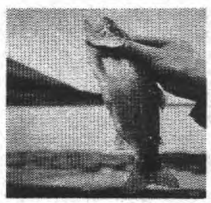
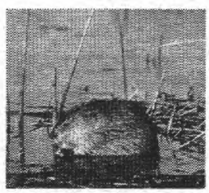
Canada Alberta Northwest Territories

Northern River Basins Study



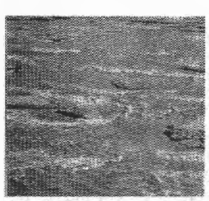




NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 141

QUALITY ASSURANCE AND QUALITY CONTROL RELATED TO ENVIRONMENTAL SAMPLES FOR THE NORTHERN RIVER BASINS STUDY






Prepared for the
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by

S. Ramamoorthy

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

NORTHERN RIVER BASINS STUDY
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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

F. J. Wrona — 14 May 96
(Dr. Fred J. Wrona, Science Director) (Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
this publication has been reviewed for scientific content and that the scientific practices represented in the report are acceptable given the specific purposes of the project and subject to the field conditions encountered.
SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [ ] No

P. A. Larkin — 24 May/96
(Dr. P. A. Larkin, Ph.D., Chair) (Date)

Whereas the Study Board is satisfied that this publication has been reviewed for scientific content and for immediate health implications,
IT IS HERE APPROVED BY THE BOARD OF DIRECTORS THAT;
this publication be released to the public, and that this publication be designated for: **[ ] STANDARD AVAILABILITY [ ] EXPANDED AVAILABILITY**

Lucille Partington — May 29/96
(Lucille Partington, Co-chair) (Date)

Robert McLeod — May 21/96
(Robert McLeod, Co-chair) (Date)

QUALITY ASSURANCE AND QUALITY CONTROL RELATED TO ENVIRONMENTAL SAMPLES FOR THE NORTHERN RIVER BASINS STUDY

STUDY PERSPECTIVE

Laboratory analyses of animal, water, and sediment samples for various substances provides a snap shot of the condition of the ecosystem. By studying the variation amongst samples over time researchers can begin to gain some insight into the impact of various changes in the study area. The validity of the analytical data measured at trace and ultra trace levels is critical to many of the present day assessments. Results can be questioned due to methodology differences between laboratories, non-adherence to established protocols, lack/poor documentation procedures and differing Quality Assurance/Quality Control (QA/QC) procedures. As the results from the laboratory analyses are taken as absolutes, it is extremely important the Northern River Basins Study (NRBS) have a sufficiently high level of confidence in the results to draw reliable interpretations that could withstand scrutiny. QA/QC programs provide users the assurance that the data are reliable and can be used with confidence.

One of the first steps taken by the NRBS was to perform an inter-laboratory performance evaluation prior to awarding analytical contracts to private analytical laboratories. The evaluation was to:
1) ensure strict adherence to the specified QA requirements, 2) ensure complete documentation and defensibility of the reported data, 3) compare the performance of low resolution mass spectrometry (LRMS) with high resolution mass spectrometry (HRMS) in the analysis of dioxin and furan in environmental samples, 4) use a scoring system to evaluate the reported data in terms of detection limit, recovery of spikes, deviation from the mean, as well as expected concentrations, and 5) rank the participating laboratories for their analytical performance.

Related Study Questions

1a)	*How has the aquatic ecosystem, including fish and /or other aquatic organisms, been affected by exposure to organochlorines or other toxic compounds?*
1b)	*How can the ecosystem be protected from the effects of these compounds?*
2)	*What is the current state of the water quality of the Peace, Athabasca and Slave river basins, including the Peace-Athabasca Delta?*
4a)	*What are the contents and nature of contaminants entering the system and what are their distribution and toxicity in the aquatic ecosystem with particular reference to water, sediments and biota?*
4b)	*Are toxic substances such as dioxin, furan and mercury etc. increasing or decreasing their rate of change?*
5)	*Are the substances added to the rivers by natural and man-made discharges likely to cause deterioration of the water quality?*
8)	*Recognizing that people drink water and eat fish from these river systems, what are the current concentrations of contaminants in water and edible fish tissue and how are these levels changing through and by location?*

Samples were sent to the various laboratories and analyzed for 2,3,7,8-PCDD/PCDF congeners, polyaromatic hydrocarbons (PAH's), polychlorinated biphenyls (PCB's) including coplanar PCB's, resin acids, chlorinated phenols, and metals. The laboratories were evaluated on closeness to mean concentrations, closeness to expected concentrations, surrogate recoveries, detection limits, sample handling program, dedicated laboratory facilities, subcontracted work, high resolution mass spectography (HRMS) results versus low resolution mass spectography (LRMS), additional QA/QC effort, non-detect data that was detected by other laboratories, flexibility and treatment of outliers. Laboratory results were also reviewed throughout the study by the Laboratory Performance Committee (LPC) using similar methods.

The results of the laboratory analyses provided the basis for the analysis and recommendations provided by the Contaminants Group. Without reliable data on contaminants and other substances, their recommendations would not be defensible. This document complements NRBS Project Report No. 142 (*A Database of Environmental Samples Collected and Analysed for the Northern River Basins Study*).

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1.0 INTRODUCTION

Due to increased activity in the environmental monitoring field, analytical data are being generated by several laboratories including government, university, private and industrial laboratories. Reports are being generated from different groups at much faster rates than before. On the one hand, it is encouraging to note the intensity of monitoring activity provides public information on what chemicals they are exposed and from which medium of the environment. On the other hand, the intense activity is also a matter of real concern regarding the validity of analytical data generated at trace and ultra-trace levels. The main reason for such a concern stems from methodology differences, non-adherance to established protocols, lack of/ poor documnetation procedures and differing QA/QC porcedures used in various laboratories. In addition, in a multi-agency, multi-year study like the Northern River Basins Study (NRBS), strict adherance to protocols for sampling biotic and abiotic matrices , preservation at site of collection, transporting samples to storage facilities, receiving and storing samples frozen (-25 C) prior to pre-analytical preparation and analysis are critical to ensure the integrity of samples. It should be borne in mind that data are only as good as the samples.

For this study (NRBS), protocols were written for sample preservation at site and for transportation to Edmonton where they were received by assigned personnel to ensure chain of custody. Samples were transferred immediately to a cold storage facility. The details are discussed elsewhere in this report.

Analytical sensitivity has increased by more than a million-fold in the last decade. The problems associated with low level detection are the variances between laboratories, poor precision within a laboratory and the lack of the level of confidence required. Unfortunately, these numbers are taken as absolute concentrations and occassionally trigger regulatory actions and incresed public concerns.

QA/QC programs validate the analytical performance of laboratories and provide for users the quality assurance of data generated. Even little data with quality assurance is superior to vast data with no quality assurance which renders them useless because the quality of data is not known. End-uses of data such as synoptic survey of comtaminants, ecological effects assessment and human exposure asessment require different levels of quality, with the highest quality needed for human health risk assessment.

2.0 INTERLABORATORY PERFORMANCE EVALUATION STUDY -I

The analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in environmental samples involves complex steps in the preanalytical and analytical stages prior to data generation. The steps include exhaustive extraction of the organic contaminants from environmental samples followed by cleanup of the extract using multi-column separation protocol to free PCDDs and PCDFs from interfering chemicals and other contaminants and ending with a quantitative analysis which is very specific for the compounds under investigation.

The extensive QA protocol described in this report evolved from the work of an analytical group created by Environment Canada's Dioxin Task Force and the two interlaboratory studies conducted by the Task Force (ref. 1). The objectives of this interlaboratory performance Evaluation Study are:

1. To ensure strict adherence to the specified QA requirements;
2. To ensure complete documentation and defensibility of the reported data;
3. To compare the performance of low resolution mass spectrometry (LRMS) with high resolutiom mass spectrometry (HRMS) in the analysis of dioxins and furans in environmental samples;
4. To use a scoring system to evaluate the reported data in terms of detection limit, recovery of spikes, deviation from the mean, as well as expected concentrations; and
5. To rank the participating laboratories for their analytical performance.

2.1 STUDY DESIGN

2.1.1 Check Samples

The four fish samples used as check samples in this study were obtained from the Federal Department of Fisheries and Oceans (DFO), Burlington, Ontario. Three samples were Reference Materials (RMs) whose concentrations for PCDD/PCDF congeners had been determined by replicate analyses. The mean concentrations of the four QA samples as provided by DFO are given in Table 1.

Each participating laboratory received four fish QA samples and three solutions in sealed glass ampoules. The solutions were analytical standard, surrogate spiking solution, and performance standard to be used for all analyses (obtained from Cambridge Isotope Laboratories, Massachusetts, U.S.A.).

Analytical (or Quanititation) Standard Solution

Table 2 lists the 16 native PCDDs and PCDFs, five ^{13}C-labelled PCDDs ranging from tetra-to-octa CDDs, one ^{17}Cl-labelled PCDD ($^{17}Cl_4$-2,3,7,8-T_4CDD) and one ^{13}C-labelled PCDD ($^{13}C_{12}$-1,2,3,4-T_4CDD) contained in the analytical standard solution. The quantitation ions and confirmation ions specified (Table 2) for all labelled and native standards and surrogates were to be used across the

tetra-to-octa range. The analytical procedures protocol (Appendix A) discusses in detail the use of the analytical standard solution and the quantitation procedure.

^{13}C-Labelled Surrogate Spiking Solution

Table 3 lists the ^{13}C-labelled PCDDs contained in the surrogate spiking solution and their concentrations. The analytical procedures protocol stipulated that surrogate recoveries were to be specified for each congener group and that all PCDD and PCDF results were to be corrected for surrogate recovery (Appendix A).

Performance (Internal) Standard Solution

^{13}C-Labelled PCDD ($^{13}C_{12}$-1,2,3,4-T_4-CDD) was used in the performance (internal) standard solution and a known volume was added to the "cleaned-up" fish extract as a recovery check just prior to analysis. The concentration of the performance standard is given in Table 4.

The standards used were for specific purposes: analytical standards for quanititation; surrogate solution for checking recovery of PCDDs from the given matrix; and the performance standard for checking recovery in the analytical stage, in particular gas-chromatography mass spectrometry (GC-MS) stage. Thge acceptable recovery ranges for the surrogate standards are given in Table 5.

All these solutions were to used in all analyses. Use of these standards was found to minimize interlaboratory variations and produce comparable analytical data for a given sample between participating laboratories (ref. 1).

2.2 PROTOCOL

The criteria for PCDD/PCDF identification, quantitation, calculation of detection limits, additional QA requirements, and data reporting and evaluation procedures were given in a detailed protocol provided to each participating laboratory (Appendix A).
For example:

2.2.1 Quantitation

Table 2 details the composition of this analytical standard and the ion masses to be monitored for determining sample results. If a $^{13}C_{12}$-T_4CDD surrogate recovery falls outside the acceptable recovery range (Table 5), the sample must be re-analyzed with the m/e 328 of the ^{37}Cl-labelled surrogate being monitored instead. This was of mutual benefit to NRBS and the participating laboratory in that the interference on the primary tetra-dioxin surrogate may not distort the percent recovery of the secondary tetra-surrogate. Alternatively the 328 ion should be routinely monitored in all samples to eliminate the need for re-analysis.

Laboratories had the option of using either internal or external standard procedures for quantitation using this mixture, however internal standard quantitation is preferred.

For quantitation by the internal standard method, the isotopically labelled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors owing to differences in injected volume and unnoticed variations in instrumental sensitivity.

2.2.2 Detection Limits

The detection limit were to be reported for all sample results, not just for not-detected (N.D.) values. The concentration units to report detection limit must be the same as those used for the samples. Detection limits were to be corrected for surrogate recovery. Table 6 lists the detection limits which were to be met for the data to be considered acceptable for the Interlaboratory Performance Study # 1.

Five laboratories participated in this Interlaboratory Performance Evaluation Study # 1. One of the laboratories agreed to analyze for dioxins and furans in fish tissues by both LRMS and HRMS. Three laboratories used LRMS only and one other laboratory used HRMS only. In total, there were four LRMS data and two HRMS data.The five laboratories were identified by assigned numbers for this study. The true identity of the participating laboratories was kept strictly confidential.

Three standard solutions in sealed glass ampoules, and four check samples of fish tissues properly preserved with refrigeration materials were sent to the participating laboratories by the third week of October 1990. Each laboratory was requested to analyze the fish check samples for PCDDs and PCDFs. The standard solutions provided were to be used in all analyses. The laboratories were requested to return a signed letter stating whether the samples and solutions were received in good condition or not. The letter also committed the laboratory to: (1) deliver results in the required format as requested by NRBS on or before November 30, 1990; (2) the understanding that results delivered after November 30, 1990 might not be included in the performance evaluation; and (3) agree to conditions of proper disposal of unused samples and standards, record keeping, data reporting, etc., as specified under Section II of the detailed analytical protocols
(Appendix A).

The following is a brief summary of the protocol and the data report format which were sent along with the QA samples to each laboratory.

BRIEF SUMMARY OF THE PROTOCOL FOR THE INTERLABORATORY PERFORMANCE EVALUATION STUDY I

Enclosed you will find four (4) fish tissue samples (15g each) and three (3) solutions in sealed glass ampoules. For the purpose of this check sample program, your laboratory is required to analyze the fish tissue samples for chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). The

solutions provided (analytical standard, surrogate spiking, performance standards) must be used for all analyses.

The data obtained for each sample are to be typed on the attached report form. Specific 2,3,7,8-substituted congeners must be individually reported along with congener group totals.

The composition of the analytical standard solution, surrogate spiking solution and performance standard solution are given in Tables 1, 2 , 3 respectively.

Each sample is to be spiked with 100 microlitres of the surrogate spiking solution prior to extraction. Prior to GS/MS analysis, the 'cleaned up' fish tissue extract is to be reconstituted with a known volume of the performance standard solution. **Please note** that if cleaned-up extracts are reconstituted with exactly 20 microlitres of the performance standard solution, the concentrations of the surrogates in the extracts would be equivalent to the concentrations of the surrogates in the analytical standard solution (assuming 100% recovery). Acceptable recovery range for the surrogate standards are given in Table 5 and Table 6 gives the detection limits which must be met for data to be considered acceptable.

For each tissue sample, the information requested on the form must be provided along with the raw GC/MS data for all standards and samples. The peaks identified as PCDDs and PCDFs must be clearly marked on the GC/MS data.

The equations used for calculating concentrations of PCDDs and PCDFs in the sample must be provided as well as the calculation sheets.

Please enclose with the final data:

1. a brief description of the methods used;
2 a description of the GC/MS system used, the operational parameters and the acquisition system;
3. the capillary column(s) used; and
4. a description of the method used for calculating detection limits.

For details, refer to the enclosed protocol.

2.3 FACTORS CONSIDERED IN THE EVALUATION OF ANALYTICAL PERFORMANCE

One of the first concerns of a major study such as NRBS who had to contract out their analytical work was how to choose a private laboratory or laboratories. For PCDDs and PCDFs, this presented a challenge because no certified reference materials were available at the time when the study was conducted (1990). The challenge was overcome by using ' Reference Materials'. These were fish samples provided by the Department of Fisheries and Oceans, Burlington, Ontario, experienced in

PCDDs and PCDFs analyses. These samples had previously been analyzed for PCDDs and PCDFs and the mean concentration of all congeners are given in Table 1. Results from previous analyses of these samples are referred to in this report as 'expected values'.

2.3.1 Analytical Performance Factors

1. Closeness to Mean Concentrations

The fish check samples used in this study were not certified reference materials (CRMs). Since the five contract laboratories participated in this study are all experienced laboratories and employed similar methodologies for this work, the mean concentrations of PCDDs and PCDFs congeners from different determinations should represent the best estimates of the true concentrations.

2. Closeness to the Expected Concentrations

Comparison of the closeness of the interlaboratory results with the expected values for the fish check samples used in this study represents another way to check analytical performance.

3. Surrogate Recoveries

One of the most important quality control operations of PCDDS and PCDFs determinations involves adding stable-isotope labelled surrogates to the samples before extraction. In the final GC-MS analysis, the amount remaining in the sample of each surrogate is determined, and expressed as a percent of the initial amount added. For PCDDs and PCDFs determinations, surrogate reecoveries in the range of 40 - 120% are considered excellent.

4. Detection Limits

To perform analyses of hundreds of samples for dioxins and furans, the analytical laboratory chosen must be able to consistently achieve low parts per trillion (10^{-12} g/g).

2.3.2 Other Factors

1. Sample Handling Plan

The contract laboratory must have an effective plan for sample receiving, storage and processing. Holding time during sample receiving must be minimized, and tissue samples must be properly refrigerated during storage prior to extraction.

2. Dedicated Laboratory Facilities

Dedicated facilities guarantee better performance and reduced possibility of sample contamination. It is not always possible for a contract laboratory to dedicate expensive GC-MS instrumentation to

a single project, but it is a common practice to analyze samples in batches of similar types. The equipment and laboratory space used for low-level dioxin/furan work must be dedicated for this project for the entire duration, or special precautions must be taken to ensure no cross-contamination of samples of different types can occur (i.e., the same extraction and cleanup equipment used for incinerator fly-ash analysis cannot be used for low-level fish tissue analysis).

3. Sub-Contracted Work

It is generally desirable to deal directly with the laboratory that will be performing the analytical services. If the work is sub-contracted by the contract laboratory to a third party not directly involved with the development of the work plan, increased possibilty exists for delays in analysis, and of mis-communicationof project goals/requirements. Regardless of whether the analytical laboratory was the initial contract laboratory for the work or not, it is essential to audit the facilities of the laboratory which carried out the analyses at any time during the project, and be able to deal directly with that laboratory regarding any questions/problems that may arise.

4 HRMS versus LRMS Analysis

If the sample cleanup was excellent, then LRMS will be adequate to achieve accurate, reproducible data at low parts per trillion determinations. The best results at the lowest detection limits (sub-parts-per-trillion) and good isomeric resolution are achieved by both excellent sample extract cleanup and use of GC-HRMS. If GC-LRMS is used, a fraction of samples should be analyzed by GC-HRMS or GC-MS-MS.

5. Additional QA/QC Effort

The internal quality control measures undertaken by the contract laboratory are critical to the quality of the data generated. The frequency and treatment of blanks, use of high quality standards from a reputable supplier and internal duplicate determinations are of additional considerations.

It is essential to internal QA/QC efforts of a contract laboratory to have a stable core of analysts who have the experience and ability to respond to unforeseen analytical problems and solve them with minimum interruption in sample analysis and without sacrificing the quality of the data. It is important that the contarct laboratory have performed verification and validation of all steps of the chosen analytical method in order to pinpoint where losses and contamination can occur and to correct the problems.

A scoring system was developed to evaluate the PCDD/PCDF data from fish tissue check samples analyses by five partipating laboratories. The scoring system was designed to take into account the following four technical factors:

1. Closeness of results to mean concentrations;
2. Closeness of results to 'expected concentrations';

3. reported percent surrogate recoveries; and
4. reported detection limits.

In addition to the above, the following considerations were important to the design of the scoring system:

- Numerical Ranking. An objective numerical score was desired, taking into account the four technical factors listed above.

- All Data Used. It is important to use all available data. Subjective comparisons of data are prone to to over-emphasis of outliers.

- Non-Detects Used. It is easy to ignore non-detects when comparing data sets. The scoring system should penalize laboratories for missing PCDD/PCDF congeners that were detected by the other laboratories.

- Flexiblity. The scoring system should be able to accommodate the needs of diiferent studies. For example, in one study accuracy may be all-important--therefore the closeness of measured values to an available certified reference material would be scored very high; whereas a different investigation concerning the sources of PCDDs and PCDFs may require very low detection limits - quantiattive accuracy would be of secondary importance. The scoring system must be able to accommodate these different needs.

- Treatment of Outliers. When comparing several sets of concentartion data that are similar, it is easy to give emphasis to the importance of a single value that is a significant outlier. While outliers must be taken into account, their importance should not be overstated.

The above considerations were dealt with in the scoring system that was developed. First, a master table of the PCDDs/PCDFs data from the Interlaboratory Perfomance Evaluation Study # I was constructed. These data are shown in Table 7 for the four laboratories participated in the interlaboratoty study # I. In each of the four samples tested, only those PCDD/PCDF congeners that were detected by at least three of the laboratories are shown in the table. The means and standard deviations of the data were calculated.

For each data point in Table 7, the number of *standard deviations units* (SDUs) by which the reported results differed from the mean for that congener was calculated. For example, in sample # 1 the mean and standard deviation for 2,3,7,8-TCDD were 2.53 and 0.55, respectively. Laboratory A reported a concentration of 2.0 ppt for 2,3,7,8-TCDD in sample # 1. This result differed by 0.37 (2.9-2.53) from the mean, which corresponded to 0.37/0.55 = 0.67 SDUs. For each laboratory, the total SDUs for all samples analyzed was the total score for that laboratory. Laboratories were then ranked numerically, and the best performance was achieved by the laboraotry with the lowest score.

To deal with non-detects, a penalty of 2 SDUs was added to the total score of a laboratory each time that laboratory failed to detect a PCDD/PCDF congener found by atleast three of the other laboratories. This was considered a suitable penalty, because the contractor wanted to minimize the possibilty of false-negative results. This analysis we call Laboratory Ranking Based on Closeness to Mean Concentrations.

A second way to rank laboratory performance was what we called Laboratory Ranking Based on Closeness to "Expected" Concentrations. For this analysis, we considered the PCDD/PCDF concentartions for these samples reported from replicate analyses by DFO to be the "correct" or "expected" values. For each individual PCDD/PCDF "expected" result, each laboratory was assigned a score of 1 to 5, based on how close their result was to the "expected" value, compared to the results reported by other laboratories. Thus, for 2,3,7,8-TCDD in sample # 3, the concentration of 46.0 reported by laboratory E was closest to the "expected" result of 45 ppt; therefore laboratory E was given a score of 1 for this result. Laboratory A and laboratory D results were tied for the third closest result, therefore they were assigned a score of 3. Because the fish samples had been archived for some time, and were not certified reference materials, we could not tell from this study whether the mean concentraions determined from this interlaboratory study or the results of previous anlyses by DFO were closer to the "actual" concentrations; therefore, the laboratory ranking was based both on the closeness to mean concentrations and according to the closeness to the "expected" concentrations.

Another way to rank laboratory performance was based on their reported percent recoveries. We assumed that 100% was the "best" recovery, and determined the total across all samples of (absolute value of) $100-R_i$, where R was the percent recovery of congener "i". The laboratory with the lowest score was best with respect to achieving consistently good surrogate recoveries.

Finally, laboratories were ranked according to their reported detection limits. This was done by determining the average (across the four samples analyzed) reported detection limit for each invidual PCDD/PCDF congener, and adding up the detection limits for all congeners. The lowest value represented the lowest reported overall detection limits.

For each of the above factors, the laboratoy with the best performance aws assigned the maximum score for that factor, and the other laboratory scores were normalized to this value in proportion to their raw score for that factor.

2.4 ANALYSIS OF RESULTS

The four technical factors listed above were assigned numerical values so that the highest possible score was 100. The advantages of the scoring system are that it uses most of the reported concentrations, takes into account false-negative results, does not over emphasize outliers, is flexible and is a quantitative relative measure of laboratory performance. Scoring for the most important technical factors (closeness to the mean concentration, closeness to the "expected" concentration, surrogate recoery, and detection limit) for this specific study were weighted accoringly. For other

investigations that have different objectives, different weights to the various factors may be applicable. Therefore, the scoring system is flexible. The analysis given below was performed using only the assigned laboratory numbers with no knowledge of which laboratory supplied which set of data.

2.4.1 Closeness to Mean Concentrations

The data used to calculate the mean and standard deviation (SD) for the different 2,3,7,8-PCDDs and PCDFs in fish check samples are given in Table 7. Table 8 gives the results of ranking based on closeness to mean concentartions. If a result was reported by a laboratory as "not detected", but was found by other laboratories, a penalty of 2.00 SD units was assigned. The case where a positive value was reported by only one or two laboratories, but not others (possible false-positive value) is not handled by this scoring system. Therefore, the presence of possible false-negatives is penalized, but not the possibility of false-positive values. The maximum score of 35 was assigned to the best performance (lowest total). Other scores were scaled proportionately to the best score. All results were scored according to their closeness to "expected" concentrations. Each reported PCDD/PCDF concentration was given a score of 1 to 5 based on how close the concentration was to the "expected" concentration determined from previous replicate analyses by DFO (closest result = 1; furthest result = 5). In the case of ties, both results were assigned thesame score. Totals for some congener groups were also considered in this comparison. Results and overall scoring for this technical factor are summarized in Table 9. The lowest total represented the best performance with respect to data being closest to the "expected" concentrations and was given the maximum score of 35.

2.4.2 Comparison of Percent Recoveries

A score for each laboratory was calculated according to how close each reported percent surrogate recovery differed from 100% recovery. All differences were summed up as positive numbers for each laboratory. The best performance (lowest total) was given the maximum score of 20, and other totals were assigned proportional scores. The results are given in Table 10.

2.4.3 Comparison of Detection Limits

A total of 10 points was assigned for the best performance for this factor. It was assigned a lower score because although important, the actual reported concentrations were by far the most important consideration in the data evaluation. The results of this comparison are given in Table 11. For each congener, the mean of the detection limits for all four samples was determined. These mean detection limits were summed across all congeners analyzed (reported detection limits for total congener groups were not considered). The lowest total represented the dataset for which detection limits were, overall, the lowest. This result was assigned the maximum score of 10 and the other totals were assigned proportional scores. The standard deviation of detection limits were not considered in this analysis.

To develop a combined score where the greatest number repesented the best performance, each of the four areas of comparison was given a maximum score as follows: *Ranking Based on Closeness to the Mean* was allocated 35 points; *Ranking based on the Closeness to "expected" Concentrations* was allocated 35 points; *Ranking Based Percent Recoveries* was allocated 20 points; *Ranking Based on Detection Limits* was allocated 10 points. Thus, the maximum score that could be obtained was 100.

For each separate rating factor, the best performing laboratory was allocated the maximum score for that factor. Other laboratories were then awarded proportional scores based on how they performed compared to the best performing laboratory. For example, Laboratory D peformed best in detection limit comparison, so labooratory D was awarded 10 points for this factor. Laboratory B was awarded (14/29 X 10) = 5 points for this factor. All of the suumary scores are given in Table 12.

2.5 DISCUSSION

Based on the choices we made concerning the relative importance of the various technical factors *for this specific comparison*, the scores in Table 12 were a quantitative measure of the relative performance of the five laboratories that participated in the PCDD/PCDF Interlaboratory Perforamance Evaluation Study # I. By weighting the technical factors differently, it is possible to get a different laboratory ranking. This is reasonable because laboratories have different strengths and limitations that make them more qualified for some types of analytical work. No single laboratory can be expected to be the best in all technical areas. Therefore, use of this scoring system can only be effective when the objectives of the study are clearly defined and the correponding technical factors are ranked in importance. Competing laboratories will perform better if they are given this information at the start of the Interlaboratory Performance Study.

It is well known that for the determination of ultra-trace levels of PCDDs/PCDFs, high resolution mass spectrometry (HRMS) is a superior technoloy compared to low resolution mass spectrometry (LRMS) - this is why laboratory D was able achieve the best overall detection limits. However, the overall performance depended on sample preparation, cleanup, and gas-chromatography separation, in addition to mass spectrometric detection.

None of the scores were low enough to suggest that any of the participating laboratories could not perform the determination of PCDDs/PCDFs in fish tissue.

The numerical scores are best used to determine the groups of laboratories judged capable of performing the required analyses. The objectives of the NRBS- Contaminants Program, and other factors such as sample handling plan, dedicated laboratory facilities, internal QA/QC programs and cost without sacrificing quality were used to choose the laboratory for analytical work.

3.0 INTERLABORATORY PERFORMANCE EVALUATION STUDY - II

The Northern River Basins Study (NRBS) had as one of its main objectives the determination of the concentrations of chlorinated organic compounds in water, suspended solids, sediment and biota throughout the Peace, Athabasca and Slave River systems.
To ensure accurate, consistent and comparable data throughout the study, competent laboratories had to be selected and their areas of expertise identified to conduct chemical analyses. Because of the need for very low detection limits an Interlaboratory Performance Evaluation Study # I was conducted in 1990. Due to start-up delays, the NRBS - contaminant Program commenced in 1992. Since the first interlaboratory study in 1990, several laboratories had improved their analytical capability significantly.

This required a second interlaboratory Performance Evaluation Study to screen the laboratories prior to final selections.

Five laboratories participated in the Interlaboratory Study # II. Each participating laboratory was sent three samples of fish, three sediment samples and one Fish check sample obtained from DFO. The samples sent were homogenized subsamples of archived materials. The fish and sediment samples chosen were from sites (i) downstream of Hinton, (ii) downstream of the Town of Athabasca and (iii) southwest shore of Lake Athabasca. Longnose sucker was chosen as the test species because it is a bottom-feeder and is found in the entire stretch of the Athabasca River. The participating laboratories were required to analyze each fish and sediment sample and the fish check sample for the following chemical parameters:

(a) 2,3,7,8-PCDD/PCDF congeners;
(b) polyaromatic hydrocarbons (PAHs);
(c) polychlorinated biphenyls (PCBs) and isomers including coplanar PCBs where the PCB results are positive;
(d) resin acids;
(e) chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
(f) total metals; lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
(g) extractable metals listed under (f) for sediment samples.

A schedule of terms of reference was sent along with the samples to each laboratory (Appendix).

Data were analyzed similar to the Interlaboratory Performance Evaluation Study # 1, using the same scoring system . The data were assessed for the performance on four technical factors (i) closeness of results to the mean concentration, (ii) closeness of results to the "expected" concentration for the one fish check sample, (iii) percent surrogate recoveries, and (iv) detection limits achieved. Table 13 lists the analytical data reported by the partipating laboratories on fish sample # 1 (from downstram of Hinton):

4.0 SELECTION OF ANALYTICAL LABORATORIES

The QA/QC results from the two interlaboratry performance evaluation studies were evaluated in April, 1992 by a team of experts familiar with routine laboratory analyses. After extensive discussion, they concluded and recommended the decisions contained in Table 20. These decisions are fully backed by the results frm the two interlaboratory performance evaluation studies. As can be seen from Table 20, the analytical workload was distributed to five different laboratories. Where the performance eas more or less the same quality, competitive processes determined the selection of the laboratory for awarding the analytical work for a given parameter(s).

Analytical laboratories chosen and the parameter(s) assigned are given below:

Dioxins/Furans/Resin Acids	Tissue - Envirotest Laboratory Sediment/water - Axys Laboratory
OCs, PCBs, PAHs & CPs**	Tissue - Zenon Laboratory Sediment/water - Chemex Laboratory
Metals, Major Ions/Physicals	All matrices - Chemex Laboratory
Fractination	Sediment - NWRI**

** OCs = Organocholrines other than PCDDs and PCDFs;
PCBs = Polychlorinated biphenyls;
PAHs = Polyaromatic hydrocarbons;
CPs = Chlorophenols;
NWRI = National Water Research Institute, Burlington, Ontario

5.0 LABORATORY PERFORMANCE COMMITTEE (NRBS)

A Laboratory Performance Committee was assembled by NRBS in 1992 by drawing analytical experts from both Provincial and Federal laboratories / departments. The terms of refernce for the NRBS Laboratory Performance Committee (NRBS - LPC) were drafted and accepted by all LPC-members and by NRBS program leaders. The names and affliations of the NRBS - LPC and the terms of reference are listed below:

Members of the NRBS Laboratory Performance Committee

1. Sub Ramamoorthy - Chair (Alberta Environmental Protection, Edmonton)
2. Earle Baddaloo - (Alberta Environmental Protection, Edmonton)
3. Dean Smillie - (Alberta Environmental Centre, Vegreville, Alberta)
4. Dave Sergeant - (Dept. of Fisheries and Oceans Canada, Burlington, Ontario)
5. John Headley - (National Hydrology Research Institute, Saskatchewan)
6. Harry Alkema - (National Water Research Institute, Burligton, Ontario)

5.1 TERMS OF REFERENCE FOR THE NRBS LPC COMMITTEE

1. Review the protocols for sampling, transient storage, shipment and pre-analytical preparation of samples of different matrices.
2. Acquire and distribute Certified Reference Materials (CRMs), Reference Materials (RMs) and analytical standards. Analyze CRMs by contract laboratories for contaminants for which CRMs are not available and serve as RMs.
3. Ascertain that each analytical laboratory has implemented an internal QA/QC program which will include GLP (Good Laboratory Practices), SOP (Standard Operating Procedures), verifiable sample log-in, valid calibration procedures, blanks, suuogate compounds and internal standards to check for extraction efficiencies and performance of instrumentation.
4. Where analytical results are questionable, advise NRBS Science Director and recommend corrective action.
5. Conduct or coordinate periodic round-robin stidies, if possible, on all analytical parameters and all matrices.

6. Verify and validate the data from analytical laboratories.

7. The chair of this committee will keep NRBS Group leaders and the NRBS Science Director informed of this committee's activities on a periodic basis.

The NRBS - LPC has identified the following members and their chemical expertise for synoptic review of anlytical data for authorization of payment. Laboratories are not to be paid until all parameters are verified and certified complete.

1. Dave Sergeant - Dioxins and Furans

2. Dean Smillie - Chlorophenols, Resin Acids, and Fatty Acids

3. John Headley - Organochlorines and Polychlorinated biphenyls

4. Sub Ramamoorthy - Metals

5. Harry Alkema - Nutrients and Inorganics

6. Earle Baddaloo - Sample receiving, log-in, deep-cold storage

6.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) DESIGN OF A TYPICAL SAMPLE BATCH

Each sample batch included upto 15% quality assurance samples including CRMs (both biotic and abiotic CRMs). The true identity of the QA samples were not revealed either to the laboratories or to NRBS office. But Qa samples were marked as QA #1, QA #2 .....etc., in the sample batch. The reason for doing so was to prevent the laboraotories contaminating their analytical system with high concentration CRNs. This could be counter-productive to NRBS-LPC/s objectives and could be expensive for the laboratories. There were additional ways of checkingsuch as screening raw data, chromatograms, etc.. The laboratories were required to anlyzed periodic laboratory blanks which would reveal with-in the laboratory cross-contamination, if any. When possible, traveling blanks were submitted along with the samples with regular sample numbers on them. This revealed that there was no transit contamination during shipemnt and prior to extraction by the laboratories. The laboratories were also required to analyze blind duplicates, low, middle and high standards with-in a sample run.

6.1 DATA EVALUATION CRITERIA

Data set on every sample batch when submitted by the laboratories were evaluated by the **NRBS - LPC** members. The data were assesses for percent and pattern, if any, of surrogate recovery on each sample, detection limits for each congener, non-detects, agreement blind duplicates, blanks, laboratory calibration standards, congener ratio (for example 2378-T_4CDD/T_4CDF), known trends, ratio of isomer/congener total, concentration of coplanar PCBs compared to total PCBs etc.. Raw data were asked for on random basis and chromatograms, calculation of recoveries and detection limits and quantitation were double-checked.

Whenever data were suspect, repeats of either re-analysis or re-extraction and re-analysis were ordered. Upon satisfactory completion, data were verified as acceptable and payment was recommended.

7.0 FLAGGING OF ANALYTICAL PROBLEMS AND CORRECTIVE ACTIONS TAKEN

Here below are examples of some analytical problems identified and corrective actions taken:

1. In the middle of 1992, one of the laboratories went through a blank problem (higher blank balues) due to cross contamination of its analytical system. Once the problem eas flagged, shipment of further samples was immediately suspended and the laboratory was alerted to clean up the analytical system. The laboratory in question undertook a major cleanup effort which required about three months. The laboratory then informed the Chair of NRBS-LPC that the problem has been rectified and blanks were clean. The LPC initiated analysis of split samples along with two soil certified reference material(CRMs) samples between the laboratory in question and one other laboratory (identity kept confidential) which had a good trck record in that analysis. The results were evaluated two independent experts who validated that the laboratory in question waws back on track to deliver high quality data. The shipment of samples resumed and the problem never did occur again.

2. The detection limits for many organo-chorine compounds other than dixoins and furans were not low enough to quantitatively report the presence or absence of several isomers of organochlorine group of compounds. The laboratories that were analyzing for these compounds were requested to improve their detection limits and they did.

3. Furan determinations in burbot livers particularly suffered from interfernce from polychlorinated biphenyl ethers (PCBE), leading to very high false-positive results for 2378-T_4CDF. This analytical problem was relayed to the laboratory, followed by discussions about how to eliminate the PCBE interference. Several cleanup methods were discussed and a few were tried by the laboratory. Finally, a validated cleanup method was put in place to eliminate the interfernce from PCBE in the analysis of PCDDs/PCDFs in fish tissues.

4. The NRBS -Contaminats Study Group decided that dioxins/furans analysis should include non-2378-substituted di-, tri- to octachloro dioxins and furans.There were several reasons for this decision: (1). non-2378-congeners are important components in bleached kraft effluents and might serve as markers of pulp mill effluent in water and suspended sediments, (2) these congeners are known to bioaccumulate in invertebrates, but mush less so in vertebrates because the latter animals could biodegrade these congeners via the MFO system, and (3) if 2378-TCDD or TCDF were non-detectable in effluent or water, some of these non-2378-substituted congeners isomers might serve as surrogates for modelling bioaccumulation.

   Hence, laboratories tested and validated their methods for di- and tri-CDDs/CDFs along with the recovery checks , thanks to the availabilty of a few CRMs for the di- and tri- CDDs and CDFs. In 1992, di- and tri-CDDs/CDFs were part of the suite of chemicals analyzed routinely.

5. The last example is the technology transfer from a federal laboratory to a contract laboratory that was analyzing for PCB congeners in sediments for NRBS. The issues at hand were: (i) identification of specific PCB congeners, (ii) analysis detection limits, and (iii) cleanup of sulfur present in sediment samples. The following corrective actions were taken:

- in consultaion with federal analytical groups, optimum analysis conditions for specific congeners were identified and instituted using the appropriate GC columns and calibration standards (CLB -1 kit from NRCC). All calibrations data were verified and validated.

- deficiencies in the laboratory's cleanup procedures to remove sulfur interference from solid abiotic samples. Several runs using the improved cleanup procedure showed the elimination of sulfur interference with a noise-free baseline for samples. Data were validated by NRBS-LPC and other independent experts in this field.

- addressing the above two items permitted the laboratory to achieve significantly lower and acceptable detection limits.

- all samples were put through the new cleanup procedure and re-analyzed for specific congener components as per the CLB-1 calibration kit.

8.0 REFERENCE

Sergeant, D.B. "Quality Assurance in Analysis of Evnrionmental Matrices for PCDDs and PCDFs". Chemosphere, V.20, 1263 - 1268, 1980.

TABLES

TABLE 1. Mean Concentrations (picogram/gram) for QA/QC Samples

Isomer	Sample #1	Sample #2	Sample #3*	Sample #4
2378-T_4CDD	<1.0	8.8	45	6.5
{ T_4CDD	<1.0	8.8	45	6.5
12378P_5CDD	<1.0	<2.0	10	<5.0
P_5CDD	<1.0	<2.0	10	<5.0
123478-H_6CDD	<2.5	<2.5	5.0	<3.0
{H_6CDD	<2.5	24.0	5.0	4.2
1234678-H_7CDD	<3.0	<3.0	2.0	<3.0
{H_7CDD	<3.0	<3.0	2.0	<3.0
O_8CDD	<10.0	<5.0	<10	<5.0
2378-T_4CDF	5.8	180	40	11.8
{T_4CDF	5.8	200	60	12.6
12378-P_5CDF	<1.0	<2.0	8.0	<2.0
23478-P_5CDF	<1.0	<2.0	30	<2.0
{P_5CDF	<1.0	<2.0	50	<2.0
234678-H_6CDF	<2.5	<2.5	5	<3.0
{H_6CDF	<2.5	<2.5	15	<3.0
1234678-H_7CDF	<3.0	<3.0	2.0	<5.0
{H_7CDF	<3.0	<3.0	2.0	<5.0
O_8CDF	<10.0	<10.0	<10.0	<10.0

*Estimations

TABLE 2. Analytical (Quantitation) Standard and Selected Ion Masses For PCDD/PCDF Analysis

Quantitation Standard	Concentration (pg/uL)	Quantitation Ion	Confirmation Ions
PCDDs			
2378-T_4CDD	100	322	320, 259
12378-P_5CDD	100	356	354, 293
123478-H_6CDD	100	390	392, 327
123678-H_6CDD	100	390	392, 327
123789-H_6CDD	100	390	392, 327
1234678-H_7CDD	100	424	426, 361
O_8CDD	100	460	458, 397
PCDFs			
2378-T_4CDF	100	306	304, 243
12378-P_5CDF	100	340	338, 277
23478-P_5CDF	100	340	338, 277
234678-H_6CDF	100	374	376, 311
123478-H_6CDF	100	374	376, 311
123678-H_6CDF	100	374	376, 311
123789-H_6CDF	100	374	376, 311
1234678-H_7CDF	100	408	410, 345
O_8CDF	100	444	442, 379
SURROGATES ($^{13}C_{12}$ - LABELLED PCDDS)			
$^{13}C_{12}$-2378-T_4CDD	100	334	332
$^{37}Cl_4$-2378-T_4CDD	100	328	None
$^{13}C_{12}$-12378-P_5CDD	100	368	366
$^{13}C_{12}$-123678-H_6CDD	200	402	404
$^{13}C_{12}$-1234678-H_7CDD	200	436	338
$^{13}C_{12}$-O_8CDD	300	472	470
PERFORMANCE (INTERNAL STANDARD) STANDARD			
$^{13}C_{12}$-1234-T_4CDD	100	334	332

Solvent = Toluene

TABLE 3. SURROGATE SPIKING SOLUTION

SURROGATE: $^{13}C_{12}$-LABELLED PCDDs	CONCENTRATION (Picogm/microlitre)
$^{13}C_{12}$ - 2378-T_4CDD	20
$^{37}Cl_4$ - 2378-T_4CDD	20
$^{13}C_{12}$ -12378-P_5CDD	20
$^{13}C_{12}$ -123678-H_6CDD	40
$^{13}C_{12}$ -1234678-H_7CDD	40
$^{13}C_{12}$ -O_8CDD	60

Solvent = Toluene

TABLE 4. PERFORMANCE (INTERNAL) STANDARD SOLUTION

$^{13}C_{12}$ -LABELLED PCDD	CONCENTRATION (Picogm/microlitre)
$^{13}C_{12}$ - 1234-T_4CDD	100

Solvent = Toluene

TABLE 5. SURROGATE STANDARD RECOVERY CRITERIA

SURROGATE STANDARD	AMOUNT SPIKED (nanogram)	ACCEPTABLE RECOVERY (%)
$^{13}C_{12}$ - 2378-T_4CDD	2	40 - 120
$^{13}C_{12}$ - 12378-P_5CDD	2	40 - 120
$^{13}C_{12}$ - 123678-H_6CDD	4	40 - 120
$^{13}C_{12}$ - 1234678-H_7CDD	4	40 - 120
$^{13}C_{12}$ - O_8CDD	4	40 - 120

TABLE 6. PCDDs/PCDFs DETECTION LIMITS IN TISSUE SAMPLES (ppt)

PCDD CONGENER	TISSUE DETECTION LIMITS (ppt)
T_4CDD	2
P_5CDD	5
H_6CDD	10
H_7CDD	15
O_8CDD	20

TABLE 7. PCDDs/PCDFs IN FISH TISSUE IN INTERLABORATORY STUDY # 1

	Laboratory Designation						
	A(L)	B(L)	C(H)	D(H)	E(L)	**Mean**	**SD**
Sample 1							
2378-T_4CDD	2.9	2.4	ND	1.8	3	2.53	0.55
123678-H_6CDD	10.0	19	16	ND	16	15.3	3.8
2378-T_4CDF (5.8)	15.8	16	19	15.0	18	16.8	1.7
12378-P_5CDF	1.7	2.0	ND	1.6	3	2.08	0.64
23478-P_5CDF	2.6	2.8	ND	2.3	4	2.93	0.75
Sample 2							
2378-T_4CDD (8.8)	7.4	9.7	10	9.4	8	8.90	1.1
2378-T_4CDF (180)	182	230	240	270	250	234	33
Sample 3							
2378-T_4CDD (45)	40	31	43	40	46	40.0	5.6
12378-P_5CDD (10)	8.6	8.8	8.1	ND	10	8.88	0.81
123678-H_6CDD	10.9	23	15	ND	10	16.0	5.1
2378-T_4CDF (40)	40.8	40	39	36.0	41	39.4	2.0
12378-P_5CDF (8)	5.6	6.2	6.2	4.4	8	6.08	1.3
23478-P_5CDF (30)	27.9	30	27	16.0	26	25.4	5.5
123478-H_6CDF	7.8	10	9.4	6.1	ND	8.33	1.8
ySample 4							
T_4CDD (6.5) 8.1	6.3	9.5	7.5	8	7.88	1.2	
1234678-H_4CDD	4.7	5.7	ND	4.7	4	4.78	0.70
O_8CDD	5.9	5.4	ND	3.7	3	4.50	1.4
2378-T_4CDD (12)	9.9	14	13	9.5	11	11.5	2.0

Notes:

1. all data are in parts per trillion
2. (L) indicates analysis was by LRMS; (H) indicates analysis was by HRMS
3. SD = Stanadard deviation
4. non-detects (ND) were not used in the calculation of means and SD
5. numbers in brackets are "expected" concentrations from previous analyses (if congeners do not have numbers in brackets, it indicates that no concentartions were reported for these congeners in the previous analysis.

TABLE 8. LABORATORY RANKING BASED ON CLOSENESS TO MEAN CONCENTRATION

	Laboratory Designation						
	Mean	**SD**	A(L)	B(L)	C(H)	D(H)	E(L)
Sample 1							
2378-T_4CDD	2.53	0.55	0.67	0.24	(2.0)	1.33	0.85
123678-H_6CDD	15.3	3.8	1.39	0.97	0.18	(2.0)	0.18
2378-T_4CDF	16.8	1.7	0.59	0.47	1.29	1.06	0.71
12378-P_5CDF	2.08	0.64	0.59	0.13	(2.0)	0.75	1.44
23478-P_5CDF	2.93	0.75	0.44	0.17	(2.0)	0.84	1.43
Sample 2							
2378-T_4CDD	8.90	1.1	1.36	0.44	1.00	0.45	0.82
2378-T_4CDF	234	33	1.58	0.12	0.18	1.09	0.48
Sample 3							
2378-T_4CDD	40	5.6	0.02	1.61	0.54	0.00	1.07
12378-P_5CDD	8.88	0.81	0.35	0.10	0.96	(2.0)	1.38
123678-H_6CDD	16	5.1	1.00	1.37	0.20	(2.0)	0.20
2378-T_4CDF	39.4	2.0	0.70	0.30	0.20	(2.0)	0.80
12378-P_5CDF	6.08	1.3	0.37	0.09	0.09	1.29	1.48
23478-P_5CDF	25.4	5.5	0.45	0.84	0.29	1.71	0.11
123478-H_6CDF	8.33	1.8	0.29	0.93	0.59	1.24	(2.0)
Sample 4							
2378-T_4CDD	7.88	1.2	0.18	1.32	1.35	0.32	0.10
1234678-H_7CDD	4.78	0.70	0.11	1.31	(2.0)	0.11	1.11
O_8CDD	4.5	1.4	1.00	0.64	(2.0)	0.57	1.07
2378-T_4CDF	11.5	2.0	0.80	1.25	0.75	1.00	0.25
TOTALS			11.9	12.6	17.6	19.5	15.5

Notes: 1. Mean and SD (standard deviation) from Table 8.
2. (2.00) indicates a congener was not detected; a penalty of 2.00 SD units is assigned.
3. (L) indicates analysis was by LRMS; (H) indicates analysis was by HRMS.

TABLE 9. LABORATORY RANKING BASED ON CLOSENESS TO "EXPECTED" VALUE

Congener/Group	"Expected" Conc. (ppt)	Laboratory Designation A(L)	B(L)	C(H)	D(H)	E(L)
Sample 1						
2378-T_4CDD	5.8	2	3	5	1	4
TOTAL PCDD+PCDF		1	3	1	3	5
Sample 2						
2378-T_4CDD	8.8	5	3	4	1	2
TOTAL H_6CDD	24	1	5	2	4	2
2378-T_4CDF	180	1	2	3	5	4
TOTAL T_4CDF	200	1	2	3	5	4
TOTAL PCDD+PCDF		1	3	2	5	4
Sample 3						
2378-T_4CDD	45	3	5	2	3	1
12378-P_5CDD	10	3	2	4	5	1
TOTAL H_6CDD	5	1	4	2	5	2
2378-T_4CDF	40	2	1	3	5	3
TOTAL T_4CDF	60	2	1	4	5	3
12378-P_5CDF	8	4	2	2	5	1
23478-P_5CDF	30	2	1	3	5	4
TOTAL P_5CDF	50	2	1	3	4	5
TOTAL H_6CDF	15	2	1	3	4	5
TOTAL PCDD+PCDF		1	2	2	5	4
Sample 4						
2378-T_4CDD	6.5	4	1	5	2	3
2378-T_4CDF	12	4	3	1	5	1
TOTAL T_4CDF	13	5	2	1	4	3
TOTAL PCDD+PCDF		3	1	4	1	5
TOTAL SCORE		50	48	59	82	66

Notes; 1. Congener group totals were only scored if more than one isomer was detected (i.e. for sample # 1, 2378 T_4CDF was the only isomer detected in previous analyses; therefore total TCDF was not included in the scoring.

2. (L) indicates analsis was by LRMS; (H) indicates analysis was by HRMS.

TABLE 10. LABORATORY RANKING BASED ON PERCENT RECOVERIES

$^{13}C_{12}$-Labelled Congener	Sample #	Laboratory Designation A(L)	B(L)	C(H)	D(H)	E(L)
2378-T_4CDD	1	173	74	71	81	76
	2	64	68	61	61	69
	3	135	75	53	84	57
	4	63	65	73	83	85
12378P_5CDD	1	84	77	52	90	91
	2	64	88	69	65	85
	3	77	81	51	88	72
	4	72	71	60	89	99
123678H_6CDD	1	74	81	34	96	77
	2	71	98	57	68	90
	3	76	78	40	104	70
	4	73	73	46	82	105
1234678H_7CDD	1	92	90	37	98	85
	2	83	107	78	66	100
	3	92	81	52	102	90
	4	102	78	54	83	87
O_8CDD	1	59	80	27	80	64
	2	51	90	64	56	68
	3	63	60	37	85	83
	4	51	58	41	66	107
Sum of (100-%R)		601	441	943	385	364

Note: 1. numbers in Table are reported percent recoveries for each four samples analyzed
2. (L) indicates analysis by LRMS; (H) indicates analysis HRMS
3. All differences in recovery from 1005 were summed up as positive numbers for each laboratory. The lowest total was assigned the maximum score 0f 20 and other totals ere assigned apprppriate scores.

TABLE 11. LABORATORY RANKING BASED ON DETECTION LIMITS

Isomer	Detection Limits in parts per trillion				
	A(L)	B(L)	C(H)	D(H)	E(L)
2378-T_4CDD	1.9	1.2	2.3	0.8	1.8
12378-P_5CDD	4.3	2.7	3.5	0.6	1.5
123478-H_6CDD	2.7	1.8	7.3	1.0	2.0
123678-H_6CDD	2.7	1.8	6.1	1.0	2.0
123789-H_6CDD	2.7	1.8	6.7	1.0	2.0
1234678-H_7CDD	2.1	2.4	7.6	0.6	3.3
O_8CDD	5.0	3.3	21.0	0.5	4.5
2378-T_4CDF	1.2	1.5	2.1	1.1	2.0
12378-P_5CDF	1.7	1.2	2.5	0.5	1.3
23478-P_5CDF	1.7	1.2	2.2	0.5	1.3
123478-H_6CDF	2.0	1.6	4.0	1.4	1.8
123678-H_6CDF	2.0	1.6	3.9	1.4	1.8
123789-H_6CDF	2.0	1.6	4.0	1.4	1.8
234678-H_6CDF	2.0	1.6	5.3	1.4	1.8
1234678-H_7CDF	2.2	1.4	5.2	0.4	2.8
O_8CDF	3.4	2.3	20.0	0.5	4.8
TOTALS	40	29	104	14	37

Notes: 1. all values are mean detection limts reported for analysis of four fish samples
2. (L) indicates analysis by LRMS; (H) indicated analysis by HRMS

TABLE 12. Over-All Score Summary of Performance in Interlaboratory Study # I

	Laboratory Designation				
Factor	A(L)	B(L)	C(H)	D(H)	E(L)
Closeness to Mean Concentrations	35	33	24	21	27
Closeness to "Expected" Concentrations	34	35	28	20	25
Percent Surrogate Recoveries	12	17	8	19	20
Detection Limits	4	5	1	10	4
Total Laboratory Score	85	90	61	70	76

Table 13. Analytical Data reported on Fish Sample # 1
Concentrations in parts per trillion (ppt)

Congener	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Mean (n)	SD
2378-TCDD	1.6	2.5	ND	2.3	1.6	2.00 (4)	0.47
2378-TCDF	7.6	8.1	6.7	8.0	7.3	7.54 (5)	0.57

n = number of data used in the calculation od mean value; SD = standard deviation

Table 14. Analytical Data on Fish Check Samples (in ppt)

Isomer	Expected Value	Reported Value Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
2378-TCDD	45	40	46	34	44.7	39
{TCDD	45	40	150	34	44.7	39
12378-P_5CDD	10	8.3	6.8	3.6	7.2	6.6
{$_5$PCDD	10	8.3	83	3.6	7.2	6.6
1234678-H_7CDD	2	1.0	ND	1.7	ND	ND
O_8CDD	<10	ND	61	2.0	ND	ND
2378-TCDF	40	37	33	40	38.2	28
12378-P_5CDF	8	5.7	5.8	5.6	6.8	4.6
23478-P_5CDF	30	26	29	12.0	30.7	20
{H_6CDF	15	16	122	46.5	15.8	12
1234678-H_7CDF	2	0.7	ND	0.00	ND	ND
O_8CDF	<10	ND	ND	2.3	2.7	5.3

Table 15. Ranking Based on Percent Recovery of Surrogates
Percent Recovery

^{13}C- Labelled Congeners	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
2378-T_4CDD	90	83	90	78	87
	115	97	86	85	78
	98	90	81	76	81
	100	80	104	113	94
	118	85	119	72	90
	108	89	90	75	94
	111	90	66	81	72
12378-P_5CDD	96	100	89	83	88
	97	111	91	86	72
	110	99	98	85	99
	131	86	126	81	75
	116	94	123	88	80
	92	98	101	82	88
	94	97	68	90	96
1234678-H_7PCDD	77	99	107	87	91
	74	109	107	93	77
	75	96	109	85	96
	67	83	69	81	89
	100	92	114	90	93
	71	95	93	86	99
	83	80	81	85	79
O_8CDD	64	90	107	68	81
	55	100	113	72	83
	54	87	113	68	91
	52	72	96	65	78
	73	90	117	71	77
	47	86	115	77	80
	54	60	104	77	72
Sum of (100-%R)	596	302	381	546	420
Total points scored (max. = 20)	10	20	16	11	14

(1). Sum of 100 - %R = Summation of (100 minus the % Recovery) values for all entries for each laboratory. The smallest total indicates the laboratory for which % recoveries were most consistently near 100%; (2). Twenty (20) points (maximum score) were given for the laboratory with the lowest total of 100 - %R (302). Scores for other laboartories were calculated as follows : Laboratory score = 302/laboratory total x 20.

Table 16. Ranking Based on Detection Limits (in ppt) for Fish Tissues

Isomer	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
2378-T_4CDD	0.17	1.22	0.92	1.12	0.62
12378-P_5CDD	0.25	2.37	2.30	1.45	0.95
123478-H_6CDD	0.37	1.92	1.27	1.30	1.30
1234678-H_7CDD	0.70	3.97	0.67	1.22	1.95
O_8CDD	1.8	5.92	0.80	2.35	2.35
2378-TCDF	0.22	0.92	0.77	0.80	0.40
12378-P_5CDF	0.17	1.62	1.40	0.92	0.52
234678-H_6CDF	0.27	1.45	1.22	1.02	1.15
1234678-H_7CDF	0.37	1.70	0.55	1.25	1.97
O_8CDF	1.62	2.70	0.80	2.05	2.20
Total	5.94	23.84	10.7	13.48	13.41
Points scored (max. = 10)	10	2.5	5.5	4.4	4.4

1. All values are mean detection limits reported for analysis of four fish samples.

2. Best overall detection limit (lowest total= 5.94) was given 10 points. Other laboratory scores were calculated as follows: Lab. score = 5.94 / Lab.total x 10.

Table 17. Ranking Based on Detection Limits (ppt) for sediments

Isomer	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
2378-T_4CDD	0.13	1.13	0.63	7.5	0.33
12378-P_5CDD	0.20	2.23	0.90	10.53	0.63
123478-H_6CDD	0.43	1.86	1.07	11.27	0.90
1234678-H_7CDD	0.67	5.67	0.67	7.8	1.17
O_8CDD	1.93	7.67	0.93	15.6	1.20
2378-T_4CDF	0.13	0.80	0.70	5.63	0.20
12378-P_5CDF	0.13	1.1	0.37	5.70	0.37
234678-H_6CDF	0.27	1.37	0.83	6.33	0.83
1234678-H_7CDF	0.37	1.70	0.50	10.5	1.43
O_8CDF	1.70	3.57	0.93	14.47	2.10
Total	5.96	27.1	7.53	95.53	9.16
Points scored (max. = 10)	10	2.2	7.9	0.6	6.5
Combined Score (sediment and fish detection limits)	10	2.3	6.7	2.5	5.4

1. All values are mean detection limits for analysis of three sediment samples.
2. Best overall detection limit summed over all congeners (lowest total = 5.96) is given the maximum score , 10 points. Other laboratories score were calculated as follows:
Laboratory score = 5.96 / Laboratory total x 10.
3. Combined score was used in calculating the total score for each laboratory.

TABLE 18. Analytical Data for Fish Samples Reported by Participating Laboratories

Polycyclic Aromatic	LAB #1			LAB #2			LAB #3			LAB #4			LAB #5		
Hydrocarbons	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
naphthalene	44	116	87	36	32	28	ND	ND	ND	3	3	5	ND	ND	ND
2-methylnaphthalene	ND	24	22	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-methylnaphthalene	8	13	14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
acenaphthylene	ND	ND	ND	3	3	2	ND	ND	ND	<1	<1	<1	ND	ND	ND
acenaphthene	ND	ND	ND	12	15	12	ND	ND	ND	<1	<1.1	<6	ND	ND	ND
fluorene	ND	ND	ND	24	22	24	ND	ND	ND	<1	<1.2	<3	ND	ND	ND
phenanthrene	ND	ND	ND	84	80	82	ND	ND	ND	2	2	1	ND	ND	ND
anthracene	ND	ND	ND	4	3	3	ND	ND	ND	<1	<1	<1	ND	ND	ND
pyrene	ND	ND	ND	6	7	7	ND	ND	ND	<1	<1	<1	ND	ND	ND
benzo(a)pyrene	ND	ND	ND	11	9	3	ND	ND	ND	<1	<1	<1	ND	ND	ND

Concentration in ng/g ND = Not Detected

DL = Detection Limits: naphthalene to pyrene 5ppb

benzo(a)anthracene to perylene 10 ppb

TABLE 19. Analytical Data for Sediment Samples Reported by Participating Laboratories

Polycyclic Aromatic	LAB #1			LAB #2			LAB #3			LAB #4			LAB #5		
Hydrocarbons	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
naphthalene	303	334	785	9	6	12	ND	ND	ND	56	250	53	ND	11	33
2-methylnaphthalene	187	150	310	ND	ND	ND									
1-methylnaphthalene	91	138	206	ND	ND	ND									
1,1-biphenyl	55	24	41	ND	ND	ND									
acenaphthene	6	6	8										ND	ND	ND
fluorene	ND	10	17	8	4	7	ND	ND	ND	15	4.6	9	14	5	11
phenanthrene	46	20	33	54	23	43	ND	ND	ND	93	39	79	71	29	60
nitroacenaphthene	8	27	6												
fluoranthene	ND	ND	ND	6	10	11	ND	ND	ND	10	13	18	7.6	10	17
pyrene	ND	8	ND	9	14	22	ND	ND	ND	13	16	32	10	17	31
benz(a)anthracene	ND	ND	ND										ND	3.9	10
chrysene	ND	ND	ND	25	16	35	ND	ND	ND	34	14	50	36	20	52
benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND				12	13	36			
benzo(k)fluoranthene	ND	ND	ND	10	7	20	ND	ND	ND	12	13	36	23	33	65
benzo(a)pyrene	ND	ND	ND	2	7	9	ND	ND	ND	2	9	24	ND	11	22
perylene	ND	ND	ND										23	230	450

Concentration in ng/g ND = Not Detected; DL = Detection Limits: naphthalene to pyrene 5ppb; benzo(a)anthracene to perylene 10 ppb

TABLE 20. Analytical Laboratory Selection

Northern River Basin Study

Parameter Group	Sample Size			Substrate		
	Tissue (Muscle/ Liver)	Sediment	Water	Tissue	Sediment	Water
Dioxins	20g/1g	40g	40L	Envirotest	Axys or BCR	Axys or BCR
OCs and PCBs (coplanar)	20g/1g	40g	4L	Zenon	Chemex	Chemex
PAHs			4L	Zenon	Chemex	Chemex
Chlorophenols			20L	Zenon	Chemex	Chemex
Resin Acids	20g	40g	------	Envirotest	Axys	------
Metals	20g/1g		1L	Chemex	Chemex	Chemex
Major Ions and Physicals	--------	--------	2L	Norwest, Chemex or Zenon	Norwest, Chemex or Zenon	Norwest Chemex or Zenon
Nutrients	--------	--------	1L	Norwest, Chemex or Zenon	Norwest, Chemex or Zenon	Norwest Chemex or Zenon

Sediment sample fractionation	-------	-------	-------	----------	NWRI	------

Notes:

1. Contract laboratories selected based on QA/QC results
2. Shaded areas indicate competitive processes determined the laboratory.
3. PAHs in fish were on selected fish only (eg. in effluent mixing zone)
4. 10g generally required for muscle analysis and a minimum of 1g for liver.
5. Analyses on sediment and water for organics were done by the same laboratory, because of partitioning information required.
6. Sediment samples were partitioned before analysis

APPENDIX A: **DETAILED PROTOCOL FOR ANALYSIS OF DIOXINS AND FURANS - STUDY I**

INTER-LABORATORY FISH CHECK SAMPLE PERFORMANCE EVALUATION STUDY QUALITY CONTROL/QUALITY ASSURANCE

I. ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find four (4) fish tissue samples (15 g each) and three (3) solutions in sealed glass ampoules. For the purpose of this check sample program, your laboratory is required to analyze the fish tissue samples for chlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-p-furans (PCDFs). The solutions provided (surrogate spiking, performance and analytical (quantitation) standards) must be used for all analyses.

2. Sample Weight

A minimum of 10g of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Surrogate Spiking

Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures provided by Alberta Environment (AE) to the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

6. Performance (Recovery) Standard/Final Extract Volume

Prior to GC/MS analysis, the cleaned up fish tissue extract will be taken just to dryness in a clean, new 100μL auto sampler vial under a gentle stream of nitrogen and exactly 20μL of the internal standard solution, (100pg/μL $^{13}C_{12}$- 1,2,3,4,-TCDD in toluene) provided by AE, will be added. This will be used to assess instrument stability, operator performance and surrogate recoveries. This final volume will produce a concentration equivalent to that in the analytical standard for the ^{13}C-surrogate if 100 per cent recovery is achieved.

7. Quantitation

A quantitation standard mixture (not provided) containing 16 native PCDD/PCDF congeners, the isotopically labelled performance standard and 6 isotopically labelled surrogates, must be used in the analysis. The composition of the analytical solution (quantitation standard), surrogate spiking solution and internal standard solution are given in Tables A, B, and C respectively.

Table A details the composition of this analytical standard and the ion masses to be monitored for determining sample results. If a $^{13}C_{12}$-TCDD surrogate recovery falls outside the acceptable recovery range (Table D), the sample must be re-analyzed with the m/e 328 of the ^{37}Cl-labelled surrogate being monitored instead. This is of mutual benefit to Northern River Basin Study (NRBS) and the participating laboratory in that an interference on the primary tetra-dioxin surrogate may not distort the % recovery of the secondary tetra-surrogate. Alternatively the 328 ion should be routinely monitored in all samples to eliminate the need for re-analysis.

Laboratories have the option of using either internal or external standard procedures for quantitation using this mixture; however, internal standard quantitation is preferred. For quantitation by the internal standard method, the isotopically labelled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors owing to differences in injected volume and unnoticed variations in instrumental sensitivity. For quantitation by the external standard method, the labelled surrogates and performance standard allow corrections to be made for processing losses and injection volume/instrument performance variability.

When using internal standard quantitation, all six isotopically labelled surrogates must be used as the internal standards. Also, the quantitation mixture must be run daily (see II.14) to determine relative response factors between the labelled and native congeners and to determine surrogate and performance standard recoveries. Results are automatically corrected for surrogate recovery; however, the actual surrogate and performance standard recoveries must be reported.

When using external standard quantitation, reported results must be recovery-corrected and the same recovery report generated as for internal standard quantitation above.

Dioxin and furan results for each homologue are corrected for the recovery of the corresponding labelled surrogate dioxin congener. Whether using internal or external quantitation methods, the participating laboratory will provide examples of all equations used to calculate surrogate recoveries, detection limits, to determine relative response factors between native and surrogate compounds and to determine PCDD/PCDF concentrations in the sample.

8. Criteria for PCDD/PCDF Identification

Since many compounds can interfere with the determination of PCDDs and PCDFs, it is of utmost importance that positive identifications be made. The criteria for PCDD/PCDF confirmation are listed below:

- Participating laboratory must demonstrate that 2,3,7,8,-TCDD is satisfactorily resolved from neighbouring tetra isomers: 1,2,3,7,-TCDD and 1,2,3,8,-TCDD for the analytical column(s) used.

- Peak responses of the monitored ions must be greater than 3 times the background noise level.

- Peak area ratios or spectral ion intensity ratios of the two monitored molecular ions for each congener group must be within +20% of the ratio obtained for the corresponding components in the QUANTITATION standard mixture.

- COCl loss must be monitored and co-maximize with the molecular ions of the analyte.

- Measures must be taken to establish retention time windows for selected ion monitoring of individual homologues, such as use of a standard mixture containing the earliest and latest eluting isomer within each homologue group. These windows must be stable and retention time shifts in excess of +2 scans between surrogates in standards and samples must not occur. Should sample surrogates shift retention time, this is an indication of column problems. All analyses must cease until problem resolved and after re-calibration, samples in question must be re-analyzed.

- Peak maxima for all three monitored ions must coincide within +2 scan units.

- For isomer specific identification, peaks may be identified as, for example, 2,3,7,8,-TCDD, 2,3,7,8,-TCDF, O_8CDD and O_8CDF, if they meet the first two criteria and co-elute with their isotopically labelled surrogates within +2 scan units.

- No response must be seen at m/e 374 at the retention time of 2,3,7,8,-TCDF. This M+ ion of hexachlorodiphenyl ether gives the same fragment ions as T_4CDF and yields a false-positive $_4$T CDF result. Monitoring for other chlorinated diphenyl ethers is optional.

- Surrogate and performance standard recoveries must fall within acceptable windows as specified in Table D.

9. Detection Limits

The detection limit must be reported for all sample results - not just for N.D. values. The concentration units used to report the detection limit must be corrected for surrogate recovery. Table E gives the detection limits which must be met for data to be considered acceptable.

A sample is detectable when the ion response is greater than 3 times S/N (signal/noise) ratio. However, if other qualitative criteria are not met, such as correct ion ratios, that measurement is reported as NDR. A sample is non-detectable when ion response is less than 3 times S/N ratio. This will be reported as ND.

For external standard, the following calculation should be used with performance standard recovery factored in:

$$\text{D.L. (ppt)} = \frac{(\text{Area 3 x S/N}) \times \text{Pq/unit area} \times 100}{\text{g sample} \times \% \text{ recovery of surrogate}} \times \frac{1}{\text{performance standard recovery}}$$

For external standard, the above calculation should be used with performance standard recovery factored in. For internal standard quantitation, the following must be used:

To determine the minimum detectable area for an individual isomer, one determines the maximum height of noise. A line is manually drawn across the top of the noise peaks in each quantitation ion in the mass chromatogram. The height of the line is determined by rationing the height of the line to the full height of the ion response times the total height counts in the window. This is next multiplied by 3 to achieve 3 times S/N. Height is then converted to area by multiplying 3 times S/N height by the peak area/peak height ratio for the surrogate in that window. This area is then used to calculate the detection limit.

In cases where the quantitation ion contains a large peak which prevents observation of the noise due to the scaling, the following procedures may be used:

1. Rescale and reprint the ion window to either side of the peak and proceed as usual.

2. Use the minimum detectable area from the same channel in the method spike run for calculation of sample detection limit.

II. ADDITIONAL QA REQUIREMENTS

Most of the following QA requirements are probably routine procedure in participating laboratories. However, they form an integral part of a QA protocol and must be followed:

1. Good laboratory practice: all equipment, sample concentrators, glassware, benches, etc. shall be kept clean during processing of these samples. No high level samples such as flyash shall be processed simultaneously. This could lead to cross-contamination problems.

2. Sample storage during workups: all sample extracts shall be refrigerated at 4°C in the dark when not needed for various cleanup steps.

3. Record keeping: a set of laboratory notebooks will be dedicated to these analyses and all records of sample treatment shall be recorded in these logs, which will be signed and dated for each sample manipulation. Such notebooks shall be available for audit upon request by NRBS and shall be delivered to NRBS at the end of the NRBS study.

4. Laboratory audits: NRBS may wish to audit individual laboratories and their operating procedures during this study. The analyst-in- charge may be required to review some of the data with NRBS.

5. Disposal: the participating laboratory is responsible for the disposal of unused samples. Such disposal shall not take place without the approval of NRBS. Samples will be suitably stored at -20°C to ensure their integrity until disposal is requested by NRBS.

6. All final sample extracts will be retained. When participating laboratory completes the analyses, these extracts (gently evaporated to dryness under nitrogen) will be delivered to NRBS in new, unused, precleaned 100 μl auto sampler vials, tightly sealed, under chain-of-custody protocols. Vial containers will not be replaced by NRBS.

7. Raw GCMS data shall be backed up onto tape or diskette daily. These tapes shall be stored in secure locations and may not be erased without express written permission from NRBS.

8. For each total congener concentration reported, the number of positive individual isomers found must be reported.

9. Analytical standards and spiking surrogate mixtures will be used for all quantitative determinations by all participating laboratories.

10. NRBS may audit positive and negative TCDF values by submitting samples to either high resolution GC - high resolution MS or GC-MS-MS analysis using appropriate columns.

11. Participating laboratory shall be responsible for GC column performance checking and shall provide details of such checks with sample reports:

    i. Check for isomer specificity for 2,3,7,8-TCDD and -TCDF.

    ii. Use of commercial window defining mixtures to set up GCMS windows for the various congener groups.

    iii. Verify calibration of column - MS by running analytical standards and maintaining a +20% response on all ions monitored across the congener groups.

    iv. Periodically a column blank shall be run to assess carryover. (2 μL injection of toluene and full analysis).

    v. Verify and demonstrate that 10 pg 2,3,7,8-TCDD can be accurately seen at 3 times S/N prior to all analyses.

12. Additional performance audits may involve blind analysis of spiked matrix samples, split audit samples sent to government labs, etc.

13. Prior to commencing analyses, linearity of system shall be determined by a minimum of 5 point calibration covering a concentration range of 0.02 to 2 ng/μl PCDD/PCDF. The participating laboratory shall be responsible for obtaining these mixtures but will provide all details to NRBS. Linearity shall be rechecked periodically and in particular, after each column change. Relative response factors (native std./labelled std.) will then be established.

14. Daily calibration will be via running the provided analytical standard using single-point calibration. The processing of samples will be performed by running the standard and comparing response to last previous standard. Control chart RRF (Relative Response Factor) plots of standards will be maintained and submitted with each data set. If value is +15% for the ions selected of natives and surrogates, analysis of samples may proceed. If responses are outside this range, a second standard must be run and similarly assessed. If this too fails, the problem must be found and corrected before any samples are run. For external standard quantitation, frequent recalibration must take place, and the following sequence should be followed when analysing samples:

    Standard, Sample, Sample, Standard

III. DATA REPORTING AND EVALUATION PROCEDURES

1. Data Reporting

   i. All results must be reported on the attached Analysis Report Form. This uniformity of reporting format is essential for ease of evaluation of data sets originating from more than one laboratory. Three copies of each data report must be provided.

   ii. It is required that each data set be accompanied by the original (not copies) legible printouts of all GCMS ion chromatograms, spectra and spectral intensity lists of all analytical standards, samples, blanks, method spikes, column blanks, and check solutions with all peaks identified as PCDD or PCDF congeners - clearly indicated directly on the printouts in ink. Retention times, peak heights, and peak areas must be clearly labelled. On Finnigan GCMS systems, the noise line must be turned "on".

   iii. For each report, all information requested on the Analysis Report Form must be supplied. The ratio ranges must be determined by the participating laboratory on their GCMS by analysis of the standard provided and determination of individual isomer's ion ratio from the areas or spectral intensities.

   iv. As an integral part of all data reports, the following additional information must be supplied:
   - Calibration reports
   - Date/time record GCMS
   - Control chart RRFs
   - Worksheet for surrogate recoveries
   - MDL calculations

   v. Please enclose the following with the final data:

      a. a brief description of the methods used;
      b. a description of the GC/MS system used, the operational parameters, and the acquisition system;
      c. the capillary column(s) used; and
      d. a description of the method for calculating detection limits.

TABLE A. ANALYTICAL (QUANTITATION) STANDARD AND SELECTED ION MASSES FOR PCDD/PCDF ANALYSIS.

QUANTITATION Standard	CONCENTRATION (pg/μL)	QUANTITATION Ion	CONFIRMATION Ions
DIOXINS			
2,3,7,8-T_4CDD	100	322	320,259
1,2,3,7,8-P_5CDD	100	356	354,293
1,2,3,4,7,8-H_6CDD	100	390	392,327
1,2,3,6,7,8-H_6CDD	100	390	392,327
1,2,3,7,8,9-H_6CDD	100	390	392,327
1,2,3,4,6,7,8-H_7CDD	100	424	426,361
O_8CDD	100	460	458,397
FURANS			
2,3,7,8-T_4CDF	100	306	304,243
1,2,3,7,8-P_5CDF	100	340	338,277
2,3,4,7,8-P_5CDF	100	340	338,277
2,3,4,6,7,8-H_6CDF	100	374	376,311
1,2,3,4,7,8-H_6CDF	100	374	376,311
1,2,3,6,7,8-H_6CDF	100	374	376,311
1,2,3,7,8,9-H_6CDF	100	374	376,311
1,2,3,4,6,7,8-H_7CDF	100	408	410,345
0_8CDF	100	444	442,379
SURROGATES (C_{13} LABELLED PCDDS)			
$^{13}C_{12}$-2,3,7,8-T_4CDD	100	334	332
$^{37}C_{14}$-2,3,7,8-T_4CDD	100	328	None
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	100	368	366
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	200	402	404
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	200	436	338
$^{13}C_{12}$-O_8CDD	300	472	470
PERFORMANCE (INTERNAL) STANDARD			
$^{13}C_{12}$-1,2,3,4-TCDD	100	334	332

Solvent = Toluene

TABLE B. SURROGATE SPIKING SOLUTION.

SURROGATE: C_{13}-LABELLED PCDDs	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 2,3,7,8-T_4CDD	20
$^{37}Cl_4$ - 2,3,7,8-T_4CDD	20
$^{13}C_{12}$ - 1,2,3,7,8-P_5CDD	20
$^{13}C_{12}$ - 1,2,3,6,7,8-H_6CDD	40
$^{13}C_{12}$ - 1,2,3,4,6,7,8-H_7CDD	40
$^{13}C_{12}$ - 0_8CDD	60

Solvent = Toluene

TABLE C. PERFORMANCE (INTERNAL) STANDARD SOLUTION.

C_{13}-LABELLED PCDD	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 1234-TCDD	100

Solvent = Toluene

TABLE D. SURROGATE STANDARD RECOVERY CRITERIA.

SURROGATE STANDARD	AMOUNT SPIKED (ng)	ACCEPTABLE RECOVERY (%)
$^{13}C_{12}$ - 2,3,7,8-T_4CDD	2	40-120
$^{13}C_{12}$ - 1,2,3,7,8-P_5CDD	2	40-120
$^{13}C_{12}$ - 1,2,3,6,7,8-H_6CDD	4	40-120
$^{13}C_{12}$ - 1,2,3,4,6,7,8-H_7CDD	4	40-120
$^{13}C_{12}$ - O_8CDD	6	40-120

TABLE E. ACCEPTABLE DETECTION LIMITS

	TISSUE DETECTION LIMITS (ppt)
T_4CDD/F	2
P_5CDD/F	5
H_6CDD/F	10
H_7CDD/F	15
O_8CDD/F	20

APPENDIX B: FISH SAMPLING PROTOCOLS - CONTAMINANT ANALYSIS

NORTHERN RIVER BASINS STUDY

SUB-PROJECT 3119 - RAP - SPECIAL FISH COLLECTION

SCHEDULE B
COLLECTION PROTOCOL

STANDARD OPERATING PROCEDURES
REPRESENTATIVE AREA PROGRAM PROJECTS

1. Fish may be collected using a variety of techniques including:

   - Electro-fishing
   - Trap nets
   - Gill nets
   - Seines
   - Set lines
   - Angling

2. It is important to obtain blood and tissue sub-samples for analyses from live fish only, which have experienced minimum handling stress. This requirement places certain restrictions on the use of the various collection techniques, namely

   i) Electro-fishing:

   Blood samples must be taken within 15 to 20 minutes, immediately followed by the remaining sub-sampling as described below.

   ii) Overnight trap net sets:

   With the exception of whitefish, it is acceptable to obtain blood samples from live fish caught in overnight sets.

   iii) Gill nets, seines and set lines:

   When nets and set lines are used, they are to be set when the desired species are most active (one hour before and after sunset for many species). They must be lifted or checked every 30 minutes to remove fish while they are still alive.

   iv) Angling:

   Angling is acceptable as long as fish are rapidly landed.

3. A sample numbering system must be designed and used to facilitate tracking of sub-samples from the same fish.

4. Captured fish must be immediately anaesthetized in the boat using MS222.

5. Immediately remove blood from the caudal vessels of the anaesthetized fish using a separate heparinized needle for each fish.

6. Transfer each blood sample to an appropriate stoppered centrifuge tube, label and store it and fish together on ice until they are transported to shore. Within 15 minutes after blood removal, transport fish and blood to shore.

7. On shore centrifuge blood, aspirate plasma into appropriate labelled storage tubes and freeze on dry ice within 15 minutes.

8. Record the fish length and weight.

9. Examine fish for external lesions and record any abnormalities. Complete the Gross Pathology Sheet (Appendix 1).

10. Open fish ventrally and examine fish for internal lesions and record any abnormalities.

11. Remove liver, weigh and record weight. Livers must be sub-sampled immediately. Mixed-function oxidase (MFO) activity decreases and the variability increases within 15 minutes of death, depending on external temperatures. Remove gall bladder and store in cryovial, specifically labelled and frozen. Livers must be removed carefully, avoiding the rupture of the gall bladder and avoiding contact with bile.

    a) Take a 1.0g sample (if liver 5.0 g or larger increase sample size to 2.0g) of the liver for MFO analysis.

    b) Each sample must be rinsed with cold 0.15m KCl to remove traces of blood and bile.

    c) Each sample must then be placed in a cryovial, specifically labelled and frozen on dry ice.

    For tissue storage, all MFO samples must be stored and maintained at -60°C or lower; storage at -20°C is not acceptable.

12. Score each fish for gender and for state of sexual development.

13. Remove gonads, weigh and record the weight. Each gonad sample must then be prepared and stored as follows:

Materials

HistoPrep Tissue Capsules (disposable polypropylene) 38 x 8 mm (Dia XH) are used in preserving and processing tissues. Pertinent information (e.g., fish sample number) and identification of the specimen should be written on each capsule with an HB pencil. The capsules are available from Fisher Scientific, product number 15-182-218.

Nalgene Square Polyethylene wide mouth bottles (Ngle 2114) of 1 litre capacity have proven to be excellent for field sampling simply because they do not leak. Bottles containing about 750 ml of Davidson's solution are packed (2 to a bag) in plastic bags (14" x 22") and secured with masking tape for transportation. The bottles are available from Fisher Scientific, product number 03-3120.

Davidson's fixative is used to preserve the pieces of gonads that have been removed from fish within 15 minutes of being brought ashore. Tissue capsules containing gonad samples are immersed in this solution for at least 24 hours and can be stored for several weeks. The Davidson solution can be prepared as follows:

95% ethyl alcohol	300.0 mL
formaldehyde	200.0 mL
glacial acetic acid	100.0 mL
distilled water	300.0 mL
glycerine	100.0 mL

These ingredients should be adequately stirred.

A 5% buffered formalin solution is also used to preserve pieces of ovary. When fresh eggs are placed directly into 5% buffered formalin, there is no significant alteration in egg weight. Labelled tissue capsules are used to hold and identify each sample. The formalin is made up as follows:

formaldehyde	50.0 mL
sodium phosphate monobasic	4.0 g
sodium phosphate dibasic	6.5 g
distilled water add to make 1 litre	

Procedure for Fixation:

One litre Nalgene bottles containing 750 mL Davidson's and 5% formalin solutions are readied. After weighing the gonads, pieces are dissected out with a scalpel. Generally, the mid-region of the gonad from one side, i.e., the left gonad is used from each fish (Burbot - take what is available). It is important that the tissue pieces do not exceed 0.5 cm in thickness but may be slightly larger (usually not greater than 1.0 cm) in the other dimensions. The tissue pieces should easily fit into the tissue capsules without being squashed, and should not take up more than half the capsule space. If a sensitive analytical balance is available, the

piece of tissue to be placed in formalin can be weighed and the weight recorded (two decimal places) in a notebook and on the capsule. A capsule containing tissue should be placed into each of the fixatives and with forceps, momentarily submersed (the tissue capsules tend to float in the fixatives). No more than 24 tissue capsules are placed in each 1 litre bottle to ensure adequate fixative volume. If the eggs in an ovary are large (>3.0mm), additional samples can be taken from the same fish to ensure an adequate number of these eggs will be taken.

14. The remaining portion of the liver with gall bladder removed is to be saved for contaminant analysis. The sample should be placed in a specifically labelled Fisheries and Oceans recommended contaminant free plastic bag. Then frozen on dry ice.

15. Gut contents from each fish are to be saved. Samples are to be placed in clean labelled containers (e.g. whirlpak bags) and frozen at -20oC. Each sample will subsequently be used to determine stable carbon, nitrogen and sulphur isotopes so contamination must be avoided. Formaldehyde and ethyl alcohol or liquids high in nitrogen, carbon and sulphur must not be used.

16. Take whole muscle fillets for contaminant and stable isotope analysis. The whole fillets are to be weighed and then placed in a specifically labelled Fisheries and Oceans recommended contaminant free plastic bag and then frozen on dry ice. Record the weight.

17. Remove the otolith for subsequent ageing. Place each sample in a specifically labelled whirlpak bag and freeze.

18. The use of dry ice for initial freezing and shipping is mandatory.

19. The use of sturdy styrofoam coolers is most practical and is recommended. Styrofoam coolers of weak construction may not assure constant freezing and may break down during shipping. Coleman type coolers may be used but not necessarily be returned immediately for repetitive use. The Contractor is responsible for picking up coolers when notified by Alberta Environment.

20. Place dry ice both on top and bottom of coolers to assure that no freeze-thaw cycles will occur during transport.

    N.B.: Any freeze-thaw, however moderate it may be, will cause contaminant migration within a sample and this may affect contaminant concentration levels in tissues.

21. Ship frozen samples and this may affect contaminant concentration levels in tissues as soon as possible or, if not possible, the majority of samples must be kept frozen in a freezer at -20°C until shipping. Samples of liver tissue for MFO analysis must be stored at -60 C or colder. Samples should be shipped to:

Alberta Environment
c/o Sub Ramamoorthy or E. Baddaloo
Standards Development Office
Oxbridge Place
9820 - 106 Street
Edmonton, Alberta T5K 2J6
(403) 427-6102

22. Any deviation from the above established protocol/procedure should be justified and accounted for in writing and a detailed description of what was done is to be submitted with the fish sample; this is to assure credibility and validity of results.

NORTHERN RIVER BASINS STUDY

SUB-PROJECT 3111 - GENERAL FISH INVENTORIES - PEACE RIVER (Downstream of Vermilion Chutes) and the SLAVE RIVER (Northwest Territories Boundary)

SCHEDULE D

A. FISH SAMPLING PROTOCOL - CONTAMINANT ANALYSIS

1. Fish may be collected using a variety of techniques including:

   - Electro-shocking
   - Gill nets
   - Seines
   - Drift nets
   - Set lines
   - Angling

2. All samples must be submitted as intact whole fish.

3. All fish samples are to be frozen as soon as possible after collection.

4. Details of species, length, date, location and the collector's name must be recorded with the sample number for each sample.

5. All fish must either be:

   (a) immediately processed (length) and directly placed into Department of Fisheries and Oceans recommended contaminant free plastic bags and the bags specifically labelled, or

   (b) placed into stainless steel buckets or basins (rinsed for each site with a solvent series as described in the "Instrument and Equipment Cleaning Procedure" provided below) and kept cool until processed, and then placed into Department of Fisheries and Oceans recommended contaminant free plastic bags and the bags specifically labelled.

   Instrument and Equipment Cleaning Procedures:

   i) washed with tap water and laboratory detergent,

   ii) rinsed with tap water and deionized water (18 meg-ohm),

iii) rinsed with pesticide grade acetone, hexane, dichloromethane and hexane, respectively, and

iv) air dried and heated to 325°C for six hours. All cleaned instruments and equipment to be wrapped in heat treated (325°C) aluminum foil until required.

N.B. Placing fish in ordinary plastic bags will contaminate the samples.

6. Pack small forage fish in composite groups of 10 or more for each species.

7. Pack large fish individually as per (5) above. Place ten (10) individually bagged fish of each major size class, for each important species, in a large bag. Record date, species, size class and sample number, and attach specific label. Important species for the various parts of the study area are:

Peace River

i) Upper reaches (above Peace River)

- Mountain whitefish, northern pike and longnose suckers.

ii) Middle reaches (Peace River to Vermilion Chutes)

- Goldeye, walleye, northern pike and long nose suckers.

iii) Lower reaches (Vermilion Chutes to Confluence with Slave River)

- Goldeye, walleye, northern pike and longnose suckers.

Slave River (All Reaches)

- Lake whitefish, goldeye, northern pike, and longnose suckers.

Athabasca River

i) Upper reaches (above Whitecourt)

- Mountain whitefish, bull trout and northern pike.

ii) Middle reaches (Whitecourt to Cascade Rapids)

- Goldeye, walleye, northern pike and longnose suckers.

iii) Lower reaches (below Cascade Rapids).

- Goldeye, walleye, northern pike, longnose suckers and lake whitefish.

8. The use of dry ice for initial freezing and shipping is the approved method. Alternatives are ice packs and then ice, and may be used only as a secondary means on occasion where there may exist a shortfall in available dry ice.

9. The use of sturdy styrofoam coolers is most practical and is recommended. Styrofoam coolers of weak construction may not assure constant freezing and may break down during shipping. Coleman type coolers may be used but may not necessarily be returned immediately for repetitive use; include return address for these.

10. Place dry ice both on top and bottom of coolers to assure that no freeze-thaw cycles will occur.

N.B.

Any freeze-thaw, however moderate it may be, will cause contaminant migration within a sample and this may affect contaminant concentration levels in tissues.

11. Ship samples as soon as possible or, if not possible, samples must be kept frozen in a freezer at -20°C until shipping. Samples should be shipped to:

Alberta Environment
c/o Sub Ramamoorthy or Earle Baddaloo
Standards Development Office
Oxbridge Place
9820 - 106 Street
Edmonton, Alberta T5K 2J6
(403) 427-6102

12. Any deviation from the above established protocol/procedure should be justified and accounted for in writing and a detailed description of what was done is to be submitted with the fish sample; this is to assure credibility and validity of results.

B. FISH SAMPLING LOCATIONS - CONTAMINANT ANALYSIS

Peace and Slave Rivers

1. Confluence to Slave River, Wood Buffalo National Park.

2. Slave River, outflow into Northwest Territories.

FISH DISSECTION PROTOCOL

1. Fish Retrieval

Upon receiving instructions from NRBS regarding the type, number and sampling site of fish collected for processing, fish samples were retrieved from VERSACOLD, the commercial cold storage facility in Edmonton. The samples were transported to the fish processing laboratory of Alberta Environmental Protection at McIntyre Centre, Edmonton.

2. Fish Characterization and Dissection

The fishes were allowed to thaw in sequence at ambient temperature on laboratory benches on clean polyethylene sheets. Once thawed, fish was identified, weighed, fork length measured as required, and sex determined. All data were recorded on page-numbered laboratory record book. The fish was then dissected using high grade filleting knife which was cleaned prior to use. The type of tissues and organs requested for analysis by NRBS were removed from the fish, muscle was weighed individually and all data were entered in the laboratory record book along with the fish sample number. These numbers were written on the dioxin-free sample bags by the consultant who collected the fish.

3. Homogenization

The tissue sample to be homogenized was thawed at ambient temperature and when moderately soft was cut into small chunks. These chunks were transferred into a clean glass blender and gently blended at low to medium speed to avoid any heating of the sample. The blending was stopped when an uniformly smooth and consistent textured sample was obtained. The sample was then transferred into pre-cleaned glass sample bottles (cleaned with water, deionized water, acetone and hexane followed by thorough drying). The bottles were clearly labelled with a cryomarker and then covered with the pre-treated aluminum foil before the lid was screwed on. The aluminum foil prevented any contact between the sample and the plastic lid. The use of dry ice was not recommended (as some commercial laboratories do) in tissue homogenization because the dry ice which is solid carbon dioxide is never more than commercially pure. This is not acceptable in sample preparation for any trace or ultra-trace analysis.

4. Sample Storage

The dissected portions of the fish such as muscle tissue, liver, fat, gonad etc. were weighed individually (generally muscle and liver), weights were recorded in the laboratory record book and then wrapped in a pre-treated aluminum foil and packaged in a dioxin-free polypropylene bag with sample #, type of tissue or organ, and weight clearly marked with a cryomarker (a pen with special ink which will not erase at low temperatures). The remnants of fish (parts of fish not taken out) were wrapped similarly in pre-treated aluminum foil and packaged in a dioxin-free polypropylene bags with details clearly marked on the outside of the bag. The bags were stored immediately in a freezer in the laboratory for subsequently transported storage at VERSACOLD.

5. Standard Operating Procedures for Eliminating Cross-Contamination

5.1 The dissection board was made of polycarbonate material free from contaminants and resistant to scratching. These procedures eliminated the possibility of any sample remnant being trapped which could cause cross-contamination. The dissection board was cleaned after each sample with water, distilled and deionized water, acetone and hexane and dried with a hot air dryer. The filleting knives were also cleaned after each dissection with water, distilled and deionized water, acetone and hexane and dried thoroughly with a hot air dryer. Acetone and hexane used were of the highest purity available from Fisher Scientific Company.

5.2 Blenders used for homogenization of tissue samples were constructed of high quality glass and they were also washed after each homogenization with water, distilled and deionized water, acetone and hexane; these were then dried thoroughly with hot air. Each batch of homogenization started with six well cleaned and dried blenders and when the fourth blender was being used, the first three used blenders were cleaned and dried. This maximized the cleaning and drying process as well as the number of samples homogenized.

5.3 The commercially available aluminum foil was cut into sheets and then cleaned well with water, deionized water, acetone and hexane. Several sheets were treated in this manner and then dried in a continuous air-flow oven at 120 C for 16 h. The sheets were then taken out of the oven and covered with a larger sheet of aluminum to avoid contamination and allowed to cool at ambient temperature. They were stored in a clean storage cooler for use.

5.4 The waste materials from fish dissection were gathered in a garbage bag, clearly marked for disposal from laboratory waste collection site.

APPENDIX C: **DETAILED PROTOCOL FOR ANALYSIS OF DIOXINS, FURANS, PAHs, PCBs, CO-PLANAR PCBs, CHLORO-PHENOLS, RESINS ACIDS AND METALS - STUDY II**

DETAILED PROTOCOL FOR THE ANALYSIS

OF DIOXINS AND FURANS

I. ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for chlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-p-furans (PCDFs). Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 20g of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

6. Performance (Recovery) Standard/Final Extract Volume

Prior to GC/MS analysis, the cleaned up fish tissue extract will be taken just to dryness in a clean, new 100μL auto sampler vial under a gentle stream of nitrogen and exactly 20μL of the internal standard solution, (100pg/μL $^{13}C_{12}$- 1,2,3,4-TCDD in toluene). This will be used to assess instrument stability, operator performance and surrogate recoveries. This final volume will produce a concentration equivalent to that in the analytical standard for the ^{13}C-surrogate if 100 per cent recovery is achieved. Use of 1,2,3,7,8,9-H_XCDD as an additional internal standard if preferred by the laboratory is acceptable.

7. Quantitation

A quantitation standard mixture (not provided) containing 16 native PCDD/PCDF congeners, the isotopically labeled performance standard and 6 isotopically labeled surrogates, must be used in the analysis. The composition of the analytical solution (quantitation standard), surrogate spiking solution and internal standard solution are given in Tables A, B, and C respectively.

Table A details the composition of this analytical standard and the ion masses to be monitored for determining sample results. If a $^{13}C_{12}$-TCDD surrogate recovery falls outside the acceptable recovery range (Table D), the sample must be re-analyzed with the m/e 328 of the ^{37}Cl-labeled surrogate being monitored instead. This is of mutual benefit to Northern River Basin Study (NRBS) and the participating laboratory in that an interference on the primary tetra-dioxin surrogate may not distort the % recovery of the secondary tetra-surrogate. Alternatively the 328 ion should be routinely monitored in all samples to eliminate the need for re-analysis.

Laboratories have the option of using either internal or external standard procedures for quantitation using this mixture; however, internal standard quantitation is preferred. For quantitation by the internal standard method, the isotopically labeled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors owing to differences in injected volume and unnoticed variations in instrumental sensitivity. For quantitation by the external standard method, the labeled surrogates and performance standard allow corrections to be made for processing losses and injection volume/instrument performance variability.

When using internal standard quantitation, all six isotopically labeled surrogates must be used as the internal standards. Also, the quantitation mixture must be run daily (see II.14) to determine relative response factors between the labeled and native congeners and to determine surrogate and performance standard recoveries. Results are automatically corrected for surrogate recovery; however, the actual surrogate and performance standard recoveries must be reported.

When using external standard quantitation, reported results must be recovery-corrected and the same recovery report generated as for internal standard quantitation above.

Dioxin and furan results for each homologue are corrected for the recovery of the corresponding labeled surrogate dioxin congener. Whether using internal or external quantitation methods, the participating laboratory will provide examples of all equations used to calculate surrogate recoveries, detection limits, to determine relative response factors between native and surrogate compounds and to determine PCDD/PCDF concentrations in the sample.

8. Criteria for PCDD/PCDF Identification

Since many compounds can interfere with the determination of PCDDs and PCDFs, it is of utmost importance that positive identifications be made. The criteria for PCDD/PCDF confirmation are listed below:

- Participating laboratory must demonstrate that 2,3,7,8-TCDD is satisfactorily resolved from neighbouring tetra isomers: 1,2,3,7-T_4CDD and 1,2,3,8-T_4CDD for the analytical column(s) used.

- Peak responses of the monitored ions must be greater than 3 times the background noise level.

- Peak area ratios or spectral ion intensity ratios of the two monitored molecular ions for each congener group must be within +20% of the ratio obtained for the corresponding components in the QUANTITATION standard mixture.

- COCl loss must be monitored and co-maximize with the molecular ions of the analyte.

- Measures must be taken to establish retention time windows for selected ion monitoring of individual homologues, such as use of a standard mixture containing the earliest and latest eluting isomer within each homologue group. These windows must be stable and retention time shifts in excess of +2 scans between surrogates in standards and samples must not occur. Should sample surrogates shift retention time, this is an indication of column problems. All analyses must cease until problem resolved and after re-calibration, samples in question must be re-analyzed.

- Peak maxima for all three monitored ions must coincide within +2 scan units.

- For isomer specific identification, peaks may be identified as, for example, 2,3,7,8-T_4CDD, 2,3,7,8-T_4CDF, O_8CDD and O_8CDF, if they meet the first two criteria and co-elute with their isotopically labeled surrogates within +2 scan units.

- No response must be seen at m/e 374 at the retention time of 2,3,7,8-T_4CDF. This M+ ion of hexachlorodiphenyl ether gives the same fragment ions as T_4CDF and yields a false-positive $_4$T CDF result. Monitoring for other chlorinated diphenyl ethers is optional.

- Surrogate and performance standard recoveries must fall within acceptable windows as specified in Table D.

9. Detection Limits

The detection limit must be reported for all sample results - not just for N.D. values. The concentration units used to report the detection limit must be corrected for surrogate recovery. Table E gives the detection limits which must be met for data to be considered acceptable.

A sample is detectable when the ion response is greater than 3 times S/N (signal/noise) ratio. However, if other qualitative criteria are not met, such as correct ion ratios, that measurement is reported as NDR. A sample is non-detectable when ion response is less than 3 times S/N ratio. This will be reported as ND.

For external standard, the following calculation should be used with performance standard recovery factored in:

$$\text{D.L. (ppt)} = \frac{(\text{Area 3 x S/N}) \times \text{Pq/unit area} \times 100}{\text{g sample} \times \%\ \text{recovery of surrogate}} \times \frac{1}{\text{performance standard recovery}}$$

For external standard, the above calculation should be used with performance standard recovery factored in. For internal standard quantitation, the following must be used:

To determine the minimum detectable area for an individual isomer, one determines the maximum height of noise. A line is manually drawn across the top of the noise peaks in each quantitation ion in the mass chromatogram. The height of the line is determined by rationing the height of the line to the full height of the ion response times the total height counts in the window. This is next multiplied by 3 to achieve 3 times S/N. Height is then converted to area by multiplying 3 times S/N height by the peak area/peak height ratio for the surrogate in that window. This area is then used to calculate the detection limit.

In cases where the quantitation ion contains a large peak which prevents observation of the noise due to the scaling, the following procedures may be used:

1. Rescale and reprint the ion window to either side of the peak and proceed as usual.

2. Use the minimum detectable area from the same channel in the method spike run for calculation of sample detection limit.

II. ADDITIONAL QA REQUIREMENTS

Most of the following QA requirements are probably routine procedure in participating laboratories. However, they form an integral part of a QA protocol and must be followed:

1. Good laboratory practice: all equipment, sample concentrators, glassware, benches, etc. shall be kept clean during processing of these samples. No high level samples such as flyash shall be processed simultaneously. This could lead to cross-contamination problems.

2. Sample storage during workups: all sample extracts shall be refrigerated at 4°C in the dark when not needed for various cleanup steps.

3. Record keeping: a set of laboratory notebooks will be dedicated to these analyses and all records of sample treatment shall be recorded in these logs, which will be signed and dated for each sample manipulation. Such notebooks shall be available for audit upon request by NRBS and shall be delivered to NRBS at the end of the NRBS study.

4. Laboratory audits: NRBS may wish to audit individual laboratories and their operating procedures during this study. The analyst-in- charge may be required to review some of the data with NRBS.

5. Disposal: the participating laboratory is responsible for the disposal of unused samples. Such disposal shall not take place without the approval of NRBS. Samples will be suitably stored at -20°C to ensure their integrity until disposal is requested by NRBS.

6. All final sample extracts will be retained. When participating laboratory completes the analyses, these extracts (gently evaporated to dryness under nitrogen) will be delivered to NRBS in new, unused, precleaned 100 μl auto sampler vials, tightly sealed, under chain-of-custody protocols. Vial containers will not be replaced by NRBS.

7. Raw GCMS data shall be backed up onto tape or diskette daily. These tapes shall be stored in secure locations and may not be erased without express written permission from NRBS.

8. For each total congener concentration reported, the number of positive individual isomers found must be reported.

9. Analytical standards and spiking surrogate mixtures will be used for all quantitative determinations by all participating laboratories.

10. NRBS may audit positive and negative T_4CDF values by submitting samples to either high resolution GC - high resolution MS or GC-MS-MS analysis using appropriate columns.

11. Participating laboratory shall be responsible for GC column performance checking and shall provide details of such checks with sample reports:

    i. Check for isomer specificity for 2,3,7,8-TCDD and -TCDF.

    ii. Use of commercial window defining mixtures to set up GCMS windows for the various congener groups.

    iii. Verify calibration of column - MS by running analytical standards and maintaining a +20% response on all ions monitored across the congener groups.

    iv. Periodically a column blank shall be run to assess carryover. (2 μL injection of toluene and full analysis).

    v. Verify and demonstrate that 10 pg 2,3,7,8-T_4CDD can be accurately seen at 3 times S/N prior to all analyses.

12. Additional performance audits may involve blind analysis of spiked matrix samples, split audit samples sent to government labs, etc.

13. Prior to commencing analyses, linearity of system shall be determined by a minimum of 5 point calibration covering a concentration range of 0.02 to 2 ng/μl PCDD/PCDF. The participating laboratory shall be responsible for obtaining these mixtures but will provide all details to NRBS. Linearity shall be rechecked periodically and in particular, after each column change. Relative response factors (native std./labeled std.) will then be established.

14. Daily calibration will be via running the provided analytical standard using single-point calibration. The processing of samples will be performed by running the standard and comparing response to last previous standard. Control chart RRF (Relative Response Factor) plots of standards will be maintained and submitted with each data set. If value is +15% for the ions selected of natives and surrogates, analysis of samples may proceed. If responses are outside this range, a second standard must be run and similarly assessed. If this too fails, the problem must be found and corrected before any samples are run. For external standard quantitation, frequent recalibration must take place, and the following sequence should be followed when analyzing samples:

    Standard, Sample, Sample, Standard

III. DATA REPORTING AND EVALUATION PROCEDURES

1. Data Reporting

   i. All results must be reported on the attached Analysis Report Form. This uniformity of reporting format is essential for ease of evaluation of data sets originating from more than one laboratory. Three copies of each data report must be provided.

   ii. It is required that each data set be accompanied by the original (not copies) legible printouts of all GCMS ion chromatograms, spectra and spectral intensity lists of all analytical standards samples, blanks, method spikes, column blanks, and check solutions with all peaks identified as PCDD or PCDF congeners - clearly indicated directly on the printouts in ink. Retention times, peak heights, and peak areas must be clearly labeled. On Finnigan GCMS systems, the noise line must be turned "on".

   iii. For each report, all information requested on the Analysis Report Form must be supplied. The ratio ranges must be determined by the participating laboratory on their GCMS by analysis of the standard provided and determination of individual isomer's ion ratio from the areas or spectral intensities.

   iv. As an integral part of all data reports, the following additional information must be supplied:

   - Calibration reports
   - Date/time record GCMS
   - Control chart RRFs
   - Worksheet for surrogate recoveries
   - MDL calculations

   v. Please enclose the following with the final data:

   a. a brief description of the methods used;
   b. a description of the GC/MS system used, the operational parameters, and the acquisition system;
   c. the capillary column(s) used; and
   d. a description of the method for calculating detection limits.

TABLE A. ANALYTICAL (QUANTITATION) STANDARD AND SELECTED ION MASSES FOR PCDD/PCDF ANALYSIS.

QUANTITATION Standard Ions	CONCENTRATION (pg/pL)	QUANTITATION Ion	CONFIRMATION
DIOXINS			
2,3,7,8-T_4CDD	100	322	320,259
1,2,3,7,8-P_5CDD	100	356	354,293
1,2,3,4,7,8-H_6CDD	100	390	392,327
1,2,3,6,7,8-H_6CDD	100	390	392,327
1,2,3,7,8,9-H_6CDD	100	390	392,327
1,2,3,4,6,7,8-H_7CDD	100	424	426,361
O_8CDD	100	460	458,397
FURANS			
2,3,7,8-T_4CDF	100	306	304,243
1,2,3,7,8-P_5CDF	100	340	338,277
2,3,4,7,8-P_5CDF	100	340	338,277
2,3,4,6,7,8-H_6CDF	100	374	376,311
1,2,3,4,7,8-H_6CDF	100	374	376,311
1,2,3,6,7,8-H_6CDF	100	374	376,311
1,2,3,7,8,9-H_6CDF	100	374	376,311
1,2,3,4,6,7,8-H_7CDF	100	408	410,345
0_8CDF	100	444	442,379
SURROGATES (C_{13} LABELLED PCDDS)			
$^{13}C_{12}$-2,3,7,8-T_4CDD	100	334	332
$^{37}C_{14}$-2,3,7,8-T_4CDD	100	328	None
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	100	368	366
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	200	402	404
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	200	436	338
$^{13}C_{12}$-O_8CDD	300	472	470
PERFORMANCE (INTERNAL) STANDARD			
$^{13}C_{12}$-1,2,3,4-TCDD	100	334	332

Solvent = Toluene

TABLE B. SURROGATE SPIKING SOLUTION.

SURROGATE: C_{13}-LABELLED PCDDs	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 2,3,7,8-T_4CDD	20
$^{37}Cl_4$ - 2,3,7,8-T_4CDD	20
$^{13}C_{12}$ - 1,2,3,7,8-P_5CDD	20
$^{13}C_{12}$ - 1,2,3,6,7,8-H_6CDD	40
$^{13}C_{12}$ - 1,2,3,4,6,7,8-H_7CDD	40
$^{13}C_{12}$ - 0_8CDD	60

Solvent = Toluene

TABLE C. PERFORMANCE (INTERNAL) STANDARD SOLUTION.

C_{13}-LABELLED PCDD	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 1234-TCDD	100

Solvent = Toluene

TABLE D. SURROGATE STANDARD RECOVERY CRITERIA.

SURROGATE STANDARD	AMOUNT SPIKED (ng)	ACCEPTABLE RECOVERY (%)
$^{13}C_{12}$ - 2378-T_4CDD	2	40-120
$^{13}C_{12}$ - 12378-P_5CDD	2	40-120
$^{13}C_{12}$ - 123678-H_6CDD	4	40-120
$^{13}C_{12}$ - 1234678-H_7CDD	4	40-120
$^{13}C_{12}$ - O_8CDD	6	40-120

TABLE E. ACCEPTABLE DETECTION LIMITS

	PRACTICAL DETECTION LIMITS		
COMPOUND	TISSUE PTT (pg/g)	SEDIMENT PPT (pg/g)	WATER PPQ (fg/g)
T_4CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
P_5CDD/F	0.4/0.4	0.4/0.4	0.4/0.4
H_6CDD/F	1.0/0.6	0.6/0.4	0.8/0.6
H_7CDD/F	1.6/1.6	1.6/1.6	1.6/1.6
0_8CDD/F	4.0/4.0	4.0/4.0	2.0/2.0

	ACHIEVABLE DETECTION LIMITS		
COMPOUND	TISSUE PTT (pg/g)	SEDIMENT PPT (pg/g)	WATER PPQ (fg/g)
T_4CDD/F	0.1/0.1	0.1/0.1	0.1/0.1
P_5CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
H_6CDD/F	0.5/0.3	0.3/0.2	0.4/0.3
H_7CDD/F	0.8/0.8	0.8/0.8	0.8/0.8
0_8CDD/F	2.0/2.0	2.0/2.0	1.0/1.0

1. These detection limits can be achieved or even lower easily by HRGC/HRMS.

2. The detection limits acceptable from LRMS will be about five times higher than those form HRMS listed here.

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBs) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under 5. for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

IV. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analytes in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001

APPENDIX D: **TERMS OF REFERENCE FOR ANALYTICAL SERVICES**

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

ANALYTICAL SERVICES

Project: **AXYS LAB**

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. **Analyze each homogenized sediment and water samples and Q.A. Check samples for the 2378-chlorine substituted congeners of polychlorinated dibenzo-p-dioxins (PCDD's) and dibenzo furans (PCDF's).**

2. Specific 2378-chlorine substituted congeners must be individually reported along with congener group totals.

3. Spike each sample with appropriate amount of the surrogate spiking solution (not provided) containing C-13 labelled PCDD's prior to extraction. Use your stock of surrogate spiking solution. Prior to GC/MS analysis, reconstitute the "cleaned up" extract with a known volume of the performance standard solution (not provided).

4. You are required to report the percent recovery of the surrogate standards.

5. You will receive a detailed protocol along with the samples.

6. **You are also required to analyze each sediment samples for resin acids.**

7. You should use the appropriate internal, surrogate standards and/or certified standards for the analysis of resin acids in sediments.

8. You are required to use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. Specific 2,3,7,8-chlorine substituted congeners must be individually reported along with congener group totals.

3. For each sample, the percent surrogate recovery of the C-13 labelled PCDD's, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike, surrogate standards or reference material in the analysis of resin acids and the associated detection limits must be individually reported on a separate report form.

5. The dioxins and furans data obtained for each sample will be provided to the Study Office on computer medium using Dbase IV as well as on a standard report form (5 copies).

6. - Analytical charts containing GC and MS chromatography for all standards and samples are to be provided to the technical officer.
   - The peaks identified as PCDD's and PCDF's and resin acids must be clearly marked on the GC/MS data.
   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase IV or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the PCDD's and PCDF's and resin acids in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

   b) a description of the GC/MS system used, the operational parameters and the acquisition system;

   c) the capillary column(s) used;

   d) a description of the method used for calculating detection limits; and

e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

For detailed information on the analysis and detection limits of PCDD's and PCDF's and resin acids, refer to Schedule B of this Agreement.

IV Re-testing and Return of Samples

1. All data provided to the technical officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the technical officer. The lab will be notified in the case where unused portions of samples are to be returned to the technical officer.

SCHEDULE A1

DETAILED PROTOCOL FOR THE ANALYSIS OF DIOXINS AND FURANS

I. ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for chlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-p-furans (PCDFs). Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 20g of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

6. Performance (Recovery) Standard/Final Extract Volume

Prior to GC/MS analysis, the cleaned up fish tissue extract will be taken just to dryness in a clean, new 100μL autosampler vial under a gentle stream of nitrogen and exactly 20μL of the internal standard solution, (100pg/μL $^{13}C_{12}$. 1,2,3.4-T_4CDD in toluene). This will be used to assess instrument stability, operator performance and surrogate recoveries. This final volume will produce a concentration equivalent to that in the analytical standard for the ^{13}C-surrogate if 100 per cent recovery is achieved. Use of 1,2,3,7,8,9-H_XCDD as an additional internal standard if preferred by the laboratory is acceptable.

7. Quantitation

A quantitation standard mixture (not provided) containing 16 native PCDD/PCDF congeners, the isotopically labelled performance standard and 6 isotopically labelled surrogates, must be used in the analysis. The composition of the analytical solution (quantitation standard), surrogate spiking solution and internal standard solution are given in Tables A, B, and C respectively.

Table A details the composition of this analytical standard and the ion masses to be monitored for determining sample results. If a $^{13}C_{12}$-T_4CDD surrogate recovery falls outside the acceptable recovery range (Table D), the sample must be re-analyzed with the m/e 328 of the ^{37}Cl-labelled surrogate being monitored instead. This is of mutual benefit to Northern River Basin Study (NRBS) and the participating laboratory in that an interference on the primary tetra-dioxin surrogate may not distort the % recovery of the secondary tetra-surrogate. Alternatively the 328 ion should be routinely monitored in all samples to eliminate the need for re-analysis.

Laboratories have the option of using either internal or external standard procedures for quantitation using this mixture; however, internal standard quantitation is preferred. For quantitation by the internal standard method, the isotopically labelled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors owing to differences in injected volume and unnoticed variations in instrumental sensitivity. For quantitation by the external standard method, the labelled surrogates and performance standard allow corrections to be made for processing losses and injection volume/instrument performance variability.

When using internal standard quantitation, all six isotopicallylabelled surrogates must be used as the internal standards. Also, the quantitation mixture must be run daily (see II.14) to determine relative response factors between the labelled and native congeners and to determine surrogate and performance standard recoveries. Results are automatically corrected for surrogate recovery; however, the actual surrogate and performance standard recoveries must be reported.

When using external standard quantitation, reported results must be recovery-corrected and the same recovery report generated as for internal standard quantitation above.

Dioxin and furan results for each homologue are corrected for the recovery of the corresponding labelled surrogate dioxin congener. Whether using internal or external quantitation methods, the participating laboratory will provide examples of all equations used to calculate surrogate recoveries, detection limits, to determine relative response factors between native and surrogate compounds and to determine PCDD/PCDF concentrations in the sample.

8. Criteria for PCDD/PCDF Identification

Since many compounds can interfere with the determination of PCDDs and PCDFs, it is of utmost importance that positive identifications be made. The criteria for PCDD/PCDF confirmation are listed below:

- Participating laboratory must demonstrate that 2378-T_4CDD is satisfactorily resolved from neighbouring tetra isomers: 1237-T_4CDD and 1238-T_4CDD for the analytical column(s) used.

- Peak responses of the monitored ions must be greater than 3 times the background noise level.

- Peak area ratios or spectral ion intensity ratios of the two monitored molecular ions for each congener group must be within +20% of the ratio obtained for the corresponding components in the QUANTITATION standard mixture.

- COCl loss must be monitored and co-maximize with the molecular ions of the analyte.

- Measures must be taken to establish retention time windows for selected ion monitoring of individual homologues, such as use of a standard mixture containing the earliest and latest eluting isomer within each homologue group. These windows must be stable and retention time shifts in excess of +2 scans between surrogates in standards and samples must not occur. Should sample surrogates shift retention time, this is an indication of column problems. All analyses must cease until problem resolved and after re-calibration, samples in question must be re-analyzed.

- Peak maxima for all three monitored ions must coincide within +2 scan units.

- For isomer specific identification, peaks may be identified as, for example, 2378-T_4CDD, 2378-T_4CDF, O_8CDD and O_8CDF, if they meet the first two criteria and co-elute with their isotopically labelled surrogates within +2 scan units.

- No response must be seen at m/e 374 at the retention time of 2378-T_4CDF. This M+ ion of hexachlorodiphenyl ether gives the same fragment ions as T_4CDF and yields a false-positive T_4CDF result. Monitoring for other chlorinated diphenyl ethers is optional.

- Surrogate and performance standard recoveries must fall within acceptable windows as specified in Table D.

9. Detection Limits

The detection limit must be reported for all sample results - not just for N.D. values. The concentration units used to report the detection limit must be corrected for surrogate recovery. Table E gives the detection limits which must be met for data to be considered acceptable.

A sample is detectable when the ion response is greater than 3 times S/N (signal/noise) ratio. However, if other qualitative criteria are not met, such as correct ion ratios, that measurement is reported as NDR. A sample is non-detectable when ion response is less than 3 times S/N ratio. This will be reported as ND.

For external standard, the following calculation should be used with performance standard recovery factored in:

$$\text{D.L. (ppt)} = \frac{(\text{Area 3} \times \text{S/N}) \times \text{Pq/unit area} \times 100}{\text{g sample} \times \%\ \text{recovery of surrogate}} \times \frac{1}{\text{performance standard recovery}}$$

For external standard, the above calculation should be used with performance standard recovery factored in. For internal standard quantitation, the following must be used:

To determine the minimum detectable area for an individual isomer, one determines the maximum height of noise. A line is manually drawn across the top of the noise peaks in each quantitation ion in the mass chromatogram. The height of the line is determined by rationing the height of the line to the full height of the ion response times the total height counts in the window. This is next multiplied by 3 to achieve 3 times S/N. Height is then converted to area by multiplying 3 times S/N height by the peak area/peak height ratio for the surrogate in that window. This area is then used to calculate the detection limit.

In cases where the quantitation ion contains a large peak which prevents observation of the noise due to the scaling, the following procedures may be used:

1. Rescale and reprint the ion window to either side of the peak and proceed as usual.

2. Use the minimum detectable area from the same channel in the method spike run for calculation of sample detection limit.

II. ADDITIONAL QA REQUIREMENTS

Most of the following QA requirements are probably routine procedure in participating laboratories. However, they form an integral part of a QA protocol and must be followed:

1. Good laboratory practice: all equipment, sample concentrators, glassware, benches, etc. shall be kept clean during processing of these samples. No high level samples such as flyash shall be processed simultaneously. This could lead to cross-contamination problems.

2. Sample storage during workups: all sample extracts shall be refrigerated at 4°C in the dark when not needed for various cleanup steps.

3. Record keeping: a set of laboratory notebooks will be dedicated to these analyses and all records of sample treatment shall be recorded in these logs, which will be signed and dated for each sample manipulation. Such notebooks shall be available for audit upon request by NRBS and shall be delivered to NRBS at the end of the NRBS study.

4. Laboratory audits: NRBS may wish to audit individual laboratories and their operating procedures during this study. The analyst-in- charge may be required to review some of the data with NRBS.

5. Disposal: the participating laboratory is responsible for the disposal of unused samples. Such disposal shall not take place without the approval of NRBS. Samples will be suitably stored at -20°C to ensure their integrity until disposal is requested by NRBS.

6. All final sample extracts will be retained. When participating laboratory completes the analyses, these extracts (gently evaporated to dryness under nitrogen) will be delivered to NRBS in new, unused, precleaned 100 μl autosampler vials, tightly sealed, under chain-of-custody protocols. Vial containers will not be replaced by NRBS.

7. Raw GCMS data shall be backed up onto tape or diskette daily. These tapes shall be stored in secure locations and may not be erased without express written permission from NRBS.

8. For each total congener concentration reported, the number of positive individual isomers found must be reported.

9. Analytical standards and spiking surrogate mixtures will be used for all quantitative determinations by all participating laboratories.

10. NRBS may audit positive and negative T_4CDF values by submitting samples to either high resolution GC - high resolution MS or GC-MS-MS analysis using appropriate columns.

11. Participating laboratory shall be responsible for GC column performance checking and shall provide details of such checks with sample reports:

    i. Check for isomer specificity for 2378-T_4CDD and -T_4CDF.

    ii. Use of commercial window defining mixtures to set up GCMS windows for the various congener groups.

    iii. Verify calibration of column - MS by running analytical standards and maintaining a +20% response on all ions monitored across the congener groups.

    iv. Periodically a column blank shall be run to assess carryover. (2 μL injection of toluene and full analysis).

    v. Verify and demonstrate that 10 pg 2378-T_4CDD can be accurately seen at 3 times S/N prior to all analyses.

12. Additional performance audits may involve blind analysis of spiked matrix samples, split audit samples sent to government labs, etc.

13. Prior to commencing analyses, linearity of system shall be determined by a minimum of 5 point calibration covering a concentration range of 0.02 to 2 ng/μl PCDD/PCDF. The participating laboratory shall be responsible for obtaining these mixtures but will provide all details to NRBS. Linearity shall be rechecked periodically and in particular, after each column change. Relative response factors (native std./labelled std.) will then be established.

14. Daily calibration will be via running the provided analytical standard using single-point calibration. The processing of samples will be performed by running the standard and comparing response to last previous standard. Control chart RRF (Relative Response Factor) plots of standards will be maintained and submitted with each data set. If value is +15% for the ions selected of natives and surrogates, analysis of samples may proceed. If responses are outside this range, a second standard must be run and similarly assessed. If this too fails, the problem must be found and corrected before any samples are run. For external standard quantitation, frequent recalibration must take place, and the following sequence should be followed when analyzing samples:

Standard, Sample, Sample, Standard

III. DATA REPORTING AND EVALUATION PROCEDURES

1. Data Reporting

   i. All results must be reported on the attached Analysis Report Form. This uniformity of reporting format is essential for ease of evaluation of data sets originating from more than one laboratory. Three copies of each data report must be provided.

   ii. It is required that each data set be accompanied by the original (not copies) legible printouts of all GCMS ion chromatograms, spectra and spectral intensity lists of all analytical standards samples, blanks, method spikes, column blanks, and check solutions with all peaks identified as PCDD or PCDF congeners - clearly indicated directly on the printouts in ink. Retention times, peak heights, and peak areas must be clearly labelled. On Finnigan GCMS systems, the noise line must be turned "on".

   iii. For each report, all information requested on the Analysis Report Form must be supplied. The ratio ranges must be determined by the participating laboratory on their GCMS by analysis of the standard provided and determination of individual isomer's ion ratio from the areas or spectral intensities.

   iv. As an integral part of all data reports, the following additional information must be supplied:

   - Calibration reports
   - Date/time record GCMS
   - Control chart RRFs
   - Worksheet for surrogate recoveries
   - MDL calculations

   v. Please enclose the following with the final data:

      a. a brief description of the methods used;
      b. a description of the GC/MS system used, the operational parameters, and the acquisition system;
      c. the capillary column(s) used; and
      d. a description of the method for calculating detection limits.

TABLE A. ANALYTICAL (QUANTITATION) STANDARD AND SELECTED ION MASSES FOR PCDD/PCDF ANALYSIS.

QUANTITATION Standard	CONCENTRATION (pg/pL)	QUANTITATION Ion	CONFIRMATION Ions
DIOXINS			
2,3,7,8-T_4CDD	100	322	320,259
1,2,3,7,8-P_5CDD	100	356	354,293
1,2,3,4,7,8-H_6CDD	100	390	392,327
1,2,3,6,7,8-H_6CDD	100	390	392,327
1,2,3,7,8,9-H_6CDD	100	390	392,327
1,2,3,4,6,7,8-H_7CDD	100	424	426,361
O_8CDD	100	460	458,397
FURANS			
2,3,7,8-T_4CDF	100	306	304,243
1,2,3,7,8-P_5CDF	100	340	338,277
2,3,4,7,8-P_5CDF	100	340	338,277
2,3,4,6,7,8-H_6CDF	100	374	376,311
1,2,3,4,7,8-H_6CDF	100	374	376,311
1,2,3,6,7,8-H_6CDF	100	374	376,311
1,2,3,7,8,9-H_6CDF	100	374	376,311
1,2,3,4,6,7,8-H_7CDF	100	408	410,345
0_8CDF	100	444	442,379
SURROGATES (C_{13} LABELLED PCDDS)			
$^{13}C_{12}$-2,3,7,8-T_4CDD	100	334	332
$^{37}C_{14}$-2,3,7,8-T_4CDD	100	328	None
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	100	368	366
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	200	402	404
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	200	436	338
$^{13}C_{12}$-O_8CDD	300	472	470
PERFORMANCE (INTERNAL) STANDARD			
$^{13}C_{12}$-1234-TCDD	100	334	332

Solvent = Toluene

TABLE B. SURROGATE SPIKING SOLUTION.

SURROGATE: C_{13}-LABELLED PCDDs	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 2,3,7,8-T_4CDD	20
$^{37}Cl_4$ - 2,3,7,8-T_4CDD	20
$^{13}C_{12}$ - 1,2,3,7,8-P_5CDD	20
$^{13}C_{12}$ - 1,2,3,6,7,8-H_6CDD	40
$^{13}C_{12}$ - 1,2,3,4,6,7,8-H_7CDD	40
$^{13}C_{12}$ - 0_8CDD	60

Solvent = Toluene

TABLE C. PERFORMANCE (INTERNAL) STANDARD SOLUTION.

C_{13}-LABELLED PCDD	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 1234-TCDD	100

Solvent = Toluene

TABLE D. SURROGATE STANDARD RECOVERY CRITERIA.

SURROGATE STANDARD	AMOUNT SPIKED (ng)	ACCEPTABLE RECOVERY (%)
$^{13}C_{12}$ - 2378-T_4CDD	2	40-120
$^{13}C_{12}$ - 12378-P_5CDD	2	40-120
$^{13}C_{12}$ - 123678-H_6CDD	4	40-120
$^{13}C_{12}$ - 1234678-H_7CDD	4	40-120
$^{13}C_{12}$ - O_8CDD	6	40-120

TABLE E. ACCEPTABLE DETECTION LIMITS

	PRACTICAL DETECTION LIMITS		
COMPOUND	TISSUE PTT (pg/g)	SEDIMENT PPT (pg/g)	WATER PPQ (fg/g)
T_4CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
P_5CDD/F	0.4/0.4	0.4/0.4	0.4/0.4
H_6CDD/F	1.0/0.6	0.6/0.4	0.8/0.6
H_7CDD/F	1.6/1.6	1.6/1.6	1.6/1.6
$0_8CDD/F$	4.0/4.0	4.0/4.0	2.0/2.0

	ACHIEVABLE DETECTION LIMITS		
COMPOUND	TISSUE PTT (pg/g)	SEDIMENT PPT (pg/g)	WATER PPQ (fg/g)
T_4CDD/F	0.1/0.1	0.1/0.1	0.1/0.1
P_5CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
H_6CDD/F	0.5/0.3	0.3/0.2	0.4/0.3
H_7CDD/F	0.8/0.8	0.8/0.8	0.8/0.8
$0_8CDD/F$	2.0/2.0	2.0/2.0	1.0/1.0

1. These detection limits can be achieved or even lower easily by HRGC/HRMS.

2. The detection limits acceptable from LRMS will be about five times higher than those form HRMS listed here.

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBS) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under 5. for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

IV. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analytes in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

ANALYTICAL SERVICES

Project: CHEMEX LABORATORIES (ALBERTA) INC.

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. Analyze each homogenized sediment and water samples and Q.A. Check samples for:

   a) polyaromatic hydrocarbons (PAHs);

   b) polychlorinated biphenyls (PCBs) and congeners including coplanar PCB's where the results are positive;

   c) chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles.

   d) Organochlorines (OCs) including toxaphene.

2. **Analyze each homogenized tissue and sediment samples for total and extractable metals; lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury.**

3. Specific congeners/isomers must be individually reported along with the totals.

4. You are required to report the percent recovery of the surrogate standards.

5. You will receive a detailed protocol along with the samples.

6. You should use the appropriate internal, surrogate standards and/or certified standards in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols, OCs and metals, in tissue samples.

7. You are required to use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. The PAHs, PCBs, Coplanar PCBs, chlorophenols, OCs and metals data obtained for each sample are to be typed on a standard report form. Specific isomers and/or congeners must be individually reported along with the group totals.

3. For each sample, the percent recovery of the surrogate standards, certified standards, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols, OCs, and metals must be individually reported.

5. Sample will be provided to the Study Office on computer medium using Dbase IV as well as in hard copy (5 copies).

6. - Analytical charts containing GC and MS chromatography for all standards and samples are to be kept on file at the Contractor's office for a minimum of three (3) years.

   - The peaks identified as PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs must be clearly marked on the GC/MS data.

   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase Iv or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the PAHs, PCBs, Coplanar PCBs, chlorophenols, OCs and metals in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

b) a description of the GC/MS system used, the operational parameters and the acquisition system;

c) the capillary column(s) used;

d) a description of the method used for calculating detection limits; and

e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

For further information on the analysis and detection limits of PAH, PCB, Coplanar PCB, chlorophenol, OC and metals, refer to Schedule A1 of this Agreement.

9. Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6, (403) 427-6102, will be the Scientific Officer for this analytical work.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the study office. The lab will be notified in the case where unused portions of samples are to be returned to the technical officer.

SCHEDULE AA - TERMS OF REFERENCE

Project: **CHEMEX LABORATORIES (ALBERTA) INC.**

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. **You are required to analyze water samples for the following major ions, physical parameters and nutrients:**

   a) **pH, conductivity, turbidity, total dissolved solids, total hardness, total alkalinity, total kjeldahl nitrogen, nitrite, nitrate, fluoride, chloride, sulfate, bicarbonate, carbonate, ammonia, dissolved orthophosphate, dissolved phosphate, total phosphate, TOC, DOC, Ca, Mg, Zn, Na, K, Fe and Mn, true colour and suspended solids.**

2. You are required to report the percent recovery to spikes and standard reference materials.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. The data obtained for each sample are to be typed on a standard report form.

3. For each sample, the percent recovery of the surrogate standards, certified standards, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike in the analysis must be individually reported.

5. Sample data will be provided to the Study Office on computer medium using Dbase IV as well as in hard copy (5 copies).

6. - Analytical charts for all standards and samples are to be provided to the technical officer.

   - The peaks identified must be clearly marked on the data sheets.

   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase IV or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the analyses in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

   b) a description of the system used, the operational parameters and the acquisition system;

   c) the columns used;

   d) a description of the method used for calculating detection limits; and

   e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

9. Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6, (403) 427-6102, will be the Scientific Officer for this analytical work.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the technical officer. The lab will be notified in the case where unused portions of samples are to be returned to the technical officer.

SCHEDULE A1

ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for PCBs and coplanar PCBs, OCs including toxaphenes, PAHs, chlorophenols, metals, routine chemistry, colour, turbidity and suspended solids, total phenolics and silicates. Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 2Og of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

SCHEDULE A1

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBS) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under V.6 for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

IV. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analyses in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

ANALYTICAL SERVICES

Project: **ENVIRO-TEST LABORATORIES**

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. **Analyze each homogenized tissue samples and Q.A. Check samples for the 2378-chlorine substituted congeners of polychlorinated dibenzo-p-dioxins (PCDD's) and dibenzo furans (PCDF's).**

2. Specific 2378-chlorine substituted congeners must be individually reported along with congener group totals.

3. Spike each sample with appropriate amount of the surrogate spiking solution (not provided) containing C-13 labelled PCDD's prior to extraction. Use your stock of surrogate spiking solution. Prior to GC/MS analysis, reconstitute the "cleaned up" extract with a known volume of the performance standard solution (not provided).

4. You are required to report the percent recovery of the surrogate standards.

5. You will receive a detailed protocol along with the samples.

6. You are also required to analyze each tissue sample for resin acids.

7. You should use the appropriate internal, surrogate standards and/or certified standards for the analysis of resin acids in tissues.

8. You are required to determine the lipid content of each tissue sample and report along with other analytical data.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. Specific 2,3,7,8-chlorine substituted congeners must be individually reported along with congener group totals.

3. For each sample, the percent surrogate recovery of the C-13 labelled PCDD's, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike, surrogate standards or reference material in the analysis of resin acids and the associated detection limits must be individually reported on a separate report form.

5. The dioxins and furans data obtained for each sample will be provided to the Study Office on computer medium using Dbase IV as well as on a standard report form.

6. - Analytical charts containing GC and MS chromatography for all standards and samples are to be provided to the technical officer.
   - The peaks identified as PCDD's and PCDF's and resin acids must be clearly marked on the GC/MS data.
   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase IV or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the PCDD's and PCDF's and resin acids in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

   b) a description of the GC/MS system used, the operational parameters and the acquisition system;

   c) the capillary column(s) used;

   d) a description of the method used for calculating detection limits; and

e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

For detailed information on the analysis and detection limits of PCDD's and PCDF's and resin acids, refer to Schedule A1 of this Agreement.

9. Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6 (403) 427-6102, will be the Scientific Officer for this analytical work.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the study office. The lab will be notified in the case where unused portions of samples are to be returned to the Coordinator, Contaminants Component.

SCHEDULE A1

DETAILED PROTOCOL FOR THE ANALYSIS OF DIOXINS AND FURANS

I. ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for chlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-p-furans (PCDFs). Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 20g of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

6. Performance (Recovery) Standard/Final Extract Volume

Prior to GC/MS analysis, the cleaned up fish tissue extract will be taken just to dryness in a clean, new 100μL autosampler vial under a gentle stream of nitrogen and exactly 20μL of the internal standard solution, (100pg/μL $^{13}C_{12}$- 1234-T_4CDD in toluene). This will be used to assess instrument stability, operator performance and surrogate recoveries. This final volume will produce a concentration equivalent to that in the analytical standard for the ^{13}C-surrogate if 100 per cent recovery is achieved. Use of 123789-H_XCDD as an additional internal standard if preferred by the laboratory is acceptable.

7. Quantitation

A quantitation standard mixture (not provided) containing 16 native PCDD/PCDF congeners, the isotopically labelled performance standard and 6 isotopically labelled surrogates, must be used in the analysis. The composition of the analytical solution (quantitation standard), surrogate spiking solution and internal standard solution are given in Tables A, B, and C respectively.

Table A details the composition of this analytical standard and the ion masses to be monitored for determining sample results. If a $^{13}C_{12}$-T_4CDD surrogate recovery falls outside the acceptable recovery range (Table D), the sample must be re-analyzed with the m/e 328 of the ^{37}Cl-labelled surrogate being monitored instead. This is of mutual benefit to Northern River Basin Study (NRBS) and the participating laboratory in that an interference on the primary tetra-dioxin surrogate may not distort the % recovery of the secondary tetra-surrogate. Alternatively the 328 ion should be routinely monitored in all samples to eliminate the need for re-analysis.

Laboratories have the option of using either internal or external standard procedures for quantitation using this mixture; however, internal standard quantitation is preferred. For quantitation by the internal standard method, the isotopically labelled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors owing to differences in injected volume and unnoticed variations in instrumental sensitivity. For quantitation by the external standard method, the labelled surrogates and performance standard allow corrections to be made for processing losses and injection volume/instrument performance variability.

When using internal standard quantitation, all six isotopicallylabelled surrogates must be used as the internal standards. Also, the quantitation mixture must be run daily (see II.14) to determine relative response factors between the labelled and native congeners and to determine surrogate and performance standard recoveries. Results are automatically corrected for surrogate recovery; however, the actual surrogate and performance standard recoveries must be reported.

When using external standard quantitation, reported results must be recovery-corrected and the same recovery report generated as for internal standard quantitation above.

Dioxin and furan results for each homologue are corrected for the recovery of the corresponding labelled surrogate dioxin congener. Whether using internal or external quantitation methods, the participating laboratory will provide examples of all equations used to calculate surrogate recoveries, detection limits, to determine relative response factors between native and surrogate compounds and to determine PCDD/PCDF concentrations in the sample.

8. Criteria for PCDD/PCDF Identification

Since many compounds can interfere with the determination of PCDDs and PCDFs, it is of utmost importance that positive identifications be made. The criteria for PCDD/PCDF confirmation are listed below:

- Participating laboratory must demonstrate that 2378-T_4CDD is satisfactorily resolved from neighbouring tetra isomers: 1237-T_4CDD and 1238-T_4CDD for the analytical column(s) used.

- Peak responses of the monitored ions must be greater than 3 times the background noise level.

- Peak area ratios or spectral ion intensity ratios of the two monitored molecular ions for each congener group must be within +20% of the ratio obtained for the corresponding components in the QUANTITATION standard mixture.

- COCl loss must be monitored and co-maximize with the molecular ions of the analyte.

- Measures must be taken to establish retention time windows for selected ion monitoring of individual homologues, such as use of a standard mixture containing the earliest and latest eluting isomer within each homologue group. These windows must be stable and retention time shifts in excess of +2 scans between surrogates in standards and samples must not occur. Should sample surrogates shift retention time, this is an indication of column problems. All analyses must cease until problem resolved and after re-calibration, samples in question must be re-analyzed.

- Peak maxima for all three monitored ions must coincide within +2 scan units.

- For isomer specific identification, peaks may be identified as, for example, 2378-T_4CDD, 2378-T_4CDF, Q_8CDD and Q_8CDF, if they meet the first two criteria and co-elute with their isotopically labelled surrogates within +2 scan units.

- No response must be seen at m/e 374 at the retention time of 2378-T_4CDF. This M+ ion of hexachlorodiphenyl ether gives the same fragment ions as T_4CDF and yields a false-positive T_4CDF result. Monitoring for other chlorinated diphenyl ethers is optional.

- Surrogate and performance standard recoveries must fall within acceptable windows as specified in Table D.

9. Detection Limits

The detection limit must be reported for all sample results - not just for N.D. values. The concentration units used to report the detection limit must be corrected for surrogate recovery. Table E gives the detection limits which must be met for data to be considered acceptable.

A sample is detectable when the ion response is greater than 3 times S/N (signal/noise) ratio. However, if other qualitative criteria are not met, such as correct ion ratios, that measurement is reported as NDR. A sample is non-detectable when ion response is less than 3 times S/N ratio. This will be reported as ND.

For external standard, the following calculation should be used with performance standard recovery factored in:

$$\text{D.L. (ppt)} = \frac{(\text{Area 3 x S/N}) \times \text{Pq/unit area} \times 100}{\text{g sample} \times \% \text{ recovery of surrogate}} \times \frac{1}{\text{performance standard recovery}}$$

For external standard, the above calculation should be used with performance standard recovery factored in. For internal standard quantitation, the following must be used:

To determine the minimum detectable area for an individual isomer, one determines the maximum height of noise. A line is manually drawn across the top of the noise peaks in each quantitation ion in the mass chromatogram. The height of the line is determined by rationing the height of the line to the full height of the ion response times the total height counts in the window. This is next multiplied by 3 to achieve 3 times S/N. Height is then converted to area by multiplying 3 times S/N height by the peak area/peak height ratio for the surrogate in that window. This area is then used to calculate the detection limit.

In cases where the quantitation ion contains a large peak which prevents observation of the noise due to the scaling, the following procedures may be used:

1. Rescale and reprint the ion window to either side of the peak and proceed as usual.

2. Use the minimum detectable area from the same channel in the method spike run for calculation of sample detection limit.

II. ADDITIONAL QA REQUIREMENTS

Most of the following QA requirements are probably routine procedure in participating laboratories. However, they form an integral part of a QA protocol and must be followed:

1. Good laboratory practice: all equipment, sample concentrators, glassware, benches, etc. shall be kept clean during processing of these samples. No high level samples such as flyash shall be processed simultaneously. This could lead to cross-contamination problems.

2. Sample storage during workups: all sample extracts shall be refrigerated at 4°C in the dark when not needed for various cleanup steps.

3. Record keeping: a set of laboratory notebooks will be dedicated to these analyses and all records of sample treatment shall be recorded in these logs, which will be signed and dated for each sample manipulation. Such notebooks shall be available for audit upon request by NRBS and shall be delivered to NRBS at the end of the NRBS study.

4. Laboratory audits: NRBS may wish to audit individual laboratories and their operating procedures during this study. The analyst-in- charge may be required to review some of the data with NRBS.

5. Disposal: the participating laboratory is responsible for the disposal of unused samples. Such disposal shall not take place without the approval of NRBS. Samples will be suitably stored at -20°C to ensure their integrity until disposal is requested by NRBS.

6. All final sample extracts will be retained. When participating laboratory completes the analyses, these extracts (gently evaporated to dryness under nitrogen) will be delivered to NRBS in new, unused, precleaned 100 μl autosampler vials, tightly sealed, under chain-of-custody protocols. Vial containers will not be replaced by NRBS.

7. Raw GCMS data shall be backed up onto tape or diskette daily. These tapes shall be stored in secure locations and may not be erased without express written permission from NRBS.

8. For each total congener concentration reported, the number of positive individual isomers found must be reported.

9. Analytical standards and spiking surrogate mixtures will be used for all quantitative determinations by all participating laboratories.

10. NRBS may audit positive and negative T_4CDF values by submitting samples to either high resolution GC - high resolution MS or GC-MS-MS analysis using appropriate columns.

11. Participating laboratory shall be responsible for GC column performance checking and shall provide details of such checks with sample reports:

    i. Check for isomer specificity for 2378-T_4CDD and -T_4CDF.

    ii. Use of commercial window defining mixtures to set up GCMS windows for the various congener groups.

    iii. Verify calibration of column - MS by running analytical standards and maintaining a +20% response on all ions monitored across the congener groups.

    iv. Periodically a column blank shall be run to assess carryover. (2 μL injection of toluene and full analysis).

    v. Verify and demonstrate that 10 pg 2378-T_4CDD can be accurately seen at 3 times S/N prior to all analyses.

12. Additional performance audits may involve blind analysis of spiked matrix samples, split audit samples sent to government labs, etc.

13. Prior to commencing analyses, linearity of system shall be determined by a minimum of 5 point calibration covering a concentration range of 0.02 to 2 ng/μl PCDD/PCDF. The participating laboratory shall be responsible for obtaining these mixtures but will provide all details to NRBS. Linearity shall be rechecked periodically and in particular, after each column change. Relative response factors (native std./labelled std.) will then be established.

14. Daily calibration will be via running the provided analytical standard using single-point calibration. The processing of samples will be performed by running the standard and comparing response to last previous standard. Control chart RRF (Relative Response Factor) plots of standards will be maintained and submitted with each data set. If value is +15% for the ions selected of natives and surrogates, analysis of samples may proceed. If responses are outside this range, a second standard must be run and similarly assessed. If this too fails, the problem must be found and corrected before any samples are run. For external standard quantitation, frequent recalibration must take place, and the following sequence should be followed when analysing samples:

    Standard, Sample, Sample, Standard

III. DATA REPORTING AND EVALUATION PROCEDURES

1. Data Reporting

   i. All results must be reported on the attached Analysis Report Form. This uniformity of reporting format is essential for ease of evaluation of data sets originating from more than one laboratory. Three copies of each data report must be provided.

   ii. It is required that each data set chosen by the Scientific Officer to a maximum of 7% of the total number of samples be accompanied **free of charge** by the original (not copies) legible printouts of all GCMS ion chromatograms, spectra and spectral intensity lists of all analytical standards samples, blanks, method spikes, column blanks, and check solutions with all peaks identified as PCDD or PCDF congeners - clearly indicated directly on the printouts in ink. Retention times, peak heights, and peak areas must be clearly labelled. On Finnigan GCMS systems, the noise line must be turned "on". Any request in addition to the agreed upon free of charge 7% of the samples will be subject to a charge of $80.00 per sample.

   iii. For each report, all information requested on the Analysis Report Form must be supplied. The ratio ranges must be determined by the participating laboratory on their GCMS by analysis of the standard provided and determination of individual isomer's ion ratio from the areas or spectral intensities.

   iv. As an integral part of all data reports, the following additional information must be supplied:
   - Calibration reports
   - Date/time record GCMS
   - Control chart RRFs
   - Worksheet for surrogate recoveries
   - MDL calculations

   v. Please enclose the following with the final data:

      a. a brief description of the methods used;
      b. a description of the GC/MS system used, the operational parameters, and the acquisition system;
      c. the capillary column(s) used; and
      d. a description of the method for calculating detection limits.

TABLE A. ANALYTICAL (QUANTITATION) STANDARD AND SELECTED ION MASSES FOR PCDD/PCDF ANALYSIS.

QUANTITATION Standard	CONCENTRATION (pg/μL)	QUANTITATION Ion	CONFIRMATION Ions
DIOXINS			
2378-T_4CDD	100	322	320,259
12378-P_5CDD	100	356	354,293
123478-H_6CDD	100	390	392,327
123678-H_6CDD	100	390	392,327
123789-H_6CDD	100	390	392,327
1234678-H_7CDD	100	424	426,361
O_8CDD	100	460	458,397
FURANS			
2378-T_4CDF	100	306	304,243
12378-P_5CDF	100	340	338,277
23478-P_5CDF	100	340	338,277
234678-H_6CDF	100	374	376,311
123478-H_6CDF	100	374	376,311
123678-H_6CDF	100	374	376,311
123789-H_6CDF	100	374	376,311
1234678-H_7CDF	100	408	410,345
0_8CDF	100	444	442,379
SURROGATES (C_{13} LABELLED PCDDS)			
$^{13}C_{12}$-2378-T_4CDD	100	334	332
$^{37}C_{14}$-2378-T_4CDD	100	328	None
$^{13}C_{12}$-12378-P_5CDD	100	368	366
$^{13}C_{12}$-123678-H_6CDD	200	402	404
$^{13}C_{12}$-1234678-H_7CDD	200	436	338
$^{13}C_{12}$-O_8CDD	300	472	470
PERFORMANCE (INTERNAL) STANDARD			
$^{13}C_{12}$-1234-TCDD	100	334	332

Solvent = Toluene

TABLE B. SURROGATE SPIKING SOLUTION.

SURROGATE: C_{13}-LABELLED PCDDs	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 2378-T_4CDD	20
$^{37}Cl_4$ - 2378-T_4CDD	20
$^{13}C_{12}$ - 12378-P_5CDD	20
$^{13}C_{12}$ - 123678-H_6CDD	40
$^{13}C_{12}$ - 1234678-H_7CDD	40
$^{13}C_{12}$ - 0_8CDD	60

Solvent = Toluene

TABLE C. PERFORMANCE (INTERNAL) STANDARD SOLUTION.

C_{13}-LABELLED PCDD	CONCENTRATION (pg/μL)
$^{13}C_{12}$ - 1234-TCDD	100

Solvent = Toluene

TABLE D. SURROGATE STANDARD RECOVERY CRITERIA.

SURROGATE STANDARD	AMOUNT SPIKED (ng)	ACCEPTABLE RECOVERY (%)
$^{13}C_{12}$ - 2378-T_4CDD	2	40-120
$^{13}C_{12}$ - 12378-P_5CDD	2	40-120
$^{13}C_{12}$ - 123678-H_6CDD	4	40-120
$^{13}C_{12}$ - 1234678-H_7CDD	4	40-120
$^{13}C_{12}$ - O_8CDD	6	40-120

TABLE E. ACCEPTABLE DETECTION LIMITS

COMPOUND	PRACTICAL DETECTION LIMITS TISSUE PPT(pg/g)	SEDIMENT PPT(pg/g)	WATER PPQ(fg/g)
T_4CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
P_5CDD/F	0.4/0.4	0.4/0.4	0.4/0.4
H_6CDD/F	1.0/0.6	0.6/0.4	0.8/0.6
H_7CDD/F	1.6/1.6	1.6/1.6	1.6/1.6
O_8CDD/F	4.0/4.0	4.0/4.0	2.0/2.0

COMPOUND	ACHIEVABLE DETECTION LIMITS TISSUE PPT(pg/g)	SEDIMENT PPT(pg/g)	WATER PPQ(fg/g)
T_4CDD/F	0.1/0.1	0.1/0.1	0.1/0.1
P_5CDD/F	0.2/0.2	0.2/0.2	0.2/0.2
H_6CDD/F	0.5/0.3	0.3/0.2	0.4/0.3
H_7CDD/F	0.8/0/8	0.8/0.8	0.8/0.8
O_8CDD/F	2.0/2.0	2.0/2.0	1.0/1.0

1. These detection limits can be achieved or even lower easily by HRGC/HRMS.
2. The detection limits acceptable from LRMS will be about five times higher than those from HRMS listed here.

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBS) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under V.6 for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

IV. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analytes in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

ANALYTICAL SERVICES

Project: **ZENON ENVIRONMENTAL LABORATORIES**

I. Sample Log-in

1. Each set of samples will be described by a Laboratory Analysis Approval Form which contains a list of samples, sample identification and analyses requested. Any discrepancies between samples described on the Approval Form and actually submitted are to be reported immediately to the Study Office (Coordinator, Contaminants Component).

2. If samples are not received by the contractor within thirty (30) days of receipt of the Approval Form, the Contractor is to notify the Study Office (Coordinator, Contaminants Component).

3. Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. Analyze each sediment or homogenized tissue sample and Q.A. Check samples for:

   a) polyaromatic hydrocarbons (PAHs);

   b) polychlorinated biphenyls (PCBs) and congeners including coplanar PCB's where the results are positive;

   c) chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles.

   d) Organochlorines (OCs) including toxaphene.

2. Specific congeners/isomers must be individually reported along with the totals.

3. You are required to report the percent recovery of the surrogate standards.

4. You will receive a detailed protocol along with the samples.

5. You should use the appropriate internal, surrogate standards and/or certified standards in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs, in tissue samples.

6. You are to use mild drying methods for sediments to avoid any possible losses of volatile chemiclas. For example, use of low temperatures and forced-air oven with convection currents is one recommended method.

7. Results for tissue samples are to be reported on a wet weight basis; results for sediments are to be reported on a dry weight basis.

8. All communications regarding analysis are to be addressed to the Chairman, Laboratory Performance Committee, with copies to the Group Leader, Contaminants Component; Contaminants Coordinator and the Component Coordinator. Their names and addresses are listed in Section V.

III. Reporting Requirements

1. Scientific Officers are: the Chairman of the Laboratory Performance Committee and the Group Leader of the Contaminants Component. The laboratory shall keep the chair of the Chairman of the Laboratory Performance Committee appraised of potential and existing performance problems at the laboratory.

2. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

3. The PAH, PCB, Coplanar PCB, chlorophenol and OC data obtained for each sample are to be typed on a standard report form. Specific isomers and/or congeners must be individually reported along with the group totals.

4. For each sample, the percent recovery of the surrogate standards, certified standards, and the detection limits achieved must be individually reported.

5. Similarly for each sample, the percent recovery of the spike in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs must be individually reported.

6. Prior to preparation of the official data report, the Contractor will provide a preliminary report of the results in spreadsheet format to the Chairman of the Laboratory Performance Committee and Group Leader of the Contaminants Component, who may request clarification and/or re-analysis where necessary. The spreadsheet should use the format shown in Schedule A2.

7. Final data obtained for each sample will be provided to the Study Office on computer medium (Quattro Pro or compatible spreadsheet format), as well as ten (10) copies of the offical hardcopy report.

8. - Analytical charts containing GC and MS chromatography for all standards and samples are to be kept on file at the Contractor's office for a minimum of three (3) years.

- The peaks identified as PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs must be clearly marked on the GC/MS data.

- Raw and manipulated data are to be provided to the Study Office on computer medium (3.5 in diskette).

9. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

10. The equations used for calculating concentrations of the PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs in the sample must be provided as well as the calculation sheets.

Also to be enclosed with the final data:

a) a brief description of the methods used;

b) a description of the GC/MS system used, the operational parameters and the acquisition system;

c) the capillary column(s) used;

d) a description of the method used for calculating detection limits; and

e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

For further information on the analysis and detection limits of PAH, PCB, Coplanar PCB, chlorophenol and OCs, refer to Schedule A1 of this Agreement.

11. The distribution of results will be to the authorization officer at the NRBS office only.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officers must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the study office. The lab will be notified in the case where unused portions of samples are to be returned to the study office.

V. Addresses

1. The chair of the Laboratory Performance Committee is Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6, (403) 427-6102.

2. The Group Leader for Contaminants is Dr. Brian Brownlee, National water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario, L7R 4A6, (416) 336-4706.

3. The Contaminants Coordinator is Greg Wagner, Northern River Basins Study, 690 Standard Life Centre, 10405 Jasper Avenue, Edmonton, Alberta, T5J 3N4, (403) 427-1742.

4. The Component Coordinator is James Choles, Northern River Basins Study, 690 Standard Life Centre, 10405 Jasper Avenue, Edmonton, Alberta, T5J 3N4, (403) 427-1742.

SCHEDULE A - TERMS OF REFERENCE

SCHEDULE A1

ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for PCBs and coplanar PCBs, OCs including toxaphenes, PAHs, chlorophenols and AOX or EOX. Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 2Og of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

SCHEDULE A - TERMS OF REFERENCE

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBS) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under V.6 for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. QA/QC

The study will submit up to 15% of every sample lot as QA/QC samples. There shall be no additional charge for these analyses.

IV. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

V. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analytes in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001

NORTHERN RIVER BASINS STUDY

SCHEDULE A - TERMS OF REFERENCE

ANALYTICAL SERVICES

Project: ZENON ENVIRONMENTAL LABORATORIES

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. Analyze each homogenized tissue samples and Q.A. Check samples for:

a) Adsorbable organic halide (AOX) and

b) Extractable organic halide (EOX).

2. You are required to report the percent recovery of the surrogate standards.

3. You will receive a detailed protocol along with the samples.

4. You should use the appropriate internal, surrogate standards and/or certified standards in the analysis.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. The data obtained for each sample are to be typed on a standard report form.

3. For each sample, the percent recovery of the surrogate standards, certified standards, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs must be individually reported.

5. Sample data will be provided to the Study Office on computer medium using Dbase IV as well as in hard copy (5 copies).

6. - Analytical charts containing GC and MS chromatography for all standards and samples are to be provided to the technical officer.

   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase IV or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

   b) a description of the GC/MS system used, the operational parameters and the acquisition system;

   c) a description of the method used for calculating detection limits; and

   d) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

9. Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6, (403) 427-6102, will be the Scientific Officer for this analytical work.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the technical officer. The lab will be notified in the case where unused portions of samples are to be returned to the technical officer.

SCHEDULE AA - TERMS OF REFERENCE

Project: **ZENON ENVIRONMENTAL LABORATORIES**

I. Sample Log-in

Maintain laboratory logs of sampling station numbers (and narratives where applicable), locations, date and times of when the samples were collected, shipped, received and analyzed, and other pertinent information. This information must be incorporated into the lab sample data reports.

II. Chemical Analysis

1. Analyze each sediment or homogenized tissue sample and Q.A. Check samples for:

   a) polyaromatic hydrocarbons (PAHs);

   b) polychlorinated biphenyls (PCBs) and congeners including coplanar PCB's where the results are positive;

   c) chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles.

   d) Organochlorines (OCs) including toxaphene.

2. Specific congeners/isomers must be individually reported along with the totals.

3. You are required to report the percent recovery of the surrogate standards.

4. You will receive a detailed protocol along with the samples.

5. You should use the appropriate internal, surrogate standards and/or certified standards in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs, in tissue samples.

III. Reporting Requirements

1. Intra-laboratory quality assurance procedures must be articulated and provided to the technical authority. All actual intra-laboratory quality control data including charts corresponding to the analytical runs involving study samples must be made available to the Study Office upon request.

2. The PAH, PCB, Coplanar PCB, chlorophenol and OC data obtained for each sample are to be typed on a standard report form. Specific isomers and/or congeners must be individually reported along with the group totals.

3. For each sample, the percent recovery of the surrogate standards, certified standards, and the detection limits achieved must be individually reported.

4. Similarly for each sample, the percent recovery of the spike in the analysis of PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs must be individually reported.

5. Sample data will be provided to the Study Office on computer medium using Dbase IV as well as in hard copy (5 copies).

6. - Analytical charts containing GC and MS chromatography for all standards and samples are to be provided to the technical officer.

   - The peaks identified as PAHs, PCBs, Coplanar PCBs, chlorophenols an OCs must be clearly marked on the GC/MS data.

   - The data may be provided in either computer or hard copy form; computerized chart data must be in Dbase IV or Lotus 123 format.

7. The laboratory will use best laboratory practices and maintain thorough records which will allow tracking of samples.

8. The equations used for calculating concentrations of the PAHs, PCBs, Coplanar PCBs, chlorophenols and OCs in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   a) a brief description of the methods used;

   b) a description of the GC/MS system used, the operational parameters and the acquisition system;

   c) the capillary column(s) used;

   d) a description of the method used for calculating detection limits; and

   e) a brief description of the methods, instruments used, internal QA/QC used and calculation methods.

   For further information on the analysis and detection limits of PAH, PCB, Coplanar PCB, chlorophenol and OCs, refer to Schedule A1 of this Agreement.

9. Dr. S. Ramamoorthy, Alberta Environment, Environmental Assessment Division, 6th Floor, Oxbridge Place, 9820 - 106 Street, Edmonton, Alberta, T5K 2J6, (403) 427-6102, will be the Scientific Officer for this analytical work.

IV. Re-testing and Return of Samples

1. All data provided to the Scientific Officer must be considered verified by the analytical laboratory. The analytical laboratory will be contacted for follow-up re-testing where data are suspect.

2. All samples are to be retained in proper storage for ninety (90) days following the release of the laboratory report to the technical officer. The lab will be notified in the case where unused portions of samples are to be returned to the technical officer.

SCHEDULE A1

ANALYTICAL PROCEDURES

1. Sample Sets

Enclosed you will find tissue samples, or water samples and sediment samples, and check samples. Your laboratory is required to analyze the fish or sediment samples for PCBs and coplanar PCBs, OCs including toxaphenes, PAHs, chlorophenols and AOX or EOX. Your laboratory must use your own solutions for surrogate spiking, performance and analytical quantitation standards for all analyses.

2. Sample Weight

A minimum of 20g of tissue homogenate must be extracted for each analysis.

3. Method Blank

Method blank is defined as all surrogates, reagents and cleanup steps, that are used on the matrices composing the sample set, with no sample matrix present.

4. Prior to extraction, each fish tissue sample must be spiked with 100μL of the surrogate standard mixtures of the participating laboratory.

5. Extraction and Cleanup

All samples will be extracted and cleaned up using the laboratory's regular validated extraction and clean-up procedures.

SCHEDULE A1

PROTOCOL FOR ANALYTES OTHER THAN DIOXINS AND FURANS

I. METHOD

The contract laboratory will use validated analytical methods for the analysis of each fish and sediment sample for:

1. polyaromatic hydrocarbons (PAHs);
2. polychlorinated biphenyls (PCBS) and isomers including coplanar PCBs where the results are positive;
3. resin acids;
4. chlorinated phenols; phenols, guaiacols, veratroles, catechols and anisoles;
5. total metals: lead, vanadium, copper, chromium, cadmium, zinc, arsenic, mercury and methylmercury in the fish tissue; and
6. extractable metals listed under V.6 for sediment samples.

II. STANDARDS

1. The contract laboratory should use appropriate ^{13}C or ^{2}H internal standards (as in EPA 625) for PAHs.
2. The contract laboratory should use ^{13}C standard-77, 126, 169 in the analysis of coplanar PCB in selected samples on consultation with the project manager.
3. The contract laboratory will use NRC certified standards in the analysis of PCB congeners in selected samples on consultation with the project manager.
4. The contract laboratory should use standard reference materials/internal standard/surrogate standard for each analyte group.

III. QA/QC

The study will submit up to 15% of every sample lot as QA/QC samples. There shall be no additional charge for these analyses.

IV. SAMPLE PREPARATION

1. The contract laboratory will use mild drying methods for sediments in order to avoid any possible losses of volatile chemicals. For example, use of low temperatures and forced-air oven with convective currents is one recommended method.

V. REPORTING REQUIREMENTS

1. For each sample, the percent recovery of the surrogate standard, internal standard or reference material in the analysis of PAHs, PCBs, chlorophenols and methylmercury and total mercury and the associated detection limits must be individually reported on a separate report form.

   The equations used for calculating concentrations of the analytes in the sample must be provided as well as the calculation sheets.

   Also to be enclosed with the final data:

   i. a brief description of the methods used;
   ii. a description of the system used, the operational parameters and the acquisition system;
   iii. a description of the method used for calculating detection limits; and
   iv. a brief description of the methods, instruments used, internal QA/QC used, calculation methods for the analysis of metals including methylmercury.

V. DETECTION LIMITS

	Analyte	Acceptable Detection Limit (Tissue and Sediment)
1.	Polyaromatic Hydrocarbons (PAHs)	1 ng/g
2.	Polychlorinated Biphenyls (PCBs)	1 ng/g
3.	Coplanar PCBs	2 pg/g
4.	Chlorophenols	0.2 pg/g
5.	Resin acids	10 ng/g

6.

Metals	Acceptable Detection Limit (ug/g) Sediment	Tissue
Arsenic	0.2	0.2
Cadmium	0.3	0.3
Chromium	0.2	0.2
Copper	0.2	0.2
Lead	0.2	0.2
Vanadium	0.2	0.2
Zinc	0.1	0.1
Mercury/methylmercury	0.0001	0.001