



Environment Canada Proficiency Testing Program / Environnement Canada Programme d'Essais d'Aptitude

Study / Étude 0101
March / Mars 2013

Rain and Soft Waters /
Eau de Pluie et Eau Douce,
Major Ions and Nutrients in Water /
Principaux ions et Substances Nutritives dans l'Eau,
Trace Elements in Water /
Éléments Traces dans l'Eau,
Total Phosphorus in Water /
Phosphore Total dans l'Eau,
Turbidity in Water /
Turbidité dans l'Eau,
Total Mercury in Water /
Mercure Total dans l'Eau

F. DeOliveira and J. Simser
IQM-2013-01



Environment
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Information and Quality Management

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March 25, 2013

To: Participants of the **Environment Canada Proficiency Testing (PT) Program**

Re: Distribution of the Final Report for **PT Study 0101** (December 2012 to March 2013)

Dear Participant,

We thank you for your co-operation and punctual responses with respect to this study. It is the aim of the PT Program to give prompt evaluations and reports, and effective remedial assistance. Our PT Program is accredited by the American Association for Laboratory Accreditation (A2LA) and conforms to the ISO/IEC 17043:2010 Conformity assessment – General requirements for proficiency testing. The scope of accreditation (A2LA 2867.01) can be viewed on the A2LA website:

<http://www.a2la.org/scopepdf/2867-01.pdf>.

This final report includes results and evaluations for **inorganic parameters in rain and soft waters (RN), major ions and nutrients in natural waters (MI), trace elements in water (TE), total phosphorus in water (TP), turbidity in water (TU) and total mercury in water (HG)**.

The evaluations include systemic bias and precision, a laboratory proficiency appraisal and a summary of z-scores. The flagging criteria, stipulated in ISO 13528:2005, Annex C, are calculated separately for each study. Each laboratory is encouraged to compare its results and evaluations with others. A complete listing of all laboratory results is included.

Laboratory managers are encouraged to discuss the attached report openly with those who manage their programs and those who use their laboratory data. Systemic bias is a major fault whose root cause can be uncovered. Systemic bias and its degree are given for each parameter in the Data Summary. In the event you disagree with any of our data evaluations, please contact us and we will discuss the item with you. The matter may also be brought forward to our Advisory Group.



Information and Quality Management
Proficiency Testing Program
Inorganic Environmental Substances

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The laboratories listed in this report submitted their data with a confidential laboratory code. This confidentiality is fully respected by our staff. Access to these codes is only possible through the relevant laboratories or program authorities.

Should you have any questions or comments regarding this study, please contact us at your earliest convenience. Your comments are instrumental to the continued improvement of our PT Program.

Sincerely,
Fedelina DeOliveira
Study Coordinator

Associated Laboratory Evaluations (2)

- 1) Laboratory Proficiency Appraisal
- 2) Z-Score Summary



Information and Quality Management
Proficiency Testing Program
Inorganic Environmental Substances

Canada

Environment Canada Proficiency Testing Program

Final Report

for

**Rain and Soft Waters
Major Ions and Nutrients in Natural Waters
Trace Elements in Water
Total Phosphorus in Water
Turbidity in Water
Total Mercury in Water**

EC PT Study 0101 - March 2013

Contributors

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March 2013

IQM-2013-01

Environment Canada Proficiency Testing Program

Glossary of Terms and Definitions

A. Statistics listed in Data Summary (Appendix A)

1. Assigned Value The **Robust Mean** of test results for a parameter and sample [1]
2. R-Std Dev Robust Standard Deviation [1]
3. Acceptable Limits See 'Limits & Flags' and Table 1
4. Warning Limits See 'Limits & Flags' and Table 1
5. Action Limits See 'Limits & Flags' and Table 1
6. N The number of usable test results for calculating the assigned value

B. Calculation of Performance Statistics (Appendix A)

Laboratory Bias: Laboratory Bias [2] $D = x - X$, 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 [3].

Limits & Flags: Acceptable Limits/No Flags: When a test result is within 2 R-Std Dev of the assigned value, flags are not assigned (see Table 1 below).

Warning Limits/Warning Flags: When a test result is between 2 and 3 R-Std Dev, the flags 'WH' or 'WL' indicate a WARNING flag, for a high or low result respectively (see Table 1 below).

Action Limits/Action Flags: When a test result deviates by more than 3 R-Std Dev from the assigned value, the flags 'AH' or 'AL' indicate an ACTION flag, high or low respectively (see Table 1 below).

Table 1 Evaluating test results, determining limits and assigning flags [2]

| Criteria | Limits | Flags |
|---|-------------------|------------------|
| Assigned value $\pm 2 \hat{\sigma}^*$ | Acceptable Limits | No Flag |
| $2 \hat{\sigma}^* - 3 \hat{\sigma}^*$ from assigned value | Warning Limits | Warning Flag (W) |
| $> 3 \hat{\sigma}^*$ from assigned value | Action Limits | Action Flag (A) |

* $\hat{\sigma}$ is the R-Std Dev

Systemic Bias: Systemic bias is indicated when a laboratory's test results (ranked by the Youden non-parametric analysis [4] for an individual parameter) are consistently higher or lower than the assigned value. Ranks are assigned to each test result for each sample, from 1 for the lowest, to N for the highest, where N is the number of usable test results. These ranks are totalled for each laboratory (Total Rank), and divided by the number of samples ranked (No. Samples Ranked). **Total Rank** and **Average Rank** for each laboratory are displayed on page 2 of the Data Summary. The **Overall Average Rank** for each parameter is shown at the bottom of the same page. Systemic bias is identified when a laboratory's **Average Rank** falls outside of the 95% confidence interval for the **Overall Average Rank**. Systemic bias may be indicated by the Youden rankings even when the test results have not been flagged (W or A) for deviation from the assigned value.

No. Samples Ranked: This is the number of test results used to determine systemic bias. A laboratory must report results for more than half of the samples in the set to allow for evaluation of bias (not including '<'). There must be ten or more laboratories participating, with sufficient test results reported, to determine systemic bias.

The two measured components of 'systemic' bias are 1) Bias Blank and 2) Bias % Slope. These components are illustrated in Figure 1: Parameter Performance. All 'systemic' biases are correctable with the investigation of the following two analytical components.

1) Bias Blank: The first component is the y-intercept of the linear regression plot (-0.0329 in Figure 1). These bias blanks are stated in the Data Summary and Evaluations for each parameter.

2) Bias % Slope: The second measured component is the % deviation of the laboratory test results versus the assigned values for a parameter. This is calculated as $[(m-1) \times 100]$, where **m** is the slope of the linear regression plot (laboratory test results) and **1** is the slope of the "ideal" line (assigned values). The Bias % Slope in Figure 1 below is minus 1.55 per cent (-1.55%). For most parameters, a Bias % Slope greater than the absolute value of 5 is considered unacceptable and requires action.

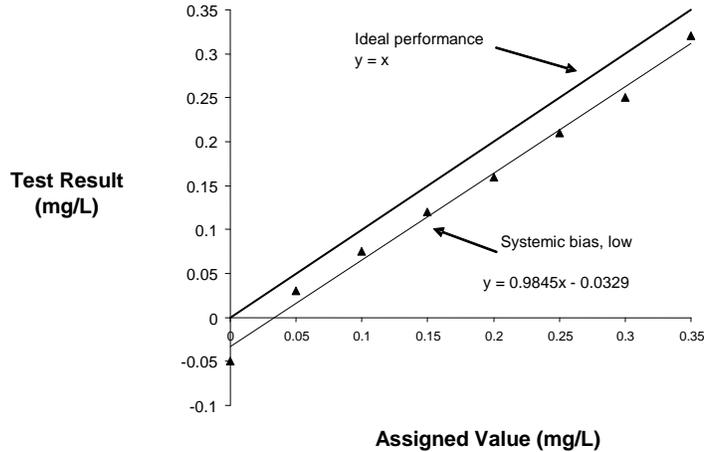


Figure 1: Parameter Performance

Bias Statement: Systemic bias is noted with the ‘BIASED HIGH’ or ‘BIASED LOW’ notations. An asterisk with the statement indicates that the bias is considered minor, yet worthy of evaluation. The minor biases are not recorded in the database and are not noted in the laboratory proficiency appraisal (see enclosed Laboratory Proficiency Appraisal). In Table 2 of the Final Report (Laboratory Performance Scores), systemic biases are calculated as the equivalent of *five* flagged values.

Method Coding: Method codes are an important part of quality assurance. These definitions are provided on the Data Reporting Forms to assist with uniform descriptions.

C. Determination of the ‘Laboratory Performance Scores’ in Table 2

The ‘Laboratory Performance Scores’ are a combination of 50% **Systemic Bias (parameters biased)** and 50% **Flagged Results**.

- Systemic bias (50%) is calculated as,

$$[(\text{No. of Parameters Biased} / \text{No. of Parameters Analyzed}) \times 100] / 2$$

- Flagged results (50%) is calculated as,

$$[(\text{No. of Flags Assigned} / \text{No. of Results Reported}) \times 100] / 2$$

These percentages are summed to obtain the % Score (Sum of Parameters Biased & Flagged Results)

The Laboratory Performance Rating is assigned according to the % Score.

- Very Good: 0 to 5%;
- Good: >5 to 12.5%;
- Fair: >12.5 to 30%
- Poor: >30%.

D. Uncertainty of Assigned Values

The standard uncertainty (u_x) of the assigned value may be estimated from the statistics presented in the data summary (Appendix A),

$$u_x = 1.25 \times \text{R-Std Dev} / \sqrt{N} \quad [5]$$

This uncertainty is not used in the performance evaluations, but may be of interest to some participants. Reporting details of the measurement uncertainty of any assigned value is a requirement of *ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing*.

E. Associated Laboratory Evaluations with the Final Report

1. Laboratory Proficiency Appraisal (see Table 2 in the Final Report for definitions)
2. Z-Score Summary [3]

References:

[1] ISO 13528:2005(E), Statistical Methods for the use in Proficiency Testing by Interlaboratory Comparisons, Annex C, Robust Analysis, Section C.1: Algorithm A, p64.

[2] ISO 13528:2005(E), Statistical Methods for the use in Proficiency Testing by Interlaboratory Comparisons, Calculation of Performance Statistics, Section 7.1.1 and 7.1.2, p18-19.

[3] ISO 13528:2005(E), Statistical Methods for the use in Proficiency Testing by Interlaboratory Comparisons, z-scores, Section 7.4.1 and 7.4.2, p25-26.

[4] Ranking Laboratories by Round-Robin Tests, W.J. Youden, Precision Measurement and Calibration, H.H. Ku, Editor, NBS Special Publication 300-Volume 1, U.S. Government Printing Office, Washington, D.C., 1969.

[5] ISO 13528:2005(E), Statistical Methods for the use in Proficiency Testing by Interlaboratory Comparisons, Standard uncertainty u_x of the assigned value , Section 5.6.2, p 9-10.

Section 4 – Total Phosphorus in Water (TP)

| | |
|------------|---|
| Table 1 | Participating Laboratories |
| Table 2 | Laboratory Performance Scores |
| Table 3 | Five-Year Historical Laboratory Performance |
| Table 4 | Sample Design |
| Table 5 | Summary of Interlaboratory Robust Means |
| Appendix A | Data Summary |

Program Name: FPTP

Study Code: 0101

Range of Samples: 1 to 10

Table 1 Participating Laboratories in FP PT for Total Phosphorus in Water

Adirondack Lakes Survey Corp., Ray Brook, NY, US
 ALS Environmental, Jacksonville, FL, US
 ALS Environmental, Winnipeg, MB, CA
 Bay of Plenty Regional Council, Whakatane, NZ
 Capital District Health Authority, QEII Lab, Halifax, NS, CA
 Environment Canada, ALET, Moncton, NB, CA
 Environment Canada, NLET, Burlington, ON, CA
 Environment Canada, NLET, Saskatoon, SK, CA
 Environment Canada, PYLET, Vancouver, BC, CA
 Environment New Brunswick, Fredericton, NB, CA
 Environnement Canada, LEEQ, Montréal, QC, CA
 Environnement Québec, CEAEQ, Gouvernement du QC, QC, CA
 Illinois State Water Survey, Champaign, IL, US
 Kinectrics Analytical and Environmental Service Lab., Toronto, ON, CA
 MB Laboratories, Sydney, BC
 NIWA, Hamilton, NZ
 NRC-Great Lakes Forestry Centre, ON Region, Sault Ste.Marie, ON,CA
 Onondaga County, WEP, Syracuse, NY, US
 Ontario Ministry of Environment, Dorset, ON, CA
 Scottish Environment Protect Agency,Edinburgh,Mid-Lothian,SC
 Servicio Geologico Minero Argentino, Buenos Aires, Argentina
 South Florida Water Management Dist., West Palm Beach, FL,US
 TAIGA Environmental Laboratory, Yellowknife, NT, CA
 U.S. Geological Survey, NWQL, Denver, CO, US
 Universidade da Coruña, A Coruña, ES
 Universite du Quebec, MITHE-RN, Ste-Foy, QC
 University of Victoria, Victoria, BC, CA
 US EPA ORD Western Ecology Division, Corvallis, OR, US

28 Laboratories.

Program Name: FFTP

Number of Labs: 30

Study Code: 0101

Range of Samples: 1 to 10

Table 2 Laboratory Performance Scores - FP PT for Total Phosphorus in Water

| <u>Lab Code</u> | Systemic Bias | | | Flagged Results | | | <u>% Score (Sum of Parameters Biased & Results Flagged)</u> |
|-----------------|-----------------------------------|---------------------------------|--------------------------------|--------------------------------|------------------------------|------------------------------|---|
| | <u>No. of Parameters Analyzed</u> | <u>No. of Parameters Biased</u> | <u>Parameters Biased (50%)</u> | <u>No. of Results Reported</u> | <u>No. of Flags Assigned</u> | <u>Results Flagged (50%)</u> | |
| F003 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F007 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F010 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F026 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F026b | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F036 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F153 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F154 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F158 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F163 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F170 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F183 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F202 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F207 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F221 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F014 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F069 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F307 | 1 | 0 | 0.00 | 10 | 0 | 0.00 | 0.00 |
| F022 | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F113 | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F069b | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F015 | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F292 | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F053 | 1 | 0 | 0.00 | 10 | 1 | 5.00 | 5.00 |
| F004 | 1 | 0 | 0.00 | 10 | 2 | 10.00 | 10.00 |
| F304 | 1 | 0 | 0.00 | 10 | 2 | 10.00 | 10.00 |
| F112 | 1 | 0 | 0.00 | 10 | 3 | 15.00 | 15.00 |
| F146 | 1 | 0 | 0.00 | 10 | 5 | 25.00 | 25.00 |
| F021 | 1 | 1 | 50.00 | 10 | 3 | 15.00 | 65.00 |
| F011 | 1 | 1 | 50.00 | 10 | 7 | 35.00 | 85.00 |

Laboratory Performance Rating

| Rating | % Score* |
|------------------|-----------------------|
| Very Good | 0 - 5 |
| Good | > 5 - 12.5 |
| Fair | > 12.5 - 30 |
| Poor | > 30 |

*Sum of Parameters Biased & Results Flagged

Program Name: FFTP

Study Code: 0101

Table 3 Five-Year Historical Laboratory Performance - FP PT for Total Phosphorus in Water

| LAB CODE | % Score Per Study (Sum of Parameters Biased & Results Flagged) | | | | | | | | | | MEDIAN | RATING | |
|----------|--|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------|--------|-----------|
| | 0092 Summer 2008 | 0093 Winter 2008 | 0094 Summer 2009 | 0095 Winter 2009 | 0096 Summer 2010 | 0097 Winter 2010 | 0098 Summer 2011 | 0099 Winter 2011 | 0100 Summer 2012 | 0101 Winter 2012 | | | |
| F003 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F004 | 25.0 | 60.0 | 0.0 | 0.0 | 10.0 | 65.0 | 60.0 | 5.0 | 0.0 | 10.0 | 10.0 | 10.0 | Good |
| F007 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F010 | 20.0 | 0.0 | 0.0 | 5.0 | 25.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F011 | 15.0 | 10.0 | 30.0 | 25.0 | 5.0 | 0.0 | 70.0 | 15.0 | 25.0 | 25.0 | 85.0 | 20.0 | Fair |
| F014 | 5.0 | | 0.0 | | 70.0 | 55.0 | 55.0 | | 5.0 | 0.0 | 5.0 | 5.0 | Very Good |
| F015 | 0.0 | 0.0 | 0.0 | 20.0 | 5.0 | 15.0 | 5.0 | 10.0 | 0.0 | 5.0 | 5.0 | 5.0 | Very Good |
| F021 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 65.0 | 0.0 | Very Good |
| F022 | 50.0 | 15.0 | 0.0 | 0.0 | 0.0 | 15.0 | 15.0 | 10.0 | 55.0 | 5.0 | 12.5 | 12.5 | Good |
| F026 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F026b | 70.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 55.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F036 | 60.0 | 0.0 | 0.0 | 5.0 | 0.0 | 0.0 | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F053 | | | | | 60.0 | 5.0 | 10.0 | 30.0 | 80.0 | 5.0 | 20.0 | 20.0 | Fair |
| F069 | 0.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | 0.0 | 0.0 | Very Good |
| F069b | 10.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 5.0 | 0.0 | 0.0 | Very Good |
| F112 | | | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 15.0 | 15.0 | 15.0 | 2.5 | 2.5 | Very Good |
| F113 | 10.0 | 5.0 | 0.0 | 0.0 | 25.0 | 0.0 | 75.0 | 65.0 | 10.0 | 5.0 | 7.5 | 7.5 | Good |
| F146 | | | | | | | | | | 25.0 | 25.0 | 25.0 | Fair |
| F153 | | | | | | | 0.0 | 55.0 | | 0.0 | 0.0 | 0.0 | Very Good |
| F154 | | | 10.0 | 0.0 | 20.0 | 10.0 | 0.0 | 0.0 | 5.0 | 0.0 | 2.5 | 2.5 | Very Good |
| F158 | | | | 15.0 | 0.0 | 60.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F163 | | | | | | | | | | 0.0 | 0.0 | 0.0 | Very Good |
| F170 | 0.0 | 0.0 | 0.0 | 0.0 | 80.0 | 0.0 | 0.0 | 0.0 | 50.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F183 | | 0.0 | | 55.0 | 10.0 | 0.0 | 65.0 | 70.0 | 60.0 | 0.0 | 32.5 | 32.5 | Poor |
| F202 | 10.0 | 5.0 | 10.0 | 0.0 | 0.0 | 10.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F207 | 0.0 | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |
| F221 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | Very Good |

Laboratory Performance Rating

| Rating | % Score |
|-----------|-------------|
| Very Good | 0 - 5 |
| Good | > 5 - 12.5 |
| Fair | > 12.5 - 30 |
| Poor | > 30 |

Program Name: FFTP

Study Code: 0101

Table 3 Five-Year Historical Laboratory Performance - FP PT for Total Phosphorus in Water

| LAB CODE | % Score Per Study (Sum of Parameters Biased & Results Flagged) | | | | | | | | | | MEDIAN | RATING |
|-----------------|--|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------|-----------|
| | 0092 Summer 2008 | 0093 Winter 2008 | 0094 Summer 2009 | 0095 Winter 2009 | 0096 Summer 2010 | 0097 Winter 2010 | 0098 Summer 2011 | 0099 Winter 2011 | 0100 Summer 2012 | 0101 Winter 2012 | | |
| F292 | | | | | | 0.0 | | 50.0 | 0.0 | 5.0 | 2.5 | Very Good |
| F304 | | | | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | | 10.0 | 0.0 | Very Good |
| F307 | | | | | | | | | 5.0 | 0.0 | 2.5 | Very Good |
| Interlab Median | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | |

Laboratory Performance Rating

| Rating | % Score |
|-----------|-------------|
| Very Good | 0 - 5 |
| Good | > 5 - 12.5 |
| Fair | > 12.5 - 30 |
| Poor | > 30 |

Table 4 Sample Design - FP PT for Total Phosphorus in Water

| Sample Number | Sample Name | Spike |
|---------------|-------------|-----------------|
| 1 | TP101-1 | organic spike |
| 2 | TP101-2 | organic spike |
| 3 | TP101-3 | inorganic spike |
| 4 | TP101-4 | no spike |
| 5 | TP101-5 | no spike |
| 6 | TP101-6 | organic spike |
| 7 | TP101-7 | no spike |
| 8 | TP101-8 | inorganic spike |
| 9 | TP101-9 | no spike |
| 10 | TP101-10 | no spike |

Samples are prepared in natural lake and river waters and preserved with 0.2% sulfuric acid. Standard phosphate solutions are prepared with potassium dihydrogen phosphate and sodium β -glycerophosphate for inorganic and organic spikes respectively.

Program Name: FPTP

Range of Samples: 1 to 10

2013-03-06

Study Code: 0101

Table 5 Summary of Interlaboratory Robust Means - FP PT for Total Phosphorus in Water

| Parameters | TP101-1 Sample 1 | TP101-2 Sample 2 | TP101-3 Sample 3 | TP101-4 Sample 4 | TP101-5 Sample 5 | TP101-6 Sample 6 | TP101-7 Sample 7 | TP101-8 Sample 8 | TP101-9 Sample 9 | TP101-10 Sample 10 |
|---------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----------------------|
| Total Phosphorus (mg/L P) | 0.00886 | 0.588 | 0.0470 | 0.0118 | 0.227 | 0.297 | 0.0247 | 0.405 | 0.00273 | 0.00190 |

Appendix A

PARAMETER: 15092 Total Phosphorus mg/L P

WATER SCIENCE & TECHNOLOGY
ENVIRONMENT CANADA

FP PT for Total Phosphorus in Water

| SAMPLE | 1= | 2= | 3= | 4= | 5= | 6= | 7= | 8= | 9= | 10= |
|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|
| LAB NO | TP101-1 LAB RESULT | TP101-2 LAB RESULT | TP101-3 LAB RESULT | TP101-4 LAB RESULT | TP101-5 LAB RESULT | TP101-6 LAB RESULT | TP101-7 LAB RESULT | TP101-8 LAB RESULT | TP101-9 LAB RESULT | TP101-10 LAB RESULT |
| F003 | 0.009 | 0.571 | 0.0469 | 0.0125 | 0.229 | 0.301 | 0.0295 | 0.409 | 0.0051 | 0.0009 |
| F004 | 0.012 WH | 0.579 | 0.053 | 0.016 AH | 0.223 | 0.294 | 0.026 | 0.396 | <0.002 | <0.002 |
| F007 | 0.009 | 0.614 | 0.049 | 0.012 | 0.233 | 0.303 | 0.025 | 0.415 | <0.002 | <0.002 |
| F010 | 0.00828 | 0.584 | 0.0434 | 0.0135 | 0.220 | 0.300 | 0.0267 | 0.406 | 0.00185 | 0.00133 |
| F011 | 0.010 | 0.617 | 0.053 | 0.032 AH | 0.284 AH | 0.331 AH | 0.030 WH | 0.434 WH | 0.015 AH | 0.008 AH |
| F014 | 0.008 | 0.60 | 0.048 | 0.012 | 0.23 | 0.30 | 0.025 | 0.40 | <0.002 | <0.002 |
| F015 | 0.008 | 0.65 WH | 0.048 | 0.012 | 0.228 | 0.31 | 0.025 | 0.43 | <0.002 | 0.003 |
| F021 | 0.008 | 0.554 | 0.043 | 0.010 | 0.210 WL | 0.271 AL | 0.022 | 0.373 WL | <0.002 | <0.002 |
| F022 | <0.02 | 0.576 | 0.054 WH | <0.02 | 0.225 | 0.289 | 0.022 | 0.401 | <0.02 | <0.02 |
| F026 | 0.009 | 0.578 | 0.046 | 0.012 | 0.228 | 0.297 | 0.025 | 0.394 | <0.001 | <0.001 |
| F026b | <0.02 | 0.615 | 0.046 | <0.02 | 0.233 | 0.312 | 0.022 | 0.424 | <0.02 | <0.02 |
| F036 | 0.008 | 0.620 | 0.047 | 0.012 | 0.230 | 0.301 | 0.023 | 0.411 | 0.001 | 0.001 |
| F053 | 0.009 | 0.554 | 0.046 | 0.012 | 0.230 | 0.286 | 0.024 | 0.365 WL | <0.005 | <0.005 |
| F069 | 0.008 | 0.603 | 0.046 | 0.013 | 0.236 | 0.303 | 0.022 | 0.414 | <0.004 | <0.004 |
| F069b | <0.01 | 0.578 | 0.039 WL | <0.01 | 0.217 | 0.292 | 0.022 | 0.391 | <0.01 | <0.01 |
| F112 | 0.008 | 0.598 | 0.047 | 0.011 | 0.180 AL | 0.248 AL | 0.024 | 0.480 AH | <0.002 | <0.002 |
| F113 | 0.010 | 0.592 | 0.045 | 0.010 | 0.226 | 0.297 | 0.032 WH | 0.407 | <0.004 | 0.004 |
| F146 | 0.009 | 0.545 WL | 0.054 WH | 0.012 | 0.245 WH | 0.321 AH | 0.034 AH | 0.380 | 0.002 | 0.001 |
| F153 | <0.02 | 0.60 | 0.044 | <0.02 | 0.23 | 0.30 | <0.02 | 0.42 | <0.02 | <0.02 |
| F154 | 0.0104 | 0.585 | 0.053 | 0.0126 | 0.234 | 0.297 | 0.0263 | 0.402 | <0.0020 | <0.0020 |
| F158 | 0.008 | 0.594 | 0.047 | 0.011 | 0.224 | 0.296 | 0.025 | 0.408 | <0.002 | <0.002 |
| F163 | 0.0102 | 0.55 | 0.048 | 0.0119 | 0.22 | 0.29 | 0.025 | 0.42 | 0.0019 | 0.0009 |
| F170 | 0.007 | 0.591 | 0.047 | 0.011 | 0.228 | 0.295 | 0.023 | 0.400 | <0.002 | 0.002 |
| F183 | 0.009 | 0.58 | 0.047 | 0.012 | 0.23 | 0.29 | 0.025 | 0.40 | <0.008 | <0.008 |
| F202 | 0.009 | 0.588 | 0.048 | 0.012 | 0.226 | 0.298 | 0.027 | 0.398 | <0.003 | <0.003 |
| F207 | 0.009 | 0.597 | 0.048 | 0.012 | 0.227 | 0.294 | 0.024 | 0.401 | <0.002 | <0.002 |
| F221 | 0.009 | 0.583 | 0.046 | 0.012 | 0.222 | 0.296 | 0.023 | 0.395 | 0.001 | 0.001 |
| F292 | 0.0117 WH | 0.598 | 0.0468 | 0.0112 | 0.228 | 0.300 | 0.0241 | 0.409 | <0.0050 | <0.0050 |
| F304 | 0.005 AL | 0.582 | 0.042 | 0.008 AL | 0.220 | 0.290 | 0.020 | 0.400 | <0.001 | <0.001 |
| F307 | 0.009 | 0.580 | 0.043 | 0.010 | 0.223 | 0.296 | 0.026 | 0.397 | <0.002 | <0.002 |
| ASSIGNED VALUE * | 0.00886 | 0.588 | 0.0470 | 0.0118 | 0.227 | 0.297 | 0.0247 | 0.405 | 0.00273 | 0.00190 |
| R-STD DEV * | 0.001093 | 0.0209 | 0.00313 | 0.00115 | 0.0065 | 0.0076 | 0.00245 | 0.0142 | 0.002357 | 0.001432 |
| ACCEPTABLE LIMITS(+ -) * | 0.002186 | 0.0418 | 0.00626 | 0.00230 | 0.0130 | 0.0152 | 0.00490 | 0.0284 | 0.004714 | 0.002864 |
| WARNING LIMITS(+ -) * | .002186- .00 | .0418- .0627 | .00626- .009 | .00230- .003 | .0130- .0195 | .0152- .0228 | .00490- .007 | .0284- .0426 | .004714- .00 | .002864- .00 |
| ACTION LIMITS(< >) * | 0.003279 | 0.0627 | 0.00939 | 0.00345 | 0.0195 | 0.0228 | 0.00735 | 0.0426 | 0.007071 | 0.004296 |
| N * | 26 | 30 | 30 | 26 | 30 | 30 | 29 | 30 | 7 | 10 |

* NOTE: SEE GLOSSARY FOR DEFINITIONS

| LAB NO. | TOTAL RANK | AVERAGE RANK | SUMMARY OF FLAGGING | BIAS STATEMENT | NO. SAMPLES RANKED | BIAS % SLOPE | BIAS BLANK | METHOD CODING |
|---------|------------|--------------|---------------------|----------------|--------------------|--------------|------------|----------------------|
| F003 | 152.0 | 15.2 | | | 10 | | | Autoclaved SnCl2 |
| F004 | 133.5 | 16.6 | WH AH | | 8 | | | Autoclaved SnCl2 |
| F007 | 173.5 | 21.6 | | | 8 | | | Autoclaved ascorbic |
| F010 | 128.5 | 12.8 | | | 10 | | | Autoclaved SnCl2 |
| F011 | 235.5 | 23.5 | AHAHAHWHAHAH | BIASED HIGH | 10 | 5.2 | 0.0117 | Colorimetric Discret |
| F014 | 137.5 | 17.1 | | | 8 | | | Flow inj. ascorbic |
| F015 | 169.5 | 18.8 | WH | | 9 | | | Autoclaved ascorbic |
| F021 | 26.0 | 3.2 | WLAL WL | BIASED LOW | 8 | -6.4 | -0.0019 | Autoclaved ascorbic |
| F022 | 69.0 | 11.5 | WH | | 6 | | | Block dig. ICP-AES |
| F026 | 102.5 | 12.8 | | | 8 | | | Autoclaved SnCl2 |
| F026b | 121.5 | 20.2 | | | 6 | | | ICP-AES |
| F036 | 148.0 | 14.8 | | | 10 | | | Autoclaved ascorbic |
| F053 | 81.0 | 10.1 | | | 8 | | | Flow inj. ascorbic |
| F069 | 144.5 | 18.0 | | | 8 | | | acid persulfate dige |
| F069b | 27.5 | 4.5 | WL | BIASED LOW* | 6 | -1.1 | -0.0053 | alkaline persulfate |
| F112 | 93.5 | 11.6 | ALAL AH | | 8 | | | Block dig. ascorbic |
| F113 | 133.0 | 14.7 | WH | | 9 | | | Flow inj. ascorbic |
| F146 | 160.0 | 16.0 | WLWH WHAHAH | | 10 | | | Flow inj. SnCl2 |
| F153 | 97.5 | 19.5 | | | 5 | | | Block dig. ICP-MS |
| F154 | 170.0 | 21.2 | | | 8 | | | Autoclaved ascorbic |
| F158 | 107.0 | 13.3 | | | 8 | | | Flow inject Ascorbic |
| F163 | 115.0 | 11.5 | | | 10 | | | Autoclaved ascorbic |
| F170 | 96.0 | 10.6 | | | 9 | | | Autoclaved ascorbic |
| F183 | 114.5 | 14.3 | | | 8 | | | ICP-MS |
| F202 | 133.0 | 16.6 | | | 8 | | | manual ascorbic acid |
| F207 | 121.5 | 15.1 | | | 8 | | | Flow inj. ascorbic |
| F221 | 93.0 | 9.3 | | | 10 | | | Flow inj. ascorbic |
| F292 | 138.0 | 17.2 | WH | | 8 | | | Flow inj. ascorbic |
| F304 | 39.5 | 4.9 | AL AL | BIASED LOW* | 8 | -0.3 | -0.0046 | Flow inj. ascorbic |
| F307 | 83.5 | 10.4 | | | 8 | | | Block dig. ascorbic |

* NOTE: INDICATED BIAS STATEMENT IS FOR CAUTION ONLY AND NOT COUNTED IN STUDY STATISTICS
PERCENT SLOPE USED FOR CAUTION COMPARISON = 5

OVERALL AVERAGE RANK IS 14.2