Quality Assessment Report for Water Quality Monitoring

January – March 2014



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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) monitoring, primarily for the following projects and their associated stations from January 1, 2014 through March 31, 2014:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356-334
- Everglades National Park Inflow East (PIE): S332DX, S18C, DS4, and BERMB3
- Everglades Protection Area (EVPA): LOX3 through LOX16

Because field quality control (QC) samples are collected for sampling events that include multiple project samples for the stations of interest, the report may also cover information on stations or projects other than those in the above list.

The SFWMD's *Field Sampling Quality Manual* (SFWMD 2013) provides the minimum requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2013) provides the minimum requirements followed in 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 the field and laboratory QC results during this quarter. The SFWMD's Laboratory Information Management System (LIMS) provided the data used in this report. These data are available in the SFWMD's DBHYDRO database. Appendix B contains all TP results for samples of interest to the Everglades Technical Oversight Committee (TOC), collected from January 1, 2014 through March 31, 2014.

This report includes an analysis of the SFWMD laboratory's performance on the EVPA split samples with the Florida Department of Environmental Protection (FDEP) for a one-year period. The report also includes the results of the National Water Research Institute Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program.

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

This period had no major procedural updates related to TP sample collection.

SAMPLES NOT COLLECTED

Table 1 lists the 55 samples that were not collected for this reporting period. Samples were not collected due to lack of flow, site dry, shallow water depth, or insufficient water level.

Project	Collection Date	Station	Comments
PIN	6-Jan-2014	S12B	No flow, no sample collected
PIN	6-Jan-2014	S12C	No flow, no sample collected
PIE	7-Jan-2014	BERMB3	No flow, no sample collected
EVPA	7-Jan-2014	LOX3	Total depth less than 0.10 m, no sample collected
EVPA	7-Jan-2014	LOX5	Total depth less than 0.10 m, no sample collected
PIN	13-Jan-2014	S12B	No flow, no sample collected
PIN	13-Jan-2014	S12C	No flow, no sample collected
PIN	13-Jan-2014	S12D	No flow, no sample collected
PIN	13-Jan-2014	S355A	No flow, no sample collected
PIN	13-Jan-2014	S355B	No flow, no sample collected
PIN	21-Jan-2014	S12B	No flow, no sample collected
PIN	21-Jan-2014	S12C	No flow, no sample collected
PIN	21-Jan-2014	S12D	No flow, no sample collected
PIE	21-Jan-2014	BERMB3	No flow, no sample collected
PIN	21-Jan-2014	S355A	No flow, no sample collected
PIN	21-Jan-2014	S355B	No flow, no sample collected
PIN	27-Jan-2014	S12B	No flow, no sample collected
PIN	27-Jan-2014	S12C	No flow, no sample collected
PIN	27-Jan-2014	S12D	No flow, no sample collected
PIN	27-Jan-2014	S355A	No flow, no sample collected
PIN	27-Jan-2014	S355B	No flow, no sample collected
PIN	3-Feb-2014	S12B	No flow, no sample collected
PIN	3-Feb-2014	S12C	No flow, no sample collected
PIN	3-Feb-2014	S12D	No flow, no sample collected
PIE	4-Feb-2014	BERMB3	Site dry, no sample collected
PIN	10-Feb-2014	S12B	No flow, no sample collected
PIN	10-Feb-2014	S12C	No flow, no sample collected
PIN	10-Feb-2014	S12D	No flow, no sample collected
PIN	10-Feb-2014	S355A	No flow, no sample collected
PIN	10-Feb-2014	S355B	No flow, no sample collected

Table 1. Samples not collected for January 1, 2014 to March 31, 2014 period.

Collection Date	Station	Comments
17-Feb-2014	_	No flow, no sample collected
17-Feb-2014	S12C	No flow, no sample collected
18-Feb-2014	S355A	No flow, no sample collected
18-Feb-2014	S355B	No flow, no sample collected
18-Feb-2014	BERMB3	No flow, no sample collected
24-Feb-2014	S12B	No flow, no sample collected
24-Feb-2014	S12C	No flow, no sample collected
24-Feb-2014	S355A	No flow, no sample collected
24-Feb-2014	S355B	No flow, no sample collected
3-Mar-2014	S12B	No flow, no sample collected
3-Mar-2014	S12C	No flow, no sample collected
4-Mar-2014	BERMB3	No flow, no sample collected
10-Mar-2014	S12B	No flow, no sample collected
10-Mar-2014	S12C	No flow, no sample collected
10-Mar-2014	S355A	No flow, no sample collected
10-Mar-2014	S355B	No flow, no sample collected
17-Mar-2014	S12B	No flow, no sample collected
17-Mar-2014	S12C	No flow, no sample collected
18-Mar-2014	S355A	No flow, no sample collected
18-Mar-2014	S355B	No flow, no sample collected
18-Mar-2014	BERMB3	No flow, no sample collected
24-Mar-2014	S12B	No flow, no sample collected
24-Mar-2014	S12C	No flow, no sample collected
24-Mar-2014	S355A	No flow, no sample collected
24-Mar-2014	S355B	No flow, no sample collected
	18-Feb-2014 18-Feb-2014 24-Feb-2014 24-Feb-2014 24-Feb-2014 24-Feb-2014 24-Feb-2014 3-Mar-2014 3-Mar-2014 10-Mar-2014 12-Mar-2014 13-Mar-2014 14-Mar-2014 14-Mar-2014 15-Mar-2014 18-Mar-2014 18-Mar-2014 24-Mar-2014 24-Mar-2014 24-Mar-2014	17-Feb-2014 S12B 17-Feb-2014 S12C 18-Feb-2014 S355A 18-Feb-2014 S355B 18-Feb-2014 S12B 24-Feb-2014 S12B 24-Feb-2014 S12C 24-Feb-2014 S12B 24-Feb-2014 S12C 24-Feb-2014 S355A 24-Feb-2014 S355B 3-Mar-2014 S12B 3-Mar-2014 S12B 3-Mar-2014 S12B 10-Mar-2014 S12B 10-Mar-2014 S12B 10-Mar-2014 S12C 10-Mar-2014 S12B 10-Mar-2014 S12B 10-Mar-2014 S12C 10-Mar-2014 S12B 17-Mar-2014 S12B 17-Mar-2014 S12C 18-Mar-2014 S12C 18-Mar-2014 S355A 18-Mar-2014 S12B 18-Mar-2014 S12B 24-Mar-2014 S12C 24-Mar-2014 S12C

Table 1. Continued.

DESCRIPTION OF WADER DEPTH MEASUREMENT

On March 5, 2014 during the project EVPA sample collection in Water Conservation Area1 (P70002), the depth measuring pole, a Paluga pole, was lost at the fourth station visited that day. The wooden meter stick typically in the tail compartment of the helicopter was missing.

The total depth and depth to consolidated sediments measurements for the five remaining stations sampled on this date—LOX6, LOX11, LOX13, LOX14, and LOXA124—were estimated using previously applied, graduated markings on the side of the waders worn by one of the sampling technicians. The waders were marked in increments of approximately ten centimeters and these markings were later verified as being within a centimeter when compared to a meter stick. While the method used to estimate the depth readings seemed reasonable, the measurements are not exact, especially for the depth to consolidated sediments measurement, and not performed according to the marsh collection method, which specifies the graduated Paluga pole.

The total depth measurements for the five stations where the measurement was estimated were qualified with a 'J' qualifier. A project manager remark was added to the remaining data associated with the five stations that identifies the depths were estimated using the marks on the waders. While the exact depths were estimated, this did not have an effect on the representativeness of the samples collected, nor the process for collecting the samples because of the precision in the marks. The process for collecting samples only changes if the total depth is less than 0.2 meters. All of the total depths where the waders were used were documented as being greater than 0.3 meters. It is therefore the conclusion of Water Quality Monitoring Quality Assurance that it is not necessary to qualify the data associated with the samples collected at these five stations.

FIELD QUALITY CONTROL

Field QC measures consist of field generated equipment blanks (EB), field-cleaned equipment blanks (FCEB), field blanks (FB), split samples (SS), and replicate samples (RS). **Table 2** summarizes EB, FCEB, and FB results for projects of interest to the TOC, as referenced in the table's footnotes. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for all three project replicates.

Table 2. Number of field blanks collected.

Type of Blank	Project	Number of Blanks Collected	Number of Blanks with Analyte Detected
	EVPA	1	0
EB	PIE	2	0
	PIN	1	0
	EVPA	6	0
FCEB	PIE	24	0
	PIN	18	0
FB	EVPA	0	0
ГВ	PIN	11	0

Type of Blank	Project	Number of Blanks Collected	Number of Blanks with Analyte Detected	
	PIE	12	0	
Total		75	0	

Notes:

- All blanks were from sampling events containing grab and auto-sampler samples collected during the sampling event on the day of collection or day adjacent to the collection date for the compliance samples.
- FCEB, EB and FB acceptance criteria: they must be less than the method detection limit (MDL).
- When sample concentrations are less than 10 times the blank values that were equal or greater than the MDL, the qualifier "J" is assigned to the associated sample(s).
- MDL 0.002 mg/L

Project Code	Number of Samples (Replicates)	Date Collected	Station	% RSD	Average Value (mg/L)	Comments
PIN	3	6-Jan-2014	TAMBR105*	3.3	0.047	The precision criterion was met.
PIN	3	3-Feb-2014	S12A	6.9	0.008	The precision criterion was met.
PIE	3	3-Feb-2014	S700*	4.2	0.014	The precision criterion was met.
PIE	3	4-Feb-2014	AJC1*	25.0**	0.004	All replicates results < PQL
EVPA	3	19-Feb-2014	CA27*	6.7	0.009	The precision criterion was met.
EVPA	3	4-Mar-2014	LOX8	0.0	0.008	The precision criterion was met.

Table 3. Precis	sion summary for	TP field replicates.
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Notes:

- The SFWMD's chemistry laboratory conducted all TP analyses.
- Field precision must be ≤ 20 percent. The laboratory applied this criterion only if sample values were greater than the practical quantitation limit (PQL).
- Qualifiers applied to samples (replicates) that a precision criterion was not met if average concentration exceeds 5 times the PQL.
- % RSD percent relative standard deviation
- *The replicate samples were collected at the stations different than stations of interest, which are listed in the Introduction section.
- **% RSD was larger than 20 percent. However, the criterion was not applied because all replicate sample values were lower than the PQL.

FIELD AUDIT

During this quarter, one audit was conducted on the sample processing of the EVPA project in Water Conservation Area (WCA) 1 collected by the Water Quality Monitoring Section and United States Fish and Wildlife Service personnel.

One process improvement was issued as a result of the *Surface Water Quality Sampling in Marshes Standard Operating Procedure* (SOP; SFWMD, SFWMD-FIELD-SOP-004); the SOP did not completely define sample description to include the amount of suspended solids. The language in the SOP was updated to clarify the procedure. This process improvement did not negatively affect the quality of the sample data.

LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

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

LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figures 1** through **6** show the TP recoveries from various types and levels of QC samples at the SFWMD laboratory from January 1, 2014 through March 31, 2014. Control charts provide a graphical means to demonstrate statistical control, monitor a measurement process, diagnose measurement problems, and document measurement uncertainty. They also are used to monitor and document critical aspects of samples and sampling operation.

Figure 1a shows the recoveries for a laboratory control sample (LCS1) at a TP concentration of 0.300 milligrams per liter (mg/L). Performance limits varied from 96 to 103 percent, and had a mean central line value of 99.3 percent based on 492 results. The acceptable control limit is 90–110 percent.

Figure 2a shows the recoveries for a laboratory control sample (LCS3) at a TP concentration of 0.020 mg/L. Performance limits varied from 91 to 107 percent, and had a mean central line value of 98.9 percent based on 89 results. The acceptable control limit is 90–110 percent.

Figure 3a shows the recoveries for a continuing calibration verification sample (CCV) at a TP concentration of 0.200 mg/L. Performance limits varied from 97 to 102 percent, and had a mean central line value of 99.6 percent based on 403 results. The acceptable control limit is 90–110 percent.

Figure 4a shows the recoveries for the method detection limit (MDL) sample (LCS5) at a TP concentration of 0.004 mg/L and results varied from 0.003 to 0.005 mg/L based on 89 results.

Figure 4c show the recoveries for the practical quantitation limit (PQL) varied from 75 to 125 percent. The acceptable control limit is 55–145 percent.

Figures 5a and **6a** present the precision and matrix spike recoveries for TP analyses during the reporting period. If QC recoveries are outside the set limits, then the SFWMD's laboratory usually rejects the analytical batch and re-analyzes.

The acceptable recoveries for the QC samples, except the PQL check, are within ± 10 percent of the true value. The daily MDL check with a true value of 0.004 mg/L indicates that the laboratory has consistently achieved the established MDL of 0.002 mg/L. The mean recovery for the organic check, a solution prepared from phytic acid and used to prepare matrix spikes, was 100.2 percent based on 318 results.

Figures 1b through **6b** show the distribution of quality control samples in the roughly symmetrical bell-shape form with most values clustered around the central line.

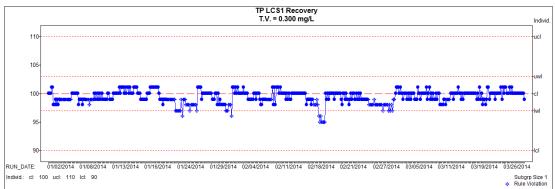


Figure 1a TP QC (Laboratory Control Sample, 0.300 mg/L) sample recoveries.

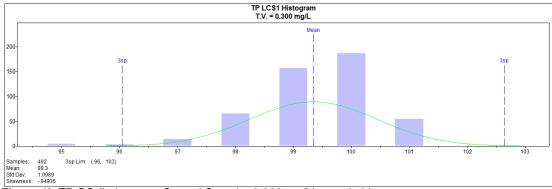


Figure 1b TP QC (Laboratory Control Sample, 0.300 mg/L) sample histogram.

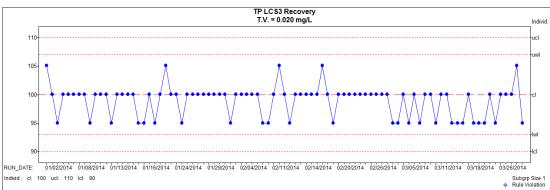


Figure 2a. TP QC (Laboratory Control Sample, 0.020 mg/L) sample recoveries.

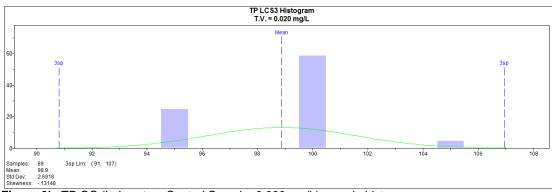
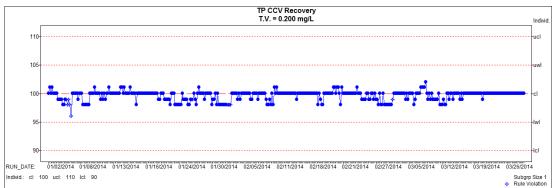
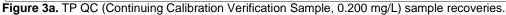


Figure 2b. TP QC (Laboratory Control Sample, 0.020 mg/L) sample histogram.





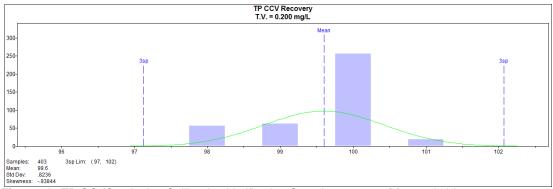


Figure 3b. TP QC (Continuing Calibration Verification Sample, 0.200 mg/L) sample histogram.

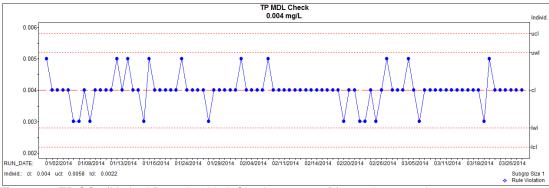


Figure 4a. TP QC5 (Method Detection Limit Check, 0.004 mg/L) sample recoveries.

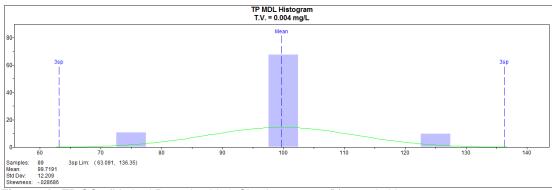
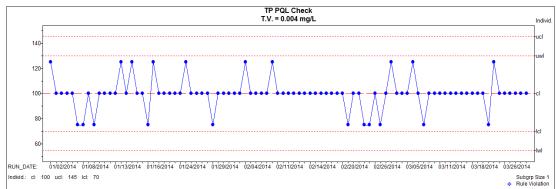
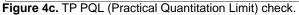
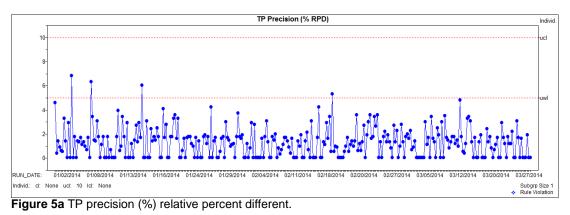


Figure 4b. TP QC5 (Method Detection Limit Check, 0.004 mg/L) sample histogram.







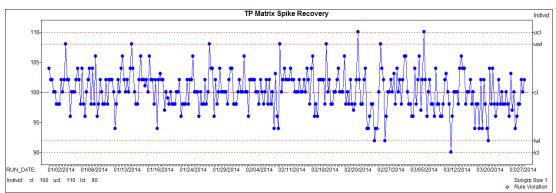
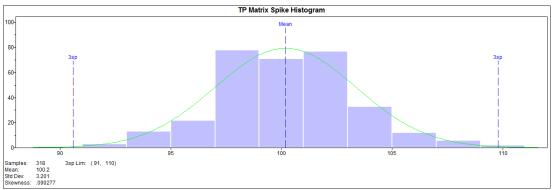
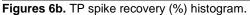


Figure 6a. TP spike recovery (%) data.





Notes for Figures 1 through 6

- T.V. true value
- ucl upper control limit
- uwl upper warning limit
- cl central line
- Iwl lower warning limit
- Icl lower control limit
- Min, Max range of acceptable limits
- Std Dev standard deviation
- Samples number of analyzed QC samples
- 3sp Lim calculated limits for subgroup based on 3 sigma factor
- y-axis label for histogram indicates number of data points

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

The reporting of estimated analytical measurement uncertainty values for all analytes was implemented in July 2012. 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. 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 uncertainty has been estimated using the nested hierarchical methodology by Ingersoll (2001) in combination with a mathematical model found in the Eurachem/CITAC (2000) guide on uncertainty. This QC-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:

$$u(x) = \sqrt{s_0^2 + (s_1^2 x^2)}$$

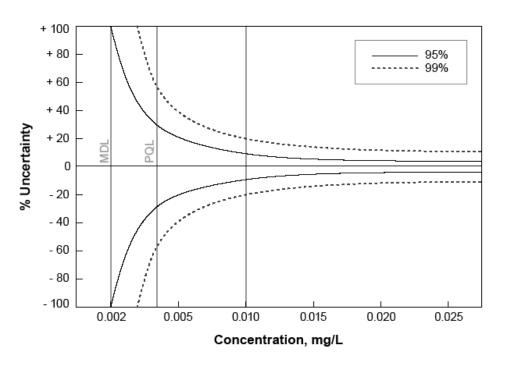
where:

 $\mathbf{u}(\mathbf{x})$ is the combined standard uncertainty in the result x.

 s_0 – a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.

 s_1 – proportionality constant derived from nested hierarchical methodology by Ingersoll.

Figure 7 is presented to clarify the concept of uncertainty of a measurement process relative to the MDL and PQL.



Uncertainty of Measurement Close to the Detection Limit

Figure 7. Uncertainty of TP measurement close to the detection limit.

METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

MDL checks are routinely analyzed with each analytical run. From January 1, 2014 to March 31, 2014, 89 results for MDL checks were reported for TP measurements. The calculated MDL from these results was determined to be 0.001 mg/L, using the procedure described in the Code of Federal Regulations (CFR), 40 CFR 136 Appendix B. These results validated the current laboratory MDL value of 0.002 mg/L.

The performance of the PQL QC sample is presented in **Figures 4a**, **4b**, and **4c**. The average recovery for the PQL was 99.7 %. The average relative standard deviation was 12.2%, which was less than acceptable criterion of 15%. These results validated the current laboratory PQL value of 0.004 mg/L.

The reported values between the MDL (0.002 mg/L) and less than PQL (0.004 mg/L) are assigned the "I" qualifier, indicating that the results are at concentrations that cannot be accurately quantified.

INTER-LABORATORY QUALITY CONTROL ASSESSMENT

SPLIT STUDIES WITH FDEP LABORATORY

To continuously assess comparability of results, the SFWMD routinely sends split samples to other laboratories. The statistical evaluation contains the data from the EVPA quarterly splits conducted by the FDEP and the SFWMD laboratories from March 2013 to March 2014 (see **Appendix A**). This comparison contains the TP qualified data. **Figure 8** presents regression analysis of all data, and **Table 4** presents summary statistics for the data pairs.

ALL DATA (TP < 0.020 mg/L)

Figure 8 shows that the intercept is not statistically different from zero and the slope is not statistically different from one for all TP data from both laboratories. The intercept of the regression is not statistically different from zero since the 95 percent confidence interval for the intercept contains zero. The slope of the regression is not different from one statistically since the 95 percent confidence interval for slope contains one. The r^2 (R-square) value of 0.83 indicates strong agreement between two laboratories results. **Table 4** shows that the mean difference (0.0002 mg/L) and the median difference (0.000 mg/L) are statistically insignificant with p-values of 0.562 and 0.5099, respectively.

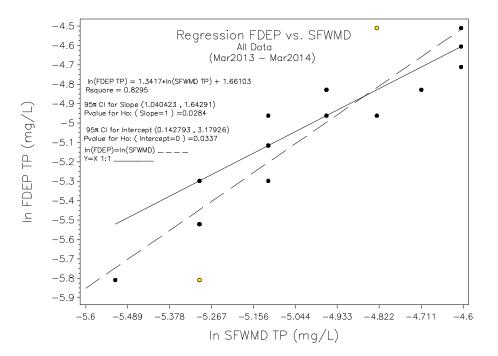


Figure 8. Regression analysis for all TP data.

	Summary Statistics								
	Lab	Ν		Mean (mg/L)	Median	(mg/L)			
	FDEP	20		0.0066	0.0065				
	SFWMD	20		0.00675	0.006				
	Statistical Test of Hypotheses								
All Data	Summary of Paired Differences (mg/L)			Hypothesis	Test	P-value			
	Mean of Differences	0.0002	Mea	n of Differences = 0	Student's t	0.562			
	Median of Differences			ian of Differences = 0	Signed Rank	0.5099			

Table 4. Comparison of SFWMD and FDEP split TP samples (December 2012–December 2013).

Notes:

- Differences calculated as the SFWMD TP minus the FDEP TP. The mean and median differences for all concentration levels are at or below the MDL.
- Data were not used in this comparison study if the FDEP value was below the FDEP's detection limit (0.002 mg/L).

TP > 0.020 mg/L

No data points were in the range where the TP was greater than or equal to 0.020 mg/L.

In summary, the mean and median differences for all TP data were below the MDL (0.002 mg/L) for both laboratories. The pair differences were statistically insignificant in both; the sign-rank test (p > 0.05) and Shapiro-Wilk (p=0.0122) for the non-normally distributed paired data and linear regression.

National Water Research Institute Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program

Environment Canada provides accredited proficiency program studies for a wide range of inorganic constituents in water. The purpose of the program is to identify sources of measurement uncertainties and variation among analytical results, and to provide information on overall data quality and reliability of analytical measurements of inorganic parameters in natural waters. The results for the SFWMD laboratory from the most recent Performance Testing Study 103 are presented in **Table 5** (March 2014). The SFWMD laboratory was rated on performance of TP as "Ideal" (highest). The evaluation includes systematic bias and precision, a laboratory appraisal and a summary of Z-scores (ISO 13528:2005).

The Z-scores, based on the International Organization of Standardization (ISO), Guide 43 can be interpreted as follows:

- |Z| < 2 Satisfactory performance 2 < |Z| < 3 Questionable performance
 - |Z| > 3 Unsatisfactory performance

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.390	0.579	0.00229	0.0257	0.333	0.0137	0.248	0.853	0.138	0.00278
Reported Results, mg/L	0.388	0.588	0.002	0.025	0.335	0.013	0.248	0.861	0.141	< 0.002
Z-score	-0.11	0.37	-0.23	-0.39	0.15	-0.28	0.00	0.19	0.47	NR

Table 5. Performance in PT Study 103 for TP, March 2014.

Notes:

- Assigned value this value is the calculated true value of the standard based upon the actual composition of the standard.
- Reported value the test result reported to the study provider for a specific analyte.
- NR Not Ranked

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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.

Equipment Blank (EB): Field QC 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, the 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 QC 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, the 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 percent 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. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the method detection limit, or can be assumed to be four times the method detection limit.

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.

Relative Percent Difference (RPD): A measure of precision, used when comparing two values. It is calculated as %RPD = [Value1–Value2]/Mean*100.

Relative Standard Deviation (RSD): A measurement of precision, used when comparing more than two results. It is calculated as %RSD = [Standard Deviation/Mean]*100.

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 RS) 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.

Split Sample (SS): A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results. Agreement between these two results is mostly an indication of laboratory precision.

Z-Score: A measure of the deviation of the result (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi-X)/\sigma$, where σ is a standard deviation) (Eurachem/CITAC 2000).

APPENDIX A

Results of TP split studies between the SFWMD and FDEP laboratories, EVPA Project, March 2013– March 2014.

Sample	Date Collected	Station	SFWMD TP result	FDEP TP result	%RPD/Comments
EVPA	5-Mar-2013	LOX8	0.009	0.008	11.8
EVPA	5-Mar-2013	LOX7	0.006	0.006	0.0
EVPA	6-Mar-2013	LOX16	0.005	0.004(I)	FDEP result < PQL
EVPA	6-Mar-2013	LOX15	0.006	0.006	0.0
EVPA	5-Jun-2013	LOX14	0.010	0.011	9.5
EVPA	5-Jun-2013	LOX16	0.010	0.009	10.5
EVPA	5-Jun-2013	LOX15	0.007	0.008	13.3
EVPA	5-Jun-2013	LOX12	0.008	0.011	31.6
EVPA	4-Sep-2013	LOX7	0.006	0.006	0.0
EVPA	4-Sep-2013	LOX4	0.007	0.008	13.3
EVPA	5-Sep-2013	LOX15	0.008	0.007	13.3
EVPA	5-Sep-2013	LOX16	0.010	0.010	0.0
EVPA	4-Dec-2013	LOX12	0.005	0.003 (I)	FDEP result < PQL
EVPA	4-Dec-2013	LOX15	0.004	0.003 (I)	FDEP result < PQL
EVPA	4-Dec-2013	LOX16	0.005	0.004 (I)	FDEP result < PQL
EVPA	4-Dec-2013	LOX14	0.005	0.004 (I)	FDEP result < PQL
EVPA	5-Mar-2014	LOX12	0.007	0.007	0.0
EVPA	5-Mar-2014	LOX15	0.005	0.005	0.0
EVPA	5-Mar-2014	LOX16	0.006	0.007	15.4
EVPA	5-Mar-2014	LOX14	0.006	0.005	18.2

Notes:

Qualifier code:

I: indicates the reported value is greater than or equal to the MDL but less than PQL. SFWMD: reported MDL = 0.002 mg/L and PQL = 0.004 mg/L. FDEP: reported MDL = 0.002 mg/L and PQL = 0.005 mg/L.

APPENDIX B

TP results for projects and their associated stations specified in the Introduction from January 1, 2014 to March 31, 2014. Among 118 reported results, 7 were qualified with a code "I".

Project	Date Collected	Station	Total Phosphorus Result (mg/L)	Uncertainty (mg/L)	Qualifier Code
PIN	1/6/2014	S12A	0.011	+/- 0.002	
PIN	1/6/2014	S12D	0.007	+/- 0.002	
PIN	1/6/2014	S333	0.007	+/- 0.002	
PIE	1/6/2014	S332DX	0.005	+/- 0.002	
PIN	1/6/2014	S356-334	0.006	+/- 0.002	
EVPA	1/7/2014	LOX4	0.006	+/- 0.002	
EVPA	1/7/2014	LOX7	0.006	+/- 0.002	
EVPA	1/7/2014	LOX8	0.007	+/- 0.002	
EVPA	1/7/2014	LOX9	0.007	+/- 0.002	
EVPA	1/7/2014	LOX10	0.004	+/- 0.002	
PIN	1/7/2014	S355A	0.007	+/- 0.002	
PIN	1/7/2014	S355B	0.007	+/- 0.002	
PIE	1/7/2014	S18C	0.007	+/- 0.002	
EVPA	1/9/2014	LOX6	0.005	+/- 0.002	
EVPA	1/9/2014	LOX11	0.004	+/- 0.002	
EVPA	1/9/2014	LOX13	0.005	+/- 0.002	
EVPA	1/9/2014	LOX14	0.004	+/- 0.002	
EVPA	1/9/2014	LOX16	0.006	+/- 0.002	
EVPA	1/9/2014	LOX15	0.005	+/- 0.002	
EVPA	1/9/2014	LOX12	0.005	+/- 0.002	
PIN	1/13/2014	S12A	0.009	+/- 0.002	
PIN	1/13/2014	S333	0.008	+/- 0.002	
PIN	1/13/2014	S356-334	0.007	+/- 0.002	
PIE	1/13/2014	S332DX	0.006	+/- 0.002	
PIE	1/14/2014	S18C	0.004	+/- 0.002	
PIN	1/21/2014	S12A	0.008	+/- 0.002	
PIE	1/21/2014	S332DX	0.005	+/- 0.002	
PIN	1/21/2014	S333	0.005	+/- 0.002	
PIN	1/21/2014	S356-334	0.006	+/- 0.002	
PIE	1/21/2014	S18C	0.003	+/- 0.002	I
PIN	1/27/2014	S12A	0.012	+/- 0.002	
PIN	1/27/2014	S333	0.007	+/- 0.002	
PIN	1/27/2014	S356-334	0.006	+/- 0.002	
PIE	1/27/2014	S332DX	0.005	+/- 0.002	
PIE	1/28/2014	S18C	0.003	+/- 0.002	I
PIN	2/3/2014	S12A	0.008	+/- 0.002	
PIN	2/3/2014	S333	0.005	+/- 0.002	
PIE	2/3/2014	S332DX	0.005	+/- 0.002	
PIN	2/3/2014	S356-334	0.007	+/- 0.002	
PIN	2/4/2014	S355A	0.008	+/- 0.002	
PIN	2/4/2014	S355B	0.008	+/- 0.002	
PIE	2/4/2014	S18C	0.003	+/- 0.002	
EVPA	2/5/2014	LOX4	0.012	+/- 0.002	

Project	Date Collected	Station	Total Phosphorus Result (mg/L)	Uncertainty (mg/L)	Qualifier Code
EVPA	2/5/2014	LOX7	0.006	+/- 0.002	
EVPA	2/5/2014	LOX8	0.009	+/- 0.002	
EVPA	2/5/2014	LOX9	0.009	+/- 0.002	
EVPA	2/5/2014	LOX10	0.007	+/- 0.002	
EVPA	2/5/2014	LOX5	0.009	+/- 0.002	
EVPA	2/5/2014	LOX3	0.011	+/- 0.002	
EVPA	2/6/2014	LOX6	0.004	+/- 0.002	
EVPA	2/6/2014	LOX11	0.006	+/- 0.002	
EVPA	2/6/2014	LOX13	0.008	+/- 0.002	
EVPA	2/6/2014	LOX14	0.006	+/- 0.002	
EVPA	2/6/2014	LOX16	0.007	+/- 0.002	
EVPA	2/6/2014	LOX15	0.006	+/- 0.002	
EVPA	2/6/2014	LOX12	0.008	+/- 0.002	
PIN	2/10/2014	S12A	0.012	+/- 0.002	
PIN	2/10/2014	S333	0.010	+/- 0.002	
PIN	2/10/2014	S356-334	0.007	+/- 0.002	
PIE	2/10/2014	S332DX	0.004	+/- 0.002	
PIE	2/11/2014	S18C	0.003	+/- 0.002	
PIN	2/17/2014	S12A	0.008	+/- 0.002	
PIN	2/17/2014	S12D	0.006	+/- 0.002	
PIN	2/17/2014	S333	0.008	+/- 0.002	
PIE	2/17/2014	S332DX	0.005	+/- 0.002	
PIN	2/17/2014	S356-334	0.007	+/- 0.002	
PIE	2/18/2014	S18C	0.002	+/- 0.002	I
PIN	2/24/2014	S12A	0.009	+/- 0.002	
PIN	2/24/2014	S12D	0.008	+/- 0.002	
PIN	2/24/2014	S333	0.008	+/- 0.002	
PIN	2/24/2014	S356-334	0.007	+/- 0.002	
PIE	2/24/2014	S332DX	0.005	+/- 0.002	
PIE	2/25/2014	S18C	0.003	+/- 0.002	I
PIN	3/3/2014	S12A	0.011	+/- 0.002	
PIE	3/3/2014	S332DX	0.006	+/- 0.002	
PIN	3/3/2014	S12D	0.007	+/- 0.002	
PIN	3/3/2014	S333	0.009	+/- 0.002	
PIN	3/3/2014	S356-334	0.021	+/- 0.002	
EVPA	3/4/2014	LOX4	0.007	+/- 0.002	
EVPA	3/4/2014	LOX7	0.006	+/- 0.002	1
EVPA	3/4/2014	LOX8	0.008	+/- 0.002	1
EVPA	3/4/2014	LOX9	0.005	+/- 0.002	1
EVPA	3/4/2014	LOX10	0.005	+/- 0.002	
EVPA	3/4/2014	LOX5	0.006	+/- 0.002	1
PIN	3/4/2014	S355A	0.013	+/- 0.002	
EVPA	3/4/2014	LOX3	0.007	+/- 0.002	

Project	Date Collected	Station	Total Phosphorus Result (mg/L)	Uncertainty (mg/L)	Qualifier Code
PIN	3/4/2014	S355B	0.015	+/- 0.002	
PIE	3/4/2014	S18C	0.004	+/- 0.002	
EVPA	3/5/2014	LOX12	0.007	+/- 0.002	
EVPA	3/5/2014	LOX15	0.005	+/- 0.002	
EVPA	3/5/2014	LOX16	0.006	+/- 0.002	
EVPA	3/5/2014	LOX14	0.006	+/- 0.002	
EVPA	3/5/2014	LOX13	0.007	+/- 0.002	
EVPA	3/5/2014	LOX11	0.006	+/- 0.002	
EVPA	3/5/2014	LOX6	0.005	+/- 0.002	
PIN	3/10/2014	S12A	0.012	+/- 0.002	
PIN	3/10/2014	S12D	0.007	+/- 0.002	
PIN	3/10/2014	S333	0.010	+/- 0.002	
PIN	3/10/2014	S356-334	0.008	+/- 0.002	
PIE	3/10/2014	S332DX	0.006	+/- 0.002	
PIE	3/11/2014	S18C	0.003	+/- 0.002	I
PIN	3/17/2014	S12A	0.014	+/- 0.002	
PIE	3/17/2014	S332DX	0.005	+/- 0.002	
PIN	3/17/2014	S12D	0.008	+/- 0.002	
PIN	3/17/2014	S333	0.008	+/- 0.002	
PIN	3/17/2014	S356-334	0.008	+/- 0.002	
PIE	3/18/2014	S18C	0.004	+/- 0.002	
PIE	3/24/2014	S332DX	0.007	+/- 0.002	
PIN	3/24/2014	S12A	0.017	+/- 0.002	
PIN	3/24/2014	S12D	0.009	+/- 0.002	
PIN	3/24/2014	S333	0.010	+/- 0.002	
PIN	3/24/2014	S356-334	0.007	+/- 0.002	
PIE	3/25/2014	S18C	0.004	+/- 0.002	
PIN	3/31/2014	S12A	0.021	+/- 0.002	
PIN	3/31/2014	S12D	0.012	+/- 0.002	
PIN	3/31/2014	S333	0.011	+/- 0.002	
PIE	3/31/2014	S332DX	0.007	+/- 0.002	
PIN	3/31/2014	S356-334	0.011	+/- 0.002	

Note:

Qualifier code "I" indicates the reported value is greater than or equal to the MDL but less than PQL.