Quality Assessment Report for Water Quality Monitoring

January - March 2002

Submitted to the
Technical Oversight Committee

Prepared by:

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I. Introduction

This report is an assessment of the SFWMD laboratory and field sampling in Total Phosphorus (TP) monitoring primarily for the following projects/stations during the first 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

The report also include information on stations other than those listed above or other projects since field QCs are collected for trips that include samples for the stations of interest.

The South Florida Water Management District's Comprehensive Quality Assurance Plan (CQAP) 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. The District's laboratory has replaced the CQAP with a Laboratory Quality Manual, to comply with National Environmental Laboratory Accreditation Conference Standards. To comply with requirements under F.A.C. 62-160, a quality manual is also being written for field sampling and testing. The District adopted changes to its water quality sampling quality control and field QC-related data assessment protocols on 3/01/02. A summary of those changes are also included in Section II of this report.

Included also in this report are the results of round robin and proficiency testing studies for which the District laboratory participates in.

II. Field Sampling Quality Assessment

A. Quality Control

Field QC measures consist of equipment blanks (EB), field blanks (FB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FB recoveries for all projects. Less than 2% of almost 600 blanks collected exceeded criteria. Data for samples associated with positive blanks are qualified according to criteria (Table 3). Table 2 summarizes field precision recoveries. 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 recoveries

Type of Blank	Project	# Blanks collected	% with value <0.004	% with value 0.004-0.008	% with value >0.008	Action Taken
FB	CAMB	235	94.4	3	2.6	Results>0.008 were qualified with "V"
	ENP	13	100	0	0	N/A
	EVPA	12	100	0	0	N/A
	NECP	3	100	0	0	N/A
EB	CAMB	237	94.5	3	2.5	Results>0.008 were qualified with "V"
	ENP	43	93	2.3	4.7	Results>0.008 were qualified with "V"
	EVPA	48	100	0	0	N/A
	NECP	4	100	0	0	N/A

Table 2. Field precision summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	45	7.9	Precision criteria were met, except in cases when the mean is <PQL.
ENP	10	10.5	Precision criteria were met, except in cases when the mean is <PQL.
EVPA	15	12.1	Precision criteria were met, except in cases when the mean is <PQL.
NECP	3	0	Precision criteria were met.

Notes

1) All TP analyses were conducted by the District's Chemistry laboratory.
2) Field precision acceptance criteria: <15%. This criteria was applied only if values >PQL.
3) FB and EB acceptance criteria: Must be </=2xMDL.
4) Associated samples are flagged when concentrations are three times the resulting blank values for possibility of contamination.
5) See Section on Changes in QA/QC and Data Assessment Protocols for changes implemented as of 3/1/02.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	1/29/02	S9S34	SAMP	V	Sample associated with positive blank
	1/29/02	S151	SAMP	V	Sample associated with positive blank
	1/29/02	S31	SAMP	V	Sample associated with positive blank
	2/12/02	USSO	SAMP	V	Sample associated with positive blank
	2/12/02	USL3BRS	SAMP	V	Sample associated with positive blank
	2/12/02	S8	SAMP	V	Sample associated with positive blank
	1/2/02	S140	SAMP	V	Sample associated with positive blank
	1/29/02	S31	FB	V	FB>2xMDL
	1/29/02	S31	FCEB	V	FCEB>2xMDL
	1/29/02	S31	SS	V	Sample associated with positive blank
	1/29/02	S31	RS	V	Sample associated with positive blank
	2/12/02	S8	SS	V	Sample associated with positive blank
	2/12/02	S8	FB	V	FB>2xMDL
	3/18/02	S11A	EB	V	EB>2xMDL
	3/19/02	S9	EB	V	EB>2xMDL
	1/2/02	S140	SS	V	Sample associated with positive blank
	1/2/02	S140	RS	V	Sample associated with positive blank
	1/2/02	S140	FB	V	FB>2xMDL
	2/5/02	S9	RS	J3	Failed field precision criteria
	3/19/02	S9	SAMP	J5	Improper field protocol
	3/12/02	S9	SAMP	J5	Improper field protocol
ENP	1/17/02	S332DAS	SAMP	V	Sample associated with positive blank
	1/17/02	S332DAS	EB	V	EB>2xMDL
	1/17/02	S332DAS	SS	V	Sample associated with positive blank
	1/31/02	S332DAS	EB	V	EB>2xMDL
EVPA	1/28/02	CA215	SS	J3	Failed field precision criteria

B. Field Audits

CAMB, ENP, NECP collection by DERM sampling team was audited on March 11, 2002. The sampling team followed proper procedures and QA/QC requirements, except for one deficiency on pH calibration.

***Corrective Action**: A look at the historical pH values reveals most of the values for the sites on this trip have been above pH 7. The pH calibration shall be performed using the pH 7 & pH 10 buffers. If values are measured below pH 7, the pH 4 buffer will be read at the end of day (in addition to the pH 7 and pH 10 buffers) to verify the instrument is reading reliably in that range.*

C. Changes in Field QA/QC and Data Assessment Protocols

The District revised its Field Quality Control program, and consequently its data assessment in terms of field QCs beginning 3/1/02. These changes were in accordance with the revised Florida Administrative Code 62-160, also known as the Florida Department of Environmental Protection's (FDEP) QA Rule. A summary of pertinent changes that are relevant to the contents of this report are presented in Table 4. These criteria presented in Table 4 are those used by SFWMD QA unit in assessing the quality and acceptability of data for all monitoring projects.

Table 4. Changes in field QC protocols and data assessment criteria and protocols for field quality control samples

FQC		Before 3/01/02	After 3/01/02
Lab/pre-Cleaned EB (EB)	Requirement	EB was collected in the beginning of every trip.	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 >2xMDL. Flag first sample on the trip if sample concentration <3x EB value. Assumption: Equipment was cleaned in the lab and affects only the first site. For subsequent sites, use FCEB as reference.	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	FCEB was collected every 20 field samples in every trip.	Collect at least one FCEB per trip.
	Corrective Action	Flag FCEB if >2xMDL. Flag affected samples (samples with concentration <3X FCEB; exclude sample from first site).	Flag FCEB if >2X MDL. Flag all affected samples (samples with concentration <3x FCEB value). Troubleshoot field-cleaning procedures.
Field Blank (FB)	Requirement	FB was collected every 20 field samples in every trip.	Optional, on as needed basis.
	Corrective Action	Flag FB if >2xMDL. Flag affected samples (all samples with concentration <3X FB value).	Troubleshoot accordingly.
Split Sample (SS)	Requirement	Collected SS every 10 samples. All submitted in the same lab as routine sample. Calculate CV (%RSD) between routine sample, SS, and RS.	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	Flag outlier of the three or all if RSD>15%. For A/S samples, flag both SS and routine sample if RPD>15%.	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	Collected RS every 10 samples. All submitted in the same lab as routine sample. Calculate CV (%RSD) between routine sample, SS, and RS.	Collect for each project quarterly, and during training of field staff.
	Corrective Action	Flag outlier of the three or all if RSD>15%. For A/S samples, flag both SS and routine sample if RPD>15%.	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%.
Field Duplicate (FD)	Requirement	For selected projects only; collected every 10 samples.	Optional, based on program requirements.
	Corrective Action	Flag routine sample and FD if RPD>15%.	Troubleshoot accordingly.

III. Laboratory Quality Control Assessment

Routine laboratory QC samples include QC checks, matrix spikes and precision checks.
The charts presented on the following pages 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. 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 after the samples have exceeded the required holding times.

Except for QC5, recoveries for the QC samples are generally within ± 10% from the true value, which are acceptable. QC5, with a true value of 0.006 mg/L, is less than the practical quantitation limit. A wider performance range can be expected at this level, 83.3 – 116.7% with a mean of 101.2%.

Organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 96.6 – 102.6%, indicating that the digestion process was effective. The same material is used to do matrix spikes, the mean recovery for which was 102.2%.

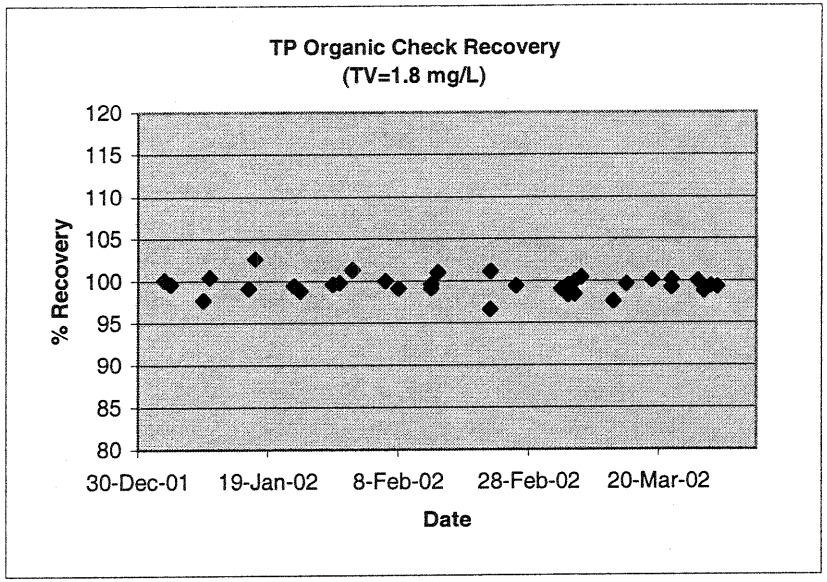
The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 0.96% and 0.49% for low and high level analyses, respectively. The maximum RPD during this period were 3.8% and 1.4% for low & high levels, respectively.

A. Split Study

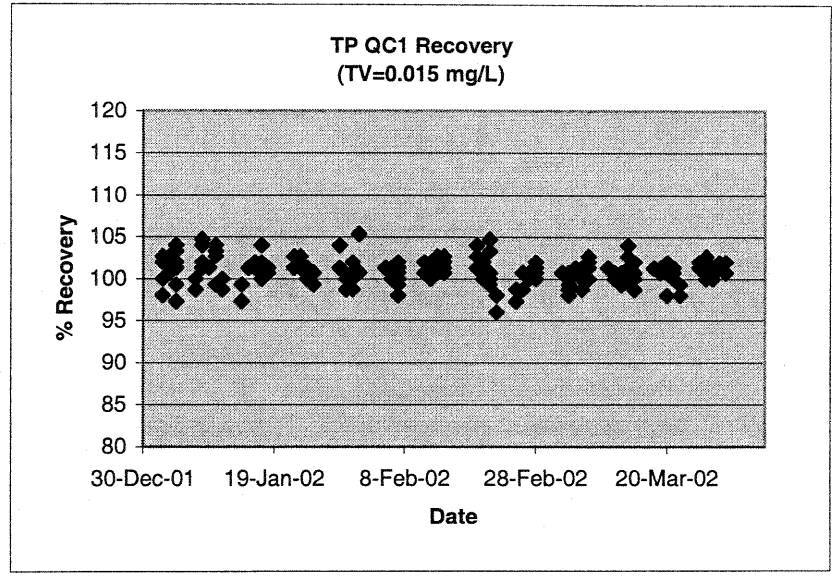
To continually assess comparability of results, the District began splitting samples, collected from the Loxahatchee National Refuge site (EVPA Project), with the Florida Department of Environmental Protection's laboratory. This split study is conducted quarterly. The result of the latest split study is presented in Table 5. Both laboratories obtained acceptable blank (EB and FB) results. Since all pairs of results were <PQL, it was not practical to compare the results. A wide range in results within and between laboratories can be expected at values below the PQL.

Table 5. Results of TP split study between SFWMD and FDEP laboratories, 3/11/02.

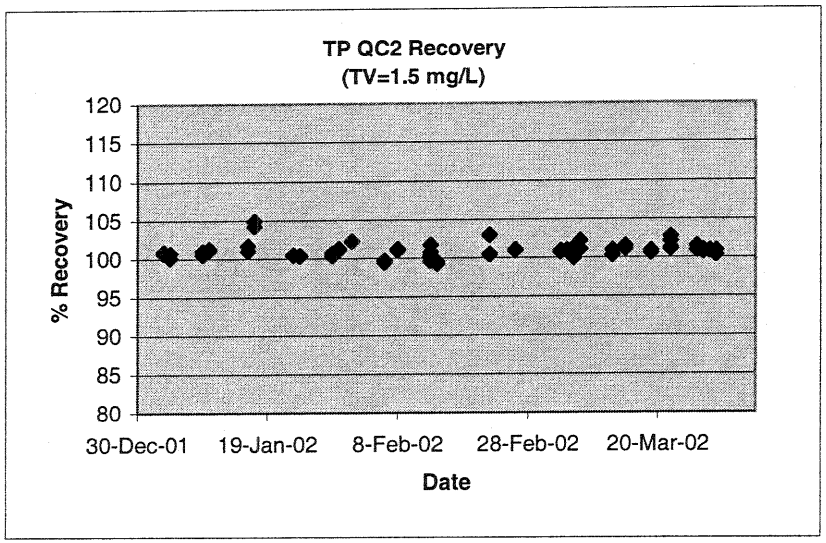
Station	Sampling Date	Type	FDEP	SFWMD	(SFWMD-FDEP)	% RPD	Comments
			mg/L				
S5AD	3/11/02	EB	<0.004	<0.004	0.000	0.0	<PQL
LOX3	3/11/02	SS	0.012	0.008	-0.004	40.0	<PQL
LOX5	3/11/02	SS	0.015	0.013	-0.002	14.3	<PQL
LOX10	3/11/02	SS	0.009	0.006	-0.003	40.0	<PQL
LOX13	3/12/02	SS	0.010	0.008	-0.002	22.2	<PQL
LOX14	3/12/02	SS	0.011	0.007	-0.004	44.4	<PQL
LOX16	3/12/02	SS	0.008	0.008	0.000	0.0	<PQL



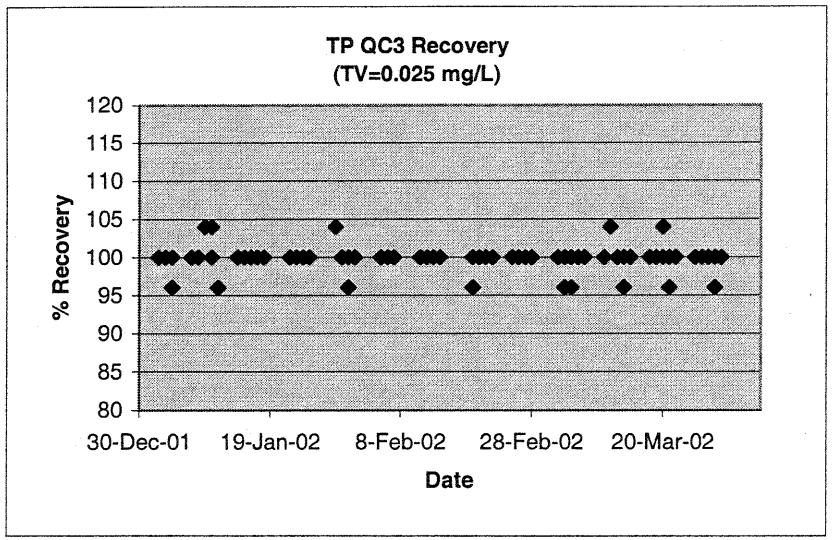
% Recovery Organic Check	MEAN	99.5
	MAX	102.6
	MIN	96.6



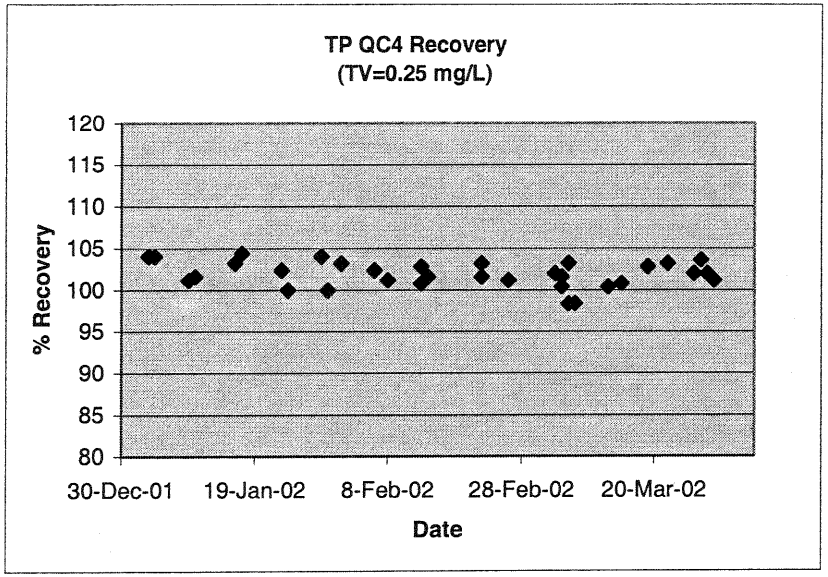
% Recovery QC1	MEAN	100.9
	MAX	105.3
	MIN	96.0

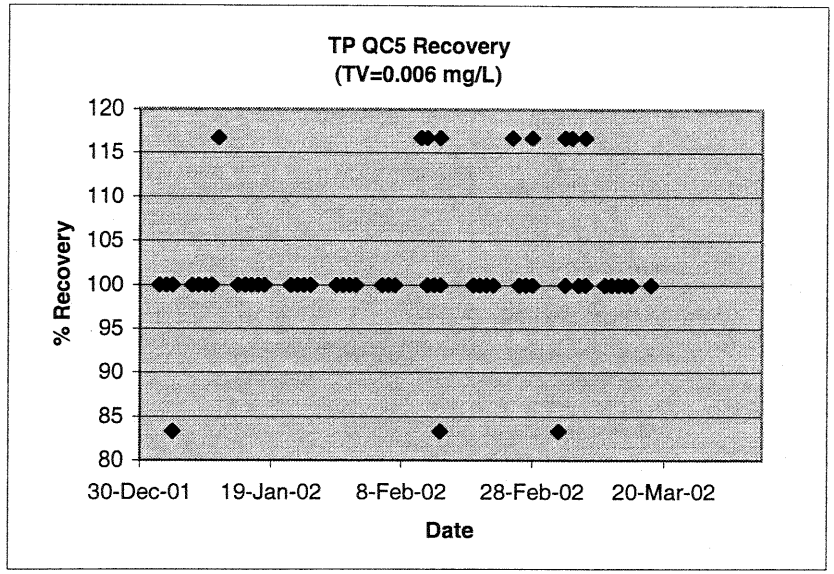


% Recovery QC2	MEAN	101.0
	MAX	104.9
	MIN	99.2



% Recovery QC3	MEAN	99.8
	MAX	104.0
	MIN	96.0





% Recovery QC4	MEAN	101.9
	MAX	104.4
	MIN	98.4

% Recovery QC5	MEAN	101.2
	MAX	83.3
	MIN	116.7

TP Precision Data 1/1/02-3/31/02 Acceptance Limit = <5.0%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	3.8	Max	1.4
Mean	0.96	Mean	0.49
SD	0.92	SD	0.35
n	314	n	37

TP Spike Recovery Data 1/1/02-3/31/02 Acceptance Limit = 90-110%			
	Min	83.3	
	Max	111	
	Mean	102.2	
	Std Dev	2.93	
	3xSD	8.78	
	LCL	93.38	
	UCL	110.94	
	# of Obser	359	

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 December 2001 study is presented in Table 6.

Table 6. Laboratory Proficiency Testing Results for TP, December 2001

Analyte	**Reported Value, mg/L**	**True Value, mg/L**	**%R**	**Status**	**National Ranking**
Sample 1 (WP)	7.42	7.43	99.9	Acceptable	#8 out of 23 laboratories
Sample 2 (APG)	9.15	9.17	99.8	Acceptable	Not ranked

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

C. SFWMD Performance Evaluation (PE) Spring 2002 Study

This is the a performance evaluation program 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 Spring 2002 study. Samples are sent blind (unknown) to all the laboratories, including District's laboratory.

Results of FDEP and District laboratories are presented in Table 7. Except for the spiked sample, the District's results were highly comparable with that of FDEP and the median. For the spiked sample, there was a wide variability in results (standard deviation=0.035).

Table 7. SFWMD and FDEP laboratories results in the Spring 2002 SFWMD PE study

Lab	Blank	QC (0.060 mg/L P)	Field Sample 1	Field Sample 2	Spiked Field Sample 1*	Sample 2 Duplicate
	mg/L					
Median (n=18)			0.018	0.032	0.079	0.032
FDEP	<0.004	0.059	0.021	0.037	0.083	0.037
SFWMD	<0.004	0.059	0.018	0.032	0.104*	0.033

**There was a wide spread on results for the spiked sample. Standard deviation was 0.035.*

D. FDEP Everglades Total Phosphorus Round Robin Study

A copy of the Everglades Round Robin 11 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.

Round Robin TP-11

Results

Laboratory	SITE																	
	G-251				G-253			G-256			S-10C				S-5A			
IFAS Everglades Research & Education Center	0.016 12	0.010 4	0.011 18	0.009 14	0.015 8	0.012 13	0.015 6	0.015 3	0.016 2	0.019 17	0.012 9	0.012 15	0.013 11	0.012 5	0.101 16	0.117 10	0.123 1	0.118 7
Collier County Pollution Department	0.012 I 4	0.012 I 18	0.014 I 14	0.011 I 5	0.014 I 15	0.015 I 6	0.015 I 2	0.018 I 7	0.018 I 17	0.018 I 8	0.012 I 12	0.014 I 1	0.015 I 11	0.012 I 16	0.137 9	0.139 13	0.139 10	0.137 3
Orange County Environmental Protection Division	0.014 5	0.014 2	0.012 14	0.013 6	0.014 16	0.014 7	0.015 9	0.017 13	0.018 12	0.019 15	0.016 4	0.015 18	0.016 1	0.013 10	0.15 17	0.14 11	0.17 3	0.15 8
US Biosystems, Inc	0.011 8	0.014 7	0.011 13	0.011 12	0.012 17	0.014 10	0.014 18	0.019 16	0.020 4	0.020 1	0.013 14	0.011 15	0.011 9	0.014 5	0.16 6	0.16 2	0.16 3	0.16 11
TestAmerica, Inc	0.023 16	0.019 12	0.019 1	0.023 11	0.023 14	0.023 5	0.023 9	0.027 17	0.027 4	0.027 6	0.023 2	0.023 10	0.023 13	0.023 3	0.241 18	0.237 8	0.233 15	0.233 7
FL Dept. of Environmental Protection	0.015 13	0.015 14	0.016 17	0.015 10	0.018 7	0.019 11	0.019 15	0.023 6	0.023 12	0.023 4	0.017 1	0.018 9	0.017 18	0.016 2	0.218 8	0.201 16	0.206 5	0.212 3
USGS - Ocala	0.0141 2	0.0151 14	0.0149 16	0.0143 15	0.0185 18	0.0185 11	0.0182 12	0.0234 4	0.023 5	0.0254 8	0.0179 3	0.0177 1	0.0171 9	0.0171 10	0.1970 13	0.1990 17	0.2000 6	0.1960 7
Duke University School of the Environment	0.014 13	0.017 14	0.014 5	0.014 15	0.014 17	0.018 18	0.017 9	0.020 2	0.020 11	0.020 8	0.017 6	0.014 1	0.017 4	0.014 12	0.208 7	0.207 3	0.209 16	0.209 10
Everglades Laboratories, Inc.	0.009 11	0.018 3	0.009 12	0.018 8	0.018 1	0.018 14	0.018 6	0.018 15	0.018 17	0.018 7	0.009 5	0.016 13	0.009 2	0.018 4	0.166 9	0.151 16	0.161 10	0.156 18
Broward County	0.017 I 9	0.020 16	0.018 I 14	0.016 I 4	0.032 18	0.020 11	0.021 12	0.031 17	0.023 8	0.024 10	0.019 I 3	0.021 2	0.020 6	0.022 5	0.238 13	0.212 15	0.219 1	0.202 7
ELAB	0.0144 7	0.0156 3	0.0144 15	0.0163 14	0.0176 2	0.0186 9	0.0189 12	0.0228 5	0.0260 1	0.0226 16	0.0185 18	0.0178 4	0.0177 17	0.0188 11	0.25 8	0.251 10	0.244 13	0.25 6
CSID Laboratory	0.020 16	0.022 4	0.022 8	0.022 6	0.024 7	0.024 5	0.024 12	0.028 15	0.028 17	0.025 1	0.027 3	0.022 18	0.024 14	0.024 13	0.187 2	0.194 11	0.195 10	0.191 9
Harbor Branch Environmental Laboratory	0.0149 18	0.0129 8	0.0136 5	0.0128 12	0.0156 3	0.0160 13	0.0158 16	0.0206 1	0.0194 6	0.0204 4	0.0155 7	0.0156 11	0.0153 2	0.0144 14	0.179 10	0.178 9	0.187 15	0.191 17
UF/IFAS-Wetlands Biogeochemistry Laboratory	0.015 1	0.015 4	0.014 8	0.015 12	0.017 9	0.018 10	0.018 3	0.022 18	0.021 7	0.022 15	0.016 14	0.016 13	0.016 6	0.016 17	0.183 2	0.180 5	0.182 11	0.183 16
PPB Environmental Laboratories, Inc.	0.012 5	0.013 1	0.012 16	0.012 4	0.016 18	0.014 9	0.014 12	0.018 11	0.019 8	0.020 15	0.014 17	0.014 14	0.014 7	0.014 13	0.195 6	0.194 2	0.199 10	0.195 3
Lee County Environmental Labs	0.0166 11	0.0124 2	0.0188 14	0.0147 7	0.213 13	0.0216 16	0.0179 1	0.0224 9	0.0232 18	0.0217 6	0.0177 12	0.0186 5	0.0172 4	0.0175 8	0 O 17	0.205 15	0.208 10	0.2155 3
STL Tallahassee	0.015 17	0.021 6	0.010 U 8	0.010 U 4	0.010 U 11	0.012 18	0.021 7	0.019 14	0.019 3	0.021 2	0.010 U 16	0.014 15	0.013 12	0.025 9	0.18 5	0.20 13	0.18 1	0.19 10
U.S. Sugar Corp.- South Bay Laboratory	0.020 16	0.020 7	0.020 13	0.020 2	0.023 5	0.023 6	0.023 11	0.027 8	0.029 12	0.027 18	0.023 17	0.023 9	0.023 1	0.023 15	0.194 3	0.196 14	0.196 4	0.194 10
DB Environmental Laboratories, Inc.	0.015 10	0.015 6	0.015 4	0.015 18	0.017 8	0.017 12	0.016 16	0.022 15	0.023 2	0.022 5	0.017 3	0.016 14	0.017 11	0.016 9	0.190 1	0.190 17	0.190 7	0.190 13
Short Enivronmental Laboratories	0.015 18	0.016 2	0.015 3	0.015 12	0.016 5	0.016 14	0.017 7	0.019 8	0.021 4	0.021 17	0.015 11	0.016 15	0.016 10	0.015 9	0.187 16	0.190 1	0.187 13	0.189 6
Columbia Analytical Services - Jax	0.022 12	0.019 17	0.015 4	0.019 11	0.017 6	0.023 3	0.020 14	0.023 1	0.023 15	0.024 10	0.017 2	0.016 7	0.017 8	0.016 13	0.190 16	0.199 18	0.188 5	0.195 9
South FL Water Mgt. District	0.016 6	0.016 14	0.015 12	0.015 4	0.018 16	0.018 2	0.019 1	0.022 8	0.023 15	0.022 18	0.017 11	0.017 5	0.017 17	0.017 7	0.188 9	0.188 3	0.188 13	0.187 10
Metro Dade County Environmental Resources Mgt.	0.014 6	0.015 13	0.014 16	0.014 14	0.017 4	0.016 15	0.017 11	0.021 10	0.021 18	0.021 1	0.016 3	0.016 2	0.015 17	0.016 12	0.180 7	0.176 9	0.175 8	0.181 5

Sample bottle number is listed under each result

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. Maybe an assessment of effectiveness of laboratory decontamination (LCEB) or on-site (field) decontamination (FCEB). EB values are indicative of effectiveness of 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 effectiveness of 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 system over a given time 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.