

DIOXINS AND FURANS IN SEDIMENT AND FISH FROM THE VICINITY OF FOUR INLAND PULP AND/OR PAPER MILLS AND ONE PETROLEUM REFINERY IN BRITISH COLUMBIA

T.M. Tuominen and M.A. Sekela September 1992

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ABSTRACT

Dioxins and furans were analysed in bed sediments and fish collected upstream and downstream of four non-chlorine bleaching pulp and/or paper mills and one petroleum refinery in inland British Columbia. Areas sampled were the Peace and Pine Rivers, Kitimat River and the lower Fraser River. The results showed that all bed sediment samples collected upstream of the mills and refinery were below the analytical detection limit for dioxins and furans. Most bed sediment samples collected downstream of the mills and refinery were also below the analytical detection limit. Exceptions were, one sample collected in the Kitimat River which had detectable levels of hexachlorodibenzodioxin and samples collected from the lower Fraser River which showed the presence of dioxins and furans, principally, octachlorodibenzodioxin.

The levels of dioxins and furans in all fish samples (composed of composites of muscle tissue) from the Peace, Pine and Kitimat Rivers were below the detection limit, with the exception of one sample. This sample, collected from the Kitimat River downstream mill. gulp had а detectable concentration of tetrachlorodibenzofuran (T4CDF). Fish samples collected from the lower Fraser River, upstream and downstream of the two pulp and/or paper mills, exhibited detectable levels of mainly T4CDF. highest levels of T4CDF were measured in the northern squawfish (Ptychocheilus oregonensis) and peamouth chub (Mylocheilus caurinus) samples.

<u>résumé</u>

Des échantillons de matériau du lit et de poissons ont été prélevés en amont et en aval de quatre usines de pâtes et/ou de papier (n'utilisant pas le chlore pour le blanchiment) et d'une raffinerie de pétrole, toutes situées à l'intérieur de la Colombie-Britannique; ces échantillons ont été analysés pour les dioxines et les furannes. Les sites d'échantillonnage étaient situés dans les rivières de la Paix, Pine et Kitimat et dans le bas du fleuve Fraser. Tous les échantillons de matériau du lit prélevés en amont des usines et de la raffinerie ont donné des valeurs qui étaient sous les limites de détection pour les dioxines et les furannes. La plupart des échantillons de matériau du lit prélevés en aval ont montré les mêmes résultats, sauf un échantillon pour la rivière Kitimat qui contenait des niveaux détectables d'hexachlorodibenzodioxines et certains échantillons pour le bas-Fraser qui montraient la présence de dioxines et de furannes, surtout l'octachlorodibenzodioxine.

Pour tous les échantillons de poisson (en fait des échantillons composites de tissu musculaire prélevé chez plusieurs individus) provenant des rivières de la Paix, Pine et Kitimat, les niveaux de dioxines et de furannes étaient sous les limites de détection, sauf pour un échantillon. Cet échantillon, prélevé en aval de l'usine pâte de Kitimat, montré un niveau détectable tétrachlorodibenzofurannes totaux (T4CDF). Certains échantillons de poissons prélevés dans le bas-Fraser, en amont comme en aval des deux usines de pâte et/ou de papier, ont montré des niveaux détectables de T4CDF. Les niveaux les plus élevés ont été mesurés chez la sauvagesse du nord (Ptychocheilus oregonensis) et le méné deux-barres (Mylocheilus caurinus).

TABLE OF CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	. v
LIST OF FIGURES	vi
ACKNOWLEDGEMENTS	vii
INTRODUCTION	1
METHODS	3
Sampling Locations and Timing	3
Sediment Sampling	. 3
Fish Sampling	18
Fish Preparation and Ageing	18
Sediment Particle Size Distribution	22
Particulate Organic Carbon Determination	22
Lipids in Fish	22
Determination of Dioxins and Furans	22
RESULTS AND DISCUSSION	23
Bed Sediment Results	23
Quality Assurance and Quality Control	23
Pine and Peace River Bed Sediments	23
Kitimat River Bed Sediments	32
Lower Fraser River Bed Sediments	33
Fish Tissue Results	36
Quality Assurance and Quality Control	36

TABLE OF CONTENTS (CONTINUED)

		Page
	Pine and Peace River Fish	36
	Kitimat River Fish	36
	Lower Fraser River Fish	44
•	Health and Welfare Evaluation of the Fish Data	45
CONCLUSIO	ons	46
REFERENCE	es :	47
APPENDIX	A	50
APPENDIX	В	52

LIST OF TABLES

			Page
Table	1.	Locations of Fish Sampling Sites, Sampling Dates and Collection Methods.	19
Table	2.	Specific Sampling Locations, Sampling Dates and Particle Sizes of Bed Sediment Samples.	24
Table	3.	Dioxin and Furan Residues, Organic Carbon Content and Moisture Content of Bed Sediments Collected Upstream and Downstream of the Pulp and/or Paper Mills and Petroleum Refinery.	27
Table	4.	Quality Control Results of Bed Sediment Splits.	29
Table	5.	Analytical Quality Control Results for Dioxin Analyses on Bed Sediments, Expressed as Percent Recovery.	30
Table	6.	Descriptions of Fish Samples Used for Dioxins and Furans Analyses.	37
Table	7.	Dioxin and Furan Residues, Lipid Content and Moisture Content of Muscle Tissue from Fish Collected Upstream and Downstream of the Pulp and/or Paper Mills and Petroleum Refinery.	39
Table	8.	Quality Control Results of Fish Tissue Splits.	41
Table	9.	Analytical Quality Control Results for Dioxin Analyses on Fish Muscle Tissue, Expressed as Percent Recovery.	42
Table	A-1.	Initial Dioxin and Furan Results for Bed Sediments that were Re-analysed.	51
Table	B-1.	Dioxin and Furan Residues and Organic Carbon Content of Suspended Sediments Collected from the Lower Fraser River.	53
Table	B-2.	Analytical Quality Control Results for Dioxin Analyses on Suspended Sediments, Expressed as Percent Recovery.	54

LIST OF FIGURES

			Page
Figure	1.	Locations of the Four Pulp and/or Paper Mills and One Petroleum Refinery Sampled.	4
Figure	2.	Locations of Areas Sampled in the Pine and Peace Rivers.	6
Figure	3.	Detail A: Locations of Fish and Sediment Sampling Sites near Fibreco Pulp Incorporated and Petro-Canada Products Limited.	8
		Detail B: Locations of Fish and Sediment Sampling Sites Upstream on the Peace River.	
Figure	4.	Detail C: Locations of Fish Sampling Sites on the Pine River near Graveyard Creek.	10
		Detail D: Locations of Fish and Sediment sampling Sites on the Pine River.	
Figure	5.	Locations of Fish and Sediment Sampling Sites in the Kitimat River Upstream and Downstream of Eurocan Pulp and Paper Company.	12
Figure	6.	Locations of Areas Sampled in the Lower Fraser River.	14
Figure	7.	Detail A: Locations of Fish and Sediment Sampling Sites near Paperboard Industries Corporation and Scott Paper Limited.	16
		Detail B: Locations of Fish and Sediment Sampling Sites near Hope.	
Figure	B-1.	Locations of Suspended Sediment Sampling Sites in the Lower Fraser River.	55

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INTRODUCTION

In 1988, Environment Canada and the Department of Fisheries and Oceans began a program to sample for dioxins and furans in sediment and biota from the vicinity of pulp and paper mills in British Columbia (B.C.). The objectives of this program were to determine levels of dioxins and furans and to identify areas of concern.

Sampling conducted in 1988 by Environmental Conservation (formerly Inland Waters) of Environment Canada concentrated on areas in the vicinity of chlorine bleaching mills in inland B.C. The results of this sampling are reported in Mah et al. (1989). In general, fish had elevated levels of tetrachlorodibenzo-para-dioxin (T4CDD) and tetrachlorodibenzofuran (T4CDF). Sediments collected downstream of the mills had elevated levels of mainly T4CDF. Of the ten mills sampled, eight utilize the chlorine bleached kraft process and two use the thermo-mechanical process. The two thermo-mechanical mills were sampled because they were located close to a chlorine bleaching mill.

Similar sampling was conducted by Environmental Protection of Environment Canada and the Department of Fisheries and Oceans in the vicinity of coastal kraft pulp mills using chlorine bleaching. The results showed that certain fish, shellfish, bivalves and sediment (Harding and Pomeroy 1990) had elevated levels of dioxins and furans. A cross-Canada survey on dioxins and furans in sediment collected downstream of pulp mills using chlorine bleaching showed elevated concentrations of dioxins and furans in the sediments (Trudel 1991). Other studies have shown that dioxins and furans are associated with chlorine bleached pulp mill effluent (Amendola et al. 1987) and in environmental samples collected from the vicinity of chlorine bleaching pulp mills (Koistinen et al. 1990; Rappe et al. 1989).

Dioxin and furan contamination from non-chlorine bleaching mills

may occur through the use of chlorophenol contaminated woodchips (Elliot et al. 1989) and recycled paper (Beck et al. 1988). In addition, a Finnish study suggested that the chlorination of process water for disinfection and decolourising may be a source of dioxins and furans precursors in some non-chlorine bleaching mills (Kitunen and Salkinoja-Salonen 1990).

In 1988, Environmental Conservation completed its program to sample for dioxins and furans in fish and bed sediments from the vicinity of ten inland B.C. pulp and/or paper mills. This report presents the results of sampling in the vicinity of the four interior pulp and/or paper mills sampled in 1989.

Sampling was conducted near an unbleached kraft mill at Kitimat, a recycled paper converting mill at Burnaby, an unbleached groundwood pulp mill at New Westminster and a bleached chemical thermomechanical mill at Taylor. None of these four mills utilizes chlorine bleaching in their process.

Samples were also collected from the vicinity of the Petro-Canada Products petroleum refinery; due to its close proximity to the pulp mill at Taylor, and because dioxins and furans have been detected in petroleum refinery wastewater (MISA 1988).

METHODS

A detailed description of methods is given in Mah et al. (1989).

Sampling Locations and Timing

Bed sediments and fish were sampled in the vicinity of: Paperboard Industries Corporation, Scott Paper Limited, Eurocan Pulp and Paper Company, Fibreco Pulp Incorporated and the Petro-Canada Products petroleum refinery (Figure 1). At each site, samples were collected upstream and downstream of the discharges. The upstream samples were collected 30 to 160 km upstream of the effluent discharges in order to avoid contamination from other potential sources of dioxins and furans (for example, wood treatment facilities). Downstream sampling was conducted in areas considered most affected by effluent. Sites containing fine grain sediments were preferentially selected for sediment sampling. The exact locations of the bed sediment and fish sampling sites are shown in Figures 2 through 7.

Sampling commenced in August 1989 and continued to October 1989. At each site sediment and fish sampling was conducted at the same time.

Sediment Sampling

Three composite bed sediment samples were collected from upstream and downstream of the discharges. Composite bed sediment samples consisted of a minimum of three grabs of the Ekman or Ponar dredge. On two occasions, samples were collected using a stainless steel spoon or ladle. In all cases only the top 2-4 cm were used. Once collected, the samples were mixed well in a stainless steel bucket and subsamples were placed into labelled Teflon jars and frozen.

Figure 1. Locations of the Four Pulp and/or Paper Mills and One Petroleum Refinery Sampled.

Figure 2. Locations of Areas Sampled in the Pine and Peace Rivers.

Details "A" and "B" are shown in Figure 3.

Details "C" and "D" are shown in Figure 4.

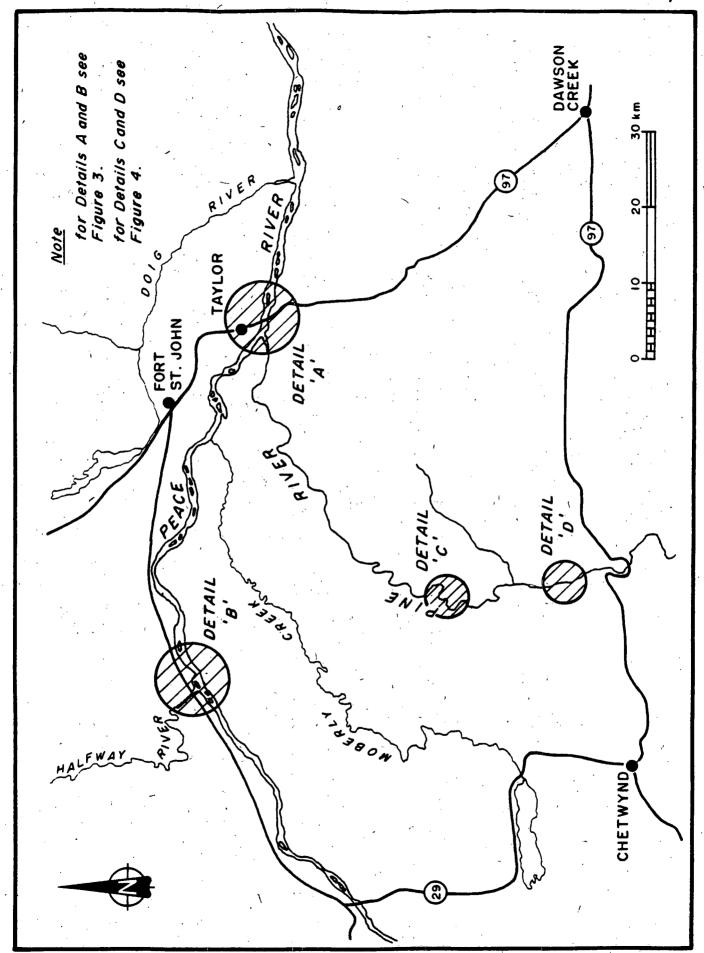


Figure 3. Detail A: Locations of Fish and Sediment Sampling Sites near Fibreco Pulp Incorporated and Petro-Canada Products Limited.

Detail B: Locations of Fish and Sediment Sampling Sites Upstream on the Peace River.

Figure 4. Detail C: Locations of Fish Sampling Sites on the Pine River near Graveyard Creek.

Detail D: Locations of Fish and Sediment Sampling Sites on the Pine River.

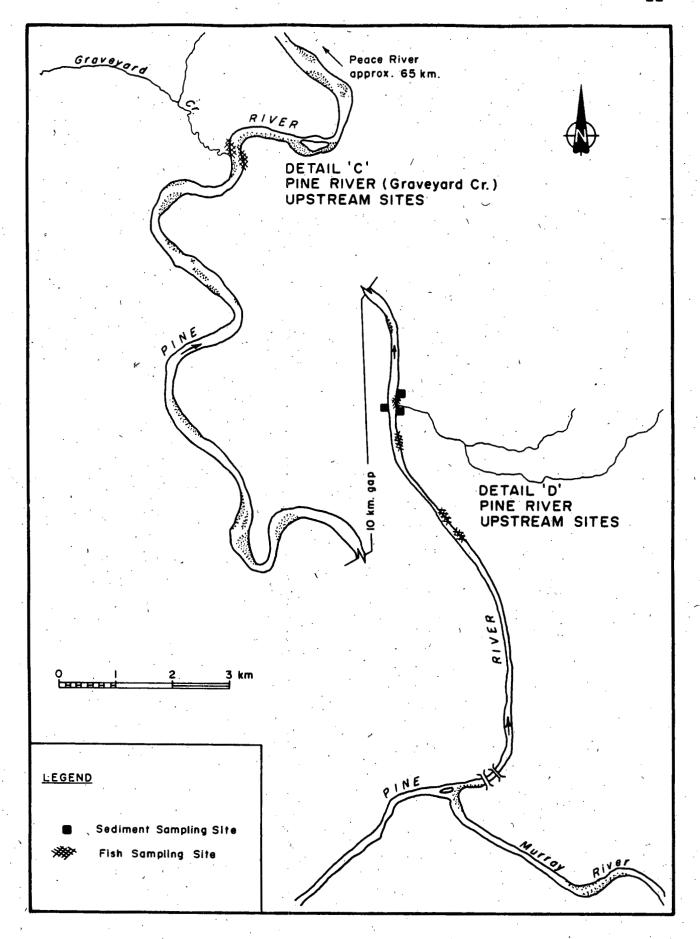


Figure 5. Locations of Fish and Sediment Sampling Sites in the Kitimat River Upstream and Downstream of Eurocan Pulp and Paper Company.

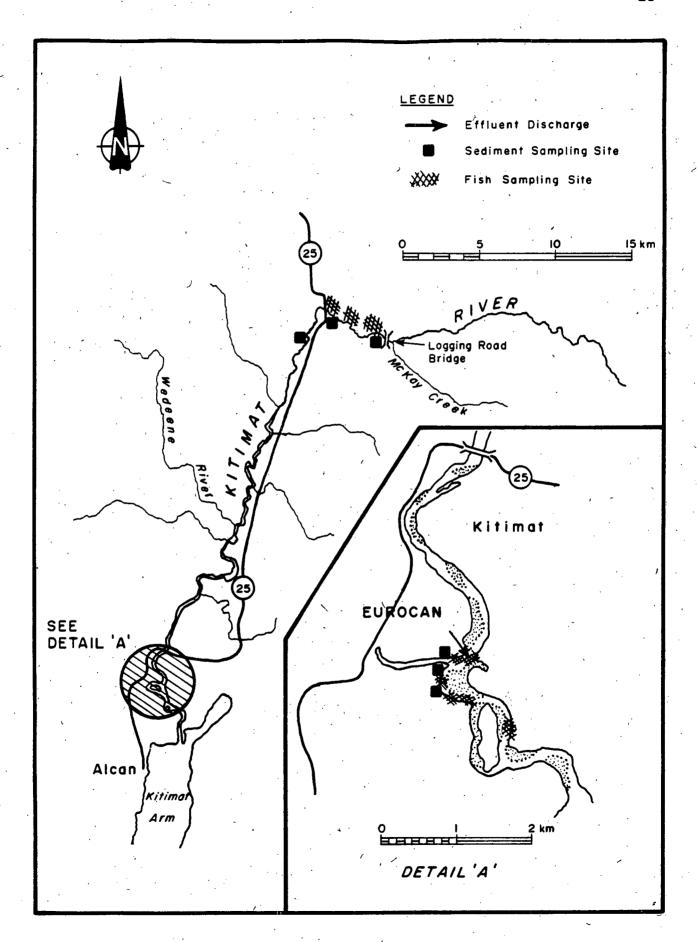


Figure 6. Locations of Areas Sampled in the Lower Fraser River.

Details "A" and "B" are shown in Figure 7.

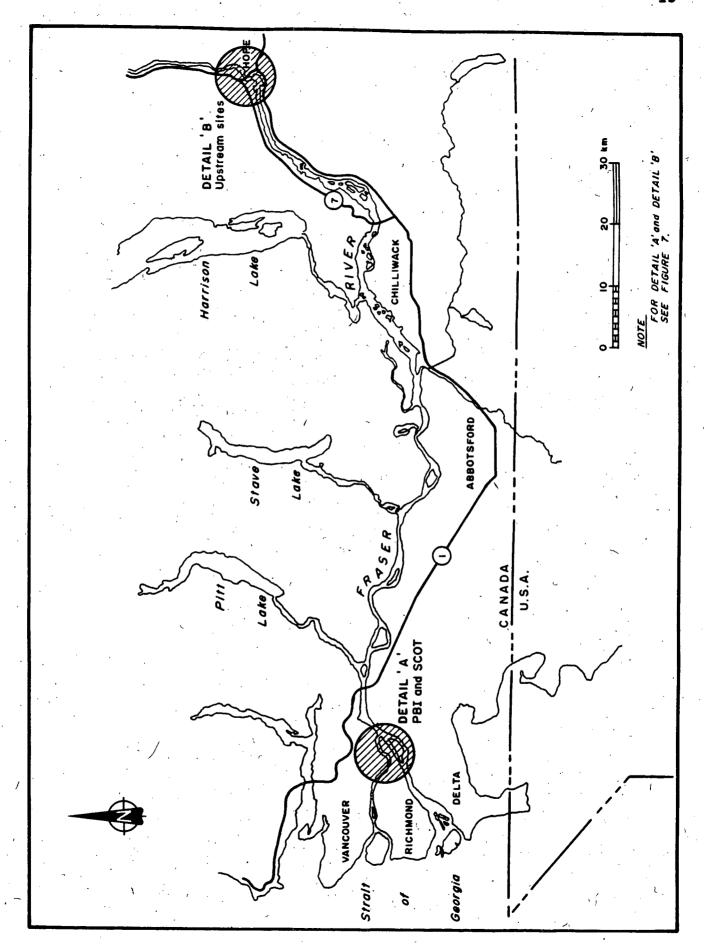
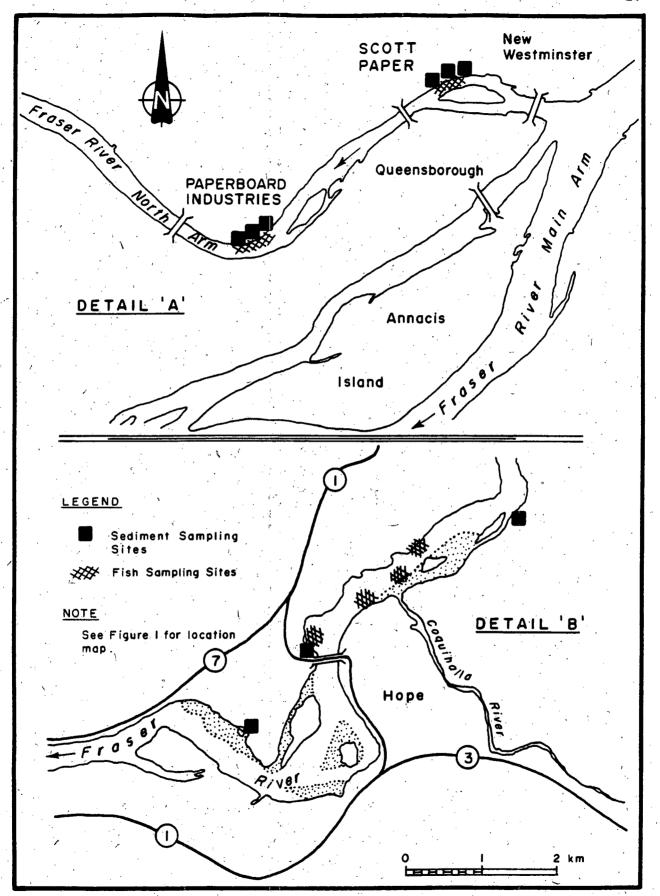


Figure 7. Detail A: Locations of Fish and Sediment Sampling Sites near Paperboard Industries Corporation and Scott Paper Limited.

Detail B: Locations of Fish and Sediment Sampling Sites near Hope.



Fish Sampling

Fish were collected using minnow traps, beach seines and sinking gill nets (mesh sizes from 3.8 cm to 11.4 cm). Captured fish were placed into stainless steel basins or buckets and kept cool until field processing. Field processing consisted of:

- identifying the species,
- recording the length,
 - assigning labels,
 - wrapping in oven baked aluminum foil,
 - and freezing with dry ice.

Details of the fish sampling locations, dates and sampling methods are presented in Table 1.

Fish Preparation and Ageing

In the laboratory the fish were thawed, weighed and re-identified to confirm field identification. The fish were then skinned, and an equal amount of epaxial muscle tissue was removed from several fish of the same species to make one composite sample. Usually, the composite sample consisted of seven fish; however, this number varied from five to sixty. The tissue was then homogenized using a blender followed by a Polytron ultrasonic dispersator and mixed well. Subsamples were placed into labelled Teflon jars and frozen. For some samples, composite liver and kidney samples were similarly prepared for future analyses.

Otoliths, pectoral fins and pelvic fins were removed and retained from each fish for age determination. Scales were retained for ageing from some species. Fish age was determined by examining annuli present in the structures listed above. The analysis was conducted at the Fish Age Determination Unit, Department of

TABLE 1. LOCATIONS OF FISH SAMPLING SITES, SAMPLING DATES AND COLLECTION METHODS

	:	•	•	4				
SAMPLING METHOD	beach seine gill nets 6.3, 11.4 cm	beach seine gill nets 6.3, 11.4 cm	beach seine	beach seine gill nets 3.8, 6.3, 11.4 cm	gill nets	beach seine	gill nets 8.9 cm	gill nets 8.9 cm
SAMPLING DATE	21/08/89	22/08/89 23/08/89 27/08/89	18/08/89	18/08/89 19/08/89	18/08/89 19/08/89	19/08/89	20/08/89* 04/10/89*	04/10/89* 05/10/89* 07/10/89*
SPECIFIC SITE	Landslide site at right bank and at confluence of the Halfway and Peace Rivers	Behind the high water island, right bank, 6 km downstream of the Halfway River	Right bank, approximately 500 m downstream of proposed Louislana Pacific discharge site	Right bank, approximately 1 km downstream of proposed Louislana Pacific discharge site	Right bank, across from proposed Louisiana Pacific discharge site	Left bank, 1 km downstream of proposed Louisiana Pacific discharge site	Left bank , 26 km downstream of Louisiana Pacific discharge site	Right bank, 26 km downstream of Louislana Pacific discharge site
GENERAL LOCATION	Near Haifway River Confluence, 58 km upstream of Fibreco	•	Pine Riyer, 80 km upstream of Fibreco	. •		•	Pine River near mouth of Graveyard Creek, 54 km upstream of Fibreco	•
SITE LOCATION	Fibreco Pulp Inc. Upstream Peace River		Fibreco Pulp Inc. Upstream Pine River					

TABLE 1. LOCATIONS OF FISH SAMPLING SITES, SAMPLING DATES AND COLLECTION METHODS (Cont'd)

SITE LOCATION	GENERAL LOCATION	SPECIFIC SITE	SAMPLING DATE	SAMPLING METHOD
Petro-Canada Products Downstream	Peace River, at Taylor, 1 km upstream of Fibreco	Left bank, back eddy 3 m from Petrocan discharge	25/08/89 26/08/89	gill nets 11.4 cm
		Right bank, across Peace River from Petrocan discharge, mouth of side channel from Pine River	26/08/89	gill nets 6.3, 11.4 cm
	•	Left bank, 200 m downstream of Petrocan discharge	26/08/89	gill nets 6.3, 11.4 cm
Fibreco Pulp Inc. Downstream	Peace River near Taylor	Left bank, in backwater behind island, 3 km downstream of Fibreco discharge	24/08/89 25/08/89	gill nets 6.3, 11.4 cm
	•	10 m downstream of Fibreco discharge, toward left bank	25/08/89 26/08/89 27/08/89	gill nets 6.3, 11.4 cm
	•	Left bank, 800 m downstream from Fibreco discharge	25/08/89	beach seine
Eurocan Puip & Paper Co. Upstream	Kitimat River, approximately 31 km upstream of Eurocan	Left bank in deep pools near Highway 25 bridge	07/09/89	minnow traps
	•	Right bank, near mouth of Chist Creek	68/60/80	minnow traps
	•	Right bank, just downstream of McKay Creek	09/09/89 to 14/09/89	minnow traps

TABLE 1. LOCATIONS OF FISH SAMPLING SITES, SAMPLING DATES AND COLLECTION METHODS (Cont'd)

SITE LOCATION	GENERAL LOCATION	SPECIFIC SITE	SAMPLING DATE	SAMPLING METHOD
Eurocan Pulp & Paper Co. Downstream	Kitimat River, near Eurocan Pulp Mill	Right and left banks, from 150 m to 2 km downstream of Eurocan discharge	07/09/89 to 14/09/89	minnow traps
	•	Directly in effluent on right bank, 1 to 3 m downstream of discharge	14/09/89	beach seine
Lower Fraser River Mills Upstream	Fraser River at Hope	Left bank, at mouth of Coquihalia River Left bank, 500 m downstream of Coquihalia River	12/10/89	gill nets 3.8, 6.3 cm gill nets 3.8, 6.3 cm
		Right bank, 1.2 km downstream of Coquihalla River	12/10/89	glll nets 3.8, 6.3 cm
		Right bank, 600 m upstream of Coquihalla River	12/10/89	gill nets 3.8, 6.3 cm
Scott Paper Limited Downstream	North Arm of the Fraser River, New Westminster	Right bank, 50 to 100 m downstream of Scott Paper discharge	05/10/89 06/10/89	gill nets 3.8, 6.3, 11.4 cm
	•	Right bank, 3 m from the Scott Paper discharge	05/10/89	gill nets 3.8, 6.3, 11.4 cm
Paperboard Industries Corp. Downstream	North Arm of the Fraser River, near Burnaby Bend	Right bank, 20 to 300 m downstream of discharge	05/10/89 06/10/89 10/10/89	gill nets 3.8, 6.3 cm
		* Collected by EVS Consultants		

Fisheries and Oceans, Pacific Biological Station, Nanaimo, B.C.

Sediment Particle Size Distribution

The particle size distribution of sediment samples was determined by hydrometer, bottom withdrawal or sieve analysis methods using procedures described in Environment Canada (1988a).

Particulate Organic Carbon Determination

The procedure for determining particulate organic carbon was identical to NAQUADAT 06903 (Environment Canada 1979; 1988b) except that the dried, acid washed sediment was pressed into a capsule and no catalyst was added.

Lipids in Fish

The lipid content was determined by extracting the fish sample with 50% methylene chloride/hexane as described in Mah et al. (1989).

Determination of Dioxins and Furans

The analytic methods used for the determination of dioxins and furans in fish and sediment, as well as the quality assurance and quality control procedures, are presented in Mah et al. (1989).

RESULTS and DISCUSSION

Bed Sediment Results

Refer to Table 2 for the bed sediment sampling locations, sampling dates and particle size distributions. Table 3 presents concentrations of dioxins and furans, moisture content and organic carbon content.

Quality Assurance (QA) and Quality Control (QC)

As part of the QA/QC procedures, composite bed sediment samples from two different locations were split into three subsamples. Each subsample was assigned a unique label and submitted for analysis. The results of the bed sediment splits (Table 4) are similar since all results were below the detection limit. However, detection limits varied among splits. Laboratory analytical QA/QC procedures are those of Mah et al., (1989). The laboratory QA/QC results for dioxin analysis on bed sediments are presented in Table 5.

Pine and Peace River Bed Sediments

Bed sediments were collected from the Pine and Peace Rivers upstream and downstream of Fibreco Pulp Incorporated and the Petro-Canada Products refinery. No detectable residues of dioxins or furans were measured except for one Pine River sample (Pine-03). Initial analysis of the Pine-03 sample showed the presence of hexachlorodibenzodioxin (H6CDD), hexachlorodibenzofuran (H6CDF) and heptachlorodibenzofuran (H7CDF) residues. Since the Pine-03 sample was collected from an upstream location with no apparent source of dioxins or furans, a re-analysis of this sample was performed. The

TABLE 2. SPECIFIC SAMPLING LOCATIONS, SAMPLING DATES AND PARTICLE SIZES OF BED SEDIMENT SAMPLES

			,				٠.	•		
	% CLAY	15.0	9 .	11.0	7.0	12.0	0.6	. 10.5	9.5	10.3
ize •	% SILT	27.8	1.61	40.0	36.8	24.0	32.2	63.8 8	41.7	52.4
PARTICLE SIZE *	% SAND	57.2	72.1	69.0	54.2	0.	58.8 8	35.7	49.1	37.3
	% GRAVEL	0:	0.5	0.0	0.0	0	, o	0.0	0.0	0.0
	SAMPLING DATE	21/08/89	21/08/89	21/08/89	18/08/69	18/08/89	19/08/89	24/08/89	24/08/89	24/08/89
	SAMPLING LOCATION	Peace River, just upetream of Halfway River Confluence, left bank	Peace River, just upstream of Halfway River Confluence across river at landslide site, right bank	Peace River, 6 km downstream of Halfway River, right side in backwater area	About 80 km upetream from Fibreco, right bank, approximately 1 km downetream of proposed Louisiana Pacific discharge	Pine River, left bank, approximately 1 km downstream of proposed Louislana Pacific discharge	Pine River, right bank, approximately 1.1 km downstream of proposed Louisiana Pacific discharge	Peace River at Taylor, 10 m downstream of discharge, left side	Peace River at Taylor, 150 m downstream of discharge, just downstream of bridge, left bank	Peace River at Taylor, 600 m downstream of discharge, at tip of island
	SITE LOCATION	Fibraco Pulp Inc. Upstream Pasce Blue			Fibreco Pulp Inc Upetream Pine River			Petro – Canada Products Downstream		·
	SAMPLE NO.	PRUS-01	PRUS-02	PRUS-03	PINE – 01	PINE-02	PINE-03	PETR-01	PETR-02	PETR-03

25

TABLE 2. SPECIFIC SAMPLING LOCATIONS, SAMPLING DATES AND PARTICLE SIZES OF BED SEDIMENT SAMPLES (Cont.d)

PARTICLE SIZE *

SAMPLE NO.	SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	% GRAVEL	% SAND	% SILT	% CLAY
FIBR-01	Fibreco Pulp Inc. Downstream	Peace River at Taylor, 650 m downstream of discharge	24/08/89	0.0	61.4	91.3	7.3
FIBR-02		Peace River at Taylor, 500 m downstream of discharge, left bank	24/08/69	0.0	23.6	61.9	14.5
FIBR-03		Peace River at Taylor, approximately 1 km downstream of discharge	24/08/89	0.0	12.8	71.6	
KITU-01	Eurocan Pulp & Paper Co. Upstream	Kitimat River, 3.5 km downstream of Hwy 25 bridge (31 km upstream of Eurocan) in side channel by right bank	68/60/80	.	1	23.6	o, o,
KITU-02		Kitimat River, just upstream of Hwy 25 bridge, left bank	68/60/80	0.2	6.53	36:9	7.0
KITU-03		Kitimat River, at logging road bridge, 4 km upetream of Hwy 25 bridge, left bank	68/60/80	0.2	8 .	11.9	4.
EUR-01	Eurocan Pulp & Paper Co. Downstream	Kitimat River, right bank, 175 m downstream of discharge	68/60/60	0.0	63.6	31.1	ro G
EUR-02		Kitimat River, right bank, 750 m downstream of discharge	69/60/60	0.1	77.6	16.9	Ą.
EUR-03		Kitimat River, right bank, 1 km downstream of discharge	68/60/60	0.0	25.4	62.6	12.0
HOPE-01	Lower Fraser River Mills Upetream	Fraser River, just upstream of Highway 1 bridge, behind rocks, in backwater by right bank	12/10/89	0.0	66.5	55 .	6

TABLE 2. SPECIFIC SAMPLING LOCATIONS, SAMPLING DATES AND PARTICLE SIZES OF BED SEDIMENT SAMPLES (Cont'd)

					PARTICLE SIZE *	SIZE *		
SAMPLE NO.	SITE LOCATION	SAMPLING LOCATION	SAMPLING DATE	% GRAVEL	% SAND	% SILT	% CLAY	
HOPE-02		Fraser River, 2 km upstream of Coquihalla River confluence, left bank	12/10/89	0.0	68.5	34.8	9.9	,
HOPE-03		Fraser River, downstream of Crott Island (3 km downstream of Hwy 1 bridge), right bank	12/10/89	0.0	12.0	1.11	10.3	
SCOT-01	Scott Paper Limited Downstreem	Fraser River, near discharge, close to shore	08/10/89	89.	59.4	30.8	6.2	
SCOT-02		Fraser River, halfway between discharge pipe and edge of Scott property (about 80 m downstream of discharge)	06/10/89	0.	46.0	43.8	10.	
SCOT-03		Fraser River, at downstream edge of Scott property by metal wall (about 200 m downstream of discharge)	06/10/89		, 3	39.	න ග්	
- PBI-01	Paperboard Industriee	Fraser River, 60 m downstream of discharge, right bank	05/10/89	4	26.0	36.	9 .	-
PBI-02	Downstream	Fraser River, 200 m downstream of discharge, right bank	05/10/89	0.0	32.7	63.0	14.3	
PBI-03		Fraser River, 300 m downstream of discharge, right bank	05/10/89	0.0	25		10.0	

* particle size categories are defined as follows: gravel = 2-64 mm, sand = 0.062-2 mm, sift = 0.004-0.062 mm, clay = <0.004 mm

DIOXIN AND FURAN RESIDUES, ORGANIC CARBON CONTENT AND MOISTURE CONTENT OF BED SEDIMENTS

COLLECTED UPSTREAM AND DOWNSTREAM OF THE PULP MILLS AND PETROLEUM REFINERY Table 3.

	1 188 179 179 179 179 179 179 179 179 179 179	1 9217 1881 1 9217 1881 1 901 1891 1 901 1891	7 27 07 1 28 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 1 29 1 2	1.08 L48 1.150 L48 1.150 L48 1.150 L48 1.150 L48 1.150 L48 1.150 L42 1.150 L42 1.150 L42	1.08 1.08 1.150 1.	1.08 1.18 1.19 1.19 1.19 1.19 1.19 1.19 1.1	1.0 E8	1.00 L48 1.00 L48 1.00 L48 1.00 L48 1.00 L42 1.00 L43 1.0	1.68 L88 1.79 L63 1.40 L48 1.30 L18 1.30 L18 1.42 L42 1.45 L44 1.45 L44 1.16 L15 1.16 L15 1.16 L15 1.16 L15 1.16 L15 1.16 L15 1.17 L18 1.18 L16 1.19 L16 1.10 L17 1.10 L16 1.10 L17 1.1	1.68	168 168 179 163 170 163 170 163 170 163 170 178 171 180 172 178 174 178 174 178 176 178 177 178 178 178 179 178 170 170 178 170 178
168 173 140 150	168 1.40 1.30 1.130	8 6 9 9 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		8 6 6 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	8 6 9 9 8 8 8 8 9 8 8 9 8 9 8 9 8 9 8 9	168 188 188 188 199 199 199 199 199 199 19	168 168 168 168 168 168 168 168 168 168	18 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	89 1 2 2 2 3 3 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	1
L40 L6	L79 L40 L30 L331 .L	67 97 97 88 89 89 89 89 89 89 89 89 89 89 89 89	L40 L33 L52 L62 L62 L62 L63	1	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	1, 64 BE 1, 188 1, 189	LS 1	LS 12 12 12 12 12 12 12 12 12 12 12 12 12	2	2	L 1
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1150		L75	175	L75 L50 L19	2 2 2 2 2 2 4		5	5	5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	55 52 52 53 55 55 55 55 55 55 55 55 55 55 55 55
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1.15		79.1	1.67 1.28 2.43	1.67 1.28 1.28 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.0	78: 12: 25: 25: 25: 25: 25: 25: 25: 25: 25: 2	79.1 2.2 3.1 5.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	1.67 1.88 1.94 1.94 1.95 1.95 1.95 1.95 1.95 1.95 1.95 1.95	79.1. 25. 26. 27. 28. 29. 27. 28. 29. 27. 29. 29. 29. 29. 29. 29. 29. 29. 29. 29	79.1	1.67 2.43 2.43 2.60 2.60 2.60 2.60 2.60 2.60 2.60 2.60	79.1 78.1 78.1 78.0 79.0 70.0
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16 26 .		3 8	e e e e e e	•				· .			
Inc. Upstream 37 Pine River 34		, 6		Petro – Canada Products Downstream Fibreco Pulp Inc.	Petro – Canada Products Downstream Pibreco Pulp Inc.	Petro – Canada Products Downstream Fibreco Pulp Inc. Downstream & Paper Co. Upstream	Petro-Canada Products Downstream Fibreco Pulp Inc. Downstream Eurocan Pulp & Paper Co. Upstream	PetroCanada Products Downstream Fibreco Pulp Inc. Downstream Eurocan Pulp & Paper Co. Upstream	Petro-Canada Products Downstream Inc. Downstream Eurocan Pulp & Paper Co. Upstream Eurocan Pulp & Paper Co.		

DIOXIN AND FURAN RESIDUES, ORGANIC CARBON CONTENT AND MOISTURE CONTENT OF BED SEDIMENTS COLLECTED UPSTREAM AND DOWNSTREAM OF THE PULP MILLS AND PETROLEUM REFINERY Table 3. (Cont'd)

				OIO	KIN CON	CENTRAT	gd) NOI	DIOXIN CONCENTRATION (pg/g dry wt.)		5	FURAN CONCENTRATION (pg/g dry wt.)	CENTRA	NOIT	3/9 dry w	•
SAMPLE	SAMPLE SAMPLING NUMBER LOCATION	MOISTURE ORGANIC CONTENT CARBON	ORGANIC CARBON (%)	2,3,7,8 T4CDD	Total T4CDD	Total Total	Total	Total Total H7CDD O8CDD	Total OecDD	2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total O8CDF
SCOT-01	SCOT-01 Scott Paper	8	1.88	113	L13	ភ	110	8	44	*	8	2	(36)	L18	8
scot-02	SCOT -02 Downstream	ຂ	1.57	115	115	2	83	- 114	8	6	, 6	L46	83	L141	8
scot-a	_	8	1.51	L10	L10	ឡ	200	118	267	L10	L10	គ្ន	5	L1 0	P
PBI-01	Paperboard	ន	0.61	91	9	112	116	83	555	8	8	° 113	L16	8	ध
PBI_02	Industries Corp.	8	8.	77	77	2	뫮	178	546	7	IJ	គ	न्त्र	L75	146
PBI-03		8	1.91	L19	L19	146	147	ន	386	L19	L19	L48	147	3	L10

denotes less than specified detection limit.

^{*} denotes no value was obtained.

⁽⁾ denotes vake was below method detection limit however a peak was detected.

Table 4. QUALITY CONTROL RESULTS OF BED SEDIMENT SPLITS

	Total OBCDF	.	1145	8	83	8	29	
dry wt.)	Total T	8	951	જુ	8	8	82	
FURAN CONCENTRATION (pg/g dry wt.)	Total T	75	997	2	24	超,	29	
PATION	=	1 24.	ا ھ	<u> </u>	_ g	ار ا	L40	
NCENT	Total P5CDF				_		. * *	. ,
PANCO	Total T4CDF	ב	Ξ	8		114 1/2 114	F 2	•
5	2,3,7,8 T4CDF	7	Ξ	82	2	12	120	
	Total	ន្ទ	L145	8	83	푎	720	
DIOXIN CONCENTRATION (pg/g dry wt.)	2,3,7,8 Total Total Total Total Total Total T4CDD 14CDD P5CDD H6CDD H7CDD 08CDD	8	, 3	3	8	3	2	
NO (pg	Total H6CDD	23	8	3	142	8	83	
ENTRATI	Total P5CDD	23	83	3	3	137	3	
IN CONC	Total T4CDD	7	5	83	2	114	F2	. ·
XOIQ	2,3,7,8 T4CDD	٦	=	23		7	L10	
•		, ``					, (°)	
٠.,	ORGANIC CARBON (%)	2	X A	¥ _N	0.20	¥ X	¥X	
	MOISTURE ORGANIC CONTENT CARBON (%) (%)	.	8	8	8	ક્ષ	38	
	SAMPLING	Fibreco Pulp	inc. Downstream		Eurocan Pulp	Downstream		• ;
	SAMPLE	FIBA-02*	Split A	Split B	EUR-01*	Split A	Split B	

L denotes less than specified detection limit.

* denotes samples reported in Table 3

N/A denotes analysis was not done.

ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON BED SEDIMENTS, EXPRESSED AS PERCENT RECOVERY

Table 5.

				SURROG/	SURROGATE SPIKE			PERFORMANCE	
SAMPLE NUMBER	SITE LOCATION	1 0	Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD	SIANDARD	
PRUS-01	Fibraco Pulp		118	110	108	86	16	145	
PRUS-02	Upstream	,	114	130	109	66	92	46	
PRUS-03			108	132	133	88	87	115	٠.
PINE-01	-Fibreco Pulp		84	96	98	64	64	60	
PINE-02	Upstream Plos Bloss		94	102	113	96	86	86	
PINE-03			20	. 982	74	42	Ξ.	100	
FIBR-01	Fibraco Pulp		22	112	119	105	86	120	
FIBR-02	Downstream		213	153	124	100	92	171	(-
Split A (FIBR-02)	į.	·	75	64	46	115	112	100	
Split B (FIBR-02)	(2)		62	82	62	191	49	100	
FIBR-03				141	125	112	88	102	
PETR-01	Petro-Canada		2	28	54	۲,	62	, 001	
PETR-02	Downstream		106	82	83	101	901	100	· .
PETR-03			28	89	69	99	28	, 100	
KITU-01	Eurocan Pulp	***	£ 23	42	92.	.	22	148	
KITU-02	Upstream		100	16		85	100	133	
KITU-03			74	118	23	111	110	95	

ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON BED SEDIMENTS, EXPRESSED AS PERCENT RECOVERY

Table 5. (Cont'd)

				SURROG	SURROGATE SPIKE	·		PERFORMANCE	
SAMPLE NUMBER	SITE LOCATION		Total C13T4CDD	Total C13P5CDD	Total Total C13P5CDD C13H6CDD	Total C13H7CDD	Total C13O8CDD	STANDARD	
EUR-01	Eurocan Pulo	• •	06	72	29	29	92	112	
Split A (EUR-01)	& Paper Co. Downstream		8		. 29	6 6	113	100	
Split B (EUR-01)			29	58	45	98	80	100	•
EUR-02		,	135	16	75	22	69	86	
EUR-03			112	100	88	32	88	112	
HOPE-01	Lower Fraser		62	29	73	140	118	100	
HOPE-02	Hiver Mills Upstream		99	29	110	. 98	122	100	
HOPE-03		•	75	74	37	99	33	100	. :.
SCOT-01	Scott Paper	•	9	82	7	42	. 89 80	100	
SCOT-02	Downstream	· •	29	999	44	20	4	100	
SCOT-03			11	86	102	107	46	95	
PBI-01	Paperboard		, 99	100	66	96	09	100	
PBI-02	Corp.		96	88	09	62	35	100	
PBI-03	DOWNSITERIN		88	84	8	, 62	98	100	

second analysis of a field split showed no detectable residues of dioxins or furans; however the detection limits were high. These differing results may be due in part to difficulties in obtaining a completely homogeneous sample for analysis. Further sampling is required to fully characterize the Pine River sediment. Appendix A, Table A-1 presents the results of the original analysis on these samples.

Kitimat River Bed Sediment

The bed sediments collected from the Kitimat River upstream of Eurocan Pulp and Paper Company had no detectable residues of dioxins or furans. One sample (EUR-03) collected downstream of Eurocan Pulp and Paper Company had a H6CDD concentration of 687 pg/g (parts per trillion or ppt). To confirm this result the sample was re-analysed. The second analysis showed a concentration of 470 ppt H6CDD; the mean of these two results is 578 ppt. Similar concentrations of H6CDD were found in marine bed sediment samples collected from Kitimat Arm in 1990 (Goyette and Boyd 1991). Goyette and Boyd measured H6CDD concentrations in bed sediments ranging from below detection to 982 pg/g. These authors also detected concentrations of heptachlorodibenzodioxin (H7CDD) and octachlorodibenzodioxin (O8CDD) in these marine sediments.

The EUR-03 sample contained higher silt-clay content (30% higher) and organic carbon content (two times higher) than the other Kitimat River samples. Dioxins and furans have low solubility in water and high affinity to soil particles with high organic carbon content (Palausky et al. 1986; Arthur and Frea 1989). In the EUR-03 sample, the presence of H6CDD may have been detected because of the higher organic carbon content.

A potential source of H6CDD in non-chlorine bleaching pulp mills is the use of chlorophenol contaminated wood chips. The production of chlorophenols is known to produce trace amounts of chlorinated dioxins including H6CDD (Hagenmaier and Brunner 1987).— In British Columbia chlorophenols have been used for preserving wood and wood products for export. The Eurocan Pulp and Paper Company plant site includes a former woodmill. Until 1977, this woodmill operated a drive-through chlorophenol dip tank for anti-sapstain treatment (S. Liu, pers. comm.). As noted by Kitunen et al. (1987), the historical use of chlorophenols (and chlorophenol contaminated wood chips) may be one source of H6CDD.

Lower Fraser River Bed Sediment

Initial analyses of bed sediment samples collected upstream of the lower Fraser River mills showed no detectable residues of dioxins or furans (Appendix A, Table A). These samples were re-analysed since detection limits in the initial analyses were high. analysis showed similar results - no dioxins or furans were detected but the detection limits were high (Table 3). detection limits may have been the result of sample matrix Samples with excessive co-extractives require interference. extensive clean-up prior to analysis. In some samples the clean-up procedure may not remove the interference thus resulting in higher detection limits. One possible source of interference may have been organic matter originating from decaying salmon that were present at the upstream site during sampling. As a result, the Hope bed sediment samples likely contained sufficient quantities of organic matter (decaying salmon) to produce the interference during analysis.

Bed sediment samples collected downstream of the lower Fraser River mills contained detectable residues of dioxins and furans. The levels of 2,3,7,8-T4CDF measured downstream of Scott Paper Limited, New Westminster (19 to 24 ppt) are similar to the level (22 ppt) measured in one sample downstream of Paperboard Industries

Corporation, Burnaby. Note that these 2,3,7,8-T4CDF levels are lower than the 2,3,7,8-T4CDF detection limits for the upstream (Hope) samples.

Similar levels of 2,3,7,8-T4CDF (5.8 to 26 ppt) were measured in lower Fraser River bed sediments collected in 1990 by Swain and Walton (1991). Their samples were collected in the vicinity of Paperboard Industries Corporation and at the mouth of the Main Arm of the Fraser River. Mah et al. (1989) measured 2,3,7,8-T4CDF in bed sediments sampled from the vicinity of six pulp mills located at least 240 km upstream of Hope in the Fraser River basin. Five of the upstream mills use the chlorine bleached kraft process. Amendola et al. (1987) state that the 2,3,7,8-T4CDD and 2,3,7,8-T4CDF isomers are the principal isomers found in chlorine-bleached pulp mill matrices.

Mah et al. (1989) measured 2,3,7,8-T4CDF in one "upstream" site. This site was located on the Fraser River upstream of pulp mills located in Quesnel but 135 km downstream of three chlorine bleaching kraft mills situated in Prince George. Their results indicate that pulp mills located upstream on the Fraser River may produce detectable residues of 2,3,7,8-T4CDF considerable distances downstream.

All six bed sediment samples collected in the vicinity of Scott Paper Limited and Paperboard Industries Corporation had measureable levels of O8CDD. Two of the six samples also had measureable residues of H6CDD and one sample contained a third isomer, H7CDD. Similar results were found by Swain and Walton (1991). They detected all five congeners of dioxin in bed sediments collected from the lower Fraser River; but the H6CDD, H7CDD and O8CDD congeners predominated.

Levels of O8CDD measured in **suspended** sediments collected from the lower Fraser River in March 1989 (Environment Canada, 1989

unpublished data) are similar to the levels measured in bed sediments in the present study. The results of the dioxin and furan analyses (Table B-1) and analytical quality control (Table B-2) on these suspended sediment samples are presented in Appendix B. Two 24 hour suspended sediment samples were collected using a Westfalia continuous flow centrifuge. Both samples were collected from the Main Arm of the lower Fraser River. The first sample (STEV-100), collected near the George Massey Tunnel (Appendix B, Figure B-1), had an OSCDD concentration of 370 ppt while the second sample (ANN-200), collected just downstream of Annacis Island (Appendix B, Figure B-1), had an OSCDD concentration of 329 ppt.

In our study, these highly chlorinated congeners of dioxin were not detected in Fraser River bed sediment samples collected upstream at Hope; nor were they detected by Mah et al. (1989) in their Fraser River Basin samples collected at least 240 km upstream of Hope. The lower Fraser River/has various potential sources of the higher chlorinated dioxin congeners. Previous studies (Czuczwa and Hites 1984; Czuczwa and Hites 1986) have shown that the primary sources of OSCDD to the environment include: municipal incinerator emissions, industrial incinerator emissions and pentachlorophenol. Czuczwa and Hites (1986) found that O8CDD predominated in airparticulate and sediment samples. Based on their historical use, Elliot et al. (1989) attribute chlorophenols as the most important potential source of dioxins to the British Columbia environment. Tetra- and pentachlorophenols have been used by the British Columbia wood industry for the prevention of sapstain fungus. Hagenmaier and Brunner (1987) found commercial pentachlorophenol and pentachlorophenate to contain measureable levels of all dioxin and furan isomers, but the octa-, hepta- and hexa- isomers Considerable chlorophenol contamination predominated. stormwater run-off to the lower Fraser River has occurred from the stacking of chlorophenol treated lumber in large outdoor storage sites (Krahn et al. 1987).

Fish Tissue Results

A detailed description of fish samples used for dioxin and furan analyses is presented in Table 6. The results of fish tissue analyses for dioxins and furans are presented in Table 7.

Quality Assurance (QA) and Quality Control (QC)

As part of the QA/QC procedures composite fish tissue samples from two different locations were split into three subsamples. Each subsample was assigned a unique label and submitted for analysis. The results of the fish tissue splits (Table 8) indicate a high level of reproducibility, with a coefficient of variation of 7.5% for the one furan isomer that was detected. Laboratory analytical QA/QC procedures are those of Mah et al. (1989). The laboratory QA/QC results for dioxin analysis on fish tissues are presented in Table 9.

Pine and Peace River Fish

Fish were collected from the Pine and Peace Rivers upstream and downstream of Fibreco Pulp Incorporated and the Petro-Canada Products refinery. These fish samples showed no detectable residues of dioxins or furans.

Kitimat River Fish

Fish collected from the Kitimat River upstream of Eurocan Pulp and Paper Company showed no detectable residues of dioxins or furans. One sample (Dolly Varden, Salvelinus malma), collected downstream of the mill, had a detectable concentration of 2,3,7,8-T4CDF and total T4CDF (24 ppt). Similar concentrations of 2,3,7,8-T4CDF (14

DESCRIPTIONS OF FISH SAMPLES USED FOR DIOXINS AND FURANS ANALYSES

Table 6.

MEDIAN AGE (Range) years	-8	20 (12-24)	5.5 (2–9)	7 (6–15)	11 (5–16)	11 (7–28)	21)	21)	3 28)	S S		· · · · · · · · · · · · · · · · · · ·	, •	•	, ति	
MEDIAN (Range) year	٥	(12-	. Š	(9)	(5,	0	9 (3-21)	16 (6-21)	16 (10–28)	3.5 (2-8)	7 7	9.5 ^ (5−23)	2 - Z	2 (1-4)	5.5 ^ (4 – 13)	6
MEDIAN WEIGHT (Range) g	60.2 (52.2–73.9)	1220.6 (767.1-1388.9)	1992.3 (884.0-3198.0)	238.1 (171.4–609.4)	666.9	1169.7 (887.5–1565.2)	860.4 (358.8-1553.2)	839.6 (668.3-1310.3)	1326.3 (1111.9–2226.0)	771.5 (723.8–960.0)	81.1 (65.1–102.0)	15.1 (10.1–25.4)	79.0 (45.8–193.4)	70.5 (36.1–280.0)	54.9 (43.0–92.0)	169.0
MEDIAN FORK LENGTH (Range) mm	172.0 (167–183)	444.0 (406 – 473)	608.5 (486-754)	272.0 (255–385)	372.0 (354–426)	465.0 (399494)	435.0 (315–504)	412.0 (374–462)	473.5 (400–556)	471.5 (440–498)	200.0 (175–205)	103.5 • (100–125)	187.0 (157–250)	178.0 (140–300)	160.5 • (150–187)	229.0
NO OF FISH IN COMPOSITE	21		©			10	•		65	•		8	Q	9	92	so.
FISH SPECIES	Prosopium williamsoni (mountain whitefish)	Catostomus catostomus (longnose sucker)	Esox Arctus (northern pike)	Cetostomus catostomus (longnose sucker)	Prosoptum williamson! (mountain whitefish)	Stizostadion vitraum (wallaya)	Strostedion vitreum (walleye)	Catostomus catostomus (longnose sucker)	Catostomus macrochellus (largescale sucker)	Exos tucius (northern pike)	Oncothynchus mykiss (rainbow trout)	Cottus aleuticus (coast range sculpin)	Salvelinus malma (dolly varden)	Oncorhynchus mykias (rainbow trout)	Cottus asper (prickly aculpin)	Salvetinus maima (dolly varden)
SAMPLING DATE	21/08/89	23/08/89 27/08/89	23/08/89 27/08/89	18/08/89 19/08/89	04/10/88 05/10/89 07/10/89	18/08/89 20/08/89 04/10/89	25/08/89 26/08/89	25/08/89 to 27/08/89	24/08/89 to 27/08/89	25/08/89 26/08/89	07/09/89 to 14/09/89			14/09/89	11/09/89 to 14/09/89	13/09/89
SITE LOCATION	Fibre co Pulp Inc. Uostream	Peace River		Fibreco Pulp Inc. Upstreem	Pine River		Petro-Canada Products Downstream	Fibreco Pulp Inc. Downstream			Eurocan Pulp & Paper Co. Upstream			Eurocan Pulp & Paper Co. Downstream		

DESCRIPTIONS OF FISH SAMPLES USED FOR DIOXINS AND FURANS ANALYSES

Table 6. (Cont'd)

SITE LOCATION	SAMPLING DATE	FISH SPECIES	NO. OF FISH IN COMPOSITE	MEDIAN FORK LENGTH (Range) mm	MEDIAN WEIGHT (Range) 9	MEDIAN AGE (Range) years	
Lower Fraser River Mills	12/08/89	Mybchelus caurinus (peamouth chub)	•	264.0 (252–280)	256.7 (224.6 – 294.4)	11 (7-17)	٠
Upstream.		Catostomus macrochellus (largescale sucker)		301.0 (287 – 335)	291.9 (253.5-426.8)	4 (4 – 5)	
•		Ptychochellus oregonensis (northern squawfish)		270.0 (260–310)	228.9 (202.1-334.9)	9 (8-12)	
Scott Paper Limited	05/10/89 06/10/89	Ptychochellus oregonensis (northem squawfish)	•	307.0 (289 – 329)	357.9 (304.1 – 481.9)	9 (7 – 19)	
Downstream	06/10/89	Myboheilus caurinus (peamouth chub)	•	189.0 (154 – 209)	69.6 (42.5–93.6)	3 (2 – 8)	
	05/10/89	Cetostomus mecrocheilus (largescale sucker)		281.0 (273~326)	281.0 (236.2–395.7)	3 (3-4)	
Paperboard Industries	06/10/89 10/10/89	Ptychochellus oregonensis (northern squawfish)		309.0 (268 – 319)	346.9 (243.0 – 426.4)	9 (8-11)	
Corp.	05/10/89 06/10/89 10/10/89	Mybohelius caurinus (peamouth chub)	9	183.0 (180-208)	82.2 (64.6 – 106.0)	(2 - 6)	
	06/10/89 10/10/89	Catostomus macrochellus (largescale sucker)	•	284.0 (276 – 307)	308.8 (245.5-338.7)	4 (3-7)	
	06/10/89	Acipensor transmontanus (white sturgeon)	6	341.5 (296–496)	270.1 (166.0–850.0)	3 (3-4)	

refers to total length rather than fork length.
 denotes only 12 fish were used for aging purposes.

DIOXIN AND FURAN RESIDUES, LIPID CONTENT AND MOISTURE CONTENT OF MUSCLE TISSUE FROM FISH COLLECTED UPSTREAM AND DOWNSTREAM.

OF THE PULP MILLS AND PETROLEUM REFINERY

•		: .		-	NOXIN C	ONCENTE	DIOXIN CONCENTRATION (pg/g wet wt.)	0/0 wet v	(1)		URANC	ONCENTI	FURAN CONCENTRATION (pg/g wet wt.)	og/g wet	£	
SITE LOCATION	FISH SPECIES	LIPID CONTENT (%_wet_wt)	MOISTURE CONTENT (%)	2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total	2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	Total H7CDF	Total	
Fibraco Pulp Inc.	Cetostomus catostomus (longnose sucker)	*	6 2.	ធ	ឡ	110	F 116	L19	115	3	3	L10	F11	L19	L15	
Opsudam Peace River	Esox lucius (northern pike)	7	78	3	,3 .	2	85	2	L19	ន	- <u>3</u>	` 5	2	8	119	
	Prosopium williamsoni (mountain whitefiah)	***	82	91	93	E E	.	.	83	9	9	क्ष	149	3	83	*
Fibraco Pulp Inc.	Calostomus caloetomus (longnose sucker)	\$2 \$2	6	<u>-</u>	3	9 .	87	L10 .	L12	2	ន	g	L16	. F10	L12	
Pine River	Prosoptum williamsoni (mountain whiteflah)	7.3	76	3	3	115	7	8	Ξ	3	.	L15	2	65 06	H	
	Stizostaction vitraum (walloye)		æ	2	3	L10	=======================================	L10	L15	<u>. 9</u>	១	L10	· 5	F10	. 115	
Fibraco Pulp Inc.	Calostomus calostomus (longnoss sucker)	8		120	L10	83	9	110	87	L10	. 120	8	5	1.10	ន្ទ	•
	Catostomus macrochellus (largescale sucker)	.	78	L10	29	170	L15	110	.	720	110	· L10	L15	L10	134	*
	Esox kicks (northern pike)	. 23	75	3	3	115	118	2	L15	7	3	112	L16	L10	112	
Petro-Canada Products Downstream	Stimetedion vitreum (walleye)	e.	8	9	3	L12	.	017	L15	ឌ	3	L12	3	. F10	. 11.	
Eurocan Pulp and Paper Co.	Oncorhynchus mydiss (minbow trout)	S. E.	75	. य	2		डा	110	F15	ជ	័ឌ	110	2	F10	L15	
	Salveiinus maima (dolly varden)	7.6	7.4	3 `	3	12	9	L10	,115	3	3 -	112	2	L10	L15	
	Cottus aleuticus (cosst range sculpin)	4.2	N.	3	9	F18	8		8	9	2	F18	8	83	8	*.
Eurocan Pulp and Paper Co.	Oncorhynchus mydiss (rainbow trout)	6 .	75	3	2	8	5	110	L15	, 3	3	ğ	[13	29	L15	
- Contaction	Salvelinus malma (dolly varden)	7.6	E E	3	3	5	133	E33	1	₹.	· %	5	झ	133	5	39
•	Cottus asper (prickty sculpin)	3.0	78	9	9	ទ	147	8	87	. 3	9	គ	75	3	8	

DIOXIN AND FURAN RESIDUES, LIPID CONTENT AND MOISTURE CONTENT OF MUSCLE TISSUE FROM FISH COLLECTED UPSTREAM AND DOWNSTREAM
OF THE PULP MILLS AND PETROLEUM REFINERY

Table 7. (Conf'd)

					DIOMN CONCENTRATION (pg/gwet wt.)	NCENTR	ATION (p	0/0 wat w	Ð	_	FURAN CONCENTRATION (pg/g wet wt.)	NCENTE	NOITA	50/0 wet	£	
SITELOCATION	FISH SPECIES	CONTENT (%_wet_wt)	MOISTURE CONTENT	2,3,7,8 T4CDD	Total T4CDD	Total PSCDD	Total	Total H7CDD	Total 08CDD	2,3,7,8 T4CDF	Total Total T4CDF P5CDF	Total	Total HBCDF	Total H7CDF	Total OBCDF) 1= 1, 1
Lower Fraser River Mills	Mytocheitus caurirus (pesmouth chub)	9	. 23	0.83	0.83	ន	3.	ন্ত	F10	. 15.4	15.4	3	3	2	710	•
Upstream	Calcstom <i>us macrocheilus</i> (argescale sucker)	0.4	8	2	2	១	2	21	110	3.8	3.8	3	3	ង	110	
	Prychochallus oregonensis (northern squawfish)	0.4	. 78	5	2	3 .	2	5 .	9	15	15	ឌ	3	Ü	93	
Scott Paper Limited	Mylochaike ceurins (peamouth chub)	9 6	. 78	១	2	១	3	ន	L10	10.3	10.3	3	3	2	L10	•
Downstream	Calostomus macrocheilus (largescale sucker)	. 60 63	22	5	5	2	.ঘ	2	ន	5	5	2	ឌ	2	ន	10
	Ptychochallus oregonensis (northern squawfish)	¥	78	2	ៗ	3	श	L10	L10	‡	1	2	3	L10	710	
Paperboard Industries	Mylocheikie ceurinus (peamouth chub)	₹	92	2	១	3	3	L10	F10	6	8	3	3	710	L10	
Corp. Downstream	Catostomus macrocheitus (Ingescale sucker)	3.2	8	2	2	3	3	ন	, 145	3	2	2	3	3	L15	ю
	Plychochellus oragonensis (northern squawfish)	4.2	78	5	5	2	3	ন্ত্	20		12	ជ	3	2	F10	
	Actoriser transmontanus (white sturgeon)	1.8	8	2	ៗ	=	ន	ន	L16	១	2	Ξ	9	<u>.</u> 2	L16	6

denotes less than specified limit
 denotes no value obtained
 MA denotes results were not available.

QUALITY CONTROL RESULTS OF FISH TISSUE SPLITS

Table 8.

· ,			i.		DIOXIN CONCENTRATION (pg/g wet wt.)	NCENTE	MTION (P	g/g wet v	ਦ	L .	URAN CC	FURAN CONCENTRATION (pg/g wet wt.)	MTION (29/g wet v	£
SITE LOCATION	FISH SPECIES	CONTENT (%_wet_wt.)_	LIPID MOISTURE TENT CONTENT of wt.) (%)	2,3,7,8 T4CDD	Total Total Total Total Total Total T4CDD PSCDD H6CDD H7CDD 08CDD	Total P5CDD	Total H6CDD	Total H7CDD	Total	2,3,7,8 T4CDF	Total Tota T4CDF P5CDF	Total PSCDF	Total H6CDF	Total Total H7CDF O8CDF	Total O9CDF
Fibreco Pulp Inc.	Esox lucius* (northern pike)	2.9	12	.7	٥.	L12	F18	710	L15	3	2	L12	L16	710	L15
Lownstream	Splt A	1.3	78	7	7	8	8	52	87	7	77	8	8	8	ន្ម
	Spit B	*	82	ន	3	2	2	8	क्ष	3	3	121	121	8	83
Scott Paper Limited	Pychocheilus oregonensis* (northern squawfish)		8 2	2	2	2	3	120	L10	4	4	3	ន		L10
	Split A	3.4	,	10	720	젊	14 9	8	. P	\$	\$	न्ध	L49	ន្ទ	L46
	Split B	3.6	82	9	2	83	8	8	L18	8	8	83	8	3	L18
			. ,	: . ,							*, *	٠	. ***		

L. denotes less than specified detection limit. * denotes samples reported in Table 7.

Table 9. ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON FISH MUSCLE TISSUE, EXPRESSED AS PERCENT RECOVERY

	•		SUR	SURROGATE	SPIKE	,	PERFOMANCE STANDARD	
SITE LOCATION	FISH SPECIES	Total C13T4CDD	Total Total C13T4CDD C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD		
Fibreco Pulp Inc.	Catostomus catostomus (longnose sucker)	8	8 8	8	8	83	001	
Upstream Peace River	Esox lucius (northern pike)	&	8 . :	8	100	8	6	, .
	Prosopkum williamsoni (mountain whitefish)	3	118	8	124	110	.00	
Fibraco Pulp Inc.	Calostomus catostomus (longnose sucker)	3	8	6	. 67	82	00	
Upstream Pine River	Prosopkum williamsoni (mountain whitefish)	92	` F	٠ ا	19	8	6	
	Stroste dion vitreum (walleye)	8	F	6	75	22	00	
Fibreco Pulp Inc.	Calostomus catostomus (longnose sucker)	8	6	\$	8	8	0	
	Catostomus mecrochellus (largescale sucker)	8	35	8	118	142	001	
•	Esox lucius (northern pike)	2	F	8	64	29	60	
	Spir A	2	22	75	8	67	8	
	Spir B	8	R	75	፬	88	8	
Petro-Canada Products Downstream	Stizoste dion vitreum (walleye)	<u>5</u>	5 0	62	&	92	8	
Eurocan Pulp and Paper Co.	Oncomynchus mykiss (rainbow trout)	a ,	8	20	8	ន	60	
	Salvelinus malma (dolly varden)	8	88	8	109	117	6	· .
	Cottus aleuticus (coast range sculpin)	8	107	8	26	02	001	

ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON FISH MUSCLE TISSUE, EXPRESSED AS PERCENT RECOVERY Table 9. (Cont'd)

Total Coation Total Coation Total Coation Tream Salvelinus malma Salvelinus caurinus (pricity eculpin) Cottus asper (pricity eculpin) Cottus asper (pricity eculpin) Cottus asper (pricity eculpin) Catostomus mecrochelius 104 Tychochelius caurinus 100 Tychochelius caurinus 100 Tychochelius caurinus 100 Spilt A Spilt B So Catostomus macrochelius 105 (Iargescale sucker) Prychochelius caurinus 105 (Iargescale sucker) Rychochelius caurinus 105 Iargescale sucker) Rychochelius caurinus 105 Rychochelius 1	•				SURROGATE	SPIKE		PERFOMANCE STANDARD	
Concontryctus mystas 83 134 103 140 131	SITE LOCATION	FISH SPECIES	Total C13T4CDD	Total C13P5CDD	Total C13H6CDD	Total C13H7CDD	Total C13O8CDD		
Cottos aspara Salvelinus mains Section	Eurocan Pulp and Paper Co.	Oncorhychus myldss (rainbow trout)	.8	131	801	6	131	85	
Cofitus saper Cofitus components Cofit cofitus cautrinus Cofitus components Cofit cofitus components Cofit c	wnstream	Salvelinus malma (dolly varden)	88	109	29	3	8	6	. ,
Preserve		Cottus asper (prickly sculpin)	8	117	8	8	22	8	•
(argascale sucker) 127 141 137 116 124 (argascale sucker) (argascole sucker)	Lower Fraser River Mills	Mylochellus caurinus (peamouth chub)	5	128	8	211	10	8	
Pychochellus oregonensis 106 113 112 102 100	stream	Catostomus macrochellus (largescale sucker)	127	5	137	116	124	8	
Paper Mytochellus caurinus 100 117 112 97 78 Ideam Cabastorius macrochellus 109 117 106 110 98 Ideam Cabastorius macrochellus 74 83 83 79 71 Prychochellus caurinus 91 116 109 91 96 Split A		Ptychochellus oregonensis (northern equewfish)	9	113	112	8	6	8	·, -
Catostomus macrochellus 109 117 109 110 98 Catostomus macrochellus organenais 74 83 83 79 71 Chorthem equawfish 83 94 89 96 73 Split A	Scott Paper Limited	Mylochellus caurinus (peamouth chub)	8	117	12	26	82	25	-
Phychochellus oregonensis 74 93 83 79 71 Contriber aquawfish 93 94 99 96 73 Split A	wnstream	Catostomus macrochellus (largescale eucker)	8	117	60	110	88	100	
Split A 83 94 98 96 73 Split B 80 72 64 107 72 board Mylochellus caurinus 91 116 109 91 86 riteam Catostomus macrochellus 105 128 127 120 Rychochellus cuesciele sucker) 102 122 117 104 88 Rychochellus surgeon) 4dipenser transmontanus 85 66 55 61 57	· • • • • • • • • • • • • • • • • • • •	Ptychochellus oregonensis (northem equawfish)	7	8	8	62	<u>ج</u>	100	•
Split B 80 72 64 107 72 board (peamouth chub) Mylochellus caurinus 81 116 109 91 96 stream Catostomus macrochellus (largascale sucker) 105 126 135 127 120 Phychochellus onegonenals (northern squawfish) 102 122 117 104 88 Adipensar transmontanus (white sturgeon) 85 66 55 61 57	٠	Spit A	8	. 2	8	8	23	6	
Mylochellus caurinus		Spir B	8	2	2	107	22	91	٠
Catostomus macrocheilus 105 126 135 127 120 (largascale sucker) (largascale sucker) 102 122 117 104 88 (northern equawfish) 4cipenser transmontanus 85 66 55 61 57 (white sturgeon) (white sturgeon) 61 57 63 64 64	perboard	Mytochelius caurinus (peamouth chub)	5	116	6 0	22	8	6	
eflus oregonensis 102 122 117 104 88 equawfish) r transmontanus 85 66 55 61 57 rrgeon)	y. wnstream	Catostomus macrochellus (largascale sucker)	105	 82	135	127	021	100	
r transmontanus 85 66 55 61 57 (rgeon)		Ptychochellus oragonensis (northern equawitsh)	2 0	<u> </u>	117	2	88	100	· .
		Acipenser transmontanus (white sturgeon)	8	8	ន	19	29	100	

ppt to 19 ppt) were found in the hepatopancreas of dungeness crab (Cancer magister) collected from Kitimat Arm by the Department of Fisheries and Oceans (Government of Canada, 1990; Harding and Pomeroy 1990). These hepatopancreas samples also had measureable concentrations of other dioxin and furan congeners. Migration studies on Dolly Varden have shown that the habitat of three to four year old fish (the age of fish used in this study) is the stream in which they were spawned (Scott and Crossman 1973). The adults (three to six years old) of anadromous populations move seaward in late May and early June, remaining short distances from the stream mouth, then move back into the streams usually in mid-July to September (Smith and Slaney 1980). The Dolly Varden collected for this study may have spent time in Kitimat Arm.

Lower Fraser River Fish

The levels of 2,3,7,8-T4CDF and total T4CDF measured in fish collected upstream and downstream of the lower Fraser River mills were similar. The dioxin, 2,3,7,8-T4CDD, was detected in only one sample, a peamouth chub (Mylocheilus caurinus) sample collected at the upstream site. These two isomers were the principal forms of dioxins and furans measured in fish collected by Mah et al. (1989) from the upper and mid-Fraser River in 1988. It should be noted that fish collected upstream of a given location may have previously resided downstream of that location, and vice versa.

In the lower Fraser River fish, the peamouth chub and northern squawfish (Ptychocheilus oregonensis) samples had higher levels of T4CDF, (24 ppt and 44 ppt, respectively) than the largescale sucker (Catostomus macrocheilus) samples (below the detection limit to 3.8 ppt). With the small sample sizes, it is difficult to comment on species-concentrations relationships. The results of this study are consistent with those observed in Mah et al. (1989). Higher levels of furans were measured in fish, like northern squawfish and

peamouth chub, that generally occupy the higher trophic levels.

Health and Welfare Evaluation of the Fish Data

Health and Welfare Canada assessed the data on dioxins and furans in fish collected in 1989 from the Peace, Pine, Kitimat, and Fraser Rivers. The assessments, as reported in Government of Canada press releases, concluded that the levels did not pose a health risk and consumption restrictions were not necessary (Government of Canada, 1990 and 1991).

CONCLUSIONS

- 1) No dioxins or furans were measured in bed sediments or fish collected from the Pine and Peace Rivers, or upstream of Eurocan Pulp and Paper Company in the Kitimat River. No dioxins or furans were detected in bed sediments collected near Hope, the upstream site for the lower Fraser River mills.
- 2) H6CDD was detected in one bed sediment sample collected from the Kitimat River downstream of Eurocan Pulp and Paper Company. Bed sediments collected from the lower Fraser River had measureable levels of dioxins and furans. The source of these dioxins and furans is unknown. The samples collected from the vicinity of Scott Paper Limited had detectable concentrations of H6CDD, H7CDD, O8CDD and 2,3,7,8-T4CDF; whereas the samples collected from the vicinity of Paperboard Industries Corporation had detectable levels of 2,3,7,8-T4CDF and O8CDD.
- One Dolly Varden (Salvelinus malma) sample collected from the Kitimat River downstream of Eurocan Pulp and Paper had a measureable concentration of 2,3,7,8-T4CDF. Northern squawfish and peamouth chub samples (Ptychocheilus oregonensis and Mylocheilus caurinus, respectively) collected from the lower Fraser River at the upstream Hope site and in the vicinity of Scott Paper Limited and Paperboard Industries Corporation also had measureable levels of 2,3,7,8-T4CDF. One peamouth chub sample collected near Hope, upstream of the lower Fraser River mills, had a detectable concentration of 2,3,7,8-T4CDD.
- 4) The Health and Welfare Canada assessment of the data on dioxins and furans in fish concluded that the levels did not pose a health risk and consumption restrictions were not necessary.

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APPENDIX A

Initial Dioxin and Furan Results for Re-analysed Bed Sediment Samples

INITIAL DIOXIN AND FURAN RESULTS FOR BED SEDIMENTS THAT WERE RE-ANALYSED Appendix A

			010	KIN CON	CENTRAI	NOIN (pg	DIOXIN CONCENTRATION (pg/g dry wt.)		FU.	AN CON	CENTRA	TION (p	FURAN CONCENTRATION (pg/g dry wt.)	(:
AOISTURE ORGAN CONTENT CARB((%) (%)	8 8 5	CARBON (%)	2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total H6CDD	Total Total Total Total PSCDD H6CDD H7CDD 08CDD	Total 08CDD	2,3,7,8 T4CDF	Total T4CDF	Total Total T4CDF P5CDF	Total- H6CDF	Total Total H6CDF H7CDF	Total O8CDF
34 0.88	9.0	8	<u>.</u> ਨ	L5	97 \	158	L130		3	L 5	97	342	969	. L77
30 0.24	0.5	Z .	120	1 70	L137	1233	L80	· 097	120	87	L137	1233	180	097
30 0.30	0.3	. 2	L15	L15	L100	L143	141	175	L15	L15	L100	L143	4	175
30 0.64	0.6	.	L15	L15	L160	L500	L100	L75	L15	115	L160	L500	L100	L75

denotes less than specified detection limit.

APPENDIX B

Suspended Sediment Sampling in the lower Fraser River,
March 1989

Table B-1.

DIOXIN AND FURAN RESIDUES AND ORGANIC CARBON CONTENT OF SUSPENDED SEDIMENTS COLLECTED FROM THE LOWER FRASER RIVER

				OIO	XIN CON	CENTRAT	OXIN CONCENTRATION (pg/g dry wt.)	/g dry wt.		FUR	IAN CON	CENTRA	TION (pg	FURAN CONCENTRATION (pg/g dry wt.)	~·
SAMPLE NUMBER	SAMPLING	SAMPLING DATE	SAMPLING ORGANIC DATE CARBON (%)	2,3,7,8 T4CDD	Total T4CDD	Total P5CDD	Total Total Total Total Total Total Total Total	Total H7CDD O	Total O8CDD	2,3,7,8 T4CDF	Total T4CDF	Total P5CDF	Total H6CDF	2,3,7,8 Total Total Total Total Total Total Total T4CDF T4CDF P5CDF H6CDF H7CDF O8CDF	Total O8CDF
STEV-100	STEV-100 Richmond	20/03/89	2.91	ह्य	क्ष	L10	967 730 736	136	370	827	EZ 1		L10 (28)	967	757
ANN-200	Delta	21/03/89 2.51	2.51	7	. 7	9	L12		124 329	7	77	.	f 4	123	181

Note: Approximate volume of water centrifuged per sample was 8300 litres.

L denotes less than specified detection limit.

() denotes value was below method detection limit; however a peak was detected.

No. Fa	PERFORMANCE STANDARD		126	001
ANALYTICAL QUALITY CONTROL RESULTS FOR DIOXIN ANALYSES ON SUSPENDED SEDIMENTS, EXPRESSED AS PERCENT RECOVERY	-		22	92
LTS FOR DIO SED AS PER		Total Total Total Total Total Total C13T4CDD C13P5CDD C13H6CDD C13H7CDD C13O8CDD	09	110
ntrol resu nts, expres	Surrogate spike	Total C13H6CDD	86	148
QUALITY CO DED SEDIME	SURROG/	Total C13P5CDD	98	136
ANALYTICAL SUSPEN		Total C13T4CDD	8	96
Table B-2.	··	SITE LOCATION	Richmond	Delta
Appendix B		SAMPLE	STEV-100 Richmond	ANN-200

Appendix B

Figure B-1. Locations of Suspended Sediment Sampling Sites in the lower Fraser River.

