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CEPA NATIONAL INTERLABORATORY COMPARISON STUDY (CP-4): ANALYSIS OF DIOXINS AND FURANS IN SEDIMENT EXTRACTS

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NWRI CONTRIBUTION 94-84

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W.C. Li and A.S.Y. Chau

Aquatic Ecosystem Protection Branch
National Water Research Institute
Burlington, Ontario L7R 4A6

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MANAGEMENT PERSPECTIVE

The highly chlorinated phenols used in pulp and paper industry across Canada contain dioxins as a manufacturing impurity. The most toxic form of dioxin is 2,3,7,8-TCDD. It has been detected in pulp and paper mill effluents. Two CEPA priority substances, dioxins and furans and effluents from pulp mills underwent CEPA assessments and were shown to be toxic as defined in the Act. These substances are presently undergoing a strategic options Process for possible regulatory control.

The successful implementation of the CEPA is dependent on the availability of reliable scientific data. To assist project managers and regulating bodies in ensuring the validity of analytical data under the Act, an interlaboratory study (CP-4) for the analysis of dioxins and furans in sediment extracts was designed and conducted. This study will help to establish the degree of comparability of dioxin and furan results among participating laboratories.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Les phénols fortement chlorés utilisés par l'industrie des pâtes et papiers de tout le Canada contiennent des dioxines, à l'état d'impuretés de fabrication. La forme la plus toxique de dioxine est la 2,3,7,8-TCDD. On a décelé sa présence dans des effluents d'usines de pâtes et papiers. Deux substances de la liste prioritaire de la LCPE, les dioxines et les furanes, et des effluents des usines de pâtes, ont été évalués conformément à la LCPE, et il a été démontré que ces substances étaient toxiques aux termes de la Loi. Présentement, celles-ci font l'objet d'un processus d'options stratégiques pour d'éventuelles mesures réglementaires de limitation.

Le succès de la mise en oeuvre de la LCPE dépend de la disponibilité de données scientifiques fiables. Pour aider les gestionnaires de projets et les organismes de réglementation à garantir la validité des données analytiques conformément à la Loi, on a conçu et effectué une étude interlaboratoire (CP-4) pour l'analyse des dioxines et des furanes dans les extraits de sédiments. Cette étude contribuera à établir le degré de comparabilité des résultats des analyses de dioxines et de furanes entre les laboratoires participants.

ABSTRACT

As part of the quality assurance program under the auspices of the Canadian Environmental Protection Act (CEPA), an interlaboratory comparison study (CP-4) for analysis of dioxins and furans in sediment extracts was designed and conducted by the Quality Assurance Group at the National Water Research Institute. Eight laboratories were sent five test samples. Each laboratory was requested to analyze 2,3,7,8-TCDD and 2,3,7,8-TCDF, and tetra-, penta-, hexa-, hept-, and octachlorinated dibenzo-p-dioxins and dibenzofurans; each homologue group in total in all test samples. Surrogate recoveries were also requested. Seven out of eight laboratories submitted results.

Since design values of dioxins and furans in test samples were unknown, median values were used as target values for the evaluation of interlaboratory results. To estimate the quality of interlaboratory results generated by participating laboratories, comparison between means and medians for dioxins and furans in all five test samples was made. The majority of means and medians for dioxins and furans agreed with each other very well with the relative % difference within ±25%.

For overall laboratory performance, five out of seven laboratories submitted satisfactory results for both of dioxins and furans in sediment extracts. Laboratory C030 had poor performance for both of dioxins and furans analyses.

RÉSUMÉ

Dans le cadre du programme d'assurance de qualité prévu par la Loi canadienne sur la protection de l'environnement (LCPE), le Groupe d'assurance de la qualité de l'Institut national de recherche sur les eaux a conçu et effectué une étude interlaboratoire comparative (CP-4) pour l'analyse des dioxines et des furanes dans des extraits de sédiments. On a envoyé cinq échantillons d'essai à huit laboratoires. Chaque laboratoire devait doser la 2,3,7,8-TCDD et le 2,3,7,8-TCDF, ainsi que les dibenzo-p-dioxines et les dibenzofuranes tétra-, penta-, hexa-, hepta- et octachlorés, soit chaque groupe d'homologues au complet dans tous les échantillons d'essai. On a également exigé les résultats des récupérations des substituts. Sept des huit laboratoires ont présenté des résultats.

Étant donné que les valeurs utilisées des dioxines et des furanes des échantillons d'essai étaient inconnues, on a pris des valeurs médianes comme valeurs cibles pour l'évaluation des résultats interlaboratoires. Afin d'évaluer la qualité de ces résultats fournis par les laboratoires participants, on a effectué des comparaisons entre les moyennes et les médianes des dioxines et des furanes pour chacun des cinq échantillons d'essai. Il y avait une très bonne concordance entre les moyennes et les médianes des dioxines et des furanes, avec une différence percentuelle relative inférieure à $\pm$ 25 %.

Pour ce qui du rendement de l'ensemble des laboratoires, cinq des sept laboratoires ont présenté des résultats satisfaisants tant pour les dioxines que pour les furanes dans les extraits de sédiments. Cependant, le rendement du laboratoire C030 laissait à désirer tant pour les analyses de dioxines que pour celles de furanes.

1 INTRODUCTION

The successful implementation of various aspects of the Canadian Environmental Protection Act (CEPA) is critically dependent on the availability of reliable scientific data. A key component of this CEPA QA program is to design and conduct, on a continual basis, a series of interlaboratory (Round Robin) studies for CEPA priority substances in a variety of matrices. These interlaboratory QA studies will assist CEPA managers and regulating bodies to ensure validity of analytical data.

In 1988, the Federal government initiated an emergency national sampling and analysis program [1] to monitor possible dioxins and furans contamination in the vicinity of Canadian pulp and paper mills using chlorine bleaching. To assist the managers in ensuring validity of analytical data, the Quality Assurance Group at the National Water Research Institute have designed and conducted several interlaboratory studies for analysis of dioxins and furans in sediments [2,3] and sediment extracts [4] to evaluate the comparability of the data generated by many different federal, provincial and private laboratories .

This CEPA interlaboratory study (No. CP-4) was distributed on February 17, 1994. The original deadline for reporting results was April 15, 1994. However, most laboratories were late in reporting, so the study was closed June 30, 1994. In August 26, 1994, a preliminary report was prepared and distributed to those participants which had submitted their results. The preliminary report allowed participants to compare their results with those of their peers. Thus any necessary corrective action could be taken in a timely manner. This final report provides information on the data summary as well as the data evaluation and laboratory performance of participants in this study.

2. STUDY DESIGN

This interlaboratory study (CP-4) for analysis of dioxins and furans in sediment extracts was initiated in December, 1993. About 70 federal, provincial and private laboratories were invited to participate. From the returned questionnaires, eight laboratories expressed interest to participate in this study. By the time the study was closed, seven out of eight participants had submitted results. The list of participants is given in Table 1.

The study consists of five sediment extract samples for the analysis of dioxins and furans. The analytes of interest were 2,3,7,8-TCDD and 2,3,7,8-TCDF, and tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans; each homologue group in total. Surrogates recoveries were also requested.

The identities and descriptions of the samples distributed in this study are given in Table 2. Briefly, the sediment extract SE-18 (samples #1) was prepared from freeze-dried sediment CRM EC-2 by soxhlet extraction using the method developed by Environment Canada [5]. This sample was used in the previous study CP-3 (samples #2 and #4). The recycle of this same sample in the present study allowed us for the evaluation of traceability of interlaboratory results in various studies and the stability of dioxins and furans in test samples. The sediment extracts SE-22 (samples #2 and 3) and SE-23 (samples #4 and 5) were prepared from bulk sediments EC-7 and EC-8a by the extraction procedure developed by Chau et. al. [6]. All the above extracts were sealed in ampules. Each ampule contained approximately 5 mL extracts in which one mL was equivalent to 1 g dry sediment. To assess reproducibility within the same laboratory, two pairs of blind duplicates were included as described earlier.

3. RESULTS AND DISCUSSION

3.1 Analytical Methodology

The participants were instructed to analyze the test samples using their in-house analytical procedure and calibration standards. The analytical procedures used by the participants in this study are presented in Table 3. All participants fortified or spiked the extracts with various surrogate standards before cleanup procedures. In general, a wide variety of cleanup procedures and quantitation were used by different participants. For cleanup of raw extracts, column chromatography with silica gel, neutral or basic alumina, various carbon columns, or various combinations of these adsorbents were used. In all cases, the dioxins and furans fraction was evaporated to a small volume (10 to 20 µL). Final analysis was performed by either GC/MSD or GC/MS (high resolution MS). For quantization of dioxins and furans in final extracts, either internal standard methods or external standard methods were used for calibrations. In most cases, correction for surrogate recoveries were made. See Table 3 for more details.

Reliable determination of dioxins and furans in environmental materials at trace and ultra-trace levels requires both high recoveries and final extracts that are free from any major interferences. In the report, "Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples" [7], the Dioxin Quality Assurance Advisory Committee (DQAAC) recommended a sample size of 5 grams for dry sediment, soil, sludge or ash, and a final volume of 20 µL for the final extract, in order to maximize capabilities for ultratrace analyses. Detection limits of dioxins and furans in sediment extracts for participating laboratories in this study are given in Table 4. In this table, the " Target MDLs" recommended by DQAAC are also included. These target method detection limit s for low resolution mass spectrometry (LRMS) are based on an assumption of high surrogate recovery and final extracts are free from any major interferences (refer to reference 7 for further details). For those laboratories (C018, C020, C025 and C034) which employed high resolution MS for the detection of final extracts, their detection limits for their respective dioxins and furans were at least 10 time more sensitive, while the remaining laboratories which employed LRMS (MSD) for detection of respective dioxins and furans, their detection limit are in same order of magnititude as those of "Target MDLs" .

Since sample size may be limited, the ability to analyze dioxins and furans at very low levels also requires that recoveries be as high as possible despite the need to employ very stringent enrichment and cleanup steps to avoid major interferences for GC/MS analysis. The amount of analyte lost during cleanup as well as concentration steps may be reflected in the recoveries of the spiked surrogates. Thus results are usually corrected for surrogate recovery losses. A summary of surrogate recoveries reported by the participants for the five sediment extracts as well as their mean values for this study is given in Table 5. On the basis of the practical experience of several government and commercial laboratories, it was recommended that the acceptable range for surrogate recoveries from all matrices except biological tissues should be 30 - 130 % [8]. Beyond these limits, it was suggested that samples should be reprocessed and reanalyzed. As can be seen from Table 5, the majority of the reported surrogate recoveries were within this 30-130% range.

3.2 Data Evaluation

All data submitted by the participants for dioxins and furans in sediment extracts are summarized in Appendix I. One laboratory (C019) submitted data after the closing dae. Their results were not included and evaluated in this final report but their data can be found in Appendix II as late results. All laboratories had the capability of analyzing all 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners, and for each of the homologue group totals in all the samples. As shown in Appendix I, interlaboratory means and standard deviations as well as interlaboratory medians were calculated after outliers (marked with a *) were removed using Grubb's test [8]. With the rejections of these outliers, the majority of the means and medians for dioxins and furans agreed with each other very well. For the evaluation of interlaboratory results, medians were used as target values because true values were unknown and a panel of reference laboratories using proven bias-free methods was not available. A summary of interlaboratory median values for dioxins and furans in this study is given Table 6. To estimate the quality of the interlaboratory results generated by participating laboratories, comparison between means and medians was made for dioxins and furans for all five test samples . As can be seen from Fig. 1.1, the relative % differences between means and medians for the five test samples and six dioxin parameters were within 25% except for samples #2, 3 and 4 for H6CDD which exceeded 25%. Where the relative % difference was expressed as [|mean - median|/(mean+median)/2] x 100. Similarly, as shown in Fig. 1.2, the relative % difference between means and medians for the five test samples and six furan parameters were within 25% except for sample #2 for 2,3,7,8-TCDF and sample #1 for T4CDF which exceeded 25%. Overall, it indicated that comparable results for dioxins and furans had been generated by these participants in this study.

Interlaboratory precision for dioxins and furans, expressed as the relative standard deviation (RSD) is given in Table 7. For the analysis of dioxins and furans in sediment extracts at trace and ultratrace concentrations at ppt levels and in the presence of a large amount of co-extractives, the larger variations of analytical results were expected because of requiring to employ very stringent enrichment and cleanup steps to avoid major interferences for GC/MS analysis. Thus the interlaboratory results demonstrated favourable comparability among participating laboratories if the RSDs were within ± 50%. As can be seen from Fig. 2.1 for the interlaboratory precision of dioxins, only 3 out of 30 results (10%) had RSD exceeding ±50% (samples #1, 2 and 4 for H6CDD). Overall, the average values of RSDs for five out of six dioxin parameters were within ±50% except H6CDD. Furan results were less precise than the dioxin results. As can be seen from Fig. 2.2 for interlaboratory precision for furans, 9 out of 30 results (30.0%) had RSD exceeding ±50% (samples #2 for 2,3,7,8-TCDF, samples # 1, 3, 4 and 5 for T4CDF and P5CDF). Overall, the average values of RSDs for four out of six furan parameters were within ±50% with the exception of T4CDF and P5CDF which exceeded ±50%. As compared with the previous study (CP-3) [4], the present study (CP-4) was less satisfactory with the higher RSDs for most of parameters of dioxins and furans.

Intralaboratory precision in this study was assessed by calculating RSD between the results provided by each participant for the two pairs of blind duplicates (i.e. SE-22 for samples #2 and #3 and SE-23 for samples #4 and #5). A summary of intralaboratory precision for participating laboratories is given in Table 8. The results show that four laboratories (C018, C020, C025 and C034) had excellent precision for both of the two pairs of duplicate samples with RSDs less than ±25% for all dioxin and furan parameters. While three other laboratories (C003, C024 and C030) were less precise with some of dioxins and furan parameters exceeding ± 25% RSD. In a few cases, the intralaboratory RSDs were higher than the interlaboratory RSDs from labs C003 and C024 as shown in Table 8. It is suggested that these above-mentioned two laboratories carefully review their internal QA/QC procedures.

3.3 Comparison of Laboratory Performance

For detailed data evaluation of each laboratory, submitted results were compared with the interlaboratory medians. As mentioned earlier, medians were used as target values because true values were unknown and results from a panel of reference laboratories using proven bias-free methods was not available. In addition, because of the small number of results available for this study, the Youden ranking technique [9] for the detection of bias as well as the computerize flagging procedure [10,11] were not used for data evaluation. Instead, a modified flagging procedure used in the national dioxin interlaboratory studies [2,3] and CEPA interlaboratory study [4] was employed in this study. This technique was a peer appraisal assessment, whereby the flags were assigned to the individual results when they deviated significantly from the interlaboratory median. Assuming that the medians had established the correct target values, the more accurate and comparable laboratories were therefore the ones with the least number of results flagged. Briefly, results within two-fold of the median for that particular parameter and sample, were deemed to be satisfactory and any values beyond this range were flagged. These ranges for the 'high' and 'low' flags were selected such that only the most extreme results would be flagged. Results recorded as "not detected" (ND) were not used for calculation of flags if the detection limits were higher than the medians. When the detection limits were lower than 1/2 (Median) , the ND results were flagged as low (L). Hence, the individual results were evaluated according to the following rating groups:

High (H)	x > 2 (Median)
Satisfactory (no flags)	1/2 (Median) ≤ x ≤ 2 (Median)
Low (L)	x < 1/2 (Median)

The appraisal for flags for each individual result is listed in appendix I. Summaries of flags for dioxins and furans in sediment extracts for the study CP-4, obtained from appendix I, are given in Tables 9.1 and 9.2, respectively.

To compare the overall laboratory performance in this study, the key step was the selection of an appropriate performance index. The performance index used for this report was the % flags within a study. This index provides a simple way to evaluate laboratory performance through acceptance criteria which are shown below:

Performance Index	Rating
≤ 25%	Satisfactory
26% - 50%	Moderate
≥ 51%	Poor

The performance index for each individual laboratory in this study is given in Tables 9.1 and 9.2 for dioxins and furans in sediment extracts, respectively. Four laboratories (C018, C020, C025 and C034) demonstrated satisfactory performance for both of dioxins and furans in sediment extracts. While performances of the other three laboratories (C003, C024 and C30) were less satisfactory especially lab C030 had provided poor rating for both of dioxins and furans in sediment extracts.

3.4 Comparison of Results between Studies and Samples

Two pairs of duplicate samples were included in this interlaboratory study for assessing reproducibility within the same laboratory as described earlier. In addition, overall interlaboratory results from these duplicate samples would provide the additional information on the homogeneity and integrity of the test samples. comparisons of interlaboratory median values between samples for the two pairs of blind duplicates (SE-22 for sample #2 and #3, and SE-23 for samples #4 and #5) are given in Tables 10.1 and 10.2. As can be seen from Table 10.1, the RSDs for samples #2 and #3 (SE-22) were within ± 25% for all twelve parameters of dioxins and furans analyses. While the RSDs for samples #4 and #5 (SE-23) were within ±25% for eleven out of 12 parameters of dioxins and furans analyses (Table 10.2). Only one parameter (T4CDD) was with the RSD exceeding ±25%. Overall, the agreement between duplicate samples was very good and this helped to verify the integrity of the test samples. In this study, sample #1 was recycled from the previous study CP-3 (Samples #2 and #4). A comparison of study to study interlaboratory median values is given in Table 10.3. Overall the agreement between studies and samples was very good (RSDs within ± 25%) for all twelve parameters of dioxins and furans analyses, and this helped to verify the stability of test samples. In conclusion, the interlaboratory results from this study also provided very valuable preliminary reference values for dioxins and furans in these sediment extract reference materials.

ACKNOWLEGEMENT

The authors are grateful to the participating laboratories for the time and effort devoted to analyze the test samples and reporting the results. This interlaboratory study would not be successful without their active participation and cooperation.

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Table 1. List of participants in CEPA interlaboratory study (CP-4).

1. Axys Analytical Services Ltd.
   Sidney, B. C.

2. Eli Eco Logic International Inc.
   Rockwood, Ontario

3. Gouvernement du Quebec
   Minnistere de I'Environnement
   Laval, Quebec

4. Research Productivity Council
   Fredericton, N. B.

5. NovaMann International
   Lachine, Quebec

6. Wellington Environmental Laboratories
   Guelph, Ontario

7. Zenon Environmental Labs.
   Burnaby, B. C.

Table 2. Samples distributed in study CP-4.

Sample No.	Identification Code	Description
1	SE-18	Soxhlet extraction of EC-2 (1 mL in toluene is equivalent to 1 g dry sediment)
2	SE-22	1: 1 mixture of solvent extraction of EC-7 and EC-8a* (1 mL in toluene is equivalent to 1 g dry sediment)
3	SE-22	Same as sample #2
4	SE-23	Solvent extraction of EC-8a* (1 mL in toluene is equivalent to 1 g dry sediment)
5	SE-23	Same as sample #4

Note: * EC-8 has not yet processed and homogenized. Samples (EC-8a) used for the preparation of SE-22 and SE-23 for this study were different from those samples (EC-8) used for the preparation of SE-20 (sample # 3) for study CP-3.

Table 3. Analytical Methodology used by participating Laboratories.

Lab No.	Sample pretreatment	Cleanup	Separation/measurement
C003	Sediment extracts fortified with surrogate standards; solvent exchange to hexane and concentrated to 5 mL.	Column chromatograph with double silica gel H2SO4, silica gel/ NaOH, silica gel/silver nitrate column; alumina column.	GC/MSD, 60 m x 0.25 mm i.d. DB-5 fused silica column; ISTD; corrected for recovery of the surrogate standards.
C018	Sediment extracts spiked with 13C-labelled PCDDs and PCDFs surrogates; solvent exchange into nonane.	Multilayer silica column (acid and base-treated silica); alumina column (basic); carbon column (PX21/celite).	HRGC/HRMS (VG70-SE high resolution mass Spec. coupled to HP 5890 GC); 60 m x 0.25 mm i.d. x 0.25 µm film thickness DB-5 capillary column; ISTD;recoveries of surrogates were accounted for all samples.
C020	Sediment extracts fortified with surrogates.	Acid/Base/Silver nitrate/silica column; Basic alumina column.	GC/MS analysis with HRMS (10000 static resolution); corrected for recoveries of surrogate standards.
C024	Sediment extracts spiked with surrogates; back extraction with KOH (3.6M),NaCl (0.9M), sulphuric acid and again NaCl.	Alumina/acid silica gel column; carbon/celite column.	HRGC/LRMS (HP 5890 series II GC /HP 5971A MSD); SIM mode; 30 m x 0.25 mm i.d. x 0.25 µm film thickness SPB-5 capillary column; ISTD; corrected for recoveries of the surrogates standards.
C025	Sediment extracts spiked with surrogate standards; solvent exchange to hexane.	alumina xolumn; acid/base/ silver nitrate/silica column.	GC/MS,HP 5890 series II GC interfaced with VG AutoSpec HRMS; multi-group selected ion recording (SIR); J & W DB-5 60 m x 0.25 mm i.d. x 0.25 µm film thickness; ISTD.
C030	Sediment extracts spiked with surrogates.	Acid-treated Biosil-A column; mixed bed silica column (acid, neutral, basic Biosil-A); celite/activated carbon column.	GC/MSD, SIM Mode; ESTD; 60 m x 0.25 mm i.d. DB-5 column; corrected for recoveries of the surrogate standards.
C034	Sediment extracts spiked with surrogates; rinsed with hexane three times; washed with KOH;washed with H2SO4.	Silca gel column; alumina column; carbon/celite; alumina column.	GC/MS (VG 70 SE high resolution MS with HP 5890 GC); MID Mode; corrected for recoveries of the surrogate standards.

Table 4. Detection limits (pg/mL) of dioxins and furans in sediment extracts.

Lab No.	Dioxins						Furans					
	2378-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	2378-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF
C003	15-29	15-29	25-41	38-70	40-63	44-80	11-57	11-57	22-48	39-47	31-80	51-70
C018	0.2	0.2	0.3	0.2	0.2	0.7	0.2	0.2	0.2	0.2	0.3	0.8
C020	1-2	1-2	1-2	1-3	9-20	2-3	1-2	1-2	1-2	2-5	2-5	2-3
C024	30	30	60	60	30	30	30	30	60	60	30	30
C025	1	1	1	8	7	7	2	2	2	5	5	9
C030	20	20	40	40	60	100	15	15	20	30	40	100
C034	0.9	0.9	0.9	1.3	1.3	1.1	1.1	1.1	0.9	1.8	2.0	2.0
Target MDLs for LRMS	-	12	24	24	36	48	-	12	24	24	36	48

Table 5. **Sample size, final volume and surrogate recoveries for study CP-4.**

Lab No.	Sample No.	Sample size (mL)	Final volume (µL)	^{13}C-Dioxins							^{13}C-Furans		
				2378-TCDD	12378-PSCDD	123478-H6CDD	123678-H6CDD	1234789-H7CDD	1234678-H7CDD	O8CDD	2378-TCDF	12378-PSCDF	1234678-H7CDF
C003	1	2.9	20	100	100		110		110	100			
	2	4.8	20	120	110		110		120	110			
	3	4.8	20		98		99		99	92			
	4	4.8	20	120	110		120		120	120			
	5	4.8	20	100	91		96		100	91			
	Mean			110	102		107		110	103			
C018	1	2	40	82	92	84	75		80	63	72	88	70
	2	2	40	82	86	95	84		79	58	68	85	77
	3	2	40	84	82	87	86		81	61	75	80	73
	4	2	40	89	97	91	86		91	72	81	89	80
	5	2	40	87	94	93	86		90	72	80	92	78
	Mean			85	90	90	83		84	65	75	87	76
C020	1			102	115		108		87	97	105	106	80
	2			103	107		110		89	93	105	103	86
	3			102	112		110		89	100	111	100	84
	4			97	115		108		92	102	95	107	87
	5			101	109		120		93	93	101	100	86
	Mean			101	112		111		90	97	103	103	85
C024	1	4	20	86	45	22			83	78			
	2	4	20	76	82	64			70	68			
	3	4	20	78	48	39			80	73			
	4	4	20	85	82	42			86	75			
	5	4	20	67	27	17			63	60			
	Mean			78	57	37			76	71			

Table 5. **Sample size, final volume and surrogate recoveries for study CP-4 (continued).**

Lab No.	Sample No.	Sample size (mL)	Final volume (µL)	^{13}C-Dioxins							^{13}C-Furans		
				2378-TCDD	12378-P5CDD	123478-H6CDD	123678-H6CDD	1234789-H7CDD	1234678-H7CDD	O8CDD	2378-TCDF	12378-P5CDF	1234678-H7CDF
C025	1	1.0	20	92	91	94	95		100	109	82	87	100
	2	1.0	20	95	104	93	91		100	109	100	97	100
	3	1.0	20	88	97	93	86		93	104	89	90	93
	4	1.0	20	94	105	106	97		105	113	92	90	105
	5	1.0	20	99	99	110	98		108	122	95	89	116
	Mean			94	99	99	93		101	111	92	91	103
C030	1	1	20	83	91		72		68	46	107		
	2	1	20	70	82		70		67	45	69		
	3	1	20	94	101		80		72	47	107		
	4	1	20	78	89		73		66	46	94		
	5	1	20	84	88		73		66	50	93		
	Mean			82	90		74		68	47	94		
C034	1	1	20	113	112		83		102	82	97	95	82
	2	1	20	95	102		70		74	42	84	86	60
	3	1	20	107	115		79		82	56	88	100	63
	4	1	20	101	99		80		82	61	84	90	63
	5	1	20	104	107		78		87	67	85	94	68
	Mean			104	107		78		85	62	88	93	67

Table 6. **Summary of interlaboratory median values for study CP-4**

Parameter	Concentration	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
Dioxins:						
2378-TCDD	pg/mL	281.5	50	47.9	95.7	100.5
T4CDD	pg/mL	422	83	93	155	225
P5CDD	pg/mL	195	69.5	61	130	126
H6CDD	pg/mL	715	245	229	468	451
H7CDD	pg/mL	1075	369.5	437	717.5	755
O8CDD	pg/mL	4025	1300	1300	2355	2400
Furans:						
2378-TCDF	pg/mL	110	40	41.7	70.2	71
T4CDF	pg/mL	829	170	203	290	371.5
P5CDF	pg/mL	751	201	234	409	403
H6CDF	pg/mL	2250	615.5	625	1250	1250
H7CDF	pg/mL	4060	1225	1140	2280	2385
O8CDF	pg/mL	7650	1750	1740	3300	3450

Table 7. **Summary of interlaboratory precision (%RSD) for study CP-4.**

Parameter	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Average
Dioxins:						
2378-TCDD	21.2	10.1	13.2	12.6	14.5	14.3
T4CDD	26.8	36.4	24.2	40.6	30.1	31.6
P5CDD	46.8	22.9	25.8	37.3	24.1	31.4
H6CDD	50.8	79.1	48.1	75.7	31.2	57.0
H7CDD	24.2	28.8	21.7	21.8	33.2	25.9
O8CDD	8.1	10.7	23.8	10.1	18.7	14.3
Furans:						
2378-TCDF	39.8	56.9	36.7	43.6	32.8	42.0
T4CDF	56.0	42.4	63.8	65.5	57.6	57.1
P5CDF	61.0	36.9	51.2	53.6	58.3	52.2
H6CDF	16.0	24.6	40.3	19.2	18.4	23.7
H7CDF	12.0	12.7	26.8	29.0	33.9	22.9
O8CDF	10.1	18.2	13.1	12.1	10.7	12.8

Table 8. Summary of intralaboratory precision (%RSD) for study CP-4.

Parameter	C003			C018			C020			C024			C025			C030			C034		
	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.	SE-22	SE-23	AVG.
Dioxins:																					
2378-TCDD	141.4	38.8	90.1	0	4.8	2.4	0	2.2	1.1	12.9	6.1	9.5	5.0	1.6	3.3	5.7	9.4	7.5	4.4	0.7	2.5
T4CDD	141.4	83.9	112.7	4.1	6.3	5.2	8.1	0	4.1	12.9	6.1	9.5	10.7	1.9	6.3	5.7	8.3	7.0	9.4	1.6	5.5
P5CDD	141.4	141.4	141.4	6.1	7.6	6.8	5.7	0	2.8	-	141.4	141.4	3.4	2.9	3.1	5.1	141.4	73.3	5.2	0	2.6
H6CDD	0	58.4	29.2	0	0.6	0.3	3.0	1.7	2.3	47.1	7.4	27.3	6.0	1.6	3.8	32.6	29.8	31.2	6.0	0.8	3.4
H7CDD	11.3	14.6	12.9	1.0	1.5	1.2	3.8	4.1	4.0	22.5	45.4	33.9	6.2	2.7	4.5	5.7	17.7	11.7	2.1	1.1	1.6
O8CDD	0	6.4	3.2	0	0.6	0.3	5.7	0.6	3.1	12.9	16.2	14.5	4.4	1.0	2.7	0	10.1	5.1	3.0	3.3	3.2
Furans:																					
2378-TCDF	39.5	61.8	50.6	8.1	1.2	4.7	0	6.8	3.4	141.4	0	70.7	4.9	0	2.5	27.7	0	13.9	0.9	1.0	1.0
T4CDF	64.5	93.6	79.0	2.5	4.6	3.6	0	1.2	0.6	141.4	0	70.7	5.9	6.4	6.2	17.2	32.6	24.9	0	0	0
P5CDF	27.8	3.1	15.5	8.5	4.1	6.3	4.6	12.9	8.7	-	76.1	76.1	10.4	1.0	5.7	39.0	33.6	36.3	1.1	1.7	1.4
H6CDF	7.5	5.7	6.6	3.5	0.5	2.0	8.9	1.1	5.0	141.4	110.6	126.0	3.8	1.9	2.9	5.7	34.6	20.1	2.9	0	1.5
H7CDF	21.8	13.5	17.6	4.1	3.9	4.0	10.4	5.8	8.1	42.8	24.6	33.7	3.3	1.0	2.2	0	10.2	5.1	2.8	2.9	2.9
O8CDF	3.8	4.3	4.1	8.4	1.8	5.1	6.8	0	3.4	4.0	2.0	3.0	4.5	2.4	3.5	1.9	9.2	5.6	2.2	2.3	2.3

Table 9.1 Performance of individual laboratory for dioxins in sediment extracts.

Lab No.	Total No. of Results Reported	No. of Results "not Detected"	No. of Results Ranked	No. of Results Flagged		% Flags (Performance Index)	Comment
				H	L		
C003	30	4	28	5	3	28.6	Moderate
C018	30	0	30	0	0	0	Satisfactory
C020	30	0	30	0	0	0	Satisfactory
C024	30	4	28	2	2	14.3	Satisfactory
C025	30	0	30	0	0	0	Satisfactory
C030	30	1	30	16	1	56.7	Poor
C034	30	0	30	0	0	0	Satisfactorty

Table 9.2 **Performance of individual laboratory for furans in sediment extracts.**

Lab No.	Total No. of Results Reported	No. of Results "not Detected"	No. of Results Ranked	No. of Results Flagged		% Flags (Performance Index)	Comment
				H	L		
C003	30	0	30	0	4	13.3	Satisfactory
C018	30	0	30	0	0	0	Satisfactory
C020	30	0	30	0	0	0	Satisfactory
C024	30	6	29	1	16	58.6	Poor
C025	30	0	30	0	1	3.3	Satisfactory
C030	30	0	30	19	0	63.3	Poor
C034	30	0	30	0	0	0	Satisfactory

Table 10.1. Comparison of interlaboratory median values between duplicate samples (SE-22).

Parameter	Concentration	Sample No.		Average Median	S.D.	RSD, %
		2	3			
Dioxins:						
2378-TCDD	pg/mL	50	47.9	49.0	1.5	3.0
T4CDD	pg/mL	83	93	88	7.1	8.0
P5CDD	pg/mL	69.5	61	65.3	6.0	9.2
H6CDD	pg/mL	245	229	237	11.3	4.8
H7CDD	pg/mL	369.5	437	403.3	47.7	11.8
O8CDD	pg/mL	1300	1300	1300	0	0
Furans:						
2378-TCDF	pg/mL	40	41.7	40.9	1.2	2.9
T4CDF	pg/mL	170	203	186.5	23.3	12.5
P5CDF	pg/mL	201	234	217.5	23.3	10.7
H6CDF	pg/mL	615.5	625	620.3	6.7	1.1
H7CDF	pg/mL	1225	1140	1182.5	60.1	5.1
O8CDF	pg/mL	1750	1740	1745	7.1	0.4

Table 10.2. **Comparison of interlaboratory median values between duplicate samples (SE-23).**

Parameter	Concentration	Sample No.		Average Median	S.D.	RSD, %
		4	5			
Dioxins:						
2378-TCDD	pg/mL	95.7	100.5	98.1	3.4	3.5
T4CDD	pg/mL	155	225	190	49.5	26.1
P5CDD	pg/mL	130	126	128	2.8	2.2
H6CDD	pg/mL	468	451	459.5	12.0	2.6
H7CDD	pg/mL	717.5	755	736.3	26.5	3.6
O8CDD	pg/mL	2355	2400	2377.5	31.8	1.3
Furans:						
2378-TCDF	pg/mL	70.2	71	70.6	0.6	0.8
T4CDF	pg/mL	290	371.5	330.8	57.6	17.4
P5CDF	pg/mL	409	403	406	4.2	1.0
H6CDF	pg/mL	1250	1250	1250	0	0
H7CDF	pg/mL	2280	2385	2332.5	74.2	3.2
O8CDF	pg/mL	3300	3450	3375	106.1	3.1

Table 10.3. **Comparison of interlaboratory median values between studies (SE-18).**

Parameter	Study No.	CP-3	CP-3	CP-4	Average Median	S.D.	RSD, %
	Sample No.	2	4	1			
Dioxins:							
2378-TCDD	pg/mL	290	285	281.5	285.5	4.3	1.5
T4CDD	pg/mL	396	380	422	399.3	21.2	5.3
P5CDD	pg/mL	202	241	195	212.7	24.8	11.7
H6CDD	pg/mL	730	760	715	735	22.9	3.1
H7CDD	pg/mL	1200	1150	1075	1141.7	62.9	5.5
O8CDD	pg/mL	3800	4000	4025	3941.7	123.3	3.1
Furans:							
2378-TCDF	pg/mL	100	110	110	106.7	5.8	5.4
T4CDF	pg/mL	640	634	829	701	110.9	15.8
P5CDF	pg/mL	778.5	1050	751	859.8	165.3	19.2
H6CDF	pg/mL	2146	2051	2250	2149	99.5	4.6
H7CDF	pg/mL	3460	3400	4060	3640	365.0	10.0
O8CDF	pg/mL	6250	7000	7650	6966.7	700.6	10.1

Fig.1.1. Comparison between Mean and Median for Dioxins

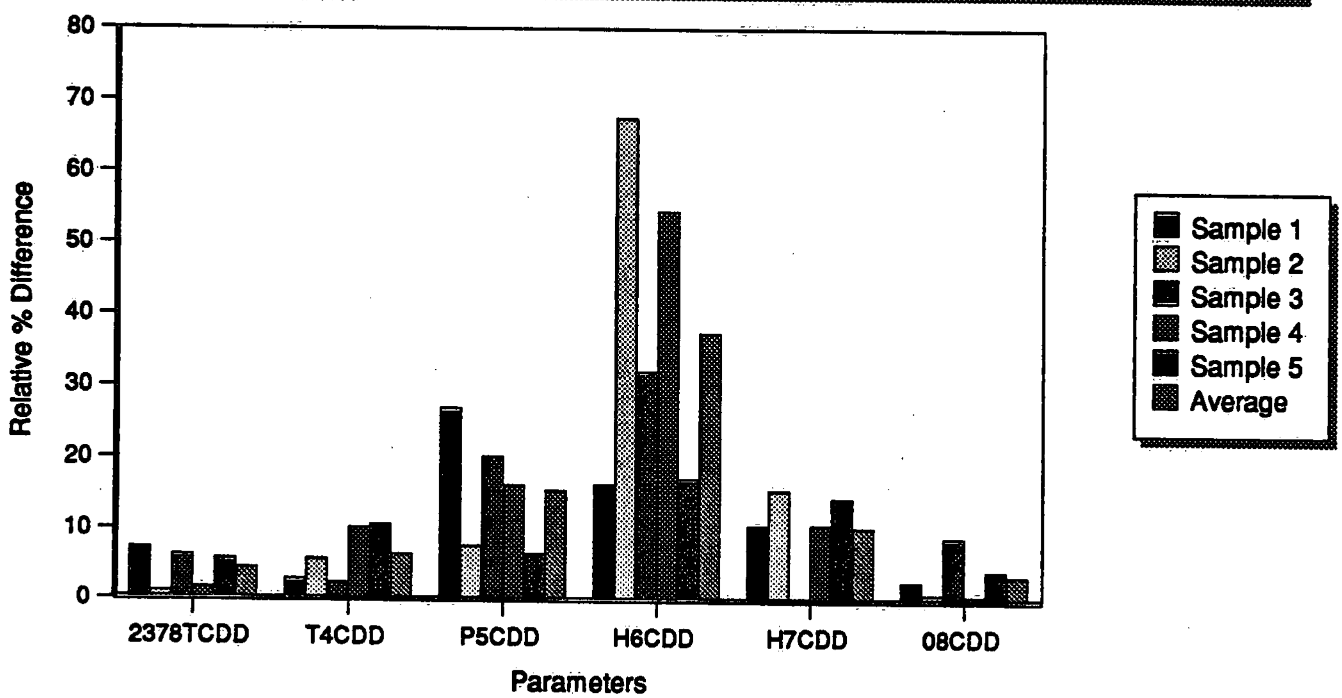


Fig. 1.2. Comparison between Mean and Median for Furans

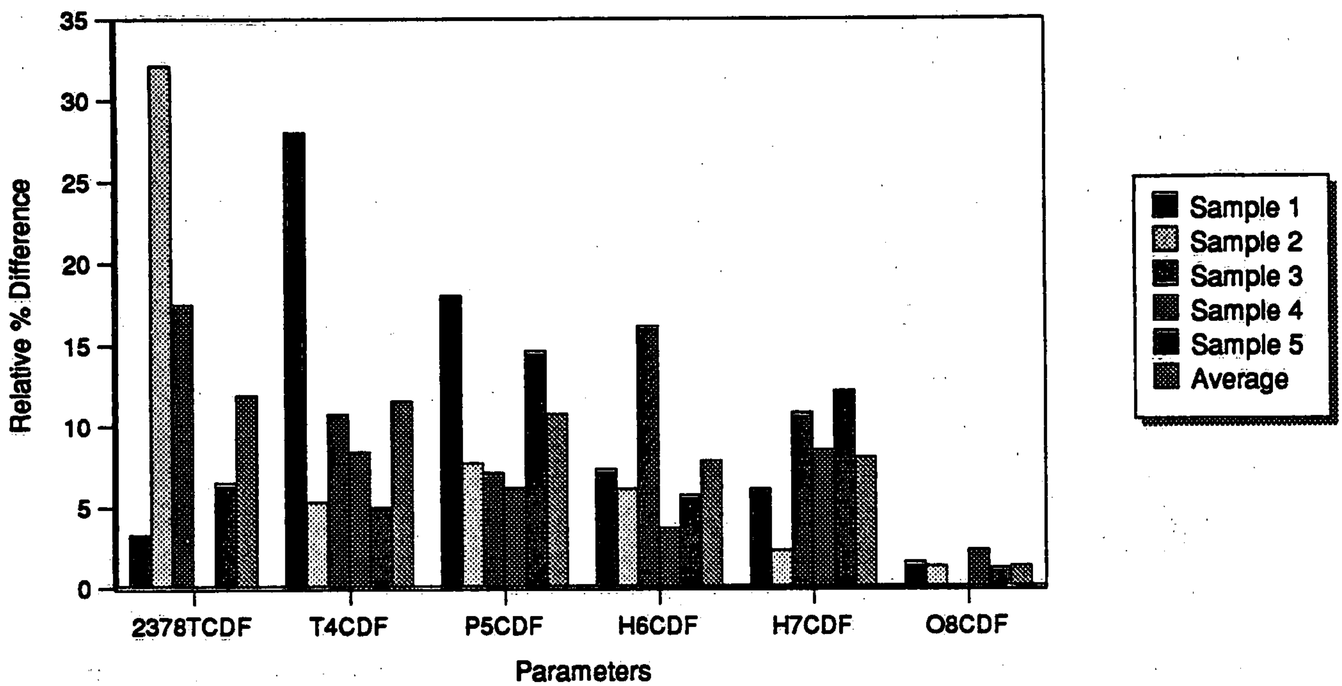


Fig. 2.1. Interlaboratory Precision for Dioxins

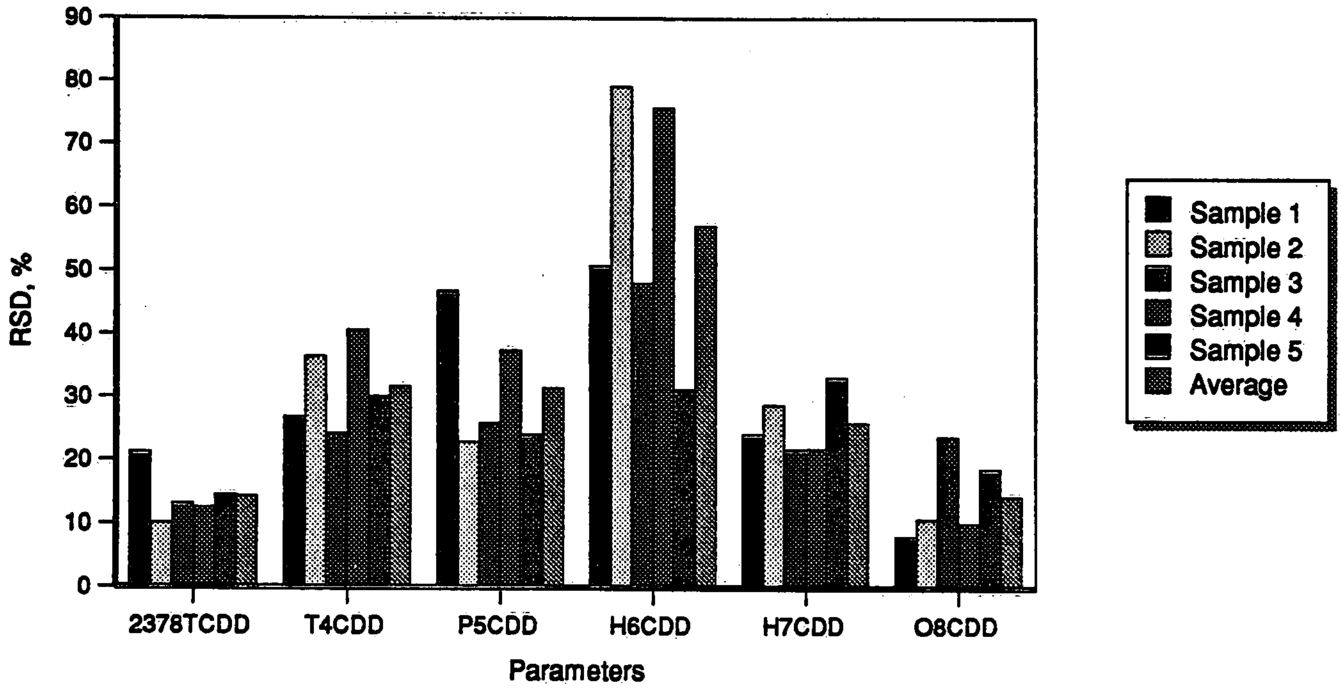
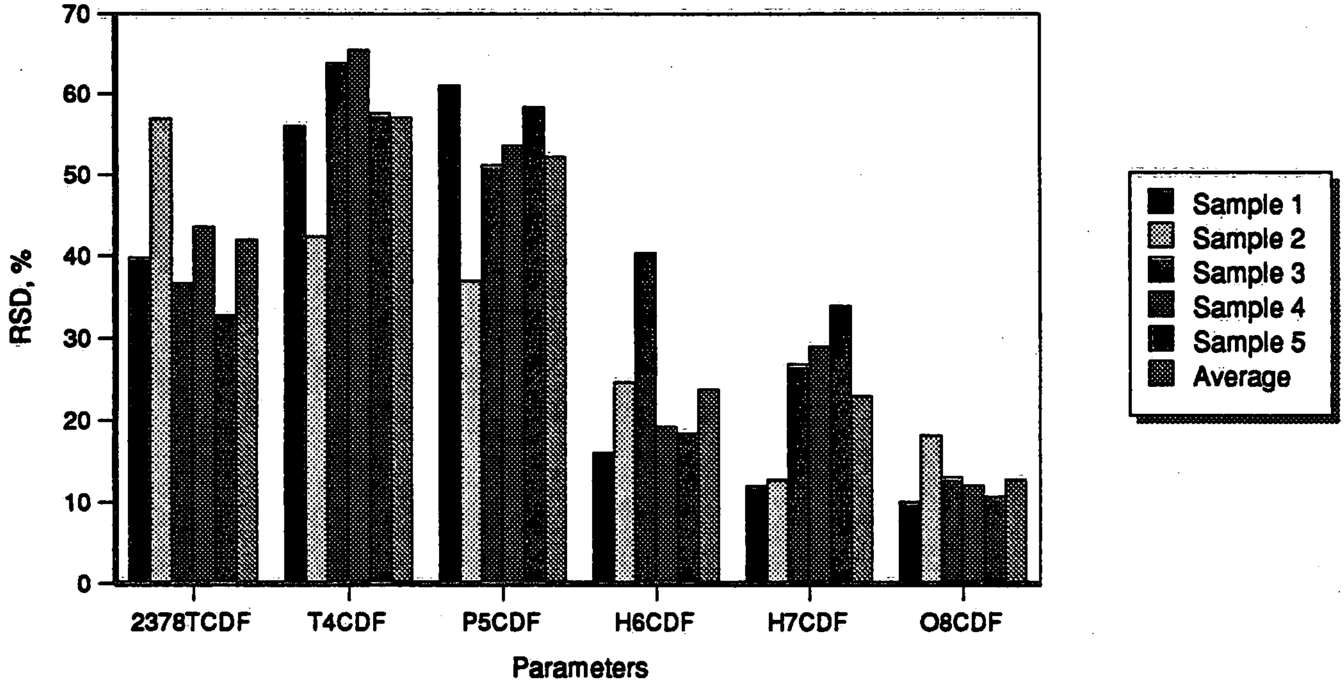


Fig. 2.2. Interlaboratory Precision for Furans



APPENDIX I

DATA SUMMARY

Table I-1. Results for 2378-TCDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	430	52	ND	74	130
C018	273	47.9	47.9	94.4	101
C020	290	56	56	97	100
C024	300	50	60	110	120
C025	254	41	44	90	88
C030	* 620 H	* 130 H	* 120 H	* 210 H	* 240 H
C034	270	50	47	99	100
MEAN	302.8	49.5	51.0	94.1	106.5
S.D.	64.3	5.0	6.7	11.9	15.4
MEDIAN	281.5	50	47.9	95.7	100.5

Table I-2. Results for T4CDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	* 960 H	52	ND L	74 L	290
C018	464	107	101	215	235
C020	380	83	74	155	155
C024	300	50	60	110	120
C025	347	73	85	148	152
C030	620	130	120	270	240
C034	495	120	105	230	225
MEAN	434.3	87.9	90.8	171.7	202.4
S.D.	116.3	32.0	22.0	69.7	60.9
MEDIAN	422	83	93	155	225

Table I-3. Results for P5CDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	450 H	74	ND	250	ND L
C018	155	55.8	60.8	95.2	106
C020	195	65	60	130	130
C024	ND L	ND	ND	ND L	120
C025	188	64	61	121	126
C030	* 820 H	100	93	130	ND L
C034	290	91	98	190	190
MEAN	255.6	75.0	74.6	152.7	134.4
S.D.	119.7	17.2	19.2	56.9	32.4
MEDIAN	195	69.5	61	130	126

Table I-4. Results for H6CDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	1700 H	470	470 H	1900 H	790
C018	753	228	228	468	472
C020	700	240	230	420	430
C024	730	1100 H	550 H	630	700
C025	570	181	197	385	394
C030	* 3100 H	1000 H	* 1600 H	1500 H	* 2300 H
C034	595	245	225	420	425
MEAN	841.3	494.9	316.7	817.6	535.2
S.D.	427.0	391.4	152.3	618.9	166.9
MEDIAN	715	245	229	468	451

Table I-5. Results for H7CDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	1600	610	520	960	780
C018	1100	369	364	715	730
C020	1520	570	540	1070	1010
C024	950	370	510	720	1400
C025	1050	327	357	711	684
C030	* 3200 H	* 1200 H	* 1300 H	* 2100 H	* 2700 H
C034	955	345	335	620	630
MEAN	1195.8	431.8	437.7	799.3	872.3
S.D.	288.9	124.2	94.8	174.6	290.0
MEDIAN	1075	369.5	437	717.5	755

Table I-6. Results for O8CDD in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	4100	1300	1300	2100	2300
C018	4100	1350	1350	2510	2530
C020	3950	1300	1200	2520	2500
C024	4300	1500	1800	2700	3400
C025	3640	1090	1160	2180	2210
C030	* 5500	* 2000	2000	* 3900	* 4500
C034	3450	1200	1150	2200	2100
MEAN	3923.3	1290	1422.9	2368.3	2506.7
S.D.	319.2	138.6	338.9	240.4	467.9
MEDIAN	4025	1300	1300	2355	2400

Table I-7. Results for 2378-TCDF in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	130	40	71	29 L	74
C018	113	36.9	41.4	70.2	71.4
C020	110	42	42	76	69
C024	60	90 H	ND	60	60
C025	73	28	30	55	55
C030	200	110 H	74	130	130
C034	110	40	39.5	72	71
MEAN	113.7	55.3	49.7	70.3	75.8
S.D.	45.2	31.4	18.2	30.7	24.9
MEDIAN	110	40	41.7	70.2	71

Table I-8. **Results for T4CDF in sediment extracts (pg/mL).**

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	1000	190	71 L	120 L	590
C018	829	247	256	429	458
C020	420	150	150	290	285
C024	60 L	90	ND L	60 L	60 L
C025	343 L	114	124	189	207
C030	880	* 600 H	470 H	600 H	960 H
C034	845	285	285	520	520
MEAN	625.3	179.3	226	315.4	353.3
S.D.	350.3	76.1	144.3	206.5	203.4
MEDIAN	829	170	203	290	371.5

Table I-9. Results for P5CDF in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	1100	140	94 L	230	220
C018	751	265	235	447	474
C020	560	150	160	300	360
C024	150 L	ND L	ND L	60 L	200 L
C025	736	201	233	409	403
C030	1900 H	* 810 H	460	610	990 H
C034	1100	330	325	635	620
MEAN	899.6	217.2	251.2	384.4	466.7
S.D.	548.8	80.2	128.6	205.9	272.3
MEDIAN	751	201	234	409	403

Table I-10. Results for H6CDF in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	2400	710	790	1200	1300
C018	2250	641	610	1420	1430
C020	2310	720	635	1300	1320
C024	ND L	380	ND L	* 110 L	900
C025	1600	434	458	960	934
C030	* 5800 H	* 1200	1300 H	1700	* 2800 H
C034	1900	590	615	1200	1200
MEAN	2092	579.2	734.7	1296.7	1180.7
S.D.	334.0	142.6	296.3	249.0	217.2
MEDIAN	2250	615.5	625	1250	1250

Table I-11. Results for H7CDF in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	4100	1200	880	1900	2300
C018	4070	1250	1180	2450	2590
C020	4150	1390	1200	2680	2470
C024	* 560 L	990	530 L	980 L	690 L
C025	3540	1050	1100	2160	2130
C030	3000	* 3000 H	* 3000 H	* 5800 H	* 6700 H
C034	4050	1300	1250	2400	2500
MEAN	3818.3	1196.7	1023.3	2095	2113.3
S.D.	459.0	151.7	274.6	607.7	716.2
MEDIAN	4060	1225	1140	2280	2385

Table I-12. Results for O8CDF in sediment extracts (pg/mL).

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	7900	1800	1900	3200	3400
C018	8610	2330	2070	4080	3980
C020	7500	1850	1680	3550	3550
C024	7800	1700	1800	3400	3500
C025	6590	1360	1450	2930	3030
C030	* 15000	* 3700 H	* 3800 H	* 7900 H	* 9000 H
C034	6750	1600	1550	3100	3000
MEAN	7525	1773.3	1741.7	3376.7	3410
S.D.	757.5	323.3	228.9	408.1	364.7
MEDIAN	7650	1750	1740	3300	3450

APPENDIX II

Late Data Submitted by Laboratory C019

Results Report Form

CEPA National Interlaboratory Study No. CP-4

Parameter	Sediment Extracts (pg/mL)					
	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Average Detection Limit
2,3,7,8-TCDD	380	48	56	100	95	1.6
T4CDD	620	120	110	240	230	1.6
P5CDD	370	110	63	200	270	1.2
H6CDD	880	310	300	590	540	3.2
H7CDD	1800	520	510	1040	1050	5.8
O8CDD	5300	1700	1500	2900	3200	6.9

Results Report Form

CEPA National Interlaboratory Study No. CP-4

Parameter	Sediment Extracts (pg/mL)					
	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Average Detection Limit
2,3,7,8-TCDF	98	32	31	56	55	9.2
T4CDF	970	270	260	440	330	9.2
P5CDF	1400	390	330	630	790	4.2
H6CDF	2300	650	650	1300	1200	15
H7CDF	4300	1300	1200	2300	2400	9.8
O8CDF	9100	1900	1900	3700	4000	4.9

Results Report form

CEPA National Interlaboratory Study No. CP-4

Sediment extract	Sample size (mL)	Final volume (µL)	Surrogate recoveries (%)								
			^{13}C-Dioxins						^{13}C-Furans		
			2378-TCDD	12378-P5CDD	123478-H6CDD	123678-H6CDD	1234678-H7CDD	O8CDD	2378-TCDF	12378-P5CDF	1234678-H7CDF
Sample #1	2.0	20.0	76	91	103	85	62	45	79	94	84
Sample #2	2.0	20.0	93	107	115	98	78	54	95	96	88
Sample #3	2.0	20.0	86	86	100	94	80	57	88	93	89
Sample #4	2.0	20.0	92	105	108	100	73	56	95	107	98
Sample #5	2.0	20.0	85	65	119	98	77	58	82	92	93

NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

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