Quality Assessment Report for Water Quality Monitoring

July - September 2005

Submitted to the
Technical Oversight Committee

Prepared by:

Delia B. Ivanoff (divanoff@sfwmd.gov)
Zdzislaw Kolasinski (zkolasin@sfwmd.gov)

Quality Assessment Report for Water Quality Monitoring
July – September 2005

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 2005:

- 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, and Everglades TP Round Robins, for a one year period.

II. Field Sampling Quality Assessment

A. 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 1 summarizes EB and FCEB results for all projects of interest to the TOC. Except for one blank result of the 125, all blanks were within the acceptance criteria. Table 2 summarizes field precision results. Field sampling precision was acceptable.

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.

Table 1. Field and equipment blank results

Type	Project	# Blanks collected	% ≤0.002	% >0.002	Action Taken
EB	CAMB	23	100	0	
	ENP	14	93	7	Blanks were flagged; samples passed criteria
	NECP	2	100	0	
FCEB	CAMB	61	100	0	
	ENP	7	100	0	
	EVPA	11	100	0	
	NECP	6	100	0	
FB	CAMB	1	100	0	

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	4	7.5	Precision criteria were met
EVPA	1	4.4	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	Flag Code	Comments
ENP	2-Aug-2005	S18C	EB	V	EB>MDL
CAMB	9-Aug-2005	S7	SAMP	Y	Improper preservation
CAMB	16-Aug-2005	S7	SAMP	Y	Improper preservation
CAMB	23-Aug-2005	S7	SAMP	Y	Improper preservation
ENP	30-Aug-2005	S174	SAMP	V	Sample associated with positive FCEB

Table 4. Samples not collected (Missing TPO4 results)

Project	Date collected	Station	Comments
CAMB	9/6/2005	S12A	Samples not shipped on ice (improper preservation), rejected by the lab
CAMB	9/6/2005	S12B	Samples not shipped on ice (improper preservation), rejected by the lab
CAMB	9/6/2005	S12C	Samples not shipped on ice (improper preservation), rejected by the lab
CAMB	9/6/2005	S12D	Samples not shipped on ice (improper preservation), rejected by the lab
CAMB	7/11/2005	S333	No flow, no samples collected
CAMB	9/6/2005	S333	No flow, no samples collected
ENP	7/12/2005	S176	No flow, no samples collected
ENP	8/9/2005	S176	No flow, no samples collected
ENP	9/6/2005	S176	No flow, no samples collected
EVPA	8/8/2005	LOX10	Total depth<0.10 m, no samples collected
EVPA	9/21/2005	LOX13	Total depth<0.10 m, no samples collected
EVPA	8/8/2005	LOX3	Total depth<0.10 m, no samples collected
EVPA	9/19/2005	LOX3	Total depth<0.10 m, no samples collected
EVPA	9/19/2005	LOX5	Total depth<0.10 m, no samples collected
NECP	7/11/2005	S334	No flow, no samples collected
NECP	9/6/2005	S334	No flow, no samples collected

B. Field Audits

During this quarter, an audit of field sampling collection activities was performed for SFWMD Sampling team collection for the CAMB project on 7/21/05.
The key findings were: a) Training documentation was not available for one of the collectors; b) The field instrument temperature thermistor had not had its quarterly check at the time of the audit. All deficiencies have been corrected.

A second audit was performed on the Tetra Tech ECI collection for the ST1W project on 9/06/05. The key findings were a) Agency quality manual was not available on site; b) Field instrument was not kept wet or rinsed between stations; c) Incomplete documentation of field sample preservation; d) Conflicting acceptance criteria for temperature verifications was being used. The corrective action plan had not been received for this audit at the time of this report.

III. Laboratory Quality Control Assessment

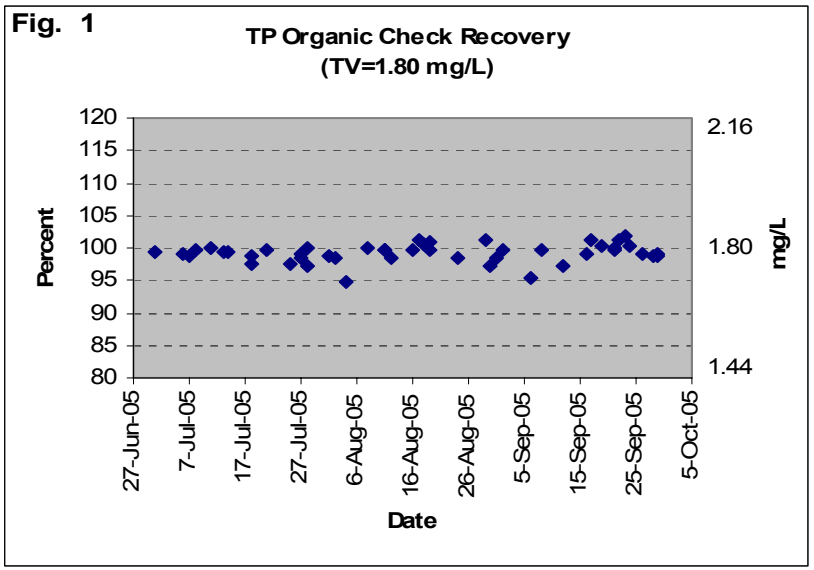
Routine laboratory QC samples include QC checks, matrix spikes, and precision checks.
The charts presented in Figures 1-6 show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. A portion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

Recoveries for the QC samples are generally within $\pm$ 10% from the true value, which are acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 102%. 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 are between 94.9 – 101.9%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.8%.

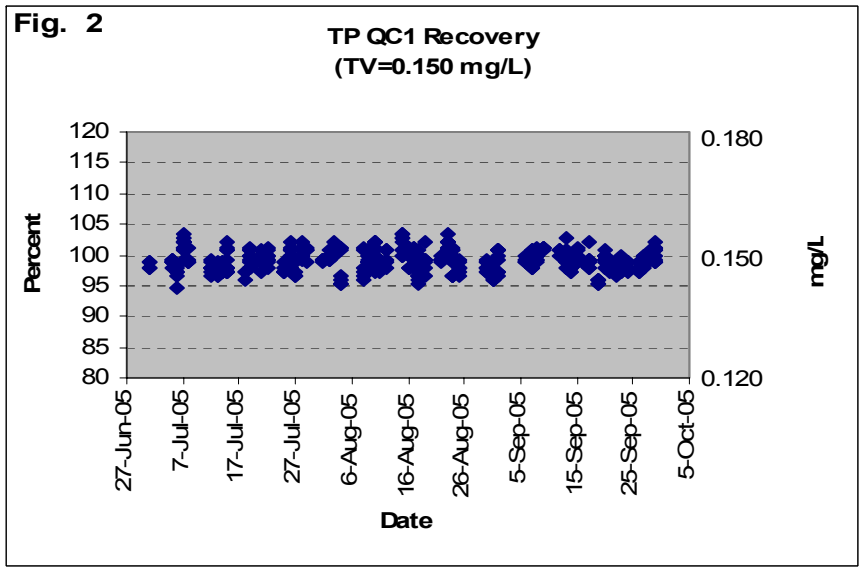
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 1.9% and 1.6% for low (0 to 0.200 mg/L) and high level (0.200-2.00 mg/L) analyses, respectively. The maximum RPD during this period were 9.8% and 5.4% for low and high levels, respectively.

Fig. 1



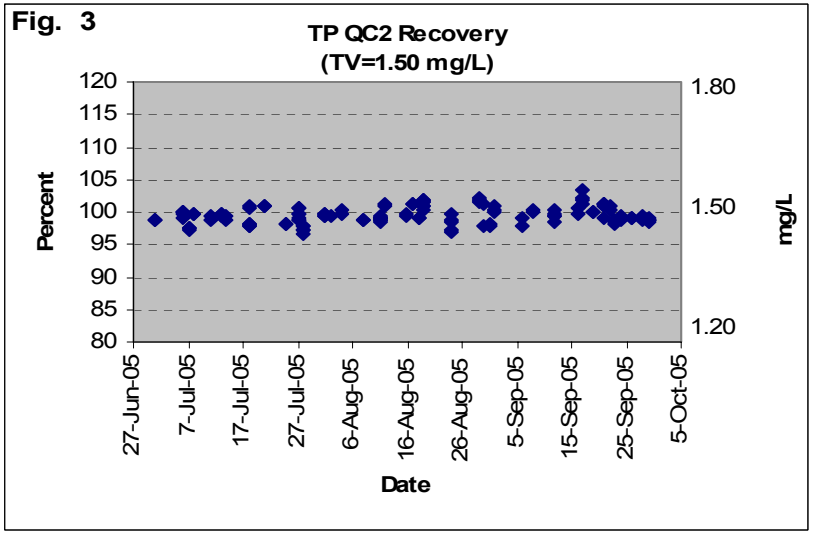
Mean = 99.2%, Max = 101.9%, Min = 94.9%

Fig. 2



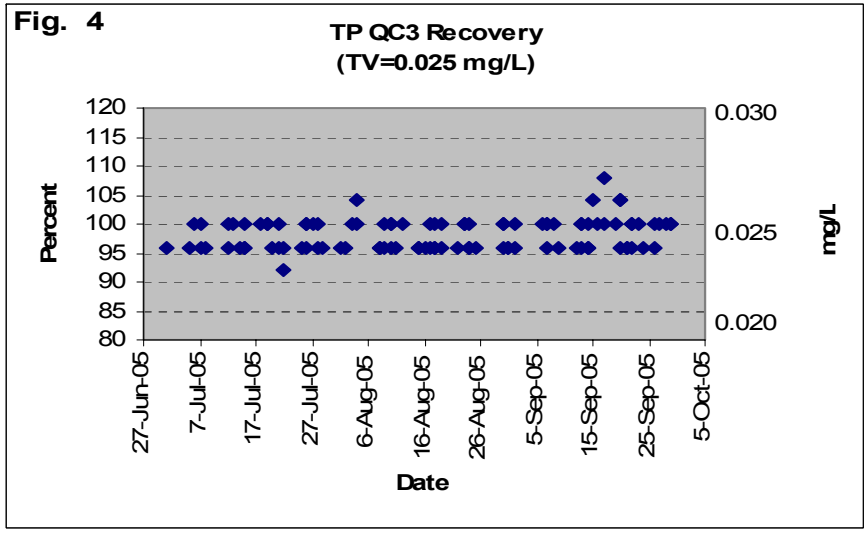
Mean = 99.2%, Max = 103.3%, Min = 94.7%

Fig. 3



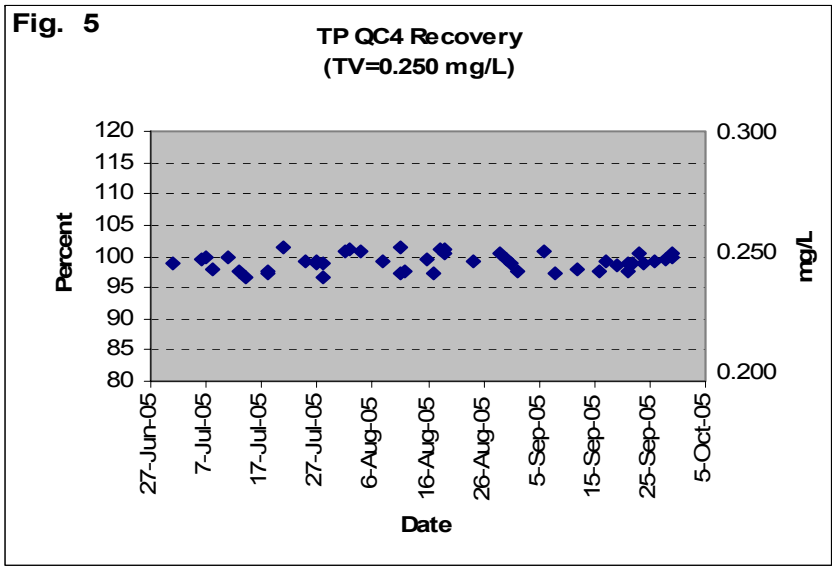
Mean = 99.5%, Max = 103.3%, Min = 96.7%

Fig. 4



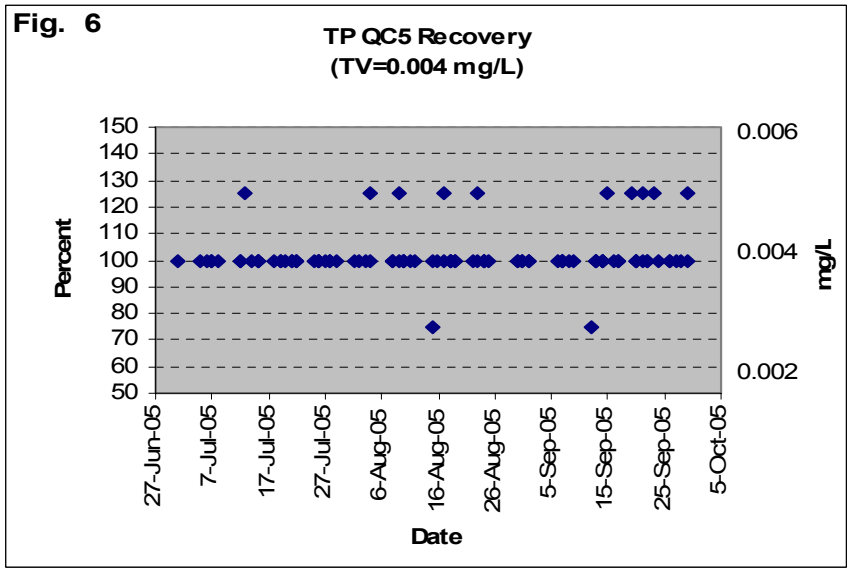
Mean = 98.2%, Max = 108%, Min = 92.0%

Fig. 5



Mean = 99.1%, Max = 101.6%, Min = 96.8%

Fig. 6



Mean = 102%, Max = 125.0%, Min = 75.0%

TP Precision Data 7/1/05-9/30/05
Acceptance Limit = <10%

Low Level (0-0.200)		High Level (0.20-2.00)	
Max	9.8	Max	5.4
Mean	1.9	Mean	1.6
Std Dev	1.76	Std Dev	1.48
3xSD	5.27	3xSD	4.44
UCL	7.2	UCL	6.0
n	286	n	41

TP Spike Recovery Data7/1/05-9/30/05
Acceptance Limit = 90-110%

Min	90.4
Max	110
Mean	100.8
Std Dev	4.09
3xSD	12.28
LCL	88.6
UCL	113.1
n	339

IV. Inter-Laboratory Quality Control Assessment

A. Split Studies

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 March 2004 to March 2005 for the following programs are presented in Table 5.

The summary statistics and signed rank test for SFWMD vs. DEP results, as presented in Table 3 below, shows that the p-value for TP ≥0.020 mg/L and TP <0.020 mg/L levels are -0.003 (Signed Rank) and 0.0387 (Student's t-test) respectively, indicating no significant difference. The mean and median of differences from both laboratories for samples with <0.02 mg/L P concentration are -0.003 and -0.002, respectively, while at higher level (>=0.02 mg/L), mean and median differences were 0.004 and -0.003, respectively. These are around the laboratories' MDLs; SFWMD's MDL is 0.002 mg/L while DEP laboratory's MDL is 0.004 mg/L. At these levels wider variability can be expected even within each laboratory.

Table 3. Statistical Comparison of TP Recoveries from SFWMD and FDEP Laboratories (Sep2004 - Sep2005)

		Summary Statistics			
	Lab	**N**	**Mean**	**Median**	
<0.02 mg/L	FDEP	15	0.013866667	0.016	
	SFWMD	15	0.011066667	0.009	
			Statistical Test of Hypotheses		
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean Of Differences	-0.0028	Mean of Differences = 0	Student's t	0.0387
	Median Of Differences	-0.002	Median of Differences = 0	Signed Rank	0.0128
		Summary Statistics			
	Lab	**N**	**Mean**	**Median**	
≥0.02 mg/L	FDEP	25	0.12028	0.14	
	SFWMD	25	0.11672	0.134	
			Statistical Test of Hypotheses		
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean Of Differences	-0.00356	Mean of Differences = 0	Student's t	-0.0036
	Median Of Differences	-0.003	Median of Differences = 0	Signed Rank	-0.003

Regression analysis of the data set, done separately for TP> 0.020 mg/L and for TP<0.020 mg/L indicate no significant difference between TP recoveries from the two laboratories (Figures 7 and 8). .

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

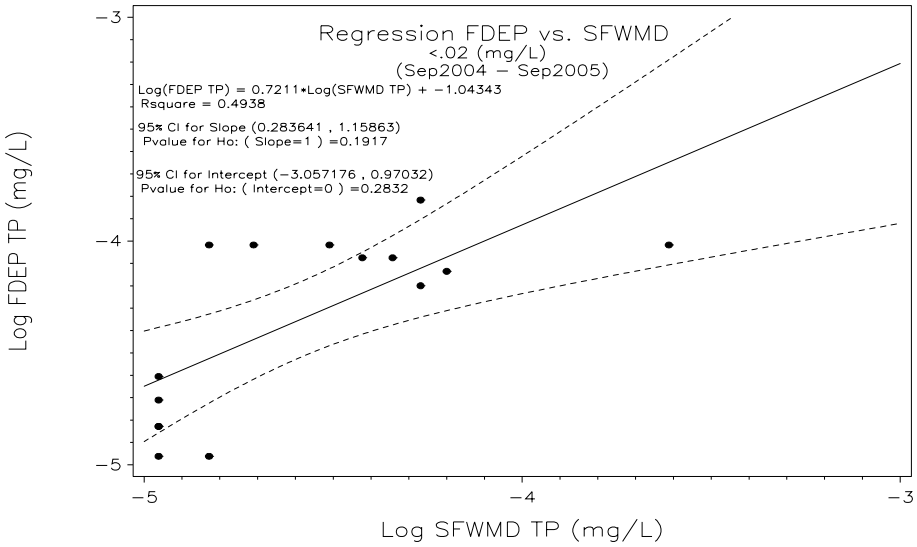


Fig.7. Regression Analysis for TP>0.020 mg/L

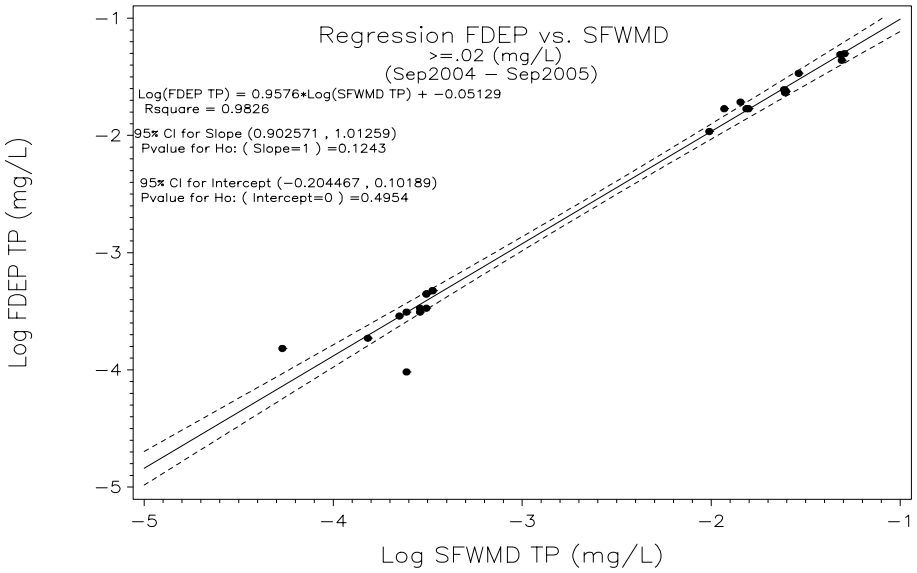


Fig.8 . Regression Analysis for TP <0.020 mg/L

Table 5. Results of TP split studies between SFWMD and FDEP laboratories, EVPA Project, March 2004 to March 2005.

Sample	Date	SFWMD	FDEP	% RPD/Comments
EVPA	21-Sep-2004	0.215	0.230	6.7 Dark brown stain
EVPA	21-Sep-2004	0.008	0.018	76.9 Light brown stain
EVPA	21-Sep-2004	0.014	0.015	6.9 Light brown stain
EVPA	21-Sep-2004	0.012	0.015	22.2 Light brown stain
ERR-15	28-Oct-2004	0.268	0.270	
ERR-15	28-Oct-2004	0.274	0.272	
ERR-15	28-Oct-2004	0.270	0.257	
ERR-15	28-Oct-2004	0.199	0.200	
ERR-15	28-Oct-2004	0.201	0.197	
ERR-15	28-Oct-2004	0200	0.195	
ERR-15	28-Oct-2004	0.200	0.199	
ERR-15	28-Oct-2004	0.030	0.031	
ERR-15	28-Oct-2004	0.030	0.035	
ERR-15	28-Oct-2004	0.031	0.036	
ERR-15	28-Oct-2004	0.031	0.036	
ERR-15	28-Oct-2004	0.029	0.030	
ERR-15	28-Oct-2004	0.029	0.031	
ERR-15	28-Oct-2004	0.030	0.035	
ERR-15	28-Oct-2004	0.007	0.009	
ERR-15	28-Oct-2004	0.007	0.008	
ERR-15	28-Oct-2004	0.007	0.007	
ERR-15	28-Oct-2004	0.007	0.008	
EVPA	13-Dec-2004	0.013	0.017	Light yellow stain, light solids
EVPA	13-Dec-2004	0.014	0.022	Dark yellow stain, light fine suspended solids
EVPA	13-Dec-2004	0.011	0.018	1-2 L bottle cracked and leaked, used only 1-2 L bottle
EVPA	13-Dec-2004	0.158	0.180	Brown stain, light suspended particles
EVPA	7-Mar-2005	0.015	0.016	6.5% / Light brown stain, heavy small suspended particles
EVPA	7-Mar-2005	0.026	0.029	10.9% /Light brown stain, heavy small suspended solids
EVPA	7-Mar-2005	0.009	0.018	66.7% / Light yellow stain, heavy small suspended solids
EVPA	13-Jun-05	0.145	0.170	15.9%
EVPA	13-Jun-05	0.027	0.018	40.0%
EVPA	13-Jun-05	0.027	0.030	10.5%
EVPA	13-Jun-05	0.022	0.024	8.7%
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

B. NWRI Environmental Canada Ecosystem Inter-laboratory Proficiency Program

SFWMD laboratory participated in the Performance Testing program provided by the National Water Research Institute, Environmental Canada. The objectives of this program are to assess and demonstrates reliability and quality of analytical measurements of inorganic parameters in natural waters.

Table 6. Laboratory Performance in PT Study 86 for TP, July 2005.

Sample #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Assigned Value	0.0016	0.001	0.0011	0.0032	0.0110	0.0677	0.218	0.1230	0.190	0.292
Reported Results	<0.002	<0.002	<0..002	0.004	0.010	0.066	0.218	0.121	0.188	0.290

The performance of total phosphorus was rated as "good" (highest).

C. U.S. Geological Survey Analytical Evaluation Program for Reference Samples

The District's laboratory participates in the USGS SRS Study on environmental samples semi-annually on a voluntary basis. The laboratory uses the study to monitor laboratory performance. Statistical analysis of results is conducted by the USGS, upon which laboratory results are based, and performance is is rated on a scale of 0 to 4.

The following rating criteria are used:

Absolute Z-value	**Rating**
0.00 to 0.50	4 (Excellent)
0.51 to 1.00	3 (Good)
1.01 to 1.50	2 (Satisfactory)
1.51 to 2.00	1 (Marginal)
greater than 2.00	0 (Unsatisfactory)

The September 2005 study is presented in Table 7.

Sample I.D	Reported Value, mg/L	Most Probable Value, mg/L	% Recovery	Z-value	Rating
M-176	0.686	0.685	101.5	0.03	Excellent

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 = [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.