Quality Assessment Report for Water Quality Monitoring

January - March 2005

Submitted to the
Technical Oversight Committee

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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 2005:

- 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 District's Field Sampling Quality Manual states the minimum requirement followed in field sample collection. The Laboratory Quality Manual states the minimum requirement followed in laboratory sample preparation and analysis, as well as in data verification and validation. The results of laboratory and field quality control during this quarter are presented in Sections II and III of this report.

Included in this report is an analysis of the District's laboratory's performance on split and inter-laboratory studies with FDEP and other laboratories for three selected projects, i.e. EVPA, C111, and Everglades TP Round Robins, for a one year period.

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 and FCEB results for all projects of interest to the TOC. Except for one blank result of the 196, 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. There are no flagged data for routine monitoring of the stations included in this report.

Table 1. Field and equipment blank results

Type of Blank	Project	# Blanks collected	% >0.002
EB	CAMB	46	0
	ENP	3	0
	EVPA	2	0
	NECP	5	0
FCEB	CAMB	66	0
	ENP	16	0
	EVPA	11	0
	NECP	1	0
FB	CAMB	11	0
	ENP	2	0
	EVPA	2	0

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	5	5.9	Precision criteria were met
EVPA	1	2.2	Precision criteria were met.
NECP	3	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 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.

B. Missing TP results

A list of stations not sampled during this quarter, including the reason for non-collection is presented in Table 3 below.

Table 3. Samples not collected

Project	Date Collected	Station	Type	Comments
CAMB	24-Jan-05	S12A	SAMP	No flow, no samples collected
CAMB	22-Feb-05	S12A	SAMP	No flow, no samples collected
CAMB	7-Mar-05	S12A	SAMP	Gate closed, no samples collected
CAMB	10-Jan-05	S12B	SAMP	No flow, no samples collected
CAMB	8-Feb-05	S12B	SAMP	No flow, no samples collected
CAMB	7-Mar-05	S12B	SAMP	No flow, no samples collected
CAMB	10-Jan-05	S12C	SAMP	No flow, no samples collected
CAMB	8-Feb-05	S12C	SAMP	No flow, no samples collected
CAMB	7-Mar-05	S12C	SAMP	Gate closed, no samples collected
CAMB	10-Jan-05	S12D	SAMP	No flow, no samples collected
CAMB	7-Feb-05	S12D	SAMP	No flow, no samples collected
CAMB	7-Mar-05	S12D	SAMP	Gate closed, no samples collected
CAMB	10-Jan-05	S333	SAMP	No flow, no samples collected
ENP	11-Jan-05	S176	SAMP	No flow, no samples collected
ENP	11-Jan-05	S177	SAMP	No flow, no samples collected
ENP	5-Jan-05	S18C	SAMP	No flow, no samples collected
ENP	11-Jan-05	S18C	SAMP	Auto-sample – power off
ENP	18-Jan-05	S18C	SAMP	Refrigeration not working, no samples collected
ENP	18-Mar-05	S18C	SAMP	No flow, no samples collected
ENP	15-Mar-05	S18C	SAMP	No flow, no samples collected
ENP	22-Mar-05	S18C	SAMP	Week 2 compliance, no samples collected
ENP	29-Mar-05	S18C	SAMP	Auto-sampler maintenance, no samples collected
EVPA	10-Jan-05	LOX3	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Feb-05	LOX3	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Mar-05	LOX3	SAMP	Tdepth<0.10 m, no samples collected
EVPA	10-Jan-05	LOX5	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Feb-05	LOX5	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Mar-05	LOX5	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Feb-05	LOX9	SAMP	Tdepth<0.10 m, no samples collected
EVPA	7-Mar-05	LOX9	SAMP	Tdepth<0.10 m, no samples collected
NECP	10-Jan-05	S334	SAMP	No flow, no samples collected

C. Field Audits

During this quarter, an audit of field sampling collection activities was performed for Miami-Dade County Department of Environmental Resources Management (DERM) sampling for the TAMB, C111D, and NECP projects – 1/26/05.

The key findings were: a) Lack of quality manual, b) unavailability of reference documentation in the field, c) insufficient documentation and documentation linkage for preservation acids, standards and specific equipment d) acidified samples were filtered, e) some document corrections were not initialed. Except for still lack of DERM quality manual, all deficiencies have been corrected as of the date of this report.

III. Laboratory Quality Assessment

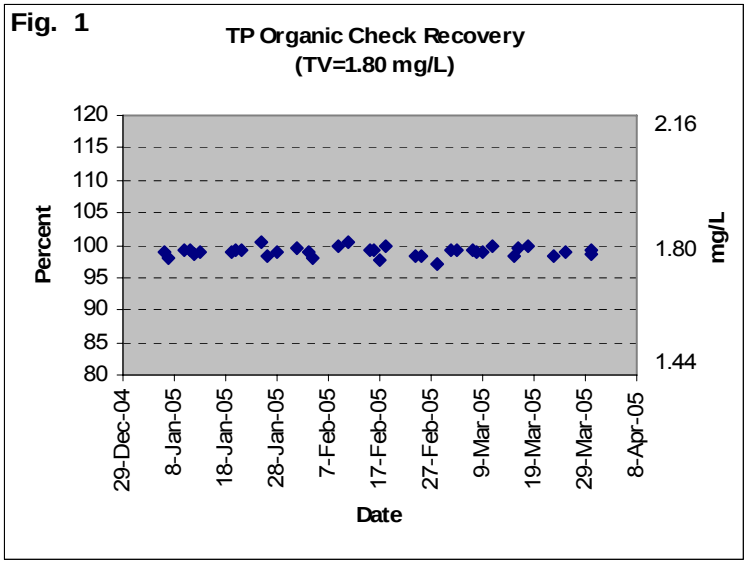
A. Routine Quality Control

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

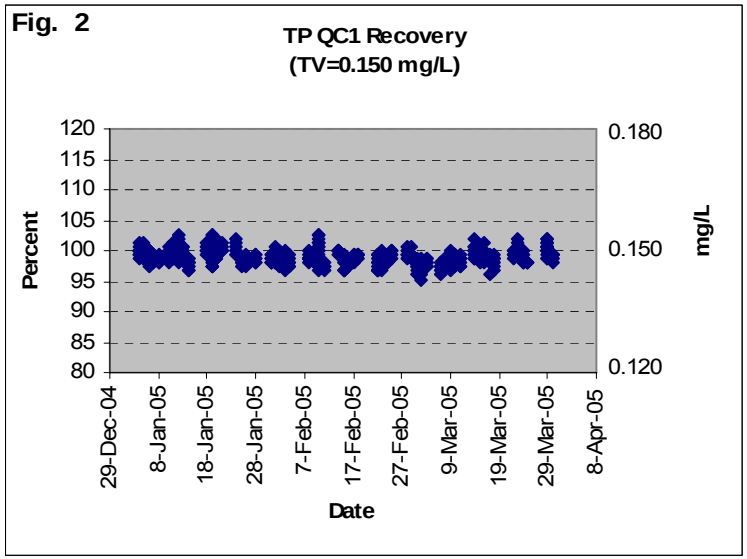
Recoveries for the QC samples are generally within $\pm$ 10% from the true value, which are acceptable. The MDL check (QC5) recovery ranged from 75-125% of the true value (0.004 mg/L), with a mean recovery of 100.2%. The MDL check results indicate the laboratory generally achieved the 0.002 mg/L MDL. Greater variance is expected at this very low range.

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 – 100.6%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 99.9%. One spike result with recovery of 57.5% was flagged due to matrix interference.

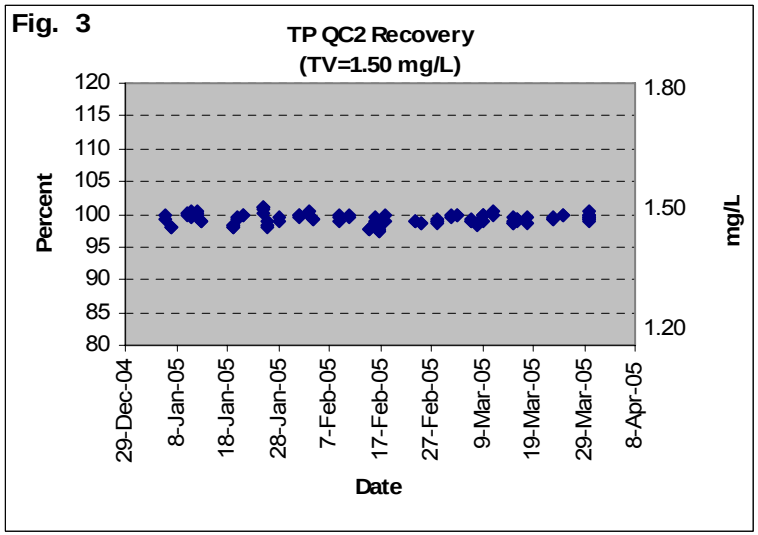
The precision target for TP analysis during this period was 10.0%, and as the report shows, mean %RPD was 2.0% and 1.4% for low (0 to 0.200 mg/L) and high level (0.200-2.00 mg/L) analyses, respectively. The maximum RPD during this period were 7.8% and 5.1% for low and high levels, respectively.



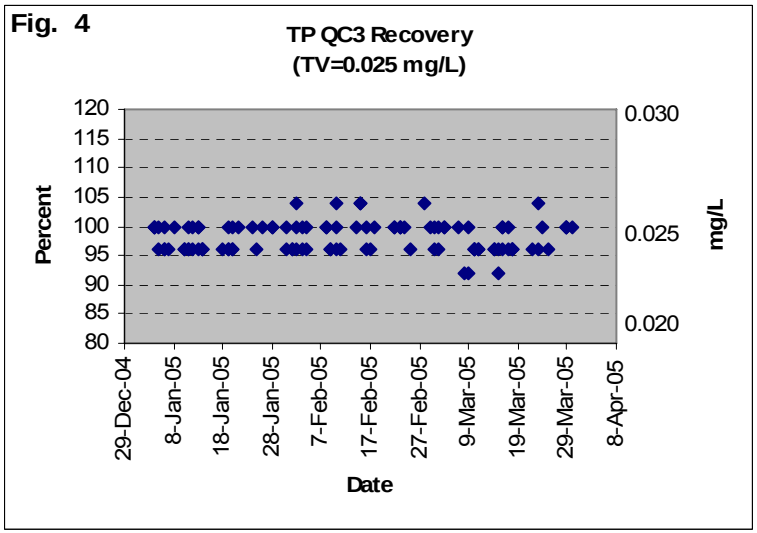
Mean = 99.0%, Max = 100.6%, Min = 97.1%



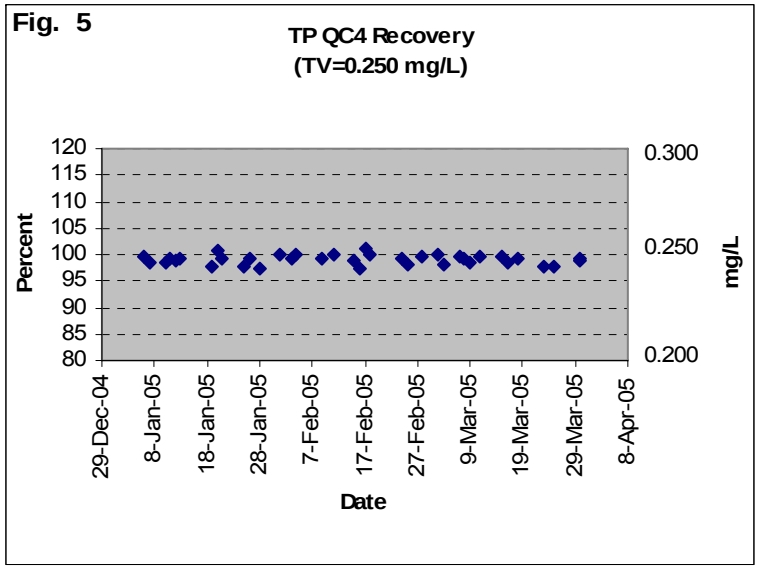
Mean = 98.9%, Max = 102.7%, Min = 95.3%



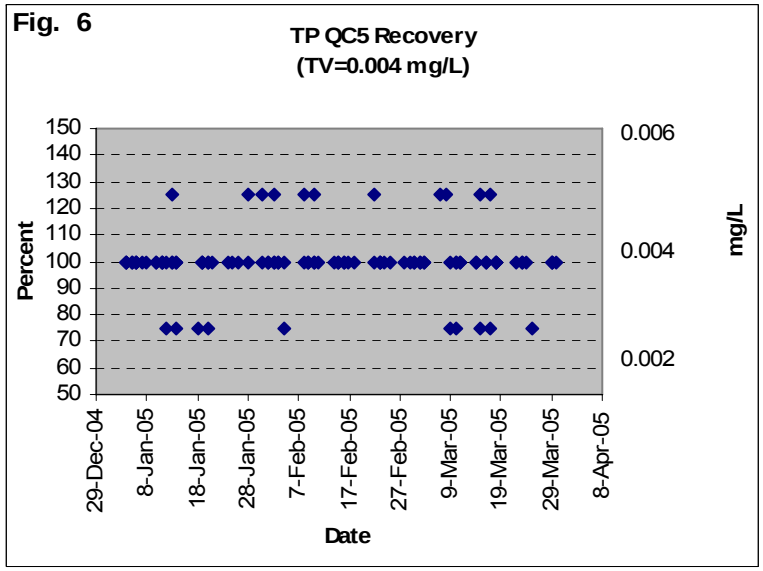
Mean = 99.2%, Max = 101.1%, Min = 97.4%



Mean = 98.1%, Max = 104%, Min = 92.0%



Mean = 99.0%, Max = 101.2%, Min = 97.2%



Mean = 100.2%, Max = 125.0%, Min = 75.0%

TP Precision Data (1/1/05-3/31/05) Acceptance Limit = <10%				**TP Spike Recovery (1/1/05-3/31/05) Acceptance Limit = 90-110%**	
Low Level (0-0.200)		**High Level (0.20-2.00)**			
Max	7.8	Max	5.1	Min, %	57.5[1]
Mean	2.0	Mean	1.4	Max. %	110
Std Dev	1.58	Std Dev	1.05	Mean, %	99.9
3xSD	4.75	3xSD	3.15	Std Dev	4.41
UCL	6.7	UCL	4.5	3xSD	13.24
n	277	n	36	LCL, %	86.6
				UCL, %	113.1
				n	326

[1] One spike recovery was reported below minimum criteria. Low recovery was attributed to matrix interference and associated data flagged.

B. Inter-Laboratory Quality Control Assessment

1. Split Studies

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. Data from split studies between DEP and SFWMD laboratories from March 2004 to March 2005 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA), Everglades TP Round Robin (ERR), and S332 sites (C111).

The summary statistics and signed rank test for SFWMD vs. DEP results, as presented in Table 3, shows that the p-value for TP >0.020 mg/L and TP <0.020 mg/L levels are 0.0165 and 0.0005 respectively. However, the mean and median of differences from both laboratories are <0.004. These are around the laboratories' MDLs; SFWMD's MDL is 0.002 mg/L while DEP laboratory's MDL is 0.004 mg/L. At these levels wider variability can be expected even within each laboratory.

Table 3. Statistical analysis of SFWMD-DEP laboratories split studies (Jan-Mar 2005)

<0.02 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	14	0.014214286	0.0165	
	SFWMD	14	0.0105	0.01	
	Statistical Test of Hypotheses				
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean of Differences	-0.00371	Mean of Differences = 0	Student's t	0.0016
	Median of Differences	-0.0025	Median of Differences = 0	Signed Rank	0.0005
>=0.02 mg/L	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	26	0.112192308	0.0495	
	SFWMD	26	0.109230769	0.0405	
	Statistical Test of Hypotheses				
	Summary Of Paired Differences		**Hypothesis**	**Statistical Test**	**Pvalue**
	Mean of Differences	-0.00296	Mean of Differences = 0	Student's t	0.042
	Median of Differences	-0.002	Median of Differences = 0	Signed Rank	0.0165

Note: Differences were calculated as (SFWMD TP - FDEP TP)

Regression analysis of the data set was done separately for TP> 0.020 mg/L and for TP<0.020 mg/L. Logarithmic transformation was needed for TP>0.020 mg/L, due to skewed data distribution. Logarithmic transformation was not needed for TP<0.020 mg/L due the fact that distribution at that concentration range is approximately normal. Regression analyses of TP data <0.020 mg/L indicate that the slope is not significantly different from 1 and intercept is not significantly different from 0, indicating that both data are highly comparable (Figures 7 and 8). Regression analyses of TP data >0.020 mg/L indicates that the slope is slightly different from 1 (<6%) and intercept is not significantly different from 0, indicating that data sets are comparable.

A paired t-test and Wilcoxon rank-sum test was also done for data that are <0.02 mg/L. These analyses indicate that there is no significant difference (ρ=0.10) between the DEP and SFWMD TP data. These statistical analyses and findings were consistent with what was in FDEP Data Comparability Report (Nearhoff, presentation to TOC, 8/26/04).

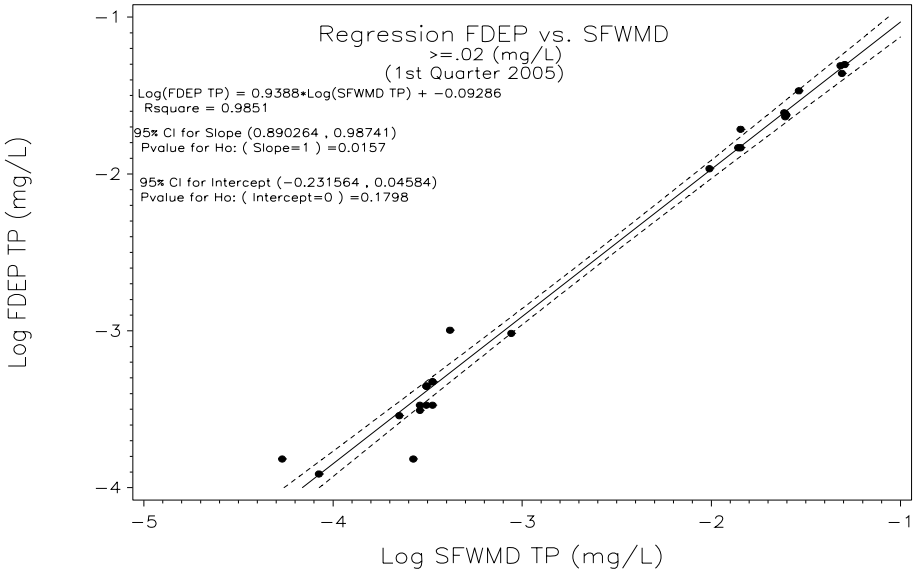


Fig.7. Regression Analysis for TP>0.020 mg/L

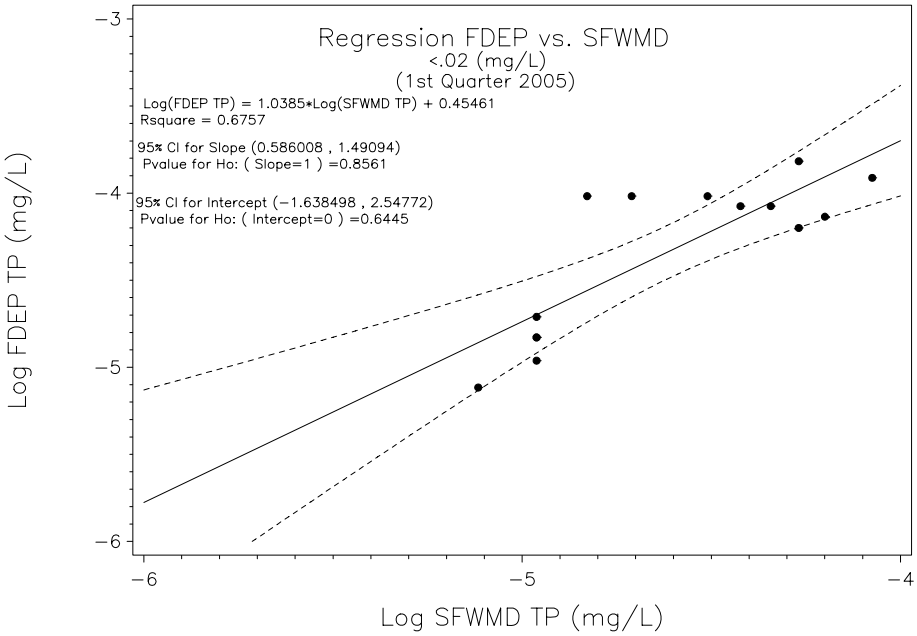


Fig. 8. Regression Analysis for TP <0.020 mg/L

Table 5. Results of TP split studies between SFWMD and FDEP laboratories, EVPA Project, March 2004 to March 2005.

Sample	Date	SFWMD	FDEP	% RPD/Comments	Sample	Date	SFWMD	FDEP	% RPD/Comments
EVPA	3/8/04	0.031	0.031	0	ERR-15	10/28/04	0.030	0.031	
EVPA	3/8/04	0.028	0.022	24.0; Heavy suspended solids	ERR-15	10/28/04	0.030	0.035	
EVPA	3/8/04	0.017	0.020	16	ERR-15	10/28/04	0.031	0.036	
EVPA	3/8/04	0.006	0.006	< PQL	ERR-15	10/28/04	0.031	0.036	
EVPA	6/14/04	0.047	0.049	4.2	ERR-15	10/28/04	0.029	0.030	
EVPA	6/14/04	0.034	0.050	38; Heavy suspended solids	ERR-15	10/28/04	0.029	0.031	
EVPA	6/14/04	0.158	0.160	1.2	ERR-15	10/28/04	0.030	0.035	
EVPA	6/14/04	0.156	0.160	2.5	ERR-15	10/28/04	0.007	0.009	
EVPA	9/21/04	0.215	0.230	6.7 Dark brown stain	ERR-15	10/28/04	0.007	0.008	
EVPA	9/21/04	0.008	0.018	76.9 Light brown stain	ERR-15	10/28/04	0.007	0.007	
EVPA	9/21/04	0.014	0.015	6.9 Light brown stain	ERR-15	10/28/04	0.007	0.008	
EVPA	9/21/04	0.012	0.015	22.2 Light brown stain	EVPA	12/13/04	0.013	0.017	Light yellow stain, light solids
ERR-15	10/28/04	0.268	0.270		EVPA	12/13/04	0.014	0.022	Dark yellow stain, light fine suspended solids
ERR-15	10/28/04	0.274	0.272		EVPA	12/13/04	0.011	0.018	1-2 L bottle cracked and leaked, used only 1-2 L bottle
ERR-15	10/28/04	0.270	0.257		EVPA	12/13/04	0.158	0.180	Brown stain, light suspended particles
ERR-15	10/28/04	0.199	0.200		EVPA	3/7/05	0.015	0.016	6.5 Light brown stain, heavy small suspended particles
ERR-15	10/28/04	0.201	0.197		EVPA	3/7/05	0.026	0.029	10.9 Light brown stain, heavy small suspended solids
ERR-15	10/28/04	0200	0.195		EVPA	3/7/05	0.009	0.018	66.7 Light yellow stain, heavy small suspended solids
ERR-15	10/28/04	0.200	0.199		EVPA	3/7/05	0.134	0.140	Sample not preserved to pH < 2; dark brown stain; heavy suspended particles

2. Total Phosphorus Round Robin XV Inter-laboratory Comparison Results

The Department of Environmental Protection (FDEP) has been providing a study of samples from Everglades research initiated in 1995. The purpose of this study is to assess the comparability of phosphorus data among 22 participating laboratories. The statistical evaluation of the results has been performed by FDEP consultant (Department of Statistics Florida State University). The scores in the table 6 are from the five sampling sites.

The TP results of October 2004 study is presented below (Table 6).

Station	S10C	S5A	WCA2E1	WCAF3	WCAU2
Consensus Study Mean	266.20	197.20	29.66	28.72	7.334
Reported Mean Results	270.67	200.00	30.50	29.33	7.00
Score*	5	5	5	5	5

*Rating of laboratories is based on the scale from 0 (unacceptable) to 5 (very good).

IV. 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 or on-site (field) decontamination (FCEB).

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" values 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.