Quality Assessment Report for Water Quality Monitoring

July - September 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 3rd 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

Field QCs are collected for trips that include multiple project samples for the stations of interest, so the report may also cover information on stations or project other than those listed above.

The South Florida Water Management District's Field and Lab Quality Manuals require 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.

Included also in this report are an analysis of the District's laboratory's performance on split or replicate studies with FDEP 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 155 blanks collected except for 6 were within the acceptance criteria. Table 2 summarizes field precision results. In general, field sampling precision was excellent. Split samples are summarized in Table 5.

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	QC Criteria met?
EB	CAMB	4	75	25	0	Y
	ENP	3	100	33	0	Y
	EVPA	3	67	33	0	Y
	NECP	1	100	0	0	Y
FB	ENP	1	100	0	0	Y
FCEB	CAMB	91	76	19	5	No, 5 blanks flagged
	ENP	23	100	0	0	Y
	EVPA	20	95	5	0	Y
	NECP	9	89	0	11	No, 1 blank flagged

Table 2. Field precision summary

Project Code	Numbers of triple	Mean % RSD	Comments
CAMB	6	5.9	Precision criteria were met.
ENP	0	N/A	N/A
EVPA	7	1.7	Precision criteria were met.
NECP	2	6.8	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 – 3% of data flagged

Project	Date Collected	Station	Type	Flag Code	Result mg/L	Comments
CAMB	9-Jul-03	S6	Sample	J5	0.063	Auto-sampler not flow proportional
CAMB	12-Aug-03	S9	Sample	V	0.025	Sample associated w/pos. FCEB value
NECP	12-Aug-03	S9A	Sample	V	0.017	Sample associated w/pos. FCEB value
CAMB	12-Aug-03	S7	FCEB	V	0.009	FCEB>2MDL
CAMB	5-Aug-03	S140	FCEB	V	0.008	FCEB>2MDL
CAMB	5-Aug-03	C123SR84	Sample	V	0.019	Sample associated w/pos. FCEB value
CAMB	5-Aug-03	G123	Sample	V	0.018	Sample associated w/pos. FCEB value
CAMB	22-Jul-03	G123	Sample	Y	0.003	Improper preservation pH<1
CAMB	4-Aug-03	S34	FCEB	V	0.008	FCEB>2MDL
CAMB	4-Aug-03	S38	Sample	V	0.015	Sample associated w/pos. FCEB value
CAMB	26-Aug-03	G123	Sample	V	0.020	Sample associated w/pos. FCEB value
CAMB	26-Aug-03	G123	Sample	V	0.017	Sample associated w/pos. FCEB value
CAMB	26-Aug-03	G123	FCEB	V	0.007	FCEB>2MDL
CAMB	18-Aug-03	S8	Sample	J5	0.057	Auto-sampler malfunction
CAMB	27-Aug-03	S6	Sample	Y	0.084	Improper preservation

Project	Date Collected	Station	Type	Flag Code	Result mg/L	Comments
CAMB	3-Sep-03	S8	Sample	J5	0.072	Auto-sampler not flow proportional
CAMB	3-Sep-03	S6	Sample	Y	0.065	Improper preservation
CAMB	2-Sep-03	G123	Sample	V	0.015	Sample associated w/pos. FCEB value
CAMB	2-Sep-03	G123	Sample	V	0.012	Sample associated w/pos. FCEB value
CAMB	2-Sep-03	G123	FCEB	V	0.005	FCEB>2MDL
CAMB	15-Sep-03	S11A	Sample	J3	0.016	Reversal OPO4>TPO4
CAMB	16-Sep-03	S9	Sample	V	0.017	Sample associated w/pos. FCEB value
CAMB	16-Sep-03	S9	Sample	V	0.015	Sample associated w/pos. FCEB value
NECP	16-Sep-03	S9A	Sample	V	0.014	Sample associated w/pos. FCEB value
NECP	16-Sep-03	S9A	FCEB	V	0.006	FCEB>2MDL
NECP	16-Sep-03	S9A	Sample	V	0.012	Sample associated w/pos. FCEB value
NECP	15-Sep-03	S142	Sample	J3	0.020	Reversal OPO4>TPO4

Table 4 Missing TPO4 results

Project	Date Collected	Station	Type	Comments
ENP	2-Jul-03	S176	Sample	Gate close, no flow
EVPA	14-Jul-03	LOX3	Sample	TDepth <0.1 m
EVPA	14-Jul-03	LOX4	Sample	TDepth <0.1 m
EVPA	14-Jul-03	LOX5	Sample	TDepth <0.1 m
EVPA	14-Jul-03	LOX9	Sample	TDepth <0.1 m
EVPA	14-Jul-03	LOX10	Sample	TDepth <0.1 m
ENP	16-Jul-03	S177	Sample	Gate close, no flow
ENP	16-Sep-03	S176	Sample	Gate close, no flow
NECP	11-Aug-03	S334	Sample	No flow
NECP	8-Sep-03	S334	Sample	Gate close, no flow
EVPA	9-Sep-03	LOX13	Sample	TDepth <0.1 m
ENP	10-Sep-03	S176	Sample	Gate close, no flow

B. Field Audits

There were three audits performed for the EVPA project and two audits performed for the CAMB project during the third quarter of 2003.

1) Summary of corrective actions for the EVPA audit conducted on 8/13/03, for the sample collection performed by The District's Research sampling group. (ERG)

- Include which equipment was cleaned in the cleaning logbook.
- Include the date and initials of the person performing the cleaning in the cleaning logbook.
- Include the time of collection on the sample bottles.
- Perform an Initial Calibration Verification (ICV) using a standard less than the expected range of readings for the sampling trip.
- Place a 'P' or 'F' on the calibration sheet in the Qualifications column denoting whether the calibration or verification passed or failed. If a calibration or verification fails, place a note concerning the failure and the action taken to correct the failure in the "Notes" section of the calibration sheet.

- Process samples within four hours of sample collection. Document the processing time in the comment section of the header sheet and in the field notes to allow assessment of compliance with the 4-hr processing time.

Responses to this audit were received and corrective action plan was satisfactory.

2) Summary of corrective actions and recommendations for the first EVPA (FWS) audit conducted on 8/11/03. for the sample collection performed by US Fish and Wildlife sampling group.

- Place the cap on the sample bottles when doing the sample bottle rinse.
- Write the open date for the preservation acid on the outside of the container. This will enable the sampling personnel to assess how long the bottle of preservative has been in use.
- Initial all corrections including the crossing off of parameters listed on the header sheet or put initials in the "Parameters crossed out by" space at the bottom of the header sheet.
- Identify "continued on" page at the bottom of the field notebook page.
- If new environmental samples are encountered outside the range of the initial verification, check the instrument calibration with standards bracketing the range of sample values.

The responses to all corrective actions were satisfactory.

3) Summary of the corrective actions recommendations for the EVPA (FWS) audit of split sample processing procedure conducted on 9/8/03.

- Thoroughly mix the composite sample in the sample bucket immediately prior to pouring the sample and split.
- It is recommended that the sample and split be processed into the appropriate sample containers consecutively (within 1-2 minutes). Alternatively, fill the sample and split containers with consecutive aliquots of the parent sample, filling one bottle half full and then the other, until both bottles are filled.

The responses to all corrective actions were satisfactory.

4) Summary of the corrective actions for the first CAMB audit conducted on 8/12/03 for the sample collection performed by District's STA sampling group.

- List collector's initials at the top of all field notes pages
- List visitors or other personnel at the sampling site in the field notes.

The response to the corrective actions was satisfactory

5) Summary of the corrective actions recommendation for CAMB audit conducted on 9/3/03 for the sample collection performed by ELC sampling group.
   - Ensure that the collection device is capable of retrieving sample at discrete/specific depth (0.5 m when appropriate). Include a notation in the field notes if samples are not collected at 0.5m.
   - Identify which equipment was cleaned in the equipment cleaning logbook.
   - Take water samples using the sample bottle dipper standing near the surface of the water and ensure the bottle is inserted neck first. If the water must be sampled from several feet above the water surface, use a discrete depth sampler (Van Dorn) to collect sample.
   - Indicate whether the calibration passed or failed in the multiparameter documentation.

The response to the corrective action was satisfactory

C. Changes in Data Assessment Protocols

Effective 10/01/03 EB and FCEB > MDL will be qualified. Also, affected samples (samples with concentrations < 5x the EB or FCEB value) will be qualified. This change is consistent with DEP, EPA and new automated data review process "ADAPT" being implemented at the District and its contract laboratories.

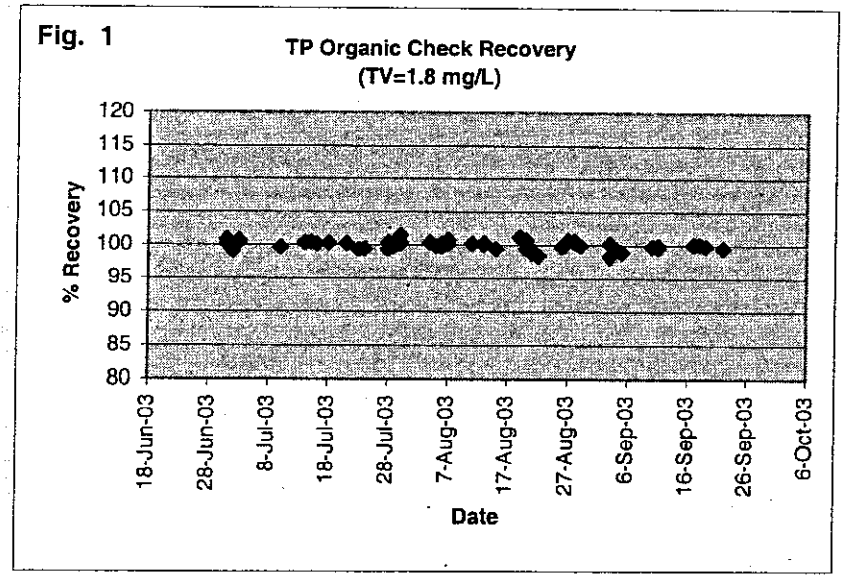
III. Laboratory Quality Control Assessment

Routine laboratory QC samples include QC checks, matrix spikes and precision checks.
The charts presented in Figures 1-5 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 are flagged accordingly if any deficiency is noted and if the samples have exceeded the required holding times and can not be reanalyzed.

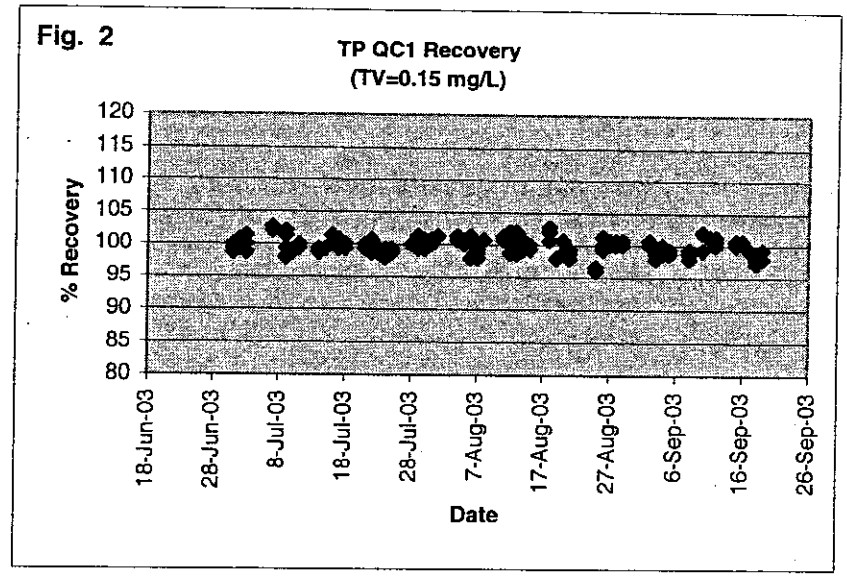
Acceptable recoveries for the QC samples are generally within ± 10% from the true value, which are acceptable. Results indicate the laboratory consistently achieved the 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 97 – 101%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.8%.

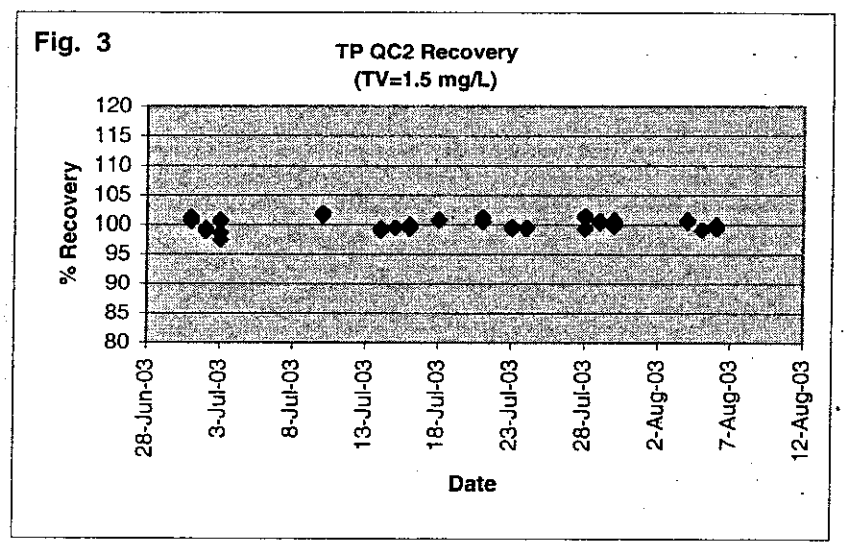
The precision target for TP analysis during this period was 10.0% and as the report shows, mean %RPD was 1.1% and 0.8% for low (0 to 0.2 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 7.1% and 3.4% for low & high levels, respectively.



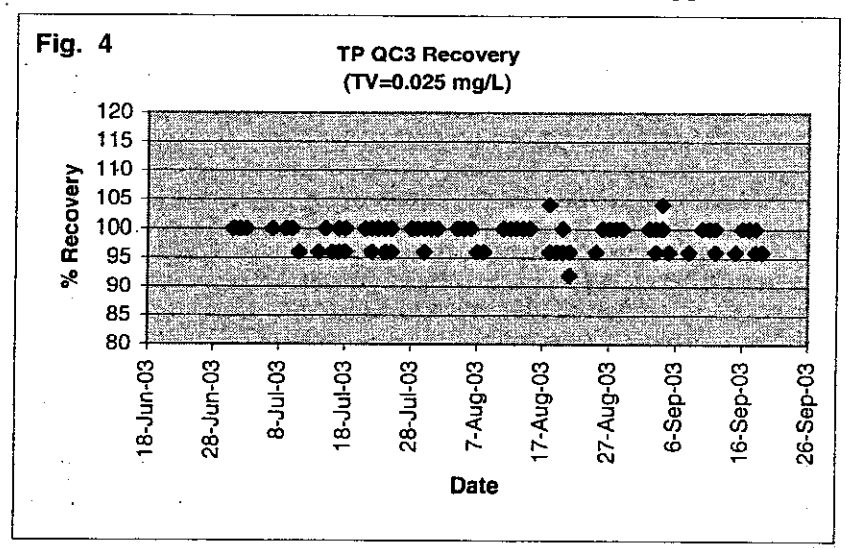
% Recovery Organic Check		
	MEAN	99.8
	MAX	101.4
	MIN	96.8



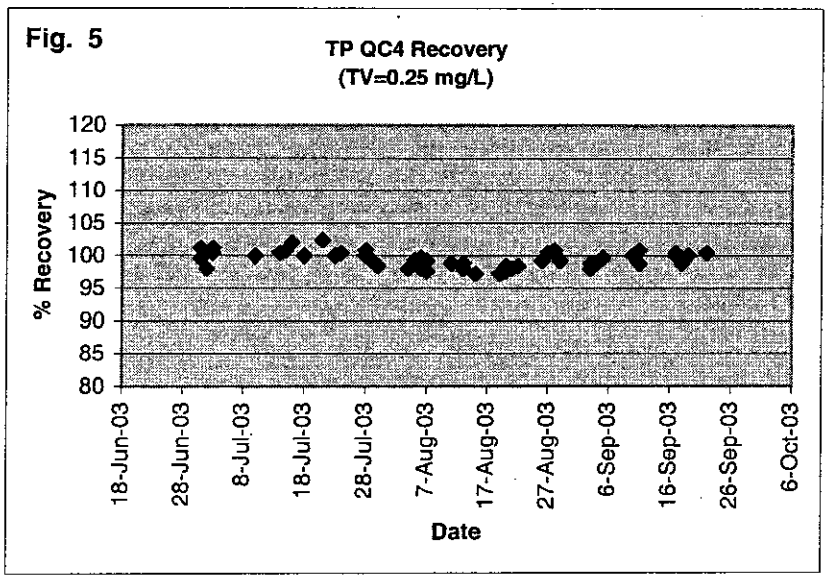
% Recovery QC1		
	MEAN	99.7
	MAX	102.7
	MIN	96



% Recovery QC2		
	MEAN	99.6
	MAX	101.9
	MIN	96.3



% Recovery QC3		
	MEAN	98.7
	MAX	104
	MIN	92



% Recovery QC4	MEAN	99.4
	MAX	102.4
	MIN	97.2

TP Precision Data 4/1/03-6/30/03 Acceptance Limit = <10%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	7.1	Max	3.4
Mean	1.1	Mean	0.8
Std Dev	1.16	Std Dev	0.75
3xSD	3.47	3xSD	2.24
UCL	4.6	UCL	3.0
n	227	n	76

TP Spike Recovery Data 4/1/03-6/30/03 Acceptance Limit = 90-110%			
	Min	89.7	
	Max	110	
	Mean	100.8	
	Std Dev	3.19	
	3xSD	9.58	
	LCL	91.2	
	UCL	110.3	
	n	293	

IV. Inter Laboratory Quality Control Assessment

A. Split and Replicate Studies

To continually assess comparability of results, among laboratories the District sends split samples to other laboratories on a routine basis. The inter laboratory QC assessment includes a special quarterly split study with the Florida Department of Environmental Protection's laboratory.for samples collected from the Loxahatchee National Refuge site (EVPA Project).

The result of the latest split study is presented in Table 5. Both laboratories obtained acceptable blank (EB) results. All results pairs met the precision criteria. Values below the PQL have inherent greater variability and thus are not good indicator of inter laboratory comparability. Results for other split studies, which the District laboratory has participated in are also attached.

Table 5. Results of TP split study between SFWMD and FDEP laboratories, EVPA Project, 9/8-9/2003

Station	Date Collected	Sample Type	TPO4 Results (mg/L)		Difference (SFWMD-FDEP)	% RPD	Comments
			SFWMD	FDEP			
S5AD	8-Sep-03	EB	0.004	<0.004 (U)	MDL	MDL	
S5AD	8-Sep-03	SS	0.148	0.160	- 0.012	7.8	
LOX3	8-Sep-03	SS	0.014	0.011	0.003	24.0	<PQL
LOX6	9-Sep-03	SS	0.006	0.008	- 0.002	28.6	<PQL
LOX11	9-Sep-03	SS	0.007	0.008	- 0.001	13.3	<PQL

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 September 2003 study is presented in Table 6.

Table 6. USGS SRS Study for TP, September 2003

Sample	Reported Value, mg/L	Most Probable Value, mg/L	%R	Rating	Z-Value
M-168	0.128	0.132	97.0	4 (Excellent)	-0.30
N-79	0.149	0.149	100.0	4 (Excellent)	0.00
N-80	1.00	1.00	100.0	4 (Excellent)	0.00

M-168=major constituents; N-79, N-80=Nutrient constituents.

C. FDEP Everglades Total Phosphorus Round Robin Study

A copy of the Everglades Round Robin 14 study results showing the District's Laboratory performance, 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 near the central tendency and that analytical precision was excellent. Statistical analysis of this study is being done by FDEP consultants.

Round Robin TP-14

Results (in ug/L)

Laboratory	SITE																	
	S10-C				S-5A				WCA215			WCA2F2			WCA2F4			
ELAB, Inc.	58.6 1	55.8 4	56.5 6	55.0 8	180 3	195 7	178 16	178 13	5.10 12	4.10 15	4.30 14	38.5 11	34.2 2	38.9 9	9.40 17	10.9 5	9.90 10	10.1 18
Everglades Laboratories, Inc.	46.0 1	63.3 13	50.3 6	58.1 12	130 8	127 17	137 15	120 2	8.67 11	6.94 10	19.9 16	40.8 4	32.9 7	41.6 5	15.6 3	15.6 14	24.3 18	19.9 9
Harbor Branch Environmental Laboratory	57.1 15	55.8 9	54.4 10	54.2 18	173 16	172 14	170 12	177 7	4.04 6	3.54 I 17	3.20 I 13	38.1 4	37.4 5	37.8 3	8.30 1	11.5 8	7.56 11	10.2 2
Lee County Environmental Labs	58 2	54 16	54 14	53 6	114 15	123 8	112 18	114 7	16 10	17 9	15 12	41 3	43 1	39 17	21 13	22 5	22 4	21 11
TestAmerica, Inc	94 15	97 11	88 13	91 7	194 12	182 16	200 3	197 5	34 18	16 2	38 10	63 1	72 9	72 4	44 8	44 14	19 17	38 6
USGS - Ocala	58.5 15	58.2 6	58.7 11	58.8 14	169 13	169 1	168 16	169 3	4.1 5	4.3 2	4.4 8	41.7 10	43.0 12	42.3 18	10.4 4	9.6 7	10.1 17	9.9 9
US Biosystems, Inc	55 16	55 11	55 13	55 5	160 17	160 1	160 8	160 4	4.1 I 10	4.4 I 3	4.4 I 6	38 2	38 14	38 18	11 7	11 15	11 9	9.8 I 12
U.S. Sugar Corp.- South Bay Laboratory	61 4	61 6	61 11	61 2	169 7	169 13	169 1	167 14	9 5	9 17	9 9	42 10	42 15	42 12	17 16	17 18	15 3	15 8
STL Miami, Inc.	62.0 17	62.0 6	64.0 3	60.0 1	184 11	184 8	174 18	182 12	11.0 7	12.0 13	11.0 2	47.0 4	43.0 9	42.0 10	19.0 16	17.0 5	17.0 15	16.0 14
Short Enivronmental Laboratories	59 3	57 9	58 2	58 10	167 5	167 17	167 14	172 12	5 13	5 18	6 7	41 1	40 11	41 6	12 4	10 16	10 15	10 8
Metro Dade County Environmental Resources Mgt.	57.77 9	56.94 7	57.05 12	57.89 18	166.75 16	163.87 8	167.75 10	166.81 4	5.29 I 13	5.49 I 15	4.66 I 11	39.44 1	39.33 3	39.91 14	10.42 6	11.19 17	10.95 2	10.90 5
Columbia Analytical Services - Jax	64 2	97 6	66 1	66 10	175 12	167 7	187 16	172 3	10 15	19 18	19 4	111 14	51 17	69 5	19 11	17 9	17 8	56 13
FL Dept. of Environmental Protection	57 11	55 13	55 4	56 10	170 17	175 18	167 15	171 8	7 I 12	6 I 3	6 I 14	42 6	41 5	40 7	12 16	10 2	7 I 1	12 9
Orange County Environmental Protection Division	54 12	53 5	53 6	53 16	166 14	171 1	168 2	162 11	3 I 7	3 I 15	6 I 4	36 18	35 17	35 9	8 I 8	8 I 13	9 3	8 I 10
Collier County Pollution Department	59 12	59 11	60 5	62 14	162 3	161 15	159 16	161 6	11 I 8	15 I 13	11 I 2	41 7	46 4	41 18	18 I 10	15 I 9	18 I 17	18 I 1
South FL Water Mgt. District	55 8	55 1	54 18	55 3	164 11	162 16	163 9	164 2	5 I 5	5 I 7	5 I 14	37 6	37 15	38 10	10 4	10 12	11 17	10 13
PPB Environmental Laboratories, Inc.	55 17	57 15	49 9	54 6	147 11	156 16	146 14	152 1	4 U 10	5 I 7	4 I 18	34 5	37 2	35 3	8 I 4	9 I 13	9 I 12	10 I 8
UF/IFAS Wetlands Biogeochemistry Laboratory	55 11	56 1	54 10	54 9	156 2	158 13	156 17	157 18	4 15	5 12	5 14	38 7	37 16	38 8	11 3	10 4	10 6	10 5
DB Environmental Laboratories, Inc.	60 7	59 4	59 3	61 6	176 15	172 17	173 14	173 12	6 I 16	6 I 10	7 I 2	40 9	40 13	40 8	11 I 5	12 1	11 I 18	11 I 11
UF/IFAS Tropical Research & Education Center	53 13	56 9	53 14	52 1	128 12	129 5	128 3	129 6	8 10	8 4	7 2	37 16	37 11	39 18	14 7	13 17	13 15	13 8
FL International University	58.21 13	59.22 11	53.15 6	59.16 7	120.75 4	109.49 9	120.38 12	119.47 14	4.65 2	4.45 5	7.85 16	38.85 1	37.85 17	42.57 10	11.84 8	10.15 15	11.13 18	6.98 3
Duke University School of the Environment	63.0 12	62.0 7	64.0 3	64.0 5	164.0 17	165.0 13	165.0 15	165.0 16	11.0 10	11.0 14	11.0 9	44.0 18	45.0 2	45.0 6	15.0 4	15.0 8	15.0 1	16.0 11

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.