Quality Assessment Report for Water Quality Monitoring

July - September 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 for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 3rd 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 District's laboratory and field quality manuals require the 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 finalized and implemented a new field QM on 12/31/02, in compliance with the new FDEP QA Rule F.A.C. 62-160.

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 recoveries. All of the 128 blanks collected were within the acceptance criteria. 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
EB	CAMB	93	96.8	3.2	0	N/A
	ENP	11	100	0	0	N/A
	EVPA	22	100	0	0	N/A
	NECP	2	100	0	0	N/A

Table 2. Field precision summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	7	5.3	Precision criteria were met.
ENP	1	0	Precision criteria were met.
EVPA	2	0	Precision criteria were met.
NECP	2	6.4	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	24-Sep-02	S5A	SAMP	J5	Possible Contamination
	24-Sep-02	S140	SAMP	J3	Not Flow Proportional
	24-Sep-02	S9	SAMP	J3	Possible Contamination
	23-Jul-02	S190	SAMP	J5	Not Flow Proportional
	26-Aug-02	S8	SAMP	J3	Not Flow Proportional
	10-Jul-02	S6	SAMP	J5	Not Flow Proportional
	17-Jul-02	S6	SAMP	J5	Not Flow Proportional
	30-Jul-02	S5A	SAMP	J5	Possible Contamination
	30-Sep-02	S38	SAMP	J3	Reversal OPO4 > TPO4
	16-Sep-02	S8	SAMP	J3	Possible Contamination
	3-Sep-02	S9	SAMP	J3	Possible Not Flow Proportional Sample
EVPA	9-Sep-02	LOX9	SAMP	Y	Improper Preservation

B. Field Audits

CAMB trace metals collection by the South Florida Water Management sampling team was audited this quarter. The sampling team followed proper procedures and QA/QC requirements. There were no deficiencies noted during the audit. Audit report listed some recommendations intended to enhance the process. The response to the audit was satisfactory concerning all recommended items.

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 100.4%.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 97.2 – 102.6%, indicating that the digestion process was effective. The same material is used to do matrix spikes, the mean recovery for which was 101.0%.

The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 0.9% and 0.5% for low (0.05 to 0.2 mg/L) and high level (0.2-2.0 mg/L) analyses, respectively. The maximum RPD during this period were 4.0% and 2.6% for low & high levels, respectively.
The range from 0 to 0.05 mg/L was evaluated for method precision by the %RSD of results for QC3 and QC5 this quarter. The %RSD were 2.2 and 5.7 for QC3 (0.025 mg/L) and QC5 (0.006mg/L) 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 might have caused the 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 is presented in Figures 7

Table 4. Results of TP REPLICATE* study between SFWMD and FDEP laboratories, 9/9/02.

Station	Sampling Date	Type	FDEP	SFWMD	(SFWMD-FDEP)	% RPD	Comments
			mg/L				
S5AD	9/9/02	EB	0.004	0.004	0	0.0	
S5AD	9/9/02	RS	0.17	0.135	-0.035	23.0	
LOX10	9/9/02	SAMP	0.009	0.007	-0.002	25.0	
LOX9	9/9/02	SAMP	0.014	0.007	-0.007	66.7	

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

B. 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.*

C. 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.

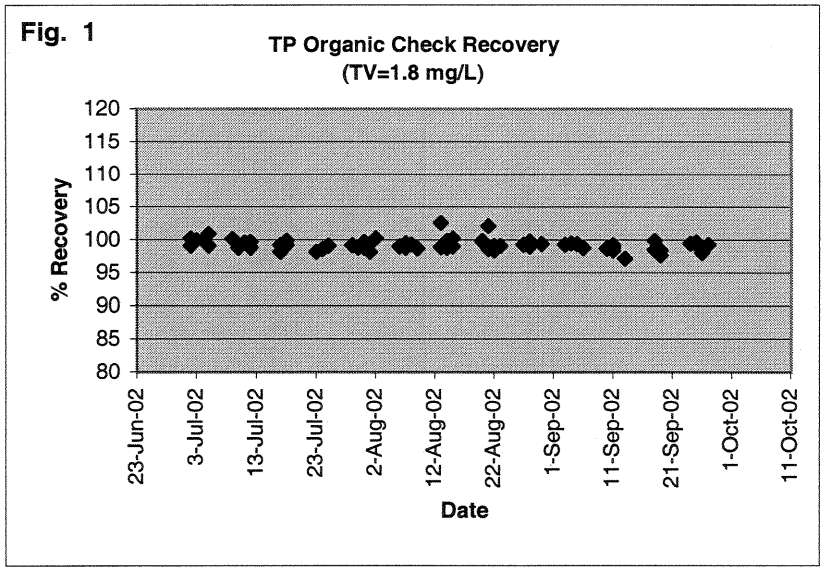
Accuracy. The agreement between the actual obtained result and the expected result. QC check samples having known or "true" value are used to test for the accuracy of a measurement system.

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.

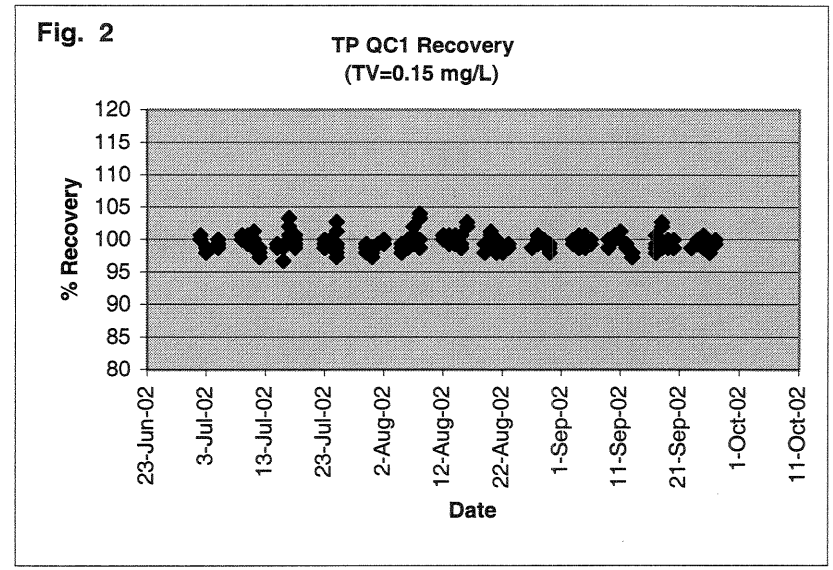
Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be 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

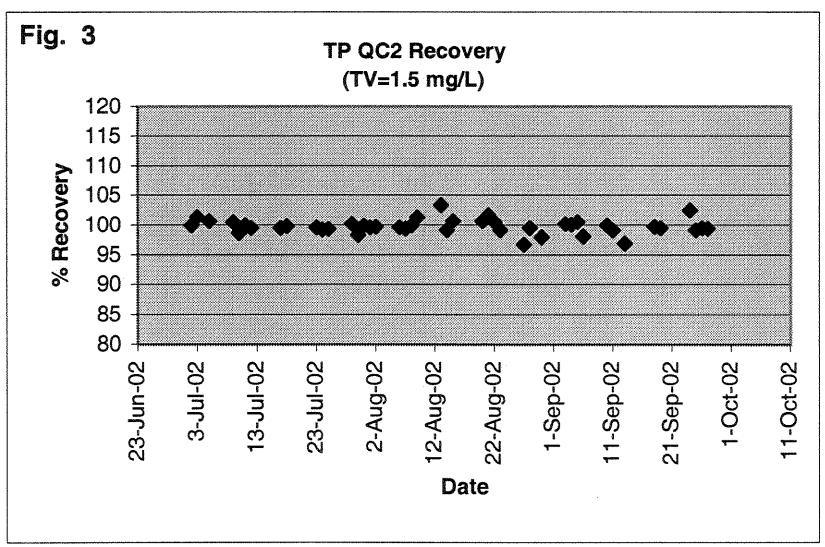
Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as: %RPD = [Value1-Value2]/Mean * 100.



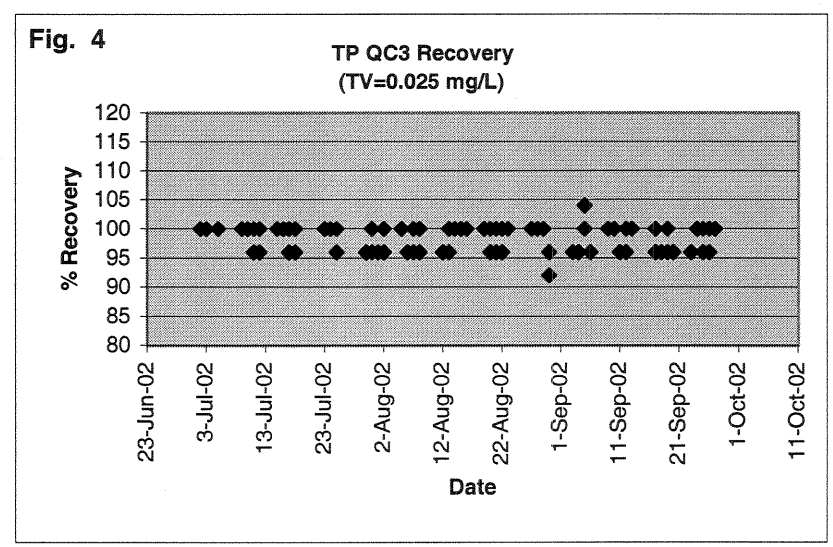
% Recovery Organic Check	MEAN	99.3
	MAX	102.6
	MIN	97.2



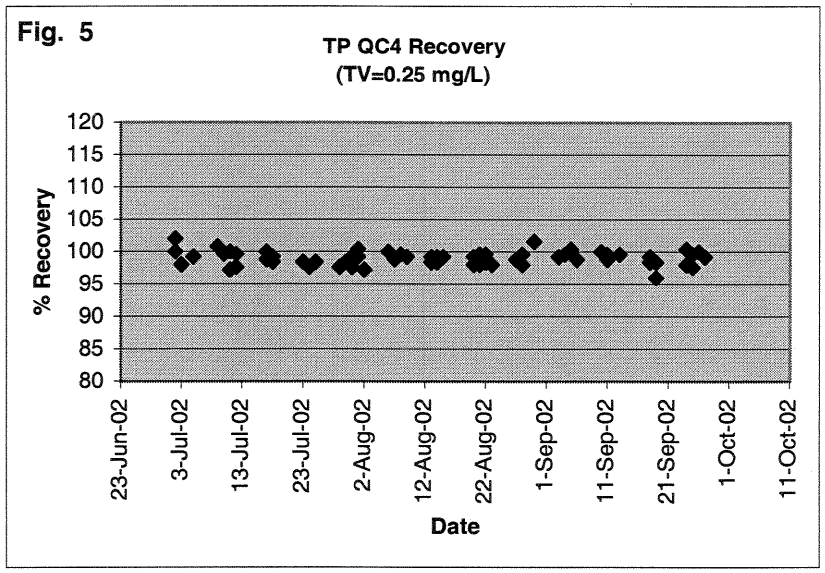
% Recovery QC1	MEAN	99.5
	MAX	103.3
	MIN	96.7

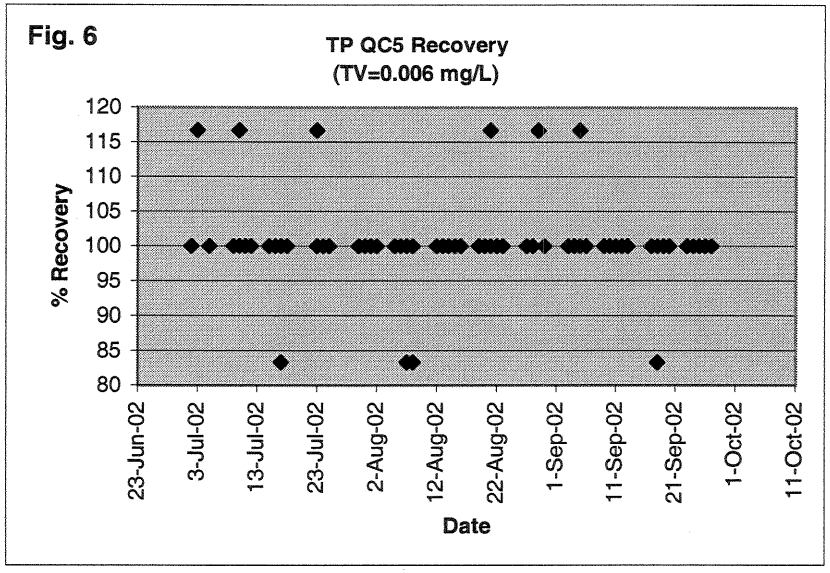


% Recovery QC2	MEAN	99.8
	MAX	103.4
	MIN	96.7



% Recovery QC3	MEAN	98.4
	MAX	104
	MIN	92





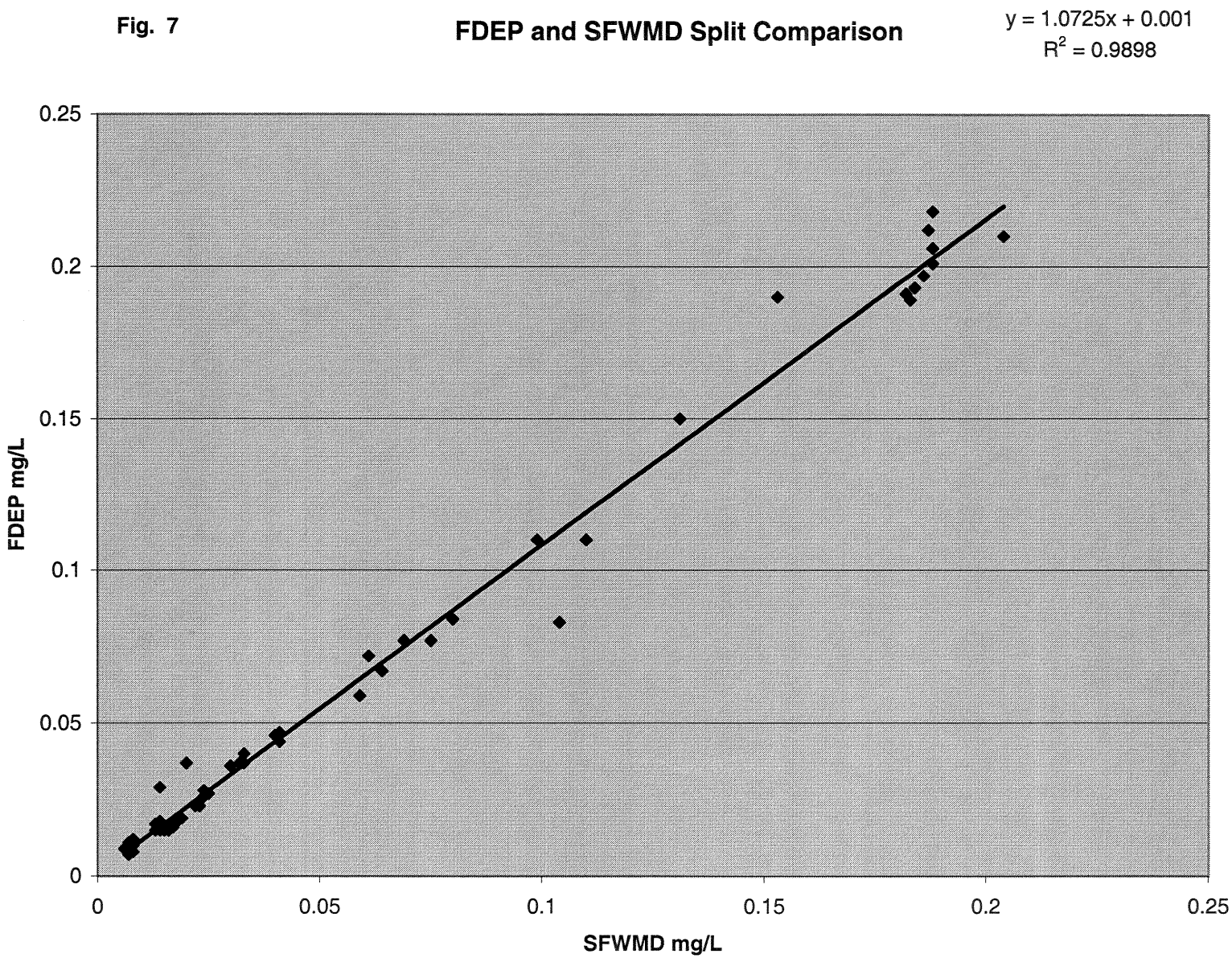
% Recovery QC4	MEAN	99.0
	MAX	102.0
	MIN	96.0

% Recovery QC5	MEAN	100.4	
	MAX	116.7	
	MIN	83.3	

TP Precision Data 7/1/02-9/30/02 Acceptance Limit = <5.0%			
Low Level (0.05-0.2)		High Level (0.2-2)	
Max	4	Max	2.6
Mean	0.9	Mean	0.5
Std Dev	0.90	Std Dev	0.47
3xSD	2.70	3xSD	1.42
UCL	3.6	UCL	2.0
n	248	n	117

TP Spike Recovery Data 7/1/02-9/30/02 Acceptance Limit = 90-110%			
	Min	78.1	
	Max	112	
	Mean	101.0	
	Std Dev	4.10	
	3xSD	12.29	
	LCL	88.7	
	UCL	113.3	
	n	375	

Fig. 7


FDEP and SFWMD Split Comparison
y = 1.0725x + 0.001
R2 = 0.9898
0.25
0.2
0.15
0.1
0.05
0
FDEP mg/L
0
0.05
0.1
0.15
0.2
0.25
SFWMD mg/L