Quality Assessment Report for Water Quality Monitoring

October 2007—December 2007

Submitted to the
Technical Oversight Committee
February 11, 2008

Zdzislaw Kolasinski (zkolasin@sfwmd.gov)

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, 2007, through December 31, 2007.

- 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

The PIE project was created for the area that has overlapping projects with duplicate or conflicting requirements including the Non-Everglades Construction Project (NECP), Everglades National Inflow Monitoring (ENP), and Project Sampling Location (C111D). The PIN supersedes portions of several existing monitoring plans for the Non-Everglades Construction Project and the Conservation Area Inflow and Outflows (CAMB). The PIE and PIN projects were both implemented on October 1, 2007. It should be noted that 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 *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 laboratory and field 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 and inter-laboratory studies with FDEP and other laboratories for the selected projects (EVPA and Everglades TP Round Robins) for a one-year period. The result of the National Proficiency Testing Program designed to evaluate the laboratory's performance is also included.

[1] SFWMD. 2006a. Field Sampling Quality Manual, Version 3.0. South Florida Water Management District, Water Quality Monitoring Division and Quality Assurance Staff. West Palm Beach, FL.

[2] SFWMD. 2006b. Chemistry Laboratory Quality Manual and Field Sampling Quality Manual (Rev. No. 06-01). 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.

FIELD AUDIT

On November 20, 2007, an audit of field sampling collection activities was performed by the District for Miami-Dade County Department of Environmental Resources Management (DERM) sampling for the PIE project stations S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356. The key findings of this audit were as follows: (1) no agency (DERM) quality manual, (2) improper equipment rinsing protocol, and (3) improper collection protocol for field-cleaned equipment blank. The corrective actions from this audit are still in process. After a review of the key findings, it was determined the quality of the data was not affected.

MISSING DATA

Table 1 presents the list of missing data for this reporting period. Thirty-five data were missing due to samples not collected because of lack of flow.

Table 1. Missing data for the period from October 1–December 31, 2007.

Project	Collection Date	Station	Comments
PIN	3-Oct-07	S12B	No flow, no sample collected
PIN	3-Oct-07	S12C	No flow, no sample collected
PIN	3-Oct-07	S12D	No flow, no sample collected
PIN	10-Oct-07	S12B	No flow, no sample collected
PIN	10-Oct-07	S12C	No flow, no sample collected
PIN	10-Oct-07	S355A	No flow, no sample collected
PIN	10-Oct-07	S335B	No flow, no sample collected
PIN	10-Oct-07	S356	No flow, no sample collected
PIN	17-Oct-07	S355A	No flow, no sample collected
PIN	17-Oct-07	S335B	No flow, no sample collected
PIN	24-Oct-07	S355A	No flow, no sample collected
PIN	24-Oct-07	S335B	No flow, no sample collected
PIN	30-Oct-07	S355A	No flow, no sample collected
PIN	30-Oct-07	S335B	No flow, no sample collected
PIN	14-Nov-07	S355A	No flow, no sample collected
PIN	14-Nov-07	S335B	No flow, no sample collected

Table 1. Missing data for the period from October 1–December 31, 2007.

Project	Collection Date	Station	Comments
PIN	20-Nov-07	S355A	o flow, no sample collected
PIN	20-Nov-07	S335B	No flow, no sample collected
PIN	27-Nov-07	S355A	No flow, no sample collected
PIN	27-Nov-07	S335B	No flow, no sample collected
PIN	04-Dec-07	S12C	No flow, no sample collected
PIN	04-Dec-07	S355A	No flow, no sample collected
PIN	04-Dec-07	S335B	No flow, no sample collected
PIN	12-Dec-07	S12B	No flow, no sample collected
PIN	12-Dec-07	S12C	No flow, no sample collected
PIN	18-Dec-07	S12B	No flow, no sample collected
PIN	18-Dec-07	S12C	No flow, no sample collected
PIN	18-Dec-07	S12D	No flow, no sample collected
PIN	18-Dec-07	S335A	No flow, no sample collected
PIN	18-Dec-07	S335B	No flow, no sample collected
PIN	27-Dec-07	S12B	No flow, no sample collected
PIN	27-Dec-07	S12C	No flow, no sample collected
PIN	27-Dec-07	S12D	No flow, no sample collected
PIN	27-Dec-07	S335A	No flow, no sample collected
PIN	27-Dec-07	S335B	No flow, no sample collected

QUALITY CONTROL

Field QC measures consist of Equipment Blanks (EB), Field-Cleaned Equipment Blanks (FCEB), Field Blanks (FB), Split Samples (SS), and Replicate Samples (RS). **Table 2** summarizes EB, FB, and FCEB results for projects of interest to the Technical Oversight Committee (TOC), as referenced in the table footnotes below. No blanks associated with samples for the stations listed in the *Introduction* section were outside the acceptance criterion. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for all four projects. Data that did not meet the set criteria for blanks, field precision, or sampling protocols were qualified using Florida Department of Environmental Protection (FDEP) data qualifier codes.

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	1	100	0
	PIE	1	100	0
	PIN	1	100	0
FCEB	EVPA	7	100	0
	PIE	13	100	0
	PIN	13	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, laboratory personnel qualified the samples for possible contamination.

Table 3. Field precision summary. [1, 2, 3]

Project Code	Number of Triplicates	Date Collected	% RSD	Comments
EVPA	1	11-Dec-07	12.5	Precision criteria met.
PIN	1	03-Oct-07	4.3	Precision criteria met.
PIN	1	14-Nov-07	5.4	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).

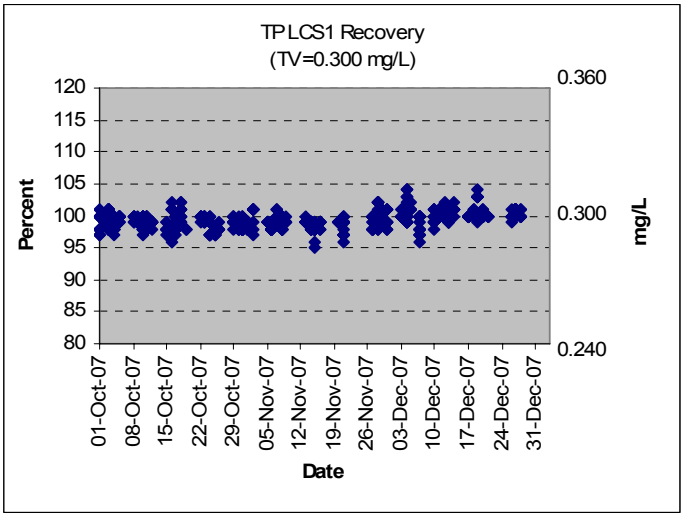
LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

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

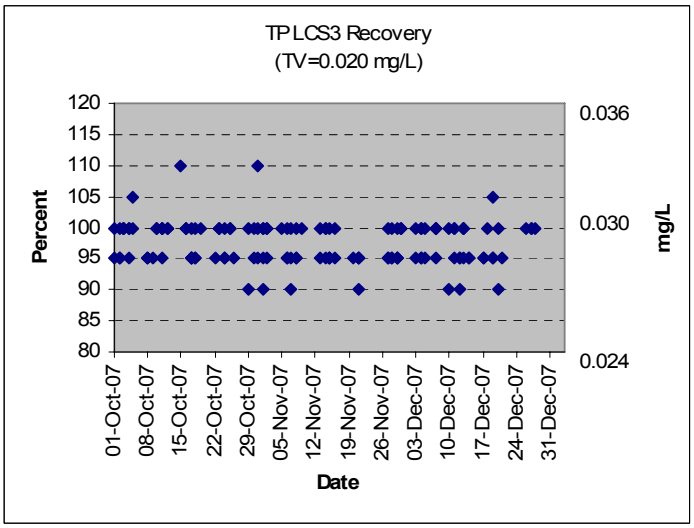
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figures 1** through **4** show recoveries from various types and levels of QC samples for the TP analysis at the District laboratory from October 1, 2007, through December 31, 2007.



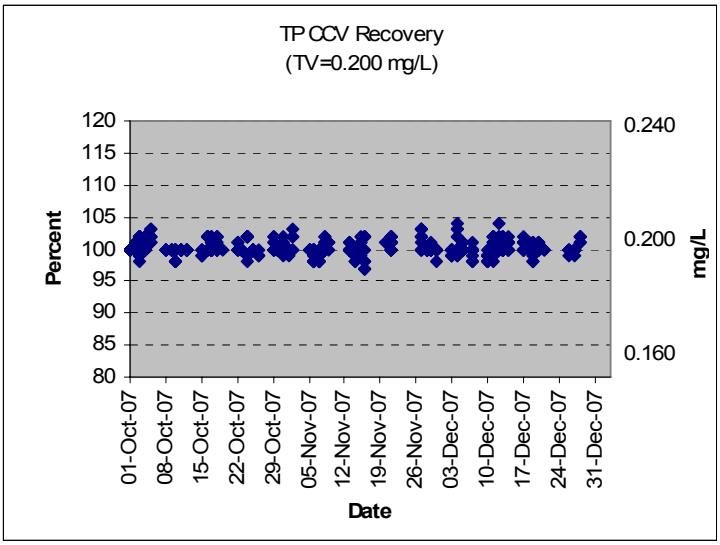
Mean = 99.4%, Max = 104.0%, Min = 95.0%

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



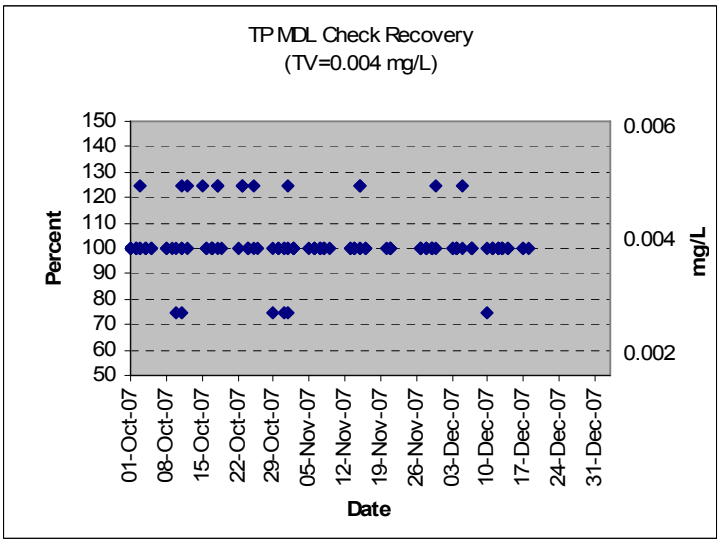
Mean = 97.5%, Max = 110.0%, Min = 90.0%

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



Mean = 100.2%, Max = 104.0%, Min = 97.0%

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



Mean = 101.8%, Max = 125.0%, Min = 75.0%

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

Tables 4 and **5** 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, the sample is qualified accordingly.

Table 4. TP Precision Data.

Acceptance Limit	<10%
Analytical Range: 0.002-0.400 mg/L	
Maximum	7.4
Mean	1.3
Standard Deviation	1.33
3xSD	3.98
UCL	5.3
n	369

UCL Upper Control Limit
n Number of data points

Table 5. TP Spike Recovery Data.

Acceptance Limit	90 – 110%
Analytical Range: 0.002-0.400 mg/L	
Minimum	90
Maximum	110
Mean	100.3
Standard Deviation	3.22
3xSD	9.66
LCL	90.6
UCL	109.9
n	369

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 101.8 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 100.3 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 December 2006 to December 2007 (see **Appendix A**) provided the data used in this analysis. **Figures 5** through **7** present regression analysis of the data, and **Table 6** 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 0.9721. This information shows that the results from the two laboratories have a very high degree of agreement (close to 1:1 correlation) between the laboratories.

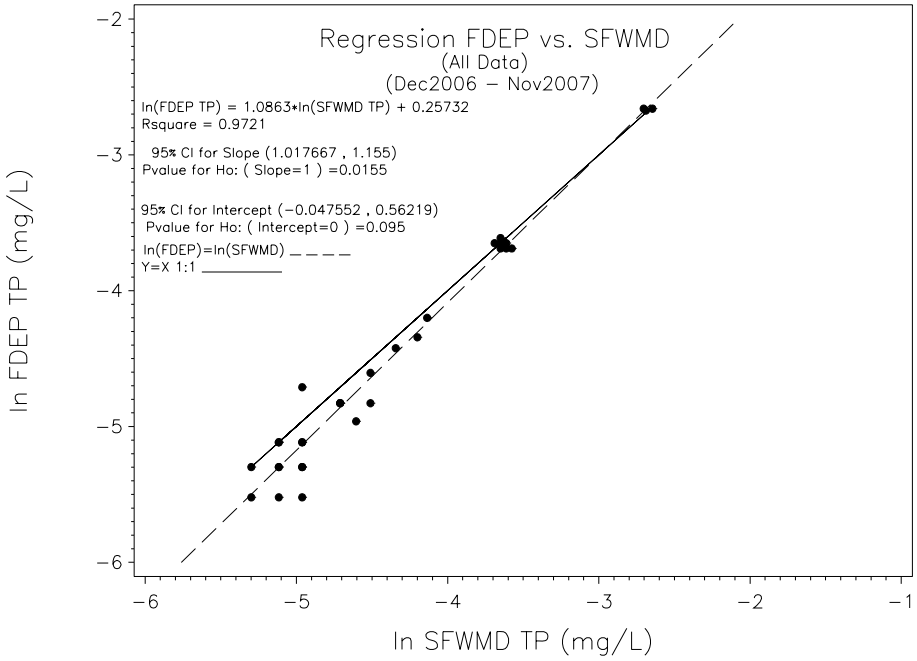


Figure 5. Regression analysis for all TP data.

The mean difference (0.00088 mg/L) and median difference (0.001 mg/L) were statistically significant. The observed differences are below the practical quantitation limit (PQL) of 0.008 mg/L. The paired t-test and signed-rank test yielded p-values of 0.0014 and 0.0001, respectively. **Note: The magnitudes of these differences are environmentally and practically insignificant.**

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 0.9894. The mean difference (0.0002 mg/L) and median difference (0.0005 mg/L) were not statistically significant. The differences are below the Practical Quantitation Limit (PQL) of the two laboratories. The paired t-test and signed-rank test yielded p-values of 0.7263 and 0.6289, respectively.

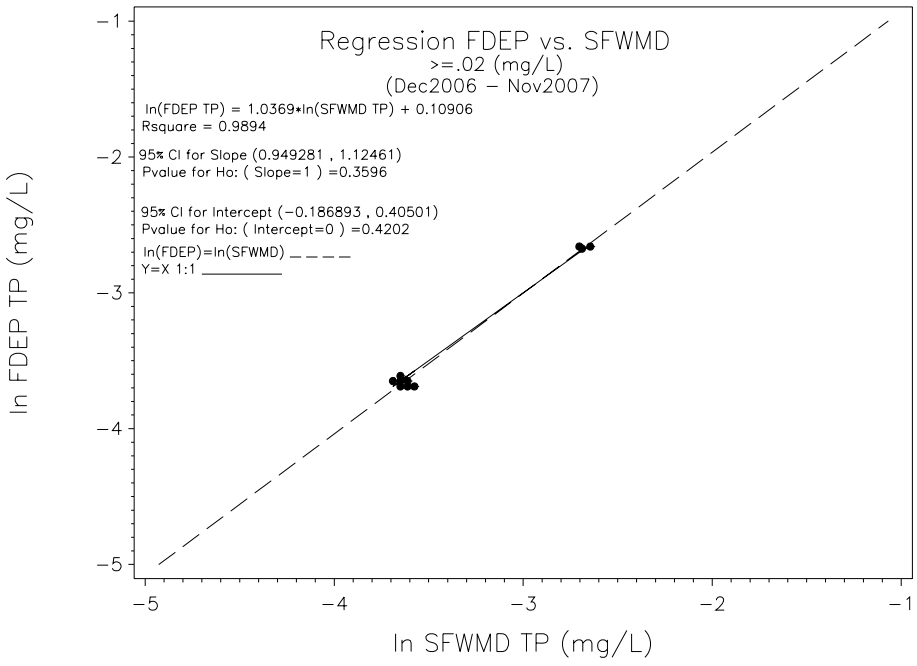


Figure 6. Regression analysis for TP greater or equal to 0.020 mg/L.

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 0.7986. At this low level, the data sets do not agree very well, as expected, due to the relatively high variability within each laboratory and between the two laboratories.

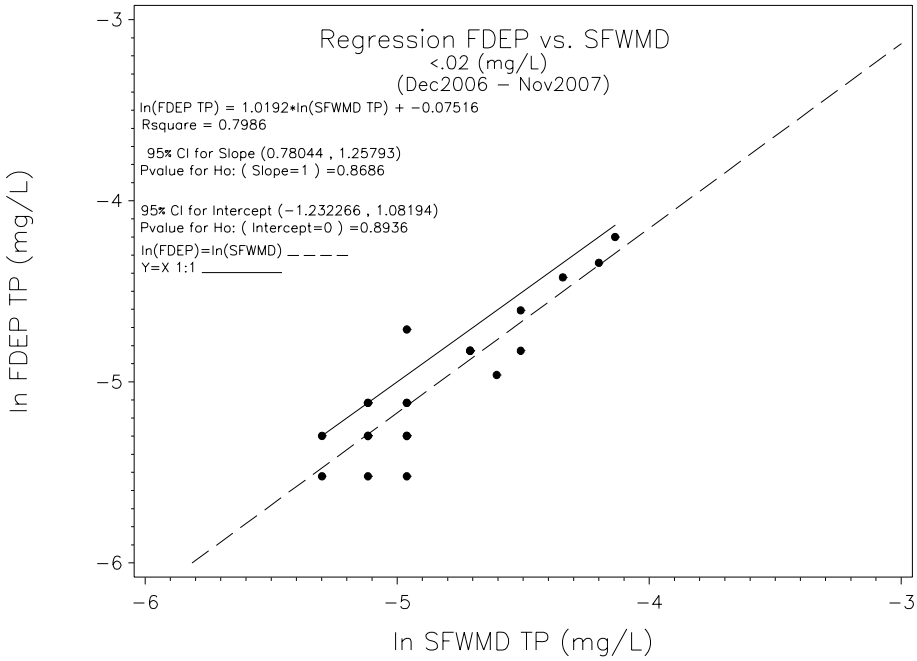


Figure 7. Regression analysis for TP less than 0.020 mg/L.

At this concentration level (< 0.020 mg/L), the mean difference (-0.0012 mg/L) and median difference (0.001 mg/L) were statistically significant. P-values for the paired t-test and signed-rank were <0.0001 and 0.0005, respectively. **Note: The magnitudes of these differences are environmentally and practically insignificant.**

Table 6. Comparison of District and FDEP split TP samples.

All Data	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	32	0.0171	0.008	
	District	32	0.0180	0.0095	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.00088	Mean of Differences = 0	Student's t	0.0014
	Median of Differences	0.0010	Median of Differences = 0	Signed Rank	0.0001
≥ 0.020 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	10	0.0389	0.026	
	District	10	0.0391	0.027	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.0002	Mean of Differences = 0	Student's t	0.7263
	Median of Differences	0.0005	Median of Differences = 0	Signed Rank	0.6289
< 0.020 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	22	0.0072	0.006	
	District	22	0.0084	0.007	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.0012	Mean of Differences = 0	Student's t	<0.001
	Median of Differences	0.0010	Mean of Differences = 0	Signed Rank	0.0005

Notes:

- Differences calculated as District TP – FDEP TP. The mean and median differences for all concentration levels are at or below the PQL.
- Data not used if FDEP value was < 0.004 (FDEP laboratory's MDL).

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 study (October to November 2007) are shown in **Table 7**.

Table 7. Proficiency testing study for TP results.

Assigned Value	1.11 mg/L
Reported Value	1.10 mg/L
Performance Evaluation	Acceptable Difference = 0.9%

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 (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi–X)/\sigma$, 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, December 2006 – December 2007.

Sample	Date	District	FDEP	% RPD/Comments
ERR-17	05-Dec-06	0.026	0.025	3.9
ERR-17	05-Dec-06	0.027	0.026	3.8
ERR-17	05-Dec-06	0.025	0.026	3.9
ERR-17	05-Dec-06	0.028	0.025	11.3
ERR-17	05-Dec-06	0.009	0.008	< PQL
ERR-17	05-Dec-06	0.009	0.008	< PQL
ERR-17	05-Dec-06	0.009	0.008	< PQL
ERR-17	05-Dec-06	0.010	0.007	< PQL
ERR-17	05-Dec-06	0.027	0.025	7.7
ERR-17	05-Dec-06	0.026	0.026	0.0
ERR-17	05-Dec-06	0.026	0.027	3.8
ERR-17	05-Dec-06	0.068	0.069	1.5
ERR-17	05-Dec-06	0.067	0.070	4.4
ERR-17	05-Dec-06	0.071	0.070	1.4
ERR-17	05-Dec-06	0.006	0.006	< PQL
ERR-17	05-Dec-06	0.007	0.006	< PQL
ERR-17	05-Dec-06	0.006	0.005	< PQL
ERR-17	05-Dec-06	0.006	0.006	< PQL
EVPA	12-Dec-06	0.005	0.004	< PQL
EVPA	12-Dec-06	0.005	0.005	< PQL
EVPA	05-Mar-07	0.010	<0.008	FDEP MDL was elevated[1]
EVPA	06-Mar-07	0.006	<0.008	FDEP MDL was elevated[1]
EVPA	06-Mar-07	0.007	<0.008	FDEP MDL was elevated[1]
EVPA	06-Mar-07	0.006	<0.008	FDEP MDL was elevated[1]
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

[1] According to the FDEP, the MDL was elevated due to sample matrix interference.