Quality Assessment Report for Water Quality Monitoring

October - December 2003

Submitted to the
Technical Oversight Committee

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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 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 Field and Lab Quality Manual 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 other laboratories and the results of the Performance Testing Program designed to evaluate the laboratory's performance on the same set of standards.

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. Except for seven blank results, EB recoveries were generally within the acceptance limits. Table 2 summarizes field precision results, and Table 6 summarizes a split study results with FDEP laboratory. Proficiency testing results are used for external quality control and are summarized in Table 7. Data comparison for new and old flagging samples criteria for 2003 is 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	% value ≤0.002	% value >0.002	QC Criteria met?
EB	CAMB	4	100	0	Y
	ENP	3	100	0	Y
	EVPA	3	100	0	Y
	NECP	2	100	0	Y
FB	CAMB	5	100	0	Y
	ENP	1	100	0	Y
FCEB	CAMB	80	91	9	No, 7 blanks flagged
	ENP	23	100	0	Y
	EVPA	20	100	0	Y
	NECP	12	100	0	Y

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	4	7.4	Precision criteria were met.
ENP	1	0.0	Precision criteria were met
EVPA	3	12.6	Precision criteria were met.
NECP	1	2.1	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 ≤MDL.
4) Associated samples are flagged when concentrations are less than five times the resulting blank values for possibility of contamination.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	8-Oct-2003	S6	FCEB	V	FCEB>MDL
CAMB	13-Oct-2003	S34	FCEB	V	FCEB>MDL
CAMB	27-Oct-2003	S145	SAMP	V	Sample associated with positive FCEB
CAMB	27-Oct-2003	S38	SAMP	V	Sample associated with positive FCEB
CAMB	27-Oct-2003	S38B	SAMP	V	Sample associated with positive FCEB
CAMB	27-Oct-2003	S34	FCEB	V	FCEB>MDL
CAMB	28-Oct-2003	G123	FCEB	V	FCEB>MDL
CAMB	12-Nov-2003	G123	FCEB	V	FCEB>MDL
CAMB	24-Nov-2003	S6	SAMP	J5	Not Flow Proportional
CAMB	24-Nov-2003	S151	SAMP	V	Sample associated with positive FCEB
CAMB	24-Nov-2003	S151	FCEB	V	FCEB>MDL
CAMB	16-Dec-2003	S140	SAMP	V	Sample associated with positive FCEB
CAMB	16-Dec-2003	S140	SAMP	V	Sample associated with positive FCEB
CAMB	16-Dec-2003	G123	SAMP	V	Sample associated with positive FCEB
CAMB	16-Dec-2003	G123	SAMP	V	Sample associated with positive FCEB
CAMB	16-Dec-2003	S140	FCEB	V	FCEB>MDL
CAMB	17-Dec-2003	S6	SAMP	J5	Not Flow Proportional

Table 4. Samples not collected or rejected by laboratory.

Project	Date Collected	Station	Type	Comments
ENP	8-Oct-2003	S176	Sample	Gate closed, no flow, no sample collected
ENP	5-Nov-2003	S176	Sample	Gate closed, no flow, no sample collected
ENP	12-Nov-2003	S18C	Sample	Gate closed, no flow, no sample collected
CAMB	17-Nov-2003	S333	Sample	Improper preservation
EVPA	17-Nov-2003	LOX3	Sample	TDepth<0.1 m, no sample collected
EVPA	17-Nov-2003	LOX5	Sample	TDepth<0.1 m, no sample collected
EVPA	17-Nov-2003	LOX9	Sample	TDepth<0.1 m, no sample collected
ENP	3-Dec-2003	S176	Sample	Gate closed, no flow, no sample collected
ENP	17-Dec-2003	S176	Sample	Gate closed, no flow, no sample collected
ENP	24-Dec-2003	S18C	Sample	Gate closed, no flow, no sample collected
CAMB	29-Dec-2003	S12A	Sample	Improper preservation

B. Field Audits

There was no field audit performed for the CAMB, ENP, EVPA or NECP projects during the fourth quarter of 2003.

C. Changes in Data Assessment Protocols

As indicated in July-August 2003 TOC report, effective 10/01/2003 EB and FCEB samples with values > MDL and affected samples (samples with concentrations < 5x the EB or FCEB value) have been qualified. This change is consistent with DEP, EPA and new Automated Data Processing Tool "ADaPT" being implemented at the District and its contract laboratories.

Comparison of Impact of Changes in MDL and Equipment Blank Criteria
As requested by Technical Oversight Committee, a comparison of flagged samples by the new vs. old criteria is summarized in Table 5.

1. **Criteria 1, Old MDL and Blank Criteria (Used until 17-Sep-2002)**
   MDL = 0.004 mg/L
   Criteria :> 2xMDL = >0.008 mg/L
   Minimum positive blank value required for data flagging = 0.009 mg/L
   Criteria for samples: <3 x positive blank value = Qualify sample data falling below this concentration (e.g., <3x 0.009 or <0.027 mg/L, minimum).

2. **Criteria 2, New MDL and Old Blank Criteria (Implemented date 17-Sep-2002)**
   MDL = 0.002 mg/L
   Criteria :> 2xMDL = >0.004 mg/L
   Minimum positive blank value require for data flagging = 0.005 mg/L
   Criteria for samples: <3 x positive blank value = Qualify sample data falling below this concentration (e.g., <3x 0.005 or <0.015 mg/L, minimum).

3. **Criteria 3, New MDL and Blank Criteria (Implemented date 01-Oct-2003)**
   MDL = 0.002 mg/L
   Criteria :> MDL = >0.002 mg/L
   Minimum positive blank value required for data flagging = 0.003 mg/L
   Criteria for samples: <5 x positive blank value = Qualify sample data falling below this concentration (e.g., <5x 0.003 or <0.015 mg/L, minimum).

Table 5. Data Comparison for all criteria and samples collected from January to December 2003

Project	Total Samples Collected	Affected Samples					
		Criteria 1		Criteria 2		Criteria 3	
	#	#	%	#	%	#	%
CAMB	1360	14	0.6	40	1.6	117	4.6
ENP	383	0	0	0	0	0	0
EVPA	582	0	0	5	0.2	7	0.3
NECP	197	0	0	2	0.1	2	0.1
Total	2522	14	0.6	47	1.9	126	5.0

Note: FCEB and EB are collected once per trip, where sampling may be conducted for multiple projects. Data sets are sorted by sampling trip.

III. Laboratory Quality Control Assessment

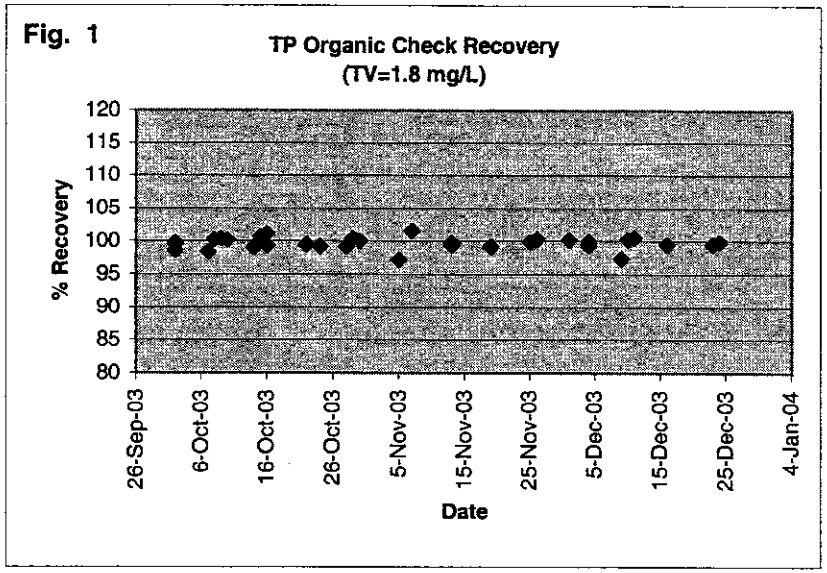
Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. The charts presented in Figures 1-6 show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. In general, an entire analytical run or a portion of the run is rejected if QC recoveries are outside the set limits. Data are flagged accordingly if any deficiency is noted and the samples have exceeded the required holding times and can not be reanalyzed.

Acceptable recoveries for the QC samples were generally within $\pm$ 10% from the true value. The PQL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 101.3%. The PQL check daily 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 – 102%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.7%

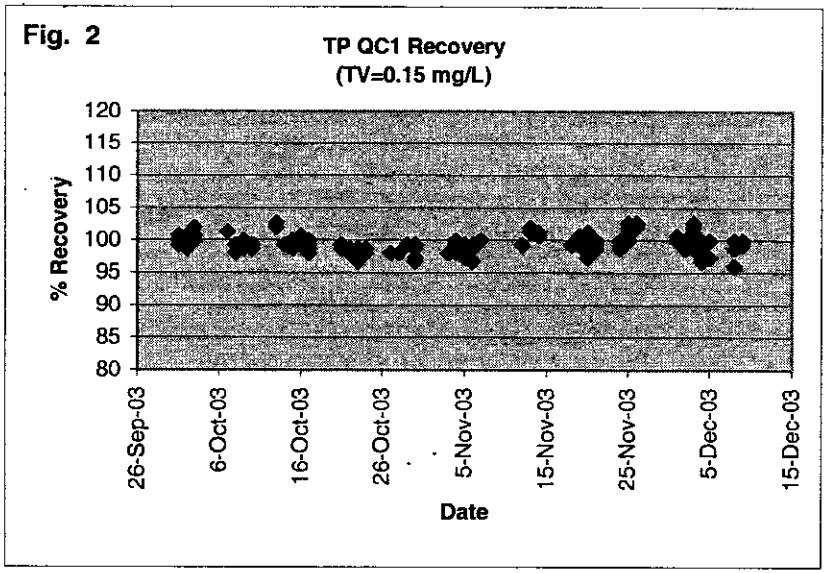
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 1.8% and 1.5% for low (0 to 0.200 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 10.5% and 5.5% for low and high levels, respectively.

Fig. 1



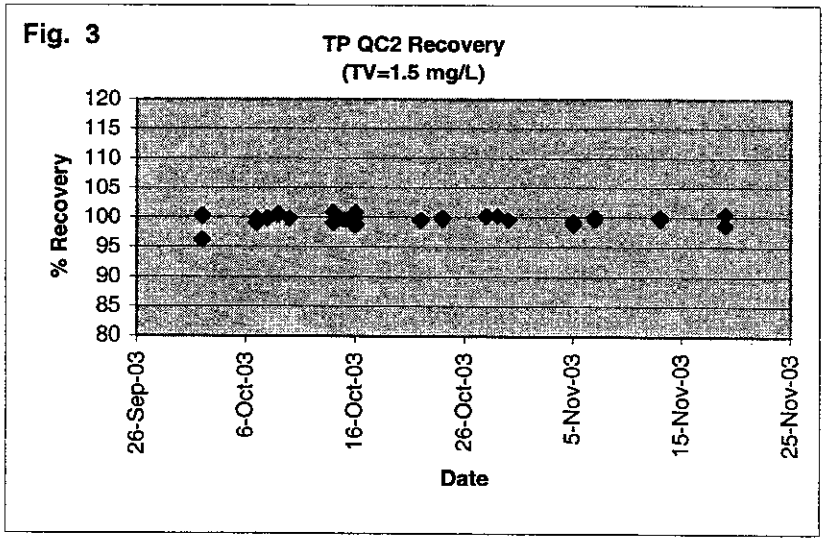
% Recovery Organic Check		
	MEAN	99.7
	MAX	101.6
	MIN	97.2

Fig. 2



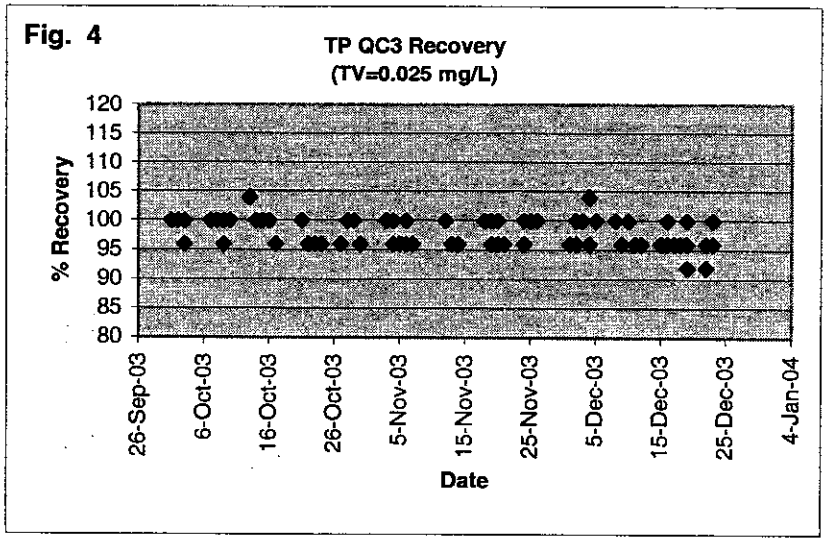
% Recovery QC1		
	MEAN	99.7
	MAX	103.3
	MIN	96

Fig. 3



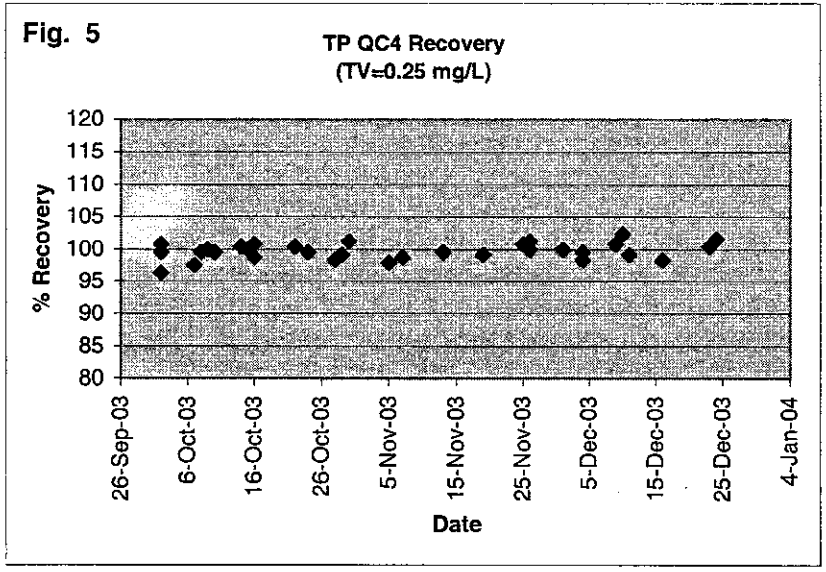
% Recovery QC2		
	MEAN	99.7
	MAX	102
	MIN	96.2

Fig. 4



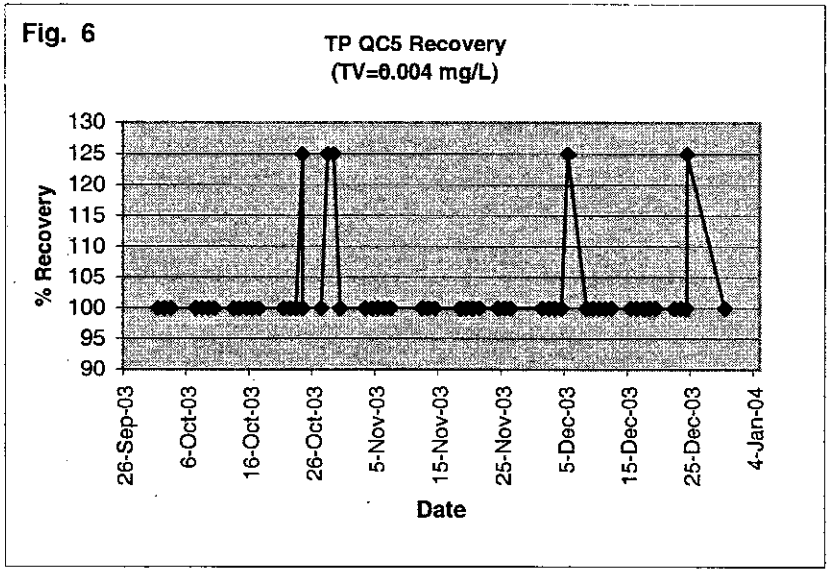
% Recovery QC3		
	MEAN	97.9
	MAX	104
	MIN	92

Fig. 5



% Recovery QC4		
	MEAN	99.7
	MAX	102.4
	MIN	96.4

Fig. 6



% Recovery QC5		
	MEAN	101.3
	MAX	125.0
	MIN	100.0

TP Precision Data 9/1/03-12-31-03 Acceptance Limit = <10%			
Low Level (0-0.2)		High Level (0.2-2)	
Max	10.5	Max	5.5
Mean	1.8	Mean	1.5
Std Dev	1.68	Std Dev	1.16
3xSD	5.05	3xSD	3.49
UCL	6.9	UCL	4.9
n	234	n	34

TP Spike Recovery Data 9/1/03-12/31/03 Acceptance Limit = 90-110%			
	Min	89.5	
	Max	108	
	Mean	100.7	
	Std Dev	3.23	
	3xSD	9.70	
	LCL	91.0	
	UCL	110.4	
	n	269	

IV. Inter Laboratory Quality Control Assessment

A. Split and Replicate Studies

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. This specific project 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 6. Both laboratories obtained acceptable blank (EB) results. Except for two pairs, where samples contained "Very heavy suspended solids" the results pairs met the precision criteria. Values below the PQL have inherent greater variability and thus are not good indicators of inter-laboratory comparability. Results for other split studies, which the District laboratory has participated in, are also attached.

Table 6. Results of TP split study between SFWMD and FDEP laboratories, EVPA Project, 15-Dec-03

Station	Date Collected	Sample Type	TPO4 Results (mg/L)		Difference (SFWMD-FDEP)	% RPD	Comments
			SFWMD	FDEP			
S5AD	15-Dec-03	EB	<0.002	<0.004	<MDL	N/A	<PQL
S5AD	15-Dec-03	SS	0.127	0.150	-0.023	16.6	Acceptable< 20% RPD
LOX3	15-Dec-03	SS	0.010	0.015	-0.005	40.0	Very heavy suspended solids
LOX5	15-Dec-03	SS	0.011	0.013	-0.002	16.7	<PQL
LOX10	15-Dec-03	SS	0.013	0.018	-0.005	32.3	Very heavy suspended solids

C. 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 October 2003 study is presented in Table 7.

Table 7. Laboratory Proficiency Testing Results for TP, October 2003

Sample I.D	Reported Value, mg/L	Assigned Value, mg/L	%Recovery	Status	Rating based on Z-Score
Sample 1 (WP)	3.56	3.49	102.0	Acceptable	Excellent
Sample 2 (APG)	7.85	7.81	100.5	Acceptable	Excellent

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

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.