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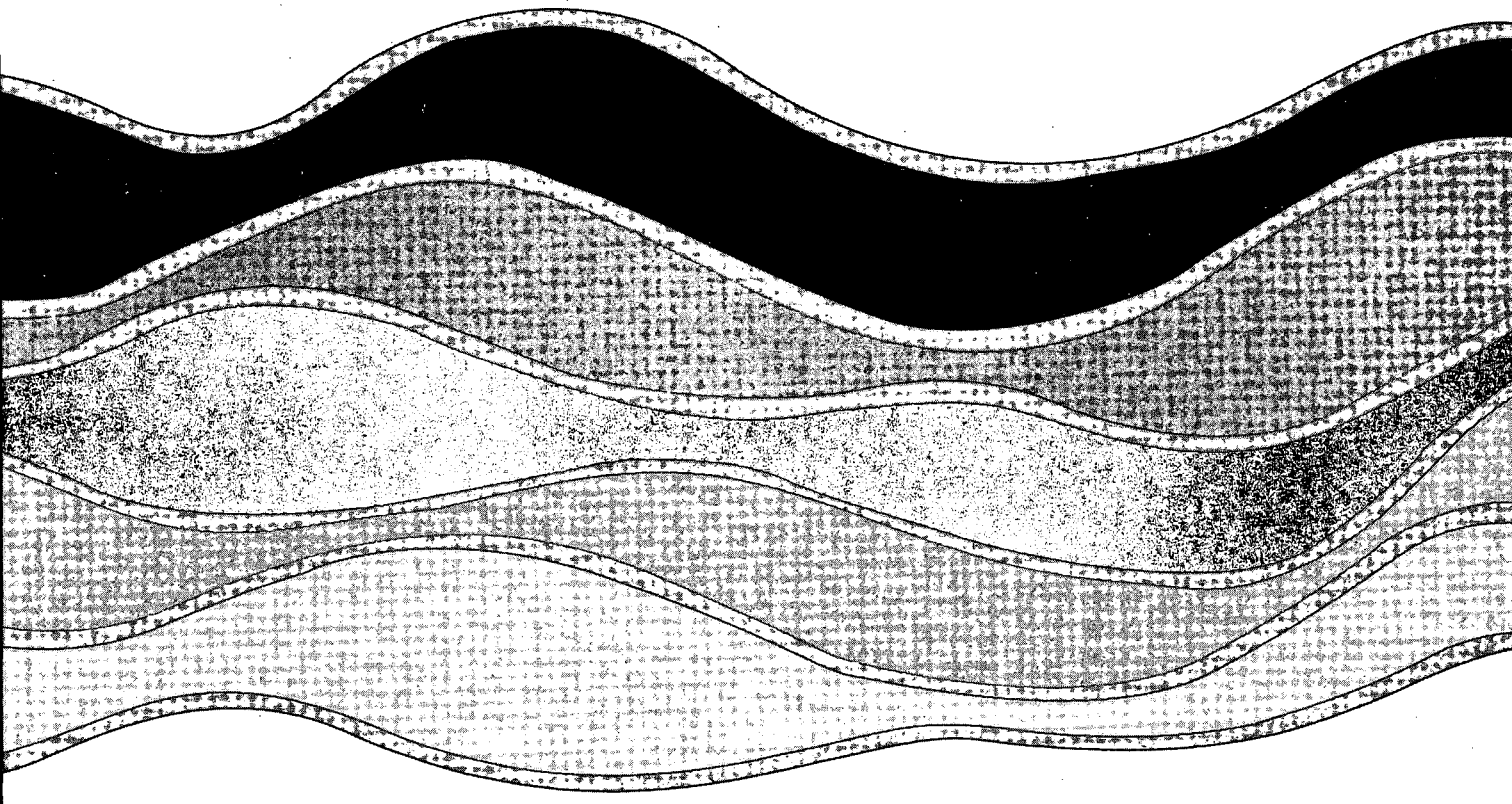

CEPA NATIONAL INTERLABORATORY COMPARISON STUDY (CP-3): ANALYSIS OF DIOXINS AND FURANS IN SEDIMENT EXTRACTS

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NWRI CONTRIBUTION 94-81

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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-3) 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 dans l'industrie des pâtes et papiers partout au pays contiennent des dioxines, sous forme d'impuretés de fabrication. La forme de dioxine la plus toxique est la 2,3,7,8-TCDD. On a décelé sa présence dans les effluents des usines de pâtes et papiers. Dans le cadre de la LCPE, on a évalué deux composés figurant sur la liste des substances d'intérêt prioritaire, les dioxines et furanes, ainsi que les effluents des usines de pâtes, et on a démontré qu'ils étaient toxiques aux termes de la Loi. Présentement, ces substances font l'objet d'un processus d'options stratégiques qui pourrait déboucher sur des mesures réglementaires de limitation.

Le succès de la mise en oeuvre de la LCPE dépend de la disponibilité de données scientifiques fiables. Afin d'aider les gestionnaires des projets et les organismes de réglementation à assurer la validité des données analytiques conformément à la Loi, on a conçu et réalisé une étude interlaboratoire (CP-3) pour l'analyse des dioxines et des furanes dans des extraits de sédiments. Cette étude contribuera à déterminer le degré de comparabilité des résultats d'analyse des dioxines et des furanes obtenus par 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-3) for analysis of dioxins and furans in sediment extracts was designed and conducted by the Quality Assurance Group at the National Water Research Institute. Ten 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 homoloque group in total in all test samples. Surrogate recoveries were also requested. Seven out of ten 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%. Overall, the average values of the relative % difference between means and medians for all six dioxin parameters were within ±10%. For the furan results, the average values of the relative % difference between means and medians were within ± 10% for five out of six furan parameters except T4CDF exceeding ± 10% (17.0%).

For overall laboratory performance, all seven laboratories submitted satisfactory results for dioxins in sediment extracts. For the furan results, six out of seven laboratories provided satisfactory results. Laboratory C024 had only a moderate performance rating for furan analysis.

RÉSUMÉ

Dans le cadre d'un programme d'assurance de la qualité mis en oeuvre en vertu de 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 réalisé une étude comparative interlaboratoire (CP-3) pour l'analyse des dioxines et des furanes dans des extraits de sédiments. Dix laboratoires ont reçu cinq échantillons. On a demandé à chaque laboratoire d'analyser le 2,3,7,8-TCDD et le 2,3,7,8-TCDF, ainsi que les dérivés tétra-, penta-, hexa-, hepta- et octachlorés des dibenzo-*p*-dioxines et dibenzofuranes, et chaque groupe d'homologues au complet dans tous les échantillons d'essai. On a également demandé les résultats des récupérations de substituts. Sept des dix laboratoires ont présenté des résultats.

Étant donné que l'on ne connaissait pas les concentrations nominales de dioxines et de furanes dans les échantillons, on a utilisé des valeurs médianes comme valeurs cibles pour l'évaluation des résultats interlaboratoires. Pour évaluer la qualité des résultats interlaboratoires présentés par les laboratoires participants, on a comparé les moyennes et les médianes obtenues pour les dioxines et les furanes de chacun des cinq échantillons d'essai. La majorité des moyennes et des médianes obtenues pour les dioxines et les furanes montraient une très bonne concordance, avec une différence relative comprise entre ±25 %. Dans l'ensemble, les valeurs moyennes des différences relatives entre les moyennes et les médianes étaient comprises entre ±10 % pour chacun des six paramètres appliqués à la dioxine. Dans le cas du furane, elles étaient comprises entre ±10 % pour cinq des six furanes, sauf dans le cas du T4CDF, pour lequel on notait un dépassement de ±10 % (17,0 %).

Pour ce qui est du rendement global des laboratoires, on note que chacun des sept laboratoires a présenté des résultats satisfaisants pour les dioxines dans les extraits de sédiments. Dans le cas des furanes, six des sept laboratoires ont fourni des résultats satisfaisants. Le laboratoire C024 n'a obtenu qu'une cote moyenne pour l'analyse des 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 ensuing 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 to evaluate the comparability of the data generated by many different federal, provincial and private laboratories [2,3].

From previous interlaboratory studies, it was noted that many variations in extraction, cleanup and quantitation existed for analysis of dioxins and furans in sediments. To eliminate the variation of sample extraction, sediment extract samples were used as test samples for the evaluation of the comparability and performance of participating laboratories in the present interlaboratory study. This CEPA interlaboratory study (No. CP-3) was distributed on November 21, 1991. The original deadline for reporting results was January 17, 1992. However, most laboratories were late in reporting, so the study was closed February 28, 1992. In April, 1992, a preliminary data summary was prepared and distributed to those participants which had submitted their results. The data summary allows participants to compare their results with those of their peers. Thus any necessary corrective action can be taken in a timely manner. This final report provides more information on the data evaluation and laboratory performance of participants.

2. STUDY DESIGN

This interlaboratory study (CP-3) for analysis of dioxins and furans in sediment extracts was initiated in August, 1991. About 70 federal, provincial and private laboratories were invited to participate. From the returned questionnaires, ten laboratories expressed interest to participate in this study. By the time the study was closed, seven out of ten 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 #2 and #4) and SE-19 (samples #1 and #5) were prepared from freeze-dried sediment CRMs EC-2 and EC-3, respectively by soxhlet extraction using the method developed by Environment Canada [4]. The sediment extract SE-20 (sample #3) was prepared from a bulk sediment EC-8 by the extraction procedure developed by Chau et. al. [5]. 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 some cases, GPC (gel permeation chromatography) was used in advance to remove high molecular weight co-extractives such as humic and fuvic acids from the extracts. 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" [6], the Dioxin Quality Assurance Advisory Committee (DQAAC) recommended a sample size of 5 grams for dry sediment, soil, sludge and 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 limits for low resolution mass spectrometry (LRMS) are based on an assumption of high surrogate recovery and final extracts that are free from any major interferences (refer to reference 6 for further details). For those laboratories (C018, C019 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, the detection limit are in same order of magnititude as those of "Target MDLs" except lab C003 which had much high detection limits.

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 are 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 % [6]. 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. 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 [7]. 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 interlaboratory results generated by participating laboratories, comparison between means and medians for dioxins and furans in all five test samples was made. 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 20% except for sample # 3 for O8CDD which exceeded 20%. Where the relative % difference was expressed as [|mean - median|/(mean+median)/2] x 100. Overall, the average values of the relative % difference for all six dioxin parameters were within 10%.. 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 20% except for sample #1 for T4CDF and sample #3 for O8CDF which exceeded 20%. While the average values of the relative % difference were within 10% for five out of six furan parameters except T4CDF (17.0%). 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% (sample #3 for T4CDD, sample #1 for P5CDD and sample #3 for O8CDD. Overall, the average values of RSDs for all six dioxin parameters were within ±50%. Furan results were less precise than the dioxin results. As can be seen from Fig. 2.2 for interlaboratory precision for furans, 4 out of 30 results (13.3%) had RSD exceeding ±50% (samples #1 and #4 for T4CDF and sample #2 for P5CDF). Overall, the average values of RSDs for five out of six furan parameters were within ±50% except T4CDF (51.7%).

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-19 for samples #1 and #5 and SE-18 for samples #2 and #4). A summary of intralaboratory

precision for participating laboratories is given in Table 8. The results show that four laboratories (C018, C024, C030 and C034) had excellent precision for both of the two pairs of duplicate samples with RSDs of less than ±25% for all parameters. While three other laboratories (C003, C005 and C019) were less precise with some dioxin and furan parameters exceeding ± 25% RSD. In a few cases, the intralaboratory RSDs were higher than the interlaboratory RSDs such as 2378-TCDF, T4CDF and P5CDF for lab C003; P5CDD and P5CDF for lab C005 and 2378-TCDF for lab C019. It is suggested that these above-mentioned three 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 [8] for the detection of bias as well as the computerize flagging procedure [9,10] were not used for data evaluation. Instead, a modified flagging procedure used in the national dioxin interlaboratory studies [2,3] 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) $\leq x \leq 2$ (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-3, 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. For the dioxins results, all seven laboratories demonstrated satisfactory performance, while for the furans results, six out of seven laboratories demonstrated satisfactory performance and only lab C024 rated moderate performance with 45.8% flags.

3.4 Comparison of Results between Duplicate 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 of the test samples. A comparison of interlaboratory median values between samples for the two pairs of blind duplicates (SE-18 for sample #2 and #4, and SE-19 for samples #1 and #5) is given in Tables 10.1 and 10.2. As can be seen from Table 10.1, the RSDs for samples #2 and #4 (SE-18) were within ± 25% for all twelve parameters of dioxins and furans. While the RSDs for samples #1 and #5 (SE-19) were within ±25% for ten out of 12 parameters of dioxins and furans (Table 10.2). Only for two parameters (P5CDD and T4CDF) did the RSDs exceed ±25%. Overall, the agreement between duplicate samples was very good and this helped to verify the integrity of the test samples. Thus these interlaboratory results 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-3).

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

2. Eli Eco Logic International Inc.
   Rockwood, Ontario

3. Enviro-Test Laboratories
   Edmonton, Alberta

4. Mann Testing Laboratories
   Mississauga, Ontario

5. Novalab Ltd.
   Lachine, Quebec

6. Wellington Environmental Consultants
   Guelph, Ontario

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

Table 2. Samples distributed in study CP-3.

Sample No.	Identification Code	Description
1	SE-19	Soxhlet extraction of EC-3 (1 mL in toluene is equivalent to 1 g dry sediment)
2	SE-18	Soxhlet extraction of EC-2 (1 mL in toluene is equivalent to 1 g dry sediment)
3	SE-20	Solvent extraction of EC-8 (1 mL in toluene is equivalent to 1 g dry sediment)
4	SE-18	Same as sample #2
5	SE-19	Same as sample #1

Table 3. Analytical Methodology used by participating Laboratories.

Lab No.	Sample pretreatment	Cleanup	Seperation/measurement
C003	Sediment extracts fortified with surrogate standards; solvent exchange to hexane and concentrated to 5 mL.	Column chromatograph with double silica gel/H_2SO_4, 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 recoveries of the surrogate standards.
C005	Sediment extract fortified with surrogate standards.	Multilayer neutral/acid/neutral/base/neutral silica column; basic alumina column.	Splitless GC/MS, MID Mode; 60 m x 0.32 mm i.d. DB-5 column; ESTD, corrected for recoveries of the surrogate standards.
C018	Sediment extracts spiked with ^{13}C-labelled PCDD surrogates.	Multilayer silica column; alumina column; carbopeck C/celite column.	GC/MS (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 apillary column; recoveries of surrogates were accounted for all samples.
C019	Sediment extracts partitioned multiple times against con. H_2SO_4; partitioned against with 5% $NaHCO_3$.	Multi-column (H_2SO_4 impregnated silica, NaOH impregnated silica, silver nitrate impregnated silica); basic alumina column; carbopeck C on celite.	GC/MS (Kratos Concept high resolution MS with HP series II GC); 50 m x 0.2 mm i.d. HP Ultra-2 column; corrected for recoveries of the surrogate standards.
C024	Sediment extracts spiked with surrogates.	GPC on SX-3; multilayer column (H_2SO_4 on silica gel , 1% deactivated alumina); Carbon/glass-fibre column.	GC/MSD, 25 m x 0.2 mm i.d. HP-5 capillary column; ESTD; corrected for recoveries of the surrogate standards.
C030	Sediment extracts spiked with surrogates.	Automated GPC; basc alumina column; 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 H_2SO_4.	Silica 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	50	140	200	150	110	110	40	110	170	200	230	140
C005	20	20	10	18	18	16	17	17	12	15	10	17
C018	0.1	0.1	0.1	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.3
C019	1.3	1.3	2.9	4.8	8.1	22	1.3	1.3	2.7	3	9.5	16
C024	6	6	80	20	10	30	6	6	40	20	8	20
C030	16	16	21	23	24	27	12	12	16	17	23	26
C034	1	1	2	3	7	5	1	1	1	3	6	6
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-3.

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
C003	1	4.9	20	110	103		106		133	125			
	2	5.1	20	113	117		116		118	114			
	3	5.2	20	92	100		117		111	90			
	4	5.1	20	107	101		117		109	105			
	5	5.1	20	103	90		110		123	107			
	Mean			105	102		113		119	108			
C005	1	4.9	20	66	69		63		82	72			
	2	5.0	20	74	123		118		47	64			
	3	5.3	20	53	50		58		75	61			
	4	5.3	20	80	44		84		124	91			
	5	5.0	20	-	57		56		80	159			
	Mean			68	69		76		82	89			
C018	1	2.5	10	93	88		106		126	130	67	97	129
	2	2.5	10	65	104		111		133	143	23	109	134
	3	2.5	10	89	118		108		126	125	62	123	128
	4	2.5	10	55	76		100		126	137	25	79	117
	5	2.5	10	91	119		110		132	132	78	119	131
	Mean			77	96		102		121	126	51	105	128
C019	1	5.0	20	90	111		90		70	63	77	116	82
	2	5.1	20	56	87		89		45	49	43	91	63
	3	5.4	20	67	35		63		96	43	96	51	57
	4	5.2	20	65	58		103		98	76	47	65	83
	5	5.0	20	33	67		76		40	48	56	86	51
	Mean			62	72		84		70	56	64	82	67

Table 5. Sample size, final volume and surrogate recoveries for study CP-3 (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
C024	1	4	20	98	111	108			103	103			
	2	4	20	87	86	80			61	48			
	3	-	-	-	-	-			-	-			
	4	4	20	81	79	69			59	43			
	5	4	20	100	108	94			82	78			
	Mean			92	96	88			76	68			
C030	1	2.5	20	80	95		84		103	108			
	2	2.5	20	83	94		76		88	86			
	3	2.5	20	75	93		81		94	95			
	4	2.5	20	88	97		76		88	81			
	5	2.5	20	80	95		80		96	94			
	Mean			81	95		79		93	93			
C034	1	4.65	20	85	75			71	104	108	69		
	2	2	20	95	75			73	118	119	74		
	3	2	20	77	71			74	92	84	67		
	4	2	20	106	88			81	111	106	81		
	5	2	20	81	98			68	97	110	71		
	Mean			89	81			73	104	105	72		

Table 6. Summary of interlaboratory median values for study CP-3.

Parameter	Concentration	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
Dioxins:						
2378-TCDD	pg/mL	285	290	100	285	280
T4CDD	pg/mL	290	396	200	380	340
P5CDD	pg/mL	182	202	166	241	266
H6CDD	pg/mL	683	730	549	760	800
H7CDD	pg/mL	1270	1200	811.5	1150	1400
O8CDD	pg/mL	4300	3800	2700	4000	4300
Furans:						
2378-TCDF	pg/mL	170	100	80	110	140
T4CDF	pg/mL	440	640	473	634	790
P5CDF	pg/mL	909	778.5	695	1050	932
H6CDF	pg/mL	1900	2146	1650	2051	2295
H7CDF	pg/mL	3600	3460	3345	3400	3680
O8CDF	pg/mL	7300	6250	4050	7000	7200

Table 7. Summary of interlaboratory precision (%RSD) for study CP-3.

Parameter	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Average
Dioxins:						
2378-TCDD	12.6	7.1	24.1	12.2	19.6	15.1
T4CDD	35.8	20.1	56.2	19.6	44.0	35.2
P5CDD	67.9	35.6	40.1	27.2	17.4	37.6
H6CDD	39.2	32.2	46.7	40.7	33.9	38.5
H7CDD	20.6	19.5	29.7	24.2	17.2	22.2
O8CDD	17.4	10.7	55.2	8.4	10.5	20.5
Furans:						
2378-TCDF	36.9	30.8	25.3	21.3	27.1	28.3
T4CDF	55.5	48.2	43.9	62.3	48.6	51.7
P5CDF	39.5	61.0	36.8	51.5	36.1	45.0
H6CDF	43.3	43.9	29.2	34.3	34.4	37.0
H7CDF	39.8	35.2	34.7	39.3	36.4	37.1
O8CDF	12.0	3.4	46.3	16.3	13.3	18.3

Table 8. Summary of intralaboratory precision (%RSD) for study CP-3.

Parameter	C905			C905			C918			C919			C924			C930			C934		
	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.	SE-19	SE-18	AVG.
Dioxins:																					
2378-TCDD	11.2	18.6	14.9	19.3	58.6	39.0	5.4	1.1	3.3	93.6	4.9	49.2	2.3	0	1.2	0	4.6	2.3	2.6	5.4	4.0
TCDD	11.2	18.6	14.9	19.3	9.1	14.2	6.2	1.1	3.7	80.0	1.1	40.6	12.9	3.9	8.3	0	6.1	3.1	2.8	1.6	2.2
PCDD	-	-	-	141.4	141.4	141.4	24.2	2.1	13.1	24.4	52.1	38.3	-	-	-	7.9	0	3.9	17.1	0	8.6
HCDD	48.2	33.7	41.0	46.0	28.6	37.3	8.0	0.8	4.4	17.4	2.9	10.2	12.4	2.6	7.5	5.7	0	2.8	0.9	0.9	0.9
HPCDD	15.7	0	7.9	1.4	16.2	8.8	1.1	0	0.6	46.0	43.9	45.0	0	6.1	3.1	0	5.2	2.6	4.9	0	2.4
OCDD	5.7	4.2	4.9	14.3	17.4	15.9	2.5	0	1.3	31.4	5.4	18.4	1.5	1.7	1.6	0	0	0	3.2	5.4	4.3
Furans:																					
2378-TCDF	3.4	141.4	72.4	17.7	33.5	25.6	3.2	7.1	5.2	42.2	141.4	91.8	4.9	0	2.4	7.9	5.7	6.8	8.8	6.7	7.9
TCDF	3.1	141.4	72.3	11.8	27.7	19.8	3.2	6.8	5.0	48.9	11.3	30.1	7.9	17.0	12.4	6.1	0.8	3.5	12.9	2.7	7.8
PCDF	26.9	78.0	52.4	19.9	81.9	50.9	4.5	4.5	4.5	22.2	12.9	17.6	2.0	29.5	15.8	0	3.4	1.7	20.2	1.6	10.9
HCDF	12.0	23.2	17.6	20.2	14.9	32.5	0.4	1.6	1.0	30.7	3.2	16.9	1.0	2.1	1.5	2.7	1.5	2.1	5.4	3.1	4.3
HPCDF	10.6	2.1	6.3	7.4	30.3	18.9	0	2.2	1.1	27.9	5.7	16.8	7.7	5.7	6.7	0	4.0	2.0	4.2	6.1	5.2
OCDF	6.1	3.3	4.7	0.8	21.6	11.2	2.0	0.8	1.4	35.8	18.0	26.9	5.1	4.2	4.6	0.9	2.8	1.8	1.0	9.0	5.0

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	5	25	0	2	8.0	Satisfactory
C005	30	3	27	1	3	14.8	Satisfactory
C018	30	0	30	0	0	0	Satisfactory
C019	30	0	30	5	1	20.0	Satisfactory
C024	24	4	24	0	4	16.7	Satisfactory
C030	30	0	30	0	0	0	Satisfactory
C034	30	0	30	1	0	3.3	Satisfactory

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	2	30	3	4	23.3	Satisfactory
C005	30	0	30	2	4	20.0	Satisfactory
C018	30	0	30	0	4	13.3	Satisfactory
C019	30	1	30	2	2	13.3	Satisfactory
C024	24	0	24	0	11	45.8	Moderate
C030	30	0	30	1	0	3.3	Satisfactory
C034	30	0	30	1	0	3.3	Satisfactory

Table 10.1. Comparison of interlaboratory median values between duplicate samples (SE-18).

Parameter	Concentration	Sample No.		Average Median	S.D.	RSD, %
		2	4			
Dioxins:						
2378-TCDD	pg/mL	290	285	287.5	3.5	1.2
T4CDD	pg/mL	396	380	388	11.3	2.9
P5CDD	pg/mL	202	241	221.5	27.6	12.4
H6CDD	pg/mL	730	760	745	21.2	2.8
H7CDD	pg/mL	1200	1150	1175	35.3	3.0
O8CDD	pg/mL	3800	4000	3900	141.4	3.6
Furans:						
2378-TCDF	pg/mL	100	110	105	7.1	6.7
T4CDF	pg/mL	640	634	637	4.2	0.7
P5CDF	pg/mL	778.5	1050	914.3	192.0	21.0
H6CDF	pg/mL	2146	2051	2098.5	67.2	3.2
H7CDF	pg/mL	3460	3400	3430	42.4	1.2
O8CDF	pg/mL	6250	7000	6625	530.3	8.0

Table 10.2. Comparison of interlaboratory median values between duplicate samples (SE-19).

Parameter	Concentration	Sample No.		Average Median	S.D.	RSD, %
		1	5			
Dioxins:						
2378-TCDD	pg/mL	285	280	282.5	3.5	1.3
T4CDD	pg/mL	290	340	315	35.3	11.2
P5CDD	pg/mL	182	266	224	59.4	26.5
H6CDD	pg/mL	683	800	741.5	82.7	11.2
H7CDD	pg/mL	1270	1400	1335	91.9	6.9
O8CDD	pg/mL	4300	4300	4300	0	0
Furans:						
2378-TCDF	pg/mL	170	140	155	21.2	13.7
T4CDF	pg/mL	440	790	615	247.5	40.2
P5CDF	pg/mL	909	932	920.5	16.3	1.8
H6CDF	pg/mL	1900	2295	2097.5	279.3	13.3
H7CDF	pg/mL	3600	3680	3640	56.6	1.6
O8CDF	pg/mL	7300	7200	7250	70.7	1.0

Fig. 1.1. Comparison between Mean and Median for Dioxins

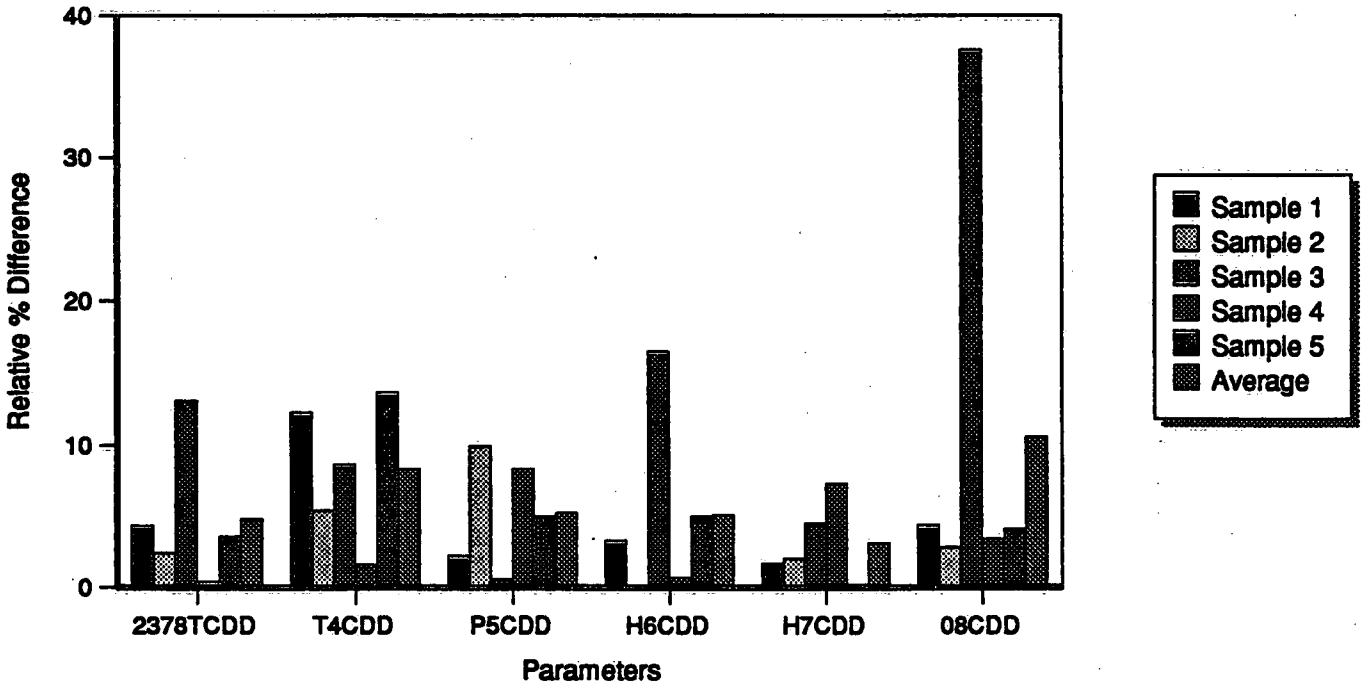
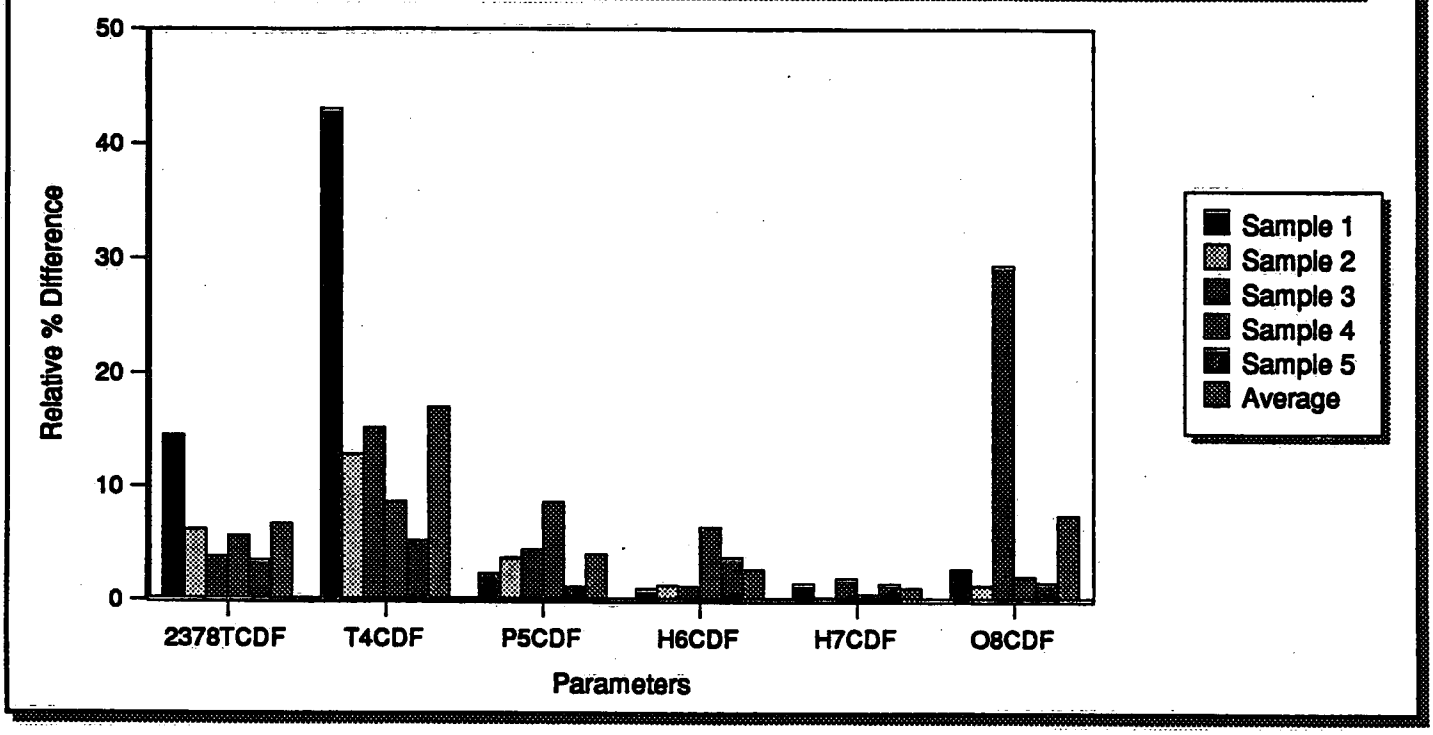


Fig. 1.2. Comparison between Mean and Median for Furans



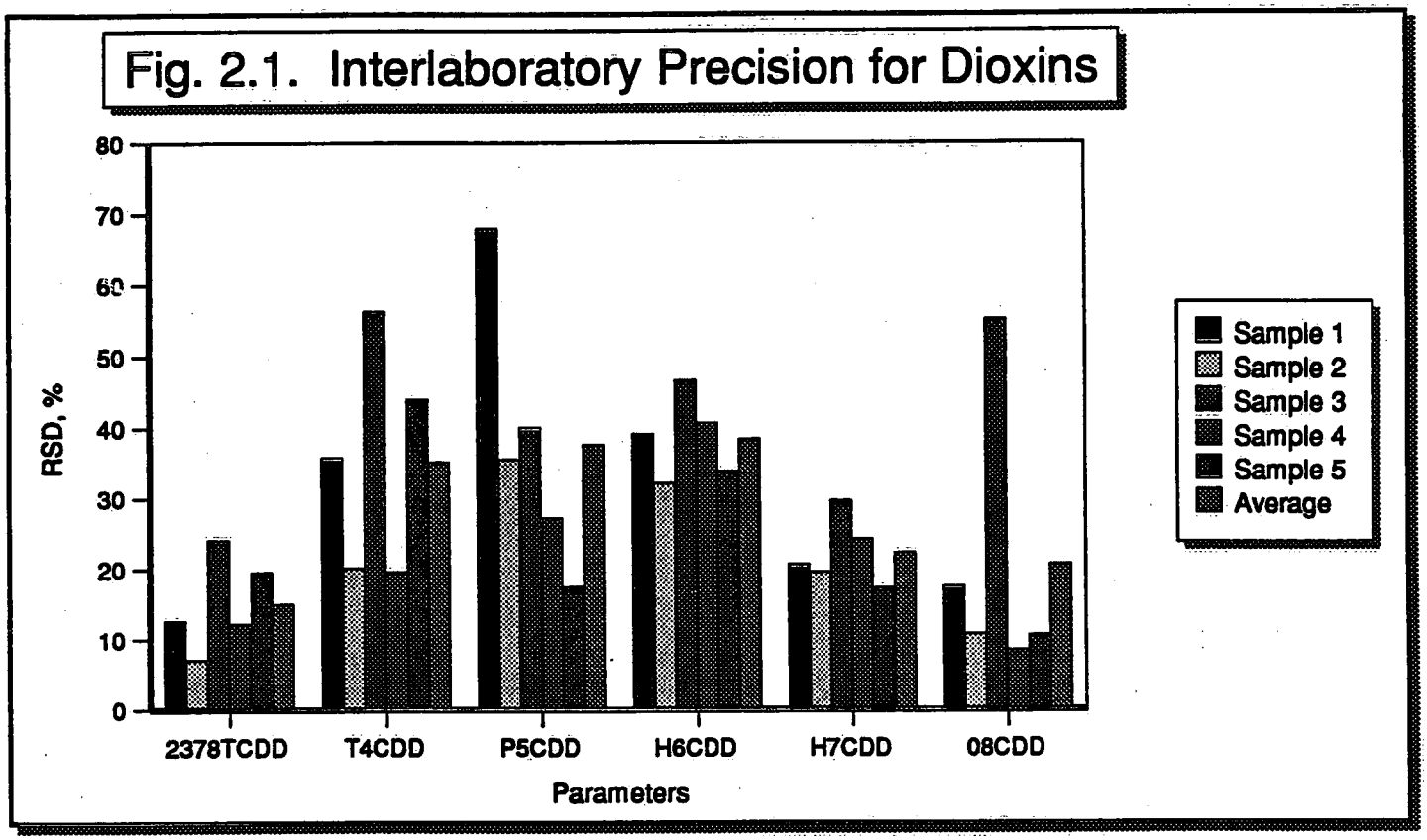


Fig. 2.1. Interlaboratory Precision for Dioxins
80
70
60
50
40
30
20
10
0
RSD, %
2378TCDD
T4CDD
P5CDD
H6CDD
H7CDD
08CDD
Parameters
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Average

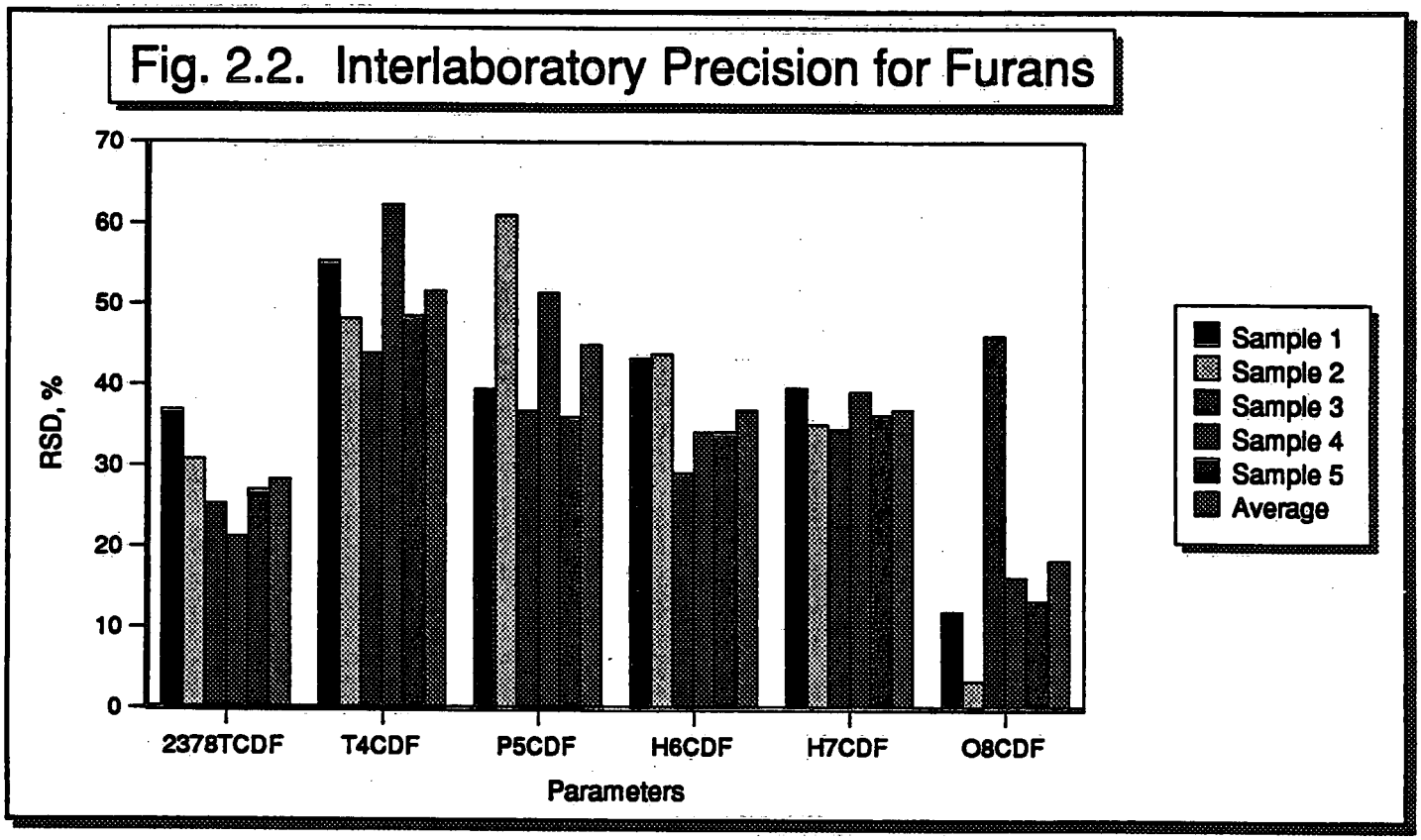


Fig. 2.2. Interlaboratory Precision for Furans
70
60
50
40
30
20
10
0
RSD, %
2378TCDF
T4CDF
P5CDF
H6CDF
H7CDF
O8CDF
Parameters
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Average

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	290	* 430	160	330	340
C005	250	290	100	* 120 L	190
C018	215	249	91.7	245	232
C019	* 110 L	300	* 340 H	280	* 540
C024	310	290	NA	290	300
C030	290	300	120	320	290
C034	280	270	100	250	270
MEAN	272.5	283.2	114.3	285.8	270.3
S.D.	34.3	20.0	27.6	35.0	53.0
MEDIAN	285	290	100	285	280

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	290	430	160	330	340
C005	250	290	100	330	190
C018	239	259	107	263	261
C019	194	396	421 H	390	700 H
C024	360	360	NA	380	300
C030	450	440	240	480	450
C034	510	450	280	440	490
MEAN	327.6	375	218	373.3	390.1
S.D.	117.2	75.5	122.6	73.1	171.7
MEDIAN	290	396	200	380	340

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	ND	ND	ND	ND	ND
C005	14 L	ND	ND	230	ND
C018	182	234	192	241	257
C019	194	156	87	338	275
C024	<80 L	<80 L	NA	<80 L	<80 L
C030	170	170	140	170	190
C034	370 H	330	240	330	290
MEAN	186	222.5	164.8	261.8	253
S.D.	126.3	79.3	66.0	71.3	44.1
MEDIAN	182	202	166	241	266

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	280 L	390	410	240 L	570
C005	560	730	360	1100	1100
C018	683	656	508	649	610
C019	732	915	1140 H	878	938
C024	680	540	NA	560	570
C030	1200	1100	880	1100	1300
C034	810	770	590	760	800
MEAN	706.4	728.7	648	755.3	841.1
S.D.	276.7	234.5	302.8	307.6	285.5
MEDIAN	683	730	549	760	800

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	1200	1200	790	1200	1500
C005	1000	780	360 L	620	980
C018	1270	1150	833	1150	1290
C019	870	1540	710	810	1710
C024	1300	1200	NA	1100	1300
C030	1600	1400	1000	1300	1600
C034	1500	1300	960	1300	1400
MEAN	1248.6	1224.3	775.5	1068.6	1397.1
S.D.	257.3	238.2	230.2	258.2	239.6
MEDIAN	1270	1200	811.5	1150	1400

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	3900	3300	2700	3500	3600
C005	4900	3200	6000 H	4100	* 6000
C018	3700	3360	2300	3360	3570
C019	2800	4100	7400 H	3800	4400
C024	4700	4100	NA	4200	4600
C030	4300	4000	2700	4000	4300
C034	4500	3800	2600	4100	4300
MEAN	4114.3	3694.3	3950	3865.7	4128.3
S.D.	717.5	396.9	2180.6	324.9	435.0
MEDIAN	4300	3800	2700	4000	4300

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	210	ND L	95	120	200
C005	180	74	69	120	140
C018	93.9	56.8	43.9	62.8	98.3
C019	54 L	ND L	86	84	100
C024	150	110	NA	110	140
C030	170	130	95	120	190
C034	170	100	74	110	150
MEAN	146.8	94.2	77.2	103.8	145.5
S.D.	54.2	29.0	19.5	22.1	39.4
MEDIAN	170	100	80	110	140

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	440	ND L	210 L	120 L	460
C005	930 H	740	560	1100	1100
C018	341	256 L	161 L	282 L	357 L
C019	384	540	426	634	790
C024	380	220 L	NA	280 L	340 L
C030	1100 H	840	560	850	1200
C034	1200 H	780	520	810	1000
MEAN	682.1	562.7	406.2	582.3	749.6
S.D.	378.5	271.1	178.5	362.7	364.2
MEDIAN	440	640	473	634	790

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	* 4700 H	* 4500 H	700	1300	* 3200 H
C005	670	480	360	1800	890
C018	905	667	580	711	964
C019	913	1622 H	1145	1948	1253
C024	340 L	190 L	NA	290 L	350 L
C030	1300	1000	880	1050	1300
C034	1200	890	690	910	900
MEAN	888	808.2	725.8	1144.1	942.8
S.D.	351.0	493.1	267.0	589.0	340.7
MEDIAN	909	778.5	695	1050	932

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

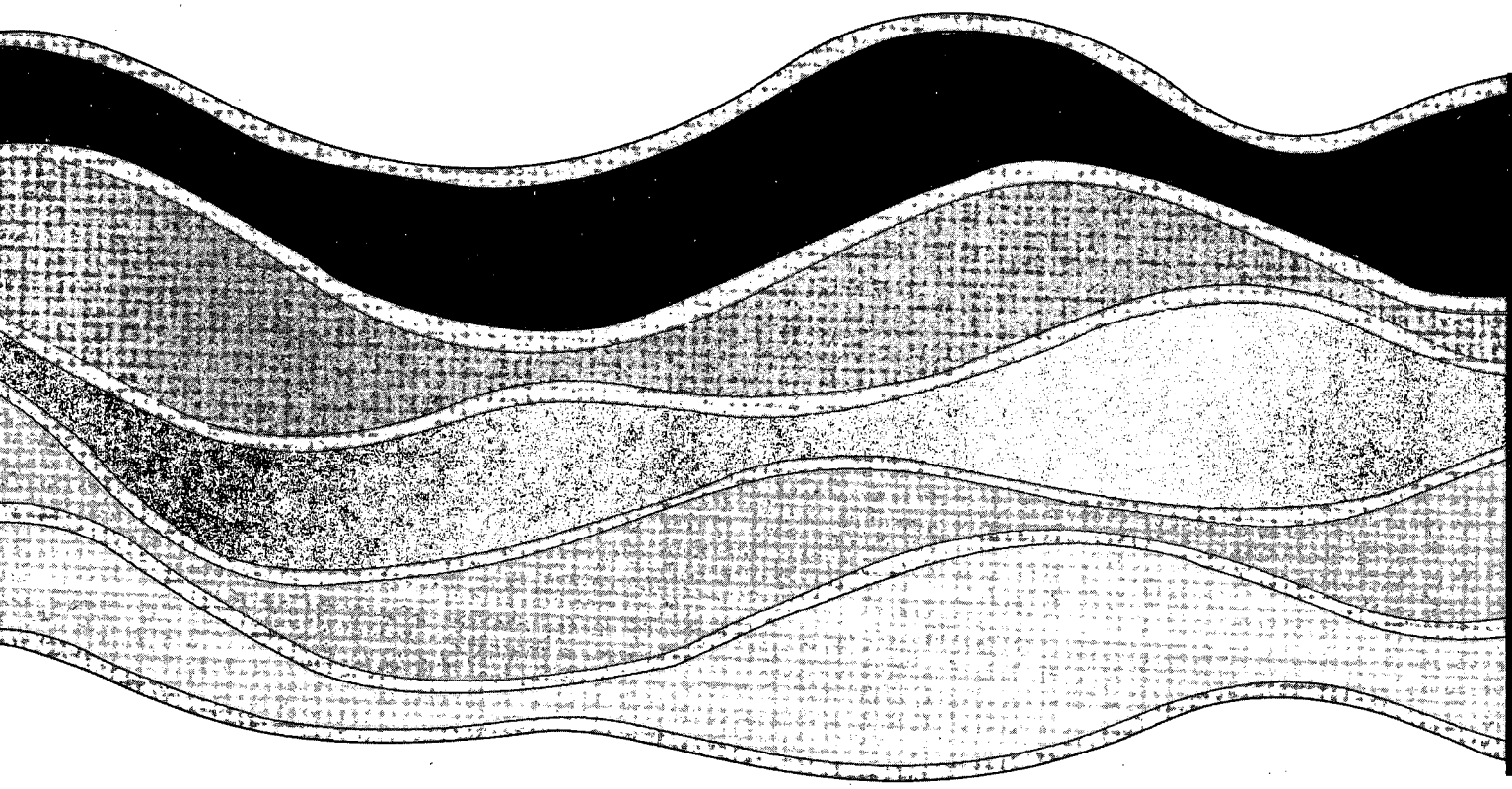
Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	2700	3900	1400	2800	3200
C005	1000	2100	970	1700	2100
C018	1900	1760	1340	1720	1890
C019	1477	2146	2274	2051	2295
C024	790 L	670 L	NA	690 L	780 L
C030	2600	2350	1900	2300	2700
C034	2700	2300	1900	2200	2500
MEAN	1881	2175.1	1630.7	1923	2209.3
S.D.	815.3	954.4	476.1	660.3	760.6
MEDIAN	1900	2146	1650	2051	2295

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	3600	3300	2600	3400	3100
C005	2000	1700 L	1600 L	1100 L	1800 L
C018	3680	3460	2910	3570	3680
C019	2560	3620	3780	3340	3820
C024	2600	2400	NA	2600	2900
C030	5950	5400	4800	5100	5950
C034	5200	4400	4000	4800	4900
MEAN	3655.7	3468.6	3281.7	3415.7	3735.7
S.D.	1455.4	1219.2	1140.2	1342.3	1364.3
MEDIAN	3600	3460	3345	3400	3680

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

Lab No.	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
C003	7200	6200	3900	6500	6600
C005	9000	6100	8700 H	8300	9100
C018	6640	6300	3510	6370	6830
C019	* 3700	6200	8700 H	4800	6200
C024	6700	6600	NA	7000	7200
C030	8100	* 7800	4200	7500	8000
C034	7400	6600	3700	7500	7300
MEAN	7506.7	6333.3	5451.7	6852.9	7318.6
S.D.	904.4	216.0	2526.5	1119.9	971.1
MEDIAN	7300	6250	4050	7000	7200



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