

Quality Assessment Report for Water Quality Monitoring

July - September 2006



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Technical Oversight Committee (TOC)
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Introduction

This report is an assessment of the South Florida Water Management District (SFWMD) laboratory analysis and field sampling for total phosphorus (TP) monitoring applicable to the following projects/stations during the third quarter of 2006.

- Water Conservation Area Inflow and Outflow Monitoring (CAMB): S12A, S12B, S12C, S12D, S333
- Everglades National Park Inflow Monitoring (ENP): S174, S176, S177, S18C
- C111 Detention Area Monitoring (C111D): S332D
- Everglades Protection Area Monitoring (EVPA): LOX3 through LOX16
- Non-Everglades Construction Project Permit Monitoring (NECP): S334

Data from stations S175 and S332 (ENP) are not included in the Field Sampling Quality Assessment section of this report. These stations are no longer the compliance stations under the Settlement Agreement (SA).

The SFWMD Field Sampling Quality Manual sets the minimum requirements to be followed in field sample collection. The Laboratory Quality Manual sets the minimum requirements to be followed in laboratory sample preparation and analysis, as well as in data verification and validation. Sections II and III of this report provide the results of laboratory and field quality control during this quarter.

Included in this report is an analysis of the SFWMD laboratory's performance on split and inter-laboratory studies with the Florida Department of Environmental Protection (FDEP) and other laboratories for three selected projects, i.e., EVPA, C111 and Everglades TP Round Robins, for a one-year period. A Glossary is also included at the end of this report.

Field Sampling Quality Assessment

PROCEDURE UPDATES

There was no major procedural update related to TP collection for this period.

FIELD AUDIT

On 7/25/2006, a field sampling collection audit was performed for Miami-Dade County Department of Environmental Resources Management (DERM) sampling for the CAMB project stations: S12A, S12B, S12C, S12D and S333.

The key findings were:

- a. The agency did not have a quality manual
- b. One document correction was obliterated from the record
- c. Rinsing protocol for the data sonde was improper
- d. The laboratory-cleaned equipment was not being rinsed with HCl for some sampling trips

Other than submittal of the DERM quality manual, all deficiencies have been corrected now. Assessment of the blanks collected by DERM indicated that the acid rinse does not affect the TP measurements.

MISSING DATA

Table 1 shows a list of missing data for this reporting period. Data may be missing because the samples were not collected or because there was a problem at sample submission to the laboratory. Out of 34 missing data, 31 were not collected due to either lack of flow, structure maintenance or shallow water depth. An autosampler malfunction missed one sample at station S18C. The laboratory cancelled analyses for two samples collected at S18C due to improper sample preservation.

Table 1. Missing Data for the Period from 7/1/06 to 9/30/06.

Project	Collection Date	Station	Comments
ENP	7/3/2006	S18C	Sample analysis cancelled by laboratory due to improper preservation or sample not analyzed by laboratory.
ENP	7/5/2006	S174	No flow, no sample collected.
EVPA	7/10/2006	LOX3	Total depth less than 0.10 m. No sample collected.
EVPA	7/10/2006	LOX5	Total depth less than 0.10m. No sample collected.
EVPA	7/10/2006	LOX9	Total depth less than 0.10m. No sample collected.
EVPA	7/10/2006	LOX4	Total depth less than 0.10m. No sample collected.
EVPA	7/11/2006	LOX13	Total depth less than 0.10m. No sample collected.

Table 1. Missing Data for the Period from 7/1/06 to 9/30/06.

Project	Collection Date	Station	Comments
ENP	7/12/2006	S174	No flow, no sample collected.
NECP	7/18/2006	S334	No flow, no sample collected.
ENP	7/19/2006	S174	No flow, no sample collected.
CAMB	7/25/2006	S12A	No flow, no sample collected.
CAMB	7/25/2006	S12B	No flow, no sample collected.
ENP	7/26/2006	S174	No flow, no sample collected.
ENP	8/2/2006	S174	No flow, no sample collected.
ENP	8/2/2006	S174	No flow, no sample collected.
EVPA	8/7/2006	LOX3	Total depth less than 0.10m. No sample collected.
EVPA	8/7/2006	LOX5	Total depth less than 0.10m. No sample collected.
EVPA	8/8/2006	LOX11	Total depth less than 0.10m. No sample collected.
ENP	8/9/2006	S174	No flow, no sample collected.
NECP	8/15/2006	S334	No flow, no sample collected.
ENP	8/16/2006	S174	No flow, no sample collected.
CAMB	8/22/2006	S12A	No flow, no sample collected.
CAMB	8/22/2006	S12B	No flow, no sample collected.
ENP	8/23/2006	S174	No flow, no sample collected.
NECP	8/31/2006	S334	No flow, no sample collected.
ENP	9/1/2006	S174	No flow, no sample collected.
ENP	9/1/2006	S174	No flow, no sample collected.
ENP	9/6/2006	S174	No flow, no sample collected.
ENP	9/6/2006	S174	No flow, no sample collected.
ENP	9/13/2006	S174	No flow, no sample collected.
ENP	9/20/2006	S174	No flow, no sample collected.
ENP	9/25/2006	S18C	Sample analysis cancelled by laboratory due to improper preservation.
ENP	9/25/2006	S18C	No sample collected due to autosampler malfunction.
NECP	9/26/2006	S334	No flow, no sample collected.

QUALITY CONTROL

Field quality control (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 and FCEB results for all projects of interest to the TOC. No blanks associated with samples for stations listed in the Introduction of this report were outside the acceptance criterion. **Table 3** summarizes field precision results, which were all acceptable.

Table 2. Field and Equipment Blank Results.

Type of Blank	Project	Blanks Collected	Percent Less than or Equal to 0.002	Percent Greater than 0.002
EB	CAMB	1	100	0
	ENP	1	100	0
	NECP	1	100	0
	EVPA	1	100	0
FCEB	CAMB	13	100	0
	ENP	33	100	0
	EVPA	7	100	0
	NECP	2	100	0
FB	ENP	1	100	0

Notes:

- Only blanks from sampling events that included samples from stations listed in the Introduction of this report were included in this analysis.
- Blanks for TP, which were collected for a short-term autosampler experimental project at some TOC stations, were not included here.
- FB, FCEB and EB acceptance criteria: Must be greater than or equal to the method detection limit (MDL).
- Samples are flagged when their concentrations are less than five times the associated blank values for possibility of contamination.

Table 3. Field Precision Summary^{1,2}.

Project Code	Number of Triplicates	Percent RSD	Comments
CAMB	1	0	Sample meets precision criteria.
CAMB	1	5.1	Sample meets precision criteria.
ENP	1	8.7	Sample meets precision criteria. Sample values are less than PQL ³ .
EVPA	1	5.4	Sample meets precision criteria.
NECP	1	1.8	Sample meets precision criteria.

¹ Only replicates from sampling events that included samples from stations listed in the Introduction of this report were included in this analysis.

² The SFWMD chemistry laboratory conducted all TP analyses.

³ Field precision acceptance criterion: Less than 20 percent. This criterion was applied only if sample values were greater than the practical quantitation limit (PQL).

Data that do not meet the set criteria for blanks, field precision or sampling protocols are flagged using FDEP data qualifier codes. **Table 4** lists data flagged for all trips that include samples during this quarter.

Table 4. List of Flagged Data.

Project	Date Collected	Station	Sample Type	Flag	Comments
CAMB	8/8/2006	S12C	G	J3	Reversal OPO4 greater than TPO4
ENP	7/31/2006	S18C	ACF	J5	Autosampler maintenance overdue, intake clogged with weeds
ENP	8/7/2006	S18C	ACF	J5	Autosampler maintenance overdue, intake clogged with weeds
ENP	8/14/2006	S18C	ACF	J5	Autosampler maintenance overdue, intake clogged with weeds

Notes:

G Grab.

ACF Autosampler Composite Flow Proportional.

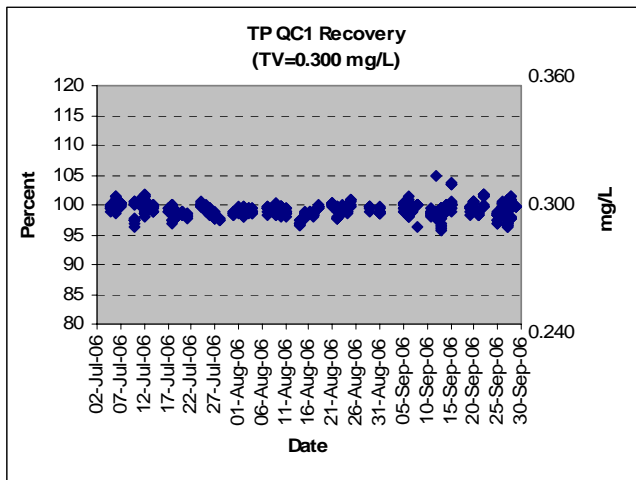
Laboratory Analysis Quality Assessment

PROCEDURE UPDATES

TP analytical procedure did not change during this reporting period.

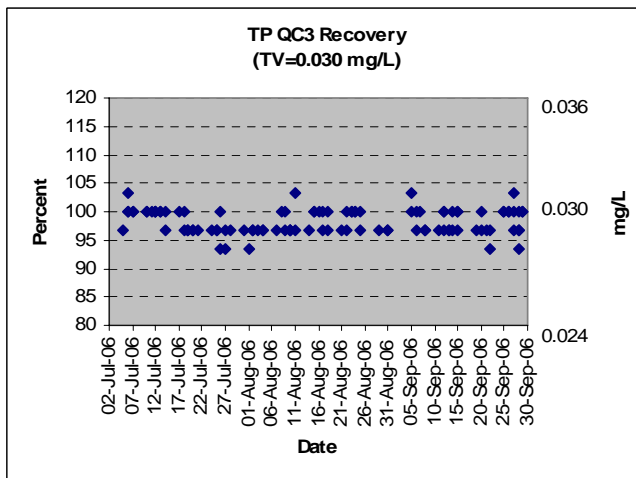
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC check samples, matrix spikes and precision check samples. **Figure 1** through **Figure 4** show recoveries from various types and levels of QC samples for the TP analysis at the SFWMD laboratory from July 1 through September 30, 2006. Recoveries for the QC samples are generally within +10 percent from the true value (TV), which are acceptable.



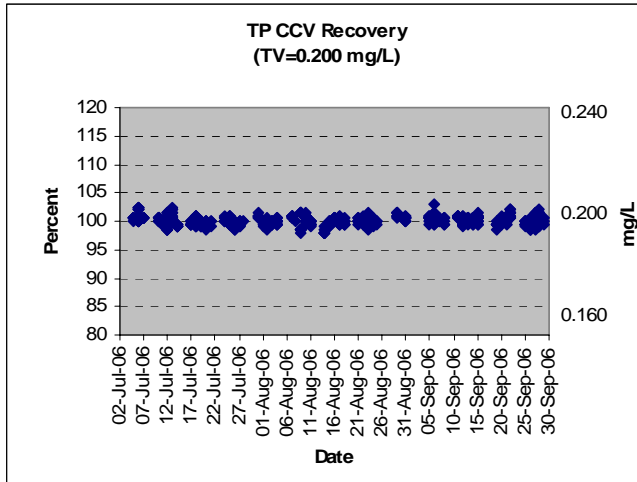
Mean = 98.2 Percent, Max. = 103.3 Percent, Min. = 93.3 Percent

Figure 1. QC (Laboratory Control Solution) Sample Recoveries for TP Analysis.



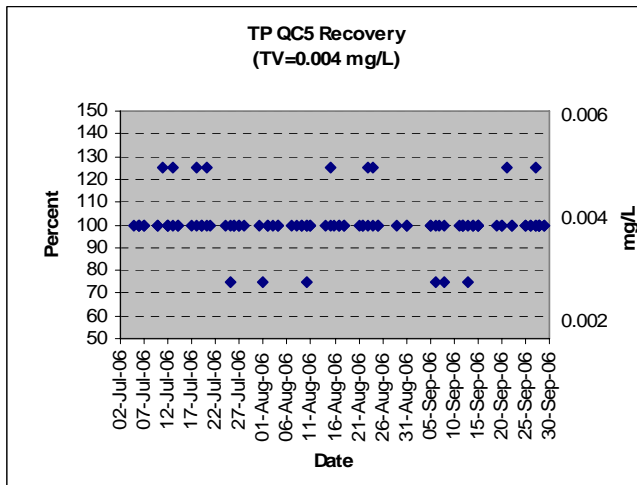
Mean = 98.2 Percent, Max. = 103.3 Percent, Min. = 93.3 Percent

Figure 2. QC (Laboratory Control Solution) Sample Recoveries for TP Analysis.



Mean = 100.1 Percent, Max. = 103.0 Percent, Min. = 98.0 Percent

Figure 3. QC (Continuous Calibration Verification) Sample Recoveries for TP Analysis.



Mean = 100.7 Percent, Max. = 125.0 Percent, Min. = 75.0 Percent

Figure 4. QC5 (Method Detection Limit Check) Sample Recoveries for TP Analysis.

Table 5 and **Table 6** show precision and matrix spike recoveries. If QC recoveries are outside the set limits, an entire analytical run is rejected. Data is flagged if deficiencies are noted but the samples cannot be re-analyzed because the required holding times have been exceeded.

Table 5. TP Precision Data, 7/01/06 through 9/30/06.

Acceptance Limit	Less than 10 Percent
Analytical Range:	0.002 - 0.400 mg/L
Maximum	8.9
Mean	1.4

Table 5. TP Precision Data, 7/01/06 through 9/30/06.

Acceptance Limit	Less than 10 Percent
Standard deviation	1.38
3xSD	4.15
Upper control limit	5.6
Number of data points	327

Table 6. TP Spike Recovery Data, 7/01/06 through 9/30/06.

Acceptance Limit	90 – 110 Percent
Analytical Range: 0.002 - 0.400 mg/L	
Minimum	90.0
Maximum	109
Mean	102.7
Standard deviation	3.04
3xSD	9.11
Lower control limit	93.6
Upper control limit	111.8
Number of data points	337

The method detection limit (MDL) check (QC5), with a true value of 0.004 mg/L, had mean recoveries of 100.7 percent. The daily MDL check results indicate the laboratory has consistently achieved the goal of 0.002 mg/L MDL.

The mean recovery for an organic check, a solution prepared from phytic acid, a stable form of organic phosphate to prepare matrix spikes, was 102.7 percent.

INTER-LABORATORY QUALITY CONTROL ASSESSMENT

Split Studies with FDEP Laboratory

To assess the comparability of results, the SFWMD sends split samples to other laboratories on a routine basis. From September 2005 through September 2006, this analysis used data from split studies between FDEP and SFWMD laboratories for the following programs:

- EVPA Quarterly Splits
- Everglades TP Round Robin (see **Appendix A**)

Figure 5 through **Figure 7** show regression analysis of the data and **Table 7** shows summary statistics for the data pairs.

ALL DATA

Figure 5 shows that the intercept of the regression is not statistically different from 0 and that the slope is not statistically different from 1 for all TP data from both laboratories. This means that the results from those two laboratories are statistically identical. The coefficient of determination (R^2) value is 0.9679. This information shows that the results from the two laboratories have a high degree of agreement (close to 1:1 correlation).

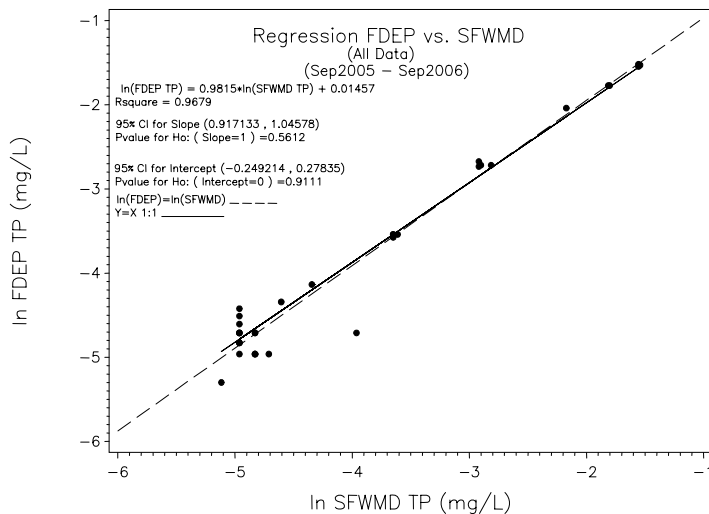


Figure 5. Regression Analysis for TP - All Data.

The mean difference (-0.0032 mg/L) and median difference (-0.0020 mg/L) were statistically significant, but these differences are at or below the FDEP laboratory's MDL. The paired t-test and signed-rank test yielded probability (of observed difference occurring by chance) values of 0.0007 and less than 0.0001 respectively.

TP GREATER THAN OR EQUAL TO 0.020 mg/L

Figure 6 shows that the intercept is not statistically different from zero, and that the slope is not statistically different from one for samples with TP greater than or equal to 0.020 mg/L. The R^2 value is 0.9944. The Mean difference (-0.0067 mg/L) and Median difference (-0.0055 mg/L) were statistically significant, but these differences are still below the Practical Quantitation Limit (PQL) of the two laboratories. The paired t-test and signed-rank test yielded probability of 0.002 and 0.0001 respectively.

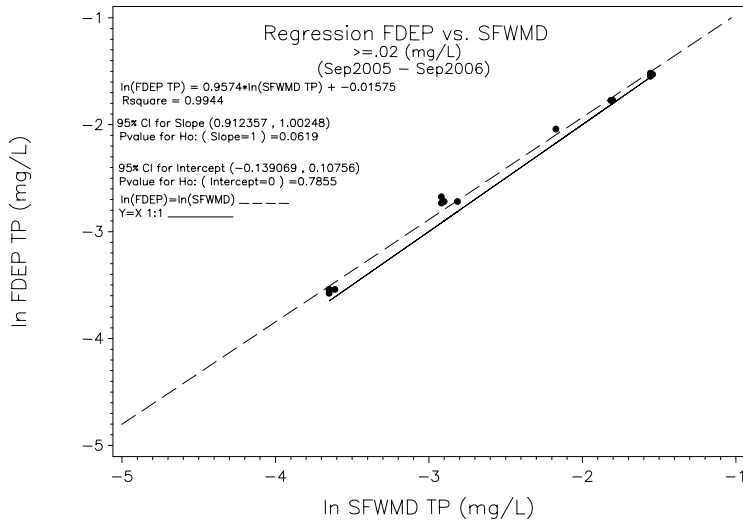


Figure 6. Regression Analysis for TP with a Concentration Greater than or Equal to 0.020 mg/L.

TP LESS THAN 0.020 mg/L

Figure 7 shows that the slope is significantly different from 1 and intercept is significantly different from 0 for samples with TP less than 0.020 mg/L, suggesting a difference between the data sets for the two laboratories. The very high variability within each laboratory and between the two laboratories at the very low concentration levels affects this outcome. The R^2 value from this regression is 0.1519.

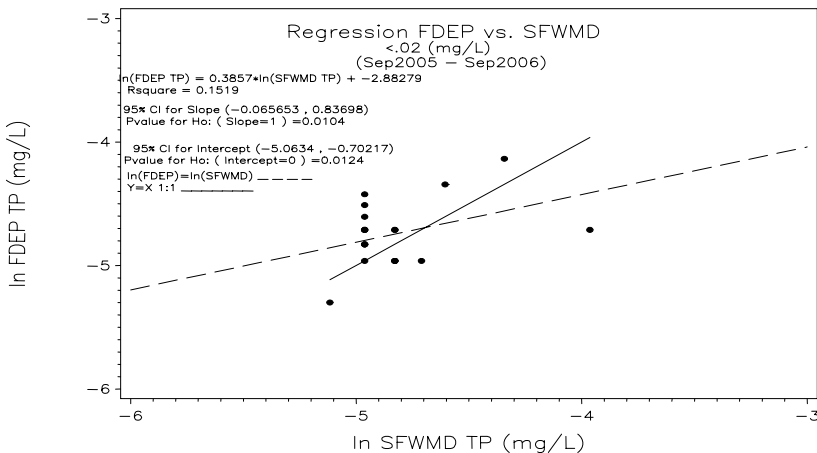


Figure 7. Regression Analysis for TP with a Concentration Less than 0.020 mg/L.

At this concentration level (less than 0.020 mg/L), the mean difference (-0.0007 mg/L) and median difference (-0.0010 mg/L) were not statistically significant. Probability values for the paired t-test and signed-rank were 0.3627 and 0.0392 respectively (see **Table 7**).

Table 7. Comparison of SFWMD and FDEP Split Phosphorus Sample Analyses (9/2005 – 9/2006).

All Data	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	34	0.0494	0.0115	
	SFWMD	34	0.0463	0.095	
Greater than or Equal to 0.020 mg/L	Statistical Test of Hypotheses				
	Summary of Paired Differences		Null Hypothesis	Test	P-value
	Mean of Differences	-0.0032	Mean of Differences = 0	Student's t	0.0007 ¹
	Median of Differences	-0.0020	Median of Differences = 0	Signed Rank	Less than 0.0001 ¹
Less than 0.020 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	14	0.1071	0.0675	
	SFWMD	14	0.1004	0.0575	
Less than 0.020 mg/L	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	-0.0067	Mean of Differences = 0	Student's t	0.0002 ¹
	Median of Differences	-0.0055	Median of Differences = 0	Signed Rank	0.0001 ¹
Less than 0.020 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	20	0.0090	0.009	
	SFWMD	20	0.0084	0.007	
Less than 0.020 mg/L	Statistical Test of Hypotheses				
	Summary of Paired Differences		Hypothesis	Test	P-value
	Mean of Differences	-0.0007	Mean of Differences = 0	Student's t	0.3627
	Median of Differences	-0.0010	Mean of Differences = 0	Signed Rank	0.0392 ²

¹ P-value indicates that the probability is very significant.

² P-value indicates that the probability is significant at 5 percent.

Notes:

- Differences were calculated as SFWMD TP minus FDEP TP. The mean and median differences for all concentration levels are at or below the PQL.
- Data were not used if FDEP value was less than 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. **Table 8** shows the results for the SFWMD’s laboratory from the most recent study (PT study 88, June 2006 through September 2006). The performance of total phosphorus analysis was rated as “ideal” (highest category) (see **Figure 8**).

Table 8. Performance in PT Study 88 for TP, June 2006 through September 2006.

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.002	0.00468	0.066	0.046	0.103	0.0171	0.090	0.138	0.270	0.226
Reported Results, mg/L	< 0.002	0.005	0.066	0.045	0.103	0.017	0.090	0.136	0.269	0.225
Z-Score		0.23	0.00	-0.23	0.00	-0.05	0.00	-0.23	-0.11	-0.09

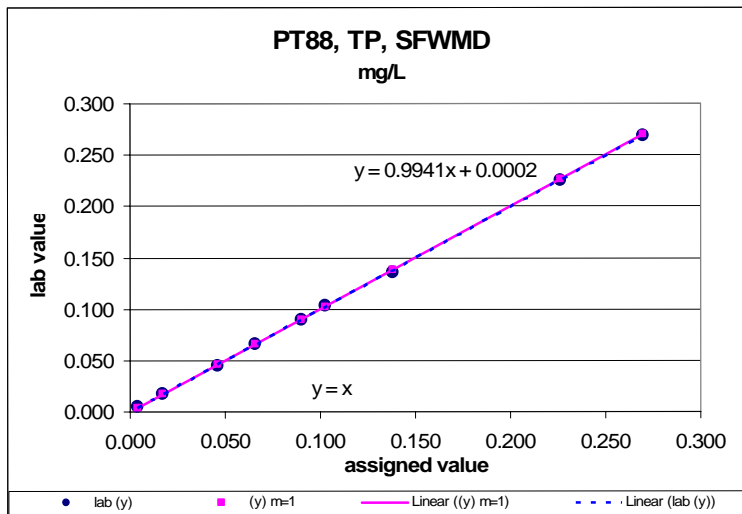


Figure 8. Linear Regression of Reported TP Results vs. Assigned Values.

Glossary

Accuracy The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random-error (precision) and systematic-error (bias) components due to sampling and analytical operations. For SFWMD application, accuracy assessment is done using percent recoveries from QC check samples and spikes.

Equipment Blank (EB) A general term used for analyte-free water, which is processed on site through all sampling equipment used in routine sample processing. It 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 completes for the routine sample at that site. FB values are indicative of environmental contamination on site.

Field Cleaned Equipment Blank (FCEB) Analyte-free water 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 lowest concentration of an analyte of interest that can be measured and reported with 99 percent confidence. 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 lowest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Usually, the PQL is 12 times the standard deviation derived from the procedure used to determine the MDL, or the PQL can be assumed to be four times the MDL.

Precision A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation. Various measures of precision exist depending on the "prescribed similar conditions." Precision is calculated from the results of replicate determinations.

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

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

Replicate Sample (RS) Samples that have been collected during the same sampling event from the same source (field replicates) or aliquots of the same sample that are prepared and analyzed at the same time (laboratory replicates). Duplicate samples are one type of RS. The analytical results from replicates are used to determine the precision of a system. If the concentration of analytes in the sample is below detectable limits,

Duplicate Spike Samples may be used to determine precision. Blind Replicates (Duplicates) are replicates that have been collected (field replicate) or prepared (laboratory replicate) and are submitted and analyzed as separate samples (analyst does not know they are replicates). Field Split samples are replicate samples that are taken from the same sample collection, or one container into which multiple collections are composited.

Split Sample (SS) Splits of the same sample volume, obtained from the same sampling device, sent to two independent laboratories for analysis or analyzed as two independent samples in the laboratory.

Z-Score 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

Table A-1. Results of TP split studies between the SFWMD and FDEP laboratories, EVPA Project, September 2005 through September 2006.

Sample	Date	SFWMD	FDEP	Percent RPD/Comments
EVPA	19-Sep-05	0.165	0.170	3.0
EVPA	19-Sep-05	0.163	0.170	4.2
EVPA	19-Sep-05	0.007	0.010	< PQL
EVPA	19-Sep-05	0.008	0.007	< PQL
ERR-16	2-Nov-05	0.027	0.029	7.7
ERR-16	2-Nov-05	0.026	0.028	7.4
ERR-16	2-Nov-05	0.026	0.029	10.9
ERR-16	2-Nov-05	0.026	0.029	10.9
ERR-16	2-Nov-05	0.007	0.008	< PQL
ERR-16	2-Nov-05	0.007	0.008	< PQL
ERR-16	2-Nov-05	0.007	0.008	< PQL
ERR-16	2-Nov-05	0.007	0.009	< PQL
ERR-16	2-Nov-05	0.060	0.066	9.5
ERR-16	2-Nov-05	0.055	0.066	18.2
ERR-16	2-Nov-05	0.054	0.065	18.5
ERR-16	2-Nov-05	0.054	0.069	24.4
ERR-16	2-Nov-05	0.214	0.217	1.4
ERR-16	2-Nov-05	0.211	0.213	0.9
ERR-16	2-Nov-05	0.211	0.219	3.7
ERR-16	2-Nov-05	0.007	0.009	< PQL
ERR-16	2-Nov-05	0.008	0.009	< PQL
ERR-16	2-Nov-05	0.007	0.009	< PQL
EVPA	12-Dec-05	0.114	0.130	13.1
EVPA	12-Dec-05	0.008	0.009	< PQL
EVPA	12-Dec-05	0.009	0.007	< PQL
EVPA	12-Dec-05	0.019	0.009	71.4
EVPA	3-Mar-06	0.009	< 0.004	< PQL
EVPA	3-Mar-06	0.007	< 0.004	< PQL
EVPA	3-Mar-06	0.008	< 0.004	< PQL
EVPA	3-Mar-06	0.007	< 0.004	< PQL
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