

Environment Canada Phosphorus and Mercury Proficiency Samples

**Onondaga Lake
Ambient Monitoring Program 2010**

Background

Environment Canada provides accredited proficiency testing (PT) studies for a wide range of inorganic constituents in water. 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. Laboratories from the U.S., Canada, and around the world participate in the PT studies; results were evaluated for precision and systematic bias (<http://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=7A20877C-1>)

The Environment Canada PT Program is comprised of two PT studies, offered on a semi-annual basis, and scheduled in the summer and winter months. The samples are prepared in natural background waters from lakes, rivers or rainwater, and are fortified or preserved as necessary. The trace elements in water samples are generally divided to reflect both low and high concentration ranges. Participating laboratories submit results for parameters they routinely analyze.

Since the fall of 2002, the Onondaga County Environmental Laboratory has routinely participated in the PT program for total phosphorus in water. In 2008, the laboratory began participating in the PT program for mercury in water. The County laboratory plans to continue to participate in the Environment Canada PT program.

Results – Total Phosphorus

In 2010, the Onondaga County Environmental Laboratory participated in PT Studies 0095 (December 2009 to March 2010) and 0096 (June to September 2010) for total phosphorus analysis. The performance of the laboratory was rated as “good” (Table 1) in both studies.

Table 1. Performance Rating of Total Phosphorus analyses by the County laboratory.

Study Code	% Score	Performance Rating
0095	0	Good
0096	0	Good

% Score = Sum of Parameters Biased and Results Flagged.

Ratings:

0-5	Good
>5-12.5	Satisfactory
>12.5-30	Moderate
>30	Poor

Previous proficiency testing (2005 through 2009) through the Environment Canada PT program has generally been “Good” to “Satisfactory”, based on the percent score per study.

The samples and results for the 2010 program are summarized in the table below (Table 2). The samples were prepared with natural lake and river waters and preserved with 0.2% sulfuric acid. Standard phosphate solutions were prepared with potassium dihydrogen phosphate and sodium β-glycerophosphate for inorganic and organic spikes, respectively.

Table 2. County analytical results for total phosphorus, 2010.

Program 0095 (Winter)				Program 0096 (Summer)			
Sample	Assigned Value (mg/l)	Measured Result (mg/l)	Acceptable Range within 2 R-Std Dev	Sample	Assigned Value (mg/l)	Measured Result (mg/l)	Acceptable Range within 2 R-Std Dev
TP95-1	0.0010	0.004	na	TP96-1	0.00200	<0.003	-0.00099-0.005
TP95-2*	0.0100	0.013	0.0048-0.015	TP96-2	0.111	0.110	0.102-0.120
TP95-3	0.0330	0.036	0.028-0.038	TP96-3**	0.00800	0.006	0.0049-0.011
TP95-4*	0.120	0.123	0.111-0.129	TP96-4	0.179	0.176	0.164-0.194
TP95-5	0.0660	0.070	0.058-0.074	TP96-5	0.00373	<0.003	0.00071-0.0068
TP95-6	0.272	0.280	0.249-0.295	TP96-6	0.0590	0.060	0.0525-0.0655
TP95-7	0.0040	0.006	0.0014-0.0066	TP96-7	0.218	0.218	0.20-0.24
TP95-8**	0.336	0.347	0.313-0.359	TP96-8*	1.13	1.16	1.04-1.22
TP95-9*	0.475	0.488	0.439-0.511	TP96-9**	0.690	0.666	0.640-0.74
TP95-10**	0.928	0.944	0.869-0.987	TP96-10*	0.400	0.393	0.372-0.428

* - inorganic spike; ** - organic spike

na – R-Std Dev was zero, therefore no range calculated.

Laboratory bias $D = x - X$, where D is the deviation, “x” is the test result, and “X” is the assigned value. This deviation was normalized with the robust standard deviation (R-Std Dev) and evaluated by the z-score. Acceptable Limits were met when the test result was within 2 R-Std Dev of the assigned value.

Results – Mercury

In 2010, Onondaga County participated in PT Studies 0095 (December 2009 to March 2010) for mercury analyses. The performance of the laboratory was rated as “good” (Table 3).

Table 3. Performance Rating of Total Phosphorus analyses by the County laboratory.

Study Code	% Score	Performance Rating
0095	0	Good

% Score = Sum of Parameters Biased and Results Flagged.

Ratings:

0-5	Good
>5-12.5	Satisfactory
>12.5-30	Moderate
>30	Poor

Previous proficiency testing (2008 and 2009) through the Environment Canada PT program was “Poor” in 2008, and “Good” in 2009, based on the percent score per study. The samples and results for the 2010 program are summarized in the table below (Table 4). The samples were prepared with natural lake water and preserved with 1% sulfuric acid and 0.05% potassium dichromate.

Table 4. County analytical results for mercury, Program 0095 (Winter) 2010.

Sample	Assigned Value (mg/l)	Measured Result (mg/l)	Acceptable Range within 2 R-Std Dev
HG95-1	0.00661	<0.0150	0.00076-0.0125
HG95-2	0.0710	0.0789	0.0481-0.0939
HG95-3	0.157	0.167	0.109-0.205
HG95-4	0.00133	<0.0150	-0.00015-0.0028
HG95-5	0.323	0.337	0.241-0.405
HG95-6	0.0478	0.0605	0.0300-0.0656
HG95-7	0.0150	0.0162	0.0092-0.0208
HG95-8	0.0280	0.0295	0.0154-0.0406
HG95-9	0.366	0.393	0.250-0.482
HG95-10	0.240	0.249	0.168-0.312

Laboratory bias $D = x - X$, where D is the deviation, “ x ” is the test result, and “ X ” is the assigned value. This deviation is normalized with the robust standard deviation (R-Std Dev) and evaluated by the z-score. Acceptable Limits are met when the test result (for measurements greater than the detection level) is within 2 R-Std Dev of the assigned value.