Quality Assessment Report for Water Quality Monitoring

July – September 2010

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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, 2010, through September 30, 2010:

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

[1] SFWMD. 2010. Field Sampling Quality Manual, Version 6.0. South Florida Water Management District, Water Quality Monitoring Division. West Palm Beach, FL.

[2] SFWMD. 2010. Chemistry Laboratory Quality Manual (Rev. No. 2010-01). South Florida Water Management District, Analytical Services Division, 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 lists the missing data for this reporting period. Thirty-eight data points were missing (not collected) due to lack of flow, shallow water depth or improper sample preservation.

Table 1. Missing data for July 1 to September 30, 2010.

Project	Collection Date	Station	Comments
PIE	6-Jul-10	BERMB3	Not enough water to sample.
PIN	8-Jul-10	S12B	No flow, no sample collected.
PIN	8-Jul-10	S12C	No flow, no sample collected.
PIE	12-Jul-10	BERMB3	Not enough water to sample.
PIN	13-Jul-10	S12B	No flow, no sample collected.
PIN	13-Jul-10	S12C	No flow, no sample collected.
PIN	13-Jul-10	S12D	Improperly preserved sample.
PIN	13-Jul-10	S355A	No flow, no sample collected.
PIN	13-Jul-10	S355B	No flow, no sample collected.
PIN	20-Jul-10	S12B	No flow, no sample collected.
PIN	20-Jul-10	S355A	No flow, no sample collected.
PIN	20-Jul-10	S355B	No flow, no sample collected.
PIE	27-Jul-10	BERMB3	Not enough water to sample.
PIN	28-Jul-10	S12B	No flow, no sample collected.
PIN	28-Jul-10	S355A	No flow, no sample collected.
PIN	28-Jul-10	S355B	No flow, no sample collected.
EVPA	2-Aug-10	LOX3	Total depth less than 0.10 m, no sample collected.
EVPA	2-Aug-10	LOX4	Total depth less than 0.10 m, no sample collected.
EVPA	2-Aug-10	LOX5	Total depth less than 0.10 m, no sample collected.
EVPA	3-Aug-10	LOX13	Total depth less than 0.10 m, no sample collected
PIN	3-Aug-10	S12B	No flow, no sample collected.
PIE	9-Aug-10	BERMB3	Not enough water to sample.
PIN	10-Aug-10	S12B	No flow, no sample collected.
PIN	10-Aug-10	S355A	No flow, no sample collected.
PIN	10-Aug-10	S355B	No flow, no sample collected.

Project	Collection Date	Station	Comments
PIN	17-Aug-10	S355A	No flow, no sample collected.
PIN	17-Aug-10	S355B	No flow, no sample collected.
PIN	24-Aug-10	S355A	No flow, no sample collected.
PIN	24-Aug-10	S355B	No flow, no sample collected.
PIN	31-Aug-10	S355A	No flow, no sample collected.
PIN	31-Aug-10	S355B	No flow, no sample collected.
PIN	14-Sep-10	S355A	No flow, no sample collected.
PIN	14-Sep-10	S355B	No flow, no sample collected.
PIE	20-Sep-10	BERMB3	No flow, no sample collected.
PIN	21-Sep-10	S355A	No flow, no sample collected.
PIN	21-Sep-10	S355B	No flow, no sample collected.
PIN	28-Sep-10	S355A	No flow, no sample collected.
PIN	28-Sep-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 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	0	NA	NA	NA
	EVPA	2	0	100	0
	PIE	1	0	100	0
FCEB	EVPA	8	0	100	0
	PIE	14	0	100	0
	PIN	13	0	100	0
FB	PIN	1	0	100	0

Notes:

- Only blanks from sampling events containing samples collected at stations listed in the Introduction are included in this analysis. 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 method detection limit (MDL).
- When sample concentrations are less than 10 times the resulting blank values that were equal or greater than the MDL, the qualifier "J9" is assigned.

Table 3. Precision summary for field replicates.

Project Code	Number of Triplicates	Date Collected	% RSD	Average Value (mg/L)	Comments
PIN	1	14-Jul-10	3.8	0.015*	Precision criterion was met
PIN	1	15-Jul-10	3.8	0.026*	Precision criterion was met
PIE	1	7-Jul-10	0.0	0.007	Precision criterion was met
EVPA	1	7-Sep-10	8.7	0.007	Precision criterion was met
EVPA	1	14-Sep-10	9.1	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 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 this quarter, two audits were conducted on the sample processing. The EVPA project in WCA-1 collected by the Water Quality Monitoring Division and United States Fish and Wildlife Services (USFWS) personnel was conducted on September 22, 2010. There were no corrective actions or recommendations as a result of this audit.

Another audit was conducted on the sample collection of the PIE project collected by Miami-Dade DERM personnel on September 13, 2010. None of the findings appear to have affected the data quality for the samples of interest in this report. The audit reports are available upon request from Quality Assurance Administrator Ming Chen (Restoration Sciences Department, SFWMD, tel. 561.682.6252).

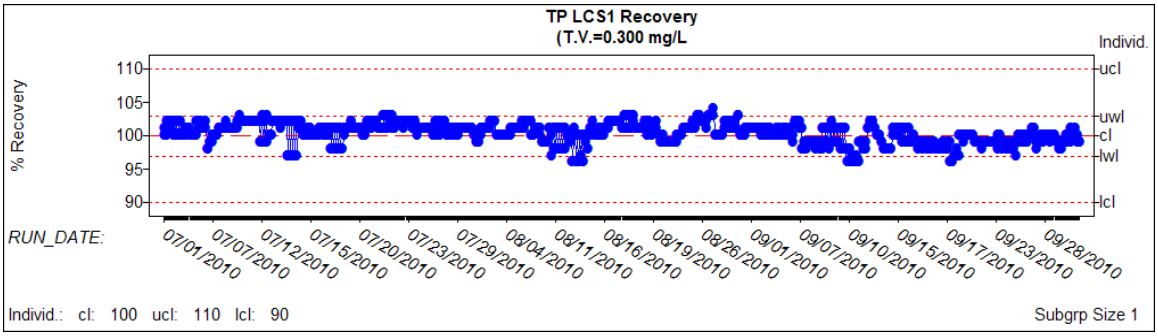
LABORATORY ANALYSIS QUALITY ASSESSMENT

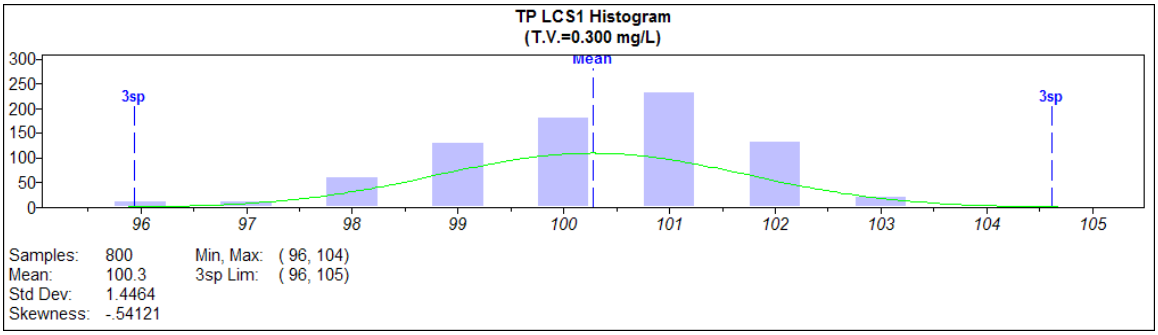
PROCEDURE UPDATES

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

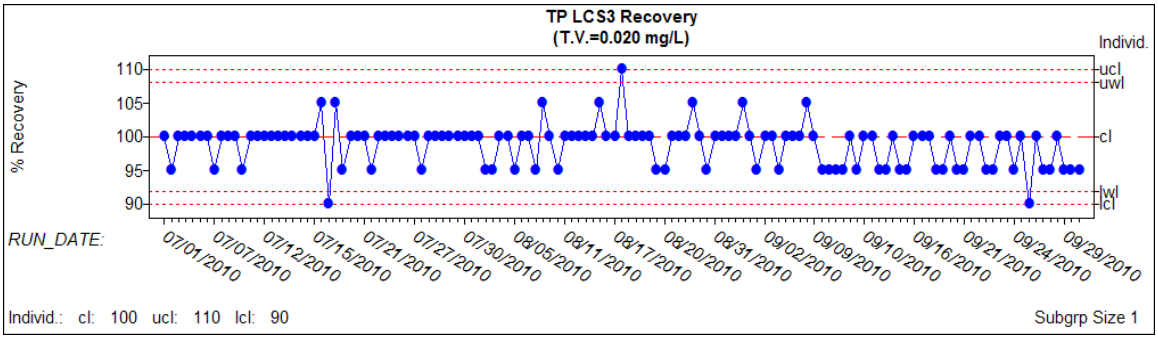
LABORATORY QUALITY CONTROL

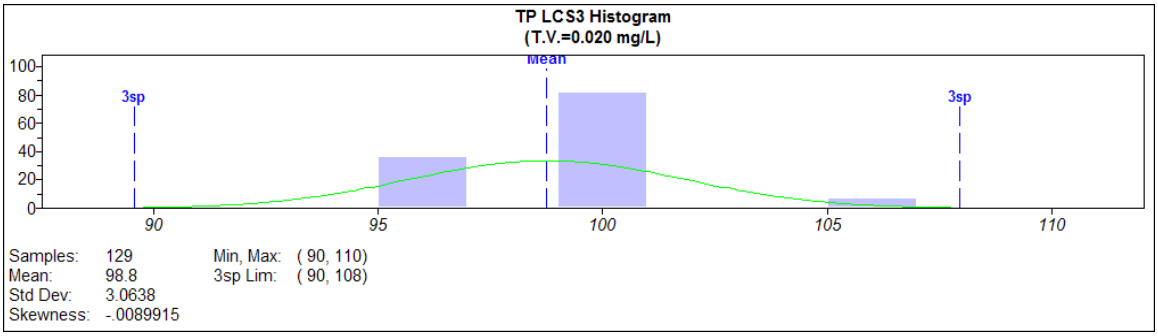
Routine laboratory QC samples include QC checks, matrix spikes, and precision checks. **Figures 1** through **6** show the TP recoveries from various types and levels of QC samples at the District laboratory from July 1, 2010, through September 30, 2010.



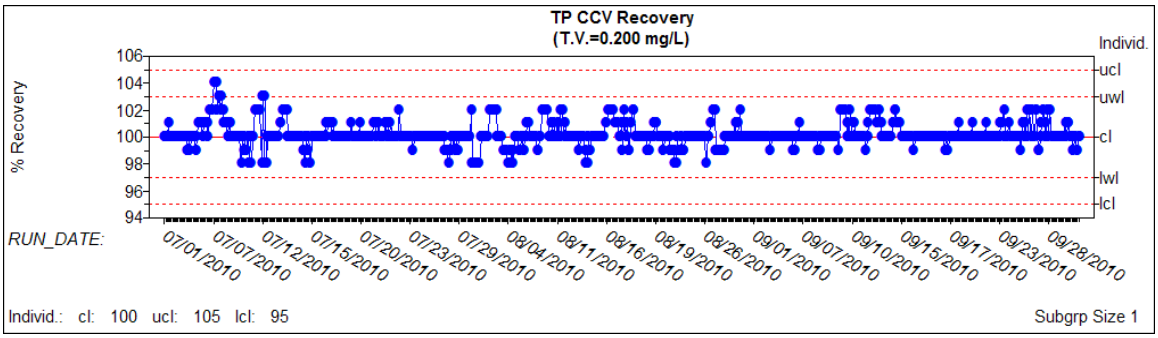


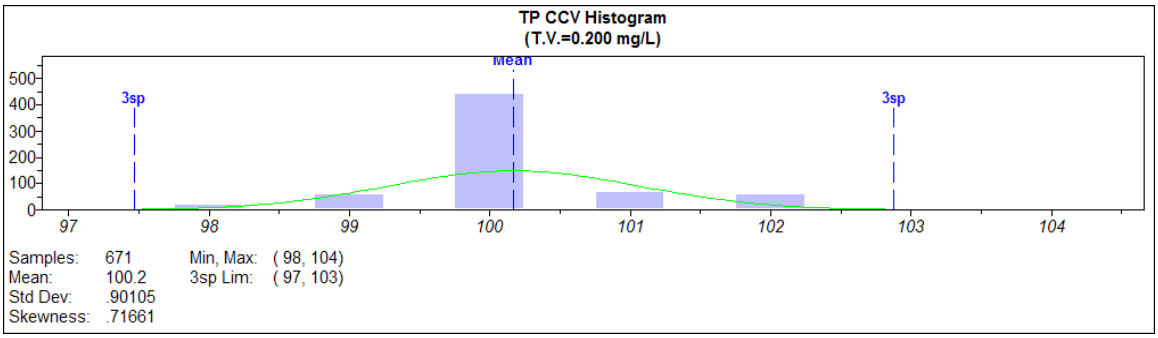
Figures 1a and 1b. TP QC (Laboratory Control Sample, 0.300 mg/L) sample recoveries and histogram.



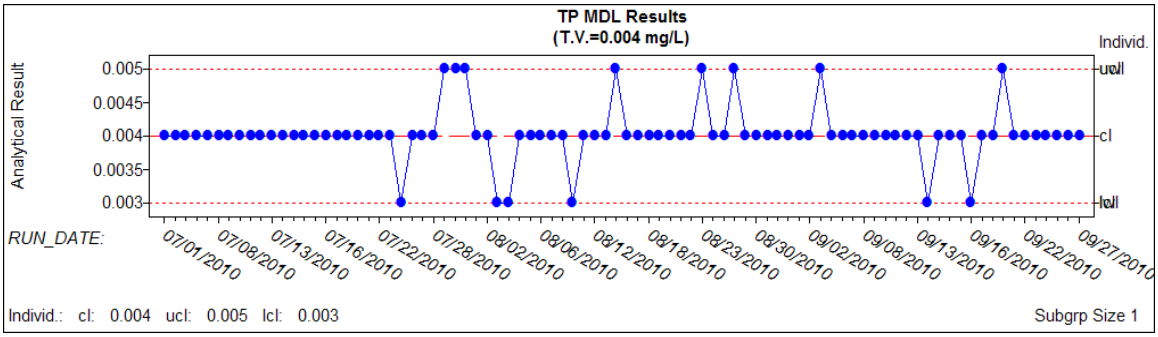


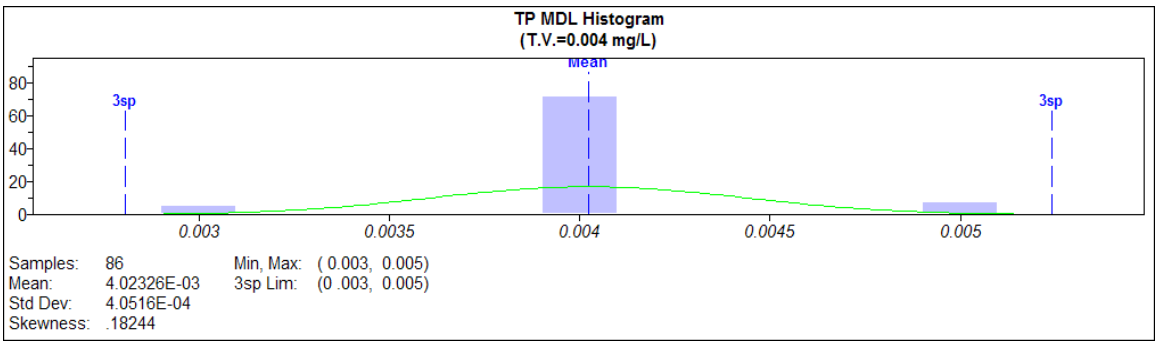
Figures 2a and 2b. TP QC (Laboratory Control Sample, 0.020 mg/L) sample recoveries and histogram.



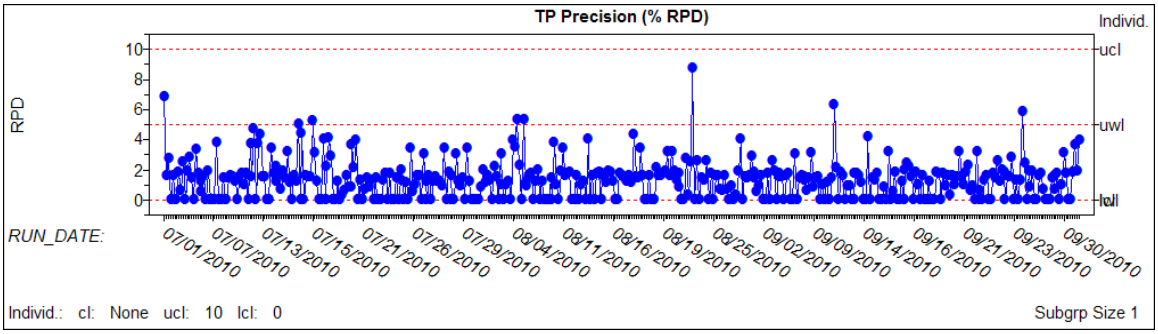


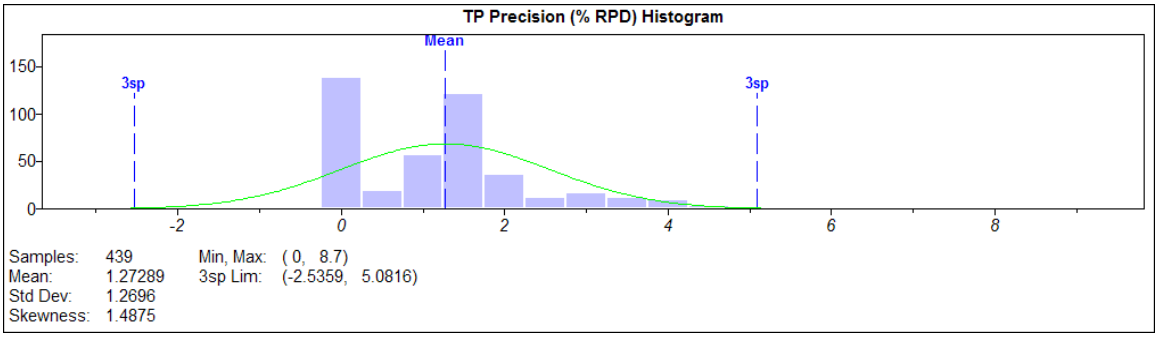
Figures 3a and 3b. TP QC (Continuing Calibration Verification Sample, 0.200 mg/L) sample recoveries and histogram.



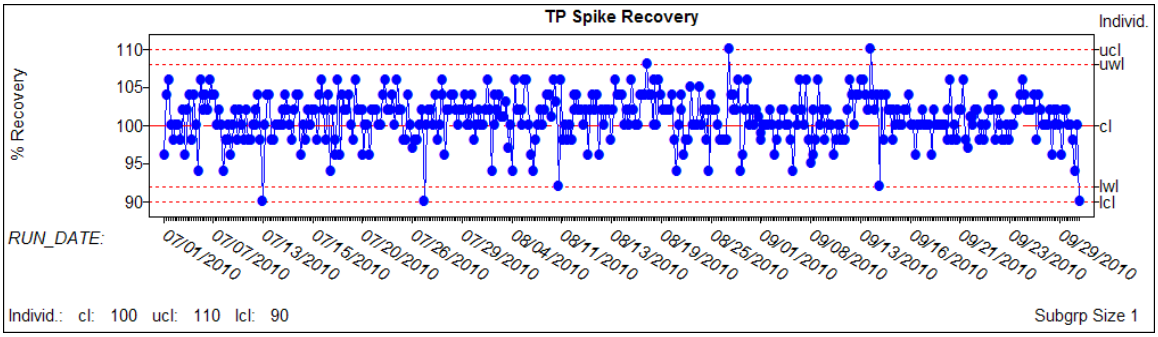


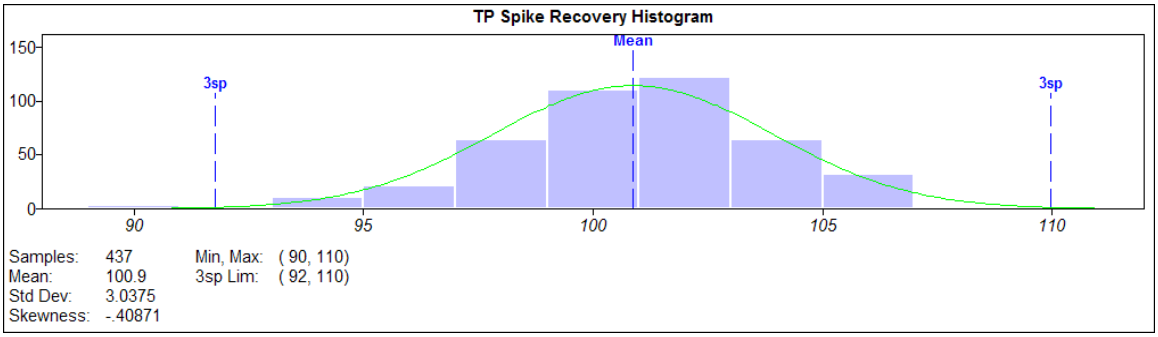
Figures 4a and 4b. TP QC5 (Method Detection Limit Check, 0.004 mg/L) sample recoveries and histogram.





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





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

Notes for Figures 1–6:

- 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 Quality Control samples
- 3sp Lim- Calculated limits for subgroup based on 3 sigma factor
- Y axis label for histogram indicates number of data points

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 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 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 Method Detection Limit (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 100.9 percent.

ESTIMATION OF ANALYTICAL MEASUREMENT UNCERTAINTY

The estimated analytical uncertainty for total phosphorus conducted by the District laboratory for the last quarter (July-September 2010) was determined to be 4.0 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).

METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LIMIT

MDL checks are routinely analyzed with each analytical run. From July 1 to September 30, 2010, 86 results for MDL checks were reported for total phosphorus measurements. The calculated MDL from these results was determined to be 1.0 µg/L, using the procedure described in 40 CFR 136 Appendix B and the calculated PQL for this period was 4.0 µg/L. At this concentration, the relative uncertainty in the measured value is estimated to be ±30 percent at the 95 percent confidence level[3].

The reported values between the MDL (established at 2 µg/L) and PQL (established at 8 µg/L) 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. 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 2009 to September 2010 (see **Appendix A**) provided the data used in this analysis. **Figure 7** presents regression analysis of all data, and **Table 6** presents summary statistics for the data pairs.

ALL DATA

Figure 7 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 0.474. 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.

Table 6 shows that the mean difference (0.001 mg/L) and the median difference (0.001 mg/L) are not statistically significant. The paired t-test and signed-rank test yield p-values of 0.102 and 0.117 respectively.

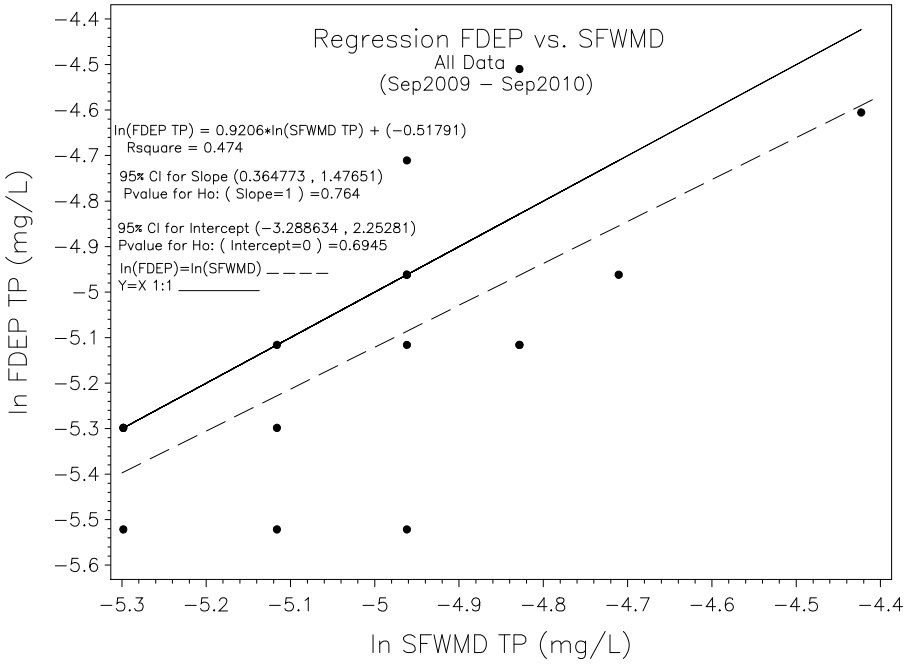


Figure 7. Regression analysis for all TP data.

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.

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.

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

All Data	**Summary Statistics**				
	Lab	**N**	**Mean (µg/L)**	**Median (µg/L)**	
	FDEP	16	0.006	0.006	
	District	16	0.007	0.007	
	Statistical Test of Hypotheses				
	Summary of Paired Differences (µg/L)		**Hypothesis**	**Test**	**P-value**
	Mean of Differences	0.001	Mean of Differences = 0	Student's t	0.102
	Median of Differences	0.001	Median of Differences = 0	Signed Rank	0.117

Notes:

- Differences calculated as the District 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).

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

The purpose of the program is to identify sources of measurement uncertainties and variation among analytical results, and to provide information on overall data quality and reliability of analytical measurements of inorganic parameters in natural waters. The results for the District's laboratory from the most recent Performance Testing (PT) Study 96 are presented in **Table 7** (June-September 2010). The District laboratory was rated on performance of TP as "Ideal" (highest). The evaluation includes systematic bias and precision, a laboratory appraisal and a summary of Z-scores.

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

Table 7. Performance in PT Study 96 for TP, June 2010-September 2010.

Sample Number	1	2	3	4	5	6	7	8	9	10
Assigned Value, mg/L	0.002	0.111	0.008	0.179	0.0037	0.059	0.218	1.13	0.690	0.400
Reported Results, mg/L	<0..002	0.111	0.007	0.178	0.003	0.056	0.219	1.15	0.690	0.400
Z-Score	NA	0.0	-0.6	-0.1	-0.4	-0.9	0.1	0.4	0.0	0.0

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 District and FDEP laboratories, EVPA Project, September 2009–September 2010.

Sample	Date	District	FDEP	%RPD/Comments
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
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

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

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

Y: sample temperature is outside acceptable range

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