Control No. AM312

DREDGING QUALITY CONTROL STUDY NO. 4 (DQC-4)
ANALYSIS OF PCBs AND TOXIC TRACE METALS IN DRY SEDIMENT REFERENCE MATERIALS

by

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EXECUTIVE SUMMARY

Quality Assurance and Methods Section was requested by EPS-OR and PWC-Toronto to set up a quality control study to evaluate the analytical capability and performance of contract and government laboratories for PCB and trace metal analysis. In Study DQC-4, 14 laboratories in Ontario, Quebec, British Columbia and Nova Scotia participated. This report compiles, evaluates and interprets the data collected for PCBs and eight trace metals. The performance of each laboratory was statistically assessed for each parameter and the results are to be used as one of the criteria in the selection of contract laboratories.

RÉSUMÉ ADMINISTRATIF

La Section de l'assurance de la qualité et des méthodes a été priée par le SPE-RO et TPC-Toronto de mettre au point une étude du contrôle de la qualité afin d'évaluer la capacité d'analyser et le rendement des laboratoires retenus à contrat et de ceux du gouvernement pour l'analyse des BPC et des métaux à l'état de traces. Quatorze laboratoires de l'Ontario, du Québec, de la Colombie-Britannique et de la Nouvelle-Écosse ont participé à l'étude DQC-4. Le présent rapport fait le bilan, évalue et interprète les données recueillies sur les BPC et huit métaux à l'état de traces. Le rendement de chaque laboratoire a fait l'objet d'une évaluation statistique pour chacun des paramètres; les résultats serviront de critère de sélection des laboratoires que l'on retiendra à contrat.

Titre : Étude de contrôle sur la qualité du dragage n^{o} 4 (DQC-4) - Analyse des BPC et des métaux à l'état de traces dans les matériaux étalons des sédiments secs
par H.B. Lee, J.A. Abbott et A.S.Y. Chau

INTRODUCTION

The Dredging Quality Control Program (DQC) initiated and supported by the Environmental Protection Service - Ontario Region (EPS-OR) was implemented by the Quality Assurance and Methods Section (QAMS) of the National Water Research Institute (NWRI). This program is part of a dredging project which ensures that the organic and inorganic contaminants in the dredged sediment is within the guidelines set by the Ontario Ministry of the Environment and the U.S. Environmental Protection Agency (1). The QC program was carried out to ensure that potential contract laboratories used by various government agencies such as the Department of Public Works, EPS, Fisheries and Oceans, etc., gave reliable analytical results on the dredged sediments. The continued use of interlaboratory QC studies provided an ongoing evaluation of a laboratory's performance for use by government agencies as a selection criterion. Interlaboratory QC studies are also used as a means for the laboratory to test the quality of its own results compared to other laboratories. The capability of these laboratories to perform specific analysis can also be determined by these QC studies.

In this study (DQC-4), the quality of sediment data for total PCBs and trace metals, two of the major classes of parameters of interest to the program, was evaluated.

STUDY PROFILE

From the returned questionnaires, a total of 17 laboratories affirmed that they would participate in this study. By the time this study was closed, 14 laboratories sent back results. Each laboratory was provided six sediment samples: four of them were freeze-dried and well characterized reference materials developed by QAMS, the rest are certified marine sediment reference materials purchased from the National Research Council of Canada. The name, sample number and reference values for the concentration of PCBs and eight toxic trace metals are given in Table 1. Note that reference materials TH-1, HR-1, Sud-1 and EC-3 are not yet fully characterized. The interim reference values were based on a limited number of in-house and external analyses. The trace metal contents in CRMs MESS-1 and BCSS-1 were determined by two or more independent analytical methods. Participants were requested to analyze all six samples for the following eight toxic trace metals: Cd, Cr, Cu, Fe, Hg, Ni, Pb and Zn. In addition, total PCB analysis for samples 1 and 2 was also requested.

RESULTS AND DISCUSSION

Analytical Methodology

In general, the dry sediment was extracted by a mixture of acetone and hexane using a shaker, ultrasonic or soxhlet technique. A few participants (D03, D04, and D17) prewetted the sample before extraction. Water was then added to the organic extract to separate acetone and the aqueous layer was back extracted with either hexane, dichloromethane, or benzene. The concentrated extract was then cleaned up on an activated or deactivated Florisil column and the PCBs were eluted by hexane. Lab D26 was the only one which used a combination of GPC (Bio-Beads S-X3) and silica gel to clean up the sediment extracts. Sulfur or sulfur compounds were removed by activated copper or metallic mercury prior to GC-ECD analysis. All but one participant used packed columns for PCB analysis and several methods of calculations including the Webb-McCall technique were used. Lab D14 analyzed PCBs with a capillary column and the total areas of PCB peaks were measured against Aroclor standards. See Table 2 for details.

For the analysis of trace metals other than mercury, digestion of sediment samples was completed using aqua regia or a combination of HNO_3, HCl, HF, and $HClO_4$ at about 100°C. This was then diluted with water and analyzed using flame or graphite furnace atomic absorption spectrophotometry (AAS). D10 was the only laboratory that did not

digest the samples. This laboratory formed sediment pellets and analyzed the trace metals by X-ray fluorescence. However, cadmium and mercury were not analyzed by this technique. See Table 3 for details. Digestion of sediment samples for mercury analysis was done by a combination of HNO_3, H_2SO_4, and HCl in the presence of $KMnO_4$, V_2O_5, or $K_2S_2O_8$. The digest was then reduced by $SnCl_2$, hydroxylamine hydrochloride or hydroxylamine sulfate. Mercury was analyzed by cold vapor AAS. See Table 4 for details.

Data Evaluation

All raw data submitted by the participants are listed in the data summary for each parameter (Appendix I). After reviewing the preliminary interlaboratory data, laboratory D25 resubmitted revised data for iron for all six test samples.

Each individual result in DQC-4 was evaluated by the Youden ranking technique (2) for the detection of biased statements as well as a computerized flagging procedure (3) for a semi-quantitative evaluation of data accuracy. Results of such evaluations were also summarized in Table 5. For each trace metal, the results of a laboratory were judged biased, i.e. consistently higher or lower, if its total rank was outside of a statistically allowable range. No biased statement was given to the PCB results since too few samples were analyzed in DQC-4 for meaningful statistics. For a more

quantitative measurement of inaccuracy, erratic results were assessed by the presence of very high (VH), high (H), low (L) and very low (VL) flags. For further explanation of the ranking and flagging procedures, please refer to Appendix II.

Interlaboratory medians rather than the reference values were used as evaluation criteria for data accuracy in the flagging procedure since not all the reference values were finalized. However, laboratory performance evaluated either by a consensus (medians) or a subjective (reference values) standard would be valid since in DQC-4 interlaboratory medians for all parameters in every sediment sample were in close agreement with the reference values. Only in a few cases did the two values differ by ±10% or more (Table 1).

SPECIFIC COMMENTS

Among the 14 participants, D04, D17, and D18 did not provide any trace metal data and D02 provided data on four of the six test samples. No results were received from D08, D09, and D10 for PCBs.

Total PCBs

Samples 1 and 2 were both naturally contaminated with Aroclors 1254 and 1260 and were derived from typical dredging sites in Lake Ontario. The interlaboratory PCB results for samples 1 and 2 were generally satisfactory. After rejection of outliers, the relative

standard deviations for the two samples were both 33% and were consistent with the results found in DQC-3 (4). PCB results from D14, D20, and especially D25 were high, while those results supplied by D07 an D18 were both low.

Chromium

The chromium results in DQC-4 were more erratic than all other trace metals in the same study with the exception of cadmium. Half (27 out of 54) of the reported results were flagged and the interlab RSD's were between 23 and 34% for samples in the 70 to 150 µg/g range. Results from D20 and D25 were identified as biased low and those from D08 were biased high by the ranking procedure. After rejection of the biased results, the interlab RSD's were between 10 and 15% for the test samples.

Iron

Other than the fact that the results from D09 were biased high and those from D25 were biased low, the interlab results for iron are satisfactory. A total of 18 out of the 64 results were flagged and after rejection of the biased results, the interlab RSD's were between 7 and 15% for samples with 3 to 4% Fe content.

Nickel

A total of 21 out of the 64 reported results were flagged for this metal. Results by D08 were biased high and those by D20 were biased low. After rejection of these results, the interlab RSD's were between 12 and 21% for sediment samples of 30 to 70 µg/g. Sample 3 was derived from Sudbury and contained an extremely high level of nickel (ca. 900 µg/g). The interlab RSD of this sample was 16% and was similar to the other samples at lower nickel concentrations.

Copper

The interlaboratory results for copper were excellent and only nine out of 64 reported results were flagged. Among the few less accurate results, those from D25 were identified as biased low. Random errors were experienced by D20 as both VH and VL results were reported in this data set. After rejection of outliers, the interlaboratory RSD's were between 5 and 9% for samples with copper levels higher than 80 µg/g and between 12 and 14% for samples at lower copper levels (ca. 20 µg/g).

Zinc

Other than a few random high results, possibly due to sample contamination, the results in this data set are precise. After

rejection of outliers, the interlaboratory RSD's were between 4 and 9% for zinc level in the 120 to 2100 µg/g range. Although D20 was identified as biased low for this metal, only one of its six results was flagged VL. The other five results from D20 were only slightly albeit consistently lower than the medians.

Cadmium

Similar to the findings in DQC-2 (5), cadmium results were the least satisfactory among all trace metals in this study. Despite a large BAE value (see Appendix) used in the flagging procedure, 19 out of 41 results were flagged. For cadmium results, D08 was identified as biased high and D21 biased low. Most laboratories reported cadmium levels to as low as 0.5 µg/g except D26, which did not report any cadmium results lower than 10 µg/g. For sediment samples with cadmium in the 1.8 to 5 µg/g range, the interlab RSD's were between 20 and 40% after rejection of outliers. There were not enough data to establish interlab precision for sediments with cadmium less than 1 µg/g.

Mercury

Mercury results are generally satisfactory in this study except for those reported by D08 which were erratic, i.e. presence of both VH and VL flags. None of the eight reporting laboratories provided biased mercury results. Interlaboratory RSD's were between 7 and 26% for mercury levels in the 0.1 to 2.5 µg/g range.

Lead

The lead results in this study are again satisfactory and only 14 of the 60 results were flagged. Results from D08 were identified as biased high and three of the six results provided by D21 were very high. On the other hand, results given by D03 were judged biased low by a small margin. The interlaboratory precision for this metal was between 12 and 20% for lead levels in the 25 to 250 µg/g range.

OVERALL PERFORMANCE OF TRACE METAL ANALYSIS

The accuracy of trace metal results in this study was summarized in Table 5. In this table, the number of results reported excluding those with a < sign as well as the number of results flagged VH, H, L, and VL for all metals were summed. The percentages of results flagged were calculated and the most accurate laboratories have the lowest % of flagged results. Laboratory D10 did extremely well in the present study since only one of the 36 (or 3%) results was flagged. However, D10 did not analyze cadmium and mercury. On the other hand, laboratories D08, D21 and D25 which had over 40% of their results flagged were among the least accurate laboratories in DQC-4. The statements of biased results included in the same table are strong evidence of systematic errors and those are the areas that the above laboratories may want to look into for improvement.

OTHER COMMENTS

Laboratory D20 indicated that significant inhomogeneity was noted in samples 2 and 3. The same comment, however, was not reported by other participants for any sample supplied in DQC-4. For each test sample, all participants received a subsample derived from the same bulk material randomly, it was then unlikely that the same laboratory would receive two inhomogeneous samples while the rest of the laboratories all received homogeneous samples. Comparison of interlab RSD's for all trace metals and PCB results did not indicate significant difference between the suspected samples (2 and 3) and the other samples when the levels were similar. Therefore, inhomogeneity among and within subsamples in test samples 2 and 3 was ruled out.

SUMMARY

Other than the biased results described above, satisfactory and accurate data were obtained from participants from iron, nickel, copper, zinc, mercury, and lead. Sediment results for chromium and PCBs were slightly more erratic than the other parameters. Cadmium results were unreliable and not comparable at 1 μg/g or lower.

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LIST OF PARTICIPANTS

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TABLE 1 **Reference values and interlaboratory medians (in brackets) for PCBs and trace metals of the six test samples distributed in DQC-4. All vaues in µg/g (dry weight basis) except for Fe (in %). Note that reference values for trace metals in Sud-1 and EC-3 are preliminary**

Parameter	Sample					
	1 (TH-1)	2 (HR-1)	3 (Sud-1)	4 (EC-3)	5 (BCSS-1)	6 (MESS-1)
Total PCBs	0.552 (0.531)	0.544 (0.501)	-	-	-	-
Cr	139 (127)	138 (141)	99.7 (91.0)	146 (139)	123 (106)	71 (66.0)
Fe	3.70 (3.65)	3.36 (3.14)	3.46 (3.20)	4.58 (4.10)	3.29 (3.21)	3.05 (2.94)
Ni	42.0 (42.1)	36.4 (40.4)	933 (896)	72.0 (69.0)	55.3 (53.0)	29.5 (29.9)
Cu	106 (105)	80.5 (80.3)	579 (562)	90.4 (97.0)	18.5 (18.5)	25.1 (26.0)
Zn	1601 (1582)	1157 (1155)	825 (801)	2117 (2111)	119 (117)	191 (192)
Cd	5.9 (5.1)	4.3 (4.1)	1.8 (1.9)	3.0 (3.1)	0.25 (0.28)	0.59 (0.60)
Hg	0.44 (0.41)	0.35 (0.30)	0.094 (0.100)	2.76 (2.46)	0.129 (0.135)	0.171 (0.168)
Pb	260 (250)	146 (141)	53.4 (63.5)	144 (140)	22.7 (25.6)	34.0 (33.0)

TABLE 2 Analytical methodology for PCBs.

Lab #	Extraction	Cleanup	GC and Quantitation
D03	1+1 acetone/hexane, shaker	Activated Florisil, hexane elution, activated Cu	3% OV-1, ECD Webb-McCall
D04	1+1 acetone/hexane, shaker	Deactivated Florisil, hexane elution	Packed column ECD. Sum of 8 peaks.
D07	41+59 hexane/acetone, soxhlet	Deactivated Florisil, hexane elution	OV-17/QF-1, ECD
D14	Acetone extract added to water, CH_2Cl_2 back extraction	Florisil, hexane elution	Capillary column, ECD, total area of PCB peaks
D17	Acetone, ultrasonic CH_2Cl_2 back extraction	Florisil, hexane elution	Packed column, ECD, total area of PCB peaks
D18	1+1 acetone/hexane, shaker	Deactivated Florisil, activated Cu	-
D21	Acetone/hexane, ultrasonic hexane back extraction	Florisil, hexane elution	ECD
D25	Acetone/hexane extract, hexane back extraction	Activated Florisil, hexane elution	ECD, Webb-McCall
D26	1+1 acetone/hexane, benzene back extraction	Bio-Beads S-X3 Silica gel, hexane elution, Hg	ECD, Webb-McCall

TABLE 3 Analytical methodology for trace metals except mercury.

Lab #	Digestion	Analysis
D02	$HClO_4/HNO_3$ at moderate heat till white fumes, cool and dilute with DW	-
D03	$HNO_3/HCl/HF$ in polyetheylene containers @ 100°C	Fe, Zn: flame AAS, other five elements graphite furnace AAS
D07	Aqua-regia	AAS with background correction
D08	Open digestion in Teflon containers	Flame AAS
D09	$HNO_3/HCl/HF$ in Teflon beakers, boil to dryness, add $H_2O/HCl/HNO_3/H_2O_2$ boil to 10 mL, make up to 30 mL	AAS or DC plasma
D10	None	X-ray fluorescence analyser
D14	Reflux with $HNO_3/HClO_4$ till white fumes in Teflon beakers, add HF and heat to dryness, redissolve in 10% HCl	Pb (AAS), other elements ICP argon plasma emission spectrophotometer
D21	Aqua-regia in Teflon beakers @ 90°C for 2 hrs. Silicious residue treated with $HF/HClO_4/HNO_3$. Fractions combined.	Flame or graphite furnace AAS background correction
D25	HNO_3/H_2O_2 boil to dryness, heat @ 400°C, cool and redissolve.	AAS

TABLE 4 Analytical methodology for mercury.

Lab #	Digestion	Analysis
D03	$HNO_3/HCl/KMnO_4$ in polystyrene containers @ 80°C for 1 hr	Cold vapor auto-analyser
D07	$H_2SO_4/HNO_3/HCl$, after digestion cool and add $KMnO_4/K_2S_2O_8$, leave overnight and add hydroxylamine sulfate/NaCl	Varian VGA76 hydride generator
D08	Open digestion in Teflon containers	Cold vapor mercury monitor
D09	V_2O_5/HNO_3 in tube @ 160°C for 10 min, cool, add HNO_3 and heat till fulmes. Transfer to BOD bottle, add water, $NH_2OH.HCl$ and $SnCl_2$.	Fisher mercury monitor
D14	$HNO_3/H_2SO_4/K_2S_2O_8/KMnO_4$ @ 90°C for 6 hrs, $SnCl_2$ reduction	Cold vapor AAS
D25	$H_2SO_4/HNO_3/HCl$ @ 50-60°C for 2-1/2 hrs. Cool, add $KMnO_4/K_2S_2O_8$/hydroxylamine sulfate/$SnCl_2$.	AAS

TABLE 5 Summary of trace metal results by lab.

Lab #	No of Results Reported*	Elements not Analyzed	No. of Results Flagged				% Flagged	Comments
			VH	H	L	VL		
D02	23	Cr, Hg	1	0	0	1	8.7	-
D03	48	none	0	2	3	1	12.5	Pb (biased low)
D04	nil	all	-	-	-	-	-	-
D07	46	none	3	0	2	1	13.0	-
D08	47	none	22	2	2	4	63.8	Cr,Ni,Cd, and Pb (biased high)
D09	48	none	4	5	0	0	18.8	Fe (biased high)
D10	36	Cd, Hg	0	1	0	0	2.8	-
D14	45	none	5	2	1	3	24.4	-
D17	nil	all	-	-	-	-	-	-
D18	nil	all	-	-	-	-	-	-
D20	47	none	2	0	5	9	34.0	Cr,Ni, and Zn (biased low)
D21	35	Cr, Hg	8	2	0	5	42.9	Cd (biased low)
D25	46	none	3	1	6	14	52.2	Fe,Cr, and Cu (biased low)
D26	39	none	1	2	3	4	25.6	-

*Excluding results with a < sign.

APPENDIX I

Data Summaries

PARAMETER: 00036 PCB IN SED UG/G

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

DOC-4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR= .50 BASIC ACCEPTABLE ERROR= .15 CONCENTRATION ERROR INCREMENT= .20
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D03	.66	7.00	.58	7.00		0.00		0.00		0.00		0.00
D04	.531	6.00	.452	5.00		0.00		0.00		0.00		0.00
D07	.29 VL	2.00	.34 L	2.00		0.00		0.00		0.00		0.00
D14	.69 H	8.00	.71 H	9.00		0.00		0.00		0.00		0.00
D17	.48	4.00	.55	6.00		0.00		0.00		0.00		0.00
D18	.278 VL	1.00	.231 VL	1.00		0.00		0.00		0.00		0.00
D20	.791 VH	9.00	.696 H	8.00		0.00		0.00		0.00		0.00
D21	.53	5.00	.4	3.00		0.00		0.00		0.00		0.00
D25	1.03 VH	10.00	.77 VH	10.00		0.00		0.00		0.00		0.00
D26	.45	3.00	.41	4.00		0.00		0.00		0.00		0.00
MEDIAN CONC.	.531		.501		0.000		0.000		0.000		0.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D03	14.00	7.000	2		INSUFFICIENT DATA
D04	11.00	5.500	2		INSUFFICIENT DATA
D07	4.00	2.000	2	VLL	INSUFFICIENT DATA
D14	17.00	8.500	2	HH	INSUFFICIENT DATA
D17	10.00	5.000	2		INSUFFICIENT DATA
D18	2.00	1.000	2	VLVL	INSUFFICIENT DATA
D20	17.00	8.500	2	VHH	INSUFFICIENT DATA
D21	8.00	4.000	2		INSUFFICIENT DATA
D25	20.00	10.000	2	VHVH	INSUFFICIENT DATA
D26	7.00	3.500	2		INSUFFICIENT DATA

OVERALL AVERAGE RANK IS 5.500

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D18	2.00	1.000	2	VLVL	INSUFFICIENT DATA
D07	4.00	2.000	2	VLL	INSUFFICIENT DATA
D26	7.00	3.500	2		INSUFFICIENT DATA
D21	8.00	4.000	2		INSUFFICIENT DATA
D17	10.00	5.000	2		INSUFFICIENT DATA
D04	11.00	5.500	2		INSUFFICIENT DATA
D03	14.00	7.000	2		INSUFFICIENT DATA
D14	17.00	8.500	2	HH	INSUFFICIENT DATA
D20	17.00	8.500	2	VHH	INSUFFICIENT DATA
D25	20.00	10.000	2	VHVH	INSUFFICIENT DATA

OVERALL AVERAGE RANK IS 5.500

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PARAMETER: 24001 CHROMIUM UG/G

QUALITY ASSURANCE AND METHODS SECTION
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DQC-4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=50.00 BASIC ACCEPTABLE ERROR=12.50 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
003	145.	7.00	169. H	7.00	113. H	7.00	147.	6.00	110.	6.50	69.	6.00
007	133.	6.00	141.	5.00	91.	5.00	139.	5.00	106.	5.00	64.	4.00
008	177. VH	9.00	189. VH	9.00	125. VH	9.00	180. VH	9.00	125. H	8.00	88. VH	9.00
009	123.	4.00	132.	4.00	103.	6.00	135.	4.00	102.	4.00	66.	5.00
010	127.	5.00	149.	6.00	81.	4.00	154.	7.00	128. H	9.00	70.	7.00
014	174. VH	8.00	181. VH	8.00	118. VH	8.00	168. H	8.00	110.	6.50	71.	8.00
020	100. L	2.00	107. VL	2.00	40.4 VL	1.00	87.2 VL	2.00	51.3 VL	2.00	29.3 VL	2.00
025	84.8 VL	1.00	87.9 VL	1.00	57.0 VL	2.00	75.5 VL	1.00	35.5 VL	1.00	21.0 VL	1.00
026	111.	3.00	112. L	3.00	76.7	3.00	130.	3.00	100.	3.00	29.8 VL	3.00
MEDIAN CONC.	127.000		141.000		91.000		139.000		106.000		66.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
003	39.50	6.583	6	HH	
007	30.00	5.000	6		
008	53.00	8.833	6	VHVHVHVHHVH	BIASED HIGH
009	27.00	4.500	6		
010	38.00	6.333	6	H	
014	46.50	7.750	6	VHVHVHH	
020	11.00	1.833	6	LVLVLVLVLVL	BIASED LOW
025	7.00	1.167	6	VLVLVLVLVLVL	BIASED LOW
026	18.00	3.000	6	LVL	

OVERALL AVERAGE RANK IS 5.000

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
025	7.00	1.167	6	VLVLVLVLVLVL	BIASED LOW
020	11.00	1.833	6	LVLVLVLVLVL	BIASED LOW
026	18.00	3.000	6	LVL	
009	27.00	4.500	6		
007	30.00	5.000	6		
010	38.00	6.333	6	H	
003	39.50	6.583	6	HH	
014	46.50	7.750	6	VHVHVHH	
008	53.00	8.833	6	VHVHVHVHHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 5.000

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PARAMETER: 26001 IRON % FE

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

DQC-4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR= 1.00 BASIC ACCEPTABLE ERROR= .25 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	2.77	3.00	3.55	2.00	2.28 VL	1.00	2.91	5.00
D03	3.55	5.00	3.15	6.00	3.43	8.50	4.11	7.00	3.21	6.00	2.94	6.00
D07	3.89	8.00	3.12	5.00	3.43	8.50	4.23	8.00	3.54	10.00	2.98	7.00
D08	3.8	7.00	3.5	8.00	3.2	6.00	4.4	9.00	3.3	7.00	3.	8.00
D09	3.99	9.00	3.85 VH	10.00	4.03 VH	11.00	4.8 H	11.00	3.76 H	11.00	3.81 VH	11.00
D10	3.45	4.00	2.96	4.00	3.33	7.00	3.92	4.00	3.32	8.00	3.03	9.00
D14	3.74	6.00	3.32	7.00	3.62	10.00	4.45	10.00	3.46	9.00	3.16	10.00
D20	2.94 L	2.00	2.46 L	2.00	2.81	4.50	3.71	3.00	2.87	3.00	2.49 L	2.00
D21	3.2	3.00	2.8	3.00	2.4 VL	2.00	4.1	6.00	3.	5.00	2.6	4.00
D25	2.6 VL	1.00	2.1 VL	1.00	2.1 VL	1.00	3.1 VL	1.00	2.3 VL	2.00	1.9 VL	1.00
D26	4.2 H	10.00	3.65 H	9.00	2.81	4.50	4.08	5.00	2.88	4.00	2.58	3.00
MEDIAN CONC.	3.645		3.135		3.200		4.100		3.210		2.940	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	11.00	2.750	4	VL	
D03	38.50	6.417	6		
D07	46.50	7.750	6		
D08	45.00	7.500	6		
D09	63.00	10.500	6	VHVHHHVH	BIASED HIGH
D10	36.00	6.000	6		
D14	52.00	8.667	6		
D20	16.50	2.750	6	LLL	
D21	23.00	3.833	6	VL	
D25	7.00	1.167	6	VLVLVLVLVLVL	BIASED LOW
D26	35.50	5.917	6	HH	

OVERALL AVERAGE RANK IS 5.844

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D25	7.00	1.167	6	VLVLVLVLVLVL	BIASED LOW
D20	16.50	2.750	6	LLL	
D02	11.00	2.750	4	VL	
D21	23.00	3.833	6	VL	
D26	35.50	5.917	6	HH	
D10	36.00	6.000	6		
D03	38.50	6.417	6		
D08	45.00	7.500	6		
D07	46.50	7.750	6		
D14	52.00	8.667	6		
D09	63.00	10.500	6	VHVHHHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 5.844

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PARAMETER: 28001 NICKEL UG/G

QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

DOC=4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=25.00 BASIC ACCEPTABLE ERROR= 6.25 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	1054. VH	10.00	74.	7.00	53.	5.50	24.	3.00
D03	47.	7.00	43.	7.00	740. VL	3.00	77.	8.00	54.	7.00	26.	5.00
D07	41.6	5.00	38.4	4.00	763. L	4.00	59.	1.00	54.6	8.00	31.8	7.00
D08	67. VH	10.00	63. VH	10.00	985.	9.00	98. VH	11.00	72. VH	11.00	44. VH	11.00
D09	39.	2.00	36.	1.00	1108. VH	11.00	69.	6.00	51.	4.00	28.	6.00
D10	40.	3.00	38.	3.00	920.	7.00	60.	2.00	53.	5.50	32.	8.50
D14	65. VH	9.00	56. VH	9.00	930.	8.00	82. H	9.00	58.	9.00	32.	8.50
D20	35.	1.00	37.	2.00	688. VL	1.00	62.	4.00	45.	2.00	21. L	2.00
D21	58. VH	8.00	50. H	8.00	847.	5.00	89. VH	10.00	61.	10.00	36. H	10.00
D25	40.1	4.00	39.9	5.00	721.2 VL	2.00	68.	5.00	50.	3.00	24.1	4.00
D26	42.6	6.00	40.9	6.00	896.	6.00	61.1	3.00	39.3 VL	1.00	<20. L	1.00
MEDIAN CONC.	42.100		40.400		896.000		69.000		53.000		28.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	25.50	6.375	4	VH	
D03	37.00	6.167	6	VL	
D07	29.00	4.833	6	L	
D08	62.00	10.333	6	VHVHVHVHVH	BIASED HIGH
D09	30.00	5.000	6	VH	
D10	29.00	4.833	6		
D14	52.50	8.750	6	VHVHH	
D20	12.00	2.000	6	VLL	BIASED LOW
D21	51.00	8.500	6	VHHVHH	
D25	23.00	3.833	6	VL	
D26	23.00	3.833	6	VLL	

OVERALL AVERAGE RANK IS 5.844

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D20	12.00	2.000	6	VLL	BIASED LOW
D25	23.00	3.833	6	VL	
D26	23.00	3.833	6	VLL	
D10	29.00	4.833	6		
D07	29.00	4.833	6	L	
D09	30.00	5.000	6	VH	
D03	37.00	6.167	6	VL	
D02	25.50	6.375	4	VH	
D21	51.00	8.500	6	VHHVHH	
D14	52.50	8.750	6	VHVHH	
D08	62.00	10.333	6	VHVHVHVHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 5.844

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QUALITY ASSURANCE AND METHODS SECTION
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BURLINGTON ONTARIO

DQC=4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=20.00 BASIC ACCEPTABLE ERROR= 5.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	616.	11.00	93.	4.00	19.	7.00	27.	8.00
D03	107.	6.50	80.	5.00	590.	8.00	87.	6.00	20.	9.00	27.	8.00
D07	102.	4.50	80.5	6.00	538.	2.00	101.	9.00	18.5	6.00	23.8	3.00
D08	108.	8.00	84.	9.00	548.	3.00	101.	9.00	23.	11.00	40. VH	11.00
D09	101.	3.00	79.2	4.00	538.	9.00	96.4	5.00	22.8	10.00	32.1 H	10.00
D10	100.	2.00	78.	3.00	570.	7.00	86.	3.00	17.	2.00	26.	6.00
D14	109.	9.00	81.2	8.00	610.	10.00	101.	9.00	19.2	8.00	25.7	5.00
D20	115.	10.00	237. VH	10.00	447. VL	1.00	107.	11.00	17.8	4.00	27.	8.00
D21	102.	4.50	81.	7.00	562.	6.00	99.	7.00	18.	5.00	25.	4.00
D25	89.3 L	1.00	67.9 L	1.00	548.2	4.00	78. L	2.00	16.	1.00	19. L	1.00
D26	107.	6.50	75.6	2.00	557.	5.00	61.6 VL	1.00	17.1	3.00	21.8	2.00
MEDIAN CONC.	104.500		80.250		562.000		97.000		18.500		26.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	30.00	7.500	4		
D03	42.50	7.083	6		
D07	30.50	5.083	6		
D08	51.00	8.500	6	VH	
D09	41.00	6.833	6	H	
D10	23.00	3.833	6		
D14	49.00	8.167	6		
D20	44.00	7.333	6	VHVL	
D21	33.50	5.583	6		
D25	10.00	1.667	6	LLLL	BIASED LOW
D26	19.50	3.250	6	VL	
OVERALL AVERAGE RANK IS		5.844			

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D25	10.00	1.667	6	LLLL	BIASED LOW
D26	19.50	3.250	6	VL	
D10	23.00	3.833	6		
D07	30.50	5.083	6		
D21	33.50	5.583	6		
D09	41.00	6.833	6	H	
D03	42.50	7.083	6		
D20	44.00	7.333	6	VHVL	
D02	30.00	7.500	4		
D14	49.00	8.167	6		
D08	51.00	8.500	6	VH	
OVERALL AVERAGE RANK IS		5.844			

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BURLINGTON ONTARIO

DQC-4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=99.00 BASIC ACCEPTABLE ERROR=25.00 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	744.	4.00	2064.	4.00	116.	5.00	190.	5.00
D03	1390. L	1.00	1200.	8.50	810.	7.00	2210.	8.50	115.	4.00	202.	8.00
D07	1656.	8.00	1183.	7.00	1119. VH	11.00	1830. L	1.00	114.	3.00	189.	4.00
D08	1674.	9.00	1103.	3.00	702. L	2.00	2210.	8.50	1538. VH	11.00	127. VL	1.00
D09	1575.	5.00	1205.	10.00	801.	6.00	2111.	6.00	126.	7.00	196.	7.00
D10	1630.	7.00	1200.	8.50	820.	9.00	2210.	8.50	117.	6.00	192.	6.00
D14	1590.	6.00	1180.	6.00	818.	8.00	2210.	8.50	128.	8.00	204.	9.00
D20	1540.	3.00	1130.	5.00	555. VL	1.00	2000.	2.00	103.	1.00	171.	2.00
D21	1678.	10.00	1093.	2.00	951. VH	10.00	2247.	11.00	1126. VH	10.00	1760. VH	11.00
D25	1530.	2.00	1073.	1.00	735.	3.00	2075.	5.00	885. VH	9.00	1498. VH	10.00
D26	1560.	4.00	1120.	4.00	749.	5.00	2010.	3.00	111.	2.00	176.	3.00
MEDIAN CONC.	1582.500		1155.000		801.000		2111.000		117.000		192.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	18.00	4.500	4		
D03	37.00	6.167	6	L	
D07	34.00	5.667	6	VHL	
D08	34.50	5.750	6	LVHVL	
D09	41.00	6.833	6		
D10	45.00	7.500	6		
D14	45.50	7.583	6		
D20	14.00	2.333	6	VL	BIASED LOW
D21	54.00	9.000	6	VHVHVH	
D25	30.00	5.000	6	VHVH	
D26	21.00	3.500	6		

OVERALL AVERAGE RANK IS 5.844

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D20	14.00	2.333	6	VL	BIASED LOW
D26	21.00	3.500	6		
D02	18.00	4.500	4		
D25	30.00	5.000	6	VHVH	
D07	34.00	5.667	6	VHL	
D08	34.50	5.750	6	LVHVL	
D03	37.00	6.167	6	L	
D09	41.00	6.833	6		
D10	45.00	7.500	6		
D14	45.50	7.583	6		
D21	54.00	9.000	6	VHVHVH	

OVERALL AVERAGE RANK IS 5.844

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QUALITY ASSURANCE AND METHODS SECTION
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DQC=4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR= 1.00 BASIC ACCEPTABLE ERROR= .50 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	1.7	3.50	2.9	4.00	<.5	0.00	.6	3.00
D03	5.29	5.00	3.87	3.00	1.88	5.00	3.43	6.00	.07	1.00	.63	4.00
D07	5.6	6.00	4.1	5.00	2.1	6.00	4.9 VH	8.00	<1.	0.00	<1.	0.00
D08	10.8 VH	8.00	8.5 VH	8.00	4.8 VH	8.00	8.4 VH	9.00	2.8 VH	3.00	<5.5	0.00
D09	5.78	7.00	4.02	4.00	2.48 H	7.00	3.65	7.00	.28	2.00	1.29 H	5.00
D14	3.4 VL	2.00	2.8 VL	2.00	<.5	0.00	2.2 L	3.00	<.5	0.00	<.5	0.00
D20	4.8	4.00	5.6 VH	7.00	<.3 VL	1.00	3.1	5.00	<.3	0.00	.5	2.00
D21	1.28 VL	1.00	.92 VL	1.00	.44 VL	2.00	.32 VL	1.00	<.1	0.00	.36	1.00
D25	4.01 L	3.00	4.29	6.00	1.7	3.50	1.7 VL	2.00	<.5	0.00	<.5	0.00
D26	<10.	0.00	<10.	0.00	<10.	0.00	<10.	0.00	<10.	0.00	<10.	0.00
MEDIAN CONC.	5.045		4.060		1.790		3.100		.280		.600	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO.OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	10.50	3.500	3		
D03	24.00	4.000	6		
D07	25.00	6.250	4	VH	
D08	36.00	7.200	5	VHVHVHVHVH	BIASED HIGH
D09	32.00	5.333	6	HH	
D14	7.00	2.333	3	VLVLL	
D20	19.00	3.800	5	VHVL	
D21	6.00	1.200	5	VLVLVLVL	BIASED LOW
D25	14.50	3.625	4	LVL	
D26	0.00	0.000	0		INSUFFICIENT DATA

OVERALL AVERAGE RANK IS 4.244

LAB NO.	TOTAL RANK	AVERAGE RANK	NO.OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D26	0.00	0.000	0		INSUFFICIENT DATA
D21	6.00	1.200	5	VLVLVLVL	BIASED LOW
D14	7.00	2.333	3	VLVLL	
D02	10.50	3.500	3		
D25	14.50	3.625	4	LVL	
D20	19.00	3.800	5	VHVL	
D03	24.00	4.000	6		
D09	32.00	5.333	6	HH	
D07	25.00	6.250	4	VH	
D08	36.00	7.200	5	VHVHVHVHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 4.244

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QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

DOC=4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR= .30 BASIC ACCEPTABLE ERROR= .10 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D03	.463	7.00	.323	7.00	.120	7.00	2.67	5.00	.180	6.00	.176	7.00
D07	.51	8.00	.29	4.00	.14	8.00	.59 VL	1.00	.11	1.00	.15	2.00
D08	.19 VL	1.00	.07 VL	1.00	.1	4.50	.81 VL	2.00	.33 VH	7.00	.06 L	1.00
D09	.402	4.00	.26	3.00	.075	3.00	2.24	4.00	.130	3.50	.185	8.00
D14	.332	2.00	.232	2.00	.070	1.50	1.96 VL	3.00	.114	2.00	.175	6.00
D20	.41	5.00	.31	6.00	.07	1.50	2.99 VH	7.00	.14	5.00	.16	3.00
D25	.39	3.00	.309	5.00	.110	6.00	2.794 H	6.00	.555 VH	8.00	.165	4.00
D26	.42	6.00	.35	8.00	.1	4.50	3. VH	8.00	.13	3.50	.17	5.00
MEDIAN CONC.	.406		.300		.100		2.455		.135		.168	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D03	39.00	6.500	6		
D07	24.00	4.000	6	VL	
D08	16.50	2.750	6	VLVLVLVHL	
D09	25.50	4.250	6		
D14	16.50	2.750	6	VL	
D20	27.50	4.583	6	VH	
D25	32.00	5.333	6	HVH	
D26	35.00	5.833	6	VH	

OVERALL AVERAGE RANK IS 4.500

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D08	16.50	2.750	6	VLVLVLVHL	
D14	16.50	2.750	6	VL	
D07	24.00	4.000	6	VL	
D09	25.50	4.250	6		
D20	27.50	4.583	6	VH	
D25	32.00	5.333	6	HVH	
D26	35.00	5.833	6	VH	
D03	39.00	6.500	6		

OVERALL AVERAGE RANK IS 4.500

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QUALITY ASSURANCE AND METHODS SECTION
NATIONAL WATER RESEARCH INSTITUTE
BURLINGTON ONTARIO

DOC-4 TOTAL PCBS AND TRACE METALS IN SEDIMENT

LOWER LIMIT FOR USE OF BASIC ACCEPTABLE ERROR=50.00 BASIC ACCEPTABLE ERROR=12.50 CONCENTRATION ERROR INCREMENT= .10
LABORATORIES YET TO REPORT: 0
LABORATORY RESULTS OMITTED ARE NONE

SAMPLE	1		2		3		4		5		6	
LAB NO	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK	REPORTED VALUE	RANK
D02		0.00		0.00	65.	6.00	156.	7.00	36.	9.00	40.	9.00
D03	202. L	1.00	110. L	1.00	50.8	3.00	120.	2.00	19.6	1.00	28.5	1.00
D07	244.	4.00	142.	6.00	72.1	9.00	212. VH	11.00	25.1	5.00	32.4	4.00
D08	322.3 VH	10.00	173.2 H	9.00	96. VH	10.00	182. VH	9.00	48. VH	10.00	<55.	0.00
D09	237.	3.00	132.	2.00	62.	5.00	140.	6.00	28.	7.00	38.	7.00
D10	250.	5.50	140.	5.00	68.	8.00	130.	3.00	24.	4.00	33.	5.00
D14	250.	5.50	138.	3.00	55.	4.00	134.	4.00	20.	2.00	32.	3.00
D20	278.	8.00	156.	8.00	50.	2.00	157.	8.00	30.	8.00	39.	8.00
D21	313. VH	9.00	188. VH	10.00	65.8	7.00	202. VH	10.00	21.9	3.00	31.1	2.00
D25	254.8	7.00	138.8	4.00	48. L	1.00	139.	5.00	26.	6.00	33.1	6.00
D26	217. L	2.00	149.	7.00	<50.	0.00	84.6 VL	1.00	<50.	0.00	<50.	0.00
MEDIAN CONC.	250.000		141.000		63.500		140.000		25.550		33.000	

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D02	31.00	7.750	4		
D03	9.00	1.500	6	LL	BIASED LOW
D07	39.00	6.500	6	VH	
D08	48.00	9.600	5	VHHVHVHVH	BIASED HIGH
D09	30.00	5.000	6		
D10	30.50	5.083	6		
D14	21.50	3.583	6		
D20	42.00	7.000	6		
D21	41.00	6.833	6	VHVHVH	
D25	29.00	4.833	6	L	
D26	10.00	3.333	3	LVL	

OVERALL AVERAGE RANK IS 5.517

LAB NO.	TOTAL RANK	AVERAGE RANK	NO. OF SAMPLES RANKED	SUMMARY OF FLAGGING	METHOD CODING
D03	9.00	1.500	6	LL	BIASED LOW
D26	10.00	3.333	3	LVL	
D14	21.50	3.583	6		
D25	29.00	4.833	6	L	
D09	30.00	5.000	6		
D10	30.50	5.083	6		
D07	39.00	6.500	6	VH	
D21	41.00	6.833	6	VHVHVH	
D20	42.00	7.000	6		
D02	31.00	7.750	4		
D08	48.00	9.600	5	VHHVHVHVH	BIASED HIGH

OVERALL AVERAGE RANK IS 5.517

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APPENDIX II

Glossary of Terms

(1) Ranking

Ranking is a non-parametric statistical technique used for the detection of pronounced systematic error (bias) in interlaboratory studies. According to Youden's procedure, rank 1 is given to the laboratory that provided the lowest result, rank 2 to the next lowest. In case of a tie, the average rank is given to the tied laboratories. Results with a < sign are not ranked. For each parameter, the total rank of each laboratory is the sum of individual rank on each samples. In the case of six test samples and ten laboratories, the 5% probability limits for ranking scores are 14 and 52. A laboratory with score lower than 14 is identified as biased low. Similarly, a laboratory with a total rank higher than 52 is biased high. In both cases, their results are classified as outliers. In cases where a laboratory did not provide all the results, or some of the results were not ranked, the average rank instead of total rank was used for the determination of biased statements.

The more comparable, i.e. better, laboratories should have ranks in the middle rather than in the extreme ends. However, laboratories with middle ranks do not necessarily mean that they provide more consistent results since very high results (high ranks)

and very low results (low ranks) would average out to yield a total rank close to the median. Therefore, ranking alone is not sufficient to determine the performance of a laboratory.

(2) Flagging

When the true values of constituents in test samples are unknown, individual results can be evaluated in terms of their absolute differences from the interlaboratory medians. Medians are chosen rather than means since they are not influenced by a moderatenumber of extreme values. By this flagging technique, all results are graded into the following three groups in the order of decreasing accuracy: (1) results with no flags, (2) results with H or L flags, and (3) results with VH or VL flags. Before evaluation is performed, three parameters, namely, Lower Limit for Use of BasicAcceptable Error (LLBAE), Basic Acceptable Error (BAE), and Concentration Error Increment (CEI) are to be set. LLBAE is usually set at the lower end of the medians in the test samples. According to our previous interlaboratory studies on PCBs, a 30% error at LLBAE is considered reasonable and thus this is used as BAE. For samples whose medians are at or below LLBAE, the reuslts are evaluated according to the following formulae:

	Absolute difference between sample and median results	$\leq$ BAE	:	acceptable
BAE <	Absolute difference between sample and median results	$\leq$ 1.5 x BAE	:	H or L
	Absolute difference between sample and median results	> 1.5 x BAE	:	VH or VL

For samples whose medians are above the LLBAE, the allowable BAE is augmented by adding an increment to BAE. This increment is calculated by multiplying the CEI by the difference between the sample median and LLBAE values. In this study, CEI is set at 0.2. Sample results are again evaluated by the above three formulae except that the augmented BAE is used instead of BAE.

For further discussion on this evaluation technique, please refer to the original paper by Clark.