48 grab sample records for the projects/locations described in the *Introduction* to this report indicate that a sample was not collected, typically due to no flow or because it was too shallow or overgrown by vegetation to collect a sample. 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
P125826	80028	PIE	07/06/2021
P124862	79545	PIE	07/06/2021
P124797	79520	PIN	07/07/2021
P125771	79999	EVPA	07/07/2021
P125779	80003	EVPA	07/08/2021
P126987	80612	PIN	07/12/2021
P124898	79563	PIE	07/13/2021
P124886	79571	PIE	07/13/2021
P126989	80613	PIN	07/19/2021
P126838	80536	PIE	07/20/2021
P126852	80543	PIE	07/20/2021
P126809	80522	PIN	07/26/2021
P126903	80569	PIE	07/27/2021
P126901	80568	PIE	07/27/2021
P126797	80516	PIN	08/02/2021
P125772	80000	EVPA	08/03/2021
P127895	81027	PIE	08/03/2021
P125780	80004	EVPA	08/04/2021
P126810	80523	PIN	08/09/2021
P127909	81040	PIE	08/10/2021
P127921	81034	PIE	08/10/2021
P126798	80517	PIN	08/16/2021
P127896	81028	PIE	08/17/2021
P126811	80524	PIN	08/23/2021
P127910	81041	PIE	08/24/2021
P127922	81035	PIE	08/24/2021
P126799	80518	PIN	08/30/2021
P127897	81029	PIE	09/01/2021
P126170	80206	EVPA	09/01/2021
P126174	80208	EVPA	09/02/2021
P126812	80525	PIN	09/07/2021
P127911	81042	PIE	09/08/2021
P127923	81036	PIE	09/08/2021
P126800	80519	PIN	09/13/2021
P127898	81030	PIE	09/15/2021
P126813	80526	PIN	09/20/2021
P127924	81037	PIE	09/21/2021
P127912	81043	PIE	09/21/2021
P126801	80520	PIN	09/27/2021
P127899	81031	PIE	09/28/2021

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

Table 2. Grab samples not collected during the reporting period.

Work Identifier	Project ^a	Sample Identifier	Station	Date	Reason Sample Was Not Collected
79520013	PIN	P124797-13	S355B	07/06/2021	Gates closed. No flow.
79520015	PIN	P124797-15	S355A	07/06/2021	Gates closed. No flow.
79520037	PIN	P124797-37	S12D	07/06/2021	Gates closed. No flow.
79520039	PIN	P124797-39	S12B	07/06/2021	Gates closed. No flow.
79999007	EVPA	P125771-7	LOX7	07/07/2021	Too shallow to sample.
79999006	EVPA	P125771-6	LOX8	07/07/2021	Too shallow to sample.
79999005	EVPA	P125771-5	LOX9	07/07/2021	Too shallow to sample.
79999004	EVPA	P125771-4	LOX10	07/07/2021	Too shallow to sample.
79999003	EVPA	P125771-3	LOX5	07/07/2021	Too shallow to sample.
79999002	EVPA	P125771-2	LOX3	07/07/2021	Too shallow to sample.
80612036	PIN	P126987-36	S12D	07/12/2021	Gates closed. No flow.
80612038	PIN	P126987-38	S12B	07/12/2021	Gates closed. No flow.
79563005	PIE	P124898-5	G737	07/13/2021	No flow. Site not visited.
79571027	PIE	P124886-27	BERMB3	07/13/2021	Too shallow to sample.
80613040	PIN	P126989-40	S12D	07/19/2021	Gates closed. No flow.
80613042	PIN	P126989-42	S12B	07/19/2021	Gates closed. No flow.
80543005	PIE	P126852-5	G737	07/20/2021	No flow. Site not visited.
80522034	PIN	P126809-34	S12C	07/26/2021	Gates closed. No flow.
80522035	PIN	P126809-35	S12B	07/26/2021	Gates closed. No flow.
80569004	PIE	P126903-4	G737	07/27/2021	No flow. Site not visited.
80568031	PIE	P126901-31	BERMB3	07/27/2021	Area overgrown by vegetation.
80516013	PIN	P126797-13	S355B	08/02/2021	Gates closed. No flow.
80516015	PIN	P126797-15	S355A	08/02/2021	Gates closed. No flow.
80516037	PIN	P126797-37	S12D	08/02/2021	Gates closed. No flow.
80516038	PIN	P126797-38	S12C	08/02/2021	Gates closed. No flow.
80516039	PIN	P126797-39	S12B	08/02/2021	Gates closed. No flow.
80000002	EVPA	P125772-2	LOX3	08/03/2021	Too shallow to sample.
81027026	PIE	P127895-26	G737	08/03/2021	No flow. Site not visited.
80523034	PIN	P126810-34	S12C	08/09/2021	Gates closed. No flow.
80523035	PIN	P126810-35	S12B	08/09/2021	Gates closed. No flow.
80523036	PIN	P126810-36	S12A	08/09/2021	Gates closed. No flow.
81034004	PIE	P127921-4	G737	08/10/2021	No flow. Site not visited.
81040026	PIE	P127909-26	BERMB3	08/10/2021	Too shallow to sample.
81028026	PIE	P127896-26	G737	08/17/2021	No flow. Site not visited.
81035004	PIE	P127922-4	G737	08/24/2021	No flow. Site not visited.
81041026	PIE	P127910-26	BERMB3	08/24/2021	Area overgrown by vegetation.
80518013	PIN	P126799-13	S355B	08/30/2021	Gates closed. No flow.
80518015	PIN	P126799-15	S355A	08/30/2021	Gates closed. No flow.
81029026	PIE	P127897-26	G737	08/31/2021	No flow. Site not visited.
80208006	EVPA	P126174-6	LOX11	09/02/2021	No bottle due to total depth below 0.1 meter
80525033	PIN	P126812-33	S12D	09/07/2021	Gates closed. No flow.
81042026	PIE	P127911-26	BERMB3	09/08/2021	Area overgrown by vegetation.
80519013	PIN	P126800-13	S355B	09/13/2021	Gates closed. No flow.
80519015	PIN	P126800-15	S355A	09/13/2021	Gates closed. No flow.
80519037	PIN	P126800-37	S12D	09/13/2021	Gates closed. No flow.
80526033	PIN	P126813-33	S12D	09/20/2021	Gates closed. No flow.
80520037	PIN	P126801-37	S12D	09/27/2021	Gates closed. No flow.
80520040	PIN	P126801-40	S12A	09/27/2021	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

To assess the quality of the sample collection process as required by the *Field Sampling Manual*, field quality control samples are collected at various sampling locations during each sampling event. The results from these quality control samples are associated with all samples collected during the sampling trip (day) and if a specific field quality control sample fails to meet the requirements set forth in the Florida Department of Environmental Protection (FDEP) *Quality Assurance Rule* (Chapter 62-160, Florida Administrative Code [F.A.C.]), 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 include 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 40 sampling events described above, a total of 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), which is 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 three J qualifiers were assigned as per the FDEP *Quality Assurance Rule* (Chapter 62-160, F.A.C.). These quality assurance process-related qualifiers are detailed in **Table 3**.

Table 3. Results with qualifiers and remark codes during the reporting period.

Work Identifier	Project ^a	Sample Identifier	Station	Collection Date	Qualifier or Remark Code/Reason
80028024	PIE	P125826-24	S328	07/06/2021	J: Sample was taken from a disconnected pool and was not representative of the surrounding wetland.
79571025	PIE	P124886-25	S328	07/13/2021	J: Sample was taken from a disconnected pool and was not representative of the surrounding wetland.
80568028	PIE	P126901-28	S328	07/27/2021	J: Sample was taken from a disconnected pool and was not representative of the surrounding wetland.

a. PIE – Everglades National Park Inflows East.

FIELD AUDITS

SFWMD did not conduct any field audits on TOC-related projects during the third quarter of 2021.

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 a total of 321 TP analyses for the grab samples collected during the 40 sampling events listed in **Table 1**. Of those 321 TP results, 153 were for grab samples collected from projects/locations listed in the *Introduction* (excluding field quality control samples). For reference, a complete set of all 321 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 153 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 153 TP results reported, no result was below the MDL and seven 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 it is accompanied by a statement of the associated uncertainty. 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.

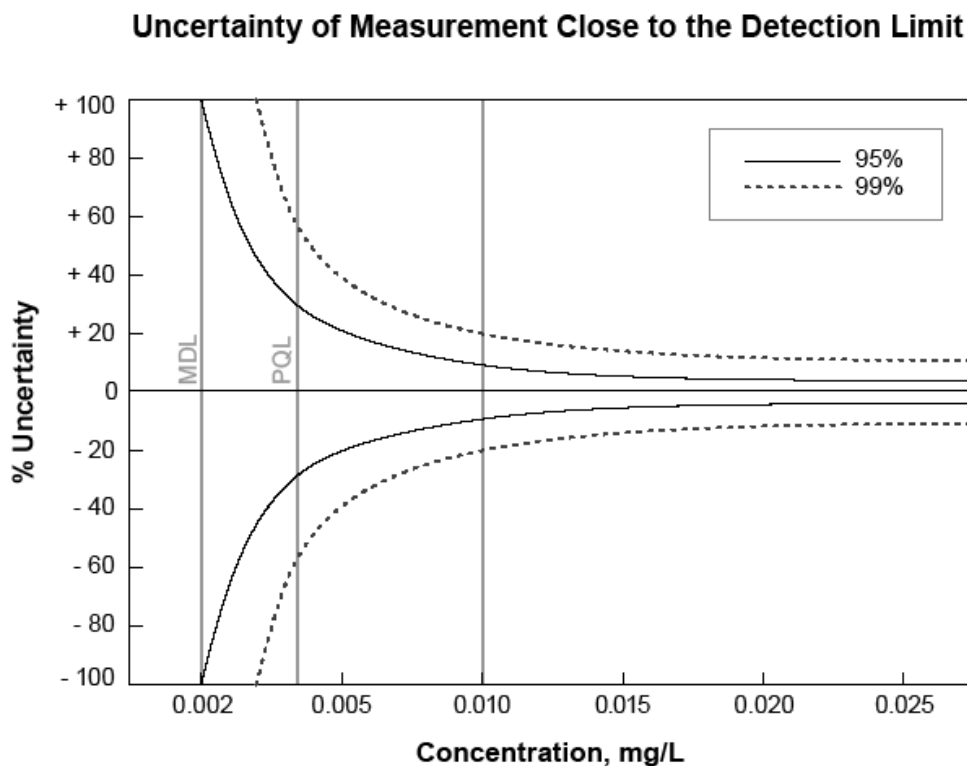


Figure 1. Estimated uncertainties at the 95% and 99% CIs relative to the MDL and PQL of the TP measurement process.

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 2021, the laboratory received results from the QUASIMEME saline / brackish waters performance evaluation study. All seven reported results were identified as "acceptable" with no Z-score exceeding ± 1.1 .

LABORATORY AUDITS

During this reporting period no quality system laboratory audits were conducted.

PROCEDURE UPDATES

The TP analytical procedure (Standard Methods 4500 P-F, Automated Ascorbic Acid Reduction Method) did not change during this reporting period.

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).