Quality Assessment Report for Water Quality Monitoring

July - September 2007

Submitted to the
Technical Oversight Committee (TOC)
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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 from July 1, 2007 through September 30, 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 through 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 the main database (DBHYDRO).

This report includes an analysis of the District laboratory's performance on the 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 Research Institute Environment Canada and U.S Geological Survey Inter-laboratory Programs 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

Field audits were conducted on the ST1W and CAMB projects during the third quarter of 2007. These audits were not included in this report due to the fact that the audited collection agencies do not collect samples at the TOC related stations.

MISSING DATA

Table 1 shows a list of missing data for this reporting period. Nineteen data were missing due to samples not collected because of either lack of flow or shallow water depth. One datum was missing due to improper sample preservation. One sample was lost during shipment.

Table 1. Missing data for the period from 07/01/07 to 09/30/07.

Project	Collection Date	Station	Comments
C111D	8/22/07	S332D	Sample was lost during shipment
CAMB	7/24/07	S12D	No flow, no sample collected
CAMB	7/24/07	S12B	No flow, no sample collected
CAMB	7/24/07	S12A	No flow, no sample collected
CAMB	8/21/07	S12D	No flow, no sample collected
CAMB	8/21/07	S12B	No flow, no sample collected
CAMB	8/21/07	S12A	No flow, no sample collected
CAMB	9/11/07	S12C	No flow, no sample collected
CAMB	9/18/07	S12D	No flow, no sample collected
CAMB	9/18/07	S12C	No flow, no sample collected
CAMB	9/18/07	S12B	No flow, no sample collected
CAMB	9/18/07	S12A	No flow, no sample collected
CAMB	9/25/07	S12C	No flow, no sample collected
ENP	7/26/07	S176	Sample not acidified
ENP	9/16/07	S176	No flow, no sample collected
ENP	9/24/07	S177	No flow, no sample collected
EVPA	7/9/07	LOX10	Total depth less than 0.10 m. No sample collected
EVPA	8/9/07	LOX13	Total depth less than 0.10 m. No sample collected
EVPA	9/17/07	LOX3	Total depth less than 0.10 m. No sample collected
EVPA	9/17/07	LOX5	Total depth less than 0.10 m. No sample collected
NECP	9/25/07	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 four projects. Routinely, data not meeting the set criteria for blanks, field precision or sampling protocols are qualified using 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
FB	ENP	1	100	0
EB	CAMB	1	100	0
	ENP	2	100	0
	EVPA	2	100	0
	NECP	1	100	0
FCEB	C111D	7	100	0
	CAMB	7	100	0
	ENP	21	100	0
	EVPA	5	100	0
	NECP	6	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 qualified the samples for possible contamination.

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

Project Code	Number of Triplicates	Date Collected	% RSD	Comments
CAMB	1	7/10/07	10.6	Precision criteria met.
C111D	1	8/08/07	0.0	Precision criteria met.
EVPA	1	9/18/07	8.7	Precision criteria met.
NECP	1	7/02/07	4.3	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).

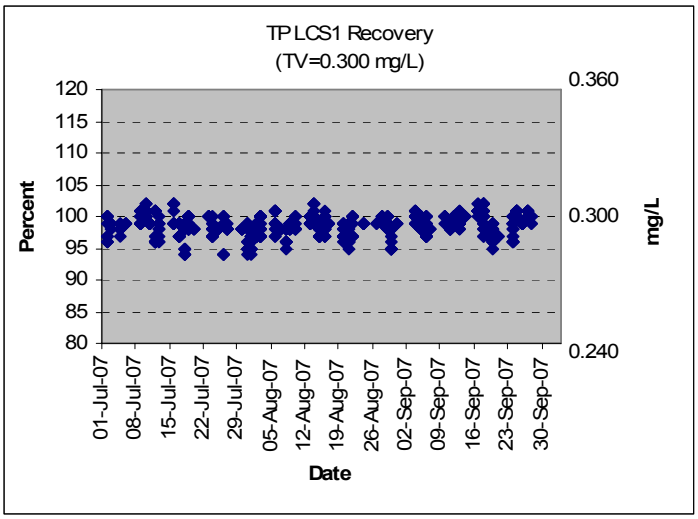
Laboratory Analysis Quality Assessment

PROCEDURE UPDATES

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

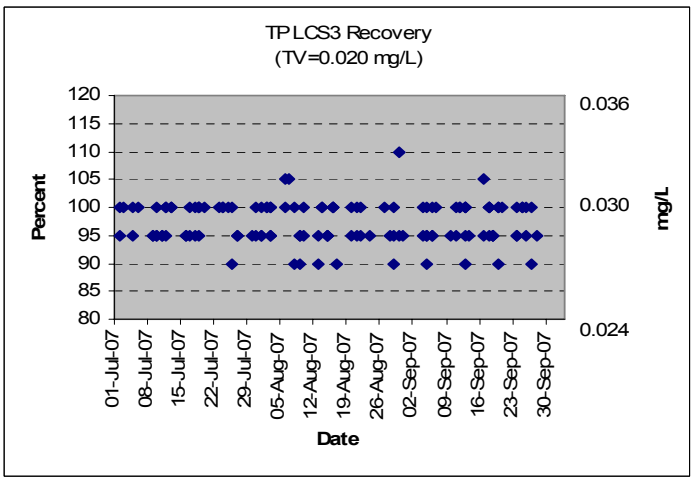
LABORATORY QUALITY CONTROL

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 July 1, 2007 through September 30, 2007.



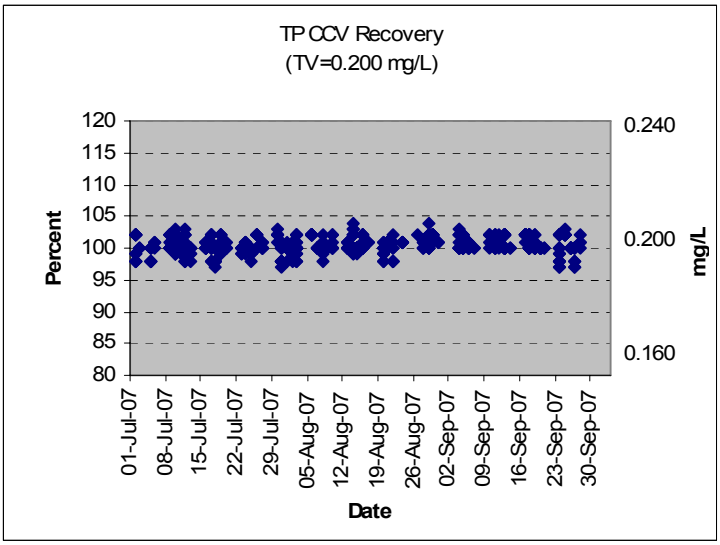
Mean = 98.5%, Max = 102.0%, Min = 94.0%

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



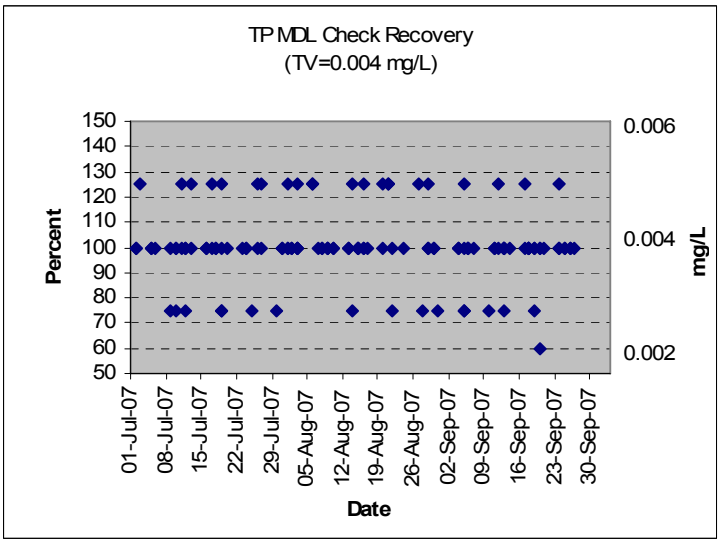
Mean = 97.3%, Max = 110.0%, Min = 90.0%

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



Mean = 100.5%, Max = 104.0%, Min = 97.0%

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



Mean = 101.0%, Max = 125.0%, Min = 60.0%

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 qualified accordingly.

Table 4. TP Precision Data, 07/01/07 – 09/30/07.

Acceptance Limit	<10%
Analytical Range: 0.002-0.400 mg/L	
Maximum	9.9
Mean	1.7
Standard Deviation	1.54
3xSD	4.62
UCL	6.4
n	375

UCL Upper Control Limit
n Number of data points

Table 5. TP Spike Recovery Data, 07/01/07 – 09/30/07.

Acceptance Limit	90 – 110%
Analytical Range: 0.002-0.400 mg/L	
Minimum	90
Maximum	110
Mean	100.4
Standard Deviation	3.89
3xSD	11.66
LCL	88.8
UCL	112.1
n	377

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 101.0%. 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 100.4%.

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 September 2006 to September 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 0.9854. 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.

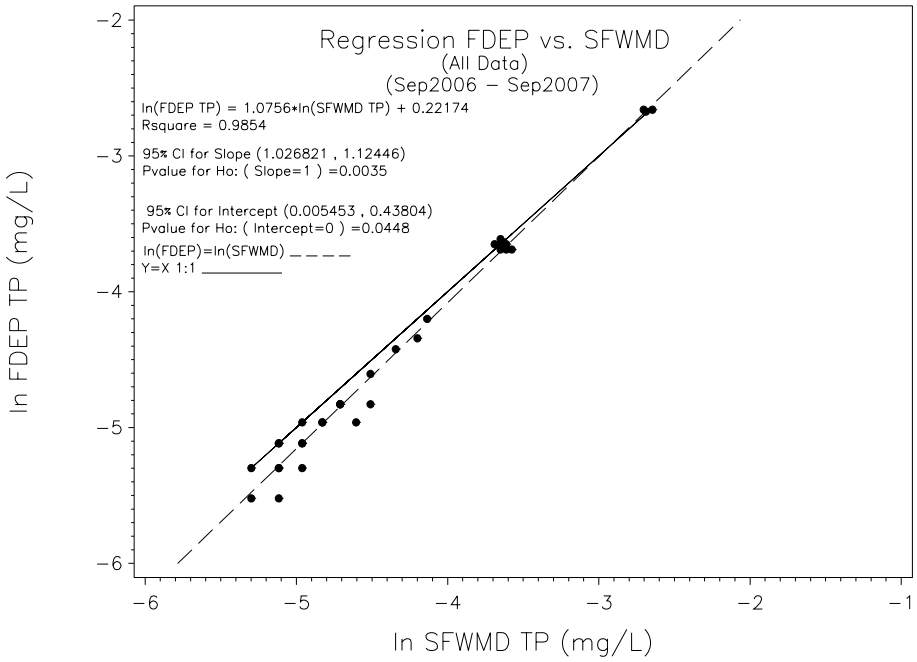


Figure 5. Regression analysis for all TP data.

The mean difference (0.00084 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 0.0006 and <0.0001, 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.

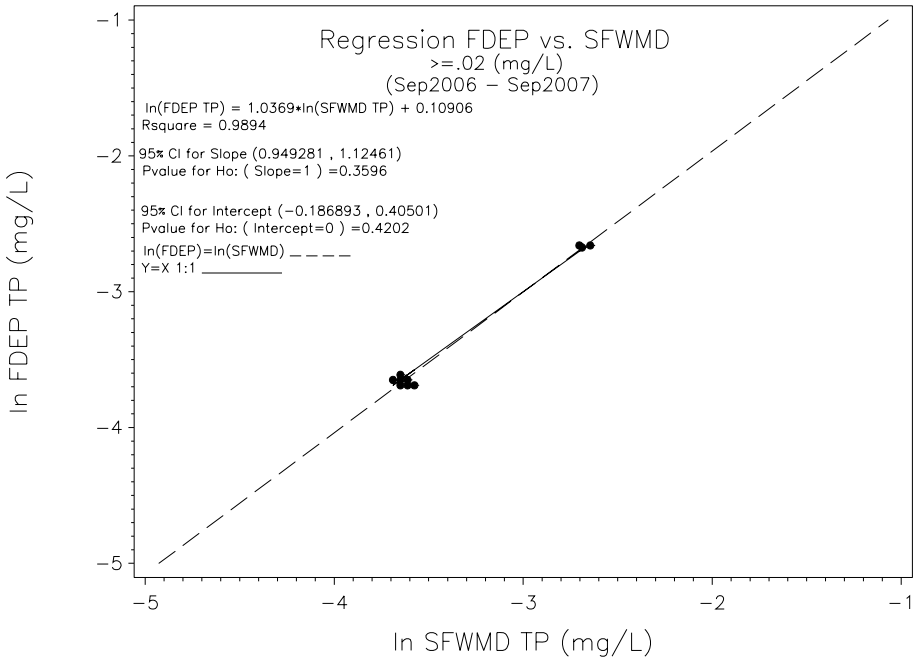


Figure 6. Regression analysis for TP greater or equal to 0.020 mg/L.

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 0.8904. 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.

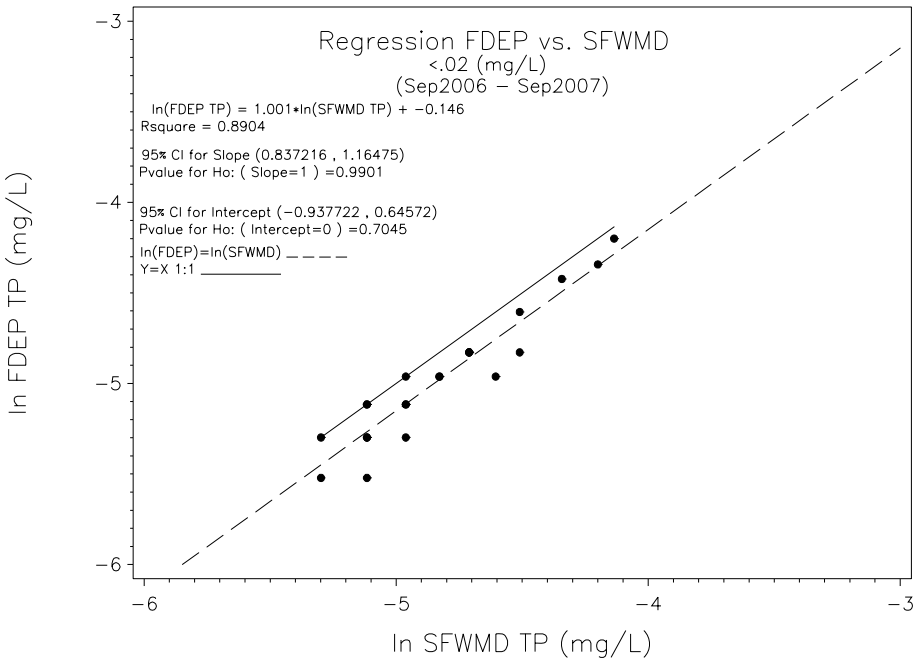


Figure 7. Regression analysis for TP less than 0.020 mg/L.

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 (09/2006 – 09/2007).

All Data	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	32	0.0172	0.008	
	District	32	0.0181	0.0095	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.00084	Mean of Differences = 0	Student's t	0.0006
	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	0.0074	0.007	
	District	22	0.0085	0.0075	
	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 Water Research Institute Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program

The objectives of this program are to assess and demonstrate reliability and quality of analytical measurements of inorganic parameters in natural waters. The results for the District's laboratory from the most recent study are presented in Table 7 (June-September 2007). The District laboratory was rated on performance of TP as "ideal" (highest category), and the linear regression shows no systematic bias (**Figure 8**).

Table 7. Performance in PT Study 90 for TP, June-September 2007

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.001	0.004	0.0065	0.088	0.0180	0.0649	0.334	0.136	0.228	0.834
Reported Results, mg/L	< 0.002	0.003	0.006	0.089	0.017	0.066	0.338	0.136	0.228	0.841
Z-value	NA	-1.4	-0.5	0.1	-0.5	0.2	0.2	0.0	0.0	0.2

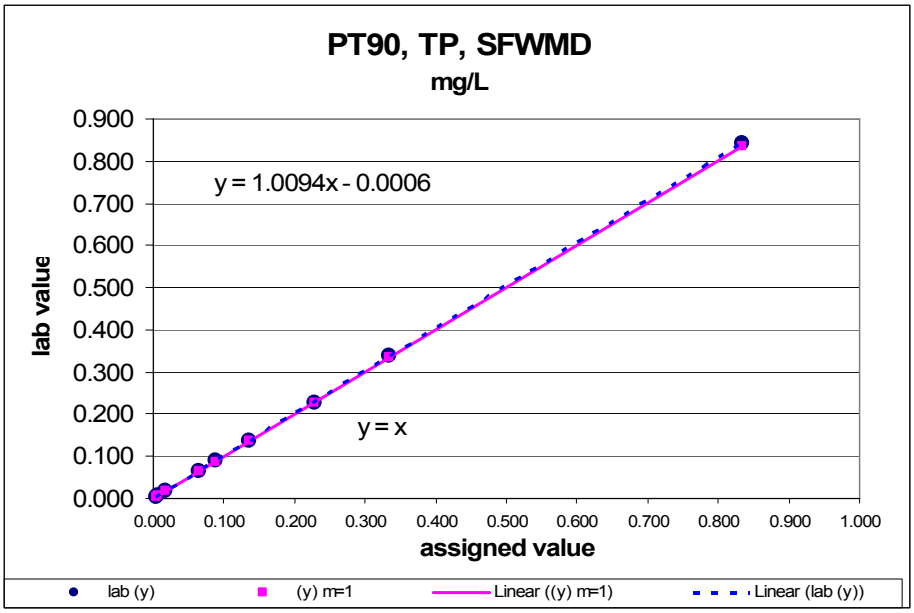


Figure 8. Linear regression of reported TP results vs. assigned values.

U.S. Geological Survey Analytical Evaluation Program

The SFWMD's laboratory voluntarily participates in a semiannual U.S Geological Survey (USGS) on environmental samples as an inter-laboratory comparison. The laboratory uses the survey results to monitor performance. Evaluation of the results is based on the deviation (z-value) from the median and percent difference. Following usual practices, a z-value less than ±2 is consider satisfactory. **Table 8** provides the results of the August-September 2007 Study.

Table 8. Performance in USGS Study for TP, August – September 2007.

Sample I.D	Reported Result, mg/L	Most Probable Value, mg/L	Z-Value	% Difference
M-184	0.929	0.910	0.46	2.09
N-95	0.232	0.231	0.08	0.43

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 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.

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

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

Sample	Date	District	FDEP	% RPD/Comments
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
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

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