Quality Assessment Report for Water Quality Monitoring

October – December 2010

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INTRODUCTION

This report is an assessment of the South Florida Water Management District (SFWMD) laboratory analysis and field sampling for total phosphorus (TP) monitoring, primarily for the following projects and their associated stations from October 1, 2010 through December 31, 2010:

- Everglades National Park Inflows North (PIN): S12A, S12B, S12C, S12D, S333, S355A, S355B, and S356-334
- 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 sampling events 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 SFWMD's *Field Sampling Quality Manual* (SFWMD 2010a) provides the minimum requirements followed in field sample collection. The *Chemistry Laboratory Quality Manual* (SFWMD 2010b) 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 available in the SFWMD's DBHYDRO database.

Additionally, this report includes an analysis of the SFWMD laboratory's performance on the split (EVPA) and inter-laboratory studies with the Florida Department of Environmental Protection (FDEP) for a one-year period. The report also includes the results of the National Proficiency Testing Program, which is designed to evaluate the laboratory's performance through analysis of unknown samples provided by an external source. Proficiency testing is one of the essential elements of the National Environmental Laboratory Accreditation Program (NELAP) accreditation process.

FIELD SAMPLING QUALITY ASSESSMENT

PROCEDURE UPDATES

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

MISSING DATA

Table 1 lists the missing data for this reporting period. Thirty-four data points were missing (not collected) due to lack of flow, shallow water depth or insufficient water level.

Table 1. Missing data for October 1 to December 31, 2010.

Project	Collection Date	Station	Comments
PIN	13-Oct-10	S355A	No flow, no sample collected.
PIN	13-Oct-10	S355B	No flow, no sample collected.
PIN	19-Oct-10	S355A	No flow, no sample collected.
PIN	19-Oct-10	S355B	No flow, no sample collected.
PIN	26-Oct-10	S355A	No flow, no sample collected.
PIN	26-Oct-10	S355B	No flow, no sample collected.
PIE	1-Nov-10	BERMB3	Site dry, no sample collected.
PIN	9-Nov-10	S12B	No flow, no sample collected.
PIN	9-Nov-10	S355A	No flow, no sample collected.
PIN	9-Nov-10	S355B	No flow, no sample collected.
PIE	15-Nov-10	BERMB3	Site dry, no sample collected.
PIN	16-Nov-10	S355A	No flow, no sample collected.
PIN	16-Nov-10	S355B	No flow, no sample collected.
PIN	23-Nov-10	S355A	No flow, no sample collected.
PIN	23-Nov-10	S355B	No flow, no sample collected.
PIE	29-Nov-10	BERMB3	Site dry, no sample collected.
PIN	30-Nov-10	S355A	No flow, no sample collected.
PIN	30-Nov-10	S355B	No flow, no sample collected.
PIN	14-Dec-10	S12B	No flow, no sample collected.
PIN	14-Dec-10	S12C	No flow, no sample collected.
PIN	14-Dec-10	S12D	No flow, no sample collected.
PIN	14-Dec-10	S355A	No flow, no sample collected.
PIN	14-Dec-10	S355B	No flow, no sample collected.
PIN	21-Dec-10	S12B	No flow, no sample collected.
PIN	21-Dec-10	S12C	No flow, no sample collected.
PIN	21-Dec-10	S12D	No flow, no sample collected.
PIN	21-Dec-10	S355A	No flow, no sample collected.
PIN	21-Dec-10	S355B	No flow, no sample collected.
PIE	27-Dec-10	BERMB3	No flow, no sample collected.
PIN	28-Dec-10	S12B	No flow, no sample collected.
PIN	28-Dec-10	S12C	No flow, no sample collected.
PIN	28-Dec-10	S12D	No flow, no sample collected.
PIN	28-Dec-10	S355A	No flow, no sample collected.
PIN	28-Dec-10	S355B	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's footnotes. **Table 3** summarizes the field precision results and shows that the field sampling precision was acceptable for all three projects. **Table 4** summarizes the contaminated field blanks. TP was detected in the EP at LOX4 and in the FCEB at S356-334) at and above the method detection limit (MDL). **Table 5** shows all TP data qualified with a "J9" code associated with these field generated blanks.

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	PIN	-	-	-	-
	EVPA	2	1	50	50
	PIE	1	0	100	0
FCEB	EVPA	9	0	100	0
	PIE	14	0	100	0
	PIN	13	1	92	8

Notes:

- Only blanks from sampling events containing samples collected at stations listed in the Introduction are included in this table. The QC blanks may have been collected during the sampling event on the day adjacent to the collection date for the compliance samples.
- FCEB and EB acceptance criteria must be less than the MDL.
- When sample concentrations are less than 10 times the blank values that were equal or greater than the MDL, the qualifier "J9" is assigned to the associated sample(s).
- mg/L – milligram per liter

Table 3. Precision summary for field replicates.

Project Code	Number of Triplicates	Date Collected	% RSD	Average Value (mg/L)	Comments
PIN	1	4-Oct-10	6.9	0.008*	Precision criterion was met.
PIN	1	7-Oct-10	5.6	0.010*	Precision criterion was met.
PIE	1	4-Oct-10	16.5	0.021*	Precision criterion was met.
EVPA	1	8-Nov-10	0.0	0.005*	Precision criterion was met.
EVPA	1	6-Dec-10	10.2	0.006	Precision criterion was met.

Notes:

- *Samples not associated with the stations of interest
- Only replicates from sampling events containing samples collected at stations listed in the Introduction are included in this analysis. The QC replicates may have been collected during the sampling event on the day adjacent to the collection date for the compliance samples.
- The SFWMD's chemistry laboratory conducted all TP analyses.
- Field precision 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.

Table 4. Field blanks ≥ MDL

Type of Blank	Project	Station	Date Collected	Value (mg/L)	Comments
EB	EVPA	LOX4	6-Dec-10	0.002	EB ≥ MDL
FCEB	PIN	S356-334	14-Dec-10	0.003	FCEB ≥ MDL

Table 5. List of qualified data

Project Code	Date Collected	Station	Flag	Result (mg/L)	Comments
EVPA	6-Dec-10	LOX4	J9	0.007	Sample associated with EB ≥ MDL and ≤ 10 times of EB (see Table4).
PIN	14-Dec-10	S333	J9	0.006	Sample associated with FCEB ≥ MDL and ≤ 10 times of FCEB (see Table4).
PIN	14-Dec-10	S12A	J9	0.006	Sample associated with FCEB ≥ MDL and ≤ 10 times of FCEB (see Table4).

Note:

- The value of 10 times the blank value equal to or greater than the sample value qualified with data code "J9" (FDEP QA Rule Chapter 62-160.700, F.A.C.)

FIELD AUDIT

There were no audits related to TOC water quality stations conducted during the fourth quarter of 2010.

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 **6** show the TP recoveries from various types and levels of QC samples at the SFWMD laboratory from October 1, 2010 through December 31, 2010. Control charts provide a graphical means to demonstrate statistical control, monitoring a measurement process, diagnose measurement problems, and document measurement uncertainty. They also are used to monitor and document critical aspects of samples and sampling operation.

Figure 1a shows the recoveries for laboratory control sample (LCS1) at TP concentration 0.300 milligrams per liter (mg/L) varied from 95 to 102%, and mean central line value of 99.3% based on 626 results. The acceptable control limit is 90-110%.

Figure 2a shows the recoveries for laboratory control sample (LCS3) at TP concentration 0.020 mg/L varied from 90 to 105%, and mean central line value of 98.0% based on 108 results. The acceptable control limit is 90-110%.

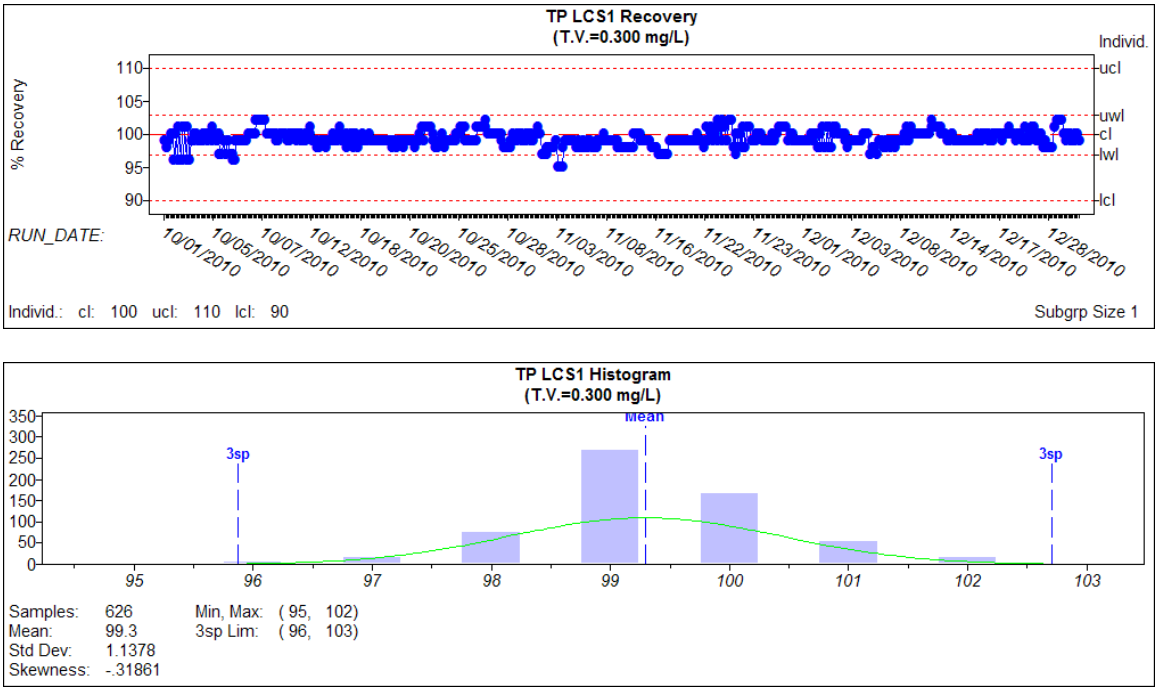
Figure 3a shows the recoveries for continuing calibration verification sample (LCS3) at TP concentration 0.200 mg/L varied from 98 to 103%, and mean central line value of 100.2% based on 518 results. The acceptable control limit is 95-105%.

Figure 4a shows the recoveries for the MDL sample (LCS5) at TP concentration 0.004 mg/L varied from 0.003 to 0.005 mg/L.

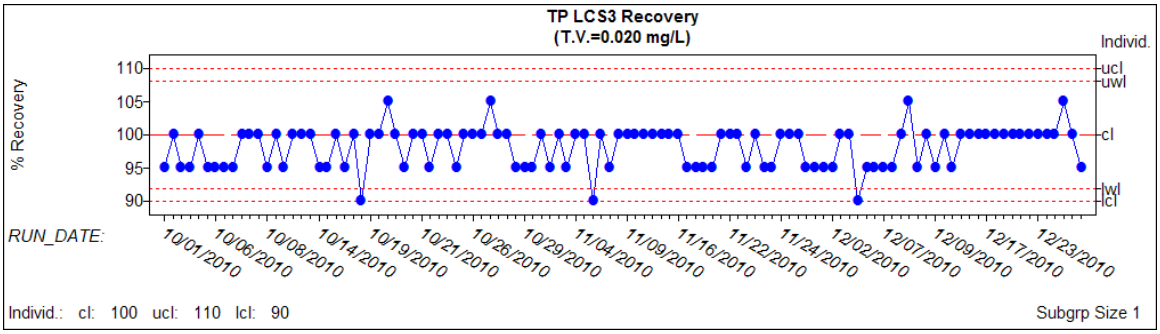
Figures 5 and **6** present the precision and matrix spike recoveries for TP analyses during the reporting period. If QC recoveries are outside the set limits, then the SFWMD's laboratory usually rejects the analytical batch. If any deficiencies are noted, the samples have exceeded the required holding times, and the laboratory cannot reanalyze the data, then the sample is qualified accordingly.

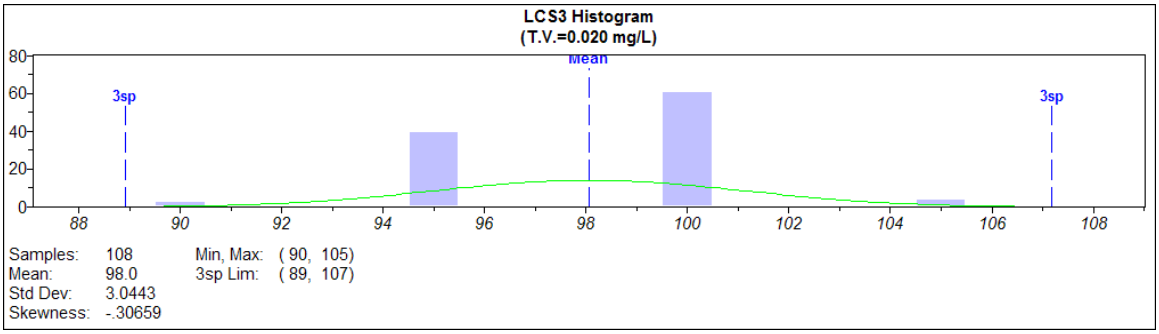
Recoveries for the QC samples are within ±10 percent of the true value, which is acceptable. The daily MDL check with a true value of 0.004 mg/L indicates that the laboratory has consistently achieved the established MDL of 0.002 mg/L. An organic check is a solution prepared from phytic acid, which is a stable form of organic phosphate used to prepare matrix spikes, the mean recovery for which was 100.6 percent.

Figures 1b through 6b show the distributed of quality control samples in the roughly symmetrical bell-shape form with most values clustered around the central line.

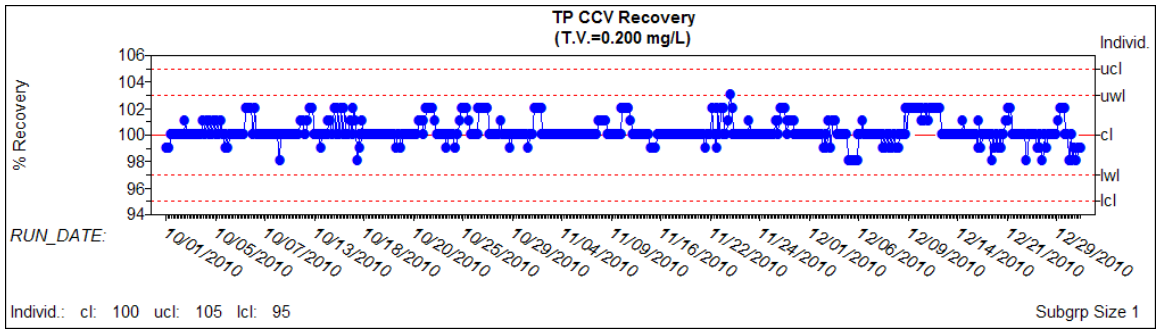


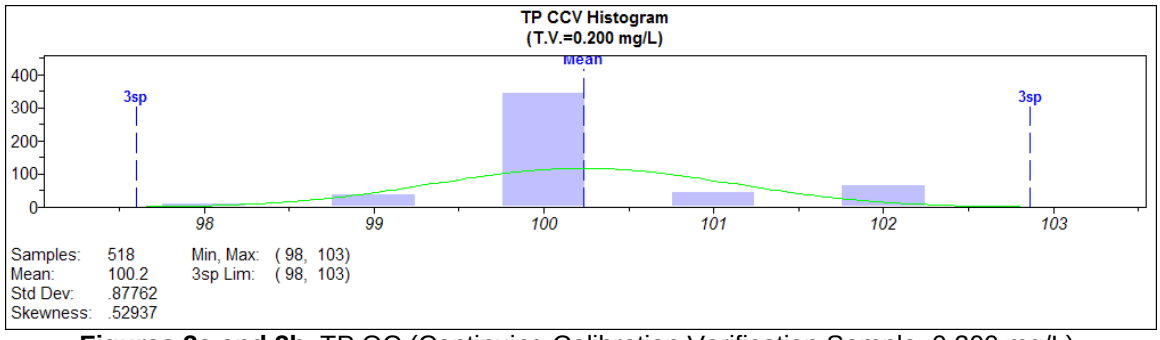
Figures 1a and 1b. TP QC (Laboratory Control Sample, 0.300 mg/L) sample recoveries and histogram.



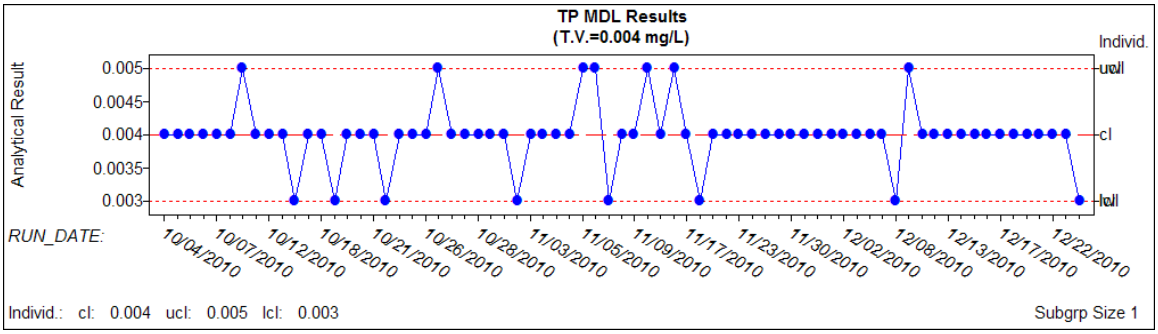


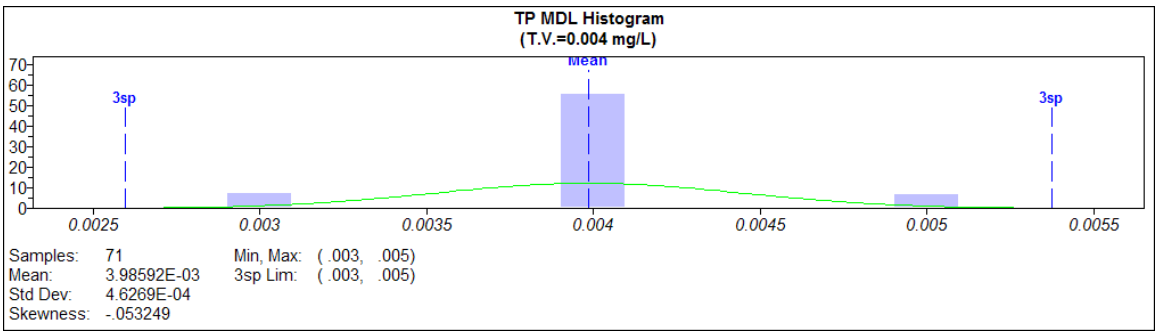
Figures 2a and 2b. TP QC (Laboratory Control Sample, 0.020 mg/L) sample recoveries and histogram.



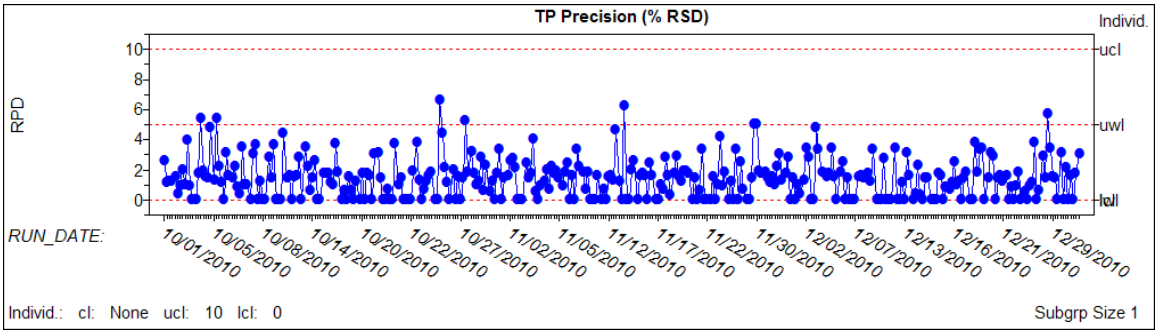


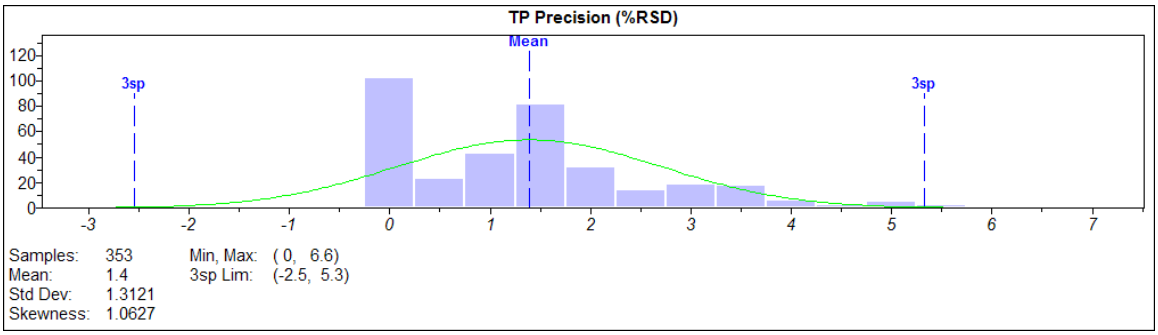
Figures 3a and 3b. TP QC (Continuing Calibration Verification Sample, 0.200 mg/L) sample recoveries and histogram.



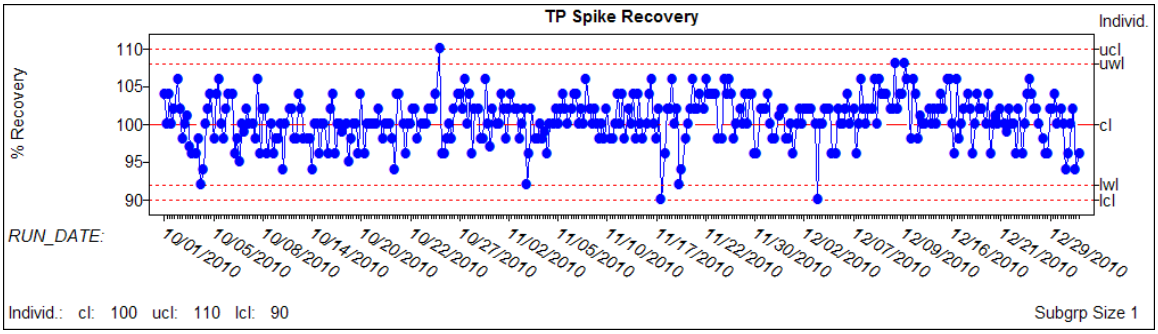


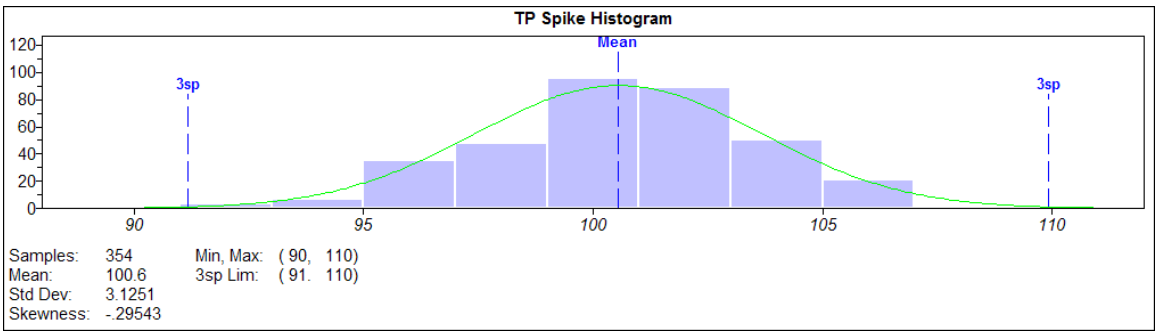
Figures 4a and 4b. TP QC5 (Method Detection Limit Check, 0.004 mg/L) sample recoveries and histogram.





Figures 5a and 5b. TP precision (%) relative percent different and histogram.





Figures 6a and 6b. TP spike recovery (%) data and histogram

Notes for Figures 1 through 6:

- T.V. - true value
- ucl - upper control limit
- uwl - upper warning limit
- cl - central line
- lwl - lower warning limit
- lcl - lower control limit
- Min, Max - range of acceptable limits
- Std Dev - standard deviation
- Samples - number of analyzed QC samples
- 3sp Lim - calculated limits for subgroup based on 3 sigma factor
- y-axis label for histogram indicates number of data points

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

The estimated analytical uncertainty for total phosphorus conducted by the SFWMD laboratory for the last quarter (October-December 2010) was determined to be 4.1 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 7** is presented to clarify the concept of MDL and practical quantitation limit (PQL) of a measurement process.

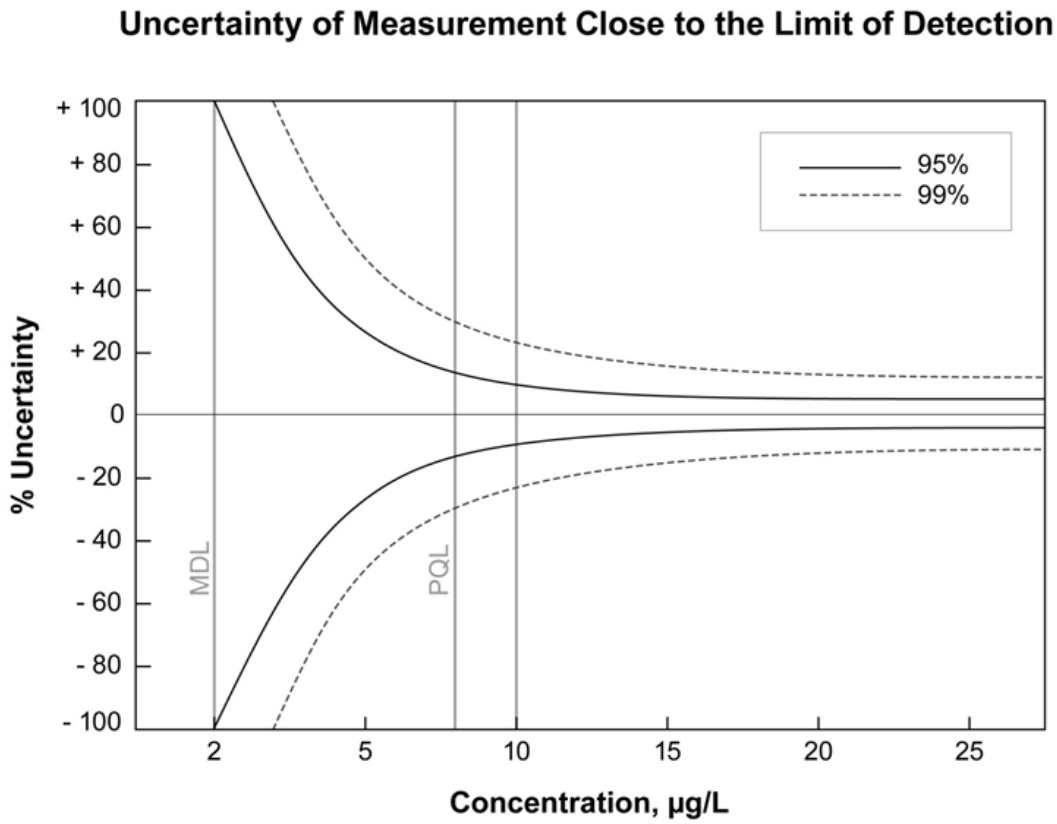


Figure 7. Uncertainty of TP measurement close to the detection limit.

METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

MDL checks are routinely analyzed with each analytical run. From October 1 to December 31, 2010, 71 results for MDL checks were reported for TP measurements. The calculated MDL from these results was determined to be 1 microgram per liter (µg/L), using the procedure described in 40 CFR 136 Appendix B and the calculated PQL for this period was 4 µg/L. At this concentration, the relative uncertainty in the measured value is estimated to be ±30 percent at the 95 percent confidence level (Taylor 1987).

The reported values between the MDL (established at 2 µg/L) and PQL (established at 8 µg/L) are assigned the "I" qualifier, indicating that the results are at concentrations that cannot be accurately quantified.

INTER-LABORATORY QUALITY CONTROL ASSESSMENT

SPLIT STUDIES WITH FDEP LABORATORY

To continuously assess comparability of results, the SFWMD routinely sends split samples to other laboratories. The EVPA Quarterly Splits conducted between the FDEP and the SFWMD's laboratory from December 2009 to December 2010 (see **Appendix A**) provided the data used in this analysis. **Figure 8** presents regression analysis of all data, and **Table 8** presents summary statistics for the data pairs.

ALL DATA

Figure 8 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 0.645. The intercept of the regression is not statistically different from zero since the 95 percent confidence interval for the intercept contains zero. The slope of the regression is not different from one statistically since the 95 percent confidence interval for slope contains one.

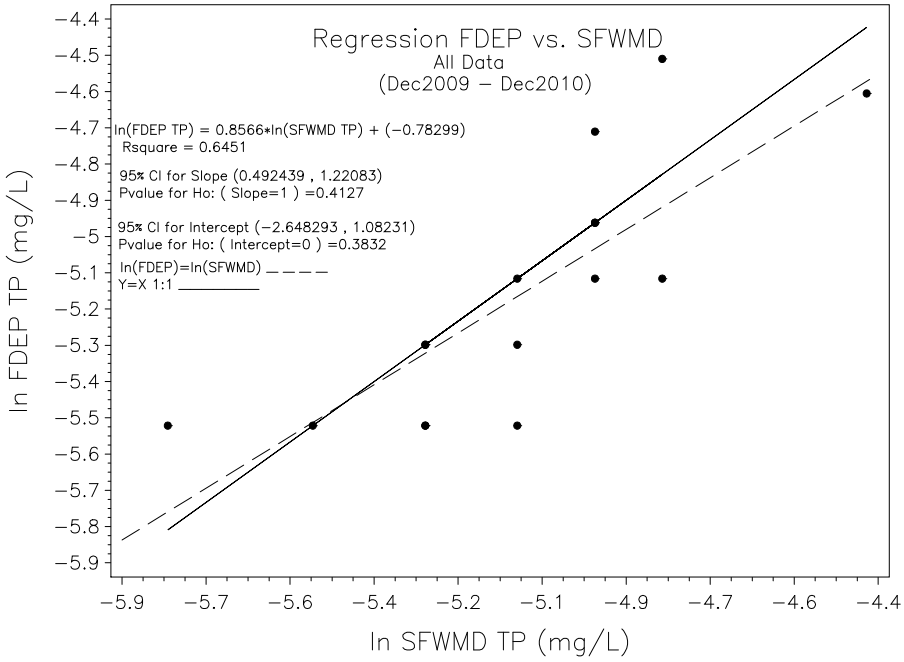


Figure 8. Regression analysis for all TP data.

Table 8 shows that the mean difference and the median difference are not statistically significant. The paired t-test and signed-rank test yield p-values of 0.483 and 0.473 respectively.

TP ≥ 0.020 mg/L

There were not any data points in this range where the TP was greater than or equal to 0.020 mg/L.

Table 8. Comparison of SFWMD and FDEP split TP samples.

All Data	**Summary Statistics**				
	Lab	**N**	**Mean (mg/L)**	**Median (mg/L)**	
	FDEP	16	0.006	0.006	
	SFWMD	16	0.006	0.006	
	Statistical Test of Hypotheses				
	Summary of Paired Differences (mg/L)		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.000	Mean of Differences = 0	Student's t	0.483
	Median of Differences	0.000	Median of Differences = 0	Signed Rank	0.473

Notes:

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

TP < 0.020 mg/L

All results for this analysis fell into the TP less than 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.

NATIONAL PROFICIENCY TESTING PROGRAM

As a requirement for laboratory certification, the SFWMD's laboratory performs proficiency testing on environmental samples on a semiannual basis. The result for the SFWMD's laboratory from the most recent proficiency testing study (September to October 2010) are shown in **Table-9**.

Table 9. Proficiency testing WP-188 study for TP.

Assigned Value	7.64 mg/L
Study Mean Value	7.66 mg/L
Reported Value	7.68 mg/L
Acceptance Limits	6.31 – 9.04 mg/L
Performance Evaluation	Acceptable

Notes:

- Assigned Value – this value is the calculated True Value of the standard based upon the actual composition of the standard.
- Study Mean Value – this value is calculated using all reported values after the removal of outliers.
- Reported Value – the test result reported to the study provider for a specific analyte.
- Acceptance Limits – this limit is calculated upon the US Environmental Protection Agency (EPA) National Standards for Water Proficiency Testing Criteria Document. For the Water Pollution Program (WP), EPA Acceptance Limits are defined as ± three (3) EPA Standard Deviation from the EPA Mean.

REFERENCES

SFWMD. 2010a. Field Sampling Quality Manual, SFWMD-FIELD-QM-001-06. South Florida Water Management District, Water Quality Monitoring Division. West Palm Beach, FL.

SFWMD. 2010b. Chemistry Laboratory Quality Manual, SFWMD-LAB-QM-2010-01. South Florida Water Management District, Analytical Services Division, West Palm Beach, FL.

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Chelsea, MI.

GLOSSARY

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.

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-Score: 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 SFWMD and FDEP laboratories, EVPA Project, December 2009–December 2010.

Sample	Date	SFWMD	FDEP	%RPD/Comments
EVPA	2-Dec-09	0.004 (I)	<0.004** (U)	<PQL
EVPA	1-Dec-09	0.008	0.011**	31.6
EVPA	2-Dec-09	0.004 (I)	<0.004** (U)	<PQL
EVPA	2-Dec-09	0.007 (I)	0.009** (I)	<PQL
EVPA	1-Mar-10	0.006 (I)	0.005 (I)	<PQL
EVPA	1-Mar-10	0.008	0.006 (I)	<PQL
EVPA	1-Mar-10	0.005 (I)	<0.004 (U)	<PQL
EVPA	2-Mar-10	0.005 (I)	<0.004 (U)	<PQL
EVPA	2-Jun-10	0.005 (I)	0.005 (I)	<PQL
EVPA	2-Jun-10	0.007 (I)	0.006 (I)	<PQL
EVPA	3-Jun-10	0.005 (I)	0.005 (I)	<PQL
EVPA	3-Jun-10	0.012	0.010	18.2
EVPA	7-Sep-10	0.006 (I)	0.006 (I), (Y)	<PQL
EVPA	7-Sep-10	0.007 (I)	0.007 (I), (Y)	<PQL
EVPA	8-Sep-10	0.005 (I)	0.004 (I), (Y)	<PQL
EVPA	8-Sep-10	0.006 (I)	0.004 (I), (Y)	<PQL
EVPA	6-Dec-10	0.007 (I) (J)	0.007 (I)	<PQL
EVPA	7-Dec-10	0.003 (I)	0.004 (I)	<PQL
EVPA	7-Dec-10	0.004 (I)	0.004 (I)	<PQL
EVPA	7-Dec-10	0.005 (I)	0.004 (I)	<PQL

Notes:

** Equipment blanks (EB) associated with this result were improperly preserved

Qualifier codes:

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

U: indicates the compound was analyzed for but not detected

Y: sample temperature is outside acceptable range

J: sample associated with EB ≥ MDL

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