



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

Study / Étude 0099  
March / Mars 2012

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**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

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C. Tinson and J. Simser  
IQM-2012-03



Environment  
Canada

Environnement  
Canada

## Information and Quality Management

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March 26, 2012

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

Re: Distribution of the Final Report for **PT Study 0099** (December 2011 to March 2012)

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.

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,  
Cheryl Tinson  
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 0099 – December 2011 to March 2012**

Contributors

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# Environment Canada Proficiency Testing Program

## Glossary of Terms and Definitions

### A. Statistics listed in Data Summary (Appendix A)

- |                      |                                                                      |
|----------------------|----------------------------------------------------------------------|
| 1. Assigned Value    | The <u>median</u> value of test results for a parameter and sample   |
| 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 $\pm 2 \sigma^*$	Acceptable Limits	No Flag
$2 \sigma^* - 3 \sigma^*$ from assigned value	Warning Limits	Warning Flag (W)
$> 3 \sigma^*$ from assigned value	Action Limits	Action Flag (A)

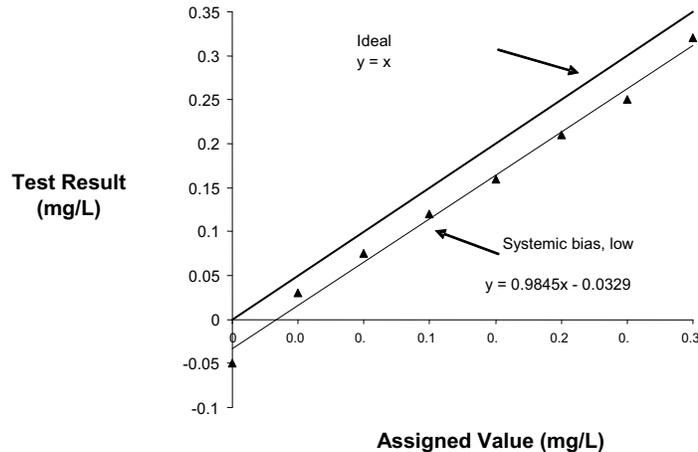
\*  $\sigma^*$  is the R-Std Dev

**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 calculate systemic bias. For programs with ten samples per set, a laboratory must report five or more test results (not including '<'). For programs with five samples per set (i.e. FPSED and FPHG low-level), a laboratory must report four or more test results (not including '<'). There must be ten or more participating laboratories regardless of the number of samples per set.

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. 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 ),

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

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*.

### **D. 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)**

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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 Median Values
Appendix A	Data Summary

**APPENDIX A**  
DATA SUMMARY

FPTP STUDY 0099

2012-03-09

PAGE 1

PARAMETER: 15092 Total Phosphorus mg/L P

WATER SCIENCE & TECHNOLOGY  
ENVIRONMENT CANADA

EC PT for Total Phosphorus in Water

SAMPLE	1=	2=	3=	4=	5=	6=	7=	8=	9=	10=	
LAB NO	TP99-1	TP99-2	TP99-3	TP99-4	TP99-5	TP99-6	TP99-7	TP99-8	TP99-9	TP99-10	
	LAB RESULT	LAB RESULT	LAB RESULT	LAB RESULT	LAB RESULT						
F003	0.002	0.070	0.225	0.128	0.594	0.001	0.390	0.013	0.016	0.175	
F004	<0.002	0.070	0.231	0.137	0.590	<0.002	0.390	0.014 WH	0.017	0.176	
F007	<0.002	0.069	0.234	0.128	0.589	<0.002	0.394	0.011	0.015	0.176	
F010	0.0025	0.072	0.225	0.122	0.592	0.0018	0.387	0.0106	0.017	0.173	
F011	<0.01	0.08 AH	0.24	0.13	0.59	<0.01	0.39	0.02 AH	0.02 AH	0.18	
F015	<0.002	0.066	0.218	0.122	0.84 AH	<0.002	0.42 WH	0.013	0.016	0.169	
F021	<0.002	0.068	0.224	0.125	0.587	<0.002	0.398	0.011	0.015	0.176	
F022	<0.002	0.079 WH	0.227	0.133	0.585	<0.02	0.391	<0.02	0.025 AH	0.170	
F026	0.001	0.068	0.218	0.124	0.572	<0.001	0.384	0.012	0.016	0.168	
F026b	<0.02	0.062	0.218	0.117	0.563	<0.02	0.383	<0.02	<0.02	0.167	
F036	0.002	0.068	0.229	0.124	0.570	0.001	0.383	0.012	0.015	0.175	
F053	0.010 WH	0.066	0.185 AL	0.023 AL	0.538	0.008 WH	0.385	0.015 WH	0.017	0.147 AL	
F069	<0.004	0.066	0.237	0.125	0.551	<0.004	0.365	0.011	0.015	0.172	
F069b	<0.010	0.064	0.223	0.125	0.587	<0.010	0.384	0.012	0.016	0.171	
F112	0.002	0.067	0.189 AL	0.104 WL	0.569	0.002	0.359	0.010	0.014	0.128 AL	
F113	<0.004	0.058 WL	0.21	0.104 WL	0.541	<0.004	0.354	0.007 WL	0.013	0.162	
F113b	0.004	0.058 WL	0.226	0.109	0.582	0.005	0.378	0.01	0.017	0.174	
F153	<0.01	0.074	0.24	0.13	0.63	<0.01	0.41	0.011	0.016	0.19 WH	
F154	0.0056	0.064	0.220	0.119	0.598	0.0040	0.368	0.012	0.015	0.168	
F158	<0.002	0.067	0.225	0.124	0.576	<0.002	0.386	0.011	0.015	0.170	
F170	0.002	0.067	0.234	0.128	0.599	<0.001	0.400	0.011	0.013	0.177	
F183	<0.008	0.0682	0.246 WH	0.129	0.66 AH	<0.008	0.437 AH	0.0107	0.0162	0.192 WH	
F202	<0.003	0.068	0.227	0.126	0.608	<0.003	0.388	0.012	0.016	0.174	
F207	<0.002	0.069	0.228	0.127	0.589	<0.002	0.391	0.011	0.015	0.173	
F221	0.001	0.061	0.215	0.117	0.563	<0.001	0.377	0.009	0.012	0.157	
F228	<0.002	0.067	0.226	0.122	0.547	<0.002	0.358	0.012	0.015	0.166	
F233	<0.0050	0.0682	0.225	0.128	0.570	<0.0050	0.406	0.0117	0.0151	0.171	
F246	<0.0010	0.0690	0.208	0.112	0.574	<0.0010	0.359	0.0104	0.0114 WL	0.158	
F248	<0.003	0.067	0.22	0.12	0.57	<0.003	0.38	0.010	0.015	0.169	
F270	<0.0020	0.059	0.21	0.11	0.55	<0.0020	0.37	0.012	0.016	0.16	
F280	<0.003	0.071	0.230	0.130	0.601	<0.003	0.385	0.011	0.017	0.172	
F292	<0.0050	0.0618	0.213	0.116	0.548	<0.0050	0.364	0.0096	0.0139	0.163	
F293	<0.004	0.062	0.224	0.122	0.577	<0.004	0.391	0.010	0.013	0.172	
F304	<0.001	0.067	0.226	0.124	0.598	<0.001	0.390	0.010	0.014	0.172	
F309	0.0711 AH	0.0655	0.224	0.120	0.578	<0.0044	0.382	0.00930	0.0140	0.168	
F317	<0.024	0.035 AL	0.237	0.092 AL	0.728 AH	<0.024	2.65 AH	<0.024	<0.024	0.159	
F324	<0.003	0.068	0.230	0.126	0.566	<0.003	0.381	0.01	0.014	0.173	
ASSIGNED VALUE *	0.0020	0.0670	0.225	0.124	0.577	0.0020	0.385	0.01100	0.0150	0.172	
R-STD DEV *	0.00266	0.00420	0.0100	0.0080	0.0240	0.00258	0.0162	0.001370	0.00159	0.0072	
ACCEPTABLE LIMITS (+-) *	0.00532	0.00840	0.0200	0.0160	0.0480	0.00516	0.0324	0.002740	0.00318	0.0144	
WARNING LIMITS (+-) *	.00532-	.00700840-	.0120200-	.03000160-	.02400480-	.072000516-	.0070324-	.0486002740-	.0000318-	.0040144-	.0216
ACTION LIMITS (<>) *	0.00798	0.01260	0.0300	0.0240	0.0720	0.00774	0.0486	0.004110	0.00477	0.0216	
N *	11	37	37	37	37	7	37	34	35	37	

\* 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	222.0	22.2			10			Autoclaved SnCl2
F004	243.5	30.4		WH BIASED HIGH*	8	0.6	0.0044	Autoclaved SnCl2
F007	208.0	26.0			8			Autoclaved ascorbic
F010	194.0	19.4			10			Autoclaved SnCl2
F011	259.5	32.4	AH	AHAH BIASED HIGH*	8	-0.2	0.0091	
F015	178.5	22.3		AH WH	8			Autoclaved ascorbic
F021	178.0	22.2			8			Autoclaved ascorbic
F022	196.0	28.0	WH	AH	7			Block dig. ICP-AES
F026	145.5	16.1			9			Autoclaved SnCl2
F026b	58.0	9.6			6			ICP-AES
F036	172.5	17.2			10			Autoclaved ascorbic
F053	117.5	11.7	WH ALAL WH WH AL		10			
F069	135.5	16.9			8			acid persulfate dige
F069b	152.0	19.0			8			b-alkaline persulfat
F112	62.0	6.2	ALWL	AL BIASED LOW*	10	-4.0	-0.0077	Block dig. ascorbic
F113	25.5	3.1	WL WL WL	BIASED LOW	8	-6.6	-0.0034	persulfate dig/FIA a
F113b	138.5	13.8	WL		10			pers dig/FIA no acid
F153	250.0	31.2		WH BIASED HIGH	8	7.8	-0.0003	Block dig. ICP-MS
F154	135.5	13.5			10			Flow inj. ascorbic
F158	140.5	17.5			8			persulfate UV
F170	201.5	22.3			9			
F183	244.5	30.5	WH AH AH WH	BIASED HIGH	8	14.2	-0.0057	ICP-MS
F202	205.5	25.6			8			manual ascorbic acid
F207	191.0	23.8			8			
F221	46.5	5.1		BIASED LOW*	9	-2.5	-0.0033	
F228	110.0	13.7			8			EPA 365.1
F233	180.0	22.5			8			Autoclaved ascorbic
F246	73.5	9.1		WL	8			Autoclvd (NH4)2S2O8
F248	101.5	12.6			8			Flow inj. ascorbic
F270	83.5	10.4			8			Autoclaved ascorbic
F280	216.0	27.0			8			Autoclaved ascorbic
F292	47.0	5.8		BIASED LOW	8	-5.6	-0.0003	Flow inj. ascorbic
F293	116.0	14.5			8			
F304	150.5	18.8			8			
F309	104.0	11.5	AH		9			Autoclaved ascorbic
F317	114.5	19.0	AL ALAH AH		6			Block dig. ascorbic
F324	139.0	17.3			8			

\* 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 17.9