

Quality Assessment Report for Water Quality Monitoring

April - June 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 2nd 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 projects other than those listed above.

The District's Field Sampling Quality Manual states the minimum requirements to be followed in field sample collection. The Laboratory Quality Manual states the minimum requirements to be 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 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. Results of other Performance Testing studies including the National Water Research Institute, Environmental Canada, and the National Proficiency Testing for laboratory certification are also included in this report

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, FCEB and FB results for all projects of interest to the TOC. Of the 131 blanks collected, only one was outside 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 of Blank	Project	# Blanks collected	% ≤0.002	% >0.002	Action Taken
EB	CAMB	8	100	0	
	ENP	1	100	0	
	EVPA	4	100	0	
	NECP	1	100	0	
FB	CAMB	5	100	0	
	ENP	1	100	0	
FCEB	CAMB	82	99	1	blank was flagged, no samples affected
	ENP	15	100	0	
	EVPA	8	100	0	
	NECP	6	100	0	

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RPD	Comments
CAMB	2	2.7	Precision criteria were met.
ENP	1	10.2	Precision criteria were met
EVPA	3	4.4	Precision criteria were met.
NECP	2	9.7	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
CAMB	22-Jul-2004	G123	FCEB	V	FCEB>MDL
ENP	1-Jun-2004	TAMBR105	SAMP	J5	Sample collected at surface, Depth 0.0 m

Table 4 Samples not collected (Missing TPO4 results)

Project	Date Collected	Station	Type	Comments
ENP	5-May-2004	S177	SAMP	Gates closed, no flow, no samples collected
ENP	7-Apr-2004	S18C	SAMP	Gates closed, no flow, no samples collected
EVPA	19-Apr-2004	LOX3	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX3	SAMP	Tdepth <0.1 m
EVPA	19-Apr-2004	LOX4	SAMP	Tdepth <0.1 m
EVPA	17-May-2004	LOX4	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX4	SAMP	Tdepth <0.1 m
EVPA	19-Apr-2004	LOX5	SAMP	Tdepth <0.1 m
EVPA	17-May-2004	LOX5	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX5	SAMP	Tdepth <0.1 m
EVPA	18-May-2004	LOX6	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX6	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX7	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX8	SAMP	Tdepth <0.1 m
EVPA	19-Apr-2004	LOX9	SAMP	Tdepth <0.1 m
EVPA	17-May-2004	LOX9	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX9	SAMP	Tdepth <0.1 m
EVPA	19-Apr-2004	LOX10	SAMP	Tdepth <0.1 m
EVPA	17-May-2004	LOX10	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX10	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX11	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX13	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX14	SAMP	Tdepth <0.1 m
EVPA	14-Jun-2004	LOX16	SAMP	Tdepth <0.1 m
ENP	21-Apr-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	28-Apr-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	5-May-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	12-May-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	19-May-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	26-May-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	2-Jun-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	9-Jun-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	16-Jun-2004	S18C	SAMP	Gate closed, no flow, no sample collected
ENP	23-Jun-2004	S18C	SAMP	Autosampler re-started
ENP	30-Jun-2004	S18C	SAMP	No sample collected by auto-sampler

B. Field Audits

An audit of sample collection by Broward Department of Planning and Environmental Protection (DPEP) Environmental Monitoring Division for CAMB and NECP projects was conducted on 6/22/2004. The following is a summary of findings for this audit. Responses received were satisfactory to correct the deficiencies.

1. Broward DPEP did not have a signed field quality manual. This is a Florida DEP requirement under Chapter 62-160, Florida Administrative Code. As a corrective action, Broward DPEP was required to provide a copy of a signed field QM.
2. The calibration report did not include the true value of the standard used for calibration. Broward DPEP was required to submit a corrected calibration report for the audited sampling event. As a long term corrective action DPEP was required to write the standard concentrations used for calibration on the calibration report.
3. There was no clear link as to which reagent used for calibration for each sampling event. As a corrective action, DPEP was required to provide a clear link of the calibration information associated with the specific field testing event.
4. There was no documentation on the chemical used to prepare conductivity calibration standard. DPEP was required to document the source of standards or reagents that are formulated in-house and used on the field testing event for these projects.
5. The grab sampling equipment was not rinsed with the site water at the first site. As a corrective action, DPEP was required to rinse the grab sampling equipment at least once with the site water prior to collection of actual sample.
6. The grab sampling equipment was rinsed with analyte-free water multiple times prior to collection of FCEB, which is not the same protocol followed when rinsing for sample collection between sites. Since the FCEB is suppose to assess the effectiveness of cleaning between sampling sites, it was recommended that the sampling equipment be cleaned the same way between each sampling effort and before collection of the FCEB.
7. The grab sampling equipment was not rinsed with ample amounts of analyte-free water immediately after completing collection at each site. It was recommended that the sampling equipment be rinsed twice with ample amounts of analyte-free water immediately after collecting the sample from each site.

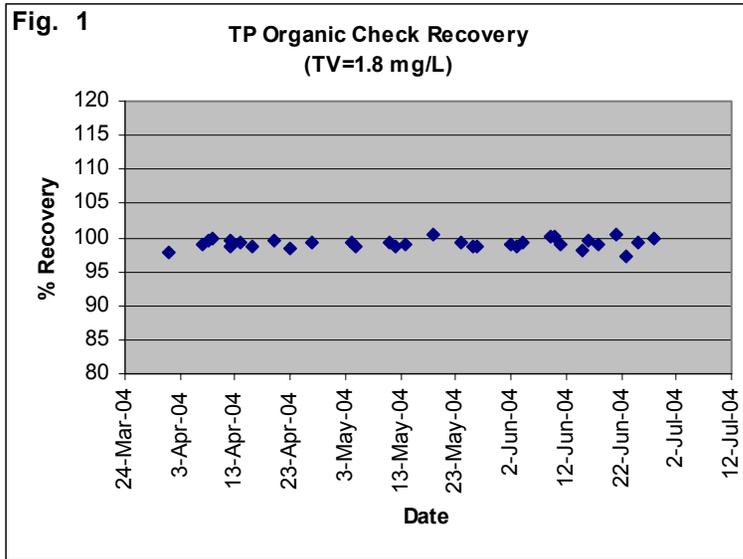
III. Laboratory Quality Control Assessment

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.

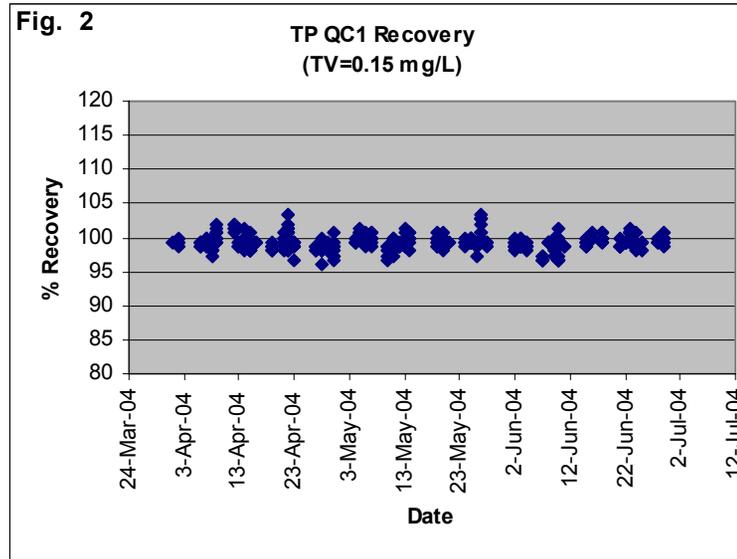
Recoveries for the QC samples are generally within $\pm 10\%$ from the true value, which are acceptable. The PQL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 100.9%. The PQL check daily results indicate the laboratory consistently achieved the 0.002 mg/L MDL. An organic check is a solution prepared from phytic acid, a stable form of organic

phosphate. Recoveries for this check sample are between 97.2 – 100.4%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.5%

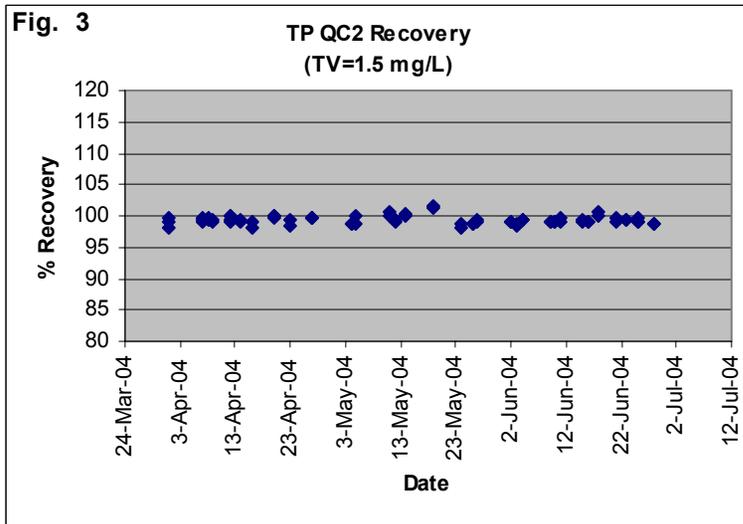
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 1.6% and 1.3% for low (0 to 0.200 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 7.1% and 3.8% for low and high levels, respectively.



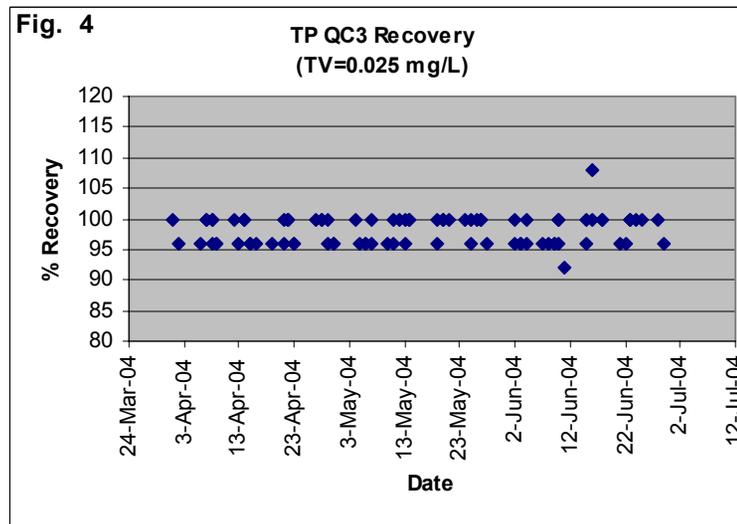
Mean=99.1%, Min=97.2%, Max=100.4%



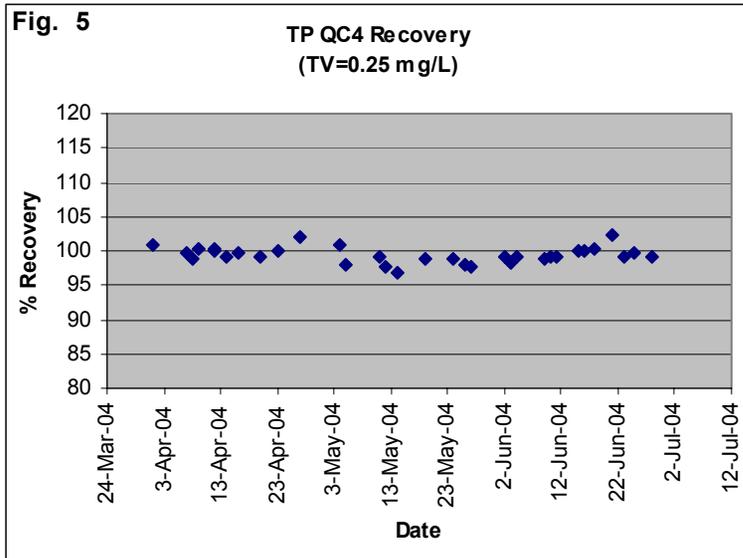
Mean=99.3%, Min=96%, Max=103.3%



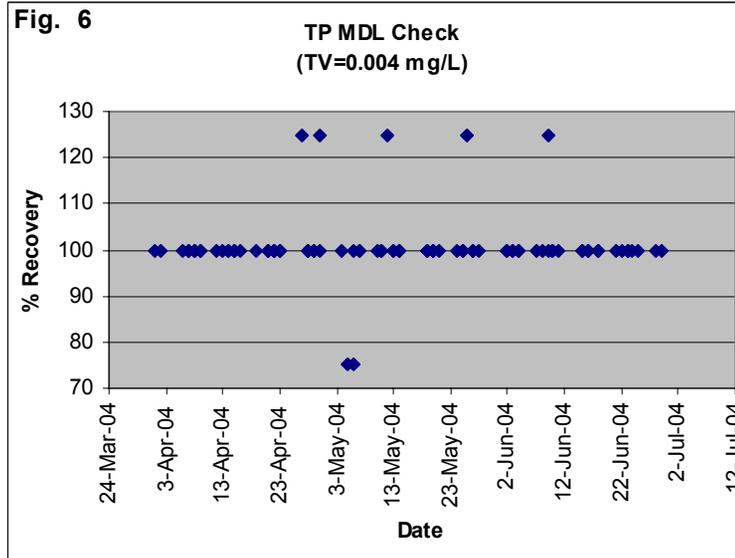
Mean=99.3%, Min=98.1%, Max=101.7%



Mean=98.2%, Min=92%, Max=108%



Mean=99.4%, Min=96.8%, Max=102.4%



Mean=100.9%, Min=75%, Max=125%

TP Precision Data 4/1/04-6/30/04 Acceptance Limit = <10%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	7.1	Max	3.8
Mean	1.6	Mean	1.3
Std Dev	1.35	Std Dev	1.02
3xSD	4.05	3xSD	3.05
UCL	5.6	UCL	4.4
n	190	n	23

TP Spike Recovery Data 4/1/04-6/30/04 Acceptance Limit = 90-110%	
Min	92.8
Max	107
Mean	100.5
Std Dev	2.80
3xSD	8.40
LCL	92.1
UCL	108.9
n	215

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 April 2003 to June 2004 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA), Everglades TP Round Robin (ERR), and S332 sites (C111) (Table 5). 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 both data are highly comparable (Figures 7 and 8).

A paired t-test and Wilcoxon rank-sum test was also done for data that are < 0.02 mg/L. These analyses indicate that there is no significant difference ($\rho=0.10$) between the DEP and SFWMD TP data.

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

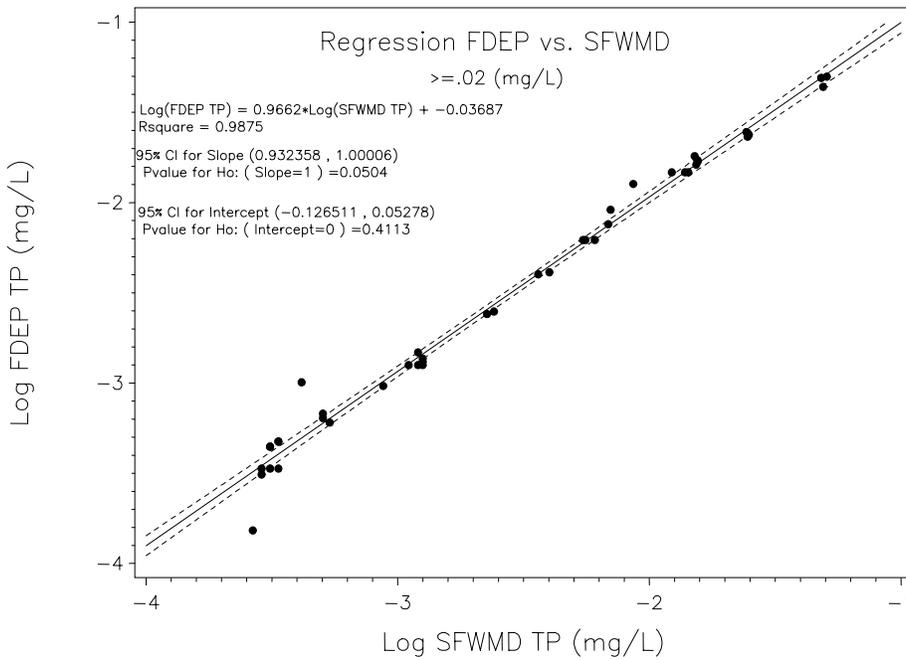


Fig. 7. Regression Analysis for TP > 0.020 mg/L

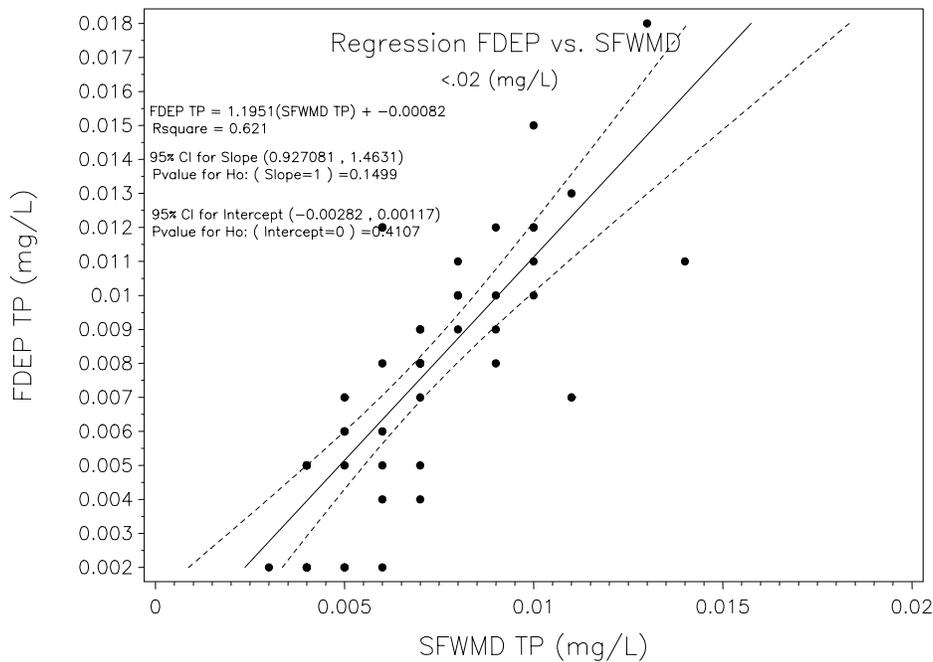


Fig. 8. Regression Analysis for TP <0.020 mg/L

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

Sample	Date	SFWMD	FDEP	% RPD/Comments
S332B-041503-1000	15-Apr-03	0.009	0.012	29
S332C-041503-1200	15-Apr-03	0.008	0.009	12
S332DDZE-041503-1400	15-Apr-03	0.004	0.005	<PQL
S332B-052703-0935	27-May-03	0.007	0.009	<PQL
S332C-052703-1130	27-May-03	0.007	0.008	<PQL
S332DDZE-052703-1430	27-May-03	0.004	0.005	<PQL
S332BWeir-062403-1100	9-Jun-03	0.010	0.011	9.5
S332DDZE-062403-1600	24-Jun-03	0.005	<0.004	<PQL
S332B-072203-1000	22-Jul-03	0.007	0.005	<PQL
S332C-072203-1200	22-Jul-03	0.006	0.004	<PQL
S332DDZE-072203-1500	22-Jul-03	0.003	<0.004	<PQL
S332B-081903-1345	19-Aug-03	0.004	0.005	<PQL
S332C-081903-1100	19-Aug-03	0.004	<0.004	<PQL
S332DDZE-081903-0830	19-Aug-03	0.005	0.005	<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

Table 5. (continued)

Sample	Date	SFWMD	FDEP	% RPD/Comments
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
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
ERR-14	1-Oct-03	0.037	0.041	10
ERR-14	1-Oct-03	0.038	0.040	5.1
ERR-14	1-Oct-03	0.010	0.012	18
ERR-14	1-Oct-03	0.010	0.010	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
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	10-Mar-03	0.116	0.130	11
EVPA	10-Mar-03	0.008	0.010	22
EVPA	10-Mar-03	0.008	0.011	32
EVPA	11-Mar-03	0.008	0.010	22
EVPA	11-Mar-03	0.008	0.010	22
EVPA	11-Mar-03	0.009	0.010	10
EVPA	16-Jun-03	0.104	0.110	5.6
EVPA	16-Jun-03	0.006	0.012	<PQL

Sample	Date	SFWMMD	FDEP	% RPD/Comments
EVPA	17-Jun-03	0.007	0.008	<PQL
EVPA	17-Jun-03	0.007	0.008	<PQL
EVPA	17-Jun-03	0.009	0.009	0
EVPA	17-Jun-03	0.009	0.008	12
EVPA	8-Sep-03	0.148	0.160	7.8
EVPA	8-Sep-03	0.014	0.011	24
EVPA	9-Sep-03	0.006	0.008	<PQL
EVPA	9-Sep-03	0.007	0.008	<PQL
ERR-15	28-Oct-03	0.268	0.27	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
ERR-15	28-Oct-03	0.031	0.036	15
ERR-15	28-Oct-03	0.031	0.036	15
ERR-15	28-Oct-03	0.029	0.03	3.4
ERR-15	28-Oct-03	0.029	0.031	6.7
ERR-15	28-Oct-03	0.030	0.035	15
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
EVPA	15-Dec-03	0.127	0.150	17
EVPA	15-Dec-03	0.010	0.015	40; Heavy suspended solids
EVPA	15-Dec-03	0.011	0.013	17; Heavy suspended solids
EVPA	15-Dec-03	0.013	0.018	32; Heavy suspended solids
EVPA	3/8/2004	0.031	0.031	0
EVPA	3/8/2004	0.028	0.022	24; Heavy suspended solids
EVPA	3/8/2004	0.017	0.020	16
EVPA	3/8/2004	0.006	0.006	<PQL
EVPA	6/14/04	0.047	0.049	4.2
EVPA	6/14/04	0.034	0.050	38%; Heavy suspended solids
EVPA	6/14/04	0.158	0.160	1.2
EVPA	6/14/04	0.156	0.160	2.5

B. National Proficiency Testing Results

As a requirement for laboratory certification, the District’s laboratory performs proficiency testing (PT) on environmental samples on a semi-annual basis. This study is administered by vendors that have been approved by the National Institute of Science and Technology as PT providers for National Environmental Laboratory Accreditation Conference.

The result of April 2004 study is presented below (Table 6).

Table 6. Laboratory Proficiency Testing Results for TP, April 2004

Sample I.D	Reported Value, mg/L	Assigned Value, mg/L	%Recovery	Status	Z-Score
Sample 1 (WP)	5.99	6.00	99.8	Acceptable	0.488
Sample 2 (APG)	1.69	1.71	98.8	Acceptable	-0.144

WP=water pollution; APG=Analytical Products Group, Inc.

C. NWRI Proficiency Testing (PT) Program for Water

SFWMD laboratory participated in the natural water samples provided by the National Water Research Institute, Environmental Canada. The objective of this program is to assess and demonstrates reliability and quality of analytical measurements.

Table 7. Laboratory performance in PT Study 0084 for TP, June 2004.

	Sample #s									
	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.003	0.002	0.012	0.035	0.054	0.079	0.147	0.208	0.159	0.32
Reported Value, mg/L	<0.002	<0.002	0.012	0.035	0.054	0.081	0.148	0.203	0.158	0.32

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

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: $\%RPD = [\text{Value1} - \text{Value2}]/\text{Mean} * 100$.