

**Quality Assessment Report for Water Quality Monitoring
April - June 2006**



**Submitted to the
Technical Oversight Committee (TOC)**

Quality Assessment Report for Water Quality Monitoring

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Introduction

This report is an assessment of the South Florida Water Management District (District) laboratory analysis and field sampling for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 2nd quarter of 2006.

- 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 QC samples are collected for trips that include multiple project samples for the stations of interest, the report may also cover information on stations or projects 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 The Florida Department of Environmental Protection (FDEP) and other laboratories for three selected projects, i.e., EVPA, C111, and Everglades TP Round Robins, for a one-year period.

Field Sampling Quality Assessment

PROCEDURE UPDATES

There were no major procedural updates related to total phosphorous collection during this time period.

FIELD AUDIT

There was no audit on sampling process performed for these projects/stations during this reporting period.

MISSING DATA

Table 1 shows a list of missing data for this reporting period. Data may not be available due to collection problems or upon sample submission to the laboratory. Out of 36 missing data, 35 were not collected due to either lack of flow, structure maintenance, or shallow water depth. One sample was missed at station S18C due to autosampler malfunction. Note that if the autosampler had collected one sample aliquot, it would have been rejected because of low pH caused by preservation.

Table 1. Missing data for the period from 4/1/06 to 6/30/06.

Project	Collection Date	Station	Comments
EVPA	4/3/06	LOX3	Total depth <0.10m. No sample collected
EVPA	4/3/06	LOX5	Total depth <0.10m. No sample collected
ENP	4/10/06	S18C	No flow, no samples collected
ENP	4/17/06	S18C	No flow, no samples collected
CAMB	4/18/06	S12D	No flow, no samples collected
CAMB	4/18/06	S12B	No flow, no samples collected
CAMB	4/18/06	S12A	No flow, no samples collected
ENP	4/24/06	S18C	No flow, no samples collected
EVPA	5/1/06	LOX3	Total depth <0.10m. No sample collected
EVPA	5/1/06	LOX5	Total depth <0.10m. No sample collected
EVPA	5/1/06	LOX10	Total depth <0.10m. No sample collected
EVPA	5/1/06	LOX9	Total depth <0.10m. No sample collected
ENP	5/1/06	S18C	1 pulse recorded, but no sample in bottles
CAMB	6/2/06	S12D	No flow, no samples collected
ENP	5/8/06	S18C	No flow, no samples collected
CAMB	5/16/06	S12D	No flow, no samples collected
NECP	5/23/06	S334	No flow, no samples collected
ENP	5/30/06	S18C	No flow, no samples collected
ENP	5/30/06	S18C	No flow, no samples collected
CAMB	5/30/06	S12A	No flow, no samples collected
CAMB	5/30/06	S12B	No flow, no samples collected
CAMB	5/30/06	S12D	No flow, no samples collected
EVPA	6/12/06	LOX3	Total depth <0.10m. No sample collected
EVPA	6/12/06	LOX5	Total depth <0.10m. No sample collected
EVPA	6/12/06	LOX10	Total depth <0.10m. No sample collected
EVPA	6/12/06	LOX9	Total depth <0.10m. No sample collected
EVPA	6/12/06	LOX7	Total depth <0.10m. No sample collected
EVPA	6/12/06	LOX4	Total depth <0.10m. No sample collected
ENP	6/12/06	S18C	No flow, no samples collected
EVPA	6/13/06	LOX6	Total depth <0.10m. No sample collected
EVPA	6/13/06	LOX11	Total depth <0.10m. No sample collected
EVPA	6/13/06	LOX13	Total depth <0.10m. No sample collected
ENP	6/19/06	S18C	No flow, no samples collected
NECP	6/20/06	S334	No flow, no samples collected
ENP	6/26/06	S18C	No flow, no samples collected
ENP	6/26/06	S18C	No flow, no samples collected

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 2** summarizes EB and FCEB results for all projects of interest to the TOC. Only one blank associated with samples for stations listed in Section I was outside the acceptance criterion. **Table 3** 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. For this reporting period, there are no flagged TP data for the stations listed in the **Introduction**.

Table 2. Field and equipment blank results*.

Type of Blank	Project	Number of Blanks Collected	% ≤0.002	% >0.002
EB	CAMB	1	100	0
	ENP	1	100	0
	EVPA	1	100	0
FCEB	CAMB	5	100	0
	ENP	38	97	3
	EVPA	7	100	0
	NECP	7	100	0
FB	ENP	1	100	0
	EVPA	1	100	0
	NECP	2	100	0

Notes

1. Only blanks from sampling events that included samples from Stations listed in Section I of this report were included in this analysis.
2. Blanks for TP which were associated with a short-term autosampler project at some TOC stations were not included here.
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. Field precision summary.

Project Code	Number of Triplicates	% RSD	Comments
CAMB	1	4.9	Precision criteria were met.
EVPA	1	6.0	Precision criteria were met.
NECP	1	4.6	Precision criteria were met.

Notes:

1. Only replicates from sampling events that included samples from stations listed in Section I of this report were included in this analysis.
2. All TP analyses were conducted by the District's Chemistry laboratory.
3. Field precision acceptance criterion: <20%. This criterion was applied only if sample values > Practical Quantitation Limit (PQL).

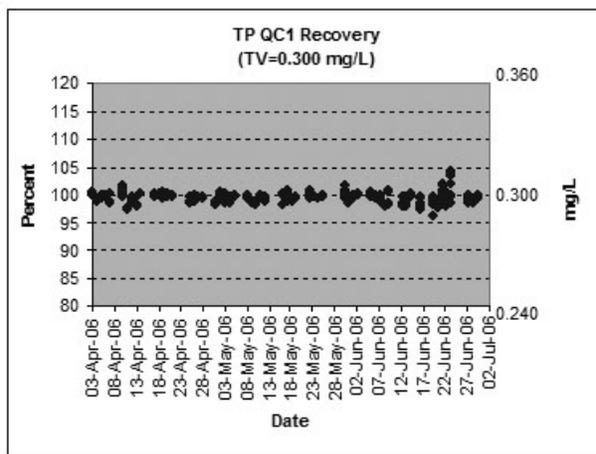
Laboratory Analysis Quality Assessment

PROCEDURE UPDATES

TP analytical procedure did not change during this reporting period. However, the District laboratory now uses an automated online dilutor, which automatically dilutes samples with concentrations exceeding the upper analytical range. Previously, the District diluted samples manually. Before diluting samples, a method performance validation was conducted, which indicated the change does not affect TP recoveries.

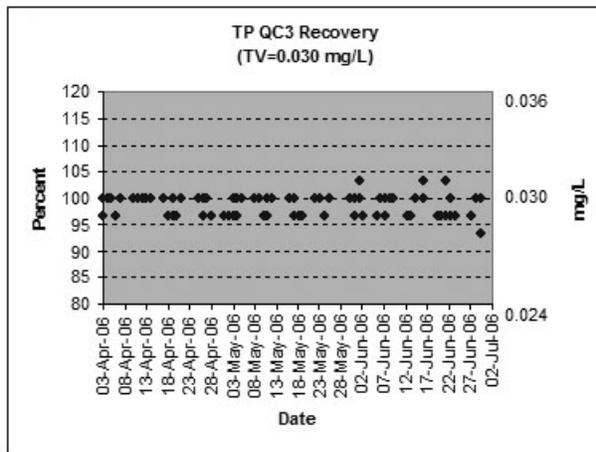
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figure 1**, **Figure 2** and **Figure 3** show recoveries from various levels of QC samples for the TP analysis at the District laboratory from April 1 through June 30, 2006.



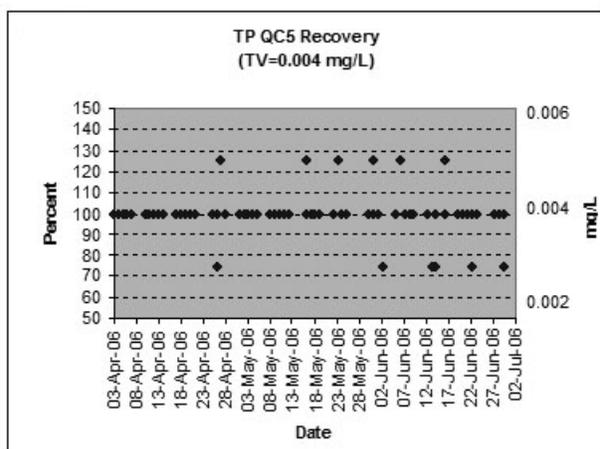
Mean = 99.6%, Max = 104.3%, Min = 96.3%

Figure 1. QC sample recoveries for TP analysis from April 1 through June 30, 2006.



Mean = 98.8%, Max = 103.3%, Min = 93.3%

Figure 2. QC sample recoveries for TP analysis from April 1 through June 30, 2006.



Mean = 99.7%, Max = 125.0%, Min = 75.0%

Figure 3. QC sample recoveries for TP analysis from April 1 through June 30, 2006.

Precision and matrix spike recoveries are shown in **Table 4** and **Table 5**. 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 deficiencies are noted and the samples have exceeded the required holding times and cannot be re-analyzed.

Table 4. TP Precision Data, 4/01/06 – 6/30/06.

Acceptance Limit	<10%
Analytical Range:	0.002-0.400 mg/L
Maximum	6.7
Mean	1.4
Standard Deviation	1.36
3xSD	4.08
UCL	5.5
n	269

UCL = Upper Control Limit
n = Number of data points

Table 5. TP Spike Recovery Data, 4/01/06 – 6/30/06.

Acceptance Limit	90 – 110%
Analytical Range:	0.002-0.400 mg/L
Minimum	91.1
Maximum	109
Mean	101.7
Standard Deviation	3.03
3xSD	9.10
LCL	92.5
UCL	110.8
n	273

LCL = Lower Control Limit
UCL = Upper Control Limit
n = Number of data points

Recoveries for the QC samples are generally within +10% from the true value, which are acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had mean recoveries of 99.7%. The daily MDL check results indicate the laboratory has consistently achieved the goal of 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate to prepare matrix spikes, the mean recovery for which was 101.7%.

INTER-LABORATORY QUALITY CONTROL ASSESSMENT

Split Studies with FDEP Laboratory

To assess comparability of results continuously, the District sends split samples to other laboratories on a routine basis. From June 2005 through June 2006, data from split studies between FDEP and District laboratories were used in this analysis for the following programs: EVPA Quarterly Splits (EVPA) and Everglades TP Round Robin (ERR) (**Appendix A**). **Figure 4** through **Figure 6** show regression analysis of the data and **Table 6** through **Table 9** show summary statistics for the data pairs.

ALL DATA

Figure 4 shows that the intercept is not statistically different from 0 and the slope is not statistically different from 1 for all TP data from both laboratories. The r^2 value is 0.966. This information shows that the results from the two laboratories have a high degree of agreement (close to 1:1 correlation).

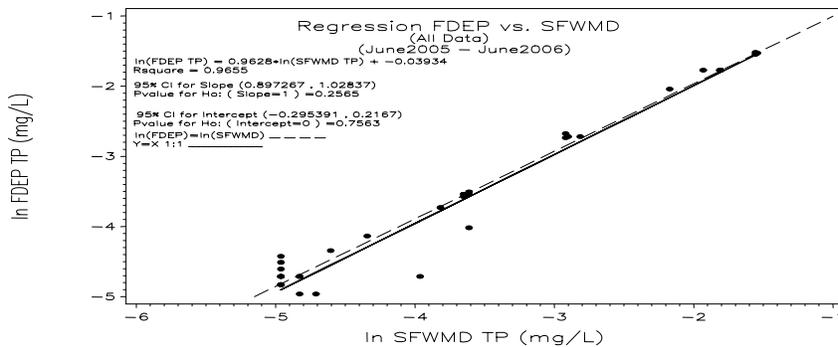


Figure 4. Regression analysis for TP all data.

The mean difference (-0.004) and median difference (-0.003) were statistically significant, but note that these differences are at or below the FDEP laboratory’s MDL. The paired t-test and signed-rank test yielded p-values of 0.0013 and <0.0001 respectively.

TP ≥ 0.02 mg/L

Figure 5 shows that the intercept is not statistically different from 0 and the slope is not statistically different from 1 for samples with TP ≥ 0.02 mg/L. The r^2 value is 0.977. The Mean difference (-0.006) and Median difference (-0.004) were statistically significant, but these differences are still below the Practical Quantitation Limit (PQL) of the two laboratories. The paired t-test and signed-rank test yielded p-values of 0.0018 and 0.0006 respectively.

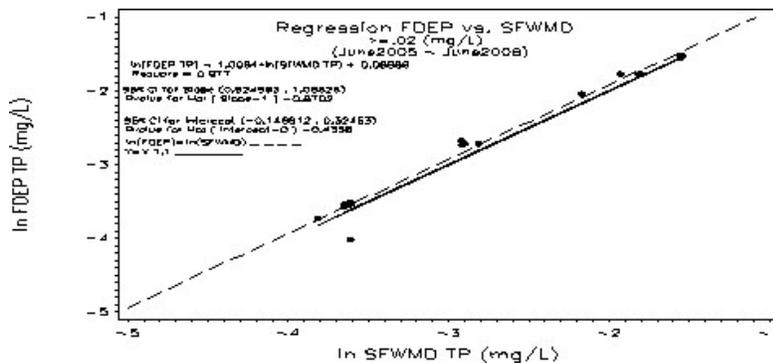


Figure 5. Regression Analysis for TP ≥ 0.020 mg/L.

TP < 0.020 mg/L

Figure 6 shows that the slope is significantly different from 1 and intercept is significantly different from 0 for samples with TP < 0.02 mg/L., suggesting a difference between the data sets for the two laboratories. It is important to note that the very high variability within each laboratory, as well as between the two laboratories at the very low concentration levels affects this outcome. The r² for this regression is 0.3527.

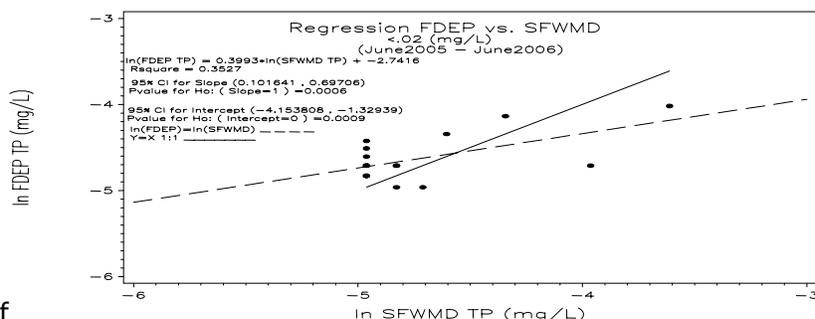


Figure 6. Regression Analysis for TP < 0.020 mg/L.

At this concentration level (<0.02 mg/L), the mean difference (-0.000) and median difference (-0.001) were not statistically significant. P-values for the paired t-test and signed-rank were 0.6838 and 0.1226 respectively (see Table 6).

Table 6. Comparison of District and FDEP Split Phosphorus Samples (6/2005 – 6/2006).

	Summary Statistics				
	Lab	N	Mean	Median	
All Data	FDEP	34	0.056	0.021	
	District	34	0.052	0.024	
	Statistical Test of Hypotheses				
	Summary of Paired Differences	Hypothesis		Test	P-value
Mean of Differences	-0.004	Mean of Differences = 0		Student's t	0.0013
Median of Differences	-0.003	Median of Differences = 0		Signed Rank	<0.0001
>=0.02 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	18	0.097	0.066	
	District	18	0.090	0.054	
Statistical Test of Hypotheses					
Summary of Paired Differences	Hypothesis		Test	P-value	
Mean of Differences	-0.006	Mean of Differences = 0		Student's t	0.0018
Median of Differences	-0.004	Median of Differences = 0		Signed Rank	0.0006
<0.02 mg/L	Summary Statistics				
	Lab	N	Mean	Median	
	FDEP	17	0.010	0.009	
	District	17	0.010	0.007	
Statistical Test of Hypotheses					
Summary of Paired Differences	Hypothesis		Test	P-value	
Mean of Differences	-0.000	Mean of Differences = 0		Student's t	0.6838
Median of Differences	-0.001	Median of Differences = 0		Signed Rank	0.1226

Notes:

1. Differences were calculated as District TP – FDEP TP. The mean and median differences for all concentration levels are at or below the PQL.
2. Data were not used if FDEP value was <0.004 (FDEP laboratory's MDL).

National Water Research Institute Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program

The objectives of this program are to assess and demonstrate reliability and quality of analytical measurements of inorganic parameters in natural waters. The results for the District's laboratory from the most recent study (December 2005/June 2006) are shown in **Table 7**.

Table 7. Performance in PT Study 87 for TP, December 2005/January 2006.

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.003	0.004	0.008	0.022	0.077	0.094	0.113	0.176	0.180	0.242
Reported Results, mg/L	<0.002	0.004	0.009	0.021	0.078	0.095	0.112	0.178	0.180	0.248

The performance of total phosphorus was rated as “ideal” (highest category).

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. A vendor approved by the National Institute of Science and Technology as PT provider for National Environmental Laboratory Accreditation Conference administers this study. **Table 8** provides the results of the April 2006 study.

Table 8. National Proficiency Testing Results.

Reported Value 8.95 mg/L

Assigned Value 9.04 mg/L

Performance Evaluation: 99% Recovery, Acceptable

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 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” 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: $\%RSD = [\text{Std. Deviation}/\text{Mean}] * 100$

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

Appendix A

Table 9. Results of TP split studies between the District and FDEP laboratories, EVPA Project, June 2005 through June 2006.

Sample	Date	District	FDEP	% RPD/Comments
EVPA	13-Jun-05	0.145	0.170	15.9
EVPA	13-Jun-05	0.027	0.018	40.0
EVPA	13-Jun-05	0.027	0.030	10.5
EVPA	13-Jun-05	0.022	0.024	8.7
EVPA	19-Sep-05	0.165	0.170	3.0
EVPA	19-Sep-05	0.163	0.170	4.2
EVPA	19-Sep-05	0.007	0.010	<PQL
EVPA	19-Sep-05	0.008	0.007	<PQL
ERR-16	2-Nov-05	0.027	0.029	7.7
ERR-16	2-Nov-05	0.026	0.028	7.4
ERR-16	2-Nov-05	0.026	0.029	10.9
ERR-16	2-Nov-05	0.026	0.029	10.9
ERR-16	2-Nov-05	0.007	0.008	<PQL
ERR-16	2-Nov-05	0.007	0.008	<PQL
ERR-16	2-Nov-05	0.007	0.008	<PQL
ERR-16	2-Nov-05	0.007	0.009	<PQL
ERR-16	2-Nov-05	0.060	0.066	9.5
ERR-16	2-Nov-05	0.055	0.066	18.2
ERR-16	2-Nov-05	0.054	0.065	18.5
ERR-16	2-Nov-05	0.054	0.069	24.4
ERR-16	2-Nov-05	0.214	0.217	1.4
ERR-16	2-Nov-05	0.211	0.213	0.9
ERR-16	2-Nov-05	0.211	0.219	3.7
ERR-16	2-Nov-05	0.007	0.009	<PQL
ERR-16	2-Nov-05	0.008	0.009	<PQL
ERR-16	2-Nov-05	0.007	0.009	<PQL
EVPA	12-Dec-05	0.114	0.130	13.1
EVPA	12-Dec-05	0.008	0.009	<PQL
EVPA	12-Dec-05	0.009	0.007	<PQL
EVPA	12-Dec-05	0.019	0.009	71.4
EVPA	3-Mar-06	0.009	<0.004	<PQL
EVPA	3-Mar-06	0.007	<0.004	<PQL
EVPA	3-Mar-06	0.008	<0.004	<PQL
EVPA	3-Mar-06	0.007	<0.004	<PQL
EVPA	13-Jun-06	0.010	0.013	26.1
EVPA	13-Jun-06	0.007	0.012	<PQL
EVPA	13-Jun-06	0.013	0.016	20.7
EVPA	13-Jun-06	0.007	0.011	<PQL