

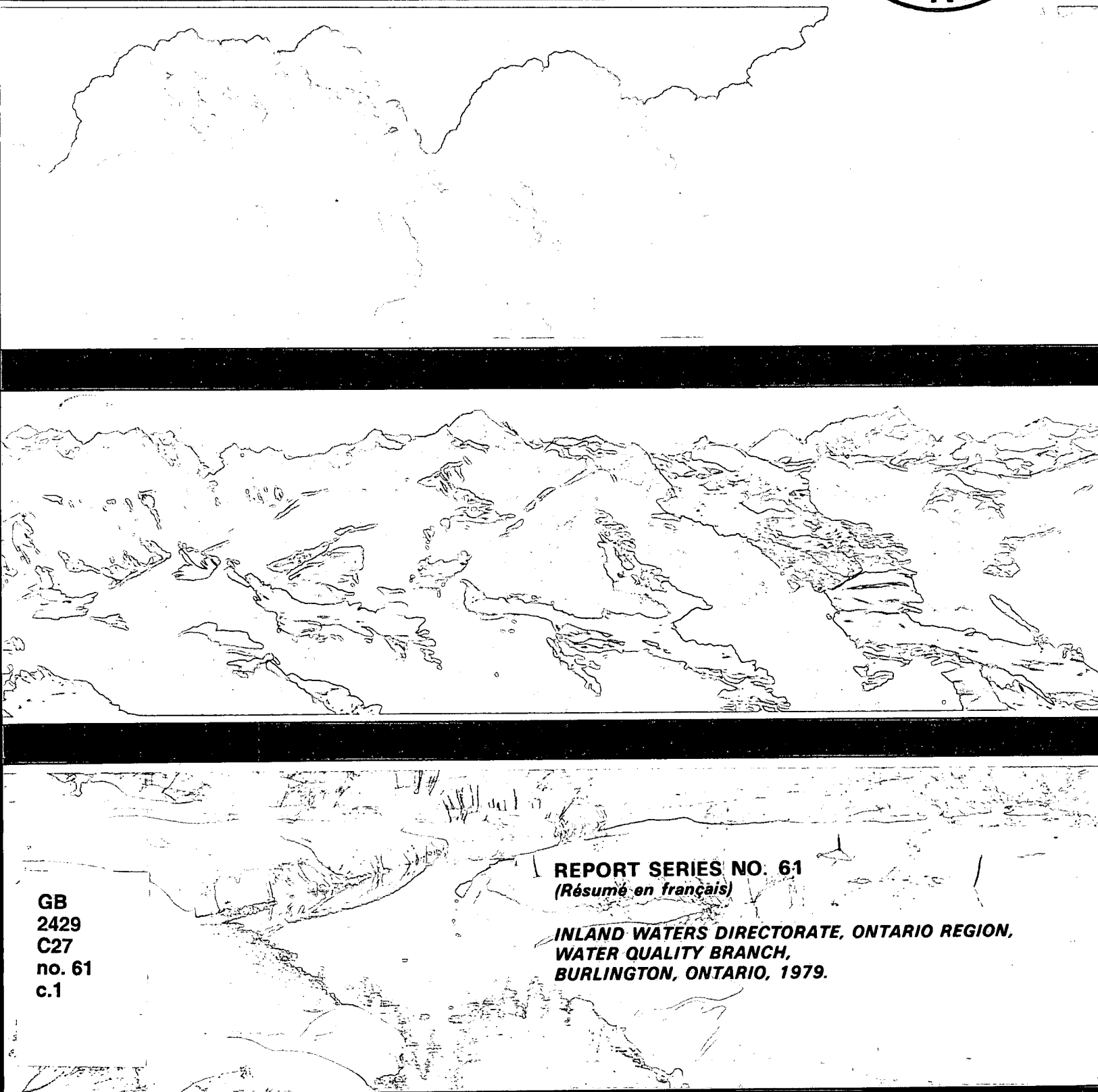


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Interlaboratory Quality Control Study No. 18 Total Mercury in Sediments

K.I. Aspila and J.M. Carron



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(Résumé en français)

**INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
BURLINGTON, ONTARIO, 1979.**



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Abstract

Results of an interlaboratory comparison study on the analysis of mercury in five lake bottom sediments are described. Twenty-eight Canadian laboratories participated. Concentrations of mercury in uncertified test samples ranged from 0.01 $\mu\text{g/g}$ to 0.6 $\mu\text{g/g}$ Hg. Mean values from participants were evaluated by rank correlation.

Estimates of the concentration of mercury in each sample were determined by sequentially eliminating all data beyond two standard deviations of adjusted mean values. Precision functions identifying average in-laboratory and interlaboratory standard deviations as a function of mean calculated mercury content are described. These precision functions identify the anticipated comparability of mercury data when a variety of different laboratories analyzes the mercury content in processed dry sediments ($<177 \mu\text{m}$) using different methods.

Résumé

Le présent rapport renferme les résultats d'une étude interlaboratoire comparative du dosage du mercure dans les sédiments de fond de cinq lacs. Vingt-huit laboratoires canadiens ont participé à l'étude. La teneur en mercure des échantillons de titre inconnu s'échelonnait entre 0,01 $\mu\text{g/g}$ et 0,6 $\mu\text{g/g}$ de Hg. Les valeurs moyennes obtenues par les participants ont été établies par corrélation des rangs.

L'estimation de la teneur en mercure de chaque échantillon s'est faite par l'élimination successive de toutes les données situées au-delà de deux écarts types calculés par rapport aux valeurs moyennes corrigées. Pour mesurer la précision des résultats, on donne des relations exprimant les écarts types moyens pour chaque laboratoire et entre les laboratoires en fonction de la teneur moyenne calculée. Ces relations servent à prévoir dans quelle mesure les données sur le mercure peuvent se comparer entre elles lorsque plusieurs laboratoires dosent le mercure des sédiments secs ($<177 \mu\text{m}$) par diverses méthodes.

List of Symbols

n Number of results used in calculating the mean value (\bar{x})

\bar{x} Mean value calculated from the equation $(\sum x_i)/n$

S.D. Standard deviation calculated from the equation

$$\text{S.D.} = \left[\frac{\sum (x_i - \bar{x})^2}{(n-1)} \right]^{1/2}$$

R.S.D. Relative standard deviation calculated from the equation

$$\text{R.S.D.} = (\text{S.D.}/\bar{x}) \times 100$$

R Designates data rejected by the method of evaluation

Interlaboratory Quality Control Study No. 18

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INTRODUCTION

Interlaboratory quality control study No. 18 was the first study of the National Interlaboratory Quality Control Program to involve interlaboratory analysis of lake bottom sediments. It was designed primarily to identify the comparability of data currently being obtained on total mercury in sediments by laboratories engaged in environmental programs in Canada. Test samples were distributed to participants in December 1976. Analyses were made between December 1976 and March 1977.

EXPERIMENTAL DESIGN

Bottom sediments selected for this study were obtained from a small bank of solid reference materials in the Quality Control Laboratories of the Water Quality Branch. A brief description of the samples is given below:

Sample	Source	Mesh	Comments
1	Lake Superior	<80 (<177 μm)	Air-dried
2	Lake Erie	<80 (<177 μm)	Air-dried
3	Lake Erie	<80 (<177 μm)	Air-dried
4	Lake Ontario	<80 (<177 μm)	Freeze-dried
5	Lake Ontario	<200 (<74 μm)	Freeze-dried

Although the source of sediment is given, the mercury content determined in these samples should not be considered representative of the Great Lakes. Samples 1 to 3 were air-dried, mechanically crushed, and passed through 80-mesh (<177 μm) stainless steel sieves. Samples 4 and 5 were originally the same material, freeze-dried and crushed. Sample 4 was passed through an 80-mesh sieve, whereas sample 5 was that fraction of the same sample that passed through a 200-mesh (<74 μm) sieve. The difference in data from samples 4 and 5 would reflect the sample processing.

After the sieving process, all test samples were homogenized for several hours in a 32-qt plastic twin-shell blender

(Patterson-Kelly Co., Pa.). Sufficient material was blended to prepare several hundred 10- to 20-g subsamples. All test samples were bottled in 1-oz borosilicate glass bottles with moisture-proof polyethylene snap caps. The freeze-drying operation for samples 4 and 5 was conducted without the aid of a mercury McLeod vacuum gauge.

Samples were distributed to participants by first-class mail. Each laboratory was requested to select a routine method and analyze for total mercury. No additional sample processing (oven-drying) was required. Participants were requested to provide their results in the form of micrograms per gram of mercury on an "as is" basis.

Several laboratories with recognized capabilities in the analysis of mercury in sediments were requested to provide replicate within-run analysis of the sediment. Other participants were encouraged to do the same.

EVALUATION OF DATA

Laboratories participating in this study were anticipated (and partially known) to represent both well-controlled high-production laboratories and some small laboratories just initiating sediment programs. For this reason the data were evaluated by a rather rigorous technique to remove potentially deviant results as well as by a method to permit each laboratory to identify its results ranked relative to the other laboratories.

Rejection of Results

Where data were received in replicate, mean values and in-laboratory standard deviations were calculated. These mean values were tabulated with each laboratory being assigned a single value. If a laboratory provided results obtained by two different methods, the mean results were identified separately by assigning an additional new laboratory number (e.g., 30a and 30b).

Laboratory values that were beyond two standard deviations of the calculated mean were arbitrarily identified as rejected. The first calculation of average interlaboratory

values resulted in an initial rejection of some data. A new mean value and a new standard deviation were then determined, and additional values were rejected. The process was continued until no further data were identified beyond plus or minus two standard deviations from the adjusted population means.

This technique of rejecting values is recognized as harsh, but it is a compromise between the use of "total laboratory data" and the alternative use of data from "select specialized laboratories" in attempting to identify a "true value" or "acceptable value" for the unknown concentration in these test materials.

Ranking of Results

Laboratory performance on test results was evaluated by a ranking method similar to that described by Youden (U.S. Department of Commerce, 1969). The laboratory that provided the lowest concentration for a sample was assigned a rank of 1. The laboratory with the highest value for a sample was given the highest rank, which for this study was 27. Although there were 28 results involved, one laboratory was excluded for convenience, since it had a "less than" value as well as an absent result owing to a broken sample bottle. Where laboratory results were identical, appropriate half-integral values were assigned in the ranking scheme of Youden. After individual laboratory ranks were assigned for each sample, a mean laboratory standing for all five samples was calculated and ranked to identify laboratories with the lowest average values through to the highest average values. The reader should note that although the mechanism of ranking data is the same as that of Youden, the assignment of low and high ranks used in this study is the reverse order.

Precision Functions

The standard deviations for in-house data and for the interlaboratory mean values were calculated using the standard formula (see List of Symbols). Assuming that all test samples behaved chemically or analytically in the same manner and that the standard deviation is directly proportional to concentration, it is possible to estimate from laboratory results a least squares line relating precision and concentration. For this study, such an equation is referred to as a precision function. In-laboratory standard deviations provided by a limited number of results permit the calculation of the in-laboratory precision function. Interlaboratory standard deviations calculated first without any data rejection and then with data rejection provide two different estimates of the interlaboratory precision functions. All such precision functions are in the form

$y = mx + b$, where y is the standard deviation, x is the concentration of mercury, m is the slope of the least squares line and b is the intercept of the line on the y -axis. Calculation of these lines from data (standard deviation and mean calculated mercury concentrations) is described by Alder and Roessler (1964) and can be determined quickly by pocket calculator.

RESULTS AND DISCUSSION

Results and Methods

Average values of results provided by participants are tabulated in Table 1. The values followed by R are classed as outliers by the method used in evaluating results. In Figure 1, the distribution of data is given. The \bar{x} identifies the mean value after rejection of outliers and the notation $G.M.$ indicates the grand mean before any data were rejected.

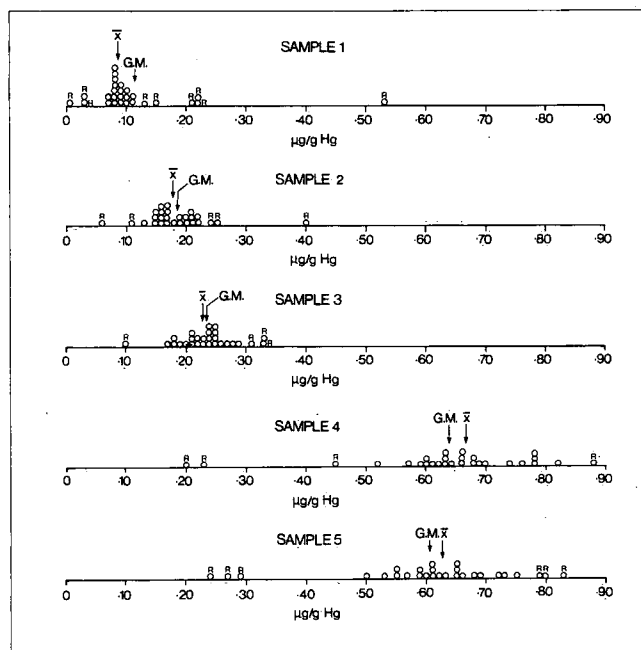


Figure 1. Distribution of results for study No. 18.

Methods used by participants varied considerably, but all included an acid digestion (with or without additional oxidants) followed by reduction with a stannous salt solution. Only one laboratory differed by using hydrazine rather than Sn^{+2} for reduction of Hg^{+2} . All methods for analyzing mercury involved cold vapour detectors. A summary of methods employed is given in Table 2. Although this summary is incomplete, it nevertheless reflects the diversity of methods used for the analysis. Methods such as neutron activation or those employing heated volatilization for extraction were unfortunately not included.

Attempts to correlate the data provided with the methods of analysis were initially considered. Correlation may still be considered by the reader but it must be handled with caution, since not only were some results suspected of being experimental (e.g., from small laboratories with low production) but also the test samples were not established with acceptable or certified concentrations. It would be more appropriate to evaluate differences between methods by in-laboratory studies, since the interlaboratory data in this present study have so many different variables.

Discussion

A summary of mean values and standard deviations calculated in evaluating the data for outliers is given in Table 3. Several borderline results were rejected by this rigorous elimination process. The end product of this exercise identifies mean values with rather tight confidence limits within which a true value is anticipated.

Rank of Laboratories

Results of ranking data for each sample by a method similar to that of Youden (Youden and Steiner, 1975; U.S. Department of Commerce, 1969) are given in Table 4. The laboratory number assigned to each participant and the mean rank of the laboratory are given as well. To place laboratories in perspective, the mean sample ranks were reordered to identify all laboratories in a relative manner (Table 5). The laboratory with the lowest average sample rank was assigned a rank of 1 and the laboratory with the highest mean sample rank, a rank of 27. One laboratory (No. 62) was not included, as two values were missing from its report. If this laboratory had been included, it would have ranked quite favourably.

Although it is difficult to rank laboratories on a single sample, ranking is significant when the precision is good and the systematic error (or bias) is large. It should be clear that a laboratory which lacks precision can inadvertently be ranked quite favourably on one sample. Yet as the number of samples used for ranking increases the systematic error (or bias) becomes more predominant, and the average laboratory rank then becomes a more suitable indicator of the accuracy of the laboratory. This accuracy is of course only implied by the fact that a laboratory with a mean rank of 14, for example, tends to have all the results near the mean values on all samples.

Laboratories that had either one or several sample results rejected in the initial screening of data (Tables 1 and 3) were ranked either very low or very high. Two labora-

tories (Nos. 10 and 23) were consistently ranked high or low, indicating a substantial systematic error. Others, notably Nos. 52, 27 and 28, had both high and low sample ranks, which imply high imprecision.

Precision

Although in-laboratory precision statements were not requested from participants, an indication of mean in-laboratory precision could be obtained from the data provided by several laboratories. The number of values reported per sample is given in Table 1. A summary of the raw data is given in Table 6. It is accepted that this information may possibly be biased slightly, since some laboratories providing such data would at times report only their best data. The results, however, are useful in describing the in-laboratory standard deviation of several of the participants. It is of interest to note that those laboratories that did identify individual results had virtually no mean values rejected in the initial evaluation (No. 13 was borderline). This coincidence is not too surprising, since several of these participants are known to have large routine analytical programs with suitable quality control programs.

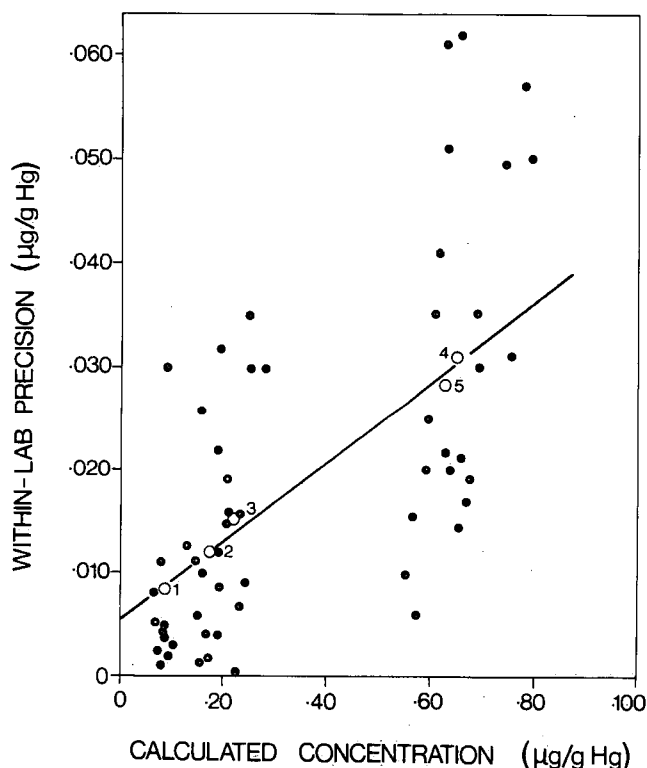


Figure 2. Estimated precision function for mean in-laboratory analysis of samples 1 to 5. Least squares line is $y = 0.038x + 0.0058$. Closed circles represent standard deviations obtained from Table 6. Open circles represent the mean values for each sample.

An estimated precision function that was calculated for the in-laboratory replication is given in Figure 2. The individual values were obtained from Table 6. The least squares line calculated is through the five co-ordinates (1, 2...5) corresponding to the mean values and mean standard deviations for the five test samples. The scatter of single laboratory data in Figure 2 is a consequence of the estimation of the standard deviations from the limited replicates provided by participants.

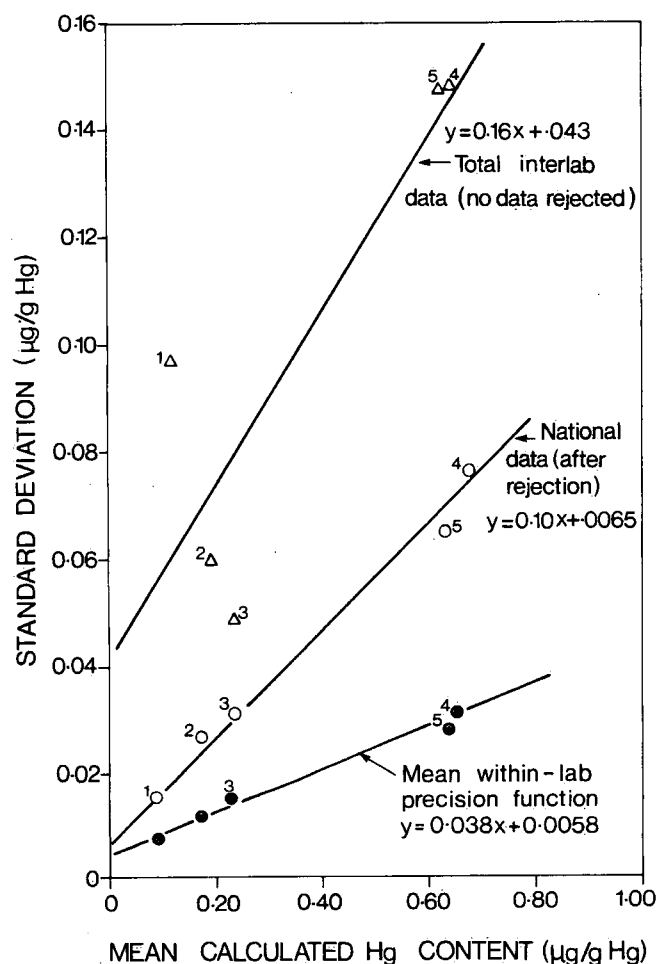


Figure 3. Estimated precision functions for in-laboratory and interlaboratory analysis of mercury in five sediments.

Interlaboratory precision functions were calculated using the overall data and then only the data accepted after the rejection of outliers (Table 3). Both such functions (in-laboratory and interlaboratory) are given in Figure 3. Caution should be exercised in the visual judgement of this graph, since the slope is exaggerated for visual clarity. The relative standard deviations (i.e., coefficient of variation) at 0.6 $\mu\text{g/g Hg}$ for the total data, adjusted data and in-laboratory data are 23%, 11% and 5%. In fact, the interlaboratory precision among laboratories in the "adjusted"

population is quite good, as it should be, since several of these participants provide a large amount of environmental data on mercury in sediments. In spite of this optimism, it must be noted that the results from this study do not reflect interlaboratory imprecision owing to field sampling. This area warrants attention, since large-scale surveys of environmental mercury can involve data from several laboratories or agencies. Study No. 18 provides direction on the anticipated quality of data if all laboratories analyze the same dry solid reference sediments.

SUMMARY

Results of an interlaboratory comparison on the analysis of mercury in five lake bottom sediments are described. The concentration of mercury in the five sediments ranged from 0.08 $\mu\text{g/g}$ to about 0.7 $\mu\text{g/g Hg}$. Although the methods of analysis used by participants were very diverse, all participants did use some form of wet chemical digestion, followed by mercury analysis using a cold vapour detection system. Major laboratories with established analytical programs on mercury in sediments were more comparable than small laboratories which had just recently developed expertise and programs. Laboratory data were rejected by sequentially removing values greater than two standard deviations from the mean. For the five test samples analyzed, the relative standard deviation on the interlaboratory results (after some data rejection) varied from 11% to 15% over the concentration range of 0.088 $\mu\text{g/g}$ to 0.667 $\mu\text{g/g Hg}$.

ACKNOWLEDGMENTS

The participating laboratories listed in the Appendix are gratefully acknowledged.

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Tables

Table 1. Mean Values of Results Provided by Participants

Laboratory number	Sample number (results in $\mu\text{g/g Hg}$)					Number of results reported per sample
	1	2	3	4	5	
9	0.084	0.160	0.218	0.633	0.601	5, 10
31	0.079	0.153	0.210	0.567	0.550	3
50	0.07	0.16	0.24	0.69	0.63	4, 5
27	0.002 R	0.056 R	0.184	0.816	0.267 R	1
30a	0.080	0.165	0.215	0.655	0.650	2
30b	0.100	0.210	0.270	0.780	0.730	1
28	0.027 R	0.15	0.24	0.23 R	0.29 R	2, 3, 4
60	0.102	0.184	0.253	0.628	0.614	5
23	0.131 R	0.240 R	0.326 R	0.878 R	0.830 R	2
53	0.145 R	0.255 R	0.305 R	0.775	0.66	2
62	<0.2	(Broken)	0.25	0.64	0.61	1
5	0.09	0.16	0.23	0.62	0.57	3
34	0.08	0.22	0.25	0.68	0.65	1
43	0.11	0.19	0.19	0.60	0.58	1
14	0.085	0.171	0.167	0.632	0.616	5, 10
52	0.22 R	0.11 R	0.206	0.45 R	0.5	1
39	0.07	0.15	0.24	0.61	0.61	1
47a	0.53 R	0.22	0.26	0.70	0.715	1
47b	0.205 R	0.205	0.285	0.765	0.80 R	2
13	0.10	0.21	0.28	0.78	0.79 R	2, 3
54	0.220 R	0.400 R	0.325 R	0.660	0.680	1
22	0.080	0.212	0.248	0.678	0.650	4, 5
6	0.080	0.153	0.21	0.587	0.593	7
57	0.080	0.170	0.233	0.597	0.555	3, 4
2	0.108	0.199	0.195	0.742	0.748	5, 10
1	0.086	0.190	0.184	0.656	0.695	5
48	0.087	0.170	0.243	0.521	0.531	5
10	0.028 R	0.129	0.096 R	0.204 R	0.237 R	1
8*	0.082	0.154	0.216	0.465	0.601	6

*Data submitted late. These results were not used in the evaluation of interlaboratory data.

R—These values were sequentially removed by rejecting results greater than two standard deviations (see Table 3). Several borderline cases were involved.

Table 2. Summary of Methods Used by Participants

Laboratory number	Extraction details		Detection system				Laboratory detection limit ($\mu\text{g/g Hg}$)
	Weight of sample analyzed (g)	Extracting agents and conditions for digestion	Reducing system	Reagents used in reducing system	Instrument	Sampler	
9	0.2-2.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 60°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$, 20°C (14 h)	Automated	a, c, d, f	Technicon Pharmacia	A	0.01
31	2.0	$\text{HNO}_3 + \text{HCl}$ (1 + 3), boil	Automated	a	Perkin-Elmer 403	A	0.005
50	0.35	$\text{HNO}_3 + \text{HCl}$ (1 + 3), heat	Manual	b, c, e	Technicon Pharmacia	M	0.01
27 R	1.0	$\text{HNO}_3 + \text{HCl}$ (1 + 3), boil (0.5 h)	Manual	b, c	Flameless atomic absorption, Perkin-Elmer (syringe)	—	0.002
30a	1.0	$\text{HNO}_3 + \text{HCl}$ (20 mL + 0.5 mL), 95°C (2 h)	Manual	a	Varian	M	0.010
30b	1.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3$ (10 mL + 2 mL), 95°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$	Manual	a,c	Varian	M	0.005
28 R	0.5-1.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3$ (10 mL + 5 mL), 50°C (12 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$	Manual	a, c, d, e	Varian	—	0.025
60	1	$\text{H}_2\text{SO}_4 + \text{HNO}_3$ (5 mL + 2.5 mL), 90°C (1 h); then KMnO_4	Manual	b, c	Spectro Products HG-2	M	0.005
23 R	0.25	$\text{HCl} + \text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{KMnO}_4$, $95-100^\circ\text{C}$ (2 h)	Manual	a, c	Coleman	—	0.020
53 R	0.25	$\text{HNO}_3 + \text{HCl}$ (1 + 3) + KMnO_4 , 90°C (45 min)	Manual	a, c	Instrumentation Laboratories	M	0.005
62	0.5	$\text{HNO}_3 + \text{HCl}$ (1 + 3) + KMnO_4 , 95°C (0.5 h)	Manual	a, c, f	Pharmacia	M	0.1
5	0.2-0.4	($\text{HNO}_3 + \text{HCl}$) (1 + 3), 95°C (0.5 h); then KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$	Manual	b, c	Pharmacia	M	0.05

Reagents used in reducing system: a— SnSO_4 e— HCl
 b— SnCl_2 f— NaCl
 c—Hydroxylamine g—Hydrazine sulphate
 d— H_2SO_4

A—Automatic sample was employed.

M—Subsampling was manual.

R—Indicates that laboratory had some results rejected by the method used in evaluating data.

Table 2. Continued

Laboratory number	Extraction details		Detection system				Laboratory detection limit ($\mu\text{g/g Hg}$)
	Weight of sample analyzed (gr)	Extracting agents and conditions for digestion	Reducing system	Reagents used in reducing system	Instrument	Sampler	
34	1.0	($\text{HNO}_3 + \text{HCl}$) (1 + 3), KMnO_4 , 170°C (0.5 h)	Manual	b, c	Pharmacia	M	0.02
43	1.0	($\text{HNO}_3 + \text{HCl}$) (1 + 3), KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$, 95°C	Manual	b	Pharmacia	—	0.01
14	0.5-2.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 60°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$ (14 h)	Automatic	b, c, d, f	Technicon Pharmacia	A	
52 R	1	$\text{HNO}_3 + \text{HCl} + \text{KMnO}_4$	Manual	b, c	Perkin-Elmer	—	0.05
39	5	$\text{HNO}_3 + \text{HCl}$ (20 mL)	Automatic	a, c, f	Technicon Pharmacia	A	—
47a R	1	$\text{HNO}_3 + \text{HCl}$ (7.5 mL + 2.5 mL), 90°C (1 h)	Manual	a	Perkin-Elmer	—	0.005
47b R	1	$\text{HNO}_3 + \text{HCl} + \text{KMnO}_4$, 90°C (1 h)	Manual	a, c	Perkin-Elmer	—	0.005
13 R	0.1-0.2	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 90°C (16 h)	Manual	b, g	Jarrell-Ash	M	0.005
54 R	0.2	$\text{H}_2\text{SO}_4 + \text{HNO}_3$ (5 + 2) + KMnO_4 , 120°C (15 min)	Manual	b, c, d, e	Laboratory Data Control	M	0.010
22	0.5-1.0	$\text{HNO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ (Teflon bomb)	Automated	b	Perkin-Elmer	A	0.05
6	0.25-0.5	$\text{HNO}_3 + \text{HCl}$ (3 mL + 5 mL) (reflux)	Manual	b	Beckman	M	0.002
57	1.0	$\text{HNO}_3 + \text{HCl}$ (4 mL + 4 mL); then KMnO_4	Manual	b	Coleman	M	0.04
2	0.5-2.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 60°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$ (14 h)	Automated	a, c, d, f	Technicon Pharmacia	A	
1	0.5-2.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 60°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$ (14 h)	Automated	a, c, d, f	Technicon Pharmacia	A	
48	0.5-2.0	$\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HCl}$, 60°C (2 h); then $\text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$ (14 h)	Automated	a, c, d, f	Technicon Pharmacia	A	
10 R	0.25	H_2O_2 (0.5 mL) + H_2SO_4 (25 mL)	Manual	b	Technicon Pharmacia	—	0.005

Table 3. Statistical Summary in Rejecting Data

Statistics	Sample number				
	1	2	3	4	5
n (total)	27	27	28	28	28
\bar{x}	0.1140	0.1849	0.2340	0.6348	0.6054
S.D.	0.0976	0.0595	0.0488	0.1493	0.1450
Rejected values	(0.53)	(0.056, 0.400)	(0.096)	(0.204, 0.23)	(0.237, 0.29, 0.267)
n	26	25	27	26	25
\bar{x}	0.098	0.1814	0.2391	0.6669	0.6463
S.D.	0.052	0.0347	0.0414	0.0950	0.0857
Rejected values	(0.22, 0.22)	(0.11, 0.255)	(0.325, 0.326)	(0.45, 0.878)	(0.830)
n	24	23	25	24	24
\bar{x}	0.0879	0.1813	0.2322	0.6672	0.6387
S.D.	0.0395	0.0289	0.0344	0.0763	0.0783
Rejected values	(0.002, 0.205)	(0.240)	(0.305)		(0.80)
n	22	22	24		23
\bar{x}	0.0865	0.1787	0.2292		0.6317
S.D.	0.0266	0.0265	0.0316		0.0719
Rejected values	(0.027, 0.028, 0.145)				(0.79)
n	19				22
\bar{x}	0.0896				0.6245
S.D.	0.0154				0.0646
Rejected value	(0.131)				
n	18				
\bar{x}	0.0873				
S.D.	0.0120				
Acceptable mean	0.0873	0.179	0.229	0.667	0.625
Acceptable range	(0.063-0.111)	(0.126-0.232)	(0.166-0.292)	(0.515-0.820)	(0.495-0.754)
R.S.D. (%)	14	15	14	11	12

Table 4. Laboratory Rank on Test Samples

Laboratory number	Sample rank					Mean sample rank
	1	2	3	4	5	
9	12	9	11	13	11	11.2
31	6	6.5	9.5	5	6	6.6
50	4.5	9	15	19	15	12.5
27	1	1	3.5	26	2	6.7
30a	9	11	8	14	17	11.8
30b	17.5	20.5	22	24.5	23	21.5
28	2	4.5	15	2	3	5.3
60	19	15	20	11	13	15.6
23	22	25	27	27	27	25.6
53	23	26	25	23	19	23.2
62	—	—	—	—	—	—
5	16	9	12	10	8	11.0
34	9	23.5	19	18	17	17.3
43	21	16.5	5	8	9	11.9
14	13	14	2	12	14	11.0
52	25.5	2	7	3	4	8.3
39	4.5	4.5	15	9	12	9.0
47a	27	23.5	21	20	22	22.7
47b	24	19	24	22	26	23.0
13	17.5	20.5	23	24.5	25	22.1
54	25.5	27	26	16	20	22.9
22	9	22	18	17	17	16.6
6	9	6.5	9.5	6	10	8.2
57	9	12.5	13	7	7	9.7
2	20	18	6	21	24	17.8
1	14	16.5	3.5	15	21	14.0
48	15	12.5	17	4	5	10.7
10	3	3	1	1	1	1.8

Table 5. Relative Laboratory Performance

Laboratory rank*	Laboratory number	Mean sample rank	Sample number rejected in evaluation of data
1	10	1.8	1, 3, 4, 5
2	28	5.3	1, 4, 5
3	31	6.6	
4	27	6.7	1, 2, 5
5	6	8.2	
6	52	8.3	1, 2, 4
7	39	9.0	
8	57	9.7	
9	48	10.7	
10.5	14	11.0	
10.5	5	11.0	
12	9	11.2	
13	30a	11.8	
14	43	11.9	
15	50	12.5	
16	1	14.0	
17	60	15.6	
18	22	16.6	
19	34	17.3	
20	2	17.8	
21	30b	21.5	
22	13	22.1	5
23	47a	22.7	1
24	54	22.9	1, 2, 3
25	47b	23.0	1, 5
26	53	23.2	1, 2, 3
27	23	25.6	1, 2, 3, 4, 5

* Laboratory ranks of 1 to 6 or 22 to 27 were assigned to participants exhibiting either imprecision or substantial systematic error.

Table 6. In-Laboratory Data on Replicate Analysis of Samples

Laboratory number	Statistics	Sample number				
		1	2	3	4	5
9	\bar{x}	0.072	0.160	0.218	0.633	0.601
	S.D.	0.0060	0.0024	0.0065	0.051	0.035
	n	5	5	5	5	5
31	\bar{x}	0.0787	0.1533	0.2100	0.5667	0.550
	S.D.	0.0021	0.0058	0	0.0153	0.010
	n	3	3	3	3	3
50	\bar{x}	0.07	0.16	0.24	0.69	0.63
	S.D.	0.008	0.0266	0.0094	0.0352	0.0617
	n	5	4	4	4	4
5	\bar{x}	0.0867	0.1600	0.2267	0.6200	0.5667
	S.D.	0.0058	0.0100	0.0153	0.020	0.0058
	n	3	3	3	3	3
14	\bar{x}	0.084	0.171	0.167	0.632	0.616
	S.D.	0.0036	0.0015	0.004	0.0169	0.0219
	n	5	5	5	5	5
13	\bar{x}	0.0967	0.2067	0.2800	0.78	0.790
	S.D.	0.0115	0.0153	0.0300	0.057	0.050
	n	3	3	3	2	3
22	\bar{x}	0.080	0.2120	0.2475	0.678	0.650
	S.D.	0.030	0.0148	0.035	0.0192	0.0141
	n	3	5	4	5	4
6	\bar{x}	0.080	0.153	0.210	0.587	0.593
	S.D.	0.011	0.011	0.019	0.020	0.025
	n	7	7	7	7	7
57	\bar{x}	0.080	0.170	0.233	0.597	0.555
	S.D.	0.008	0.0	0.013	0.015	0.013
	n	4	4	4	3	4
2	\bar{x}	0.1225	0.1986	0.1954	0.7418	0.7478
	S.D.	0.0126	0.0319	0.0085	0.0497	0.0312
	n	4	5	5	5	5
1	\bar{x}	0.086	0.190	0.184	0.656	0.695
	S.D.	0.004	0.004	0.012	0.021	0.030
	n	5	4	5	5	5
60	\bar{x}	0.102	0.184	0.253	0.628	0.614
	S.D.	0.003	0.022	0.030	0.061	0.041
	n	5	5	5	5	5
Grand mean*		0.0863	0.177	0.222	0.651	0.634
Mean standard deviation†		0.0088	0.012	0.015	0.032	0.028

* The grand mean is the average \bar{x} for the data above.

† The mean standard deviation is the average S.D. for the 12 laboratories listed above.

Appendix
List of Participants

List of Participants

Fisheries and Environment Canada, Environmental Management Service

- Atlantic Region, Water Quality Branch Laboratory (Moncton)
- Ontario Region, Water Quality Branch Inorganic Laboratory (Burlington)
- Pacific-Yukon Region, Water Quality Branch Laboratory (Vancouver)
- Quebec Region, Water Quality Branch Laboratory (Longueuil)
- Western Region, Water Quality Branch Laboratory (Calgary)

Fisheries and Environment Canada, Environmental Protection Service

- Atlantic Region, Environmental Services Branch (Halifax)
- Northwest Region, Alberta (Edmonton)

Fisheries and Environment Canada, Fisheries and Marine Service

- Fisheries Services Laboratory (West Vancouver)
- Freshwater Institute (Winnipeg)

Provincial Government Laboratories

- British Columbia Ministry of the Environment, Environmental Laboratory (Vancouver)
- British Columbia Research Council, Division of Applied Biology (Vancouver)

- Manitoba Department of Mines, Resources and Environmental Management, Environmental Protection Branch, Technical Services Laboratory (Winnipeg)
- Ontario Ministry of the Environment, Inorganic Trace Contaminants Laboratory (Rexdale)
- Ontario Ministry of the Environment, Thunder Bay Regional Laboratory (Thunder Bay)
- Ontario Ministry of Natural Resources, Mineral Research Branch (Toronto)
- Province of Nova Scotia, Pathology Institute (Halifax)

Municipal Government Laboratories

- City of Winnipeg Waterworks and Waste Disposal Division (Winnipeg)

Industrial and Consulting Laboratories

- Acres Consulting Services Ltd. (Niagara Falls, Ontario)
- Aluminum Company of Canada Ltd. (Arvida Analytical Centre, Arvida, Quebec)
- Barringer Research Ltd. (Rexdale, Ontario)
- Beak Consultants Ltd. (Mississauga, Ontario)
- Beak Consultants Ltd. (Richmond, British Columbia)
- Bondar-Clegg & Co., Ltd. (Ottawa, Ontario)
- Chemex Labs Ltd. (North Vancouver, British Columbia)
- Cominco Ltd. (Trail, British Columbia)
- Enviroclean Ltd. (London, Ontario)
- B.H. Levelton and Associates Ltd. (Vancouver, British Columbia)
- Renewable Resources Consulting Services Ltd. (Edmonton, Alberta)

Environment Canada Library, Burlington



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