Quality Assessment Report for Water Quality Monitoring

April - June 2002

Submitted to the
Technical Oversight Committee

Prepared by:

Delia B. Ivanoff and Juan Manzano
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
April-June 2002

I. Introduction

This report is an assessment of the SFWMD laboratory and field sampling for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 2nd 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 may also cover information on stations or project other than those listed above 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. Effective 2/26/2000, the District's laboratory Quality Manual replaced the CQAP, to comply with National Environmental Laboratory Accreditation Conference Standards requirements. This also makes the laboratory in compliant with the new FDEP QA Rule F.A.C. 62-160. This QA rule also requires the development of a field quality manual by 10/10/2002. The District, with approval from the FDEP, adopted the revised FDEP Rule changes to its water quality sampling quality control and field QC-related data assessment protocols on 3/01/02. A summary of those changes is also included in Part II, Section C, Table 4 of this report.

Included also in this report are an analysis of District's laboratory's performance on split or replicate studies with FDEP and other laboratories, the results of U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples, and the FDEP Everglades Round Robin Studies 11 and 12 (draft).

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, FCEB and FB recoveries for all projects under the purview of the TOC. Under the new criteria, the collection of field blanks are reduced and left to the discretion of the project manager. Less than 1% of the 106 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	8	100	0	0	N/A
	ENP	1	100	0	0	N/A
	EVPA	0	0	0	0	N/A
	NECP	0	0	0	0	N/A
EB	CAMB	62	96.8	3.2	0	N/A
	ENP	15	93.3	0	6.7	Results>0.008 were qualified with "V"
	EVPA	14	100	0	0	N/A
	NECP	6	100	0	0	N/A

Table 2. Field precision summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	7	30.5	Precision criteria were met, except in cases when the value is <PQL, or for 4/2/02 and 4/16/02 pairs which are flagged.
ENP	1	13.3	Precision criteria were met.
EVPA	2	2.75	Precision criteria were met.
NECP	2	9.0	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 values >PQL.
3) FB, FCEB 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	5/14/02	S5AU	SAMP	J5	Not Flow Proportional
	5/21/02	USL3BRS	SAMP	J3	Possible Contamination
	6/18/02	S5A	SAMP	J5	Not Flow Proportional
	6/26/02	S6	SAMP	J5	Not Flow Proportional
	4/2/02	S7	SAMP	J3	Failed Field Precision Criteria
	4/2/02	S7	RS	J3	Failed Field Precision Criteria
	4/16/02	S5A	SAMP	J3	Failed Field Precision Criteria
ENP	4/11/02	S332DAS	EB	V	Blank > 2xMDL
NECP	4/22/02	S334	SAMP	Y	Improper Preservation

B. Field Audits

EVPA collection by the United States Fish and Wild Life Service (USFWS) sampling team was audited on April 9th, 2002. The sampling team followed proper procedures and QA/QC requirements, except for a deficiency concerning documentation of equipment cleaning.

The response to this audit report adequately addressed this deficiency.

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. Summaries 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 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 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 102.1%.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 97.1 – 101.1%, indicating that the digestion process was effective. The same material is used to do matrix spikes, the mean recovery for which was 99.3%.

The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 1.7% and 0.6% for low and high level analyses, respectively. The maximum RPD during this period were 4.1% and 2.2% for low & high levels, respectively.

A. Split and Replicate Studies

To continually assess comparability of results, the District send 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
For this quarter, due to a field error, **RS** were collected instead of **SS** and this resulted in higher % RPD as shown in Table 5. Because replicate samples (RS) were collected from two separate grabs, higher variability is expected. The District's laboratory also participates in other split studies throughout the year. An analysis of District's laboratory TP recoveries on these various split studies as compared to FDEP and other laboratories, is presented in Figures 7-9.

Table 5. Results of TP REPLICATE* study between SFWMD and FDEP laboratories, 6/17/02.

Station	Sampling Date	Type	FDEP	SFWMD	(SFWMD-FDEP)	% RPD	Comments
			mg/L				
S5AD	6/17/02	EB	0.004	0.004	0	0	
S5AD	6/17/02	SAMP	0.15	0.131	-0.019	13.5	
LOX4	6/17/02	SAMP	0.037	0.020	-0.017	59.6	
LOX7	6/17/02	SAMP	0.029	0.014	-0.015	69.8	
LOX8	6/17/02	SAMP	0.017	0.013	-0.004	26.7	

** Replicate samples (RS) were from two separate grabs, as opposed to true splits which should have come from the same grab sample.*

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 on a semi-annual basis on a voluntary basis. The Laboratory uses the study to monitor laboratory performance. Statistical Analysis of results are conducted by the USGS, based on which laboratory results performance are rated on a scale 4 to 0.

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 - April 2002 study is presented in Table 6.

Table 6. USGS SRS Study for TP, March-April 2002

Sample	**Reported Value, mg/L**	**Most Probable Value, mg/L**	**%R**	**Rating**	**Z-Value**
M-162	0.507	0.510	99.4	4(Excellent)	-0.12
N-72	0.139	0.132	105.3	3(Good)	0.79
N-74	0.745	0.755	98.7	4(Excellent)	-0.25

M-162=major constituents; N-72, N-74=Nutrient constituents.

C. SFWMD Performance Evaluation (PE) Spring 2002 Study

This is the 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 the 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

Copies of the Everglades Round Robin Studies 11 and 12 study results showing the District's Laboratory performance, as compared with the other participating laboratories are also included 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 these studies 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. 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.