Quality Assessment Report for Water Quality Monitoring

January - March 2003

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 1st quarter of 2003:

- 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 131 blanks collected except for six 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	78	22	0	N/A
	ENP	3	100	0	0	N/A
	EVPA	3	100	0	0	N/A
	NECP	2	100	0	0	N/A
FB	CAMB	3	100	0	0	N/A
FCEB	CAMB	75	76	16	8	Results > 0.004 were qualified with a "V"
	ENP	12	92	8	0	N/A
	EVPA	19	100	0	0	N/A
	NECP	5	60	40	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	3	4	Precision criteria were met.
NECP	2	13	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	1/8/2003	G136	SS	J3	FAILED QC CRITERIA
CAMB	1/8/2003	S5AU	SAMP	J5	A/S NOT FLOW PROPORTIONAL.
CAMB	1/8/2003	S5AU	SAMP	J5	A/S NOT FLOW PROPORTIONAL.
CAMB	1/8/2003	S7	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	S150	FCEB	V	FCEB > 2 X MDL
CAMB	1/8/2003	S150	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	G123	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	G123	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	S9	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	S9	FCEB	V	FCEB > 2 X MDL
CAMB	1/8/2003	S151	FCEB	V	FCEB > 2 X MDL
CAMB	1/8/2003	S9	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
CAMB	1/8/2003	S150	FCEB	V	FCEB > 2 X MDL
CAMB	1/8/2003	G123	FCEB	V	FCEB > 2 X MDL.
CAMB	1/8/2003	S9	FCEB	V	FCEB > 2 X MDL
NECP	1/8/2003	S9A	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.
NECP	1/8/2003	S9A	SAMP	V	SAMPLE ASSOCIATED WITH POSITIVE FCEB.

B. Field Audits

There was one audit performed for the CAMB and NECP projects during the first quarter of 2003. This collection is done by Broward County Department of Planning and Environmental Protection (DPEP). There was one recommendation and one corrective action concerning their documentation process. The recommendations and corrective actions were communicated verbally at the time of the audit during the exit conference and will be addressed with the next sampling event. The formal written response to the audit report is in process.

Summary of Audit Corrective (CA) and Recommendations (R) for CAMB and NECP Surface Water sample collection (2/25/03)

- (R) Whenever possible, corrections should be made by someone who participated in the sampling event. If not possible, provide a reason for corrections.
- (CA) Note the location where calibration and continuing calibration verification took place in the calibration documentation (DEP SOP FT1000 Section 4.2.2).
- (CA) NIST-traceable thermometer used to check the calibration of the field instruments must have scale marks for every 0.1°C increment (DEP SOP FT1400 Section 1.2).

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, 75 – 125% with a mean of 101.8%.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 98 – 102%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 99.1%.

The precision target for TP analysis during this period was 10.0% and as the report shows, mean %RPD was 1% and 0.8% for low (0.03 to 0.2 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 3.6% and 2.1% for low & high levels, respectively.
There was no data available in the 0 to 0.03 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.

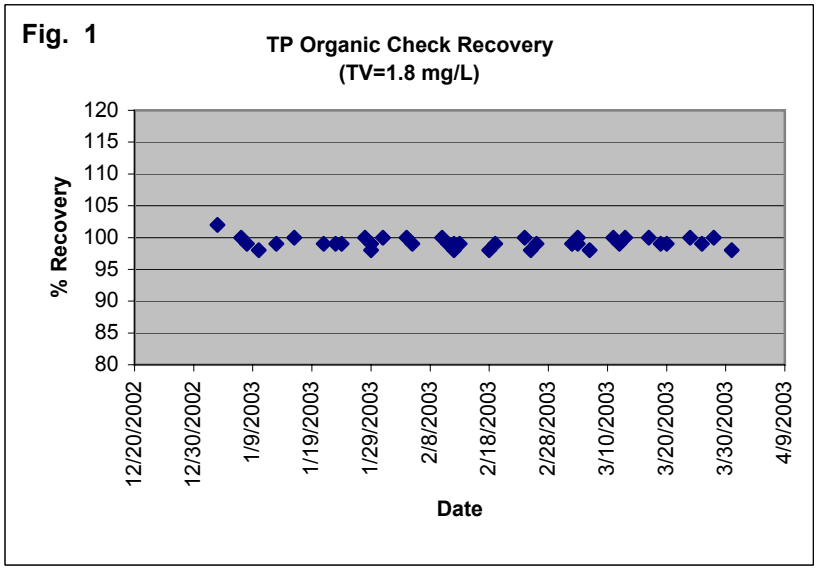
A. Split and Replicate Studies

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 (EB) 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. A Mann-Whitney Test was used to compare the data sets at the different ranges. The null hypothesis was not rejected. The data does not support the hypothesis that there is a difference between the two populations. A Paired t-test of the differences was performed disproving the null hypothesis at the 0-20 ppb range, but not by practical levels.

Table 5. Results of TP split study between SFWMD and FDEP laboratories, EVPA Project, 3/10/03

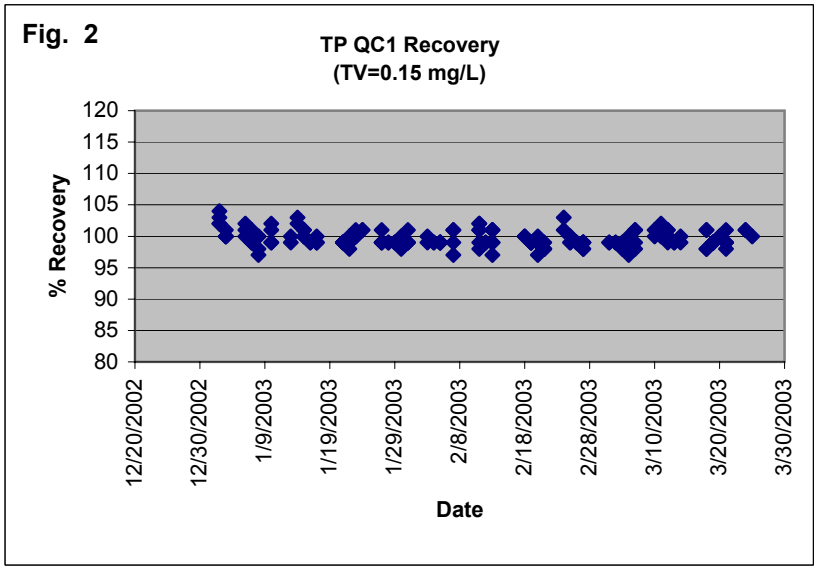
Station	Date Collected	Sample Type		TPO4 Results (mg/L)		Difference (SFWMD-FDEP)	% RPD	Comments
		SFWMD	FDEP	SFWMD	FDEP			
S5AD	3/10/03	EB	EB	<0.002	<0.004	0.000	0.0	<PQL
S5AD	3/10/03	SS	SS	0.116	0.13	-0.014	11.4	
LOX8	3/10/03	SS	SS	0.008	0.010	-0.002	22.2	<PQL
LOX7	3/10/03	SS	SS	0.008	0.011	-0.003	31.6	<PQL
LOX11	3/11/03	SS	SS	0.008	0.010	-0.002	22.2	<PQL
LOX13	3/11/03	SS	SS	0.008	0.010	-0.002	22.2	<PQL
LOX14	3/11/03	SS	SS	0.009	0.010	-0.001	10.5	<PQL

Fig. 1



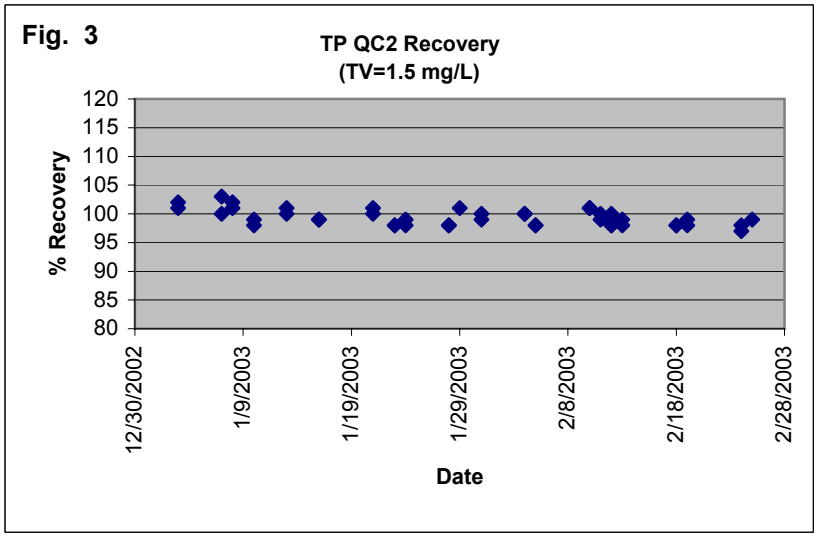
% Recovery Organic Check	MEAN	99.2
	MAX	102
	MIN	98

Fig. 2



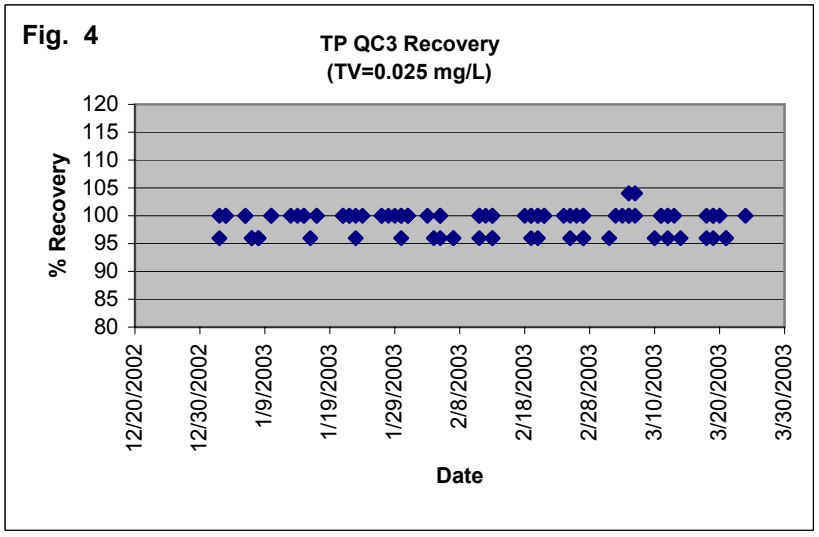
% Recovery QC1	MEAN	99.7
	MAX	104
	MIN	97

Fig. 3



% Recovery QC2	MEAN	99.3
	MAX	103
	MIN	97

Fig. 4



% Recovery QC3	MEAN	98.8
	MAX	104
	MIN	96

Fig. 5

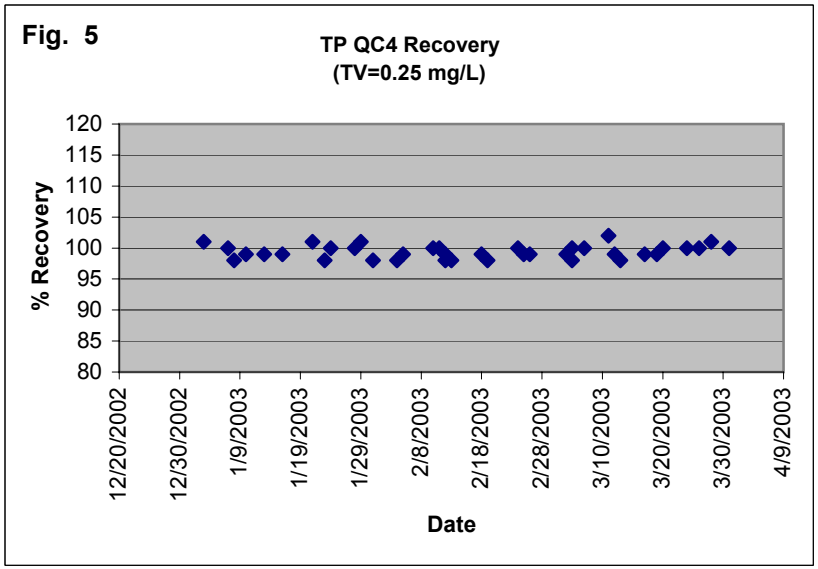
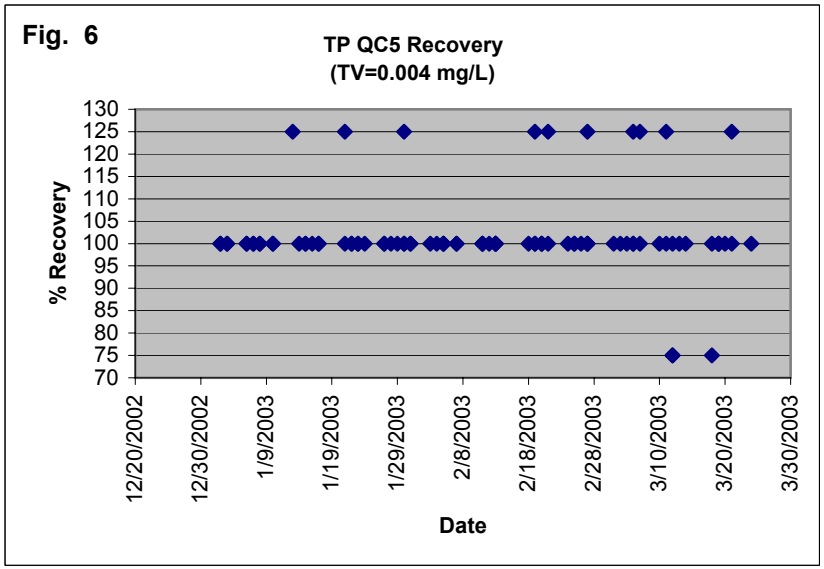


Fig. 6



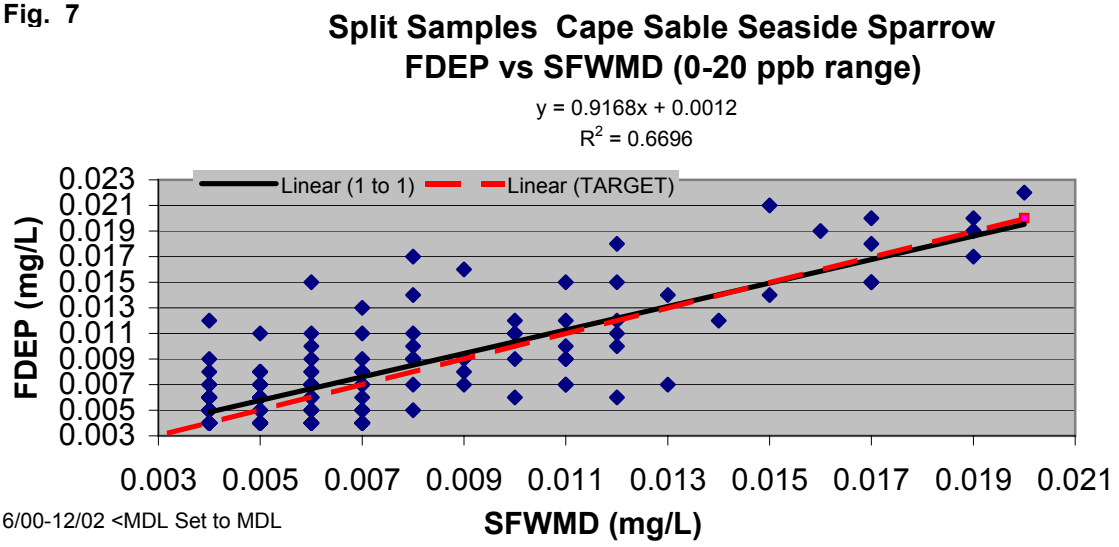
% Recovery QC4	MEAN	99.4
	MAX	102.0
	MIN	98.0

% Recovery QC5	MEAN	101.8
	MAX	125.0
	MIN	75.0

TP Precision Data 1/1/03-3/31/03 Acceptance Limit = <10%			
Low Level (0.03-0.2)		High Level (0.2-2)	
Max	3.6	Max	2.1
Mean	0.8	Mean	0.8
Std Dev	0.86	Std Dev	0.53
3xSD	2.58	3xSD	1.58
UCL	3.4	UCL	2.4
n	255	n	74

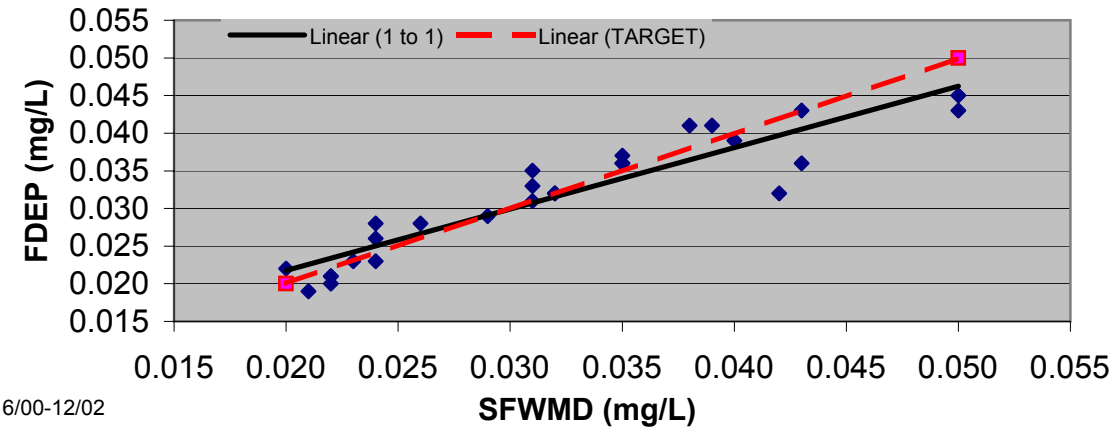
TP Spike Recovery Data 1/1/03-3/31/03 Acceptance Limit = 90-110%			
	Min	70	
	Max	109	
	Mean	99.1	
	Std Dev	4.83	
	3xSD	14.50	
	LCL	84.6	
	UCL	113.6	
	n	318	

Fig. 7



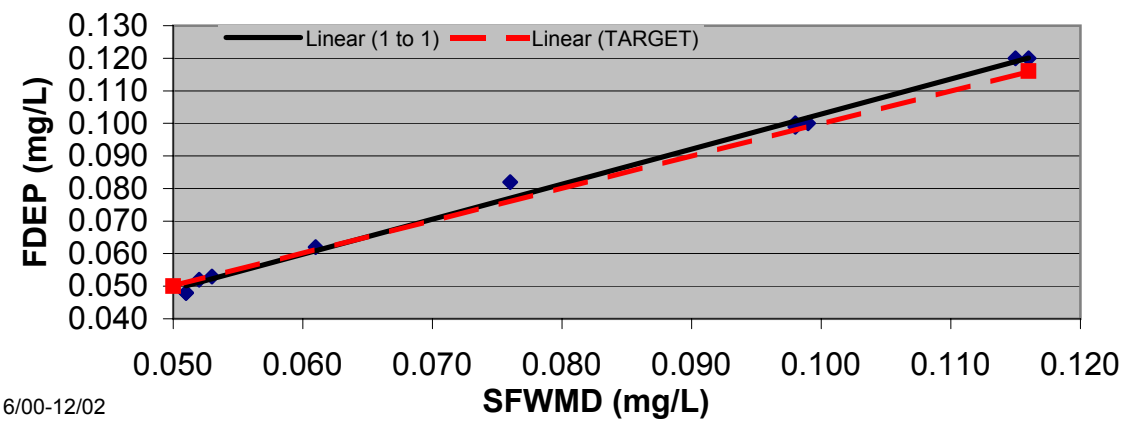
6/00-12/02 <MDL Set to MDL

Fig. 8



6/00-12/02

Fig. 9



6/00-12/02

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 March 2003 study is presented in Table 6.

Table 6. USGS SRS Study for TP, March 2003

Sample	**Reported Value, mg/L**	**Most Probable Value, mg/L**	**%R**	**Rating**	**Z-Value**
M-166	0.057	0.056	1.02	4 (Excellent)	0.11
N-77	0.069	0.065	1.06	3 (Good)	0.83
N-78	0.634	0.640	0.99	4 (Excellent)	-0.19

M-166=major constituents; N-77, N-78=Nutrient constituents.

C. FDEP Everglades Total Phosphorus Round Robin Study

A copy of the Everglades Round Robin 13 study results showing the District's Laboratory performance, as compared with the other participating laboratories is also provided in this report. A general evaluation of the study indicates that the District's results, at all levels, were at or around the central tendency and that analytical precision was excellent. Statistical analysis of this study is being done by FDEP consultant.

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.

Round Robin TP-13

Results (reported as micrograms/liter)

Laboratory	SITE																	
	CA215				S10C			S5A				WCA2F4			WCA2U2			
Metro Dade County Environmental Resources Mgt.	7.43 I 1	7.33 I 5	6.76 I 13	7.41 I 3	61.79 9	59.76 2	60.18 14	108.73 17	109.79 7	109.75 6	110.35 12	12.00 16	12.24 8	12.41 4	36.57 11	37.40 10	35.70 15	35.88 18
U.S. Sugar Corp.- South Bay Laboratory	0.009 17	0.009 16	0.009 7	0.009 9	0.063 11	0.063 18	0.061 1	0.120 3	0.118 10	0.120 8	0.120 2	0.015 14	0.015 12	0.015 15	0.040 4	0.040 5	0.040 13	0.038 6
Everglades Laboratories, Inc.	10.9 15	9.7 6	13.3 2	10.9 11	35.8 7	45.9 14	43.4 8	91.0 12	91.0 3	85.6 13	82.9 17	18.3 18	13.3 1	20.7 16	33.2 4	30.7 9	28.2 10	28.2 5
ELAB, Inc.	0.00680 9	0.00690 18	0.0102 5	0.00740 10	0.0650 13	0.0668 7	0.0641 11	0.123 15	0.120 17	0.124 12	0.123 14	0.0123 4	0.0128 8	0.0107 16	0.0377 1	0.0429 2	0.0397 3	0.0444 6
Duke University School of the Environment	5.0 I 17	4.0 I 1	5.0 I 9	5.0 I 15	63.0 18	63.0 4	63.0 11	115.0 5	116.0 7	115.0 3	114.0 13	10.0 12	10.0 14	10.0 6	35.0 2	36.0 8	35.0 10	36.0 16
Orange County Environmental Protection Division	8 16	7 10	7 2	7 5	64 17	61 13	50 4	120 6	110 18	120 8	120 14	12 15	11 7	12 12	37 11	31 3	37 1	36 9
Columbia Analytical Services	4.6 5	5.2 13	5.2 16	8.4 3	59.0 8	55.8 7	58.1 10	114 12	113 14	113 15	117 1	11.5 18	11.8 2	14.8 11	33.0 17	35.5 6	36.8 4	32.7 9
Harbor Branch Environmental Laboratory	3.77 12	5.31 13	5.62 4	4.30 14	61.0 11	61.4 5	58.0 8	117 16	142 17	116 9	113 15	9.07 6	11.8 10	10.7 1	31.2 7	54.2 18	34.9 2	34.5 3
TestAmerica, Inc	7.0 11	7.0 12	7.0 16	7.0 17	67.0 4	64.0 1	64.0 13	121 5	127 15	121 9	121 18	13.0 14	10.0 8	10.0 2	34.0 7	37.0 6	37.0 10	34.0 3
Short Enivronmental Laboratories	6 17	6 6	7 18	6 4	61 1	62 10	62 14	116 11	115 7	116 16	112 15	12 9	12 13	12 8	36 2	35 5	38 12	35 3
US Biosystems, Inc	6.4 I 3	6.5 I 5	6.2 I 13	6.1 I 8	60 16	60 12	60 10	111 15	114 4	111 9	113 18	11 6	11 7	11 14	34 17	34 11	34 1	34 2
FL Dept. of Environmental Protection	7 I 12	7 I 4	6 I 5	8 I 17	63 3	63 13	60 18	114 9	115 7	115 16	113 15	11 10	11 14	11 6	34 1	36 2	37 11	36 8
South FL Water Mgt. District	7 1	7 11	7 9	7 17	62 10	63 13	63 4	112 18	111 3	108 7	111 6	11 15	12 14	11 12	36 8	34 16	35 2	34 5
USGS - Ocala	6.5 10	6.5 8	6.7 15	6.5 13	56 4	56.3 7	56.5 11	86.2 3	86.4 17	86.4 6	85.7 14	10.1 2	9.5 16	9.8 9	36.1 12	36.4 18	35.8 5	36.1 1
Collier County Pollution Department	0.012 I 4	0.012 I 14	0.011 I 7	0.012 I 10	0.030 6	0.030 8	0.031 3	0.084 15	0.087 12	0.087 2	0.104 17	0.017 I 9	0.019 I 5	0.019 I 16	0.041 18	0.038 13	0.035 11	0.041 1
Lee County Environmental Labs	0.001 T 16	0.001 T 9	0.001 T 8	0.000 TU 3	0.043 17	0.054 7	0.048 18	0.111 10	0.076 11	0.086 12	0.043 4	0.006 15	0.007 2	0.009 1	0.025 14	0.029 13	0.042 5	0.024 6
IFAS Everglades Research & Education Center	10 I 9	8 T 7	9 T 6	7 T 3	60 11	59 8	60 18	112 10	108 2	108 5	108 12	12 I 15	10 I 13	12 I 16	33 4	35 1	36 14	33 17
FL International University	7 13	10 7	10 6	7 18	57 9	62 8	62 17	114 16	114 15	118 5	113 11	10 14	13 2	12 12	38 1	36 3	37 10	36 4
STL-Miami Lab	20.0 7	18.0 14	9.0 1	11.0 6	61.0 13	57.0 4	64.0 15	130.0 3	136.0 17	132.0 8	137.0 2	14.0 11	14.0 5	24.0 9	43.0 18	36.0 16	38.0 10	40.0 12
DB Environmental Laboratories, Inc.	6 I 1	7 I 16	7 I 12	8 I 3	58 15	58 2	61 13	113 8	114 4	112 7	114 9	11 I 6	13 10	11 I 17	34 11	35 18	34 14	35 5
PPB Environmental Laboratories, Inc.	7 I 6	7 I 18	7 I 4	7 I 5	65 1	63 15	64 7	119 8	119 17	120 13	120 12	12 I 14	12 I 10	12 I 9	37 3	37 16	38 11	37 2
UF/IFAS-Wetlands Biogeochemistry Laboratory	6 17	5 1	6 5	6 15	62 6	60 18	60 14	110 11	110 8	113 13	110 3	11 9	11 4	11 10	36 12	36 2	34 7	35 16