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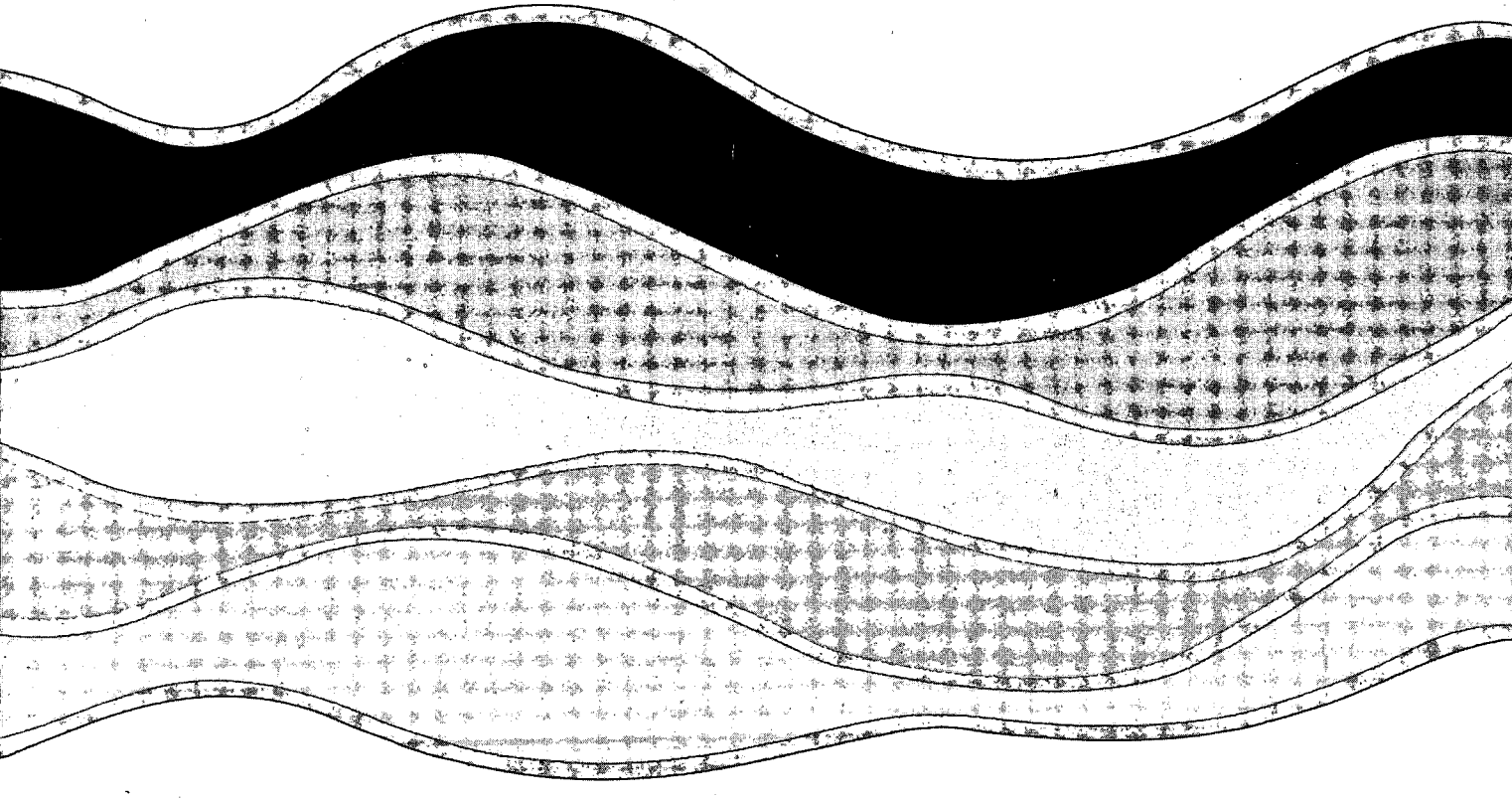

NATIONAL DIOXIN LABORATORY QC STUDY NO. 1 - The Analysis of Dioxins and Furans in Sediment

Yvonne D. Stokker, Eleanor A. Kokotich and Alfred S.Y. Chau

NWRI CONTRIBUTION 91-113

MANAGEMENT PERSPECTIVE

National Dioxin Interlaboratory Quality Control Study No.1 was conducted by the Quality Assurance Group at the National Water Research Institute to evaluate the quality and comparability of data generated by Canadian government and commercial laboratories for the analysis of polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans in naturally-contaminated sediments. As part of a larger national dioxin quality assurance program, one of the goals for this study was to assist Canadian laboratories in identifying analytical problems and improving their analytical performance on dioxin and furan analyses. Furthermore, the results from this series of interlaboratory round-robin studies would contribute to a continual and long-term database on laboratory performance that would, in future, serve as a preliminary screening criteria for potential commercial contracts for dioxin and furan analysis. Therefore, this national dioxin QA program would ultimately enable faster and more reliable response to environmental crises requiring this highly specialized type of analysis. The results from this first dioxin round-robin study indicate that, despite the many different methodologies and quantitation techniques being employed, there are several Canadian laboratories who have the capability of performing sensitive, accurate and comparable analyses for dioxins and furans in sediments. By providing an assessment of the capabilities of potential contract laboratories to perform these specific sediment analyses in a precise and accurate manner, this report may also be used as a guide for federal agencies in the granting of contracts to commercial laboratories for the testing of sediments for dioxins and furans.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVE-GESTION

L'étude nationale de contrôle de la qualité n° 1, portant sur les dioxines, a été menée par le Groupe chargé du programme d'assurance de la qualité à l'Institut national de recherche sur les eaux, afin d'évaluer la qualité et la comparabilité des données obtenues par des laboratoires gouvernementaux et commerciaux canadiens en ce qui concerne l'analyse des polychlorodibenzo-para-dioxines et des polychlorodibenzofuranes présents dans des sédiments naturellement contaminés. Dans le cadre d'un vaste programme national d'assurance de la qualité portant sur les dioxines, l'un des objectifs de la présente étude était d'aider les laboratoires canadiens à déterminer les problèmes d'analyse et à améliorer leur efficacité analytique pour ce qui est des dioxines et des furanes. De plus, les résultats de cette série d'études comparatives interlaboratoires alimenteront une base de données continue et à long terme sur l'efficacité des laboratoires qui servira, dans l'avenir, de critère de dépistage préliminaire pour l'octroi d'éventuels contrats commerciaux pour l'analyse des dioxines et des furanes. Ce programme national d'assurance de la qualité pour les dioxines permettrait donc, en fin de compte, de réagir plus rapidement et de façon plus fiable aux crises écologiques nécessitant ce type d'analyse hautement spécialisée. Les résultats de cette première étude comparative interlaboratoire pour les dioxines montrent que malgré les nombreuses méthodes et techniques de dosage différentes employées, plusieurs laboratoires canadiens peuvent effectuer des analyses sensibles, précises et comparables pour déceler des dioxines et des furanes dans les sédiments. En évaluant l'expertise d'éventuels laboratoires soumissionnaires chargés d'exécuter ces analyses particulières dans des sédiments, de manière précise et juste, le présent rapport peut également servir de guide aux organismes fédéraux pour l'attribution de contrats à des laboratoires commerciaux chargés de la recherche de dioxines et de furanes dans les sédiments.

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ABSTRACT

This report describes National Dioxin Interlaboratory QC Study No.1, the first in a series of intercomparison studies conducted by the Quality Assurance Group at the National Water Research Institute on the analysis of polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans in sediment. The purpose of the present study was to evaluate the quality and comparability of the data generated by commercial and government laboratories for the analysis of these highly toxic compounds in naturally-contaminated freeze-dried sediments. The analytical data submitted by eleven Canadian laboratories for National Dioxin Study No.1 were evaluated by various statistical treatments to identify outlying results and to assess laboratory performance with respect to precision, accuracy and bias. The dioxin data in this study were, for the most part, satisfactory, and showed favourable comparability between laboratories despite the multitude of different methodologies employed. The furan results were also satisfactory for several of the participants, but there were some extreme outliers among the results for the tetra- and heptachlorinated furans as well as several sets of biased data submitted for the pentachlorinated dioxins and heptachlorinated furans. A comparison of the different methodologies employed by the participants in this study is also presented in this report.

RÉSUMÉ

Le présent rapport décrit l'étude nationale du contrôle de la qualité interlaboratoire n° 1, portant sur les dioxines, la première d'une série d'études de comparaison interlaboratoire menée par le Groupe de l'assurance de la qualité de l'Institut national de recherche sur les eaux et portant sur l'analyse des polychlorodibenzo-para-dioxines et des polychlorodibenzofuranes dans les sédiments. La présente étude visait à évaluer la qualité et la comparabilité des données de laboratoires commerciaux et gouvernementaux concernant l'analyse de ces composés très toxiques dans des sédiments lyophilisés naturellement contaminés. On a évalué par divers traitements statistiques les données d'analyse présentées par onze laboratoires canadiens participant à l'étude nationale n° 1 portant sur les dioxines afin de déterminer les résultats aberrants et d'évaluer l'efficacité des laboratoires sur le plan de la précision, de la justesse et des erreurs. Dans la présente étude, les données sur les dioxines étaient, en grande partie, satisfaisantes, et elles présentaient une bonne comparabilité entre les laboratoires malgré la multitude de méthodes appliquées. Dans le cas des furanes, les résultats étaient également satisfaisants chez plusieurs participants, mais on a relevé certaines valeurs extrêmes aberrantes en ce qui concerne les tétrachlorofuranes et les heptachlorofuranes ainsi que pour plusieurs ensembles de données biaisées concernant les pentachlorodioxines et les heptachlorofuranes. On trouve également dans le présent rapport une comparaison portant sur les différentes méthodes utilisées par les participants à l'étude.

LIST OF TABLES

NATIONAL DIOXIN INTERLABORATORY QC STUDY NO.1
The Analysis of Dioxins and Furans in Sediment

by
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INTRODUCTION

Contaminated sediments have long been of great concern to many government agencies, environmentalists, toxicologists, and the general public alike. The discovery of several compounds from the closely-related families of polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in Canadian sediments and fish[1] stirred a flurry of activity in methods development throughout the last decade. These dioxins and furans entered the environment inadvertently, as byproducts from the synthesis of chlorinated phenols[1,2], from the manufacture of materials derived from chlorophenols and related materials[3], as a result of combustion processes including that of leaded gasoline[2], from domestic and industrial waste incineration[1,2], and from the bleaching of wood pulp[1,2]. The intense concern over the presence of these chemicals in the environment stems from their pronounced toxicity, especially that of the 2,3,7,8-tetrachlorodibenzo-para-dioxin isomer (2,3,7,8-TCDD), and from their potential to bioaccumulate up the foodchain due to their stability[2].

With the multitude of analytical methods being developed and used across Canada[4,5], there arose a question of the comparability of the dioxin and furan data being generated. Moreover, an external control system was lacking whereby the dioxin laboratories could validate their methods, verify their data and regularly monitor their analytical systems. To check the validity of their data, the individual laboratories could implement in-house quality control programs that included frequent analysis of standards of known concentration, the analysis of blank and spiked samples, repeats of samples showing high levels, replicate analyses and, if available, interlaboratory comparisons[1,6]. However, there were no external assurances for these laboratories to monitor and verify the quality of their in-house program on a regular basis. In particular, naturally-contaminated reference materials as quality control samples were lacking.

Therefore, in the late 1980's, a national dioxin quality assurance program was initiated to offer verification of comparability between the data generated by the many different Canadian laboratories, both within the government and in the private sector. One of the key components of this program was to be a series of interlaboratory studies, whose purpose would be:

(a) to assist Canadian laboratories in identifying analytical problems and improving their analytical performance;

(b) to enable faster response to environmental crises that needed dioxin/furan analyses; and

(c) to form a continual and long-term database on laboratory performance to serve as preliminary screening criteria for potential commercial contracts for dioxin and furan analysis.

Participation/non-participation would also be part of the laboratory evaluation criteria to be established at a later date. In addition to the above goals, the data generated by the participants in the round-robin studies would populate the databases being formed for several potential sediment reference materials for dioxins and furans. These materials would then be available to the study participants at a later date as check samples to confirm their analytical performance over time.

In January 1989, a survey of more than 200 Canadian government and private laboratories was conducted to assess the interest and capabilities of these laboratories to participate in the first dioxin interlaboratory study. One desirable element for participation in this study was the capability to complete the analysis of four sediment samples within two months. Samples were sent in early March to the seventeen qualified laboratories who had expressed an interest in participating, with a request for results by April 20, 1989. When only three sets of results were received by May 1, the study deadline was extended. By late July, eleven laboratories had provided full or partial results. A list of these participants is provided in Table 1.

This report, on National Dioxin Interlaboratory Study No. 1, evaluates the quality and comparability of the data submitted by eleven government and private laboratories for the analysis of dioxins and furans in sediment.

STUDY DESIGN

The identities and a brief description of the samples distributed in this study are given in Table 2. The sample set was comprised of four freeze-dried sediments that had been prepared at the National Water Research Institute (NWRI) in Burlington, Ontario. Samples #1 and #2 were identical subsamples of a blended material that had been fortified to 100 pg/g and 50 pg/g, respectively, with each of 2,3,7,8-TCDD and 2,3,7,8-TCDF. These two 'sediments' were a homogeneous blend of one part St. Basile-Le-Grand soil, collected in September 1988 from the vicinity of the PCB warehouse fire, and nine parts of a Lake St. Clair freeze-dried sediment. The mixing was accomplished according to a procedure established by the Quality Assurance group of NWRI and is described elsewhere[7]. The two congeners of interest were spiked into each individual subsample and mixed well. However, because these samples may not have been fully homogeneous with respect to the two spiked compounds, the participants were instructed to extract and analyze the entire contents of each jar for samples #1 and #2. Samples #3 and #4 were fully homogeneous, naturally-contaminated reference materials specially developed for trace organic analyses. Originating from the Great Lakes basin, they were naturally-contaminated with polynuclear aromatic hydrocarbons, PCBs, chlorobenzenes, and dioxins and furans. However, while the concentration levels of PAHs, PCBs and chlorobenzenes were well-established, previous dioxin and furan analysis of these materials had been limited. Consequently, the true concentrations of these latter parameters in the sediments were not known with absolute certainty.

The participants were requested to analyze the four sediment samples for 2,3,7,8-TCDD and 2,3,7,8-TCDF, and for tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and dibenzofurans, each homologue group in total. Surrogate recoveries were also requested. Each sediment was to be extracted and analyzed using the laboratory's own routine method of analysis and their own in-house calibration standards and quantitation techniques. Because the base material for samples #1 and #2 was identical, an estimate of precision could be made for the results provided by the participants for each homologue group total, except, of course, for the tetrachlorinated congeners.

RESULTS AND DISCUSSION

Analytical Methodologies

Summaries of the analytical procedures employed by the participants for the dioxin and furan analyses in this study are presented in Table 3. A wide variety of techniques were used by the different laboratories, primarily among the procedures used for cleanup of the raw extracts, as well as for the quantitative measurement of the parameters of interest.

The most commonly used method for extracting the dioxins and furans from the sediment samples in this study was by soxhlet apparatus. Only one participant used an agitation technique with an acetone/hexane mixture as the extracting solvent. Toluene was employed by six laboratories for their soxhlet extractions, while the other participants used benzene, dichloromethane, or a benzene/acetone blend. In one laboratory, the sediments were soxhlet-extracted twice, first using a hexane/acetone mixture, followed by toluene, and then the two extracts were combined before cleanup procedures were applied. One participant soxhlet-extracted their sediment samples with granular copper and two laboratories applied metallic mercury to their raw extracts after soxhlet extraction in order to remove some of the sulpher-containing contaminants. Two participants washed their sediment extracts with concentrated sulphuric acid and one applied a trisodium phosphate washing step to the raw extract. All other participants in this study used column chromatography only as cleanup procedures.

Each method described in this study used column chromatography on silica gel, neutral or basic alumina, carbon fibre columns, or various combinations of these adsorbents as the means to clean up the sediment extracts before analysis for dioxins and furans. As listed in Table 3, nine participants used multilayer columns with or without additional column cleanup steps, while two employed multiple columns in a sequential manner. Most of the multilayer columns exposed the dioxin and furan-containing extracts to acid-coated silica

gel followed by base-coated silica gel, while one also included a third layer of silica gel coated with silver nitrate. One of the multilayer columns was composed of acid-coated silica gel and alumina only. In short, all eleven laboratories included a step whereby the extract was cleaned to some extent of easily oxidized organics by exposure to acid-coated silica gel, while all but two of the eleven methods also included base-coated silica gel. The two participants who did not use base-coated silica gel, employed gel permeation chromatography as a preliminary cleanup procedure prior to their other column cleanup steps. Seven of the eleven participants included silver nitrate, coated on either silica gel or alumina, to eliminate sulpherous compounds from the extracts. Six participants employed neutral alumina and four used basic alumina to isolate the polychlorinated dioxins and furans from other potential interferents such as PCBs. A final polishing step with a carbon-fibre column of one type or another was used by five participants before analysis of the extracts.

For the detection and quantitation of the dioxins and furans, seven laboratories used GC-MSD techniques while four employed GC/MS. All participants analyzed their extracts on bonded phase DB-5 columns, or equivalent. Eight of the eleven laboratories in this study used 25 or 30 meter columns and the remaining three employed 60 meter columns. Of the latter three, two were narrowbore columns and one was a widebore column. Six of the 25-30 meter columns were narrowbore and two were widebore columns. Refer to Table 3 for details. All six participants who quantitated the dioxins and furans by internal standard methods, corrected their results for surrogate recoveries. Among the five participants who used the external method of calibration for quantitation, two did not correct their results for surrogate recoveries. Inspection of the sediment sample results in this study gave no clear indication of which technique or column provided more accurate dioxin and furan results.

Data Evaluation

The raw data submitted by the participants for the dioxins and furans in the four sediment samples are listed in Tables 4 to 11. Only one laboratory did not analyze for the individual 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners, but all laboratories reported results for each of the homologue group totals requested. Interlaboratory means and medians were determined for each homologue group using all data reported by the participants (except the 'less than' values with high detection limits). Outliers were not rejected when calculating these medians since most of the results fell within a two to three-fold range. The majority of interlaboratory means agreed with the median results. The discrepancies occurred primarily among the pentachlorinated dioxins and heptachlorinated furans where strong biases were significant. The widest ranges of results were found among the data for the tetra- and heptachlorinated furans where outlying results were more predominant. The most comparable data in this study were submitted for 2,3,7,8-TCDD and for total T4CDD. In general, comparability between laboratories was significantly greater among the dioxin data than among the furan data.

Accuracy of the data submitted in this study was evaluated in two ways. The first was by assessing the participants' recoveries of spiked amounts of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the first two samples. The base material for these samples was a soil/sediment composite mix that had previously been shown to be free of, or to contain, at most, only very low levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF. This material was then fortified with each of the two compounds of interest to 100 pg/g and 50 pg/g, for samples #1 and #2, respectively. Because the background levels of this composite sediment may have included some 2,3,7,8-TCDD and 2,3,7,8-TCDF, the percent recoveries listed in Table 14 were calculated relative to the interlaboratory medians rather than to the expected concentrations from the spikes only. As can be seen in this table, most participants in this study submitted results that were within 30% of the interlaboratory medians in each sample.

The second way of assessing the data for accuracy was by means of a flagging procedure described more fully in Appendix I. 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 then, 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. Tables 15 and 16 provide summaries of each laboratory's performance with respect to accuracy, based on the percentage of their results that were flagged. In Table 15, it can be seen that laboratories F066 and F089 received flags on nearly 40% of their dioxin results while Table 16 highlights the higher percentages of flagged data reported by laboratories F058, F065 and F088 for their furan analyses.

Intralaboratory precision could not be fully assessed in this study because blind duplicate sediments were not included in the set of four samples. However, samples #1 and #2 were prepared from the same composite sediment, and only the 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations were altered by fortification in the two samples. One of the recommendations made by the Joint Federal/Industrial Dioxin Quality Assurance Committee for the analysis of dioxins and furans is that for blind duplicate samples, "relative percent differences must agree to within ±50% for TCDD, TCDF, OCDD and OCDF".[1] Because two of the tetrachlorinated congeners had been spiked into samples #1 and #2, precision in this study could therefore only be assessed on the two octachlorinated congeners. The relative percent difference between OCDD in samples #1 and #2 was less than 50% for all participants in this study except laboratory F089, while all participants achieved better than 30% repeatability on their OCDF analyses.

Bias was determined by the technique of Youden ranking, as described in Appendix I. The bias statements listed for each laboratory in Table 17 refer to the tendency of their entire set of results for that particular parameter or homologue series to be higher or lower than those of the other participants in the study. In this study, all participants except laboratory F061 provided

biased data for at least one of the congener groups. Laboratory F061, however, did not analyze sample #2, nor did they report results for 2,3,7,8-TCDD and 2,3,7,8-TCDF. The furan data submitted by laboratory F058 was biased in three of the homologue groups, while laboratories F066 and F089 submitted biased results on three or more of the dioxin parameters. Generally, these statements of biased results are strong evidence of systematic error and are the specific areas that the laboratories should look to for improvement. Over the entire homologue series for both dioxins and furans, the data submitted by laboratory F065 tended to be considerably higher than those provided by the other participants. Overall, laboratory F058 reported the lowest furan results and both laboratories F058 and F066 generally submitted lower results for the dioxins than the other participants. These comments are graphically presented in Figure 1, where the participating laboratories have been placed according to their total rank, in windows of ten percentile ranges. The position of each laboratory relative to the others, represents a general ranking of overall bias for each of the dioxin and furan sets of analyses.

Being able to reliably measure contaminants at trace and ultra-trace levels involves coping with a variety of problems common to all types of analysis close to the limits of detection. It is of interest to note, therefore, that the participants' method detection limits (MDLs) listed in Table 12, cover a more than 1000-fold range for several of the homologue group totals. These large ranges can be partly attributed to variations in the size of samples, the laboratories' capabilities and experience in dealing with complex samples, variations in the effectiveness of their individual cleanup procedures for handling the removal of interfering substances in the sediments, and the different means of quantifying the parameters of interest. Some of these values listed in Table 12, however, represent a generalized statement of detection limit capabilities under optimum conditions (e.g. minimal number of matrix interferences), while other participants reported their detection limits for each of the specific samples undergoing analysis. Examples of optimum MDLs would be those reported by laboratories F065 and F066 who reported detection capabilities for dioxin and furan homologue totals that

were as much as 200-fold lower than their submitted 'less than' values for some of the homologue totals in sediments #3 and #4. Nevertheless, it is encouraging to see that most of the other laboratories were able to achieve detection limits close to those recommended by the Dioxin Quality Assurance Advisory Committee (DQAAC), and which are also listed in Table 12. These target MDLs 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".[6] For high resolution mass spectrometry, they expected MDL values to be 20-fold lower. In their report, "Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples"[6], the DQAAC also recommended a sample size of 5 grams for dry sediment, soil, sludge or ash, and a final volume of 20 uL for the injection-ready extract, in order to maximize capabilities for detection limit analyses.

Since sample size may be limited, the ability to analyze for dioxins and furans at very low levels, requires that recoveries be as high as possible even though enrichment and cleanup must also be very stringent to avoid chromatographic interferences. The amount of analyte lost during sample extraction and cleanup may be reflected in the percentage recovery of the spiked surrogates and is one of the reasons for correcting the data for surrogate recoveries. Table 13 provides a listing of the surrogate recoveries reported by the participants for the four sediment samples in this study. In the DQAAC[6] document referred to above, it was recommended, on the basis of the practical experiences of several government and commercial laboratories, that the acceptable range for surrogate recoveries from all matrices except tissue should be 30-130%. Beyond these limits, it was suggested that the samples should be reprocessed and reanalyzed. In this study, it was encouraging to see that the majority of the reported surrogate recoveries were within this 30-130% range. However, half of the surrogate recoveries reported by laboratory F033 for samples #3 and #4 were less than 30%, and laboratory F061 reported 22-26% recovery of all five of their surrogate standards in sample #4. It is interesting to note that this latter participant was one of the two laboratories who did not correct their data for surrogate recoveries. It may

be significant, then, that they also reported the lowest results for the native dioxins and furans in sample #4. This seems to indicate that they may have experienced problems with extraction and/or cleanup of this sample. On the other hand, it was noted in another round-robin dioxin study conducted by the QA group at NWRI, "that the surrogate recoveries do not necessarily reflect the quality of the recoveries of the compounds in question".[7] These authors further suggested that "care should be taken in interpreting the results of surrogate recoveries, in using surrogate recoveries as a QC practice, and in the application and practice of surrogates".[7]

In the performance evaluation database that will be set up at NWRI for the National Dioxin QA Program, participation in these dioxin interlaboratory studies will be an important consideration to ensure that all samples generated can be analyzed efficiently by laboratories of known competence. Nevertheless, while it will be the quality of the data that is of the utmost importance, it must be recognized that these procedures are complicated, time-consuming and involve the use of complex and sensitive instrumentation. Therefore, for a laboratory's performance to indicate thorough competence, they must demonstrate that they are able to provide quality results in an efficient and timely manner. In this study, most participants provided full or partial results within four months of having received the sediment samples, and only five Canadian laboratories who requested samples did not submit any results.

CONCLUSION

Despite the various extraction and cleanup procedures and the different quantitative techniques used by the participants, the dioxin data in this study were, for the most part, satisfactory and comparable. The data submitted for the analysis of furans in the sediment samples were also satisfactory for several of the participants, but were generally not as comparable as those for the dioxins. Some extreme outlying results were submitted by a few of the participants, especially for the tetra- and heptachlorinated furans. Strong biases were most apparent among the data reported for the pentachlorinated dioxins and heptachlorinated furans. Only one laboratory, in particular, submitted data that was consistently higher than those of the other participants for both the dioxins and furans. Our rating system for evaluating laboratory performance in this study is tentative and is based in part on the assumption that the interlaboratory medians target the true concentrations of the dioxins and furans in these sediment samples. Thus, each laboratory was rated for accuracy relative to the performance of the other participants. However, some of the limitations to this technique occur with laboratories which do not provide complete sets of data, or which submit a large number of 'not detected' results.

At the present time, the analysis of dioxins and furans is universally accomplished by GC-MSD and GC/MS techniques which utilize the elution parameters (retention time) of high resolution gas chromatography to provide isomer specificity within a given homologue, while the mass spectrometer provides the required sensitivity and specificity for class (dioxin vs. furan) and homologue group (chlorine no.). On the other hand, the extraction and cleanup procedures are as individual as the laboratories themselves. Nevertheless, it was beyond the scope of this study to recommend one method over another. It is recognized that different laboratories have developed a variety of sample workup procedures applicable to specific sample matrices and analyte concentration ranges and that these methodologies are tailored to the

needs of their particular GC/MS or GC-MSD instrumentation. It has been reported elsewhere[1] that, in most cases, the sample workup and the GC/MS technique form a 'matched set', and suboptimal results are obtained when the cleanup procedure favoured by one laboratory is applied without modification for determination by another laboratory's GC/MS technique. It was not the purpose of this study to seek out relationships between the generation of quality data and methods of analysis. Rather, the data assessment provided in this report, should identify common trends and problems experienced by the majority of the participants in their dioxin and furan analyses, yet should also highlight individual biases or inaccuracy in the results submitted by each participant relative to those of their peers. Future studies in the National Dioxin Interlaboratory QA Program will provide additional information on these sediment samples and will address improvements (or declines) in the quality of data generated by these laboratories in their analyses for dioxins and furans.

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Table 1. List of Participants in National Dioxin QC Study No. 1.

Federal Government:		
1.	Environment Canada C&P (EPS) Laboratory Services River Road Environmental Technology Centre Ottawa, Ontario	
2.	Environment Canada National Water Quality Laboratory Burlington, Ontario	
3.	Environment Canada National Water Research Institute Analytical Chemistry Research, RAB Burlington, Ontario	Results requested for samples #3 and #4 only
Provincial Governments:		
4.	Gouvernement du Québec Ministère de l'Agriculture, des Pêcheries et de l'Alimentation Sainte-Foy, Québec	No results submitted
5.	Gouvernement du Québec Ministère de l'Environnement Laboratoire de Montréal St-Vincent-de-Paul (Laval), Québec	
University Laboratories:		
6.	Kyung Hee University School of Medicine Department of Preventive Medicine Seoul, Korea	No results submitted
7.	University of Manitoba Department of Soil Science Pesticide Research Laboratory Winnipeg, Manitoba	No results submitted
Private Laboratories:		
8.	B.C. Research Corporation Vancouver, B.C.	Requested and received a second set of samples #3 and #4

continued

Table 1 (continued). List of Participants in National Dioxin QC Study No. 1.

9. Chemex Labs Alberta Inc. Calgary, Alberta	No results submitted
10. ELI EcoLaboratories Inc. Rockwood, Ontario	
11. Enviro-Test Laboratories Edmonton, Alberta	No results submitted for sample #2
12. Mann Testing Laboratories Ltd. Mississauga, Ontario	
13. Novalab Ltée Lachine, Québec	
14. OceanChem Group Dartmouth, Nova Scotia	No results submitted
15. Wellington Environmental Inc. Guelph, Ontario	
16. Whiteshell Research Pinawa, Manitoba	No results submitted
17. Zenon Environmental Inc. Burlington, Ontario	

Table 2. Description of Samples.

Sample #	Identification Code	Origin
1	Q-1 #2*	fortified St. Basil-Le-Grand/Lake St. Clair sediment
2	Q-1 #1**	fortified St. Basil-Le-Grand/Lake St. Clair sediment
3	EC-2	blended Lake Ontario sediments
4	EC-3	Niagara River Plume sediment

* Sample 1 was a 1:10 blend of St. Basil-Le-Grand soil:Lake St. Clair sediment fortified with 100 pg/g each of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

** Sample 2 was a 1:10 blend of St. Basil-Le-Grand soil:Lake St. Clair sediment fortified with 50 pg/g each of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Note: All samples were freeze-dried sediments prepared at the National Water Research Institute.

Table 3. Summary of Methodologies for the Analysis of Dioxins and Furans in Sediments.

Lab no.	Extraction	Cleanup	Analysis & Quantitation*
F033	soxhlet-extracted with toluene; Hg cleanup	multi-layer acid/base silica column; alumina column; carbon-fibre column	splitless GC-MSD; 30m x 0.2mm Ultra-2; ISTD, corrected for recoveries
F058	agitation with (30+70) acetone/hexane; wash with H_2O, then H_2SO_4, then H_2O	acid silica column; base silica column; two sequential $AgNO_3$/alumina columns	splitless GC-MSD, SIM mode; 30m x 0.32mm SPB-5; ISTD, corrected for recoveries
F061	soxhlet-extracted with benzene	multi-layer acid/base silica column; $AgNO_3$ column; alumina column	GC-MSD, SIM mode; 60m x 0.25mm Rtx-5; ESTD, uncorrected for recoveries
F065	soxhlet-extracted with toluene	multi-layer neutral/acid/neutral/base/neutral silica column	on-column GC/MS, SIM mode; 30m x 0.32 mm DB-5; ESTD, corrected for recoveries
F066	soxhlet-extracted with CH_2Cl_2	multi-layer neutral/acid/neutral/base/neutral silica column; $AgNO_3$/silica column; basic alumina column	splitless GC-MSD, MID mode; 60m x 0.32mm DB-5; ISTD, corrected for recoveries
F077	soxhlet-extracted with toluene	multi-layer neutral/acid/neutral/base/neutral silica column; $AgNO_3$/silica column; basic alumina column	on-column GC-MSD, SIM mode; 30m x 0.25mm DB-5; ESTD, uncorrected for recoveries
F088	soxhlet-extracted with (1+1) benzene/acetone	multi-layer acid/base/$AgNO_3$ silica column; basic alumina column; carbon column	splitless GC/MS, SIM mode; 30m x 0.25 mm DB-5; ISTD, corrected for recoveries
F089	sediment + granular copper soxhlet-extracted with (40+60) hexane/acetone; then soxhlet-extracted with toluene (extracts combined)	GPC on SX-3; multi-layer acid silica/alumina column; glass fibre/carbon column	GC-MSD; 25m x 0.2mm HP-5; ESTD, corrected for recoveries
N090	soxhlet-extracted with toluene	multi-layer acid/base silica column; $AgNO_3$/silica column; basic alumina column	on-column GC/MS; 60m x 0.25mm DB-5; ISTD, corrected for recoveries
N122	soxhlet-extracted with (1+1) acetone/benzene; wash with H_2SO_4	multi-layer neutral/acid/neutral/base/neutral silica column; $AgNO_3$/silica column; alumina column; CARBOPAK C/Celite column	splitless GC/MS, SIR mode; 30m x 0.25mm DB-5; ESTD, corrected for recoveries
N187	soxhlet-extracted with toluene; wash with 0.05M $Na_3PO_4 \cdot 12H_2O$; Hg cleanup	GPC; alumina column; acid silica column; carbon-fibre polish	GC-MSD; 25m x 0.2mm DB-5; ESTD, corrected for recoveries

* Quantitation techniques: (1) ESTD (external standard) vs. ISTD (internal standard);
(2) "corrected/uncorrected" refers to whether reported data has/has not been corrected for surrogate recoveries.

Table 4: DIOXIN Results (pg/g) for Sample 1 **

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	Total PCDD
F033	108	108	<20	<25	113	355	576
F058	97	97	<26	<23	100	260	457
F061	-	107	<67	<87	152	967 H	1226
F065	110	110	<50	<110	190	540	840
F066	48 L	48 L	<25	<22	170	380	598
F077	130	130	<150	<120	<160	370	500
F088	125	125	<19	23	159	795	1102
F089	83	83	9.4	38	220	700	1050
N090	91	91	<61	<58	132	473	696
N122	150	150	<10	<10	88	280	518
Interlab Mean	105	105	*	*	147	512	756
SD	30	28	*	*	43	237	280
Interlab Median	108	108	*	*	152	427	647

* not detected by majority of participants
** fortified with 100 pg/g each of 2,3,7,8-TCDD & 2,3,7,8-TCDF

See Appendix I for an explanation of codes for tables 4-12.

Table 5: DIOXIN Results (pg/g) for Sample 2 **

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	Total PCDD
F033	52	52	<20	<25	120	415	587
F058	130	130	<26	<23	87	290	507
F061	-	-	-	-	-	-	-
F065	90	90	<20	<44	140	450	680
F066	22 L	22 L	<18	<21	120	240	382
F077	81	81	<160	<130	<170	380	461
F088	73	73	<19	24	200	874 H	1171
F089	44	54	13	47	420 H	2100 H	2634 H
N090	40	40	<61	<58	125	421	586
N122	84	84	<10	<10	99	270	453
Interlab Mean	68	70	*	*	164	604	829
SD	33	32	*	*	109	591	715
Interlab Median	73	73	*	*	123	415	586

* not detected by majority of participants
** fortified with 50 pg/g each of 2,3,7,8-TCDD & 2,3,7,8-TCDF

Table 6: DIOXIN Results (pg/g) for Sample 3

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	Total PCDD
F033	355	443	129	322	1546	3520	5960
F058	270	270	45 L	590	1300	3100	5305
F061	-	293	<67	811	1387	4537	7028
F065	510	720	<570	<1100	2700	4500	7920
F066	<160 L	<1100	<600	<230 L	1500	2000 L	3500
F077	490	540	150	650	1600	4700	7640
F088	396	396	119	740	2240	6690	10185
F089	140 L	330	1100 H	2700 H	3800 H	7300	15230 H
N090	281	353	<61 L	573	1191	4388	6505
N122	500	500	130	590	910	2900	5030
N187	320	420	156	663	1367	4192	6798
Interlab Mean	362	427	261	849	1776	4348	7373
SD	125	134	372	707	834	1558	3130
Interlab Median	355	408	129	620	1500	4388	6798

Table 7: DIOXIN Results (pg/g) for Sample 4

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	Total PCDD
F033	353	481	133	396	2354	4486	7850
F058	310	310	79	140 L	1800	3700	6029
F061	-	179 L	<67	454	877 L	2542	4052
F065	510	620	<1000	<1800	2000	4700	7320
F066	<150 L	<1500	<2200	<340 L	2200	4000	6200
F077	420	420	130	880	2300	6600	10330
F088	259	274	75	733	1950	7620	10652
F089	140 L	400	860 H	3200 H	2700	6200	13360
N090	301	380	<61 L	774	1347	4479	6980
N122	580	580	160	660	1100	3600	6100
N187	379	551	185	915	1408	4349	7408
Interlab Mean	361	420	232	906	1821	4752	7844
SD	132	141	280	896	573	1481	2629
Interlab Median	332	410	130	733	1950	4479	7320

Table 8: FURAN Results (pg/g) for Sample 1 **

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	Total PCDF
F033	127	127	<20	<25	<50	80	207
F058	100	100	<11	<15	28 L	83	211
F061	-	111	<105	<131	86	383 H	580
F065	120	240	<120	<110	460 H	140	840 H
F066	83	120	<12	<67	88	88	296
F077	110	110	<60	<140	<80	140	250
F088	335 H	335 H	<27	107	265 H	662 H	1369 H
F089	120	160	3.8	47	79	110	400
N090	146	316 H	211	109	74	101	811 H
N122	99	110	18	<10	49	100	277
Interlab Mean	138	173	*	*	141	189	524
SD	76	90	*	*	148	189	380
Interlab Median	120	124	*	*	79	106	348

* not detected by majority of participants
** fortified with 100 pg/g each of 2,3,7,8-TCDD & 2,3,7,8-TCDF

Table 9: FURAN Results (pg/g) for Sample 2 **

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	Total PCDF
F033	65	65	<20	<25	<50	81	146
F058	68	68	<11	<15	22 L	79	169
F061	-	-	-	-	-	-	-
F065	56	170 H	<50	<44	460 H	120	750 H
F066	38	38	<14	<19	68	66	172
F077	52	52	<60	<150	<80	170	222
F088	252 H	252 H	61	129	289 H	654 H	1385 H
F089	110	170 H	9.7	41	76	120	417
N090	62	62	28	<30	<86	90	180
N122	61	71	19	35	45	99	269
Interlab Mean	85	105	*	*	160	164	412
SD	66	74	*	*	176	186	412
Interlab Median	62	68	*	*	68	99	222

* not detected by majority of participants
** fortified with 50 pg/g each of 2,3,7,8-TCDD & 2,3,7,8-TCDF

Table 10: FURAN Results (pg/g) for Sample 3

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS						
	2,3,7,8-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	Total PCDF
F033	188	1239 H	665	1469	3514	6699	13586
F058	95	95 L	210 L	4000 H	1600 L	7100	13005
F061	-	213	403	1940	3634	8660	14850
F065	140	790 H	2000 H	<1100	11000 H	9600	23390
F066	110	650	770	1500	2200	3400 L	8520
F077	88	150 L	620	3700 H	3000	13000	20470
F088	100	150 L	375	1280	3330	10500	15635
F089	59	390	1000	1200	3500	4100	10190
N090	135	446	700	1805	3511	7604	14066
N122	53	160 L	670	1800	2100	7600	12330
N187	106	402	529	1090	2553	5940	10514
Interlab Mean	107	426	722	1978	3631	7655	14232
SD	40	350	474	1027	2540	2763	4399
Interlab Median	103	390	665	1650	3330	7600	13586

Table 11: FURAN Results (pg/g) for Sample 4

Laboratory No.	HOMOLOGUE GROUP CONCENTRATIONS					
	2,3,7,8-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF	Total PCDF
F033	171	1294	765	1944	4066	8252	16321
F058	130	203 L	150 L	2400	800 L	7100	10653
F061	-	<115 L	261 L	1116	2224	4498	8099
F065	157	940	1500	<1800	10000 H	9400	21840
F066	170	950	1100	2400	4900	6400	15750
F077	170	920	1100	3800	5300	16000	27120
F088	134	305 L	320 L	1360	3710	14200	19895
F089	93	600	550	1600	3700	6800	13250
N090	184	712	944	2236	3995	8900	16787
N122	82	280 L	830	2000	2700	9700	15510
N187	169	741	552	1320	3001	8402	14016
Interlab Mean	146	695	734	2018	4036	9059	16295
SD	35	352	414	777	2340	3362	5249
Interlab Median	163	712	765	1972	3995	8402	15750

Table 12. Detection Limits (pg/g).

Lab No./ Sample No.*	Dioxins						Furans					
	2,3,7,8-TCDD	T4CDD	P5CDD	H6CDD	H7CDD	O8CDD	2,3,7,8-TCDF	T4CDF	P5CDF	H6CDF	H7CDF	O8CDF
F033	15	15	20	25	50	75	15	15	20	25	50	75
F058	20	20	26	23	24	27	16	16	11	15	19	19
F061	21-92	21-92	47-67	51-87	48-99	88-140	22-115	22-115	77-105	42-131	36-121	69-187
F065	18	18	18	29	70	70	18	18	18	29	70	70
F066	7.5	7.5	10	11	12	16	6.3	6.3	8.3	10	11	15
F077-1	50	50	150	120	160	110	40	40	60	140	80	130
F077-2	60	60	160	130	170	120	40	40	60	150	80	140
F077-3	30	30	80	70	90	60	20	20	40	80	40	80
F077-4	40	40	70	70	90	80	20	20	30	80	70	120
F088-1&2	13	13	19	18	31	64	80	21	27	51	156	123
F088-3&4	12	12	24	14	25	45	14	14	11	13	12	34
F089	2	2	2	4	4	4	2	2	2	2	2	4
N090	15-22	15-22	44-61	41-58	32-45	50-78	8-15	8-15	11-23	17-30	60-86	43-66
N122	10	10	10	10	20	20	10	10	10	10	20	20
N187	10-15	10-15	10-15	10-15	10-15	30-45	10-15	10-15	10-15	10-15	10-15	30-45
Target MDLs for LRMS**	-	12	24	24	36	48	-	12	24	24	36	48

* The detection limits listed apply to all samples unless the laboratory specified different limits for each sample.

** 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.

Table 13. Sample Size, Final Volume and Surrogate Recoveries.

Lab No./ Sample No.	Sample Size (g)	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
F033-1	5.0	25	88	85	73	-	45	35	-	-	-
F033-2	5.0	25	82	89	75	-	62	55	-	-	-
F033-3	5.0	25	58	38	23	-	20	20	-	-	-
F033-4	5.0	25	82	82	44	-	28	22	-	-	-
F058-1	5.00	10	94.2	-	-	-	-	101	-	-	-
F058-2	4.99	10	86	-	-	-	-	127	-	-	-
F058-3	10.0	10	82.6	-	-	-	-	124	-	-	-
F058-4	10.0	10	93.2	-	-	-	-	103	-	-	-
F061-1	5.0	100	46	59	-	67	77	77	-	-	-
F061-3	5.1	100	49	48	-	50	53	50	-	-	-
F061-4	5.0	100	22	26	-	25	24	26	-	-	-
F065-1	5	50	55	-	-	-	-	54	-	-	-
F065-2	5	50	130	-	-	-	-	124	-	-	-
F065-3	5	50	121	-	-	-	-	85	-	-	-
F065-4	5	50	58	-	-	-	-	73	-	-	-
F066-1	5.004	25	79	-	-	100	-	115	-	-	-
F066-2	5.002	25	69	-	-	70	-	73	-	-	-
F066-3	10.001	25	148	-	-	104	-	105	-	-	-
F066-4	10.03	25	93	-	-	120	-	170	-	-	-
F077-1	5.0	50	96.7	95.2	-	-	98.2	91.8	100	95.9	92.9
F077-2	5.0	50	94.8	90.6	-	-	95.4	85.0	98.4	96.0	88.8
F077-3	10.0	50	94.4	107	-	-	107	103	102	107	102
F077-4	10.0	50	97.9	98.8	-	-	122	123	97.8	98.8	114
F088-1	4.98	20	69	87	-	101	95	65	33	-	-
F088-2	4.99	20	61	79	-	87	86	57	29	-	-
F088-3	5.00	20	59.8	74.0	-	101	107	86.2	54.9	-	-
F088-4	5.01	20	64.7	79.8	-	98.2	103	73.8	65.8	-	-
F089-1	5.00	20	78	85	-	85	86	86	-	-	-
F089-2	4.99	20	92	95	-	95	89	70	-	-	-
F089-3	10.20	20	76	38	-	80	50	65	-	-	-
F089-4	10.13	20	94	56	-	83	65	67	-	-	-
N090-1	5	25	64	64	-	63	61	63	74	-	-
N090-2	5	25	68	64	-	67	62	61	72	-	-
N090-3	5	50	89	85	-	88	85	81	122	-	-
N090-4	5	25	62	67	-	59	59	62	88	-	-
N122-1	5.0	25	70	78	-	96	128	123	-	-	-
N122-2	5.0	25	63	74	-	90	120	114	-	-	-
N122-3	5.0	25	61	59	-	77	124	122	-	-	-
N122-4	5.0	25	75	102	-	144	111	107	-	-	-
N187-3	5.020	25	79	73	81	-	82	50	-	-	-
N187-4	5.108	25	78	81	94	-	116	88	-	-	-

- not used in surrogate mixture

Table 14. % Recovery of 2,3,7,8-TCDD and 2,3,7,8-TCDF in Samples #1 and #2.

Lab no.	Sample #1		Sample #2	
	2,3,7,8-TCDD	2,3,7,8-TCDF	2,3,7,8-TCDD	2,3,7,8-TCDF
Spike (pg/g)	100	100	50	50
Mean (pg/g)	105	138	68	85
Median (pg/g)	108	120	73	62
F033	100	106	71	105
F058	90	83	178	110
F065	102	100	123	90
F066	44	69	30	61
F077	120	92	111	84
F088	116	279	100	406
F089	77	100	60	177
N090	84	122	55	100
N122	139	83	115	98

Note: % Recoveries were calculated to the interlaboratory medians.

Table 15. Summary of Dioxin Results Flagged to the Interlaboratory Medians.

Lab no.	Total No. of Results Reported	No. of Results "Not Detected"	No. of Ranked Results*	No. of Flags		% Flagged**
				H	L	
F033	28	4	28	0	0	0
F058	28	4	28	0	2	7
F061	18	4	18	1	2	17
F065	28	8	24	0	0	0
F066	28	12	24	0	9	38
F077	28	6	26	0	0	0
F088	28	2	28	1	0	4
F089	28	0	28	9	2	39
N090	28	6	28	0	2	7
N122	28	4	28	0	0	0
N187	14	0	14	0	0	0

* "Less than" values reported with high detection limits could not be ranked by the Youden method.

** $\%\ \text{Flagged} = \dfrac{\text{No. Flags}}{\text{No. Ranked Results}} \times 100$

Table 16. Summary of Furan Results Flagged to the Interlaboratory Medians.

Lab no.	Total No. of Results Reported	No. of Results "Not Detected"	No. of Ranked Results*	No. of Flags		% Flagged**
				H	L	
F033	28	6	26	1	0	4
F058	28	4	28	1	8	32
F061	18	3	18	1	2	17
F065	28	6	26	9	0	35
F066	28	4	28	0	1	4
F077	28	6	26	1	1	8
F088	28	1	28	10	3	46
F089	28	0	28	1	0	4
N090	28	2	27	2	0	7
N122	28	1	28	0	2	7
N187	14	0	14	0	0	0

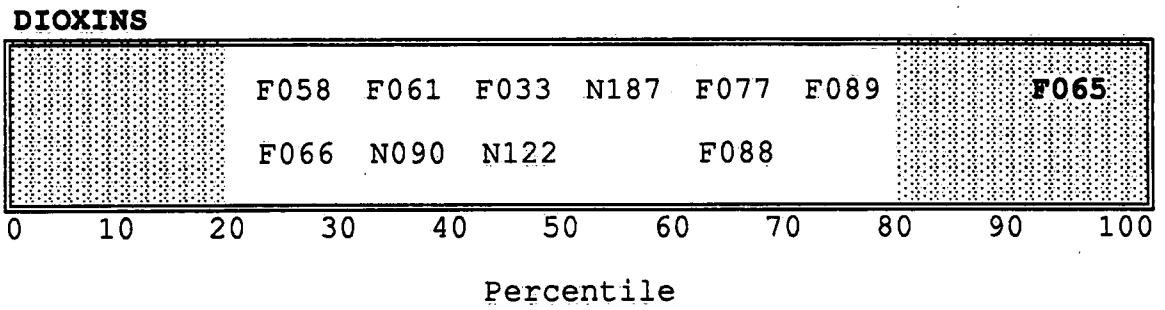
* "Less than" values reported with high detection limits could not be ranked by the Youden method.

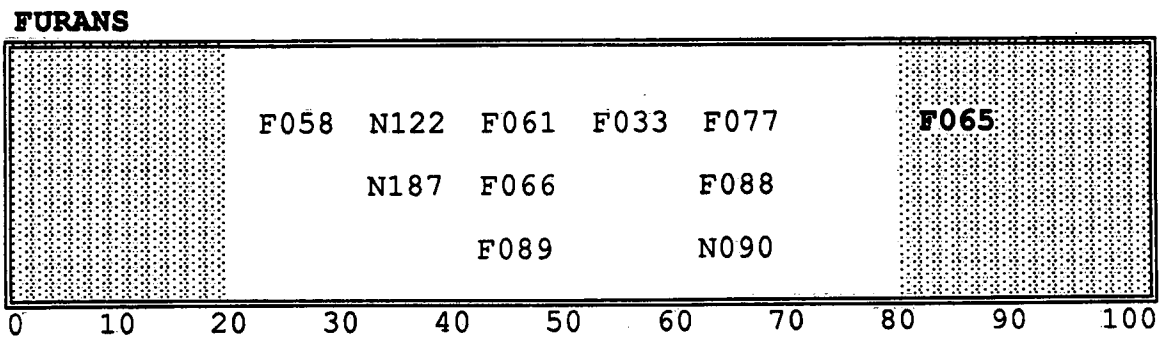
** $\%\ \text{Flagged} = \dfrac{\text{No. Flags}}{\text{No. Ranked Results}} \times 100$

Table 17. Summary of Bias Statements.

Lab no.	Comments
F033	biased high on H7CDF
F058	biased low on P5CDF and H7CDF biased high on H6CDF
F061	did not analyze sample #2 did not analyze for 2,3,7,8-TCDD or 2,3,7,8-TCDF no bias determined for remaining parameters
F065	biased high on P5CDF and H7CDF
F066	biased low on 2,3,7,8-TCDD, T4CDD and H6CDD
F077	biased high on H6CDF
F088	biased high on O8CDF
F089	biased high on P5CDD, H6CDD, H7CDD and Total PCDD
N090	biased low on P5CDD
N122	biased low on H7CDD
N187	biased low on H6CDF biased high on P5CDD

Figure 1. Summary of Total Ranks.





APPENDIX I

Glossary of Terms and Symbols

Legend for Tables 4-12:

-	not analyzed
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
T4CDD	total tetrachlorinated dibenzo-p-dioxin isomers
P5CDD	total pentachlorinated dibenzo-p-dioxin isomers
H6CDD	total hexachlorinated dibenzo-p-dioxin isomers
H7CD	total heptachlorinated dibenzo-p-dioxin isomers
O8CDD	octachlorodibenzo-p-dioxin
Total PCDD	total polychlorinated dibenzo-p-dioxin congeners = Σ (T4CDD + P5CDD + H6CDD + H7CDD + O8CDD)
2,3,7,8-TCDF	2,3,7,8-tetrachlorodibenzofuran
T4CDF	total tetrachlorinated dibenzofuran isomers
P5CDF	total pentachlorinated dibenzofuran isomers
H6CDF	total hexachlorinated dibenzofuran isomers
H7CDF	total heptachlorinated dibenzofuran isomers
O8CDF	octachlorodibenzofuran
Total PCDF	total polychlorinated dibenzofuran congeners = Σ (T4CDF + P5CDF + H6CDF + H7CDF + O8CDF)

Explanation of Terms for Data Evaluation Techniques:

A set of results is said to be biased when the set exhibits a tendency to be either higher or lower than some standard. The standard which has been used in the analysis of our studies thus far has been the performance of all other participating laboratories. The ranking procedure employed in testing for bias and the rationale for evaluating laboratories' performances by ranking results are described in more detail elsewhere[9-11] but a brief synopsis is presented below. In our use of the procedure, there is about one chance in twenty of deeming a set of results biased, when in fact it is not, (i.e. α=0.05).

Ranking is a non-parametric statistical technique used for the detection of pronounced systematic error (bias) in interlaboratory studies. According to Youden's procedure[9], rank 1 is given to the laboratory that provided the lowest result, rank 2 to the next lowest. In the case of a tie, the average rank is given to the tied laboratories. Results with a "<" (less than) sign are generally not ranked. In this study, however, the extremely low detection limits provided by some participants for their "not detected" results, allowed ranking of these particular low values. For each parameter, (or in the case of the dioxins and furans, each homologue series of isomers), the total rank of a laboratory is the sum of the individual ranks they received for that parameter in each sample. In the present case of the dioxins and furans in National Dioxin Study No.1, statistically, the permissable score limits for eleven laboratories and four test samples are 7 and 41 (for a full set of data at 5% probability). A laboratory with a score lower than 7 is identified as biased low for that particular set of data. Similarily, a laboratory with a total rank higher than 41 is identified as biased high. In both cases, their results are classified as outliers. In cases where a laboratory did not provide all of the results, or where some of the results were not ranked, the average rank instead of total rank was used for the determination of bias statements.

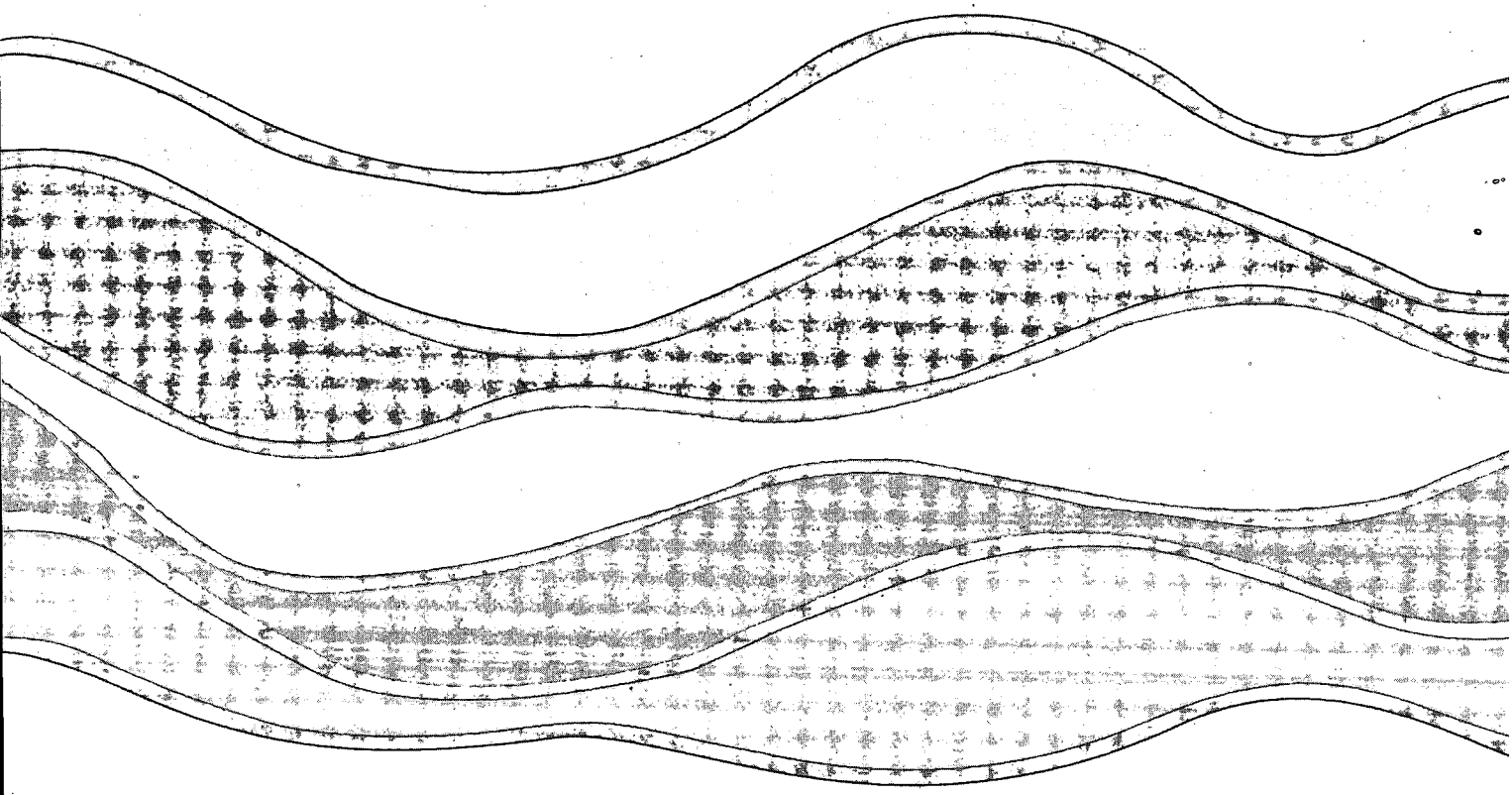
The more comparable laboratories should have ranks in the middle rather than on the extreme ends. However, laboratories with middle ranks did not necessarily provide more consistent results since very high results (high ranks) and very low results (low ranks) would average out to yield a total rank close to the middle. Therefore, ranking alone is not sufficient to determine the performance of a laboratory.

Flagging: When the true values of constituents in test samples are unknown, individual results can be evaluated by a peer group assessment technique in terms of their absolute differences from the interlaboratory medians. A more detailed discussion on this evaluation technique has been reported elsewhere[10]. Medians are chosen rather than means since they are not influenced by a moderate number of extreme values.

In order to assess the dioxin and furan results provided by each laboratory in this study, a modified approach to the technique of flagging was used. Arbitrarily, 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. Hence, the individual results were evaluated according to the following rating groups:

High (H)	$X > 2$ (Median)
Satisfactory (no flags)	$\frac{1}{2}$(Median) $\leq X \leq 2$ (Median)
Low (L)	$X < \frac{1}{2}$ (Median)

It is important to remember that some participants may appear to have provided satisfactory results (i.e. having received few flags), yet they may have submitted an incomplete set of results, a large number of 'not detected' values, and/or be biased for one or a number of parameters. Furthermore, because the results were flagged relative to the interlaboratory medians, this assessment is a peer appraisal technique and the "% flagged" ratings are therefore dependent on the assumption that the median values had established the correct target values.



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