Quality Assessment Report for Water Quality Monitoring

July – September 2009

Revisions were made to this document on December 11, 2009
(See footnote and details on page 3)

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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD or District) laboratory analysis and field sampling for total phosphorus (TP) monitoring, primarily for the following projects and their associated stations from July 1, 2009, through September 30, 2009:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356
- Everglades National Park Inflow East (PIE): S332DX, S18C, DS2, DS4, and BermB3
- Everglades Protection Area (EVPA): LOX3 through LOX16

Because field quality control (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 in the above list.

The District's *Field Sampling Quality Manual*[1] provides the minimum requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual*[2] provides the minimum requirements followed in preparing and analyzing laboratory samples, as well as data verification and validation. The *Field Sampling Quality Assessment* and *Laboratory Analysis Quality Assessment* sections in this report provide the field and laboratory QC results during this quarter. The SFWMD's Laboratory Information Management System (LIMS) provided the data used in this report. These data are considered preliminary until release into the District's DBHYDRO database.

Additionally, this report includes an analysis of the District laboratory's performance on the split (EVPA project) with the Florida Department of Environmental Protection (FDEP) for a one-year period. The report also includes the results of the U.S. Geological Survey Analytical Evaluation Program for Standard Reference Samples of the laboratory's performance and the results of the National Water Research Institute Environment Canada Ecosystem Inter-laboratory Proficiency Testing Program.

[1] SFWMD. 2009. Field Sampling Quality Manual, Version 5.0. South Florida Water Management District, Water Quality Monitoring Division and Quality Assurance Staff. West Palm Beach, FL.

[2] SFWMD. 2009. Chemistry Laboratory Quality Manual (Rev. No. 2009-01). South Florida Water Management District, Water Quality Monitoring Division, Environmental Resource Assessment Department. West Palm Beach, FL.

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

This period had no major procedural updates related to TP sample collection.

MISSING DATA

Table 1 presents the list of missing data for this reporting period. Twenty-five data points were missing (not collected) due to lack of flow or shallow water depth.

Table 1. Missing data for July 1 to September 30, 2009.

Project	Collection Date	Station	Comments
PIN	7-Jul-09	S12B	Gates closed, no flow, no sample collected.
PIN	7-Jul-09	S12C	Gates closed, no flow, no sample collected.
PIE	13-Jul-09	BERMB3	Insufficient depth to sample, thick algal mats on surface.
PIN	14-Jul-09	S12B	Gates closed, no flow, no sample collected.
PIN	14-Jul-09	S12C	Gates closed, no flow, no sample collected.
PIN	14-Jul-09	S355A	Gates closed, no flow, no sample collected.
PIN	14-Jul-09	S355B	Gates closed, no flow, no sample collected.
PIN	21-Jul-09	S355A	Gates closed, no flow, no sample collected.
PIN	21-Jul-09	S355B	Gates closed, no flow, no sample collected.
PIN	28-Jul-09	S355A	Gates closed, no flow, no sample collected.
PIN	28-Jul-09	S355B	Gates closed, no flow, no sample collected.
PIE	10-Aug-09	BERMB3	Insufficient depth to sample, algae covered water surface.
PIN	18-Aug-09	S355A	Gates closed, no flow, no sample collected.
PIN	18-Aug-09	S355B	Gates closed, no flow, no sample collected.
PIN	24-Aug-09	BERMB3	Insufficient depth to sample.
PIN	25-Aug-09	S355A	Gates closed, no flow, no sample collected.
PIN	25-Aug-09	S355B	Gates closed, no flow, no sample collected.
PIN	9-Oct-09	S355A	Gates closed, no flow, no sample collected.
PIN	9-Oct-09	S355B	Gates closed, no flow, no sample collected.
PIN	15-Oct-09	S355A	Gates closed, no flow, no sample collected.
PIN	15-Oct-09	S355B	Gates closed, no flow, no sample collected.
PIN	22-Oct-09	S355A	Gates closed, no flow, no sample collected.
PIN	22-Oct-09	S355B	Gates closed, no flow, no sample collected.
PIN	29-Oct-09	S355A	Gates closed, no flow, no sample collected.
PIN	29-Oct-09	S355B	Gates closed, no flow, no sample collected.

FIELD QUALITY CONTROL

Field QC measures consist of equipment blanks (EB), field-cleaned equipment blanks (FCEB), split samples (SS), and replicate samples (RS). **Table 2** summarizes EB and FCEB results for projects of interest to the Technical Oversight Committee (TOC), as referenced in the table footnotes below. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for two projects. The samples collected for the PIE project on July 13, 2009 failed the field precision[3].

Table 2. Field and equipment blank results.

Type of Blank	Project	Number of Blanks Collected	Number of Detected Blanks	% < 0.002 mg/L	% ≥ 0.002 mg/L
EB	EVPA	1	0	100	0
	PIE	1	0	100	0
	PIN	1	0	100	0
FCEB	EVPA	11	0	100	0
	PIE	14	0	100	0
	PIN	13	0	100	0

- Only blanks for sampling events from samples collected at stations listed in the Introduction are included in this analysis.
- Blanks for TP, which were associated with a short-term auto-sampler project at some TOC stations, are not included in this analysis.
- FCEB and EB acceptance criteria must be less than the method detection limit (MDL).
- When sample concentrations are less than ten times the resulting blank values *that were equal to or greater than the MDL*, "J9" is added[4].

[3] The associated samples were qualified but none of them were related to the stations of interest to the TOC.
[4] Text in italics added to clarify note.

Table 3. Field precision summary.

Project Code	Number of Triplicates	Date Collected	% RSD	Average Value (mg/L)	Comments
PIN	1	7-Jul-09	6.2	0.009	Precision criteria were met
PIE	1	13-Jul-09	39.2	0.029	Precision criteria were not met
EVPA	1	8-Sep-09	6.7	0.009	Precision criteria were met

- Only replicates for sampling events from samples collected at stations listed in the Introduction are included in this analysis.
- The District's chemistry laboratory conducted all TP analyses.
- Field precision acceptance criterion must be ≤ 20%. The laboratory applied this criterion only if sample values were greater than the practical quantitation limit (PQL), which is four times the MDL.

FIELD AUDIT

During the third quarter, one field audit of the PIN project was conducted related to the TOC water quality stations.

The findings were: a) improper sample collection protocol which was resolved by the auditor on site, and b) the NIST-traceable thermometer had not been calibrated in the past year. This thermometer has been calibrated successfully since the audit took place.

The corrective actions from this audit are complete. After a review of the key deficiencies, it was determined the quality of the data were not affected.

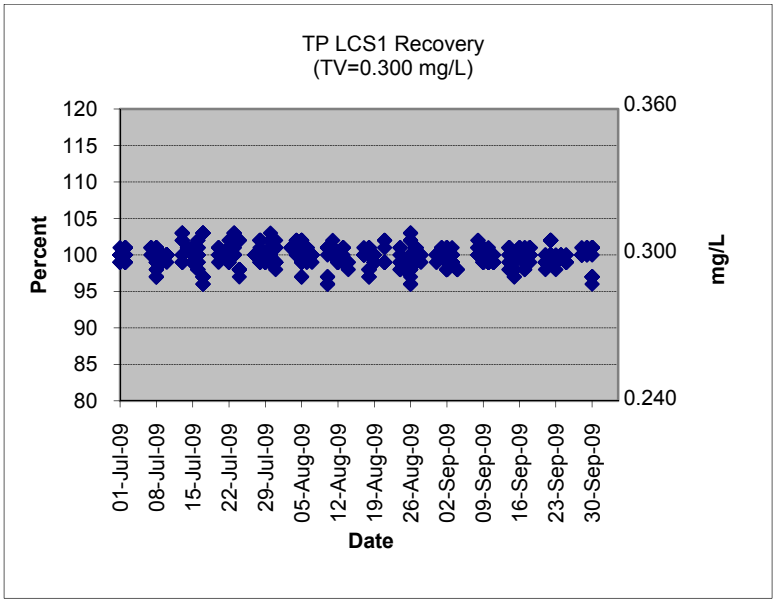
LABORATORY ANALYSIS QUALITY ASSESSMENT

PROCEDURE UPDATES

The TP analytical procedure did not change during this reporting period.

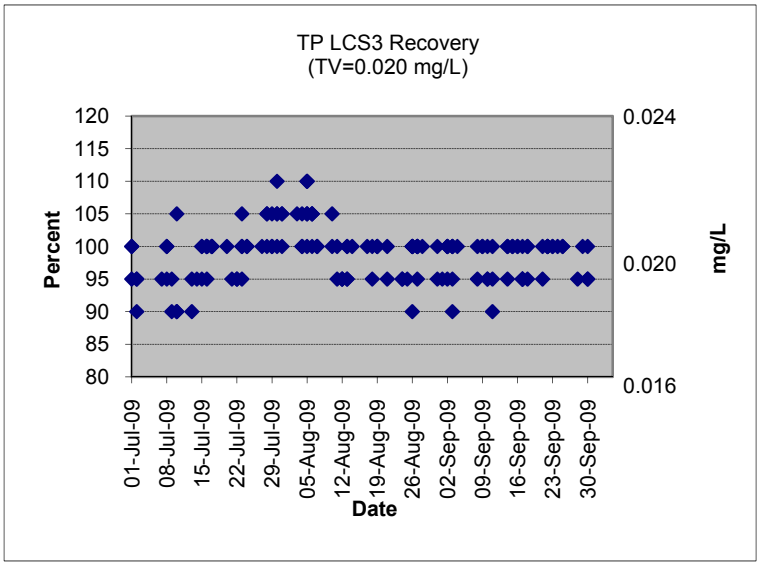
LABORATORY QUALITY CONTROL

Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figures 1** through **4** show the TP recoveries from various types and levels of QC samples at the District laboratory from July 1, 2009, through September 30, 2009.



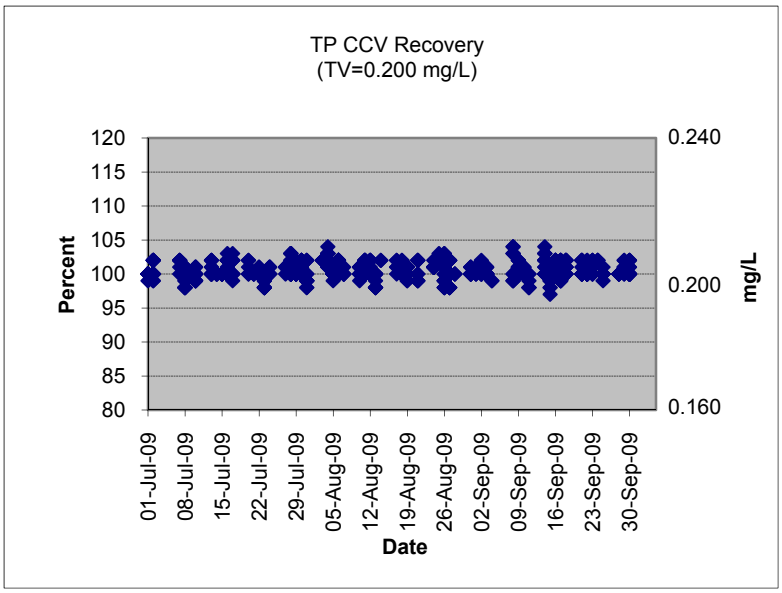
Mean = 99.9%, Max = 103%, Min = 96%

Figure 1. QC (laboratory control sample) recoveries for TP analysis.



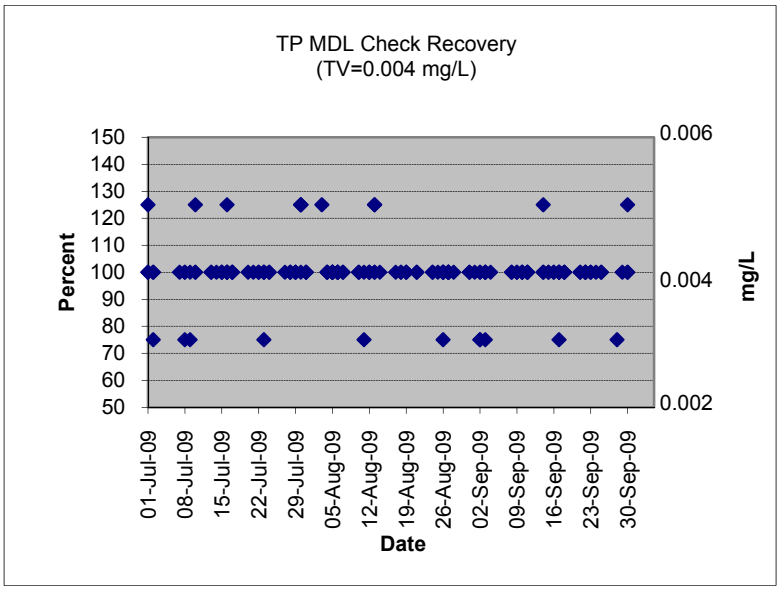
Mean = 98.8%, Max = 110%, Min = 90%

Figure 2. QC (laboratory control sample) recoveries for TP analysis.



Mean = 100.5%, Max = 104%, Min = 97%

Figure 3. QC (continuing calibration verification) sample recoveries for TP analysis.



Mean = 100%, Max = 125.0%, Min = 75.0%

Figure 4. QC5 (MDL check) sample recoveries for TP analysis.

Tables 4 and **5** present the precision and matrix spike recoveries for TP analyses during the reporting period. If QC recoveries are outside the set limits, then the District's laboratory usually rejects the analytical batch. If any deficiencies are noted, the samples have exceeded the required holding times, and the laboratory cannot re-analyze the data, then the sample is qualified accordingly.

Table 4. TP Precision Data.

Acceptance Limit	**<10 %**
Analytical Range: 0.002-0.400 mg/L	
Maximum	8.3 %
Mean	1.6 %
Standard Deviation	1.5 %
3xSD	4.6 %
UCL	6.2 %
n	396

UCL Upper Control Limit (Calculated)
n Number of data points

Table 5. TP Spike Recovery Data.

Acceptance Limit	**90 – 110 %**
Analytical Range: 0.002-0.400 mg/L	
Minimum	90 %
Maximum	110 %
Mean	100.2 %
Standard Deviation (SD)	3.7 %
3xSD	11.1 %
LCL	89 %
UCL	111 %
n	398

LCL Lower Control Limit (Calculated)
UCL Upper Control Limit (Calculated)
n Number of data points

Recoveries for the QC samples are within ±10 percent of the true value, which is acceptable. The Method Detection Limit (MDL) check (QC5), with a true value of 0.004 mg/L, had mean recoveries of 100 percent. The daily MDL check results indicate that the laboratory has consistently achieved the established MDL of 0.002 mg/L. An organic check is a solution prepared from phytic acid, which is a stable form of organic phosphate used to prepare matrix spikes, the mean recovery for which was 100.2 percent.

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

The estimated analytical uncertainty for total phosphorus conducted by the District laboratory for the last quarter was determined to be 6.2 percent (with a 95 percent confidence level). This result applies to the analytical process and does not include uncertainty attributed to field sampling activities (e.g., sample collection and sample location effects). **Figure 5** is presented to clarify the concept of MDL and Practical Quantitation Limit (PQL) of a measurement process.

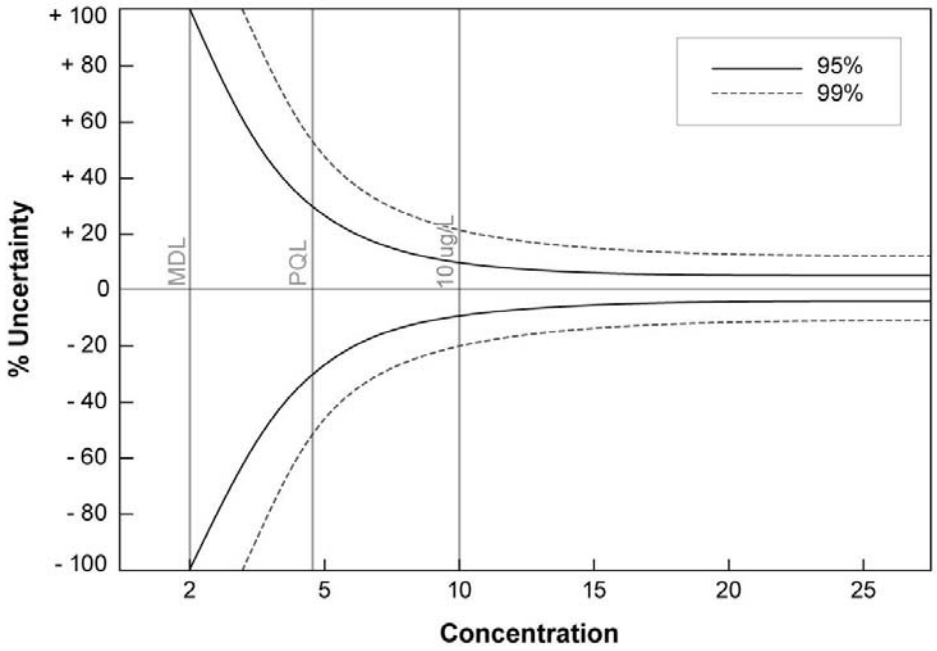


Figure 5. Uncertainty of TP measurement close to the detection limit.

METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

MDL checks are routinely analyzed with each analytical run. From July 1 to September 30, 2009, 156 results for MDL checks were reported for total phosphorus measurements. The calculated MDL from these results was determined to be 0.9 µg/L, using the procedure described in 40 CFR 136 Appendix B and the calculated PQL for this period was 3.6 µg/L. At this concentration, the relative uncertainty in the measured value is estimated to be ±30 percent at the 95 percent confidence level[5].

The reported values between the MDL (established) and PQL are assigned the "I" qualifier, indicating the uncertainty is sufficiently high that the reported values should be considered an estimate of the actual concentration.

[3] Taylor, J.K. 1987. Quality Assurance of Chemical Measurements (1987) Lewis Publishers, Chelsea, MI.

INTER-LABORATORY QUALITY CONTROL ASSESSMENT

Split Studies with FDEP Laboratory

To continuously assess comparability of results, the District routinely sends split samples to other laboratories. The EVPA Quarterly Splits conducted between the FDEP and the District's laboratory from September 2008 to September 2009 (see **Appendix A**) provided the data used in this analysis. **Figure 6** presents regression analysis of all data, and **Table 6** presents summary statistics for the data pairs.

ALL DATA

Figure 6 shows that the intercept is not statistically different from zero and the slope is not statistically different from one for all TP data from both laboratories. The r^2 (R-square) value is 0.402. The intercept of the regression is not statistically different from zero since the 95 percent confidence interval for intercept contains zero. The slope of the regression is not different from one statistically since the 95 percent confidence interval for slope contains one.

Table 6 shows that the mean difference (0.0003 mg/L) and median difference (0.0005 mg/L) are statistically insignificant. The paired t-test and signed-rank test yield p-values of 0.639 and 0.148 respectively.

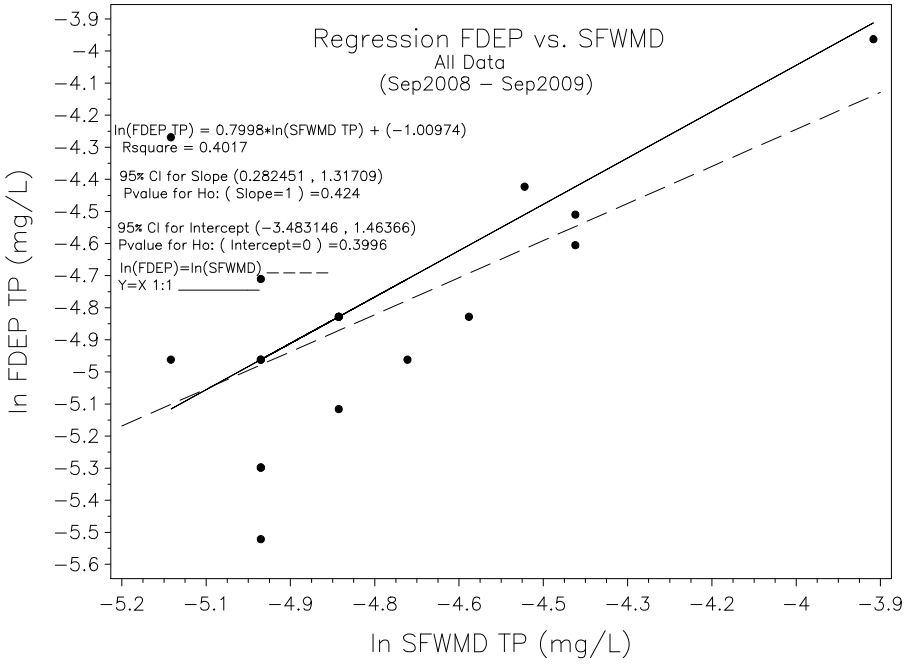


Figure 6. Regression analysis for all TP data.

TP ≥ 0.020 mg/L

There was only one data pair in this range where the TP ≥ 0.020 mg/L. The comparison of concentration at this level is not possible.

TP < 0.020 mg/L

All results for this analysis fell into the TP < 0.020 mg/L range. The results for all "All Data" range are comparisons of concentration at this level.

In summary, the differences for all TP levels were below the MDL for both laboratories and the difference was statistically insignificant in both; the sign-rank test ($p>0.05$) for non-normally distributed paired data and linear regression.

Table 6. Comparison of District and FDEP split TP samples.

All Data	**Summary Statistics**				
	Lab	**N**	**Mean**	**Median**	
	FDEP	18	0.009	0.008	
	District	18	0.009	0.008	
	Statistical Test of Hypotheses				
	Summary of Paired Differences		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.0003	Mean of Differences = 0	Student's t	0.639
	Median of Differences	0.0005	Median of Differences = 0	Signed Rank	0.148

Notes:

- Differences calculated as District TP minus FDEP TP. The mean and median differences for all concentration levels are at or below the MDL.
- Data were not used if FDEP value was below FDEP's detection limit (0.004 mg/L).

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 (PT 94) are presented in **Table 7** (June-September 2009). The District laboratory was rated on performance of TP as "Ideal" (highest) and the linear regression shows no systematic bias (**Figure 7**).

The interpretation of a Z-value is based on the International Organization of Standardization (ISO), Guide 43. A Z-value < 2 is classified satisfactory, 2 > Z < 3 is questionable and Z > 3 is unsatisfactory.

Table 7. Performance in PT Study 94 for TP, June-September 2009

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.0910	0.008	0.345	0.055	0.225	0.004	0.0015	0.696	0.0200	0.158
Reported Results, mg/L	0.091	0.007	0.339	0.054	0.227	0.003	<0.002	0.706	0.019	0.154
Z-value	0.0	-0.4	-0.4	-0.2	0.1	-0.6	NA	0.3	-0.5	-0.5

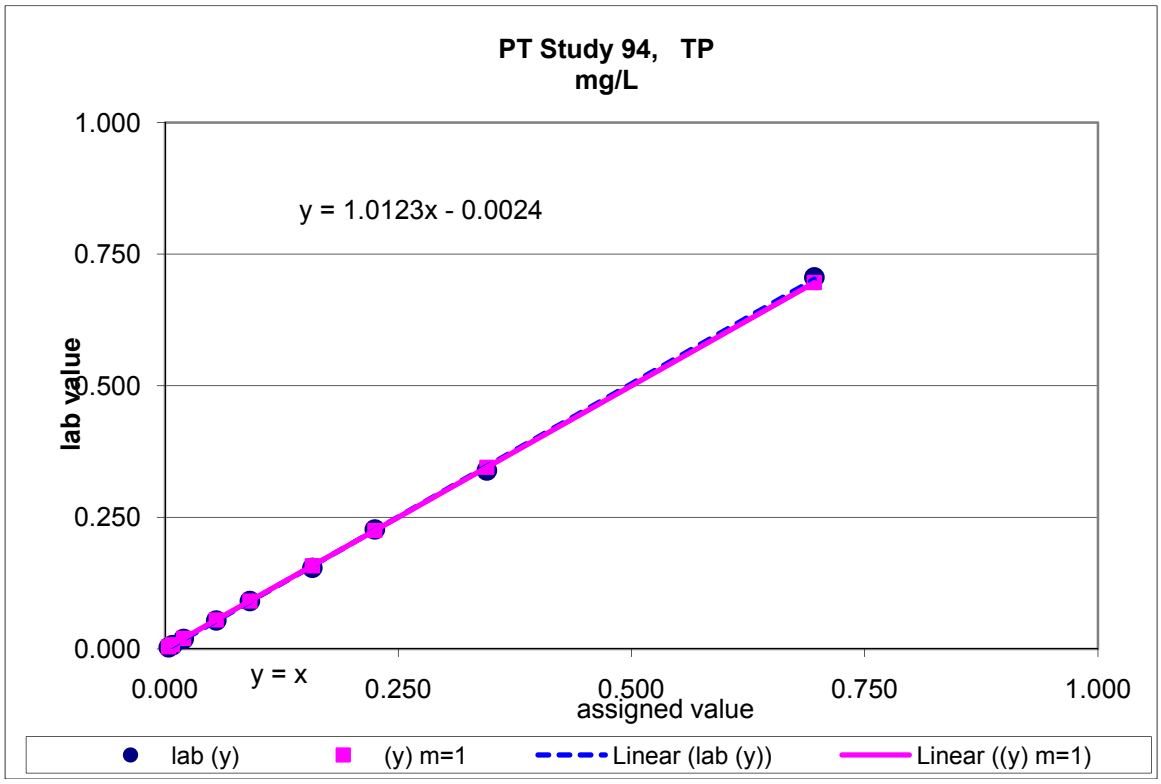


Figure 7. Regression analysis of reported TP results

U.S. Geological Survey Analytical Evaluation Program

The SFWMD's laboratory participates in the semiannual U.S Geological Survey (USGS) performance evaluation program on environmental samples for the Comprehensive Everglades Restoration Plan (CERP). The results have been published in a final report to the CERP Quality Assurance Oversight Team. Evaluation of the results is based on the deviation (Z-value) from the median and percent difference. **Table 8** provides the results of the fall (June–September) 2009 study.

Table 8. USGS Performance Evaluation study for TP results.

Sample I.D	Reported Result, mg/L	Most Probable Value, mg/L	Z-Value	% Difference
M-192	0.075	0.072	0.43	4.17
N-103	0.299	0.293	0.46	2.05

GLOSSARY

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.

Equipment Blank (EB). A general term 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 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.

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.

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 MDLs 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 U.S. Environmental Protection Agency.

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 four times the MDL.

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.

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

Relative Standard Deviation (RSD). A measurement of precision, used when comparing more than two results. It is calculated as %RSD = [Std. Deviation/Mean]*100.

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.

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.

Z-Value. A measure of the deviation of the result (Xi) from the assigned value (X) for that determinant (calculated as $z = (Xi–X)/\sigma$, where σ is a standard deviation) (EURACHEM).

APPENDIX A

Results of TP split studies between the District and FDEP laboratories, EVPA Project, September 2008–September 2009.

Sample	Date	District	FDEP	%RPD/Comments
EVPA	18-Sep-08	0.007 (I)	0.007 (I)	<PQL
EVPA	18-Sep-08	0.008	0.008 (I)	<PQL
EVPA	18-Sep-08	0.008	0.008 (I)	<PQL
EVPA	18-Sep-08	0.008	0.008 (I)	<PQL
EVPA	09-Dec-08	0.007 (I)	0.005 (I)	<PQL
EVPA	09-Dec-08	0.009	0.007 (I)	<PQL
EVPA	09-Dec-08	0.007 (I)	0.005 (I)	<PQL
EVPA	09-Dec-08	0.004 (I)	<0.004 (U)	<PQL
EVPA	09-Mar-09	0.005* (I)	0.012* Y	<PQL
EVPA	09-Mar-09	0.006 (I)	0.014	80.0
EVPA	09-Mar-09	0.006 (I)	0.007 (I)	<PQL
EVPA	10-Mar-09	0.011	0.012	8.7
EVPA	02-Jun-09	0.020	0.019	5.1
EVPA	02-Jun-09	0.012	0.010	18.2
EVPA	02-Jun-09	0.012	0.011	8.7
EVPA	02-Jun-09	0.010	0.008 (I)	<PQL
EVPA	8-Sep-09	0.007 (I)	0.007 (I)	<PQL
EVPA	9-Sep-09	0.008	0.006 (I)	<PQL
EVPA	9-Sep-09	0.007 (I)	0.004 (I)	<PQL
EVPA	8-Sep-09	0.009	0.007 (I)	<PQL

*Result not included in the statistical evaluation due to improper sample preservation (qualifier code "Y")

Qualifier codes:

I: indicates that the reported value is greater than or equal to the MDL but less than PQL

U: indicates that the compound was analyzed for but not detected

SFWMD: Actual MDL = 0.002 mg/L and PQL = 0.008 mg/L
FDEP: Actual MDL = 0.004 mg/L and PQL = 0.010 mg/L