el 300885 1 B

ENVIRONMENT CANADA
ENVIRONMENTAL PROTECTION
CONSERVATION AND PROTECTION
PACIFIC AND YUKON REGION
NORTH VANCOUVER, B.C.

DIOXIN, FURAN AND CHLORINATED PHENOLIC LEVELS IN SEDIMENTS FROM THE FRASER RIVER ESTUARY AND BRITISH COLUMBIA WEST COAST REFERENCE SITES

Regional Data Report: DR 90-3

by

L. E. Harding

November, 1990

LIBRARY
ENVIRONMENT CANADA
CONSERVATION AND PROTECTION
PACIFIC REGION

REVIEW NOTICE

Data reports are prepared to make preliminary data available without full analysis or interpretation. This report has been reviewed by the Marine and Estuarine Programs Division, Environmental Protecion, and approved for limited distribution. For further information please contact:

Lee Harding
Manager, Marine and Estuarine Programs
Environmental Protection
Conservation and Protection
224 West Esplanade Avenue
North Vancouver, B.C.
V7M 3H7

TABLE OF CONTENTS

	PAGE
REVIEW NOTICE	i
TABLE OF CONTENTS	ii
List of Tables	iii
List of Figures	iii
1.0 INTRODUCTION	1
2.0 MATERIALS AND METHODS	2
2.1 Sample Collection	2
2.2 Analytical Procedures	2
2.3 Quality Assurance/Quality Control	2
3.0 RESULTS	6
ACKNOWLEDGEMENTS	9

APPENDICES:

I - Quality Assurance Guidelines for Determination of Dioxins and Furans for Environmental Monitoring Programs

II - Environment Canada Chlorinated Phenols Analysis

LIST OF TABLES

TABLE		PAGE
1	DIBENZODIOXIN/DIBENZOFURAN RESULTS (PPT WET WT.) - FRASER ESTUARY	4

LIST OF FIGURES

FIGURE		PAGE
1	STATION LOCATIONS	3
2	LEVELS OF TOTAL HEXACHLORODIBENZODIOXIN (PG/G) ..	7
3	LEVELS OF 2,3,7,8 TETRACHLORODIBENZOFURAN (PG/G)	8

1.0 INTRODUCTION

This study was undertaken as part of a joint investigation with the Department of Fisheries and Oceans, of levels of chlorinated dibenzo-p-dioxins ("dioxins") and chlorinated dibenzofurans ("furans") in the Fraser River Estuary and southern Georgia Strait.

2.0 MATERIALS AND METHODS

2.1 Sample Collection

Samples of marine sediment for this study were collected during October 23 - November 10, 1990, at north coast reference sites using the fisheries research vessel CSS Vector; on November 30, 1989 in the southern Georgia Strait, using the fisheries research vessel, CSS Parizeau; and during February 27-28, 1990, on Roberts and Sturgeon Banks using the Canadian Coast Guard Hovercraft (Figure 1). Subtidal sediments were collected with a Smith-McIntyre grab by taking undisturbed sediment from the top 2 cm. of the surface in a hexane-washed jar. Exposed intertidal sediments were taken directly into hexane-washed glass jars at low tide. Samples of river sediment were taken similarly (access by road) at low tide during March 17-18. Jars were kept dark and cool until delivered to the laboratory.

2.2 Analytical Procedures

All chemical analysis was by Zenon Environmental Inc. Methods of analysis and quality assurance/quality control program specified for this contract are given in Appendix I.

2.3 Quality Assurance/Quality Control

Three of the 19 samples (GS-6, DFO-6 and NA-1) were analysed in duplicate. Surrogates 12C12-T4CDF, 13C-T4CDD, 13C12-P5CDD, 13C12-H6CDD, 13C12-H7CDD and 13C12-OCDD were added to each sample to check for recovery, and all results were corrected for percent recovery. Three blanks were analysed.

All duplicate pairs of samples varied less than 10% for total dioxins and total furans. Only the second of each duplicate pair is given in Table 1. Samples with <50% recovery in any congener were C-6, 23, SB-2, RB-1, RB-2,

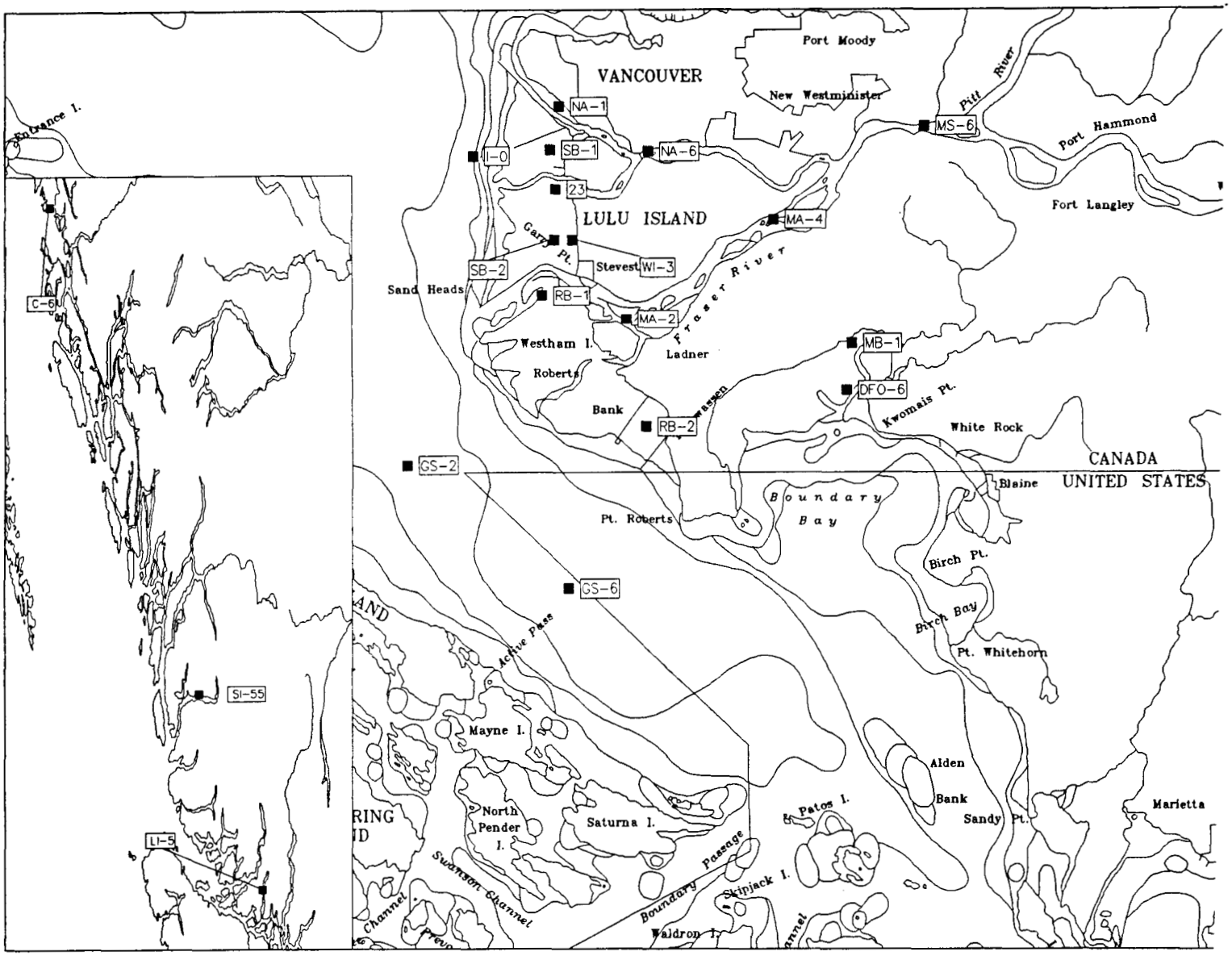


Figure 1 Station locations.

Table 1 **DIBENZODIOXIN/DIBENZOFURAN RESULTS (PPT)**

SITE NO.	SITE	2378 T4CDD	TOTAL T4CDD	12378 P5CDD	TOTAL P5CDD	123478 H6CDD	TOTAL H6CDD	1234678 H7CDD	TOTAL H7CDD	TOTAL O8CDD	2378 T4CDF	TOTAL T4CDF	12378 P5CDF	23478 P5CDF	TOTAL P5CDF	234678 H6CDF	TOTAL H6CDF	1234678 H7CDF	TOTAL H7CDF	TOTAL O8CDF
C-6	CHATHAM SOUND	<5.0	<5.0	<3.0	<3.0	<5.0	28.0	14.0	26.0	41.0	25.0	25.0	<3.0	<3.0	<3.0	<4.0	<4.0	<7.0	<7.0	<7.0
I-0	IONA OUTFALL	<6.0	<6.0	<3.0	<3.0	<5.0	<5.0	9.0	20.0	49.0	4.0	4.0	<3.0	<3.0	<3.0	<4.0	<4.0	<7.0	<7.0	<6.0
LI-5	LOUNGBOROUGH INLET	<8.0	<8.0	<4.0	<4.0	<8.0	27.0	29.0	50.0	100.0	<5.0	<5.0	<4.0	<4.0	<4.0	<6.0	<6.0	<11.0	<11.0	<9.0
GS-6	GEORGIA STRAIT	<2.0	<2.0	<1.0	<1.0	<2.0	<2.0	<2.0	3.0	12.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<3.0	<3.0	<2.0
GS-2	GEORGIA STRAIT	<3.0	19.0	<4.0	<4.0	<8.0	<8.0	19.0	39.0	65.0	<4.0	<4.0	<4.0	<4.0	<4.0	<6.0	<6.0	<11.0	<11.0	<10.0
SI-55	SEYMOUR INLET	<3.0	<7.0	<4.0	<4.0	<6.0	<6.0	<7.0	<7.0	<9.0	<4.0	<4.0	<4.0	<4.0	<4.0	<5.0	<5.0	<9.0	<9.0	<8.0
23	STURGEON B.	<3.0	<5.0	<3.0	<3.0	<3.0	<3.0	<4.0	<4.0	<6.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<5.0	<5.0	<5.0
SB-2	STURGEON B.,W. OF LULU IS	<3.0	<5.0	<3.0	<3.0	<4.0	<4.0	<4.0	<4.0	<6.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<5.0	<5.0	<5.0
RB-1	ROBERTS B.,W. OF WESTHAM	<3.0	<4.0	<2.0	<2.0	<3.0	<3.0	<4.0	<4.0	<7.0	<2.0	<2.0	<2.0	<2.0	<2.0	<3.0	<3.0	<6.0	<6.0	<6.0
MA-2	MAIN ARM-WOODWARD IS.	<3.0	<3.0	<2.0	<2.0	<3.0	<3.0	6.0	14.0	40.0	3.0	3.0	<2.0	<2.0	<2.0	<2.0	<2.0	<4.0	9.0	<4.0
RB-2	ROBERTS B.,W. OF FERRY C.	<3.0	<4.0	<3.0	<3.0	<4.0	<4.0	<4.0	<4.0	13.0	<3.0	<3.0	<2.0	<2.0	<2.0	<3.0	<3.0	<5.0	<5.0	<5.0
MB-1	MUD BAY	<3.0	<3.0	<2.0	<2.0	<3.0	<3.0	<4.0	<4.0	13.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<4.0	<4.0	<4.0
DFO-6	BOUNDARY BAY	<3.0	<3.0	<2.0	<2.0	<2.0	<2.0	<3.0	<3.0	<5.0	<2.0	<2.0	<1.0	<1.0	<1.0	<2.0	<2.0	<4.0	<4.0	<4.0
NA-6	NORTH ARM,RIVER RD AT OAK	<3.0	<3.0	<2.0	<2.0	<3.0	<3.0	31.0	90.0	119.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	26.0	86.0	17.0
MS-6	FRASER RIVER AT PORT MANN	<3.0	<2.0	<1.0	<1.0	<2.0	<2.0	9.0	17.0	60.0	<1.0	<1.0	<1.0	<1.0	<1.0	<2.0	<2.0	<4.0	<4.0	<5.0
NA-4	ANNACIS IS.	<3.0	<4.0	<3.0	<3.0	<6.0	<6.0	<8.0	<8.0	<12.0	<3.0	<3.0	<3.0	<3.0	<3.0	<5.0	<5.0	<10.0	<10.0	<9.0
SB-1	STURGEON B.,W. OF SEA IS.	<3.0	<4.0	<6.0	<6.0	<11.0	<11.0	<18.0	<18.0	81.0	4.0	4.0	<6.0	<6.0	<6.0	<9.0	<9.0	<25.0	<25.0	<27.0
WI-3	LULU IS.,UPPER INTERTIDAL	<3.0	<4.0	<6.0	<6.0	<13.0	<13.0	20.0	38.0	100.0	8.0	8.0	<5.0	<5.0	<5.0	<10.0	<10.0	<19.0	<19.0	<19.0
NA-1	NORTH ARM	<3.0	<2.0	<1.0	<1.0	<2.0	5.0	29.0	59.0	161.0	<1.0	<1.0	<1.0	<1.0	<1.0	<2.0	<2.0	33.0	88.0	19.0

NA-6, MA-4, SB-1 and WI-3. Recoveries varied as follows:

12C12-T4CDF	45-105%
13C-T4CDD	41-96%
13C12-P5CDD	37-108%
13C12-H6CDD	30-92%
13C12-H7CDD	27-93%
13C12-OCDD	31-87%

These recoveries were within acceptable limits (Appendix I, Table 3). All blanks were blank, with recoveries in the range 67-108% overall.

3.0 RESULTS

Table 1 shows the levels of dioxins and furans measured in Fraser Estuary and reference site sediments. In general, levels were very low, and 2,3,7,8 TCDD was not detected in any sample. Other TCDD's were detectable in only one sample, GS-2 in the southern Strait of Georgia. Otherwise, only dioxin congeners with 6 or more chlorine atoms were detected. Furans detected included those with 4, 7 and 8 chlorine atoms.

Samples in which some dioxins or furans were detected were from the references sites at Chatham Sound (a pulp mill is located in nearby Porpoise Harbour) and Loughborough Inlet (no known source); in Georgia Strait off the new, deepwater outfall of the Iona sewage treatment plant and at stations GS-2 and GS-6 in the plume of the Fraser River; at Station RB-2 on Roberts Bank; at Stations SB-1 and WI-3 on Sturgeon Bank; at Station MB-1 in Mud Bay; and at Stations MA-2, MA-6, MS-6 and NA-1 in reaches of the lower Fraser River.

Figure 2 shows the relative amounts of total hexachlorodibenzodioxin at each station and Figure 3 shows the relative amounts of total 2,3,7,8 chlorodibenzofuran at each station. Circles are proportional to 10 times the log of the concentration given in Table 1. Triangles indicate values below detection limits.

All chlorophenols, chloroguaiacols and chlorocatechols were non-detectable (Appendix II).

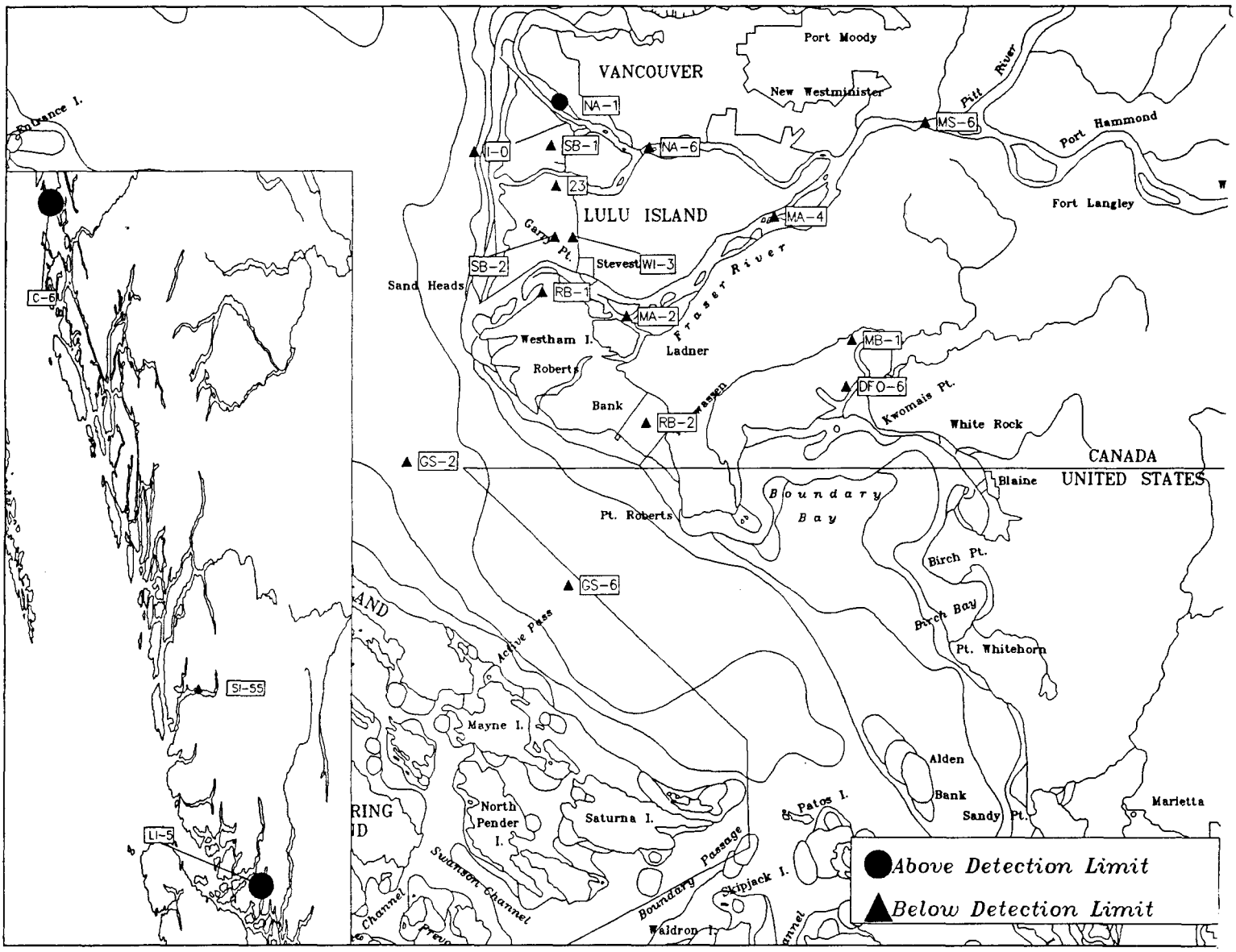
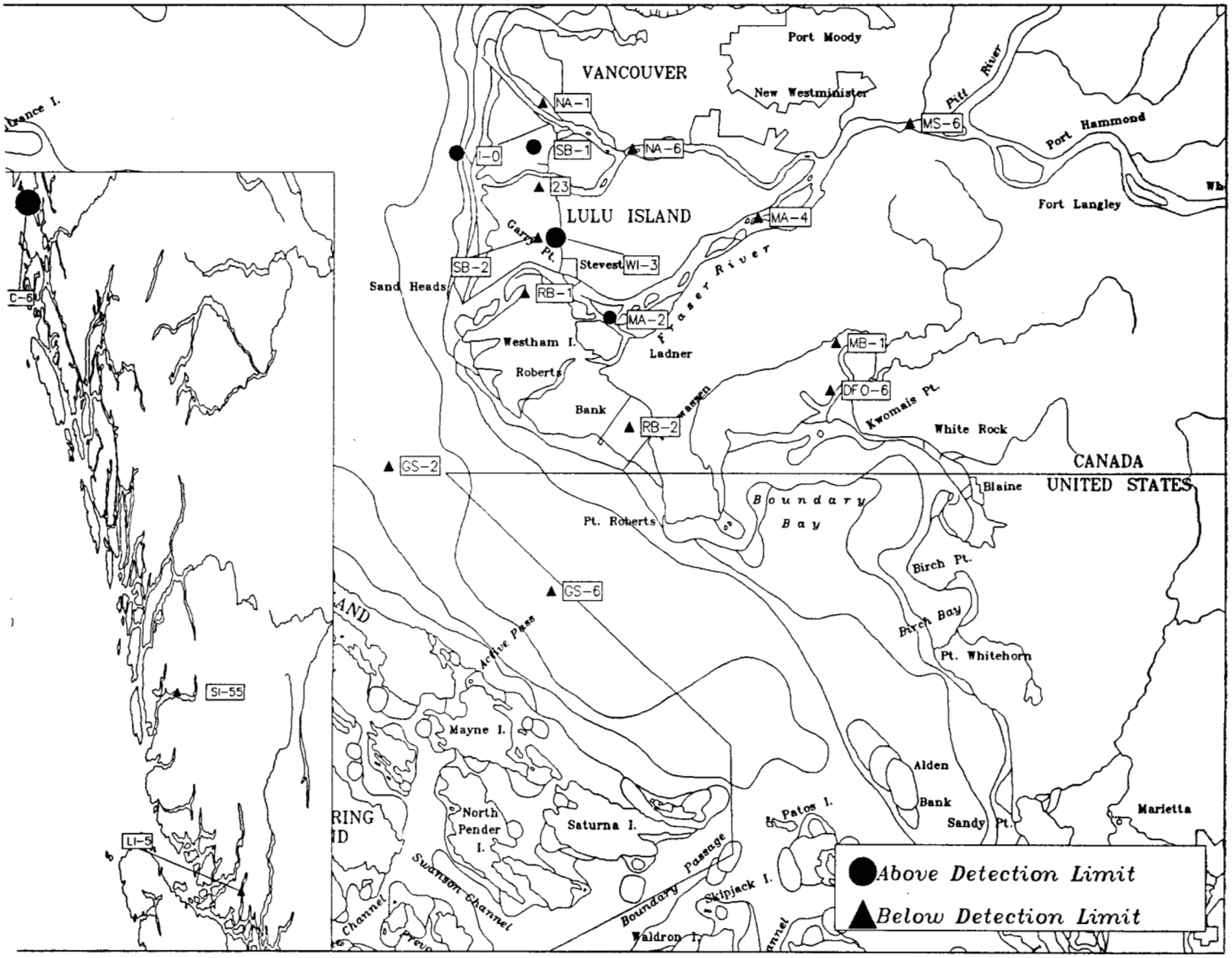


Figure 2 Levels of total hexachlorodibenzodioxin (pg/g).



gure 3 Levels of 2,3,7,8 tetrachlorodibenzofuran (pg/g).

ACKNOWLEDGEMENTS

Marine sediments were collected by Darcy Goyette and Janice Boyd in north coast reference sites and by Al Colodey and Janice Boyd in southern Strait of Georgia. River sediments were collected by Janice Boyd. Michael Makhijani prepared the data tables and maps using the geographic information system QUIKMap, by E.S.L. Environmental Sciences Ltd., Sidney, B.C. Special thanks to Captain John McGrath and crew of the Canadian Coast Guard Hovercraft Unit, Richmond, B.C. Martin Pomeroy provided helpful editorial comments.

APPENDIX I

ASSURANCE GUIDELINES FOR DETERMINATION OF DIOXINS AND FURANS FOR ENVIRONMENTAL MONITORING PROGRAMS

QUALITY ASSURANCE GUIDELINES FOR DETERMINATION OF DIOXINS AND FURANS FOR ENVIRONMENTAL MONITORING PROGRAMS

Version 1.0 November

INTRODUCTION

These quality assurance guidelines has been developed for analytical laboratories providing dioxin/furan data on water, sediment and tissue samr for environmental monitoring programs. They are based on a QA protocol developed by the Dioxin Quality Assurance Committee, comprised of analytica and Quality Assurance experts from Environment Canada and the Department of Fisheries and Oceans. The objectives of this intensive QA are:

- to maximize the generation of quality analytical data;
- to ensure complete documentation and defensibility of all data;
- to expedite data evaluation and acceptance with a minimur inconvenience to Environment Canada and contract labs; ar
- to clearly define the various QA requirements that must b followed.

Since highly accurate and precise results at the parts-per-trillion and -quadrillion level are required, it is essential that laboratories follow these guidelines closely. This does not infer that they should not follow their own internal QA program as well.

These guidelines are divided into 4 sections:

(a) Analytical Procedures

(b) Data Reporting and Evaluation Procedures

(c) Additional QA Requirements

(d) Reference Materials

For further information, contact:

Director, Laboratories
Conservation and Protection
Environment Canada
4195 Marine Drive
West Vancouver, B. C. V7V 1N8

tel. (604)666-6767 FAX (604)666-4895

contd. ...

A. ANALYTICAL PROCEDURES

1. Sample Sets

All samples will be processed in batches. A minimum of 20% of the samples must be analyzed in duplicate. For a batch size of 9 samples or less, a minimum of 1 method blank and one reference sample must be processed with the samples. For more than 9 samples, at least two method blanks and two reference samples must be analyzed. (A method blank is defined as all surrogates, reagents and cleanup steps with no sample matrix present.) The reference material may be spiked with known quantities of various isomers. Laboratories will follow their own internal QA protocols as well.

Example of sample batch =	6 samples
	1 method blank
	2 replicates
	1 reference

	10

The National Water Research Institute has available two freshwater sediment reference materials which are considered satisfactory where sediment analyses are being conducted (see Section D for further information). Other reference materials may be acceptable as well.

2. Sample Sizes

It is expected that 4 L of each fresh water sample will be required to achieve the detection limits specified in Table 2. One liter of each effluent sample must be analyzed.

A minimum of 10 g (wet weight) of tissue must be analyzed. Results are to be reported in wet weight.

A minimum of 5 g (air-dried weight) of each sediment sample must be analyzed. Oven-dried (O.D.) weight must be determined and used in calculations.

contd. ...

3. Surrogate Spiking

Prior to extraction, each sample must be spiked in its extraction vessel with 100 uL of the surrogate standard solution (see Table 1).

4. Extraction and Cleanup

All samples will be extracted and cleaned up by the lab's regular validated extraction and cleanup procedures.

5. Recovery Standard and Final Extract Volume

The cleaned up extract will be taken just to dryness in a clean, new 100 uL cone-shaped vial under a gentle stream of nitrogen and 20 uL of the Recovery Standard solution (see Table 1) added. This will be used to assess surrogate recoveries.

6. Quantitation

The Daily Calibration Standard solution, containing native and labelled PCDD/PCDF compounds, is listed in Table 1. The ion masses to be monitored for determining sample results are also shown in Table 1. This solution must be run daily (at the beginning of the day and every 8 hrs. thereafter, including after the last sample analysis) to update relative response factors (RRFs) determined during periodic multi-level calibrations (see Section C, para. 9). The daily RRF's must be +/- 15% of the originally determined values, or they must be completely re-established by multi-level calibration.

Laboratories are to use internal standard procedures for quantitation using the Surrogate Standard Solution detailed in Table 1. The isotopically labelled surrogates serve as internal standards to correct for losses during processing of samples and to compensate for errors due to differences in injected volume and unnoticed variations in instrumental sensitivity.

Dioxin and furan results for each homologue are corrected for the recovery of the corresponding labelled surrogate dioxin congener, except for tetra-furan which are corrected for the recovery of their own labelled surrogates. The contractor will provide examples of all equations used to calculate surrogate recoveries, to determine relative response factors between native and surrogate compounds, and to determine PCDD/PCDF concentrations in the sample.

contd. ...

7. 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:

C1 - Peak responses of the quantitation ions must be greater than 3 times the background noise level.

C2 - Peak area (or height) ratios or spectral ion intensity ratios (from intensity list of spectrum of analyte peak) of the two monitored molecular ions for each congener group must be within +/- 20% of the ratio obtained for the corresponding components in the Daily Calibration Standard solution.

C3 - Peak maxima for all three monitored ions must coincide within +/-2 scan units for it to be included in total congener summation.

C4 - For isomer specific identification, peaks may be identified as 2,3,7,8-TCDD, 2,3,7,8-TCDF, P5CDD, H6CDD, H7CDD and O8CDD if they meet the first two criteria and co-elute with their isotopically-labelled surrogates within +/- 2 scan units.

C5 - no response must be seen at the m/e ratios identified for the M+ ions of hexachlorodiphenyl ethers identified in Table 1. These compounds can give the same fragment ions as the associated furans and yield a false positive result.

C6 - surrogate recoveries must fall within acceptable windows in Table 3 below.

8. Detection Limits

The detection limit must be reported for all sample results - not just for non-detectable values. The concentration units used to report the detection limit must be the same as that used for the sample. Detection limits must be corrected for surrogate recovery.

Table 2 below gives detection limits which must be met for data to be considered acceptable.

contd. ...

TABLE 1 - STANDARDS AND SELECTED ION MASSES FOR PCDD/PCDF ANALYSIS

Standard	CONCENTRATION (pg/L)	QUANTITATION ION	CONFIRMATION IONS	INT. (1)
1. Daily Calibration Standard (Set B)				
DIOXINS -				
2,3,7,8-T4CDD	100	322	320, 259	
1,2,3,7,8-P5CDD	200	356	354, 293	
1,2,3,4,7,8-H6CDD	200	390	392, 327	
1,2,3,6,7,8-H6CDD	200	390	392, 327	
1,2,3,7,8,9-H6CDD	200	390	392, 327	
1,2,3,4,6,7,8-H7CDD	200	424	426, 361	
O8CDD	300	460	458, 395	
FURANS -				
2,3,7,8-T4CDF	100	306	304, 243	376
1,2,3,7,8-P5CDF	200	340	338, 277	410
2,3,4,7,8-P5CDF	200	340	338, 277	410
1,2,3,4,7,8-H6CDF	200	374	376, 311	446
1,2,3,6,7,8-H6CDF	200	374	376, 311	446
1,2,3,7,8,9-H6CDF	200	374	376, 311	446
2,3,4,6,7,8-H6CDF	200	374	376, 311	446
1,2,3,4,6,7,8-H7CDF	200	408	410, 345	478
1,2,3,4,7,8,9-H7CDF	200	408	410, 345	478
O8CDF	300	444	442, 379	514

(plus the Surrogates and Recovery Standards listed below)

2. Surrogate Standard Solution (Set C)			
13C12-2,3,7,8-T4CDD	100	334	332
13C12-1,2,3,7,8-P5CDD	100	368	366
13C12-1,2,3,6,7,8-H6CDD	200	402	404
13C12-1,2,3,4,6,7,8-H7CDD	200	436	438
13C12-O8CDD	300	472	470
13C12-2,3,7,8-T4CDF	100	318	316
3. Recovery Standard (Set D)			
13C12-1,2,3,4,-T4CDD	100	334	332

Note (1): molecular ion of possible chlorodiphenyl ether interferences.

contd. ...

TABLE 2 DETECTION LIMITS

	Water (ppq)	Effluent (ppq)	Sediment (ppt)	Tissue (ppt wet)
T4CDD/F	2	10	10	2
P5CDD/F	5	20	20	5
H6CDD/F	10	30	30	10
H7CDD/F	15	40	40	15
O8CDD/F	20	50	50	20

An analyte is detectable when the quantitation ion response is greater than 3 times S/N ratio. However, if other qualitative criteria, such as correct ion ratios (congener specific determinations only), are not met, that measurement is reported as ND(R). An analyte is non-detectable when the quantitation ion response is less than 3 times S/N ratio. This will be reported as ND.

Detection limits corrected for surrogate recovery will be calculated in both cases as follows:

$$\text{D.L. (ppt)} = \frac{(3 \times N) \times (\text{Pg of internal std. added})}{\text{g sample} \times (\text{peak area for int. std.}) \times \text{RRF}}$$

RRF is the response factor for a native standard relative to the response factor for the surrogate. Noise (N), the estimated sum of electronic and chemical background, can be determined by manually drawing a line across the top of the average maximum noise peaks in the ion chromatogram of the quantitation ion for each homologue window. The height of the line is converted to area by multiplying by the peak area/peak height ratio determined from a surrogate peak.

Whenever possible, the noise for each homologue group will be determined from the actual chromatogram of the sample of interest. However, in cases where the quantitation ion channel contains a large peak which prevents observation of the noise (without rescaling and reprinting), the noise from the same channel in the method blank run may be used as a default value.

contd. ...

B. DATA REPORTING AND EVALUATION PROCEDURES

1. Data Reporting

All results must be reported in a format similar to Form A (attached).

The laboratory must retain, and provide for inspection on request, hard copies of all GCMS ion chromatograms, with areas and retention times clearly marked in ink for positive analyte peaks not printed by printer, spectra and spectral ion intensity lists used for ratio calculations for all analytical standards, sample and blank extracts and check solutions with all peaks identified as PCDD or PCDF congeners clearly indicated directly on the printouts in ink.

2. Data Evaluation

Environment Canada will examine all material requested and either accept or reject the data based upon the identification criteria, surrogate recoveries, comparison of duplicates and reference materials, performance on solutions of standards, etc. Duplicates must agree to within 50% for all target analytes.

Surrogate recoveries outlined in Table 3 below must be achieved for all matrices. In cases where recoveries of surrogates are less than the minimum recovery (in the 20 - 40% range with all other criteria being met) and there is a significant positive congener value at greater than twice the detection limit the data will be closely examined and may be accepted. However, if results are non-detectable, repeat analysis will be requested.

Laboratory performance may be further evaluated by inter-laboratory study with spiked or unspiked matrices. Environment Canada may also wish to audit individual laboratories and their operating procedures on-site.

C. ADDITIONAL QA REQUIREMENTS

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

1. Methodology Documentation must be available, kept up to date, and provided to Environment Canada on request.

2. 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 with the sediment samples. This could lead to cross-contamination problems.

contd. ...

TABLE 3 SURROGATE STANDARD RECOVERY CRITERIA

Surrogate Standard	Amount Spiked (ng)	Acceptable Recovery (%)
13C12-2,3,7,8-T4CDD	2	40-120
13C12-1,2,3,7,8-P5CDD	2	35-120
13C12-1,2,3,6,7,8-H6CDD	4	30-120
13C12-1,2,3,4,5,7,8-H7CDD	4	25-120
13C12-O8CDD	6	20-120
13C12-2,3,7,8-T4CDF	2	40-120

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

4. Record keeping: - a set of laboratory notebooks will be dedicated these analyses and all records of sample treatment shall be recorded in these logs, which will be checked, signed and dated daily by a senior chemist. Such notebooks shall be available for audit upon request by Environment Canada.

5. Samples and final sample extracts will be suitably stored until Environment Canada accepts the analytical data.

6. Laboratories shall be responsible for GC column performance checking and shall provide details of such checks with sample reports:

   (i) check for isomer specificity (2,3,7,8-TCDD and -TCDF)

   (ii) use commercial window defining mixtures to set up GCMS windows for the various congener groups.

   (iii) run a column blank frequently to assess carryover.

contd. ...

(iv) verify and demonstrate that 5 pg 2,3,7,8-TCDD can be accurately seen at greater than 3 times S/N prior to each set of analyses.

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

8. Instrument mass range shall be calibrated daily.

9. Quantitation linearity of the system shall be determined periodically by a 6 point calibration covering a concentration range of 5 to 1500 pg/uL PCDD/PCDF. Relative response factors (RRF's) (native std./labelled std.) are established using these 6 solutions. It is recommended that RRF's be calculated on the basis of triplicate analysis of each solution. The relative standard deviation (RSD) for each set of three RRFs determined from a single standard must be less than 10%. If this precision criterion is met, average RRFs over the entire calibration range can be calculated from the single point averages. The RSD of the six point average RRFs must be less than 20%. This latter value effectively corresponds to a response linearity criterion.

12. COCl loss must be monitored.

D. REFERENCE MATERIALS

The National Water Research Institute has two uncertified freshwater reference materials suitable for use under this protocol. They are available at a cost of $200 per bottle (containing approximately 20 g). Certified values are available for other organic compounds. Order these materials from:

Environment Canada
National Water Research Institute
Quality Assurance Program
P. O. Box 5050, 867 Lakeshore Road
Burlington, Ont. L7R 4A6

tel. (416) 336-4877
FAX (416) 336-4989

Cheques must be made payable to the Receiver General for Canada.

REVISION HISTORY

Version 1.0	Nov 89	Introduction

contd. ...

FORM A. ANALYTICAL RESULTS (for sediment samples)

Lab Name: Date:
Sample ID: GC/MS:
Sample Description:
Sample Weight: g (air dry) Final Volume: uL
g (oven dry)

Congener	pg/O.D.g (1)	DL (2)	Homologue	pg/O.D.g (1)	DL (2)
2378-T4CDD			TCDD		
12378-P5CDD *			P5CDD		
123478-H6CDD *			H6CDD		
123678-H6CDD *			H7CDD		
123789-H6CDD *			OCDD		
1234678-H7CDD					
			Total PCDD		
2378-TCDF *					
12378-P5CDF *			TCDF		
23478-P5CDF *			P5CDF		
123478-H6CDF *			H6CDF		
234678-H6CDF *			H7CDF		
123789-H6CDF *			OCDF		
1234678-H7CDF					
1234789-H7CDF					
			Total PCDF		

Surrogate	Amount Added (ng)	Recovery (%)
13C12-TCDF		
13C12-TCDD		
13C12-P5CDD		
13C12-H6CDD		
13C12-H7CDD		
13C12-OCDD		

1. Results are corrected for surrogate recovery. Value for asterisked (*) isomer represents maximum possible amount, as it could co-elute with oth isomers. O.D.g = oven-dried weight in grams. ND = not detected. ND(R) = detected due to incorrect ratio.
2. DL = Detection Limit (ng/g).
3. NP = number of analyte peaks.

APPENDIX II

ENVIRONMENT CANADA CHLORINATED PHENOLICS ANALYSIS

Environment Canada - Chlorinated Phenolics Analysis
(ng/g)

Zenon ID	22881	22882	22883	22884	22885
Enviroment Canada ID	**STN C-6**	**STN I-0**	**STN LI-5#14**	**STN GS-6#4**	**STN GS-2#5**
2,6-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,5-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,6-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5,6-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
Surrogate Recovery	69%	76%	67%	76%	69%

Environment Canada - Chlorinated Phenolics Analysis
(ng/g)

Zenon ID	22886	22887	22888	22889	22890
Enviroment Canada ID	**STN SI-55#10**	**STN 23#3**	**STN 5B-2 #4**	**STN RB #6**	**STN MA-2 #8**
2,6-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,5-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,6-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5,6-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
Surrogate Recovery	55%	69%	65%	59%	63%

Environment Canada - Chlorinated Phenolics Analysis
(ng/g)

Zenon ID	22891	22892	22893	23312	23313
Enviroment Canada ID	**STN RB-2 #9**	**STN MB-1#10**	**STN DFO-6#11**	**NA6 #14**	**MS-6 #12**
2,6-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,5-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,6-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichloroguaiacol	<0.05	<0.05	<0.05	0.90	<0.05
3,4,5-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5,6-Trichloroguaiacol	<0.05	<0.05	<0.05	0.15	<0.05
3,4,5,6-Tetrachloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,5-Dichlorocatechol	<0.05	<0.05	<0.05	0.10	<0.05
4,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
Surrogate Recovery	71%	62%	53%	50%	57%

Environment Canada - Chlorinated Phenolics Analysis
(ng/g)

Zenon ID	23314	23315	23316	23317	blank1
Enviroment Canada ID	**MA-4 #13**	**SB-1 #19**	**WI-3 #1**	**NA-1 #25**	
2,6-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4-Dichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,4,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,6-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4-Trichlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,4,5-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
2,3,5,6-Tetrachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,6-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5,6-Trichloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachloroguaiacol	<0.05	<0.05	<0.05	<0.05	<0.05
4-Chlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
4,5-Dichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5-Trichlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
3,4,5,6-Tetrachlorocatechol	<0.05	<0.05	<0.05	<0.05	<0.05
Surrogate Recovery	64%	55%	69%	44%	79%

Environment Canada - Chlorinated Phenolics Analysis
(ng/g)

Zenon ID Enviroment Canada ID	blank1	blank3
2,6-Dichlorophenol	<0.05	<0.05
2,4-Dichlorophenol	<0.05	<0.05
2,4,6-Trichlorophenol	<0.05	<0.05
2,4,5-Trichlorophenol	<0.05	<0.05
2,3,6-Trichlorophenol	<0.05	<0.05
2,3,5-Trichlorophenol	<0.05	<0.05
2,3,4-Trichlorophenol	<0.05	<0.05
2,3,4,6-Tetrachlorophenol	<0.05	<0.05
2,3,4,5-Tetrachlorophenol	<0.05	<0.05
2,3,5,6-Tetrachlorophenol	<0.05	<0.05
Pentachlorophenol	<0.05	<0.05
4-Chloroguaiacol	<0.05	<0.05
4,6-Dichloroguaiacol	<0.05	<0.05
4,5-Dichloroguaiacol	<0.05	<0.05
3,4,5-Trichloroguaiacol	<0.05	<0.05
4,5,6-Trichloroguaiacol	<0.05	<0.05
3,4,5,6-Tetrachloroguaiacol	<0.05	<0.05
4-Chlorocatechol	<0.05	<0.05
3,5-Dichlorocatechol	<0.05	<0.05
4,5-Dichlorocatechol	<0.05	<0.05
3,4,5-Trichlorocatechol	<0.05	<0.05
3,4,5,6-Tetrachlorocatechol	<0.05	<0.05
Surrogate Recovery	82%	75%