Quality Assessment Report for Water Quality Monitoring

January - March 2004

Submitted to the
Technical Oversight Committee

Prepared by:

Delia B. Ivanoff and Zdzislaw Kolasinski
Water Quality Analysis Division
South Florida Water Management District
1480-9 Skees Road
West Palm Beach, FL 33411-2642
(561) 681-2500

Quality Assessment Report for Water Quality Monitoring
January-March 2004

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 first quarter of 2004:

- 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 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 other laboratories, the results of the U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples, and the statistical results of the Everglades Total Phosphorus Round Robin XIV.

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 one blank result of the 129, all blanks were within the acceptance criteria. Table 2 summarizes field precision results. Field sampling precision was acceptable.

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	QC Criteria met?
EB	CAMB	6	100	0	Y
	ENP	2	100	0	Y
	EVPA	3	100	0	Y
	NECP	1	100	0	Y
FB	CAMB	6	100	0	Y
FCEB	CAMB	79	99	1	No, 1 blank was flagged
	ENP	12	100	0	Y
	EVPA	12	100	0	Y
	NECP	8	100	0	Y

Table 2. Field precision summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	4	1.9	Precision criteria were met.
ENP	0	N/A	N/A
EVPA	1	0.0	Precision criteria were met.
NECP	2	8.3	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 for possibility of contamination when concentrations are less than three times the resulting blank values.

Table 3. List of flagged data

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	10-Feb-04	S6	SAMP	Y	Autosampler Refrigerator failed
CAMB	16-Mar-04	S5AS	EB	V	FCEB>MDL

Table 4. Samples not collected or rejected by laboratory.

Project	Date Collected	Station	Type	Comments
ENP	14-Jan-2004	S176	Sample	Gate closed, no flow, no sample collected
ENP	29-Jan-2004	S18C	Sample	Quarterly maintenance of auto-sampler
ENP	11-Feb-2004	S18C	Sample	Gate closed, no flow, no sample taken in autosampler
ENP	11-Feb-2004	S176	Sample	Gate closed, no flow, no sample collected
ENP	14-Jan-2004	S177	Sample	Gate closed, no flow, no sample collected
ENP	11-Feb-2004	S177	Sample	Gate closed, no flow, no sample collected
NECP	22-Mar-2004	S334	Sample	Gate closed, no flow, no sample collected

B. Field Audits

Two audits were performed for the CAMB project during the first quarter of 2004. Generally, the field teams were sampling according to approved procedure and QA/QC requirements, except for key findings and corrective actions listed below.

1. CAMB audit conducted on 1/28/2004 by SFWMD field sampling team:
   - The DO probe membrane for multiparameter instrumentation should be changed at least monthly if used regularly.
   - The Calibration Summary Report must include the field sample identification for the samples so the sample readings can be associated with the calibration.
   - The calibration information must include specific standard identification numbers.
   - The calibration information must be recorded to include whether the check met or failed the acceptance criteria.
   - The calibration information must be recorded to include any corrective actions associated with a failed check.

2. CAMB audit conducted on 3/31/2004 by SFWMD field sampling team:
   - Training for the tasks performed by all participants must be documented.
   - Each field logbook entry for a given project day must include the trip frequency (weekly, biweekly, quarterly, etc.).
   - EBs must be collected by pouring analyte-free water into the sample collection container and through each piece of sampling equipment.
   - DO membrane and electrolyte solution should be changed monthly and documented with regular use.
   - Document the field sample identification of the EB for the batch of tubing used at each site for the quarterly autosampler maintenance activity.

The audits indicated general compliance to requirements and standard procedures by the two sampling teams involved and acceptable quality of collection process. The findings were common problems and primarily involved documentation improvement. None of the findings are known to have affected data quality for these projects.

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 spike 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 the samples have exceeded the required holding times and can not be reanalyzed.

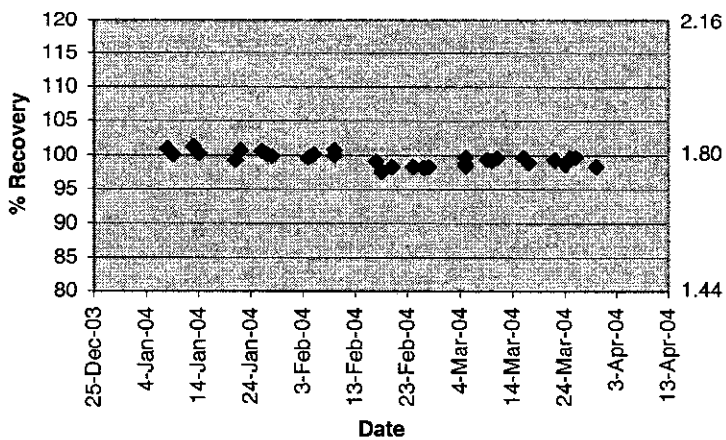
Acceptable recoveries for the QC samples are generally within $\pm$ 10% from the true value. The MDL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 102%. The MDL check daily results indicate the laboratory consistently achieved the 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 97.6 – 101.3%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes; the mean recovery for which was 100.3%.

The precision target for TP analysis during this period was 10.0% and as the report shows, mean %RPD was 1.8% and 1.6% for low (0 to 0.200 mg/L) and high level (0.200-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 8.6% and 4.6% for low and high levels, respectively.

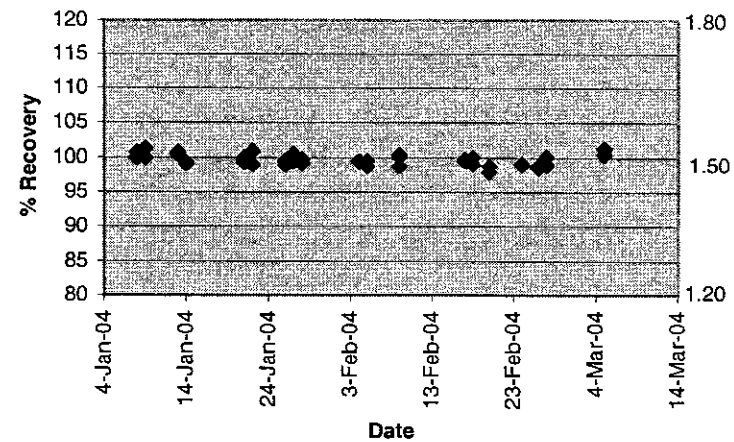
Based on these QC results, it is evident that the District laboratory's performance on TP analysis was excellent and highly acceptable for the various projects analyzed during this reporting period.

Fig. 1



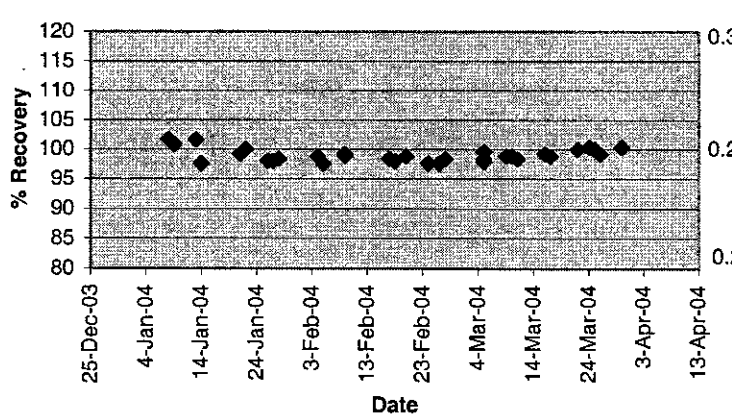
% Recovery Organic Check	MEAN	99.5
	MAX	101.3
	MIN	97.6

Fig. 2



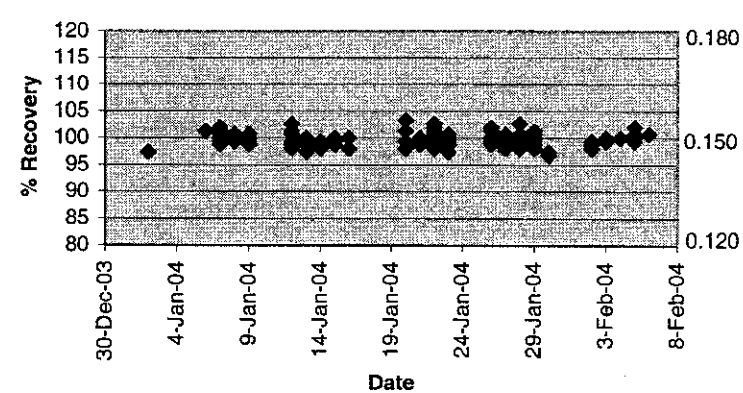
% Recovery QC2	MEAN	99.6
	MAX	101.3
	MIN	97.9

Fig. 3



% Recovery QC4	MEAN	99.0
	MAX	101.6
	MIN	97.6

Fig. 4



% Recovery QC1	MEAN	99.7
	MAX	103.3
	MIN	96

Fig. 5

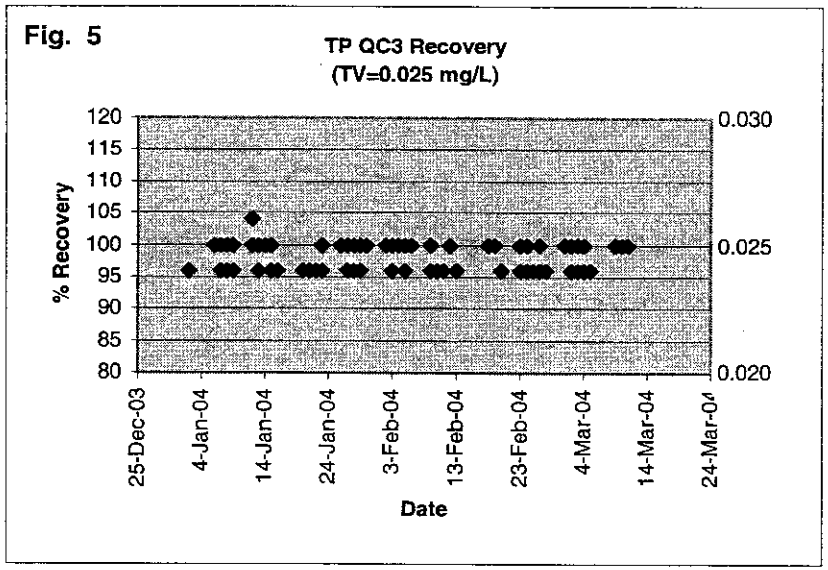
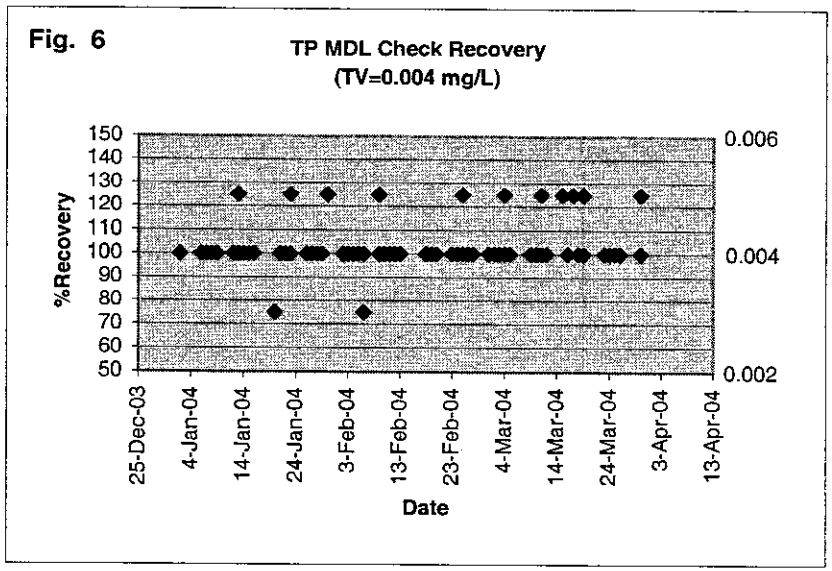


Fig. 6



% Recovery QC3	MEAN	98.4
	MAX	104
	MIN	96

MDL Check QC5	MEAN	102.0
	MAX	125.0
	MIN	75.0

TP Precision Data 1/1/04-3/31/04 Acceptance Limit = <10%			
Low Level (0-0.200)		High Level (0.200-2.0)	
Max	8.6	Max	4.6
Mean	1.8	Mean	1.6
Std Dev	1.75	Std Dev	1.16
3xSD	5.26	3xSD	3.48
UCL	7.1	UCL	5.1
n	239	n	29

TP Spike Recovery Data 1/1/04-3/31/04 Acceptance Limit = 90-110%			
	Min	81.7	
	Max	109	
	Mean	100.3	
	Std Dev	3.27	
	3xSD	9.82	
	LCL	90.4	
	UCL	110.1	
	n	285	

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 5. Both laboratories obtained acceptable blank (EB) results. Except for one pair where samples contained "Very heavy suspended solids", the results pairs met the precision criteria. The RPDs of 24.0 and 16.2% for LOX5 and LOX10, respectively, could be attributed to the fact that the samples collected had very heavy amounts of coarse suspended solids. Presence of solid materials generally results in such or larger differences due to heterogeneity of the samples and the difficulty in maintaining particulates in suspension during subsampling the splitting process and while taking aliquots in the laboratory. The current limit for within laboratory precision is 20%. Interlaboratory precision, particularly at very low concentration levels, can be expected to be much higher.

Table 5. Results of TP split study between SFWMD and FDEP laboratories, EVPA Project, 3/8/04

Station	Date Collected	Sample Type	TPO4 Results (mg/L)		Difference (SFWMD-FDEP)	% RPD	Comments
			SFWMD	FDEP			
S5AD	3/8/2004	EB	<0.002	<0.004	<MDL	N/A	Acceptable
S5AD	3/8/2004	SS	0.031	0.031	0.000	0.0	Acceptable
LOX5	3/8/2004	SS	0.028	0.022	0.006	24.0	Very heavy coarse suspended solids
LOX10	3/8/2004	SS	0.017	0.020	-0.003	16.2	Very heavy coarse suspended solids
LOX9	3/8/2004	SS	0.006	0.006	0.000	0.0	Acceptable

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 of 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)	Greater than 2.00

The result of March 2004 study is presented in Table 6.

Table 6. USGS SRS Study for TP, March 2004

Sample	Reported Value, mg/L	Most Probable Value, mg/L	%R	Rating	Z-Value
M-170	0.910	0.932	97.6	4 (Excellent)	-0.47
N-81	0.085	0.085	100	4 (Excellent)	0.00
N-82	0.840	0.856	98.1	4 (Excellent)	-0.47

M-170=major constituents; N-81, N-82=Nutrient constituents.

C. FDEP Everglades Total Phosphorus Round Robin Study

The Report of Statistical Analysis and Summary of the Everglades Total Phosphorus Round Robin XIV Inter-laboratory Comparison Program for samples submitted in October 2003 was published in July, 2004. The 5-point scoring scale was used to assess a laboratory's performance on each site, with 5.0 = the best and 0.0= the worst. The score for each side of the analytical results performed by the SFWMD laboratory are presented in the table below. Full reports for these DEP interlaboratory studies can be found at http://www.dep.state.fl.us/labs/everglades/index.htm.

Table 7. Everglades TP Round Robin XIV, October 2003

Site	CA215	WCA2F2	WCA2F4	S5A	S10C	Average Score
Score	5	4	5	5	4	4.6

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.