

Quality Assessment Report for Water Quality Monitoring

October – December 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 October 1, 2008 through December 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 report also includes the results of the National Proficiency Testing Program, which is designed to evaluate the laboratory's performance.

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. Twenty-two data points were missing (not collected) due to lack of flow.

Table 1. Missing data for October 1 to December 31, 2008.

Project	Collection Date	Station	Comments
PIN	16-Oct-2008	S355A	Gate closed, no flow, no sample collected.
PIN	16-Oct-2008	S355B	Gate closed, no flow, no sample collected.
PIN	22-Oct-2008	S355A	Gate closed, no flow, no sample collected.
PIN	22-Oct-2008	S355B	Gate closed, no flow, no sample collected.
PIN	29-Oct-2008	S355A	Gate closed, no flow, no sample collected.
PIN	29-Oct-2008	S355B	Gate closed, no flow, no sample collected.
PIN	12-Nov-2008	S355A	Gate closed, no flow, no sample collected.
PIN	12-Nov-2008	S355B	Gate closed, no flow, no sample collected.
PIN	25-Nov-2008	S355A	Gate closed, no flow, no sample collected.
PIN	25-Nov-2008	S355B	Gate closed, no flow, no sample collected.
PIN	09-Dec-2008	S355A	Gate closed, no flow, no sample collected.
PIN	09-Dec-2008	S355B	Gate closed, no flow, no sample collected.
PIN	17-Dec-2008	S355A	Gate closed, no flow, no sample collected.
PIN	17-Dec-2008	S355B	Gate closed, no flow, no sample collected.
PIN	23-Dec-2008	S12B	Gate closed, no flow, no sample collected.
PIN	23-Dec-2008	S12C	Gate closed, no flow, no sample collected.
PIN	23-Dec-2008	S12D	Gate closed, no flow, no sample collected.
PIN	23-Dec-2008	S355A	Gate closed, no flow, no sample collected.
PIN	23-Dec-2008	S355B	Gate closed, no flow, no sample collected.
PIN	29-Dec-2008	S12B	Gate closed, no flow, no sample collected.
PIN	29-Dec-2008	S355A	Gate closed, no flow, no sample collected.
PIN	29-Dec-2008	S355B	Gate closed, 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. In **Table 3**, one blank associated with samples for the stations listed in the *Introduction* section was outside the acceptance criterion. **Table 4** 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 5**).

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

Type of Blank	Project	Number of Blanks Collected	Number of Detected Blanks	% < 0.002 mg/L	% ≥ 0.002 mg/L
EB	EVPA	2	0	100	0
	PIE	1	0	100	0
	PIN	1	0	100	0
FCEB	EVPA	11	0	100	0
	PIE	20	1	95	5
	PIN	14	0	100	0

- 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, "J" is added.

Table 3. Field blanks ≥ MDL

Type of Blank	Project	Station	Date Collected	Value mg/L	Comments
FCEB	PIE	S178	27-Oct-2008	0.012	FCEB>MDL

Table 4. Field precision summary ^{1, 2, 3}

Project Code	Number of Triplicates	Date Collected	% RSD	Comments
PIE	1	6-Oct-2008	4.2	Precision criteria met.
PIN	1	2-Dec-2008	0.0	Precision criteria met.
EVPA	1	9-Dec-2008	6.9	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 $\leq 20\%$. The laboratory applied this criterion only if sample values > Practical Quantitation Limit (PQL), which is four times the MDL.

Table 5. List of flagged data

Project Code	Date Collected	Station	Flag	Result, mg/L	Comments
PIE	27-Oct-08	S18C	J	0.005	Sample associated with contaminated FCEB. Possible sample mix-up

FIELD AUDIT

During this quarter, an audit was conducted on the sample collection procedures of the EVPA project. Samples for the project were collected by the Water Quality Monitoring Division and USFWS personnel. This was an audit of the simulated marsh collection process. This simulated collection process took place in STA-1E. There were no deficiencies noted during the course of this audit.

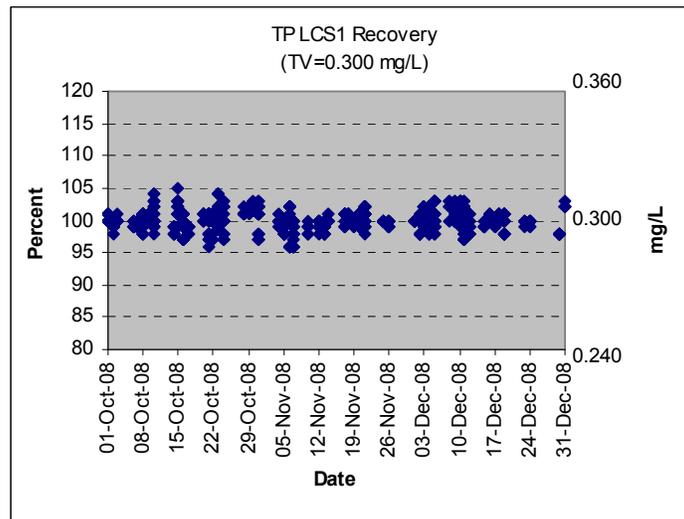
LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

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

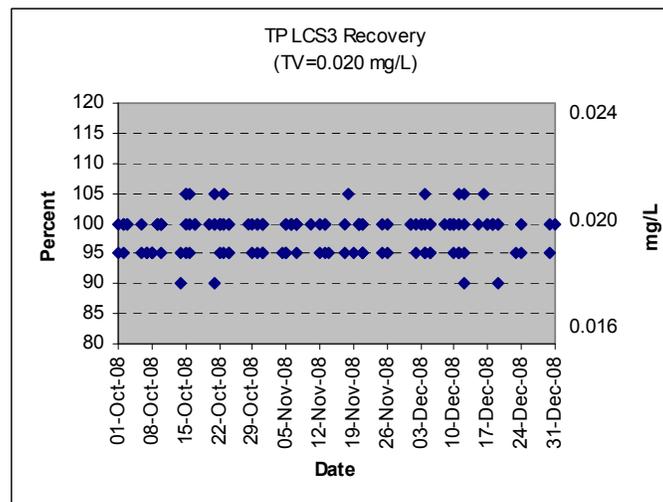
LABORATORY QUALITY CONTROL

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 October 1, 2008 through December 31, 2008.



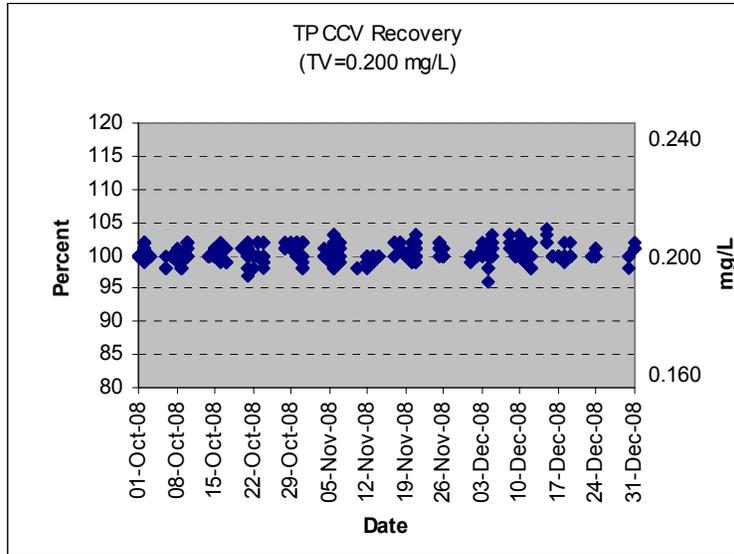
Mean = 100.0%, Max = 105.0%, Min = 96.0%

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



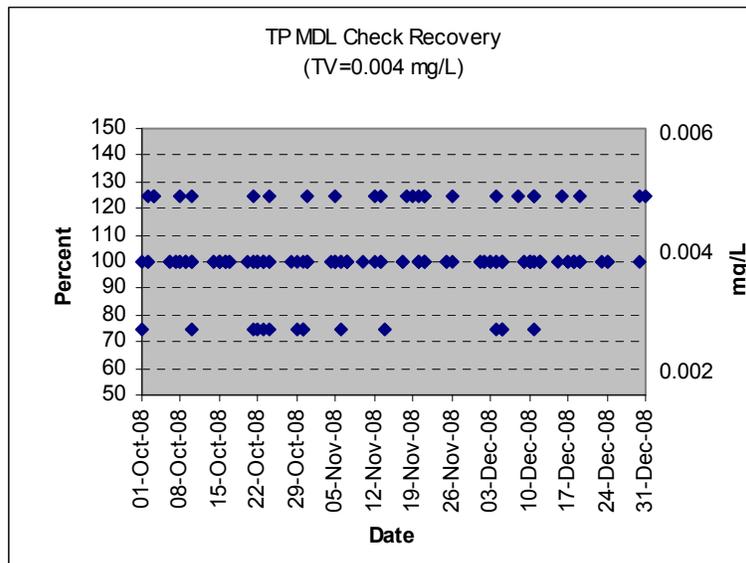
Mean = 98.5%, Max = 105.0%, Min = 90.0%

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



Mean = 100.3%, Max = 104.0%, Min = 96.0%

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



Mean = 101.7%, Max = 125.0%, Min = 75.0%

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

Tables 6 and 7 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, the samples have exceeded the required holding times, and the laboratory cannot re-analyze the data, then the sample is qualified accordingly.

Table 6. TP Precision (%) Data.

Acceptance Limit	<10
Analytical Range: 0.002-0.400 mg/L	
Maximum	8.1
Mean	1.5
Standard Deviation	1.5
3xSD	4.5
UCL	6.0
n	406

UCL Upper Control Limit
n Number of data points

Table 7. 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	3.2
3xSD	9.6
LCL	91
UCL	110
n	402

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

Recoveries for the QC samples are 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 101.7 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.

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

One of the prime objectives of the District laboratory's quality assurance program is to evaluate measurement uncertainty. The analytical uncertainty must always be known and taken into account when using data to make decisions. In the District's laboratory, estimates of measurement uncertainty are determined using the Nested Hierarchical Methodology suggested by Ingersoll³. This approach is widely applied in the environmental industry and is data driven (as opposed to methodology or procedure driven); therefore, the resulting estimate of uncertainty is based on actual District quality control results and is computed using a Microsoft Excel spreadsheet developed by Ingersoll.

A measurement result is complete when accompanied by a quantitative statement of its uncertainty. The estimated analytical uncertainty for total phosphorus determinations conducted by the District laboratory for the last quarter was determined to be 5.6 percent (with a 95 percent confidence level). Therefore, if a single sample measurement of total phosphorus is reported to be 20 µg/L, the uncertainty interval is 18.9 to 21.1 µg/L. This result applies to the analytical process and does not include uncertainty attributed to field sampling activities (e.g., sample collection and sample location effects).

Estimates of relative uncertainty derived in this fashion are considered constant above the Practical Quantitation Limit up to the limit of linearity.

PRACTICAL QUANTITATION LIMIT

Method Detection Limit (MDL) checks are routinely analyzed with each analytical run. From October to December 2008, 144 results for MDL checks were reported for total phosphorus measurements. As required under NELAP certification, the reportable MDL is formally reviewed on an annual basis. The formal review and quarterly calculations have consistently supported a conservative MDL of 2 µg/L for the past six years. The calculated MDL from these results was determined to be 1.2 µg/L, using the procedure described in 40 CFR 136 Appendix B. However, the lower level where measurement becomes quantitatively meaningful is the Practical Quantitation Limit (PQL). According to the District *Laboratory's Quality Manual*, the PQL is equal to four times the MDL. Therefore, the calculated PQL for the period from October to December 2008 was 4.8 µg/L. At this concentration, the relative uncertainty in the measured value is estimated to be ±30 percent at the 95 percent confidence level⁴.

Figure 5 is presented to clarify the concept of MDL and PQL of a measurement process.

³ [Ingersoll, W.S., Estimation of Analytical Measurement Uncertainty \(2001\)](#)

⁴ Taylor, J.K., *Quality Assurance of Chemical Measurements* (1987)

Uncertainty of Measurement Close to the Limit of Detection

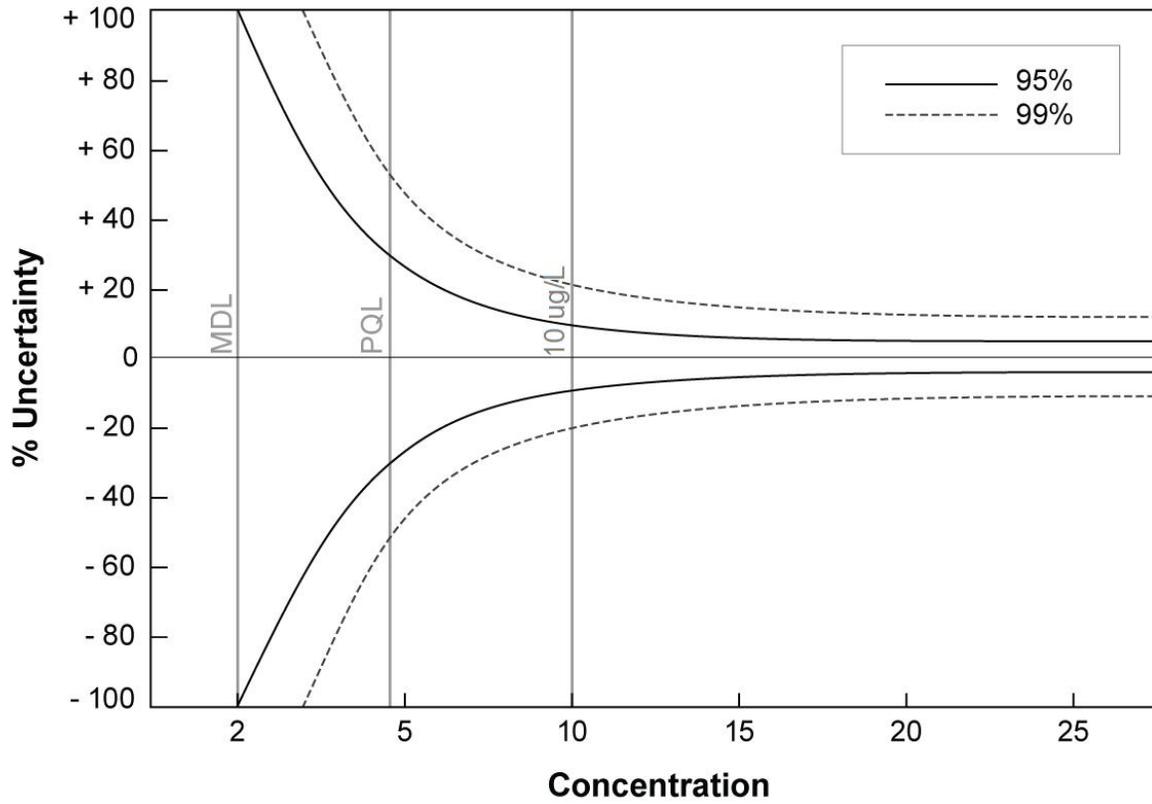


Figure 5. Uncertainty of TP measurement close to the detection limit.

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 November 2007 to December 2008 (see **Appendix A**) provided the data used in this analysis. **Figures 6** through **8** present regression analysis of the data, and **Table 8** presents summary statistics for the data pairs.

ALL DATA

Figure 6 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 0.932. The intercept of the regression is not different from zero statistically since the 95 percent confidence interval for intercept contains zero. The slope of the regression is not different from one statistically since the 95 percent confidence interval for slope contains one. This information indicates a very high degree of agreement between the laboratories.

Table 8 shows that the mean difference (0.0004 mg/L) was statistically insignificant (p-value 0.230). The median difference (0.001 mg/L) was statistically significant (p-value 0.032). **Note: The magnitudes of these differences are environmentally and practically insignificant.**

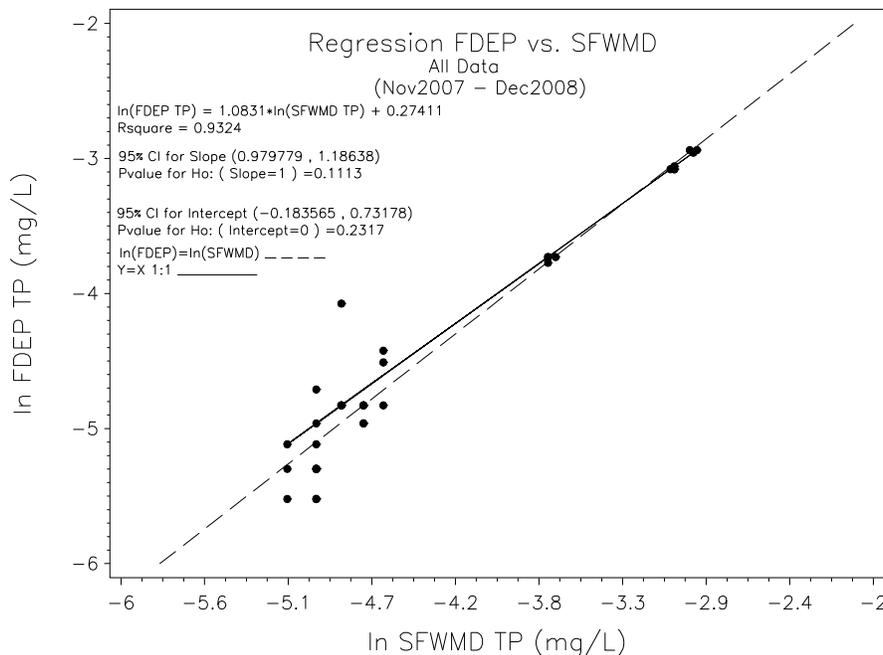


Figure 6. Regression analysis for all TP data.

$TP \geq 0.020 \text{ mg/L}$

Figure 7 shows that the intercept is not statistically different from zero and the slope is not statistically different from one for samples with $TP \geq 0.020 \text{ mg/L}$. The r^2 value is 0.997. This information also indicates a very high level of agreement between both laboratories.

Table 8 shows that the mean difference (0.0002 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.

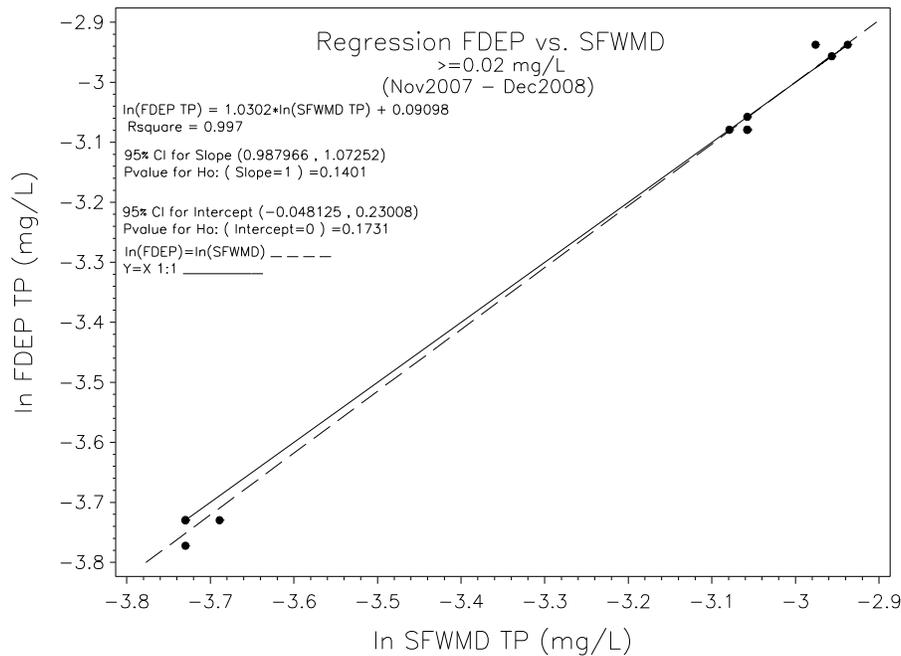


Figure 7. Regression analysis for TP greater than or equal to 0.020 mg/L.

TP < 0.020 mg/L

Figure 8 shows that the slope is not significantly different from one and the intercept is not significantly different from zero for samples with TP < 0.020 mg/L. The r^2 for this regression is 0.445. 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 8 shows that the mean difference (0.0005 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.**

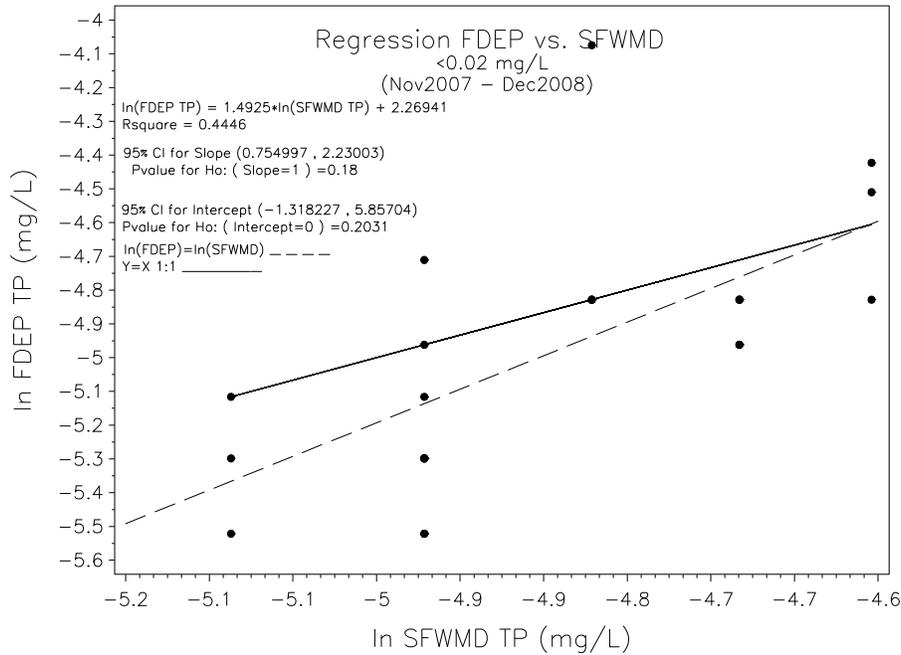


Figure 8. Regression analysis for TP less than 0.020 mg/L.

In summary, the differences for all TP levels were below the MDL for both laboratories. The differences were not normally distributed (Shapiro-Wilk, p-value was <0.002), so the results of the Sign-Rank test are appropriate for the comparison.

Table 8. Comparison of District and FDEP split TP samples.

All Data	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	35	0.018	0.008	
	District	35	0.018	0.009	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	0.0004	Mean of Differences = 0	Student's t	0.230
Median of Differences	0.001	Median of Differences = 0	Signed Rank	0.032	
≥ 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	0.0002	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	24	0.007	0.007	
	District	24	0.008	0.008	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	0.0005	Mean of Differences = 0	Student's t	0.290
Median of Differences	0.001	Mean of Differences = 0	Signed Rank	0.033	

Notes:

- Differences calculated as District TP minus FDEP TP. The mean and median differences for all concentration levels are at or below the MDL.
- Data were not used if FDEP value was below FDEP's detection limit (0.004 mg/L).

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 (October to November 2008) are shown in **Table 9**.

Table 9. Proficiency Testing Evaluation study for TP results.

Sample ID	Reported Result, mg/L	Assigned Value, mg/L	Comments
WP-165	6.51	6.55	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, November 2007–December 2008.

Sample	Date	District	FDEP	% RPD/Comments
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	<PQL
EVPA	18-Sep-08	0.007	0.007	<PQL
EVPA	18-Sep-08	0.008	0.008	<PQL
EVPA	18-Sep-08	0.008	0.008	<PQL
EVPA	18-Sep-08	0.008	0.008	<PQL
EVPA	09-Dec-08	0.007	0.005	<PQL
EVPA	09-Dec-08	0.009	0.007	<PQL
EVPA	09-Dec-08	0.007	0.005	<PQL
EVPA	09-Dec-08	0.004	<0.004	<PQL