Quality Assessment Report for Water Quality Monitoring

April - June 2007

Submitted to the
Technical Oversight Committee (TOC)
on
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Zdzislaw Kolasinski (zkolasin@sfwmd.gov),

Introduction

This report is an assessment of the South Florida Water Management District (District) laboratory analysis and field sampling for Total Phosphorus (TP) monitoring, primarily for the following projects/stations during the second quarter of 2007.

- Conservation Area Inflow and Outflows (CAMB) S12A, S12B, S12C S12D, S333
- Everglades National Park Inflow Monitoring (ENP) S174, S176, S177, S18C
- Everglades Protection Area (EVPA) LOX3 to LOX16
- Non-Everglades Construction Project (NECP) S334
- C111 Project Sampling Location (C111D) S332D

Since field 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 this list.

The District's *Field Sampling Quality Manual* provides the minimum requirements followed in field sample collection. The *Laboratory Quality Manual* provides the minimum requirements followed in preparing and analyzing laboratory samples, as well as in-data verification and validation. **Field Sampling Quality Assessment** and **Laboratory Analysis Quality Assessment** in this report provide the laboratory and field quality control results during this quarter.

The SFWMD Laboratory Information Management System (LIMS) provided the data used in this report. This data is considered preliminary until the District releases it to their main database (DBHYDRO).

This report includes an analysis of the District laboratory's performance on split and inter-laboratory studies with FDEP and other laboratories for three selected projects (EVPA, C111 and Everglades TP Round Robins) for a one-year period. The results of the National Proficiency Testing Program designed to evaluate the laboratory's performance are also included.

Field Sampling Quality Assessment

PROCEDURE UPDATES

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

FIELD AUDIT

During this quarter on June 11, 2007, an audit was conducted to evaluate the field sampling collection activities for Miami-Dade County Department of Environmental Resources Management (DERM). The ENP project stations included in the audit were S178, S177 and S18C; and for NECP project station S197.

The key findings were: a) no agency quality manual, b) errors in documentation and documentation procedure and c) improper rinsing protocol for the data sonde during calibration.

The DERM is currently in the process of implementing corrective actions to address the deficiencies identified during the audit. After a review of the key findings it was determined the quality of the data were not affected.

MISSING DATA

Table 1 shows a list of missing data for this reporting period. All 44 missing data were not collected due to either lack of flow, site construction or shallow water depth.

Table 1. Missing data for the period from 04/01/07 to 06/30/07.

Project	Collection Date	Station	Comments
EVPA	4/16/07	LOX10	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX10	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX10	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX11	Total depth is less than 0.1 m. No sample collected
EVPA	6/12/07	LOX12	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX13	Total depth is less than 0.1 m. No sample collected
EVPA	4/17/07	LOX14	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX14	Total depth is less than 0.1 m. No sample collected
EVPA	4/17/07	LOX15	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX15	Total depth is less than 0.1 m. No sample collected
EVPA	6/12/07	LOX15	Total depth is less than 0.1 m. No sample collected
EVPA	4/17/07	LOX16	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX16	Total depth is less than 0.1 m. No sample collected
EVPA	6/12/07	LOX16	Total depth is less than 0.1 m. No sample collected
EVPA	4/16/07	LOX3	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX3	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX3	Total depth is less than 0.1 m. No sample collected

Table 1. Missing data for the period from 04/01/07 to 06/30/07.

Project	Collection Date	Station	Comments
EVPA	4/16/07	LOX4	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX4	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX4	Total depth is less than 0.1 m. No sample collected
EVPA	4/16/07	LOX5	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX5	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX5	Total depth is less than 0.1 m. No sample collected
EVPA	4/17/07	LOX6	Total depth is less than 0.1 m. No sample collected
EVPA	5/15/07	LOX6	Total depth is less than 0.1 m. No sample collected
EVPA	6/12/07	LOX6	Total depth is less than 0.1 m. No sample collected
EVPA	4/16/07	LOX7	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX7	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX7	Total depth is less than 0.1 m. No sample collected
EVPA	4/16/07	LOX8	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX8	Total depth is less than 0.1 m. No sample collected
EVPA	4/16/07	LOX9	Total depth is less than 0.1 m. No sample collected
EVPA	5/14/07	LOX9	Total depth is less than 0.1 m. No sample collected
EVPA	6/11/07	LOX9	Total depth is less than 0.1 m. No sample collected
CAMB	4/17/07	S12A	No flow. No sample collected.
CAMB	5/1/07	S12A	No flow. No sample collected.
CAMB	5/30/07	S12A	No flow. No sample collected.
CAMB	4/17/07	S12B	No flow. No sample collected.
CAMB	5/1/07	S12B	No flow. No sample collected.
CAMB	5/30/07	S12B	No flow. No sample collected.
CAMB	4/3/07	S12D	Site under construction.
CAMB	5/30/07	S12D	No flow. No sample collected.
NECP	4/24/07	S334	No flow. No sample collected.
NECP	5/22/07	S334	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 all projects of interest to the TOC. No blanks associated with samples for the stations listed in the Introduction were outside the acceptance criterion. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for all three projects. Routinely, data not meeting the set criteria for blanks, field precision or sampling protocols are flagged using FDEP data qualifier codes. **Table 4** lists flagged data for all trips that include samples for CAMB, ENP, EVPA, C111D and NECP projects during this quarter.

Table 2. Field and equipment blank results [1, 2, 3, 4].

Type of Blank	Project	Number of Blanks Collected	% < 0.002	% ≥ 0.002
FB	EVPA	1	100	0
EB	ENP	1	100	0
	EVPA	2	100	0
FCEB	C111D	6	100	0
	CAMB	8	100	0
	ENP	20	100	0
	EVPA	2	100	0
	NECP	5	100	0

[1] Only blanks for sampling events from samples collected at stations listed in the Introduction of this report 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 < MDL.

[4] When sample concentrations are less than five times the resulting blank values, laboratory personnel flagged the samples for possible contamination.

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

Project Code	Number of Triplicates	% RSD	Comments
CAMB	1	13.2	Precision criteria met.
ENP	1	20.0	Precision criteria met.
EVPA	1	3.7	Precision criteria met.

[1] Only replicates for sampling events from samples collected at stations listed in the Introduction of this report 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).

Table 4. List of flagged data.

Project	Date Collected	Station	Sample Type	Flag	Comments
EVPA	5/15/07	LOX12	G	J5	Dry patches in area, not a continuous body of water.

G - Grab sample

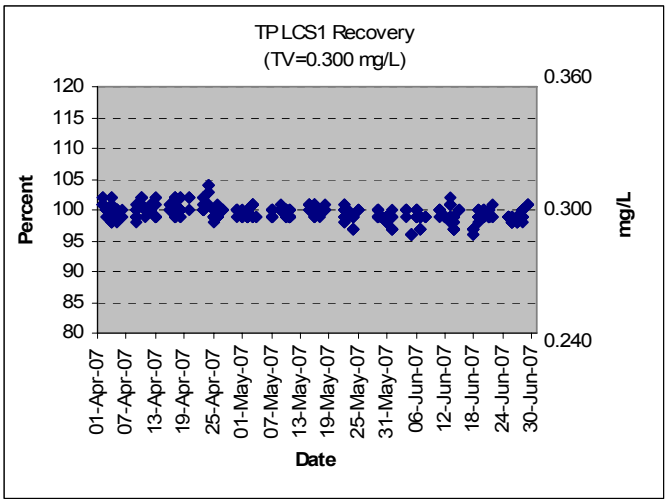
Laboratory Analysis Quality Assessment

PROCEDURE UPDATES

Total Phosphorus (TP) analytical procedure did not change during this reporting period.

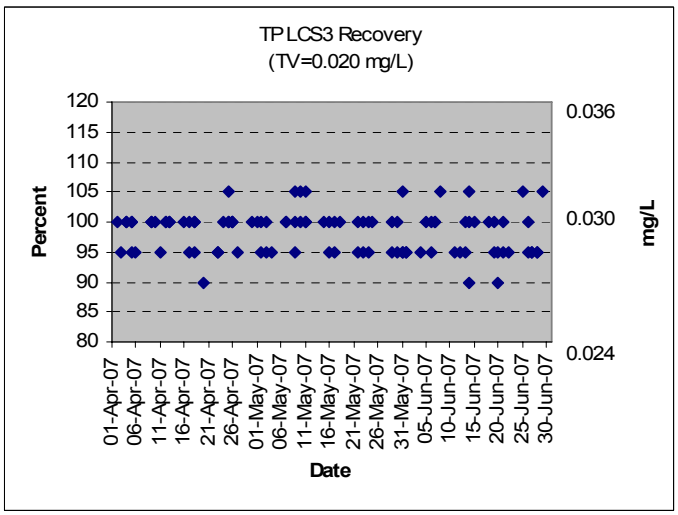
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figure 1** through **Figure 4** show recoveries from various types and levels of QC samples for the TP analysis at the District laboratory from April 1 through June 30, 2007.



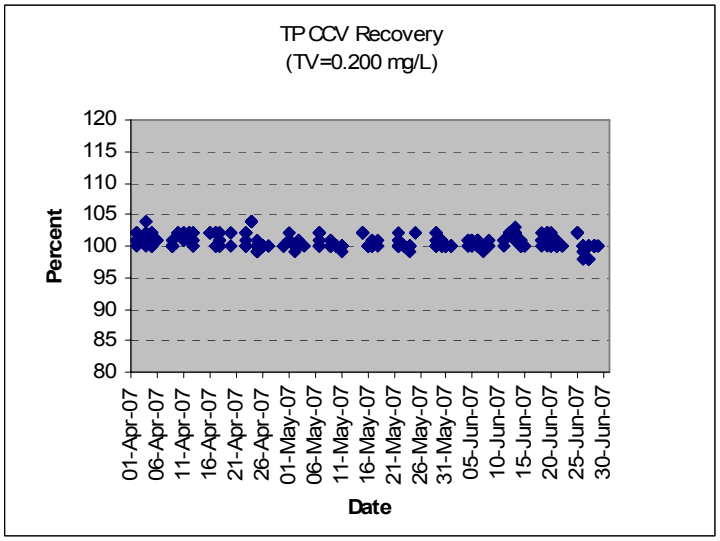
Mean = 99.5%, Max = 104.0%, Min = 96.0%

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



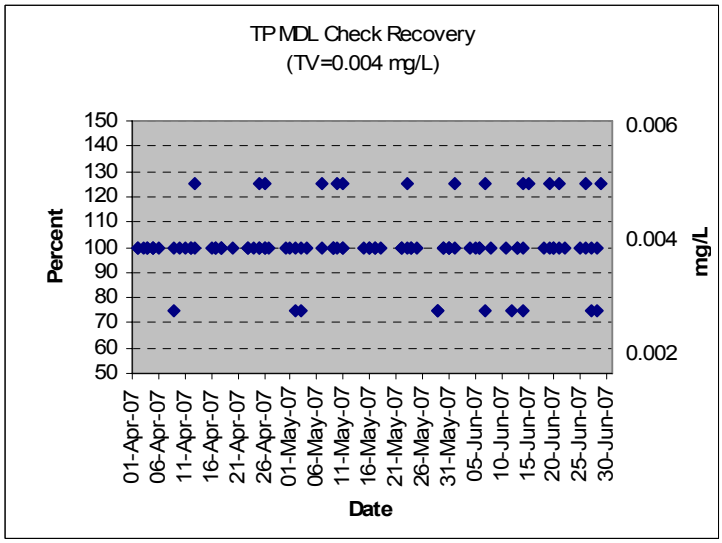
Mean = 98.3%, Max = 105.0%, Min = 90.0%

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



Mean = 100.6%, Max = 104.0%, Min = 98.0%

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



Mean = 101.2%, Max = 125.0%, Min = 75.0%

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

Table 4 and **Table 5** show precision and matrix spike recoveries. If QC recoveries are outside the set limits, the District 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 flagged accordingly.

Table 4. TP Precision Data, 04/01/07 – 06/30/07.

Acceptance Limit	<10%
Analytical Range: 0.002-0.400 mg/L	
Maximum	6.8
Mean	1.4
Standard Deviation	1.35
3xSD	4.05
UCL	5.5
n	280

UCL Upper Control Limit
n Number of data points

Table 5. TP Spike Recovery Data, 04/01/07 – 06/30/07.

Acceptance Limit	90 – 110%
Analytical Range: 0.002-0.400 mg/L	
Minimum	90
Maximum	110
Mean	100.1
Standard Deviation	3.46
3xSD	10.38
LCL	89.7
UCL	110.4
n	278

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

Recoveries for the QC samples are usually within ±10% from the true value, which is acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had mean recoveries of 101.2%. The daily MDL check results indicate the laboratory has consistently achieved the established MDL of 0.002 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 100.1%.

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 2006 to June 2007 (see **Table A-1**) provided the data used in this analysis. **Figure 5** through **Figure 7** show regression analysis of the data and **Table 6** shows summary statistics for the data pairs.

ALL DATA

Figure 5 shows that the intercept is not statistically different from zero (0) and the slope is not statistically different from one (1) for all TP data from both laboratories. The r^2 value is 0.9502. This information shows that the results from the two laboratories have a high degree of agreement (close to 1:1 correlation).

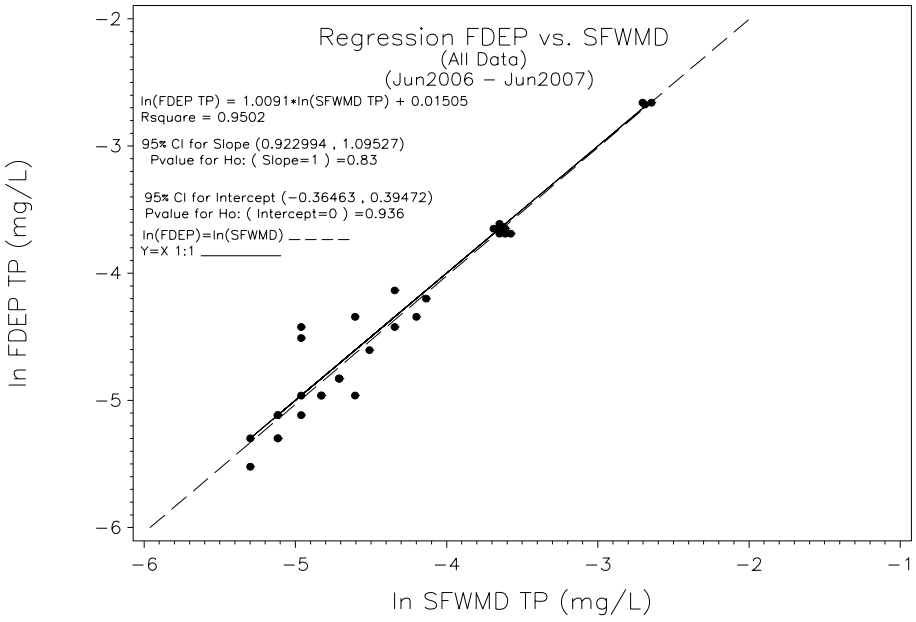


Figure 5. Regression analysis for all TP data.

The mean difference (0.00013 mg/L) and median difference (0.0010 mg/L) were not 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 0.712 and 0.1783, respectively.

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.

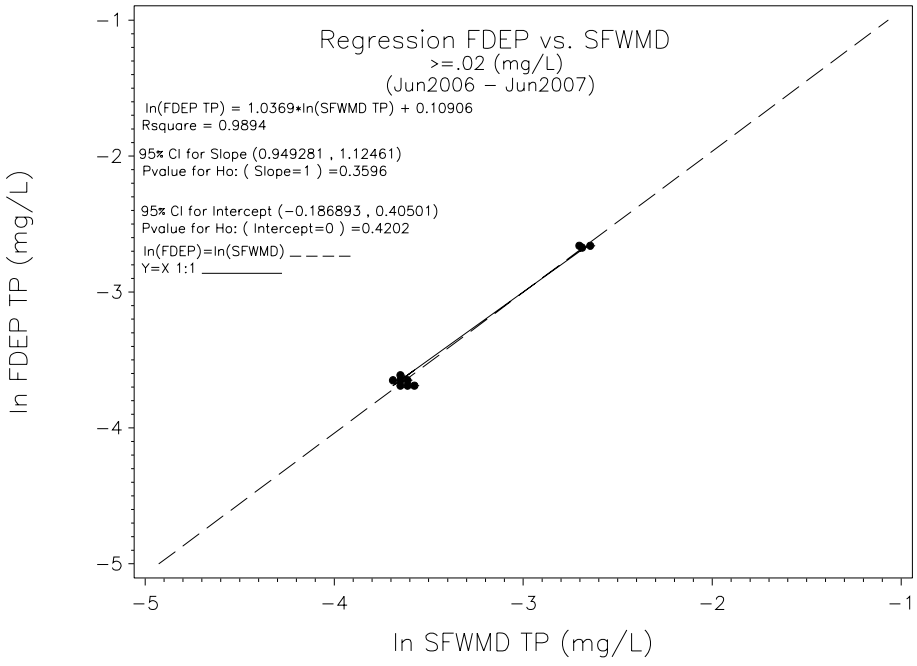


Figure 6. Regression analysis for TP greater or equal to 0.020 mg/L.

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 0.7045. 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.

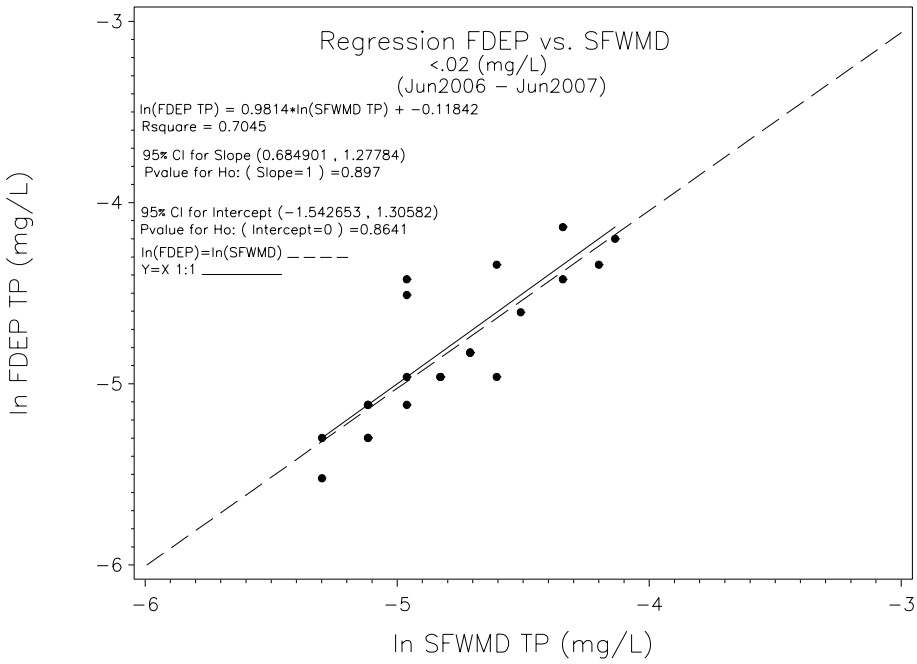


Figure 7. Regression analysis for TP less than 0.020 mg/L.

At this concentration level (< 0.020 mg/L), the mean difference (-0.0002 mg/L) and median difference (0.0010 mg/L) were not statistically significant. P-values for the paired t-test and signed-rank were 0.833 and 0.3967 respectively.

Table 6. Comparison of District and FDEP Split Phosphorus Samples (06/2006 – 06/2007).

All Data	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	32	0.0181	0.0115	
	District	32	0.0183	0.01	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.00013	Mean of Differences = 0	Student's t	0.7118
	Median of Differences	0.0010	Median of Differences = 0	Signed Rank	0.1783
≥ 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	0.0087	0.0075	
	District	22	0.0088	0.008	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.0001	Mean of Differences = 0	Student's t	0.833
	Median of Differences	0.0010	Mean of Differences = 0	Signed Rank	0.3967

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 (PT) on environmental samples on a semi-annual basis. The results for the District's laboratory from the most recent study (April-May 2007) are shown in **Table 7**.

Table 7. PT study April – May 2007 TP results.

Most Probable Value	2.72 mg/L
Reported Value	2.72 mg/L
Performance Evaluation	Acceptable Difference = 0.0%

Glossary

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 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.

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.

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.

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.

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.

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.

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 EPA.

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 4 times the MDL.

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

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

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

Table A-1. Results of TP split studies between the District and FDEP laboratories, EVPA Project and Everglades Round Robin, June 2006 – June 2007.

Sample	Date	District	FDEP	% RPD/Comments
EVPA	13-Jun-06	0.010	0.013	26.1
EVPA	13-Jun-06	0.007	0.012	< PQL
EVPA	13-Jun-06	0.013	0.016	20.7
EVPA	13-Jun-06	0.007	0.011	< PQL
EVPA	19-Sep-06	0.006	0.005	< PQL
EVPA	19-Sep-06	0.008	0.007	< PQL
EVPA	19-Sep-06	0.007	0.007	< PQL
EVPA	19-Sep-06	0.008	0.007	< PQL
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	[1]FDEP MDL was elevated
EVPA	06-Mar-07	0.006	<0.008	[1]FDEP MDL was elevated
EVPA	06-Mar-07	0.007	<0.008	[1]FDEP MDL was elevated
EVPA	06-Mar-07	0.006	<0.008	[1]FDEP MDL was elevated
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

[1] FDEP comment: The MDL was elevated due to sample matrix interference.