

Quality Assessment Report for Water Quality Monitoring

July - September 2004



Submitted to the
Technical Oversight Committee

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I. Introduction

This report is an assessment of the SFWMD laboratory analysis and field sampling for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 3rd quarter of 2004:

- Conservation Area Inflow and Outflows (CAMB)
S12A, S12B, S12C S12D, S333
- Everglades National Park Inflow Monitoring (ENP)
S175, S176, S177, S18C, S332, S332D
- Everglades Protection Area (EVPA)
LOX3 to LOX16
- Non-Everglades Construction Project (NECP)

S334

Since field QCs are collected for trips that include multiple project samples for the stations of interest, the report may also cover information on stations or project other than those listed above.

The District's Field Sampling Quality Manual states the minimum requirement followed in field sample collection. The Laboratory Quality Manual states the minimum requirement followed in laboratory sample preparation and analysis, as well as in data verification and validation. The results of laboratory and field quality control during this quarter are presented in Sections II and III of this report.

Included in this report is an analysis of the District's laboratory's performance on split and inter-laboratory studies with FDEP and other laboratories for three selected projects, i.e. EVPA, C111 (S332D), and Everglades TP Round Robins, for a one year period.

II. Field Sampling Quality Assessment

A. Quality Control

Field QC consist of equipment blanks (EB), field-cleaned equipment blanks (FCEB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FCEB results for all projects of interest to the TOC. Except for one blank result, blanks were within the acceptance criteria.

Field sampling precision was also acceptable for all sampling events, except for Station S6, collected 7/7/04 that had a precision of 39% (Table 2).

Data not meeting the set criteria for blanks, field precision or sampling protocols are flagged using FDEP data qualifier codes. A comprehensive list of flagged data for all trips that include samples for CAMB, ENP, EVPA and NECP during this quarter is presented in Table 3. Due to Hurricane Frances, the SFWMD Laboratory lost power and samples stored in the refrigerators reached the ambient temperature for 34 hours. This resulted in 26 TP data points being flagged with the qualifying code “Y” (analysis was performed from improperly preserved sample).

Table 1. Field and equipment blank results

Type of Blank	Project	# Blanks collected	% ≤0.002	% >0.002	Action Taken
EB	CAMB	6	100	0	
	ENP	2	100	0	
	EVPA	3	100	0	
FB	CAMB	2	100	0	
	ENP	2	100	0	
FCEB	CAMB	95	99	1	blank was flagged, sample mix-up
	ENP	9	100	0	
	EVPA	12	100	0	
	NECP	7	100	0	

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	4	12.6	Precision criteria were generally met, except for one triplicate precision that was 38.8%- for Station S6, collected 7/7/04. Data were flagged.
ENP	0	-	
EVPA	3	4.1	Precision criteria were met.
NECP	1	14.8	Precision criteria were met.

Notes

- 1) All TP analyses were conducted by the District’s Chemistry laboratory.
- 2) Field precision acceptance criteria: <20%. This criteria was applied only if sample values >PQL.
- 3) FB, FCEB and EB acceptance criteria: Must be ≤MDL.
- 4) Associated samples are flagged when concentrations are less than five times the resulting blank values for possibility of contamination.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Result, mg/L	Flag Code	Comments [†]
CAMB	12-Jul-2004	USSO	SAMP	0.075	V	Sample associated w positive FCEB
CAMB	7-Jul-2004	S6	SAMP	0.027	J3	Failed field precision criteria
CAMB	7-Jul-2004	S6	SAMP	0.015	J3	Failed field precision criteria
CAMB	2-Aug-2004	S145	SAMP	<0.002	J5	Sample mix up
CAMB	2-Aug-2004	S145	FCEB	0.018	V	FCEB>MDL
CAMB	4-Aug-2004	S6	SAMP	0.048	J5	Sample not flow proportional
CAMB	28-Sep-2004	S5A	SAMP	0.192	PMF	Auto-sampler malfunction
ENP	1-Sep-2004	S18C	SAMP	0.004	Y	Sample storage exceeded 6°C [†]
ENP	1-Sep-2004	S18C	SAMP	0.006	Y	Sample storage exceeded 6°C [†]
CAMB	31-Aug-2004	S190	SAMP	0.107	Y	Sample storage exceeded 6°C [†]
CAMB	31-Aug-2004	S190	SAMP	0.111	Y	Sample storage exceeded 6°C [†]
CAMB	31-Aug-2004	L28I	SAMP	0.103	Y	Sample storage exceeded 6°C [†]
CAMB	31-Aug-2004	S190	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	31-Aug-2004	S190	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S151	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S145	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S151	SAMP	0.016	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S11B	SAMP	0.011	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S11C	SAMP	0.012	Y	Sample storage exceeded 6°C [†]
NECP	30-Aug-2004	S142	SAMP	0.012	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S145	SAMP	0.008	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S38	SAMP	0.019	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S34	SAMP	0.023	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S11A	SAMP	0.012	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	ACME1C	SAMP	0.065	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	G94D	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	USSO	FCEB	0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	USSO	FCEB	<0.002	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	S10E	SAMP	0.039	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	G94D	SAMP	0.055	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	L3BRS	SAMP	0.197	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	USSO	SAMP	0.102	Y	Sample storage exceeded 6°C [†]
CAMB	30-Aug-2004	USSO	SAMP	0.113	Y	Sample storage exceeded 6°C [†]

[†] Due to Hurricane Frances, SFWMD Laboratory lost power and samples stored in the refrigerators reached the ambient temperature for 34 hours. All samples stored above the acceptable maximum limit of 6°C were flagged with qualifying code "Y"(analysis was performed from improperly preserved sample).

Table 4 Samples not collected (Missing TPO4 results)

Project	Date Collected	Station	Type ¹	Comments
CAMB	20-Sep-2004	12B	G	Sample cancelled due to improper preservation
ENP	28-Jul-2004	S176	G	Gate closed, no flow, no sample collected
ENP	11-Aug-2004	S176	G	Gate closed, no flow, no sample collected
ENP	8-Sep-2004	S176	G	Gate closed, no flow, no sample collected
ENP	8-Sep-2004	S177	G	Gate closed, no flow, no sample collected
ENP	30-Jun-2004	S18C	ACF	No flow, no samples taken by auto-sampler
EVPA	12-Jul-2004	LOX3	G	Tdepth<0.10 m
EVPA	9-Aug-2004	LOX3	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX4	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX5	G	Tdepth<0.10 m
EVPA	9-Aug-2004	LOX5	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX6	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX7	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX8	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX9	G	Tdepth<0.10 m
EVPA	12-Jul-2004	LOX10	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX11	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX13	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX14	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX15	G	Tdepth<0.10 m
EVPA	13-Jul-2004	LOX16	G	Tdepth<0.10 m
NECP	12-Jul-2004	S334	G	Gate closed, no flow, no sample collected
NECP	9-Aug-2004	S334	G	Gate closed, no flow, no sample collected

¹ACF= Autosampler Composite Flow Proportional; G=Grab Sample.

B. Field Audits

There was no field audit performed for the CAMB, ENP, EVPA or NECP projects during the third quarter of 2004.

III. Laboratory Analysis Quality Assessment

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. The charts presented in Figures 1-6 show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. A portion of or an entire analytical run is generally rejected if QC recoveries are outside the set limits. Data are flagged accordingly if any deficiency is noted, or the samples have exceeded the required holding times, or can not be reanalyzed.

Recoveries for samples QC-1, QC-2, QC-3, and QC-4 are within $\pm 10\%$ from 100%, which are acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 101.9%. The MDL check daily results indicate the laboratory consistently achieved the 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample were between 96.8 – 101.9%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 99.5%.

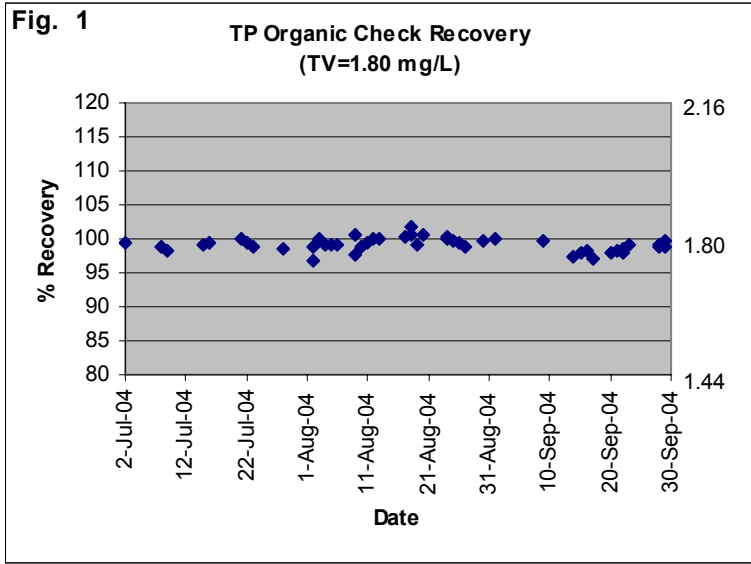
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 1.6% and 1.4% for low (0 to 0.200 mg/L) and high level (0.200-2.00 mg/L) analyses, respectively. The maximum RPD during this period were 9.2% and 5.2% for low and high levels, respectively.

Recoveries for two matrix spikes (77.4 and 79%) are below the minimum criterion of 90%. The poor recoveries are attributed to matrix interference and associated data have been flagged.

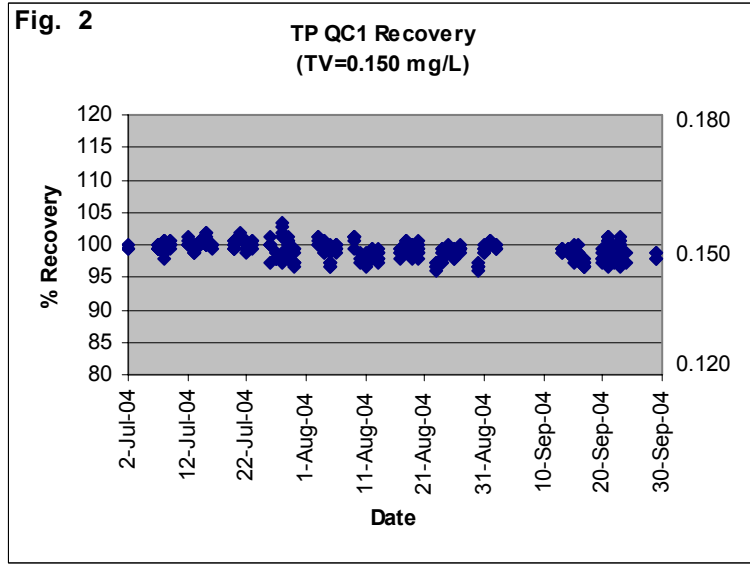
IV. Inter-Laboratory Quality Control Assessment

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. Data from split studies between DEP and SFWMD laboratories from September 2003 to September 2004 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA), Everglades TP Round Robin (ERR), and S332 sites (C111). Regression analysis of the data set was done separately for TP > 0.020 mg/L and for TP < 0.020 mg/L. Logarithmic transformation was needed for TP > 0.020 mg/L, due to skewed data distribution. Logarithmic transformation was not needed for TP < 0.020 mg/L due the fact that distribution at that concentration range is approximately normal. Both regression analyses indicate that the slope is not significantly different from 1 and intercept is not significantly different from 0, indicating that the data sets are highly comparable (Figures 7 and 8). Paired t-test for TP < 0.02, n=30, yielded a p-value of 0.0484; signed rank sum p-value was 0.0787, also indicating no significant difference in the results from the two laboratories.

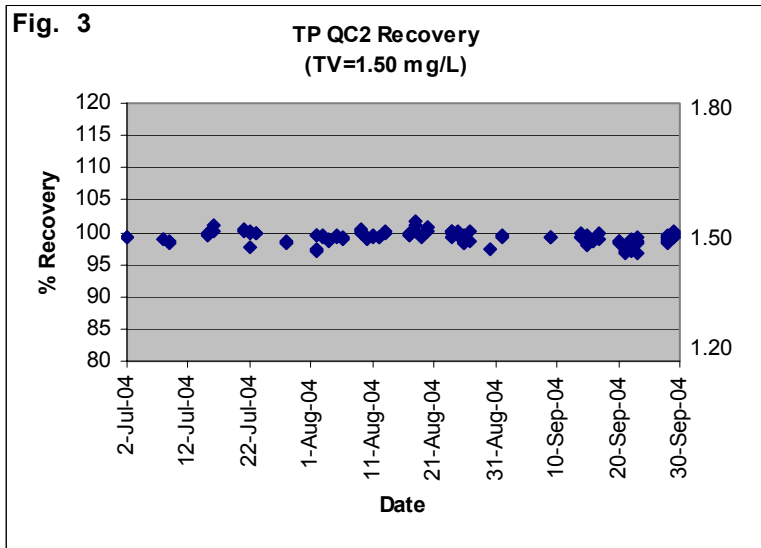
These statistical analyses and findings were consistent with what was in FDEP Data Comparability Report (Nearhoff, presentation to TOC, 8/26/04).



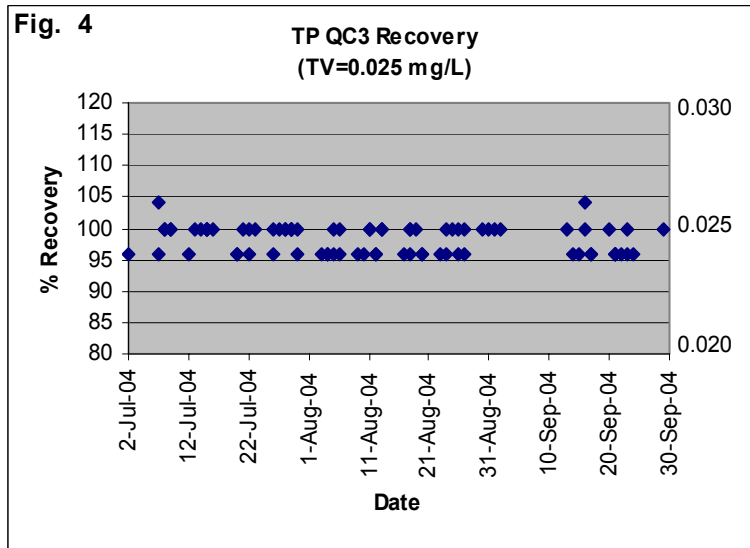
Mean = 99.2%, Max = 101.9%, Min = 96.8%



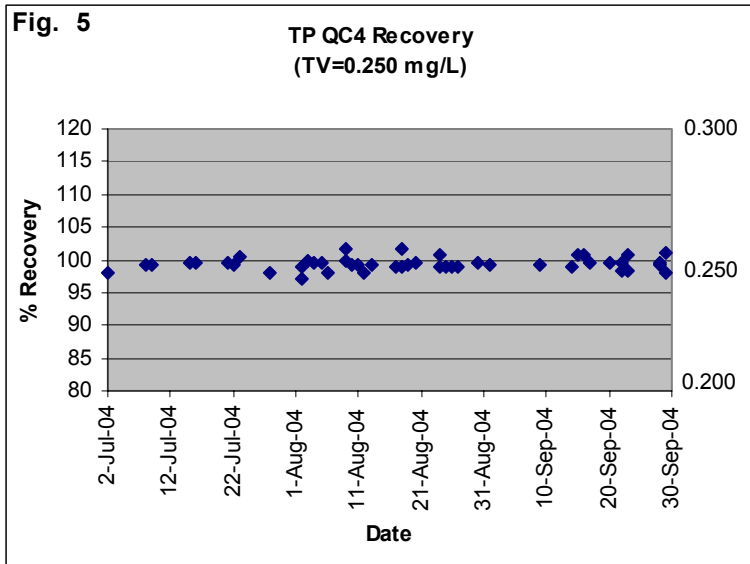
Mean = 99.3%, Max = 103.3%, Min = 96.0%



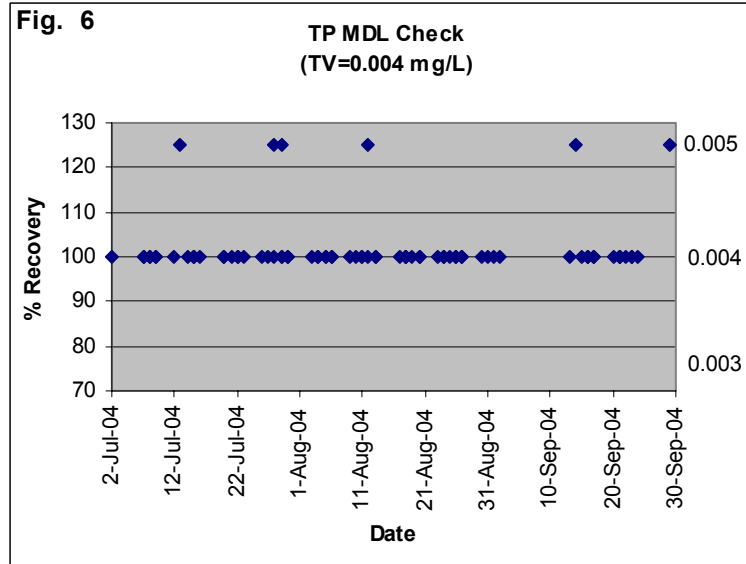
Mean = 99.2%, Max = 101.7%, Min = 96.6%



Mean = 98.3%, Max = 104%, Min = 96.0%



Mean = 99.3%, Max = 101.6%, Min = 97.2%



Mean = 101.9%, Max = 125%, Min = 100%

TP Precision Data 7/1/04-9/30/04 Acceptance Limit = <10%			
Low Level (0-0.200)		High Level (0.200-2.0)	
Max	9.2	Max	5.2
Mean	1.6	Mean	1.4
Std Dev	1.53	Std Dev	1.35
3xSD	4.59	3xSD	4.04
UCL	6.2	UCL	5.4
n	209	n	59

TP Spike Recovery Data 7/1/04-9/30/04 Acceptance Limit = 90-110%	
Min	77.4 ¹
Max	109
Mean	99.5
Std Dev	3.60
3xSD	10.81
LCL	88.7
UCL	110.4
n	272

¹Two spike recoveries were reported below minimum criteria. Low recoveries were attributed to matrix interference and associated data flagged.

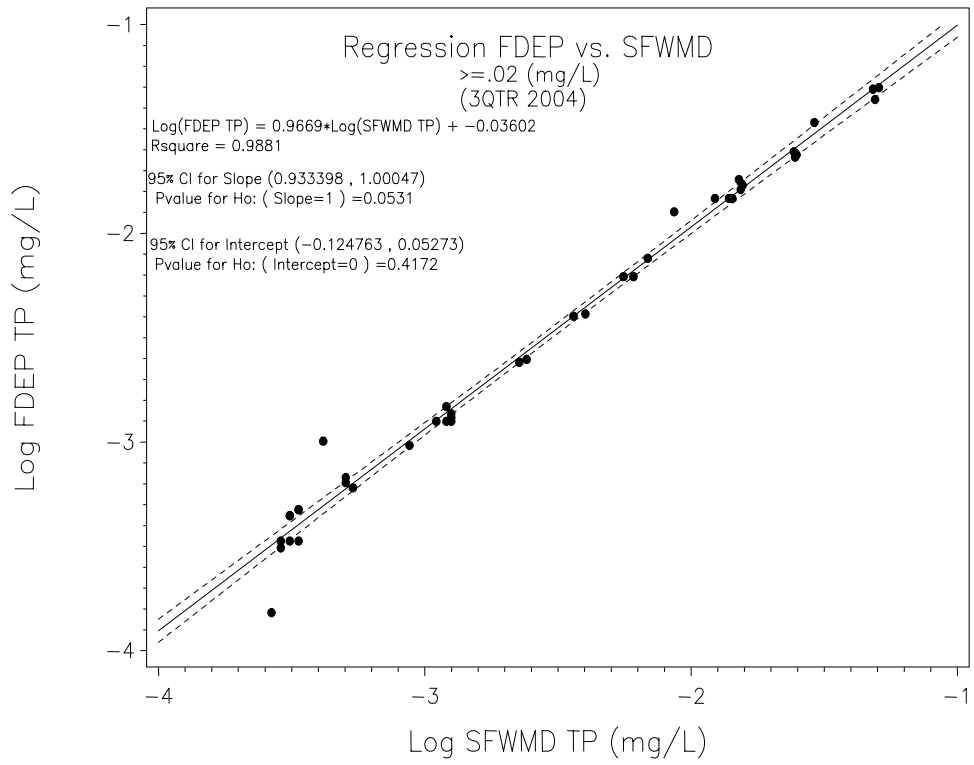


Fig.7. Regression Analysis for TP > 0.020 mg/L

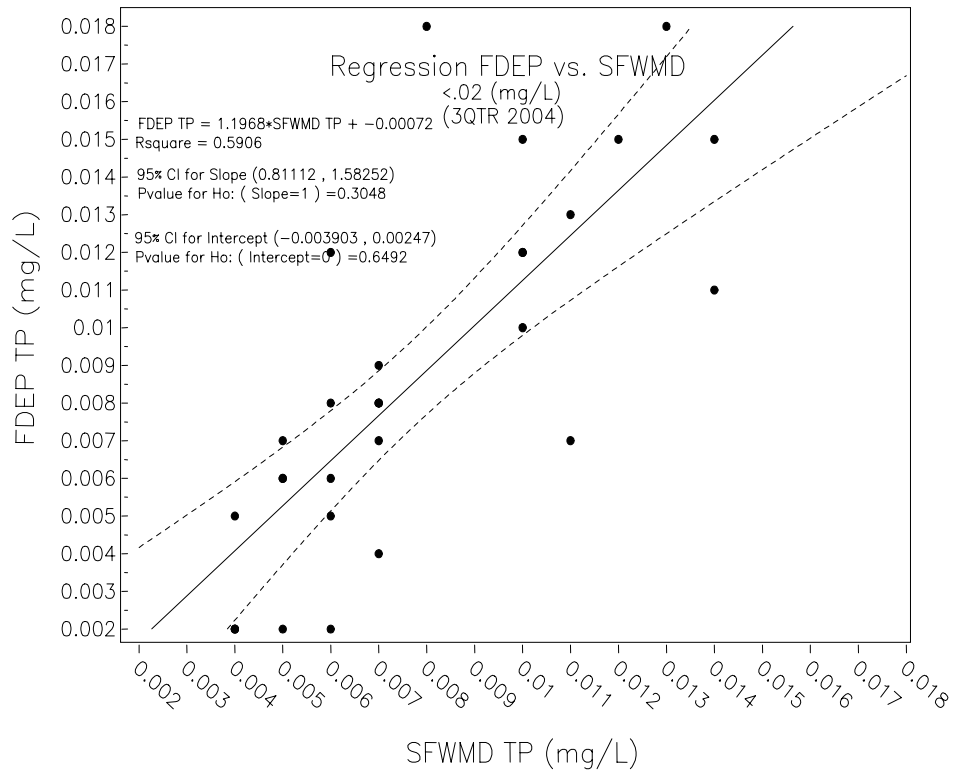


Fig.8 . Regression Analysis for TP < 0.020 mg/L

Table 5. Results of TP split studies between SFWMD and FDEP laboratories, EVPA Project, September 2003 to September 2004.

Sample	Date	SFWMD	FDEP	% RPD/Comments
EVPA	8-Sep-03	0.148	0.160	7.8
EVPA	8-Sep-03	0.014	0.011	24.0
EVPA	9-Sep-03	0.006	0.008	<PQL
EVPA	9-Sep-03	0.007	0.008	<PQL
S332B-093003-1200	30-Sep-03	0.004	0.005	<PQL
S332C-093003-1030	30-Sep-03	0.006	0.005	<PQL
S332DDZE-093003-0800	30-Sep-03	0.004	<0.004	<PQL
S339-093003-0000	30-Sep-03	0.052	0.055	5.6
S339-093003-0800	30-Sep-03	0.087	0.091	4.5
S339-093003-1600	30-Sep-03	0.105	0.110	4.6
ERR-14	1-Oct-03	0.055	0.057	3.6
ERR-14	1-Oct-03	0.055	0.055	0.0
ERR-14	1-Oct-03	0.054	0.055	1.8
ERR-14	1-Oct-03	0.055	0.056	1.8
ERR-14	1-Oct-03	0.164	0.170	3.6
ERR-14	1-Oct-03	0.162	0.175	7.7
ERR-14	1-Oct-03	0.163	0.167	2.4
ERR-14	1-Oct-03	0.164	0.171	4.1
ERR-14	1-Oct-03	0.005	0.007	<PQL
ERR-14	1-Oct-03	0.005	0.006	<PQL
ERR-14	1-Oct-03	0.005	0.006	<PQL
ERR-14	1-Oct-03	0.037	0.042	13.0
ERR-14	1-Oct-03	0.037	0.041	10.0
ERR-14	1-Oct-03	0.038	0.040	5.1
ERR-14	1-Oct-03	0.010	0.012	18.0
ERR-14	1-Oct-03	0.010	0.010	0.0
ERR-14	1-Oct-03	0.011	0.007	<PQL
ERR-14	1-Oct-03	0.010	0.012	18
S332B-102803-1500	28-Oct-03	0.005	<0.004	<PQL
S332C-102803-1300	28-Oct-03	0.006	<0.004	<PQL
S332DDZE-102803-0800	28-Oct-03	0.004	<0.004	<PQL
S339-102803-0000	28-Oct-03	0.071	0.073	2.8
S339-102803-0800	28-Oct-03	0.054	0.059	8.8
S339-102803-1600	28-Oct-03	0.109	0.110	0.9
ERR-15	28-Oct-03	0.268	0.270	0.7
ERR-15	28-Oct-03	0.274	0.272	0.7
ERR-15	28-Oct-03	0.270	0.257	4.9
ERR-15	28-Oct-03	0.199	0.200	0.5
ERR-15	28-Oct-03	0.201	0.197	2.0
ERR-15	28-Oct-03	0.200	0.195	2.5
ERR-15	28-Oct-03	0.200	0.199	0.5
ERR-15	28-Oct-03	0.030	0.031	3.3
ERR-15	28-Oct-03	0.030	0.035	15.0
ERR-15	28-Oct-03	0.031	0.036	15.0
ERR-15	28-Oct-03	0.031	0.036	15.0
ERR-15	28-Oct-03	0.029	0.030	3.4
ERR-15	28-Oct-03	0.029	0.031	6.7

Sample	Date	SFWMD	FDEP	% RPD/Comments
ERR-15	28-Oct-03	0.030	0.035	15.0
ERR-15	28-Oct-03	0.007	0.009	<PQL
ERR-15	28-Oct-03	0.007	0.008	<PQL
ERR-15	28-Oct-03	0.007	0.007	<PQL
ERR-15	28-Oct-03	0.007	0.008	<PQL
S332B-120903-1300	9-Dec-03	0.006	0.012	<PQL
S332C-120903-1100	9-Dec-03	0.007	0.004	<PQL
S332DDZE-120903-0800	9-Dec-03	0.004	<0.004	<PQL
S339-120903-0000	9-Dec-03	0.115	0.120	4.2
S339-120903-0800	9-Dec-03	0.073	0.074	1.4
S339-120903-1600	9-Dec-03	0.091	0.092	1.1
EVPA	15-Dec-03	0.127	0.150	17
EVPA	15-Dec-03	0.010	0.015	40.0; Heavy suspended solids
EVPA	15-Dec-03	0.011	0.013	17.0; Heavy suspended solids
EVPA	15-Dec-03	0.013	0.018	32.0; Heavy suspended solids
EVPA	8-Mar-04	0.031	0.031	0
EVPA	8-Mar-04	0.028	0.022	24.0; Heavy suspended solids
EVPA	8-Mar-04	0.017	0.020	16
EVPA	8-Mar-04	0.006	0.006	<PQL
EVPA	14-Jun-04	0.047	0.049	4.2
EVPA	14-Jun-04	0.034	0.050	38; Heavy suspended solids
EVPA	14-Jun-04	0.158	0.160	1.2
EVPA	14-Jun-04	0.156	0.160	2.5
EVPA	21-Sep-04	0.215	0.230	6.7 Dark brown stain
EVPA	21-Sep-04	0.008	0.018	76.9 Light brown stain
EVPA	21-Sep-04	0.014	0.015	6.9 Light brown stain
EVPA	21-Sep-04	0.012	0.015	22.2 Light brown stain

Glossary

Equipment blank (EB). A general terminology used for analyte-free water that is processed on-site through all sampling equipment used in routine sample processing. May be an assessment of effectiveness of laboratory decontamination (LCEB) or on-site (field) decontamination (FCEB). EB values are indicative of the effectiveness of the decontamination process.

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” value 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 MDL’s 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: $\%RSD = [\text{Std. Deviation}/\text{Mean}] * 100$

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