Quality Assessment Report for Water Quality Monitoring

October - December 2002

Submitted to the
Technical Oversight Committee

Prepared by:

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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 4th quarter of 2002:

- 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 South Florida Water Management District's Quality Manual requires analysis of laboratory quality control (QC) samples and the collection and analysis of field QC samples along with routine samples to assess the data quality. A summary of current QC protocols, data assessment criteria and protocols for field quality control samples is included in Part II, Section C, Table 4 of this report.

Included also in this report are an analysis of the District's laboratory's performance on split or replicate studies with FDEP and other laboratories and the results of the U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples.

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. All of the 130 blanks collected except one were within the acceptance criteria. Table 2 summarizes field precision results. Field sampling precision was generally excellent.

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	% with value <0.002	% with value 0.002-0.004	% with value >0.004	Action Taken
EB	CAMB	9	66.7	33.3	0	N/A
	ENP	3	66.7	33.3	0	N/A
	EVPA	3	100.0	0	0	N/A
	NECP	2	100.0	0	0	N/A
FB	CAMB	4	100	0	0	N/A
FCEB	CAMB	75	85.3	13.3	1.3	Results > 0.004 were qualified with a "V"
	ENP	9	100.0	0	0	N/A
	EVPA	19	5.3	0	0	N/A
	NECP	6	100.0	0	0	N/A

Table 2. Field precision summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	5	7	Precision criteria were met.
ENP	0	N/A	N/A
EVPA	2	0	Precision criteria were met.
NECP	2	5	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 </=2xMDL.
4) Associated samples are flagged when concentrations are less than three times the resulting blank values for possibility of contamination.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	1-Oct-02	S140	SAMP	J3	Possible Sample Contamination
	10-Oct-02	S39	SAMP	Y	Improper Preservation
	10-Oct-02	S39	SAMP	Y	Improper Preservation
	25-Nov-02	S11A	SAMP	V	Sample Associated with Positive FCEB
	25-Nov-02	S145	SAMP	V	Sample Associated with Positive FCEB
	25-Nov-02	S145	SAMP	V	FCEB >2XMDL

B. Field Audits

The CAMB project sample collection team was audited this quarter. The overall auditor's assessment was satisfactory. There were some deficiencies noted during the audit that dealt with minor errors in documentation. Also, two recommendations intended to enhance the process were listed.
The response to the audit was satisfactory concerning all items.

Summary of Audit Corrective (CA) and recommendations (R)

- (CA) Identify each trip as W, BW, and Q for Weekly, Biweekly, Quarterly respectively.
- (CA) List all responsibilities of sample collection personnel in the field notes.
- (CA) If there is more than one page for a sampling event, the "continued on" and "Continued from" blanks should be completed on each page.
- (CA) List visitors or other personnel at the site in the field notes.
- (CA) Note location where calibration and continuing calibration verification took place.
- (R) Whenever possible, one person should collect all three replicates. Apply the same level of mixing among replicates to help ensure that we are obtaining true sampling replicates.
- (R) For proper tracking purposes, place temperature reading in the "Adj." column only if the reading is for the monthly check of the thermistor and the reading is from the NIST Traceable thermometer.

C. Current Field QA/QC and Data Assessment Protocols

The criteria presented in Table 4 are those used by the SFWMD QA unit in assessing the quality and acceptability of data for all monitoring projects.

Table 4. Current field QC protocols, data assessment criteria and protocols for field quality control samples.

FQC		**As of 3/01/02**
Lab/pre-Cleaned EB (EB)	Requirement	Laboratory cleaning monthly check for re-usable containers and equipment. For A/S: test for NH3 and OPO4. Field: Collect one pre-cleaned EB per quarter.
	Corrective Action	Flag EB if >2x MDL. Flag affected samples only if the problem is evident and consistent. Troubleshoot laboratory or off-site cleaning procedures.
Field Cleaned EB (FCEB)	Requirement	Collect at least one FCEB per trip.
	Corrective Action	Flag FCEB if >2X MDL. Flag all affected samples (samples with concentration <3x FCEB value). Troubleshoot field-cleaning procedures.
Field Blank (FB)	Requirement	Optional, on as needed basis.
	Corrective Action	Troubleshoot accordingly.
Split Sample (SS)	Requirement	Collect quarterly for selected projects only. Two SS per site from 4 sites per selected project. The routine samples are sent to routine lab while the other two sets are sent to two other laboratories.
	Corrective Action	Provide feedback to the affected lab and initiate troubleshooting or other corrective action with that lab. New RPD or RSD criteria: 20%.
Replicate Sample (RS)	Requirement	Collect for each project quarterly, and during training of field staff.
	Corrective Action	Verify if this is lab or field deficiency. Provide feedback to the affected group and initiate troubleshooting or other corrective action, if necessary. New RPD or RSD criteria: 20% @ > PQL.
Field Duplicate (FD)	Requirement	Optional based on program requirements.
	Corrective Action	Troubleshoot accordingly.

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.

Except for QC5, recoveries for the QC samples are generally within $\pm$ 10% from the true value, which are acceptable. QC5, with a true value of 0.004 mg/L, is less than the practical quantitation limit. A wider performance range can be expected at this level, 76 – 126% with a mean of 100.8%.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 96.7 – 102.4%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 98.2%.

The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 0.9% and 0.6% for low (0.04 to 0.2 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 3.8% and 2.2% for low & high levels, respectively. There was no data available in the 0 to 0.04 mg/L range thus no evaluation. Laboratory and split sample field collection precision at the low range was evaluated using split data from the Cape Sable Seaside Sparrow project. See figures 7, 8 and 9.

The method detection limit for Total Phosphorous is now 2 ppb instead of the previous 4 ppb level.

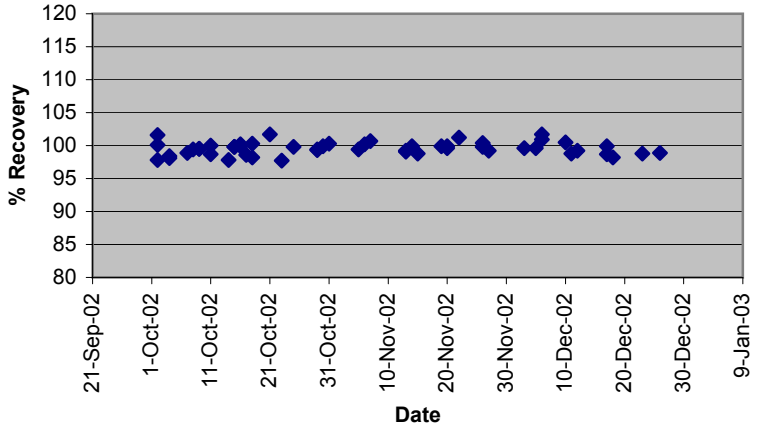
A. Split and Replicate Studies

To continually assess comparability of results, the District sends split samples to other laboratories. This includes a special quarterly split study for samples collected from the Loxahatchee National Refuge site (EVPA Project), with the Florida Department of Environmental Protection's laboratory
The result of the latest split study is presented in Table 5. Both laboratories obtained acceptable blank (FCEB) results. All results pairs met the field precision criteria. The District's laboratory also participates in other split studies throughout the year. An analysis of District's laboratory TP results on the Cape Sable Seaside Sparrow split studies as compared to FDEP, is presented in Figures 7, 8 and 9. Results were compared at ranges where sufficient data was available. The R^2 values ranged from 0.67 to 0.99 based on range, having good correlation at the lowest range (0-20 ppb) and the best correlation at the highest level (50-200 ppb) as expected.

Table 5. Results of TP split study between SFWMD and FDEP laboratories, 12/16/02.

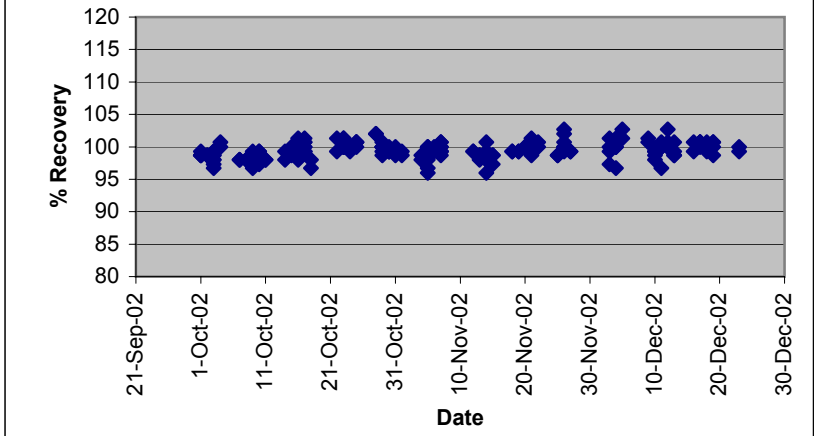
Station	Sampling Date	Type	FDEP	SFWMD	(SFWMD-FDEP)	% RPD	Comments
			mg/L				
LOX4	12/16/02	FCEB	<0.004	<0.002	N/A	N/A	<PQL
S5AD	12/16/02	SS	0.23	0.206	-0.024	11.0	< 20% RPD
LOX3	12/16/02	SS	0.009	0.007	-0.002	25.0	<PQL
LOX5	12/16/02	SS	0.008	0.006	-0.002	28.6	<PQL
LOX6	12/17/02	SS	0.006	0.006	0.000	0	<PQL
LOX11	12/17/02	SS	0.008	0.007	-0.001	13.3	<PQL
LOX13	12/17/02	SS	0.008	0.007	-0.001	13.3	<PQL

Fig. 1



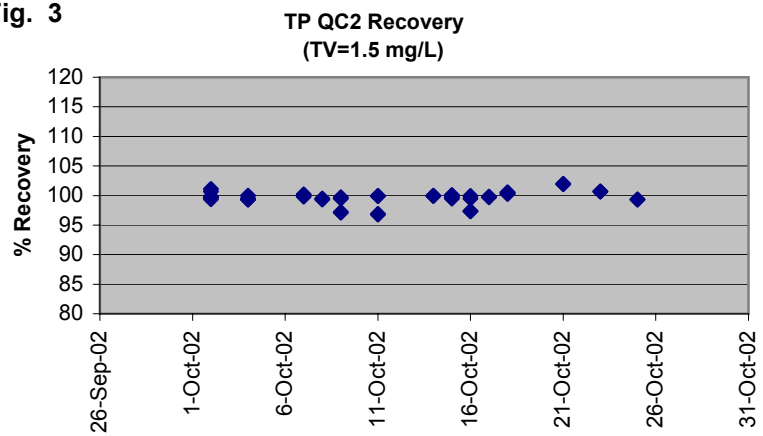
% Recovery Organic Check	MEAN	99.6
	MAX	101.7
	MIN	97.7

Fig. 2



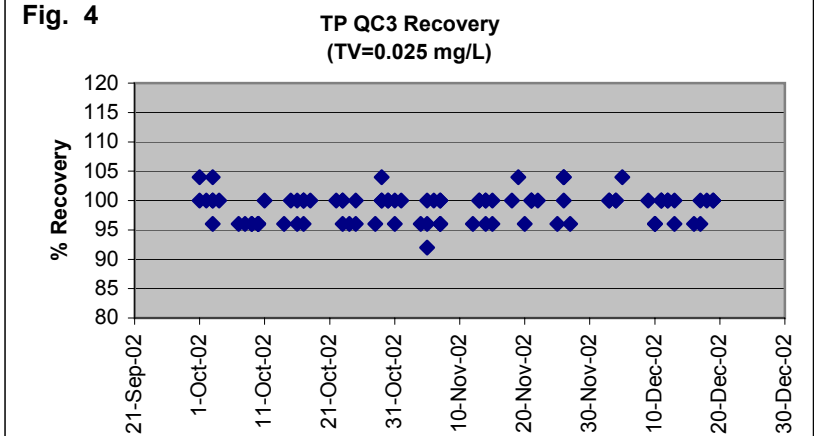
% Recovery QC1	MEAN	98.8
	MAX	101.3
	MIN	96.7

Fig. 3



% Recovery QC2	MEAN	99.6
	MAX	102
	MIN	96.8

Fig. 4



% Recovery QC3	MEAN	98.8
	MAX	104
	MIN	92

Fig. 5

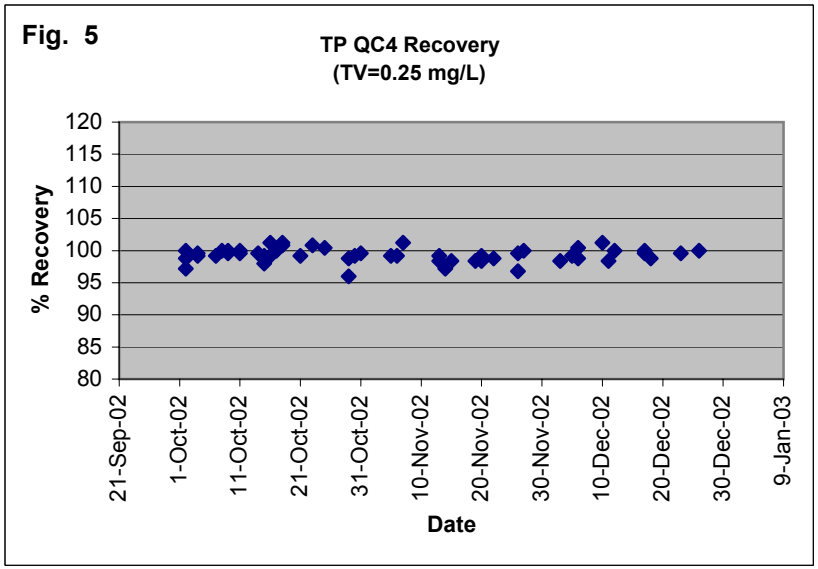
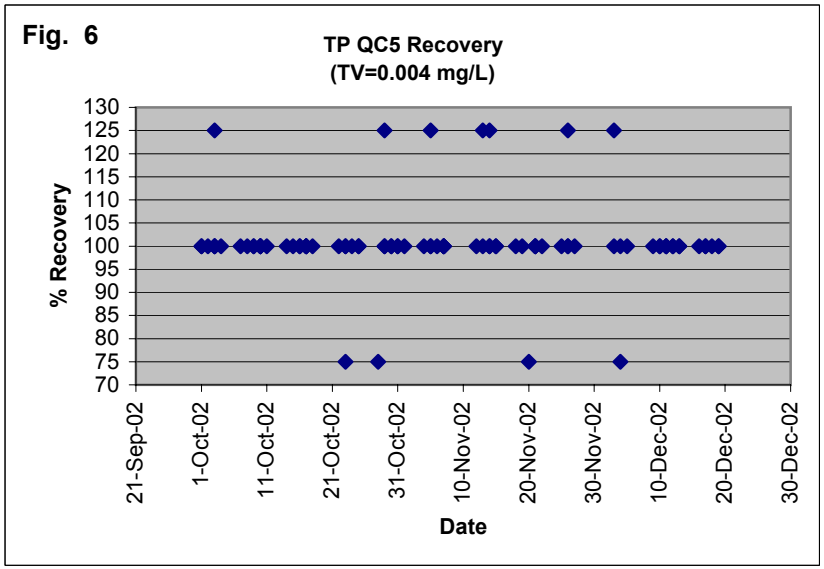


Fig. 6



% Recovery QC4	MEAN	99.3
	MAX	101.2
	MIN	96.0

% Recovery QC5	MEAN	100.8
	MAX	125.0
	MIN	75.0

TP Precision Data 10/1/02-12/31/02 Acceptance Limit = <5.0%			
Low Level (0.04-0.2)		High Level (0.2-2)	
Max	3.8	Max	2.2
Mean	0.9	Mean	0.6
Std Dev	0.87	Std Dev	0.47
3xSD	2.62	3xSD	1.42
UCL	3.5	UCL	2.0
n	224	n	71

TP Spike Recovery Data 10/1/02-12/31/02 Acceptance Limit = 90-110%			
	Min	68.2	
	Max	109	
	Mean	98.2	
	Std Dev	6.06	
	3xSD	18.19	
	LCL	80.0	
	UCL	116.3	
	n	254	

Fig. 7

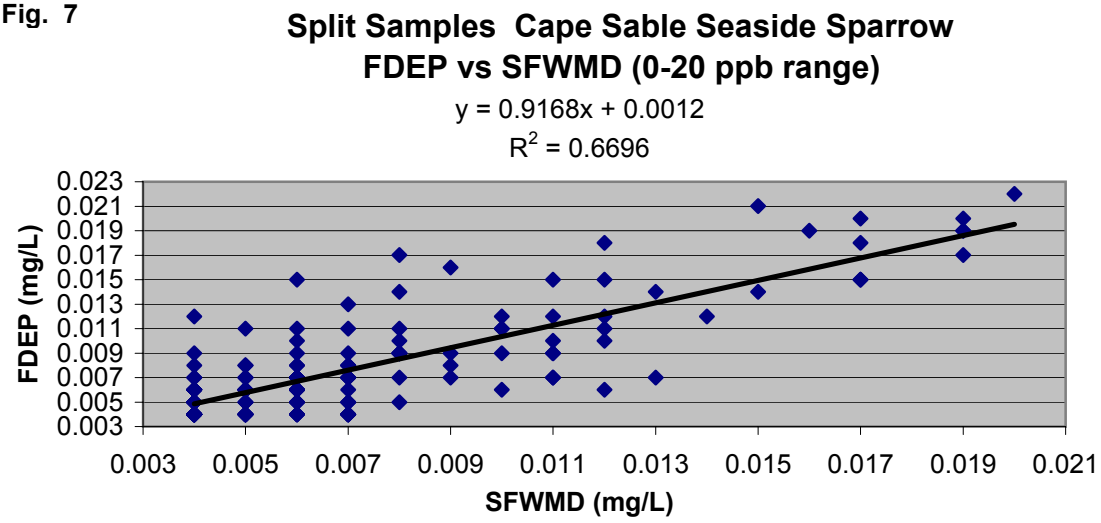


Fig. 8

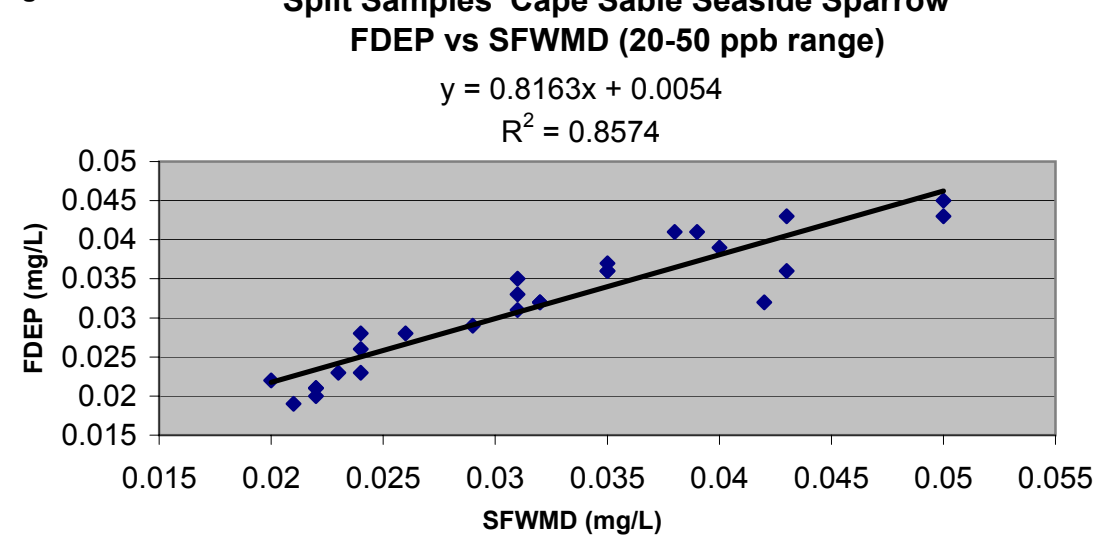
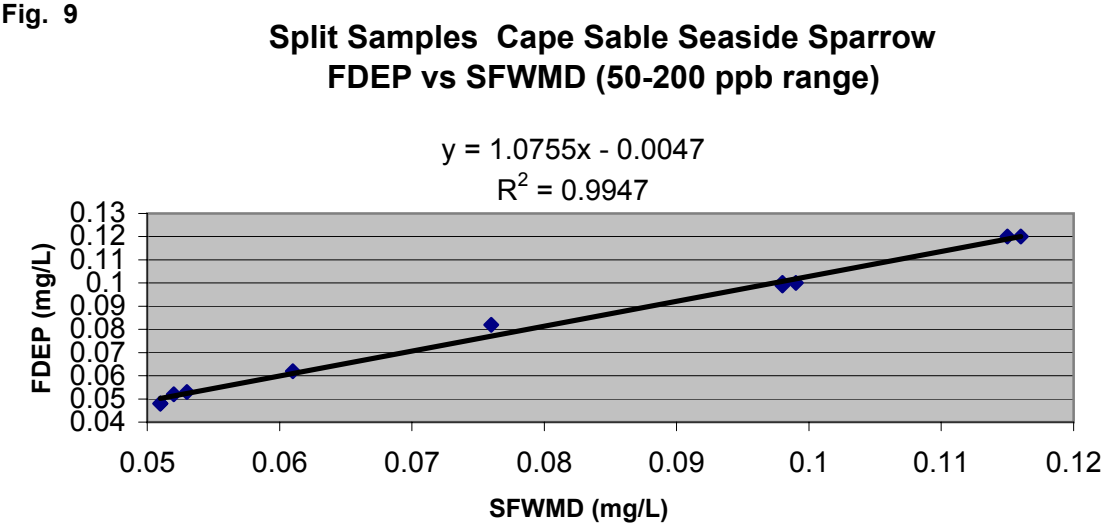


Fig. 9



B. U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples (USGS SRS Study)

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 rated on a scale 0 to 4.

Rating	Absolute Z-value (Rating based on)
4(Excellent)	0.00 to 0.50
3(Good)	0.51 to 1.00
2(Satisfactory)	1.01 to 1.50
1(Marginal)	1.51 to 2.00
0(Unsatisfactory)	>2.01?

The result of the September - October 2002 study is presented in Table 6.

Table 6. USGS SRS Study for TP, September - October 2002

Sample	Reported Value, mg/L	Most Probable Value, mg/L	%R	Rating	Z-Value
M-164	0.248	0.249	99.6	4(Excellent)	-0.05
N-75	0.125	0.128	97.6	4(Excellent)	-0.34
N-76	0.944	0.958	98.5	4(Excellent)	-0.29

M-164=major constituents; N-75, N-76=Nutrient constituents.

C. SFWMD Performance Evaluation (PE) October 2002 Study

This performance evaluation program is coordinated by the District's Quality Assurance Section. A set of samples consisting of a blank, quality control solution, and freshwater field samples is sent to different laboratories, primarily those that are under contract to the District. There were eighteen laboratories that participated in the Fall 2002 study. Samples are sent blind (unknown) to all the laboratories, including the District's laboratory.

Results of the District laboratory are presented in Table 7. The District's results were highly comparable with the median and the QC true value.

Table 7. SFWMD laboratory results in the Fall 2002 SFWMD PE study

Lab	Blank	QC (0.030 mg/L P)	Field Sample 1	Field Sample 2	Spiked Field Sample 2	Sample 1 Duplicate
	mg/L					
Median (n=13)		0.030	0.108	0.026	0.055	0.108
SFWMD	<0.002	0.030	0.105	0.024	0.052	0.105

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.