

Quality Assessment Report for Water Quality Monitoring

April–June 2008



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Technical Oversight Committee
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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD or District) laboratory analysis and field sampling for total phosphorus (TP) monitoring, primarily for the following projects/stations from April 1, 2008, through June 30, 2008.

- Everglades National Park Inflows North (PIN) S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356
- Everglades National Park Inflow East (PIE) S332DX, S18C, DS2, DS4, and Berm B3
- Everglades Protection Area (EVPA) LOX3 through LOX16

Because field quality control (QC) samples are collected for trips 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 District's *Field Sampling Quality Manual*¹ provides the minimum requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual*² 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 provided the data used in this report. These data are considered preliminary until release into the District's DBHYDRO database.

Additionally, this report includes an analysis of the District laboratory's performance on the split (EVPA) and inter-laboratory studies with the Florida Department of Environmental Protection (FDEP) and other laboratories for the selected projects (Everglades TP Round Robins) for a one-year period. The result of the National Proficiency Testing Program designed to evaluate the laboratory's performance and the final evaluation of total phosphorus of the Everglades Round Robin XVIII are also included.

¹ SFWMD. 2008. Field Sampling Quality Manual, Version 4.0. South Florida Water Management District, Water Quality Monitoring Division and Quality Assurance Staff. West Palm Beach, FL.

² SFWMD. 2008. Chemistry Laboratory Quality Manual (Rev. No. 08-01). South Florida Water Management District, Water Quality Monitoring Division, Environmental Resource Assessment Department. West Palm Beach, FL.

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

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

MISSING DATA

Table 1 presents the list of missing data for this reporting period. Sixty-one data points were missing (not collected) due to lack of flow or shallow water depth.

Project	Collection Date	Station	Comments
PIN	04/01/08	S12C	No flow, no sample collected.
PIN	04/01/08	S12C	No flow, no sample collected.
PIN	04/01/08	S355A	No flow, no sample collected.
PIN	04/01/08	S355B	No flow, no sample collected.
PIN	04/09/08	S12B	No flow, no sample collected.
PIN	04/09/08	S12C	No flow, no sample collected.
PIN	04/15/08	S12B	No flow, no sample collected.
PIN	04/15/08	S12C	No flow, no sample collected.
PIN	04/15/08	S355A	No flow, no sample collected.
PIN	04/15/08	S355B	No flow, no sample collected.
PIN	04/22/08	S12B	No flow, no sample collected.
PIN	04/22/08	S12C	No flow, no sample collected.
PIN	04/22/08	S355A	No flow, no sample collected.
PIN	04/22/08	S355B	No flow, no sample collected.
PIN	04/29/08	S12B	No flow, no sample collected.
PIN	04/29/08	S12C	No flow, no sample collected.
PIN	04/29/08	S355A	No flow, no sample collected.
PIN	04/29/08	S355B	No flow, no sample collected.
PIN	05/06/08	S12B	No flow, no sample collected.
PIN	05/06/08	S12C	No flow, no sample collected.
PIN	05/13/08	S12B	No flow, no sample collected.
PIN	05/13/08	S12C	No flow, no sample collected.
PIN	05/13/08	S355A	No flow, no sample collected.
PIN	05/13/08	S355B	No flow, no sample collected.
EVPA	05/14/08	LOX3	Total depth less than 0.10 m. No sample collected.

EVPA	05/14/08	LOX4	Total depth less than 0.10 m. No sample collected.
EVPA	05/14/08	LOX5	Total depth less than 0.10 m. No sample collected.
EVPA	05/14/08	LOX9	Total depth less than 0.10 m. No sample collected.
EVPA	05/14/08	LOX10	Total depth less than 0.10 m. No sample collected.
PIN	05/20/08	S12B	No flow, no sample collected.
PIN	05/20/08	S12C	No flow, no sample collected.
PIN	05/20/08	S355A	No flow, no sample collected.
PIN	05/20/08	S355B	No flow, no sample collected.
PIN	05/28/08	S12B	No flow, no sample collected.
PIN	05/28/08	S12C	No flow, no sample collected.
PIN	05/28/08	S355A	No flow, no sample collected.
PIN	05/28/08	S355B	No flow, no sample collected.
PIN	06/03/08	S12B	No flow, no sample collected.
PIN	06/03/08	S12C	No flow, no sample collected.
PIN	06/03/08	S12D	No flow, no sample collected.
PIN	06/10/08	S12B	No flow, no sample collected.
PIN	06/10/08	S12C	No flow, no sample collected.
PIN	06/10/08	S12D	No flow, no sample collected.
PIN	06/10/08	S355A	No flow, no sample collected.
PIN	06/10/08	S355B	No flow, no sample collected.
EVPA	06/11/08	LOX3	Total depth less than 0.10 m. No sample collected.
EVPA	06/11/08	LOX4	Total depth less than 0.10 m. No sample collected.
EVPA	06/11/08	LOX5	Total depth less than 0.10 m. No sample collected.
EVPA	06/11/08	LOX9	Total depth less than 0.10 m. No sample collected.
EVPA	06/11/08	LOX10	Total depth less than 0.10 m. No sample collected.
EVPA	06/12/08	LOX6	Total depth less than 0.10 m. No sample collected.
PIN	06/17/08	S12B	No flow, no sample collected.
PIN	06/17/08	S12C	No flow, no sample collected.
PIN	06/17/08	S12D	No flow, no sample collected.
PIN	06/17/08	S355A	No flow, no sample collected.
PIN	06/17/08	S355B	No flow, no sample collected.
PIN	06/24/08	S12B	No flow, no sample collected.
PIN	06/24/08	S12C	No flow, no sample collected.
PIN	06/24/08	S12D	No flow, no sample collected.
PIN	06/24/08	S355A	No flow, no sample collected.
PIN	06/24/08	S355B	No flow, no sample collected.

QUALITY CONTROL

Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), Split Samples (SS), and Replicate Samples (RS). **Table 2** summarizes EB, and FCEB results for projects of interest to the Technical Oversight Committee (TOC), as referenced in the table footnotes below. One blank associated with samples for the stations listed in the *Introduction* section was outside the acceptance criterion. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for all three projects. Data that did not meet the set criteria for blanks, field precision, or sampling protocols were qualified using FDEP data qualifier codes. (**Table 4**)

Table 2. Field and equipment blank results ^{1, 2, 3, 4}

Type of Blank	Project	Number of Blanks Collected	% < 0.002	% ≥ 0.002
EB	EVPA	2	100	0
	PIE	1	100	0
	PIN	1	100	0
FCEB	EVPA	4	100	0
	PIE	14	100	0
	PIN	13	92	8

- ¹ Only blanks for sampling events from samples collected at stations listed in the *Introduction* section were included in this analysis.
- ² Blanks for TP, which were associated with a short-term autosampler project at some TOC stations, were not included in this analysis.
- ³ FB, FCEB, and EB acceptance criteria must be < Method Detection Limit (MDL).
- ⁴ When sample concentrations are less than five times the resulting blank values, “V” or “J” is added.

Table 3. Field precision summary ^{1, 2, 3}

Project Code	Number of Triplicates	Date Collected	% RSD	Comments
EVPA	1	12-Jun-08	6.7	Precision criteria met.
PIN	1	09-Apr-08	15.1	Precision criteria met.
PIE	1	07-Apr-08	11.9	Precision criteria met.

- ¹ Only replicates for sampling events from samples collected at stations listed in the *Introduction* section were included in this analysis.
- ² The District’s chemistry laboratory conducted all TP analyses.
- ³ Field precision acceptance criterion must be ≤ 20%. The laboratory applied this criterion only if sample values > Practical Quantitation Limit (PQL), which is 4 times of the MDL.

Table 4. List of flagged data.

Project Code	Date Collected	Station	Flag	Comments
PIN	01-Apr-08	S356	J	Sample associated with contaminated FCEB.
PIN	01-Apr-08	S12D	J	Sample associated with contaminated FCEB.
PIN	01-Apr-08	S12A	J	Sample associated with contaminated FCEB.

FIELD AUDIT

Field audits were not conducted on TOC related projects during the second quarter of 2008.

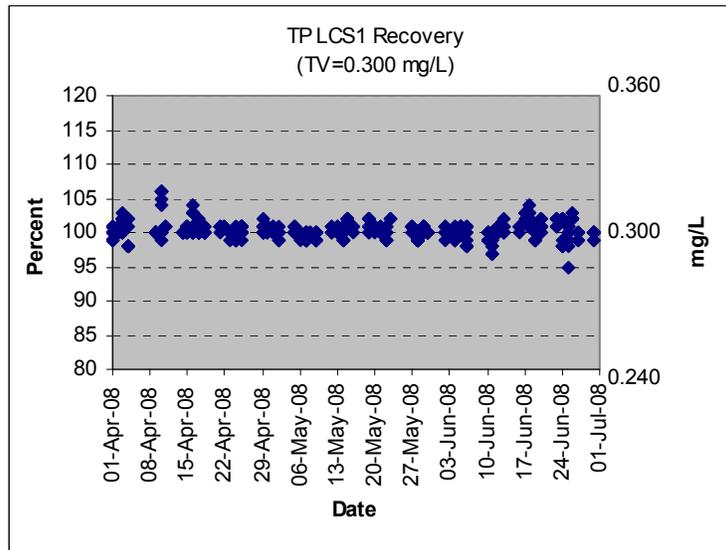
LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

The TP analytical procedure did not change during this reporting period.

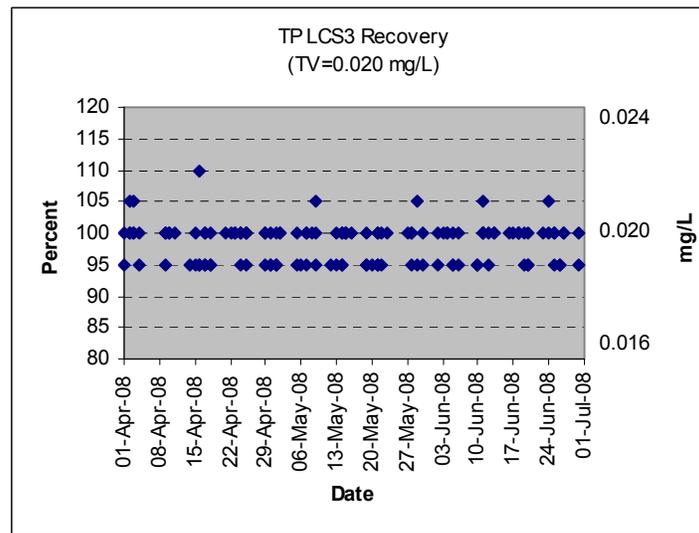
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figures 1 through 4** show the TP recoveries from various types and levels of QC samples at the District laboratory from April 1, 2008, through June 30, 2008.



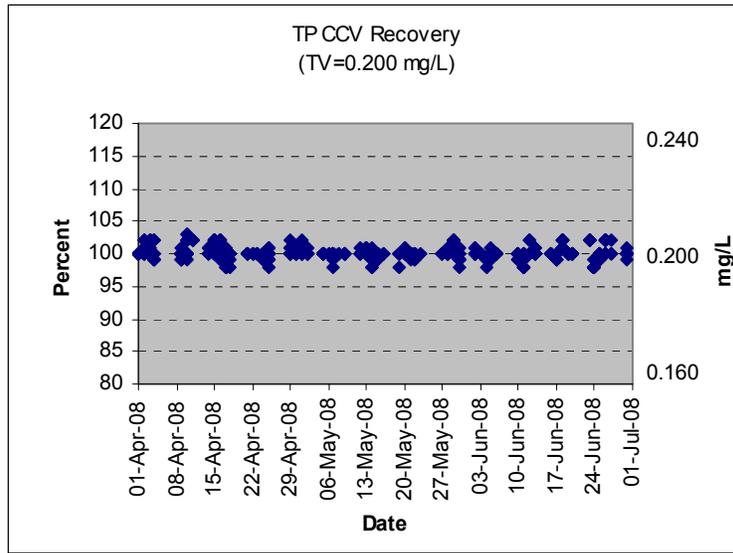
Mean = 100.4%, Max = 106.0%, Min = 95.0%

Figure 1. QC (Laboratory Control Solution) sample recoveries for TP analysis.



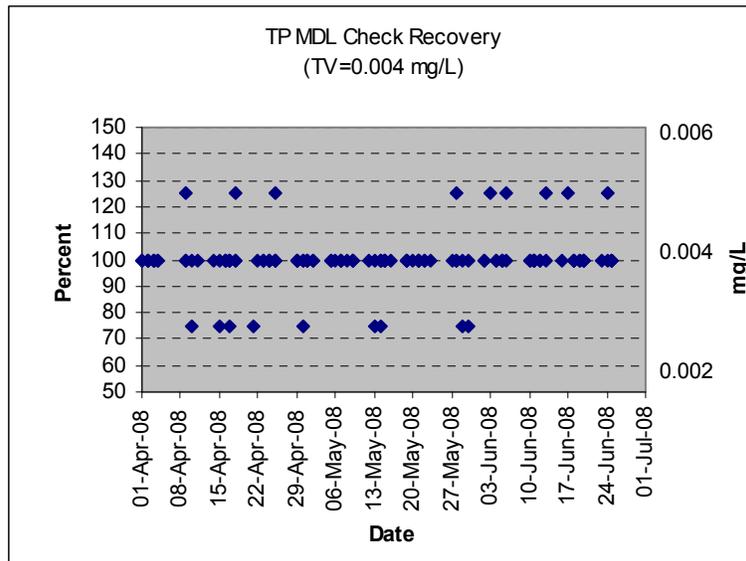
Mean = 98.5%, Max = 110.0%, Min = 95.0%

Figure 2. QC (Laboratory Control Solution) sample recoveries for TP analysis.



Mean = 100.1%, Max = 103.0%, Min = 98.0%

Figure 3. QC (Continuing Calibration Verification) sample recoveries for TP analysis.



Mean = 100.2%, Max = 125.0%, Min = 75.0%

Figure 4. QC5 (Method Detection Limit check) sample recoveries for TP analysis.

Tables 5 and 6 present the precision and matrix spike recoveries for TP analyses during the reporting period. If QC recoveries are outside the set limits, then the District’s laboratory usually rejects the analytical batch. If any deficiencies are noted and the samples have exceeded the required holding times and the laboratory cannot re-analyze the data, then the sample is qualified accordingly.

Table 5. TP Precision (%) Data.

Acceptance Limit	<10
Analytical Range: 0.002-0.400 mg/L	
Maximum	8.4
Mean	1.5
Standard Deviation	1.54
3xSD	4.63
UCL	6.1
n	328

UCL Upper Control Limit
n Number of data points

Table 6. TP Spike Recovery (%) Data.

Acceptance Limit	90 – 110
Analytical Range: 0.002-0.400 mg/L	
Minimum	90
Maximum	110
Mean	100.4
Standard Deviation	3.70
3xSD	11.1
LCL	89.3
UCL	111.6
n	329

LCL Lower Control Limit
UCL Upper Control Limit
n Number of data points

Recoveries for the QC samples are usually within ±10 percent from the true value, which is acceptable. The Method Detection Limit (MDL) check (QC5), with a true value of 0.004 mg/L, had mean recoveries of 100.2 percent. The daily MDL check results indicate that the laboratory has consistently achieved the established MDL of 0.002 milligram per liter (mg/L). An organic check is a solution prepared from phytic acid, which is a stable form of organic phosphate used to prepare matrix spikes, the mean recovery for which was 100.4 percent.

INTER-LABORATORY QUALITY-CONTROL ASSESSMENT

Split Studies with FDEP Laboratory

To continuously assess comparability of results, the District routinely sends split samples to other laboratories. The EVPA Quarterly Splits and the Everglades TP Round Robin (ERR) split-study programs conducted between the FDEP and the District's laboratory from June 2007 to June 2008 (see **Appendix A**) provided the data used in this analysis. **Figures 5** through **7** present regression analysis of the data, and **Table 7** presents summary statistics for the data pairs.

ALL DATA

Figure 5 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 r^2 value is 0.934. This information indicates a very high degree of agreement between the laboratories.

Table 7 shows that the mean difference (0.001 mg/L) was statistically insignificant (p-value 0.088). The median difference (0.001 mg/L) was statistically significant (p-value 0.005). **Note: The magnitudes of these differences are environmentally and practically insignificant.**

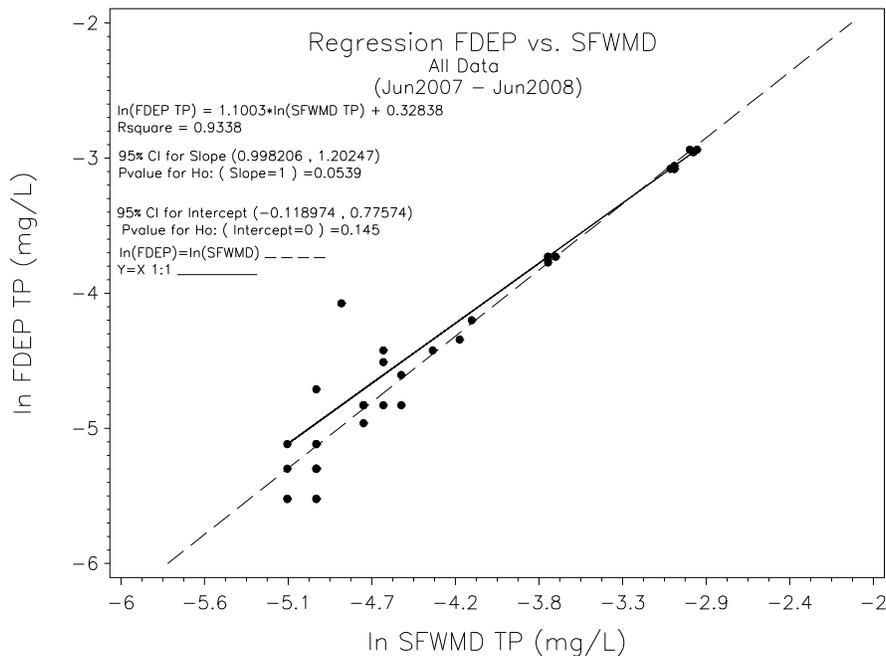


Figure 5. Regression analysis for all TP data.

TP ≥ 0.020 mg/L

Figure 6 shows that the intercept is not statistically different from 0 (zero) and the slope is not statistically different from 1 (one) for samples with TP ≥ 0.020 mg/L. The r^2 value is 0.997. This information also indicates a very high level of agreement between both laboratories.

Table 7 shows that the mean difference (0.000 mg/L) and median difference (0.000 mg/L) were not statistically significant. The paired t-test and signed-rank test yielded p-values of 0.506 and 0.750, respectively.

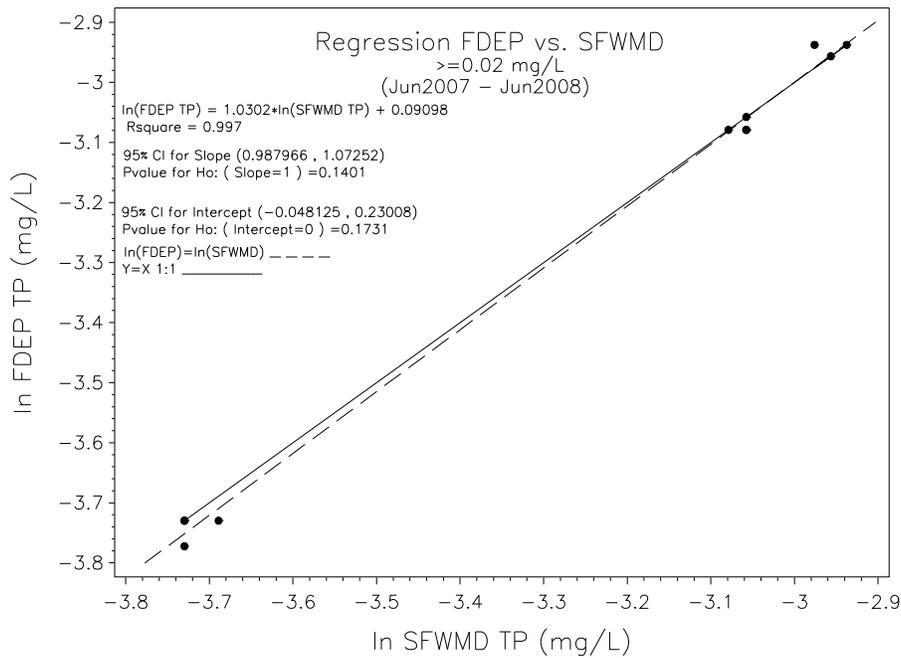


Figure 6. Regression analysis for TP greater or equal to 0.020 mg/L.

TP < 0.020 mg/L

Figure 7 shows that the slope is not significantly different from 1 (one) and the intercept is not significantly different from 0 (zero) for samples with TP < 0.020 mg/L. The r^2 for this regression is 0.632. At this low level, the data sets do not agree very well, as expected, due to the relatively high variability/uncertainty within each laboratory and between the two laboratories.

Table 7 shows that the mean difference (0.008 mg/L) was statistically insignificant and median difference (0.001 mg/L) was very small but statistically significant at this concentration level (< 0.020 mg/L). **Note: The magnitudes of these differences are environmentally and practically insignificant.**

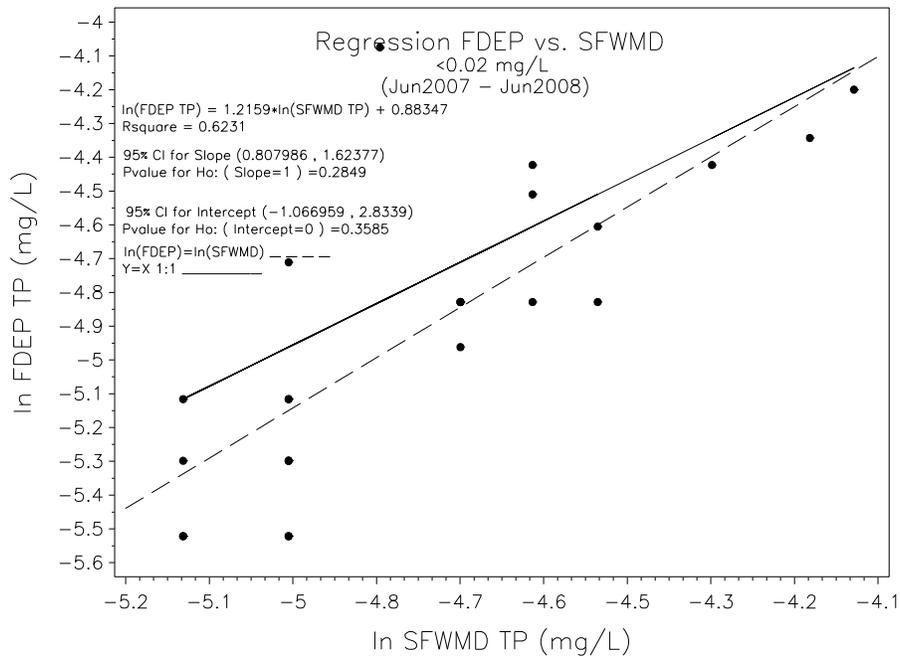


Figure 7. Regression analysis for TP less than 0.020 mg/L.

In summary, the differences for all TP levels were below the Method Detection Limit (MDL) for both laboratories.

Table 7. Comparison of District and FDEP split TP samples.

All Data	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	36	0.018	0.010	
	District	36	0.018	0.010	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	0.001	Mean of Differences = 0	Student's t	0.088
Median of Differences	0.001	Median of Differences = 0	Signed Rank	0.005	
≥ 0.020 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	11	0.040	0.046	
	District	11	0.040	0.047	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	0.000	Mean of Differences = 0	Student's t	0.506
Median of Differences	0.000	Median of Differences = 0	Signed Rank	0.750	
< 0.020 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	25	0.008	0.008	
	District	25	0.009	0.008	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	0.001	Mean of Differences = 0	Student's t	0.113
Median of Differences	0.001	Mean of Differences = 0	Signed Rank	0.004	

Notes:

- Differences calculated as District TP minus FDEP TP. The mean and median differences for all concentration levels are at or below the PQL.

Total Phosphorus Everglades Round Robin Inter-laboratory Comparison Program

The final report was published by the Florida Department of Environmental Protection for the statistical analysis and summary of the total phosphorus round robin XVIII Inter-laboratory comparison program. The SFWMD Chemistry Laboratory's performance was evaluated with the average score of 5.0 on the 5-point scale, where 5.0 = the best and 0.0 = the worst from the five sampling sites.

National Proficiency Testing Program

As a requirement for laboratory certification, the District's laboratory performs proficiency testing on environmental samples on a semiannual basis. The results for the District's laboratory from the most recent PT study (April to May 2008) are shown in **Table 8**.

Table 8. Proficiency testing study for TP results.

Assigned Value	16.9 mg/L
Reported Value	16.3 mg/L
Performance Evaluation	Acceptable

GLOSSARY

Accuracy. The agreement between the actual obtained result and the expected result. QC-check samples, having known or “true” values, are used to test for the accuracy of a measurement system.

Equipment Blank (EB). A general terminology used for analyte-free water that is processed onsite through all sampling equipment used in routine sample processing. May be an assessment of effectiveness of laboratory decontamination or on-site (field) decontamination (FCEB).

Field Blank (FB). Analyte-free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Field Cleaned Equipment Blank (FCEB). Analyte-free water that is processed on-site, after the first sampling site, through all sampling equipment used in routine sample processing. EB values are indicative of the effectiveness of the decontamination process.

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 section 40 CFR, Part 136, Appendix B, as established by the U.S. 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 MDL, or can be assumed to be four times the MDL.

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 $\%RSD = [Std. Deviation / Mean] * 100$.

Replicate Sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared to routine sample 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-Value. 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).

APPENDIX A

Results of TP split studies between the District and FDEP laboratories, EVPA Project and Everglades Round Robin, June 2007–June 2008.

Sample	Date	District	FDEP	% RPD/Comments
EVPA	12-Jun-07	0.013	0.012	8.0
EVPA	12-Jun-07	0.016	0.015	6.5
EVPA	12-Jun-07	0.015	0.013	14.3
EVPA	12-Jun-07	0.011	0.010	9.5
EVPA	18-Sep-07	0.006	0.004	<PQL
EVPA	18-Sep-07	0.007	0.006	<PQL
EVPA	18-Sep-07	0.007	0.005	<PQL
EVPA	18-Sep-07	0.011	0.008	<PQL
EVPA	12-Nov-07	0.006	0.005	<PQL
EVPA	12-Nov-07	0.007	0.004	<PQL
EVPA	12-Nov-07	0.007	0.009	<PQL
EVPA	12-Nov-07	0.007	0.005	<PQL
ERR-18	12-Feb-08	0.007	0.004	<PQL
ERR -18	12-Feb-08	0.007	<0.004	<PQL
ERR-18	12-Feb-08	0.006	0.004	<PQL
ERR-18	12-Feb-08	0.024	0.023	4.2
ERR-18	12-Feb-08	0.024	0.024	0.0
ERR-18	12-Feb-08	0.024	0.024	0.0
ERR-18	12-Feb-08	0.025	0.024	4.1
ERR-18	12-Feb-08	0.009	0.008	<PQL
ERR-18	12-Feb-08	0.009	0.008	<PQL
ERR-18	12-Feb-08	0.009	0.008	<PQL
ERR-18	12-Feb-08	0.009	0.007	<PQL
ERR-18	12-Feb-08	0.046	0.046	0.0
ERR-18	12-Feb-08	0.047	0.046	2.2
ERR-18	12-Feb-08	0.047	0.047	0.0
ERR-18	12-Feb-08	0.047	0.046	2.2
ERR-18	12-Feb-08	0.053	0.053	0.0
ERR-18	12-Feb-08	0.051	0.053	3.8
ERR-18	12-Feb-08	0.052	0.052	0.0
EVPA	06-Mar-08	0.010	0.011	9.5
EVPA	06-Mar-08	0.007	0.005	<PQL
EVPA	06-Mar-08	0.006	<0.004	<PQL
EVPA	06-Mar-08	0.007	0.006	<PQL
EVPA	11-Jun-08	0.010	0.012	18.2
EVPA	12-Jun-08	0.008	0.017	72.0
EVPA	12-Jun-08	0.006	0.006	<PQL
EVPA	12-Jun-08	0.010	0.008	22.2