Quality Assessment Report for Water Quality Monitoring
January – March 2006

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 1st quarter of 2006:

- 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 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 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. Procedure Updates

Sampling is conducted following the 9/2005 version of monitoring plan and improvements that were discussed among and decided by the Sampling Work Group, as tasked by the TOC in August 2005. The latest meeting of this group was on 2/9/2006. Minutes of these workshops have been distributed and posted at the TOC website.

The following are highlights of those improvement areas:

Minimize Helicopter Disturbance: Samplers are expected to guide the helicopter pilot to an appropriate landing location to minimize disturbance at the target sampling location. Generally, sampling off the helicopter float should not be done unless if the water is >1m. Samplers should continue to use judgment on sampling from the helicopter float if water is deep or if sediments are easily disturbed, such as if the ground is uneven and riddled with holes.

Discontinue Submersing Capped Bottles: Uncapping bottles underwater can cause unnecessary disturbance. Samplers have switched to uncapping sample bottles before submersing. Entrainment of surface film and particulates can be minimized by holding the inverted bottle, mouth facing down,

with the bottle perpendicular to the water surface, immersing it neck opening first to the appropriate depth, and then turning it upright. Surface film should be avoided when retrieving samples.

Implement a consistent method of measuring depth to consolidated substrate (DCS), effective 2/2006. District staff designed a pole (the "Paluga pole") to better and more consistently measure the DCS. The prototype was constructed from ¾-inch PVC pipe with a white cap on the bottom and a metric scale (0-150 cm) on the side. The white cap allows the sampler to see when the tip of the pole begins to sink into the sediments. Using the pole, instead of a meter stick, helps in achieving consistency in depth measurements. Holes drilled in the pipe reduce buoyancy and a yellow float attached to the top aid in visibility and retrieval. Additional "Paluga poles" have been fabricated and distributed to the marsh sampling teams.

Enhance field documentation. The standard District field sheet has been revised with additional space for observations. A checklist for typical field observations will also be added as a reference for samplers.

- Any unusual conditions must be documented in the field notes (e.g., "no distinguishable water column").
- Reasons for deviation from sequence of sampling stations
- Reason for sampling from helicopter pontoon
- Observed impacts of sampling from pontoon
- Clear description of site conditions vs. sample conditions
- A description of the "visible nature of the water"
- Type of common plants (e.g., cattails) present
- Roles of each member of the team in each site

Use smaller sample collection bottle, effective 2/2006. The larger the container, the more risk of disturbing detrital material during sampling, especially in areas with dense submerged aquatic vegetation. The collection bottle size was changed from 2 L to 1 L capacity; samplers are collecting a total volume of up to 3 liters of water. Samplers must make a determination to ensure that the gap in submerged vegetation is at least twice the size of bottle being used. If a gap is not large enough for the 1L bottle then the sampler should leave the area to find a gap of sufficient size. If in the rare instance that a gap is not available to use 1L bottle, then the sampler must use a 250 mL bottle to fill the bottles. If the visibility of the water column is low, then the collector should collect sample using a smaller bottle.

Allow sampling outside the poled (marked) perimeter, effective 2/2006. Sampling has been usually conducted within the marked perimeter at most stations since the early 90s. Restricting collection within this perimeter sometimes makes it difficult for samplers to obtain undisturbed samples. Tracks are visible where samplers have repeatedly visited sample stations. Over time, holes in the sediment column are created by the sampler by merely walking through the marsh to the sampling location. Eventually, there are too many holes within the designated perimeter. The sampler should make the necessary judgment to sample in a location that is representative of the bulk surface water in the area. As an improvement, the samplers are now permitted to decide on the specific sampling location using GPS coordinates and distance from helicopter as a reference. Samplers will vary their approach to each station to minimize impacts depending on wind direction and the presence of cattails and tree islands. Samplers should sample at least 10 m from helicopter propeller disturbance and within 50 m of where the helicopter lands.

B. Missing Data

Table 1 shows a list of missing data for this reporting period. Data may not be available due to problems in collection or upon sample submission to the laboratory. Out of 25 missing data, 23 were because no samples were collected due to either lack of flow, structure maintenance, or depth was too shallow. The cooler containing S12C sample, collected on 3/14/06, was lost by the courier and did not make it to the laboratory. A S175 sample, collected on 3/1/06, was not properly preserved and was rejected by the laboratory.

Table 1. Missing data for the period from 1/1/06 to 3/31/06

Project	Collection Date	Station	Comments
CAMB	1/9/06	S12A	No flow, no samples collected
CAMB	1/9/06	S12B	No flow, no samples collected
CAMB	1/23/06	S12C	No flow, no samples collected
CAMB	2/7/06	S12D	No flow, no samples collected
CAMB	2/7/06	S12B	No flow, no samples collected
CAMB	2/21/06	S12A	No flow, no samples collected
CAMB	3/14/06	S12C	No sample submitted. Cooler was lost by courier.
CAMB	3/21/06	S12A	No flow, no samples collected
CAMB	3/21/06	S12B	No flow, no samples collected
CAMB	3/21/06	S12D	No flow, no samples collected
ENP	1/10/06	S177	No flow, no samples collected
ENP	1/10/06	S176	No flow, no samples collected
ENP	1/17/06	S18C	No flow, no samples collected
ENP	1/24/06	S18C	No flow, no samples collected
ENP	2/7/06	S18C	No flow, no samples collected
ENP	2/14/06	S18C	No flow, no samples collected
ENP	2/21/06	S18C	No flow, no samples collected
ENP	2/27/06	S18C	No flow, no samples collected
ENP	3/1/06	S176	Improper preservation. Sample was not acidified; rejected by the laboratory; tests canceled.
ENP	3/14/06	S18C	Autosampler shut down for structure maintenance.
ENP	3/20/06	S18C	Autosampler shut down for structure maintenance.
EVPA	3/6/06	LOX5	Total depth <0.10m. No sample collected
NECP	1/31/06	S334	No flow, no samples collected
NECP	2/14/06	S334	No flow, no samples collected
NECP	2/28/06	S334	No flow, no samples collected

C. 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 and FCEB results for all projects of interest to the TOC. All blanks associated with samples for stations listed in Section I were within the acceptance criteria. Table 3 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. For this reporting period, there are no flagged TP data for the stations listed in Section I.

Table 2. Field and equipment blank results*

Type of Blank	Project	# Blanks collected	% ≤0.002	% >0.002
EB	CAMB	6	100	0
	ENP	1	100	0
	EVPA	2	100	0
FCEB	CAMB	6	100	0
	ENP	12	100	0
	EVPA	6	100	0
	NECP	1	100	0
FB	ENP	1	100	0

Notes

1) Only blanks from sampling events that included samples from Stations listed in Section I of this report were included in this analysis.
2) Two blanks greater than the MDL for TP which were associated with a short term autosampler project at stations S12C and S333 were not included here.
3) Two blanks greater than the MDL for TP not included here were associated with the CAMB project at stations S190 and S8. These sampling trips do not include TOC compliance stations.

Table 3. Field precision summary

Project Code	# of triplicates	% RSD	Comments
CAMB	1	0	Precision criteria were met
ENP	1	10.8	Sample results were less than PQL
EVPA	1	0	Precision criteria were met

Notes

1) Only replicates from sampling events that included samples from Stations listed in Section I of this report were included in this analysis.
2) All TP analyses were conducted by the District's Chemistry laboratory.
3) Field precision acceptance criteria: <20%. This criteria was applied only if sample values >PQL.
4) FB, FCEB and EB acceptance criteria: Must be ≤MDL.
5) Associated samples are flagged when concentrations are less than five times the resulting blank values for possibility of contamination.

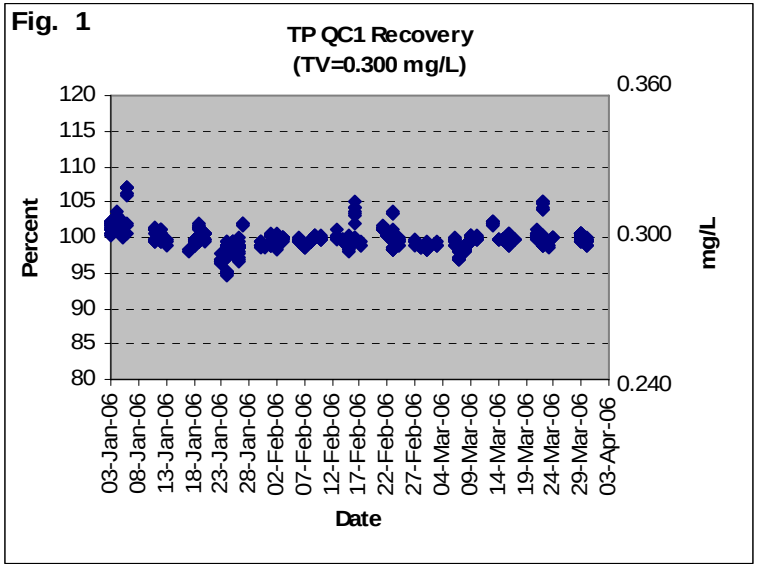
III. Laboratory Quality Control Assessment

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. The charts presented in Figures 1-3 show recoveries from various levels of QC samples for the TP analysis at the SFWMD laboratory for the period from January 1 through March 31, 2006. Precision and matrix spike recoveries are shown in Tables 4 and 5. A portion of or an entire analytical run is generally re-analyzed or rejected if QC recoveries are outside the set limits. Data is flagged accordingly if any deficiencies are noted and the samples have exceeded the required holding times and cannot be re-analyzed.

Recoveries for the QC samples are generally within ±10% from the true value, which are acceptable. The PQL check (QC5), with a true value of 0.004 mg/L, mean recoveries of 100.3%. The daily PQL check results indicate the laboratory has consistently achieved the goal of 0.002 mg/L MDL.

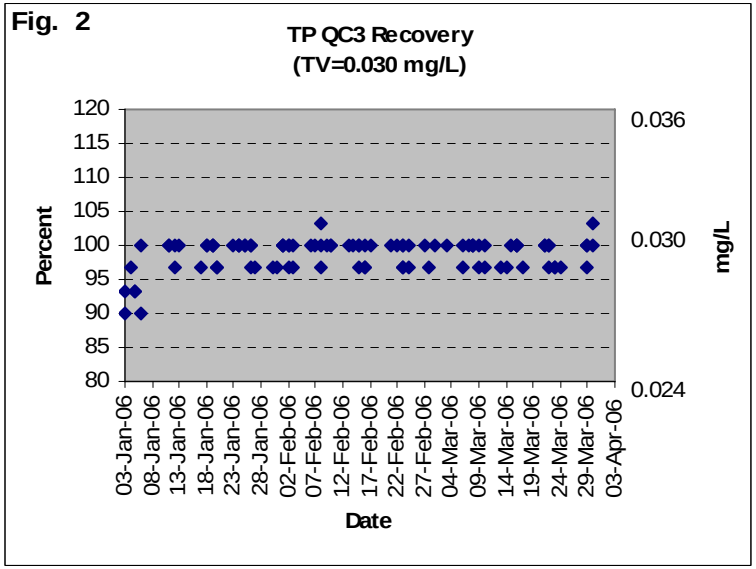
Accuracy based on matrix spikes, prepared by adding a solution of phytic acid, a stable form of organic phosphate, was 102%. Precision, based on mean and maximum relative standard deviation were 1.1 and 7.0%, respectively, which are well within the precision target of 10.0%.

Fig. 1



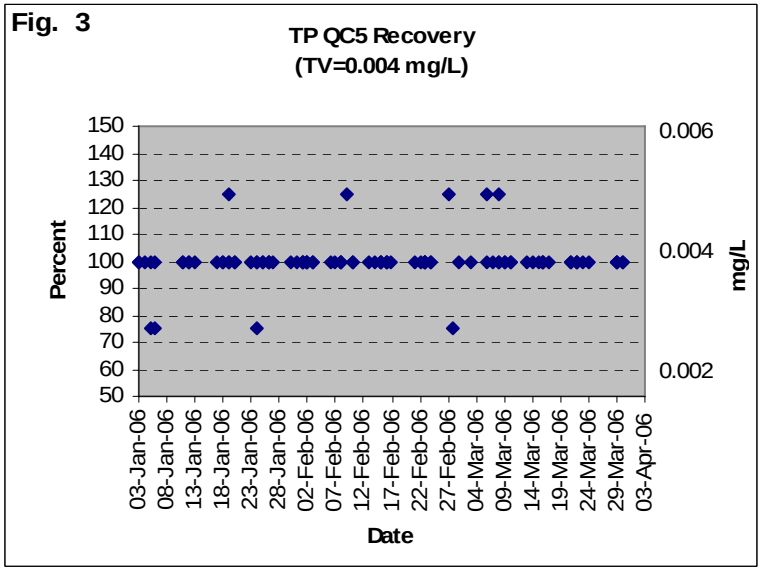
Mean = 99.8%, Max = 107.0%, Min = 94.7%

Fig. 2



Mean = 98.7%, Max = 103.3%, Min = 90.0%

Fig. 3



Mean = 100.3%, Max = 125.0%, Min = 75.0%

Table 4. TP Precision Data, 1/01/06-3/31/06

Acceptance Limit	<10%
Working Range	0.002-0.400 mg/L
Max	7.0
Mean	1.1
Std Dev	1.15
3 x SD	3.44
UCL	4.6
n	299

Table 5. TP Spike Recovery Data, 1/01/06-3/31/06

Acceptance Limit	90-110%
Working Range	0.002-0.400 mg/L
Min	60.4[1]
Max	110
Mean	102.2
Std Dev	3.96
3 x SD	11.88
LCL	90.4
UCL	114.1
n	305

[1] One spike recovery was reported below minimum criteria. Low recovery was attributed to matrix interference and associated data flagged.

IV. Inter-Laboratory Quality Control Assessment

A. Split Studies with FDEP Laboratory

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. Data from split studies between FDEP and DISTRICT laboratories from March 2003 to November 2005 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA) and Everglades TP Round Robin (ERR) (Appendix Table 1). Regression analysis of the data set was done separately for TP≥0.020 mg/L and for TP<0.020 mg/L (Figures 4-6). Logarithmic transformation was done because of skewed data distribution. At <0.02 mg/L level, the slope is significantly different from 1 and intercept is significantly different from 0, suggesting a difference in the data sets. It is important to note that the very high variability within each laboratory, as well as between the two laboratories at the low concentration levels affects this outcome.

At ≥0.02 mg/L, regression analysis shows that the slope is not significantly different from 0 and intercept is not significantly different from 1.

Although Wilcoxon rank-sum test indicate that there is a significant difference in the results between the two laboratories at concentrations <0.02 mg/L (Table 5), the mean difference was 0 (<MDL). At ≥0.02 mg/L TP concentrations, there was a significant difference between the two laboratory results, however, even at this higher concentration range, the mean difference is 0.006 mg/L, which is still below the two laboratories' practical quantitation limit (PQL).

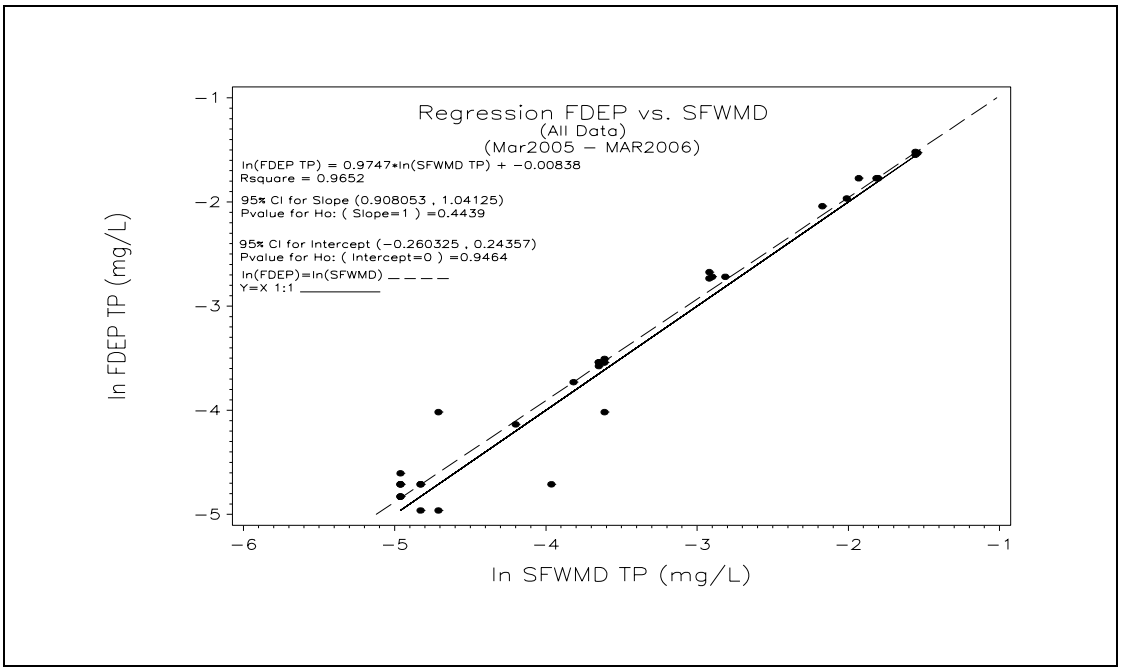


Fig. 4. Regression Analysis for TP<0.020 mg/L

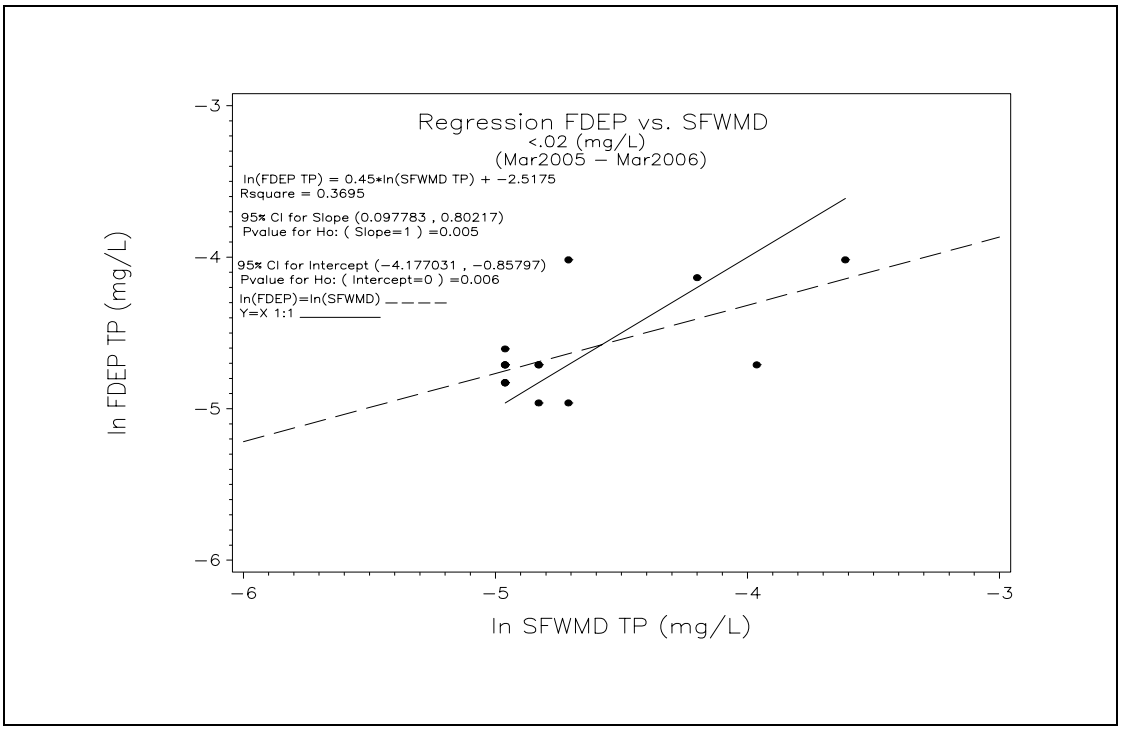


Fig. 5. Regression Analysis for TP<0.020 mg/L

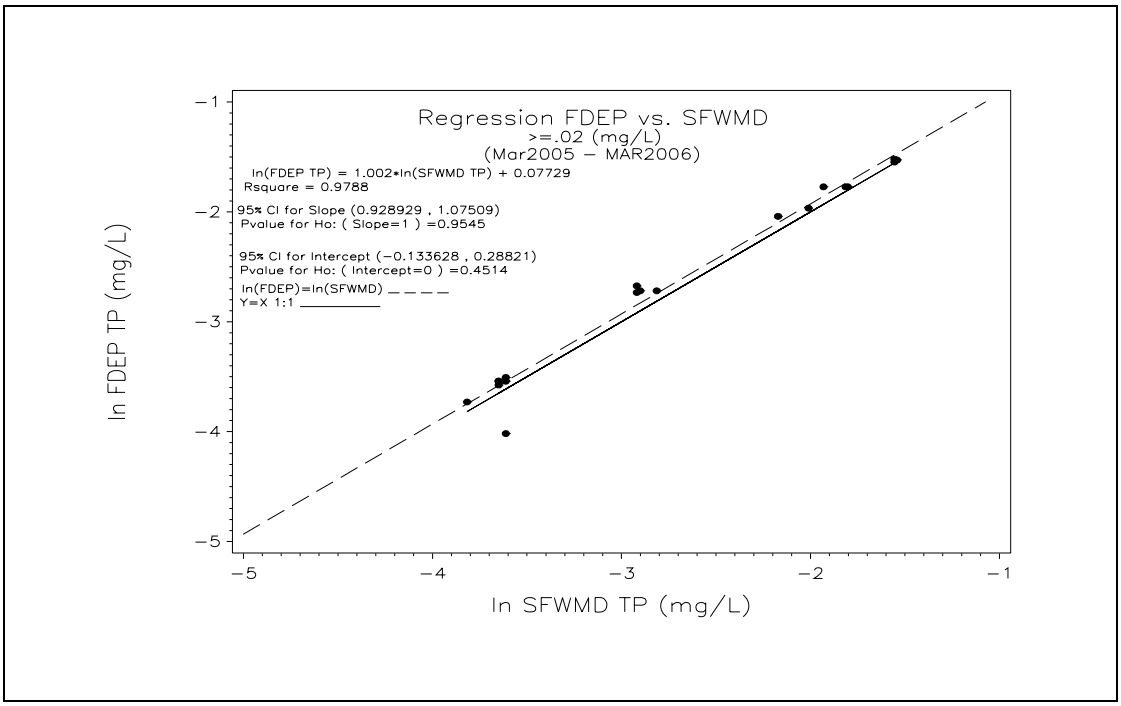


Fig. 6. Regression Analysis for TP≥0.020 mg/L

Table 6. Statistical Comparison of SFWMD and FDEP Split Phosphorus Samples (3/2005 – 3/2006).

All Data	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	34	0.060	0.028	
	SFWMD	34	0.056	0.026	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean of Differences	-0.004	Mean of Differences = 0	Student's t	0.0011
	Median of Differences	-0.002	Median of Differences = 0	Signed Rank	<.0001
<0.02 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	15	0.010	0.009	
	SFWMD	15	0.010	0.008	
	Statistical Test of Hypotheses				
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean of Differences	-0.000	Mean of Differences = 0	Student's t	0.9118
	Median of Differences	-0.001	Median of Differences = 0	Signed Rank	0.2706
≥0.02 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	20	0.096	0.066	
	SFWMD	20	0.089	0.054	
	Statistical Test of Hypotheses				
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean of Differences	-0.006	Mean of Differences = 0	Student's t	0.0008
	Median of Differences	-0.004	Median of Differences = 0	Signed Rank	0.0003

Notes:
1) Differences were calculated as (SFWMD TP - FDEP TP). *The mean and median differences for all concentration levels are at or below the PQL.*
2) Data were not used if FDEP value was below detection limit (-.004).

B. U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples

The District's laboratory participates in the USGS SRS Study on environmental samples semi-annually on a voluntary basis, as an external QC program to monitor laboratory performance. This study is participated in by multiple laboratories all over the country. The result of the March 2006 study is presented in Table 7.

Table 7. USGS SRS Study for TP, March 2006

Sample	Reported Value, mg/L	Most Probable Value, mg/L	%Recovery	Z-Value
M-178	0.060	0.064	93.7	-0.40

B. NWRI Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program

SFWMD laboratory participated in the Performance Testing program provided by the National Water Research Institute, Environment Canada. The objectives of this program are to assess and demonstrate reliability and quality of analytical measurements of inorganic parameters in natural waters. The results from the most recent study are shown in Table 8.

Table 8. Laboratory Performance in PT Study 87 for TP, December/January 2006.

Sample #	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.003	0.004	0.008	0.022	0.077	0.094	0.113	0.176	0.180	0.242
Reported Results, mg/L	<0.002	0.004	0.009	0.021	0.078	0.095	0.112	0.178	0.180	0.248

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

IV. 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 or on-site (field) decontamination (FCEB).

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.

APPENDIX TABLE 1. Results of TP split studies between SFWMD and FDEP laboratories, EVPA Project, March 2005 to March 2006.

Sample	Date	SFWMD	FDEP	% RPD/Comments
EVPA	7-Mar-2005	0.134	0.140	4.4, Dark brown stain, heavy 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
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