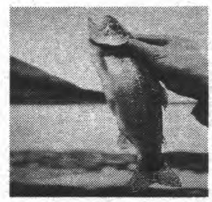
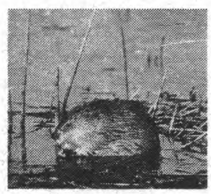
Canada Alberta Northwest Territories

Northern River Basins Study

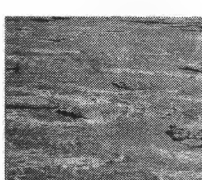
  

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 44

CONTAMINANTS IN ENVIRONMENTAL SAMPLES:

PCDDs AND PCDFs DOWNSTREAM OF BLEACHED KRAFT MILLS PEACE AND ATHABASCA RIVERS, 1992

Prepared for the
Northern River Basins Study
under Project 2381-C5

by

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PREFACE:

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

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

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

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

F.J. Wrona — 2 Feb 95

(Dr. F.J. Wrona, Ph.D., Science Director) — (Date)

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

P.A. Larkin — 2 Feb 95

(Dr. P. A. Larkin, Ph.D., Chair) — (Date)

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

Lucille Partington — 2 Feb 95

(Lucille Partington, Co-chair) — (Date)

Robert McLeod — 3 Feb 95

(Robert McLeod, Co-chair) — (Date)

CONTAMINANTS IN ENVIRONMENTAL SAMPLES: PCDDs AND PCDFs DOWNSTREAM OF BLEACHED KRAFT MILLS PEACE AND ATHABASCA RIVERS, 1992

STUDY PERSPECTIVE

> ***Related Study Questions***
>
> *4a) Describe the contents and nature of the contaminants entering the system and describe their distribution and toxicity in the aquatic ecosystem with particular reference to water, sediment and biota.*
>
> *8) Recognizing that people drink water and eat fish from these rivers systems, what is the current concentration of contaminants in water and edible fish tissue and how are these levels changing through time and by location?*
>
> *13a) What predictive tools are required to determine the cumulative effects of man-made discharges on the water and aquatic environment?*
>
> *b) What are the cumulative effects of man-made discharges on the water and aquatic environment?*

One of the main objectives of the Northern River Basins Study is to determine the effects of contaminants from industrial and municipal sources on the aquatic ecosystem of the Peace, Athabasca and Slave rivers. Historical contaminant information for these basins was sparse, thus additional research was required to describe the nature and distribution of chemical contaminants entering the rivers. Such information would allow scientists to assess contaminant fate and toxicity for aquatic life and people using these rivers. People are particularly interested in the dioxin/furan group of chlorinated hydrocarbons, noted for their toxicity and ability to bioaccumulate in animal and fish tissue. Two Alberta pulp mills used chlorine in their pulping processes and were known contributors of dioxins and furans. The presence, abundance and effects of these compounds in the basins are a particular concern.

In 1992, a number of projects were initiated to assess the incidence and concentration of chemical contamination, including dioxins and furans, in the Athabasca and Peace River drainages. In addition to water, sediment and biological samples being collected at six locations on the Athabasca River downstream of Hinton, fish samples were collected from several other locations in the Athabasca and Peace River basins.

This report provides an interpretation of analytical results for dioxins and furans in water, biofilm, sediment, invertebrates and fish samples collected on the Athabasca and Peace rivers in 1992. Of the approximately 210 dioxins and furans known to occur, 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachloro dibenzofuran (TCDF) have the greatest potential to bioaccumulate in animal tissue. The latter compound is considered to be 10 times less toxic than the former, yet they act in an additive manner. Analysis focused on the partitioning, fate and bioaccumulation of this group of compounds to assist in the assessment of ecosystem health and long-term effects.

Analytical results from the Athabasca river showed that the highest levels of dioxins/furans were found within 50 km downstream from the Weldwood Canada-Hinton combined effluent. Concentrations returned to upstream levels for fish sampled greater than 116 km downstream from the bleached kraft mill effluent source. The most prominent dioxin/furans in the effluent were mono-, di- and trichloro dibenzofurans, but these compounds were either not detected or found in much lower levels in fish than 2,3,7,8-TCDD and 2,3,7,8-TCDF. Toxic equivalent concentrations (TEQs) in sediment, water, invertebrates and fish downstream from the Weldwood Canada pulp mill were generally low. The levels detected were lower than the guideline limits recommended under the Canadian Environmental Quality Guidelines for PCDD/Fs in sediment and water, and Health Canada guidelines for fish tissue. Comparison with previous analyses of mountain whitefish indicated that concentrations of TCDD/F had declined by 2.5 fold. Based on stable isotope assessment, it appears the most important food chain pathway for the uptake of dioxins and furans in the Athabasca River is the transfer from effluent to fine suspended particulates in the water, which are subsequently trapped by filter feeding organisms (e.g., caddisfly larvae), which are in turn fed upon by fish like mountain whitefish. In the Peace River drainage, the highest TCDD/F concentrations were found in burbot liver, ranging from 40 to 53 pg/g TCDD TEQs at two sampling locations nearest the Weyerhaeuser Canada bleached kraft mill on the Wapiti River near Grand Prairie. These levels exceed the Health Canada guidelines for human consumption (20 pg/g).

During 1993, Weldwood Canada and Weyerhaeuser Canada went to complete substitution of molecular chlorine with chlorine dioxide. This alteration in pulp processing is expected to further reduce emissions of all chlorinated organic compounds, including dioxins and furans. Environmental samples from 1993 and 1994 will provide additional information on the changing concentrations of dioxins and furans in the ambient environment. The estimates of dissolved and particulate bound levels of PCDD/Fs from this study, along with levels in various food chain components, will be used to develop approaches to predict future trends for the environmental fate and bioaccumulation of dioxins and furans.

Report Summary

This report summarizes the levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in water, sediment, suspended sediment, invertebrates, and mountain whitefish and northern pike samples collected during the spring of 1992 as part of the Reach Specific Study (RSS) downstream of Hinton, Alberta. Concentrations of PCDD/Fs in mountain whitefish, long-nosed suckers, goldeye, and walleye collected further downstream on the Athabasca River and in burbot from the Wapiti/Smoky/Peace system are also discussed. The emphasis in the report is on the pathways of accumulation of 2,3,7,8-TCDD and 2,3,7,8-TCDF, the two PCDD/Fs congeners with highest bioaccumulation potential.

Highest levels of PCDD/Fs were found in environmental samples within 50 km downstream from the Weldwood of Canada Ltd. (combined) effluent. PCDD/F levels returned to upstream levels (control site) for fish sampled ≥ 116 km downstream from the bleached kraft mill (BKM) effluent source. The most prominent PCDD/Fs in the effluent were mono-, di- and trichlorodibenzofurans. These compounds proved to be excellent markers of BKM effluent downstream of the mill because they were present in all abiotic samples. However, they were not detected, or were present at lower levels (<2 pg g^{-1}), in fishes than 2,3,7,8-TCDD and 2,3,7,8-TCDF. TCDD toxic equivalent concentrations (TEQs) in effluent (centrifugate) was less than the 15 pg L^{-1} level set by the Canadian Environmental Protection Act (CEPA) to be achieved by pulp and paper mills as of January 1, 1994.

TCDD TEQs in suspended sediment, sediment, water (centrifugate), invertebrates, and fishes downstream from the Weldwood of Canada Ltd. BKM were generally in the low pg g^{-1} range. 2,3,7,8-TCDF was the major PCDD/F congener in fish (fillet) samples. Levels of TCDD TEQs in fish samples from the RSS were lower than the the 20 pg g^{-1} Health Canada guideline limit for human consumption. Comparison with previous analyses of mountain whitefish collected in 1987 to 1989 by Alberta Environment and the DFO National Dioxin program at sites within 40 km of the BKM indicated that concentrations of TCDD/F had declined by about 2.5 fold. Levels of TCDD in two invertebrate samples within 48 km downstream of the BKM exceeded the draft Canadian Environmental Quality Guideline value for aquatic biota. PCDD/F TEQs in burbot livers at the two sampling sites nearest to the Grande Prairie BKM also exceeded the Health Canada guideline limit.

This study has demonstrated that stable isotope analysis using sulphur and nitrogen isotopes (^{34}S and ^{15}N) may help to characterize fish with unusually low PCDD/Fs by identifying mainstem and tributary feeders. The age length, and weight of northern pike were strongly correlated with 2,3,7,8-TCDD and -TCDF levels, but not for mountain whitefish. Other variables, such as the sex of the fish and lipid content had little effect on the results. There were few statistically significant differences between 2,3,7,8-TCDD and -TCDF levels in mountain whitefish and northern pike. Mountain whitefish consistently had higher levels of 2,3,7,8-TCDD and -TCDF than long-nosed suckers at the sample site one km downstream of Hinton.

The results from the RSS represent a "snapshot" of the environmental distribution of PCDD/Fs prevailing in the spring of 1992 prior to high water flows in the Athabasca River that occur in May and June as a result of snow melt in the Rockies. The RSS study has yielded valuable information for use in fate and food chain modelling of PCDD/Fs in the Athabasca River. The estimates of dissolved and particulate bound levels of PCDD/Fs along with levels in various food chain components will be useful for calibrating models with which to predict future trends in PCDD/F contamination.

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1.0 INTRODUCTION

The Northern River Basin Study (NRBS) is a 4.5 year project, extending to 1996, examining the impact of development on ecosystem health and integrity on three large river basins in Alberta and the Northwest Territories: Athabasca, Peace, and Slave. There are over 100 projects in eight study areas: contaminants, nutrients, hydrology/hydraulics, drinking water, food chain, synthesis/modelling, traditional knowledge, and other uses. This report summarizes results for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in environmental samples collected downstream from bleached kraft pulp and paper mills (BKMs) on the Athabasca River during April through June 1992 and burbot livers on the Peace River during October to November 1992.

The NRBS study board has prepared 16 guiding questions to ensure project leaders address a common mandate. The two questions most relevant to this report are:

4-a) "What are the contents and nature of the contaminants entering the system and what is their distribution and toxicity in the aquatic ecosystem with particular reference to water, sediments and biota?"

8) "... what is the current concentration of contaminants in water and edible fish tissue and how are these levels changing through time and by location?"

The Reach Specific Study (RSS) initiated in the spring of 1992 was designed to address these questions by determining spatial and temporal trends of a large suite of contaminants (metals, polyaromatic hydrocarbons, organochlorine pesticides, PCDD/Fs) in abiotic and biotic samples collected at six locations on the Athabasca River downstream of Hinton, Alberta. Basin-wide studies on contaminants in fishes, the General Fish Collection and the Special Burbot Collection, were also conducted to examine levels on a larger scales within the Athabasca and Peace River basins.

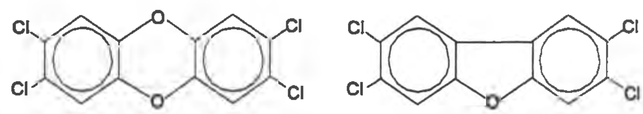
The two most common PCDD/F congeners found in environmental samples downstream of BKMs are 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In January 1994, the Canadian Environmental Protection Act (CEPA) promulgated a new regulation requiring "non measurable" (at a detection limit of 15 ppt expressed in 2,3,7,8-TCDD TEQs) concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in final effluent discharged from BKMs. To achieve this goal, the pulp and paper industry has reduced the use of molecular chlorine. Weyerhauser Canada Ltd. at Grande Prairie (Wapiti River) had implemented a 25% substitution of molecular chlorine with chlorine dioxide in 1989, which rose to 70% in early 1991, and 100% during the summer of 1992. In June 1993, the Weldwood of Canada Ltd. at Hinton (Athabasca River) shifted from 45% to 100% substitution of molecular chlorine with chlorine dioxide. These changes in the pulp bleaching technology were expected to reduce the concentrations of PCDD/Fs emitted to the Wapiti and Athabasca Rivers and the quantities bioavailable to riverine biota.

The purpose of this report is to summarize the levels of PCDDs and PCDFs from spring 1992 samples in water, sediment, suspended sediment, invertebrates, and fish and to describe the partitioning, fate, and bioaccumulation of this group of compounds following their discharge into the northern Alberta river systems.

2.0 BACKGROUND INFORMATION

2.1 PHYSICOCHEMICAL PARAMETERS OF CHLORINATED DIOXINS AND FURANS

PCDDs and PCDFs are large families of chlorinated hydrocarbons consisting of 75 PCDD and 135 PCDF congeners (each congener having a different Cl substitution pattern). The core molecules are tricyclic aromatic structures: two benzene rings connected by a third ring containing a single oxygen atom for the furans and two oxygen atoms for the dioxins (see structures below). PCDD/Fs display similar molecular, physical, and chemical properties. An increase in chlorine substitution of PCDD/Fs is positively correlated to greater hydrophobicity (insolubility in water), lipophilicity (strong affinity for lipids), and environmental persistence.



2,3,7,8-TCDD 2,3,7,8-TCDF

Structures of 2,3,7,8-TCDD and 2,3,7,8-TCDF

Knowledge of physical and chemical properties of organic contaminants is essential to understanding their environmental transport and fate as well as their pharmacokinetic and toxicological behaviour. The physicochemical properties of PCDD and PCDFs commonly found in BKM effluent are summarized below in Table 1 and 2, respectively.

2.2 INTERNATIONAL TOXICITY EQUIVALENT FACTORS (I-TEFS)

International Toxicity Equivalent Factors (I-TEFs) have been assigned to 17 of the most hazardous PCDD/Fs (Safe et al. 1990). I-TEFs allow the total toxicity to be expressed as a single Toxic Equivalent (TEQ) value (Equation 1). The most toxic congener, 2,3,7,8-TCDD, has been appointed a value of 1. The remaining 16 PCDD/F congeners were given I-TEF values in proportions to their relative toxicity to 2,3,7,8-TCDD. For example the I-TEF for 2,3,7,8-TCDF is 0.1. The I-TEFs for lower chlorinated PCDD/Fs, such as dichlorodibenzodioxin (DCDD), have not been assigned but are assumed to be zero. The I-TEFs have been adopted by the scientific and regulatory community in eight countries: Canada, United States, United Kingdom, Norway, The Netherlands, Denmark, Italy, and the Federal Republic of Germany. TEQs are calculated in the following way:

$$TEQ = \sum (\text{I-TEF}_i \times [\text{contaminant}]_i)_{n=1 \text{ to } 17} \qquad \text{(Equation 1)}$$

where $[\text{contaminant}]_i$ = the concentration of a PCDD or PCDF congener.

Table 1. Physicochemical Properties for PCDD Congeners[a]: C_s (Water Solubility), VP (Vapour Pressure), H_c (Henry's Law Constant), K_{ow} (Octanol-Water Partition Coefficient), K_{oc} (Organic Carbon-Water Partition Coefficient), I-TEF (International Toxic Equivalent Factors), and MW (Molecular Weight).

Properties	2,3-DiCDD[b]	2,7-DiCDD[b]	2,8-DiCDD[b]	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD
C_s (ng L^{-1} @ 25° C)	14,900	3,750	16,700	8 to 200[c]	ND[d]	ND	ND	0.090 to 2.4	0.074[c]
VP (μPa @ 25°C)	390	120	140	0.15 to 0.62[c]	0.058 to 17.5	0.0048	0.0065	0.00075 to 1.02	0.00011[c]
H_c (Pa m^3 mol^{-1})[e]	6.61	8.11	2.13	1.62	ND	ND	ND	ND	0.683
Log K_{ow}	5.60	4.70	4.70	6.80[c]	7.0 to 7.8	7.6 to 7.8	6.9	8.0 to 11.4	8.20[c]
Log K_{oc}[f]	ND	ND	ND	6.8	6.8	7.6	6.6	7.8	7.9
I-TEF	ND	ND	ND	1	0.5	0.1	0.1	0.01	0.001
MW	253	253	253	322	356	391	391	425	461

[a] Adapted from original table in Environment Canada (1993)
[b] Source: Mackay et al. (1992)
[c] Source: Shiu et al. (1988)
[d] Symbol: ND = No Data
[e] Source: USEPA (1992) - calculated values
[f] Source: Broman et al. (1991)

Table 2: Physicochemical Properties for PCDF Congeners[a]: C_s (Water Solubility), VP (Vapour Pressure), H_c (Henry's Law Constant), K_{ow} (Octanol-Water Partition Coefficient), K_{oc} (Organic Carbon-Water Partition Coefficient), I-TEF (International Toxic Equivalent Factors), and MW (Molecular Weight)[a].

Properties	2,8-DiCDF[b]	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
C_s (ng L^{-1} @ 25° C)	14,500	419[c]	ND[d]	8.25
VP (μPa @ 25°C)	390	123[e]	0.23 to 36	0.032 to 8.1
H_c (Pa m^3 mol^{-1})[f]	ND	1.46	ND	ND
Log K_{ow}	5.30[g]	6.53[g]	7.8	7.6
Log K_{oc}[h]	ND	7.5	ND	7.4
I-TEF	ND	0.1	0.05	0.5
MW	237	306	340	340

[a] Adapted form original table in Environment Canada (1993)
[b] Source: Mackay et al. (1992)
[c] Source: Friesen et al. (1990a)
[d] Symbol: ND = No Data
[e] Source: Eitzer and Hites (1988)
[f] Source: USEPA (1992) -calculated values
[g] Source: Burkhard and Keuhl (1986)
[h] Source: Broman et al. (1991)

2.3 PERSISTENCE OF PCDD AND PCDF

PCDD/Fs are characterized as environmentally stable and persistent compounds. Recent reviews by Fletcher and McKay (1993) and Hites (1990) provide good overviews of current information on the environmental behavior of PCDD/Fs. The two major pathways of degradation of PCDD/Fs in the aquatic environment are photolysis and biodegradation.

Sunlight photolysis is thought to be an important pathway of degradation of PCDD/Fs in environmental samples because these compounds have UV absorption spectra which overlap the sunlight spectrum (i.e. > 290 nm) (Podoll et al. 1986). 2,3,7,8-TCDF has been shown to be photodechlorinated by sunlight in natural waters with a half-life of less than 1 day (Foga 1991; Dung and O'Keefe 1994). Sunlight photodegradation of PCDD/Fs is much more rapid in the presence of dissolved organic materials than in distilled water and is affected by the degree of chlorination of the pollutant of interest (USEPA 1990a; Friesen et al. 1990b).

Microbial degradation of PCDD/Fs with one or two chlorines has been shown to occur in laboratory incubations. Aerobic degradation of mono-, di- and trichloro-dioxins was slower in bacterial cultures containing suspended sediment than in sediment-free cultures indicating that the rate of desorption is critical to the extent of biotransformation (Parsons 1992). More highly chlorinated congeners are extremely resistant to biodegradation in sediments or water. Slow microbial degradation of 2,3,7,8-TCDD and 1,3,6,8-TCDD (1 to 7% over periods of 588 to 675 days) has been observed in sediment/water incubations under laboratory conditions (Ward and Matsumura 1978; Muir et al. 1985). No degradative products were seen for ^{14}C-labelled 1,3,6,8-TCDD or OCDD in sediments after 700 days in a natural mesocosm experiment on a Canadian shield lake (Servos et al. 1992). The major removal process of 1,3,6,8-TCDD in sediments was found to be diffusion back into the water column (Segstro et al. 1995). Historical profiles of PCDD/Fs in sediment cores from large lakes show no evidence of transformation of congeners (such as anaerobic dechlorination) over time (Hites 1990).

The evidence of degradative products or low recovery of the parent compound suggests metabolic transformation of some PCDD/F congeners by fish (Table 3).

Table 3: Metabolic Transformation of Specific PCDD/F Congeners by Aquatic Organisms.

Organism	Congener	Degradative Products	Source
mussel (Anodonta grandis)	1,3,6,8-TCDD	< 5%	Servos (1988)
crayfish (Procambarus spp.)	1,2,3,4,7-PeCDD	5 to 9%	Friesen (1988)
rainbow trout	2,3,7,8-TCDD	≈ 30%	Mehrle et al. (1988)
rainbow trout	2,3,7,8-TCDD	20 to 30 %	Branson et al. (1985)
goldfish	2,8-DCDD	ND[a]	Sijm et al. (1988)
rainbow trout	1,3,6,8-TCDD	68 to 77 %	Muir et al. (1986)
rainbow trout	2,3,7,8-TCDF	<2% (whole body)	Muir et al. (1992a)
rainbow trout	2,3,4,7,8-PnCDF	<25%	Muir et al. (1990)

[a] Symbol: ND = No Data

2.4 TOXICITY

A recent report by the US Environmental Protection Agency has thoroughly reviewed the toxicity of 2,3,7,8-TCDD to aquatic life (USEPA 1993). Most studies support the hypothesis that fish are more sensitive to 2,3,7,8-TCDD than mammals or aquatic macroinvertebrates (Yockim 1978, Adams et al. 1986, USEPA 1993). Toxic effects caused by 2,3,7,8-TCDD/F in fish are species-specific and include effects on mixed function oxidase (MFO) enzyme induction, reproduction (e.g., hormone dysfunction and fetotoxicity), behaviour, immune systems, development (e.g., wasting syndrome), hepatoxicity (e.g., liver lesions) and teratogenicity (Cooper 1989, USEPA 1993). Increases in mortality occurred in lake trout fry when body burdens exceeded 0.055 ng g^{-1} (Walker et al. 1991). The levels of 2,3,7,8-TCDD required to generate a 50% lethality (LD_{50}) in carp and rainbow trout ranged from one to two ng g^{-1} (Cook et al. 1991). MFO enzyme activity responses to 2,3,7,8-TCDD have been observed in rainbow trout liver at 0.02 ng g^{-1} (Parrott et al. 1994).

2.5 SOURCES OF PCDDs and PCDFs

2.5.1 Bleached Kraft Mills (BKMs)

There are approximately 47 bleached kraft pulp and paper mills in Canada which generate a wide range of low and high molecular weight organics including PCDD/Fs (Environment Canada 1993). PCDDs/Fs have been detected in the pulp, effluent, and sludge from BKMs using chlorine (Keuhl et al. 1987, Merriman 1988, Swanson et al. 1988, Amendola et al. 1989, Clement et al. 1989, Safe 1991) and in many pulp products such as paper, coffee filters, and diapers (Safe 1991). The predominant PCDD/Fs identified in the effluent of BKMs were 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 1,2,7,8-TCDF (Muller and Halliburton 1990). Beginning in 1989, the pulp and paper industry in Canada has reported annually on levels of PCDD/Fs in BKM effluents (PPRIC 1991).

The site of dioxin or furan formation has been narrowed to either the chlorination or extraction stages during paper production (USEPA 1990a). During these stages, a complex series of reactions takes place, chlorination, oxidation, and demethylation. This ultimately produces the chlorinated phenolic precursors for PCDD/Fs (Alasdair et al. 1990, Fiedler et al. 1990, USEPA 1990b, Safe 1991). Sources for dioxin/furan precursors, such as unsubstituted dibenzo-*p*-dioxin and dibenzofuran, have been identified in treated wood (e.g., anti-sapstain fungicide pentachlorophenol), natural wood constituents (i.e., lignin), paper additives, and contaminated pipes (Muller and Halliburton 1990, USEPA 1990b). The production of PCDD/F is the result of aqueous chlorination of the precursor molecules. The substitution of the strong chlorination agent, molecular chlorine, with other oxidants such as ClO_2 and hydrogen peroxide has reduced emissions of the chlorinated byproducts (Swanson et al. 1988, Craig et al. 1990).

2.5.2 Other Sources

PCDD/Fs are also generated during the production or combustion of industrial, agricultural, and commercial chemicals such as pentachlorophenol and the herbicide 2,4,5-T (Ree et al. 1988, Christmann et al. 1989a, Fiedler et al. 1990, Rappe et al. 1989). They are detected in the emissions from both municipal and industrial incinerators (Meyerson et al. 1981) as well as in the chemical and biological wastes from municipalities and wood treatment plants (Weerasinghe et al. 1985, Christmann et al. 1989b).

Other anthropogenic sources include exhaust from automobile combustion of diesel and leaded fuels, cigarette smoke, and forest fires (Ontario Ministry of Environment 1985, Buchert and Ballschmiter 1986, Marklund et al. 1990). PCDD and PCDF congeners have also been found associated with other chlorinated hydrocarbons at scrap metal refineries and copper smelters (Cooper 1989).

2.6 FATE AND TRANSPORT OF CHLORINATED HYDROCARBONS

Hydrophobic compounds such as 2,3,7,8-TCDD and 2,3,7,8-TCDF can be found associated with the organic carbon (OC) content of suspended particulate matter (SPM), dissolved organic carbon (DOC), and sediment particles in the aquatic environment (Eadie et al. 1982, McCarthy et al. 1985). Once accumulated by aquatic organisms they are found associated with lipid pools and are termed lipophilic (Thomann et al. 1992). In aquatic ecosystems, the smallest particle sizes ($< 1.0\ \mu m$) generally contain the highest OC and are potentially good carriers of bound PCDD/Fs. Approximately 90% of all riverine particles (by total weight) fall into the smallest class (Hynes 1970, Ross et al. 1981).

2.7 ENVIRONMENTAL LEVELS AND BIOMAGNIFICATION OF PCDD/Fs

The presence of 2,3,7,8-TCDD and other PCDD/Fs in fish near BKMs was first observed in 1987 (Kuehl et al. 1989). Since then there have been numerous surveys in Europe and North America to measure prevailing PCDD/F concentrations in resident fish populations near BKMs. A characteristic "BKM" pattern of congeners usually observed with environmental samples were high levels of tetra- and penta-CDD/Fs (especially the 2,3,7,8-congeners) as seen in a study by Swanson et al. (1988). In 1989, the Dept. of Fisheries and Oceans (DFO) initiated a national program to measure PCDD/Fs in fish captured near Canada's 47 BKMs. High levels of the 2,3,7,8-congeners in crustaceans in the vicinity of some BKM required the closure of some Canadian crustacean fisheries (Muller and Hallibuton 1990). In 1990, Health and Welfare Canada recommended consumption restrictions to safeguard the health of those who consume mountain whitefish, burbot, and bull trout due to elevated dioxin and furan levels on the Athabasca River near Hinton (Government of Canada News Release 1990-66). Restrictions were also placed on mountain whitefish from the Wapiti River near Grande Prairie. The DFO National Dioxin Survey data are currently being entered into a geographical information system for access by researchers and interested members of the public (Duncan 1994).

Dietary transfer may help to explain the significant levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF detected in insect-eating fish sampled downstream from BKMs (Owens et al. 1994). One study conducted on the Fraser River, British Columbia, in the winter revealed that chinook salmon (Family Salmonidae, Oncorhynchus tshawytscha (Walbaum)) eating a diet of predominantly insect larvae downstream from BKMs contained body burdens that approached 68 ng kg^{-1} of 2,3,7,8-TCDD and 370 ng kg^{-1} of 2,3,7,8-TCDF (Rodgers et al. 1989). In another study, levels of 2,3,7,8-TCDD/F in mountain whitefish (Family Salmonidae, Prosopium willamsoni (Girard)) exceeded those in suckers (Family Catostomidae, Catostomus sp.) by two to five fold at five out of six western Canadian kraft mills investigated (Muir et al. 1992b). Evidence for a trophic transfer is supported by the fact that mountain whitefish are predominantly insectivorous (Davies et al. 1976, Thompson et al. 1976) and suckers are non-discrimatory benthic foragers (Marshall 1965, McPhail et al. 1970). A more recent study found that the gut contents of mountain whitefish consisted of 71.5% trichoptera and contained 2,3,7,8-TCDD/F (TEQs) body burdens 15 times greater than long-nosed suckers consuming a diet of 43.5% sediment and 39.3% chironomids sampled downstream from a BKM (Owens et al. 1994). Recent accumulation and depuration studies with filter-feeding invertebrates showed relatively short half-lives for 2,3,7,8-TCDD and OCDD when compared to freshwater fish species (Pastershank 1994).

3.0 METHODOLOGY

3.1 SITE LOCATIONS AND SAMPLE DESCRIPTIONS

This report discusses PCDD/F data for environmental samples collected downstream from the BKM on the Athabasca River (Spring 1992) and burbot sampled from the Peace and Wapiti Rivers (Fall 1992). The sample descriptions, site locations, lab reference numbers, and the laboratories performing the PCDD/F analysis are compiled in Table 4. The sample site locations are indicated in Figure 1.

3.1.1 Reach Specific Study (RSS) Survey (Project No. 3119 - Spring 1992)

PCDD/F concentrations were determined for water (centrifuged with a continuous flow centrifuge), suspended sediments (centrifuged solids), depositional sediments, invertebrates, mountain whitefish (Family Salmonidae, Prosopium willamsoni (Girard)), and northern pike (Family Esocidae, Esox lucius (Linnaeus)) samples collected from the Athabasca River at Hinton during April and May of 1992. The RSS was designed to examine bioaccumulation of hydrophobic contaminants such as the PCDD/Fs from water/effluent to fish. PCDD/F levels were determined for samples from all the major river compartments. Six sites were located downstream from the Weldwood of Canada Ltd. pulp and paper mill and one site upstream:

Site 1. Upstream-control (REF). Located 10 km upstream.
Site 2. Weldwood Haul Road Bridge (HB). Located 1 km downstream.
Site 3. Obed Mountain Coal Bridge (OB). Located 19 km downstream.
Site 4. Emerson Lakes Road Bridge (EL). Located 48 km downstream.
Site 5. Knight Bridge (KB). Located 116 km downstream.
Site 6. Windfall Bridge (WB). Located 176 km downstream.

3.1.2 General Fish Collection (Project No. 3117 - Spring 1992)

Long-nosed suckers (Family Catostomidae, Catostomus catostomus (Forster)) and mountain whitefish samples were collected from two sites: HB, and Whitecourt (200 km downstream). Samping

Table 4: Laboratory Samples Received and Analyzed for PCDD/Fs.

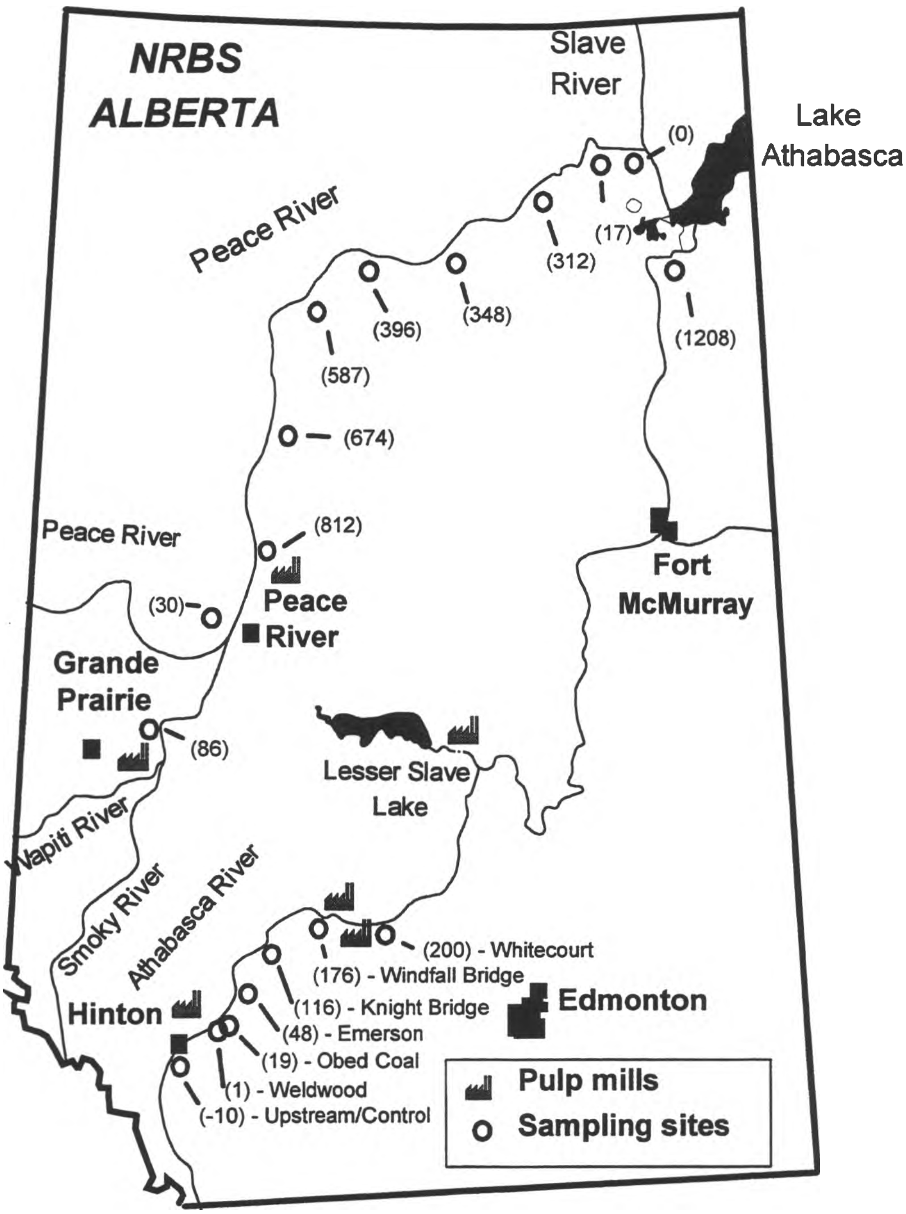
LAB SAMPLE #	LAA NO.	Lab	Sample Description	Sample Information
92-D1393	3,4	ETL	38 fish muscles, 13 invertebrates, 6 biofilms, 4 blanks, 4 QA/QC	Athabasca River - mountain whitefish and northern pike: upstream Hinton, Obed Coal Bridge, Windfall Bridge
92-D1491		ETL	2 fish muscles (repeats for 92-D1393)	
92-D1509	34	ETL	12 invertebrates	Site 2 (Weldwood Haul Road) Site 4 (Emerson Lake Bridge) Site 5 (Knight Bridge)
92-D1551 2815	48 --	ETL AXYS	6 sediments, 2 QA/QC 4 depositional and erosional sediments	Lake Athabasca West end (Sites B,G,I) Weldwood Bridge, Obed Coal Bridge, Emerson Lake Bridge
92-D1552	41,42	ETL	53 fish muscles	mountain whitefish: upstream Hinton, Haul Bridge, Emerson Lake Bridge northern pike: Haul Bridge, Emerson Lake Bridge, Knight Bridge
E3-01-003	68	ETL	40 fish muscles, 6 QA/QC	mountain whitefish: Athabasca River Km. 1238 and 1024 long-nosed suckers: Athabasca River Km. 1238 and 1024
E3-02-011	99	ETL	28 fish livers, 3 QA/QC	burbot livers, Special Burbot Collection

continued

Table 4. Concluded.

LAB SAMPLE #	LAA NO.	Lab	Sample Description	Sample Information
E3-02-110 E3-02-170	98,100, 105	ETL	36 fish muscles, 4 QA/QC 32 fish muscles, 4 QA/QC	walleye: Athabasca River, Km. 627-634, Km. 230-300, Delta and Lake Athabasca goldeye: Athabasca River, Km. 627-634, Km. 230-300, Delta
E3-020246	99	ETL	32 fish livers	burbot livers, Special Burbot Collection: Smoky (km 86), Peace (312, 348, and 396)
E3-03-064	99	ETL	40 fish livers	burbot livers, Special Burbot Collection: Wapiti (30), Peace (312, 396, 587, 674, and 812)
2815	12,19,36, 94	AXYS	suspended sediment, effluent	Weldwood, Obed Coal Bridge, Emerson Lake, Knight Bridge and Windfall Bridge
ENVI113-0501	--	Chemex	water centrifugate: total dissolved solids, TOC, DOC	Control, Weldwood, Obed Coal Bridge, Emerson Lake, Knight Bridge, and Windfall Bridge
ENVI113-0501	--	Chemex	water grab: TOC, DOC, total filterable residue (TDS), and non-filterable residue (TSS)	Control, Weldwood, Obed Coal Bridge, Emerson Lake, Knight Bridge, and Windfall Bridge
		J. Dalton	sediment: total carbon, and percent organic carbon	Control, Weldwood, Obed Coal Bridge, Emerson Lake, Knight Bridge, and Windfall Bridge
	18,93	AXYS	6 water (centrifugate)	Weldwood, Obed Coal Bridge, Emerson Lake, Knight Bridge, and Windfall Bridge

Figure 1. General Map Showing Study Area



Note: On Athabasca km are measured downstream of Hinton, whereas on the Peace-Smoky-Wapiti, km are upstream of river mouth.

Note: All values in brackets ( ) are kilometers used in this study.

dates were from May 5 to May 20, 1992.

Goldeye (Family Hiodontidae, Hiodon alosoides (Rafinesque)) and walleye (Family Percidae, Stizostedion vitreum (Mitchill)) muscle samples were collected from an additional seven sites: Goose Island, Jackfish Lake Fishing Village, and five other sites located 230.4, 299.8, 627, 630, and 633.8 km downstream from Hinton. Jackfish Lake Fishing Village is located 1208 km downstream from the Weldwood Pulp and Paper Mill (35 km before Lake Athabasca). The sampling period was from May 5 to June 11, 1992.

3.1.3 Special Burbot Collection (Project No. 3118 - Fall 1992)

Concentrations of PCDD/Fs were determined in burbot (Family Gadidae, Lota lota (Linnaeus)) livers from seven sites located downstream from a BKM on the Peace River (km 0, 17, 348, 396, 587, 674, and 812), one site on the Wapiti River (km 30) and one site from the Smoky River (km 86). Burbot were captured between October and November, 1992.

3.2 PCDD/F ANALYSIS PROCEDURES ON ENVIRONMENTAL SAMPLES

Field sampling procedures are outlined in a recent NRBS Project Report by Crosley (1994). The two laboratories conducting PCDD/F analysis were AXYS Analytical Services, Sidney, BC, and Enviro·Test Laboratories Ltd (ETL)., Edmonton, AB.

3.2.1 Water and Effluent Samples

Water (REF, HB, OB, EL, KB, and WB) and effluent (HCE - Hinton combined discharge from the Weldwood of Canada Ltd. pulp and paper mill) samples were obtained in the field using a continuous-flow centrifuge. For PCDD/F analysis, centrifugate samples (20 L) were extracted using a Goulden extractor in which dichloromethane was mixed with a continuous flow of water. Sample extracts were shipped to AXYS. The extracts received consisted of a dichloromethane layer and an aqueous layer. A surrogate standard solution was added. The two distinct layers were divided in a separatory funnel. The aqueous layer was further extracted two times with 100 ml dichloromethane. The dichloromethane extracts were combined and followed the washing procedure outlined below. All extracts were cleaned by a series of base/acid washes and four chromatographic columns. PCDD/F surrogate standards were added to the cleaned samples and analyzed by high resolution gas chromatography (HRGC) with high resolution mass spectrometer (HRMS) using a Hewlett Packard 5890 GC equipped with a 60 m DB-5 column. Further details on methodology can be found in data reports submitted by AXYS (1994).

3.2.2 Sediment Samples

The field methodology for sediment sampling are summarized in a report by R.L. & L. Environmental Services (1993). Sediments were collected at REF, HB, OB, EL, KB, and WB with a stainless steel Ekman Grab, spoon, and tray. Samples were stored on dry ice and delivered to the National Water Research Institute (NWRI) in Burlington ON. The sediment samples were freeze dried, and fractionated to the different particle size classes with brass sieves as described by Duncan (1992). The finer fraction of sediments ($< 0.63 \mu m$) from the REF, OB, and WB sites were analyzed for PCDD/F levels by both ETL and AXYS laboratories. The samples were not ground. The organic carbon content (OC) was determined by NWRI for the bulk sediments. Samples of the fine fraction are currently submitted to NWRI for OC analysis.

ETL laboratories received the sediment in a dried, fine powder. The powder was Soxhlet extracted according to ETL MSOP 18.02 (ETL 1993). Clean-up consisted of a series of column chromatographies: sulfuric acid charring, followed by multisilica, florisil, basic alumina (ETL MSOP 94.00) and carbon. Extracts were brought to dryness and internal standards were added. Samples were first spiked with a surrogate solution of nine ^{13}C-labelled dioxin and furans (higher chlorinated congeners) and one ^{13}C-labelled mono-, di-, tri-CDD/F (lower chlorinated congeners). Sediment was ground with anhydrous sodium sulphate in a mortar and pestle in to a free-flowing powder. Sediment samples were Soxhlet extracted in a toluene/acetone solution in a 80:20 ratio. The cooled extract was concentrated by a rotary evaporator. Extracts were than cleaned with base/acid washes and a series of four chromatographic columns: Silica Gel, Alumina, Carbon/Celite, and Alumina. Recovery standards were added at the point the extract became dried. PCDD/Fs were assayed by a Kratos Concept high resolution mass spectrometer linked with a high resolution gas chromatography (Hewlett Packard 5890) and a Sun data system. The chromatograph column was a 60 m Restek Rtx-5, 0.25 mm i.d. x 0.1 μm film thickness.

Similar sediment analysis procedures were employed by AXYS. Approximately 5 g (wet wt) sediment samples were ground with anhydrous sodium sulphate in a mortar and pestle to a free-flowing powder. The powder and an aliquot of surrogate standard solution was Soxhlet refluxed for 20 h with a toluene and acetone mixture (80:20). The extract was cooled and then rotary evaporated prior to the washing procedure. Chromatographic clean-up procedures consisted of transferring the extract through a series of columns: Silica Gel, Alumina, Carbon/Celite, and Alumina. The extract was evaporated just to dryness, and an aliquot of recovery solution was added. The sample was analyzed by a high resolution GC/MS, Hewlett Packard 5890 GC with a VG 70SE high resolution mass spectrometer. The chromatography column was a 60 m DB-5, 0.25 mm i.d. x 0.1 μm film thickness. Data were acquired in the voltage selected ion recording mode.

3.2.3 Suspended Sediment Samples

Suspended sediments were removed from the water at REF, HCE, HB(2), OB, El, KB, and WB sites with a Alfa-Laval MB103 centrifuge and stored in IChem glass sediment jars with Teflon liners. Samples were weighed then stored on dry ice and sent to NWRI (National Water Research Institute), Burlington, ON for freeze drying. Particle sizes for suspended sediments were determined by Dalton

(1993) at NWRI. The fraction of OC for suspended sediments at each sample site was determined by NWRI. Dried suspended sediment samples (≈ 5 g) were analyzed for PCDD/Fs by AXYS using the same methodology outlined above for sediments.

3.2.4 Biological Tissues

Field mcollection methods for invertebrates and fish are summarized in three NRBS Project Reports (Barton et al. 1993, Hvenegaard et al. 1993, and R. L. & L, Environmental Services 1993). Concentrations of PCDD/Fs in biological tissues were determined by ETL. Samples of fish muscle and macroinvertebrate tissues (≈ 10 g) were mixed with Na_2SO_4 and Soxhlet-extracted following addition of $^{13}C_{12}$-surrogates. A portion of this extract was analyzed for lipid content. The remainder of the extract was initially subjected to sulfuric acid charring, followed by multisilica, florisil, basic alumina and carbon column chromatography. The extracts were dried prior to adding a solvent containing internal standards. Analysis for specific PCDD/F congeners was performed by a Kratos Concept high resolution mass spectrometer. Further details are summarized in ETL reports reference numbers: E3-09-116.REP, E3-07-406.REP, E3-11-330.REP, E3-09-515.REP.

3.3 QUALITY ASSURANCE

Quality assurance protocols carried out by the analytical labs are described in the analytical data reports by AXYS and ETL. In brief, both laboratories followed quality assurance requirements set out by Environment Canada (1992) which include the use of ^{13}C-PCDD/F surrogates, blank analyses to demonstrate laboratory cleanliness, multi-level instrument calibration to demonstrate linearity of mass spectrometer response, and analyses of duplicate samples once every 10 samples. Sample extraction and analyses were repeated if surrogate recoveries were less than 40% or greater than 120%. Detection limits were calculated for each congener in each sample, based on a method detection limit (MDL) of three times the standard deviation of the analyte peak in the sample blank.

3.4 STATISTICAL ANALYSIS

The Univariate Procedure was used to test the normality of all data. While conducting Student's t-test, if the assumptions of normality or homogeneity of variances were not met, the data was analyzed with the nonparametric Wilcoxon Rank Sum test (PROC NPAR1WAY, $p = 0.05$). The Wilcoxon Rank Sum test is also called the Mann-Whitney U test and deals with unequal sample sizes. All statistical tests conducted on 2,3,7,8-TCDD/F levels in fish were on a wet wt and lipid normalized basis.

Arc-sine transformation was applied to the percent fraction of lipid measured in 63 mountain whitefish, 29 northern pike, and 20 long-nosed suckers. Student's t-tests ($p = 0.05$) were conducted on the transformed data to determine if there were interspecies differences in lipid content, and if intraspecies differences in lipid content exited due to the sex of the fish. In addition, Student's t-tests ($p = 0.05$) were conducted at each sampling location to compare the levels of 2,3,7,8-TCDD/F in mountain whitefish due to its sex. Proc Corr was used to determine if the levels of 2,3,7,8-TCDD/F correlated with the length, wet weight, and age of the fish for each site.

Non-parametric tests (PROC NPAR1WAY, $p = 0.05$) were conducted to determine if there were significant differences in the levels of 2,3,7,8-TCDD/F between mountain whitefish and northern pike fore each sample site. To test the effect of location (upstream vs. downstream BKM sits) on the bioaccumulation of TCDD/F in mountain whitefish, the "post hoc" comparison procedure chose was Wilcoxon Rank Sum test (PROC NPAR1WAY, $p = 0.05$) was chosen. The levels of 2,3,7,8-TCDD/F in northern pike caught at the upstream site were compared with those obtained from each downstream site using PROC NPAR1WAY ($p = 0.05$).

In order to calculate mean concentrations and TEQs in environmental samples, the analytical detection limits were substituted for all PCDD/F congeners not detected. This decision was based on the fact that as many as 38 (mono- to octachloro) PCDD/F congeners were detected in the suspended particulate matter in BKME. Thus all 38 PCDD/F congeners could reasonably be assumed to be present in environmental samples collected downstream, although below analytical detection limits.

4.0 <u>RESULTS AND DISCUSSION: THE RSS SURVEY</u>

4.1 CONCENTRATION OF PCDD/Fs IN ABIOTIC SAMPLES

The lower and higher chlorinated dioxin and furan congeners detected in environmental samples collected in the spring of 1992 from the Athabasca River downstream of Hinton are summarized in Figures 2 and 3. Concentrations of PCDD/Fs in effluent, water, biofilm, depositional sediments, suspended sediments, invertebrates, and fish are given in Appendix A.

4.1.1 <u>Effluent</u>

The suspended particulate matter associated with the HCE was analyzed for 41 PCDD/Fs ranging from monochloro- to octachloro-substituted congeners (Appendix A: Tables A1 and A2). Most congeners were detected except 1-MCDD, 1,2,4-TriCDD, and 1,2,3,7,8,9-HxCDF. The lower chlorinated mono-, di-, and tri-CDDs ($\leq$ 24 pg g^{-1} (dry wt)) were found at much lower concentrations than the CDFs ($\leq$ 1400 pg g^{-1} (dry wt)). The concentrations of tetra-, penta-, hexa-CDFs (pg g^{-1} (dry wt)) were also higher than their dioxin counterparts. However, the levels of HpCDDs ($\leq$ 38 pg g^{-1} (dry wt)) and OCDD (140 pg g^{-1} (dry wt)) exceeded those obtained for HpCDFs ($\leq$ 7.3 pg g^{-1} (dry wt)) and OCDF (9.1 pg g^{-1} (dry wt)). 2,3,7,8-TCDD (11 pg g^{-1} (dry wt)) was found in a ratio of 1:10 with 2,3,7,8-TCDF (110 pg g^{-1} (dry wt)).

The concentrations of PCDD/Fs associated with the HCE centrifugate water samples are summarized in Tables A3 to A5 of Appendix A. Only mono-, di-, and tri-CDD/Fs, 2,3,7,8-TCDD/Fs, and non-2,3,7,8-substituted TCDDs were measured in HCE centrifugate (water) samples. All lower chlorinated furans found associated with supended particulate matter (Appendix A: Table A1) were also detected in low concentrations in the centrifugate HCE samples (Appendix A: Table A3).

Figure 2: Presence of Mono-, Di-, and Tri-CDD/Fs in Environmental Samples Downstream from the Weldwood of Canada Pulp and Paper Mill, Athabasca River, AB, (Spring 1992)

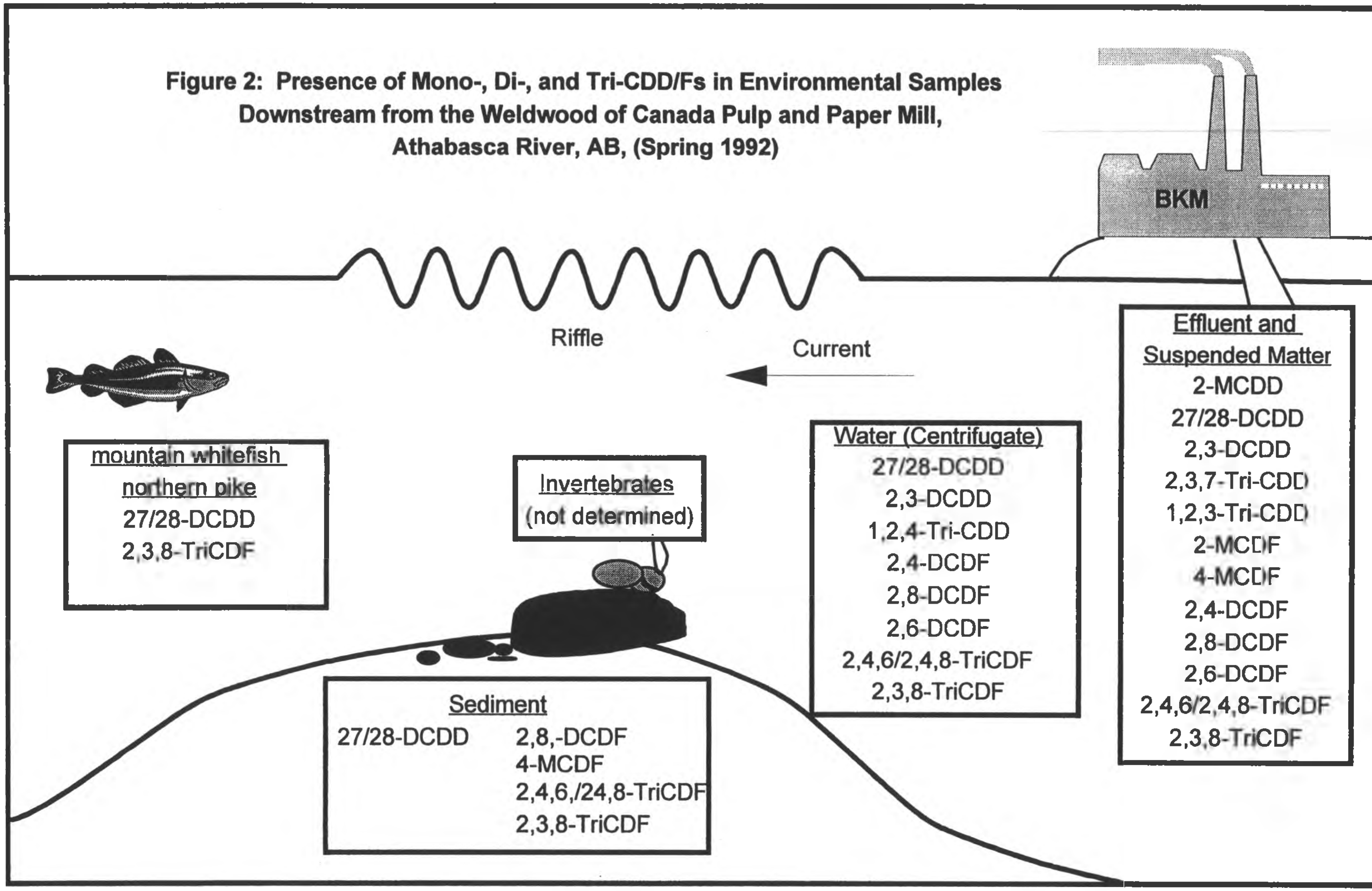
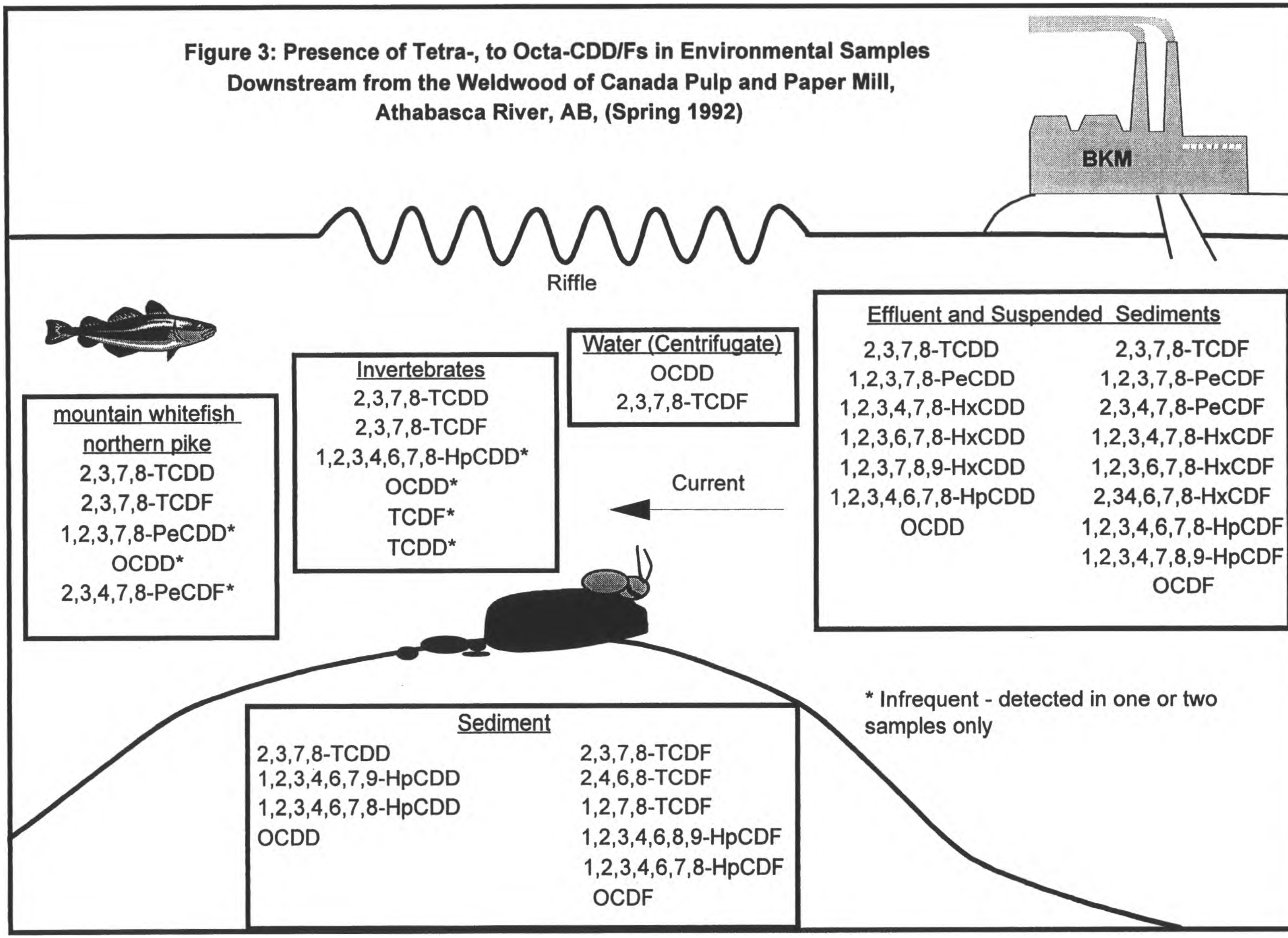


Figure 3: Presence of Tetra-, to Octa-CDD/Fs in Environmental Samples Downstream from the Weldwood of Canada Pulp and Paper Mill, Athabasca River, AB, (Spring 1992)



4.1.2 Water (Centrifugate)

Within one km downstream of the Weldwood Pulp and Paper Mill the levels of all PCDD/Fs congeners in centrifuged water were generally below the detection limits (Appendix A: Table A3 to A5). The low PCDD/F concentrations could be attributed to the dilution capacity of the Athabasca River, and to the association of the more highly chlorinated PCDD/Fs congeners with the SPM.

The total aqueous concentrations for the PCDD/Fs (pg L^{-1}) ranged from < 2.6 pg L^{-1} for DiCDFs to < 0.80 pg L^{-1} for OCDD. Concentrations of 2,3,7,8-TCDF concentrations were above the detection limits at two sites: Weldwood Haul Road site (0.10 pg L^{-1}) and Emerson Lake (0.09 pg L^{-1}). The only other congener surpassing the detection limit was OCDD at three sites: Weldwood Haul Road (0.80 pg L^{-1}), Emerson Lake (0.60 pg L^{-1}), and Knight Bridge sites (0.30 pg L^{-1}).

In order to determine the PCDD/F TEQs for water, the detection limits were substituted for non-detect values. The total PCDD/F TEQs were $\leq$ 0.40 pg L^{-1} at all the sites (Figure 4). The major TEQ contributors were 2,3,7,8-TCDD and 2,3,7,8-TCDF. These TEQs should be regarded as worst-case estimates because of the use of detection limits for non-detect values. Unfortunately these detection limits vary between samples due to sample size and instrument sensitivity. Results from the Knight Bridge sample (TEQ of 0.06 pg L^{-1}) which had the lowest detection limits for 2,3,7,8-substituted congeners are probably more realistic. Recent draft Canadian Environmental Quality Guidelines have suggested a limit of 0.06 pg TEQ L^{-1} for protection of freshwater aquatic life (CCME 1995) but it is clearly at or just beyond the limit of the analytical methodology used in the RSS study.

4.1.2.1 Freely dissolved concentrations of 2,3,7,8-TCDD/TCDF. Although congeners like 2,3,7,8-TCDD/F are highly hydrophobic and lipophilic, there will always be some in the freely dissolved state in aqueous mediums. The majority of the contaminant will be associated with two other phases: suspended particulate matter (SPM) and Dissolved Organic Carbon (DOC). Freely dissolved contaminants can bioaccumulate in aquatic organisms via gills or respiratory surfaces in the case of invertebrates. Knowledge of freely dissolved concentrations allows comparisons with bioaccumulation studies in the laboratory and with other field studies. Equation (2) describes the mass balance of the contaminants among three phases: freely dissolved, dissolved organic carbon (DOC), and particulate organic carbon (POC) (USEPA 1993). The total chemical concentration in water can be expressed as:

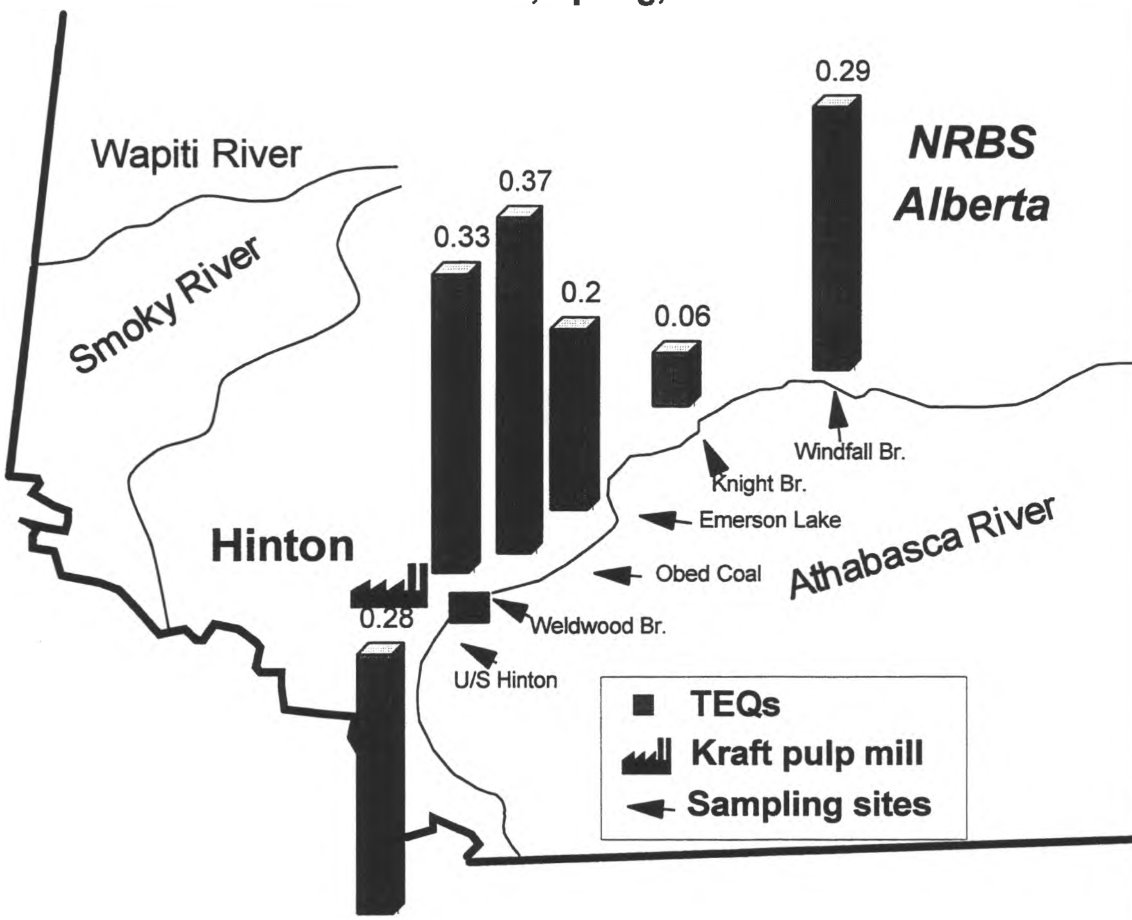
$$\mathbf{C_T = C_{fd} + (POC * C_{POC}) + (DOC * C_{DOC})} \qquad \text{(Equation 2)}$$

where C_T = total concentration of chemical in the water (pg L^{-1}), C_{fd} = concentration of chemical freely dissolved in the water (pg L^{-1}), POC = mass fraction of particulate organic carbon in water (kg L^{-1}) DOC = mass fraction of dissolved organic carbon in water (kg L^{-1}), C_{POC} = concentration of chemical associated with particulate organic carbon (pg kg^{-1}) and C_{DOC} = concentration of chemical associated with dissolved organic carbon (pg kg^{-1}). At equilibrium, Equation (2) can be expressed as Equation (3):

$$\mathbf{C_T = C_{fd} \cdot (1 + POC \cdot K_{POC} + DOC \cdot K_{DOC}) = C_{fd}/f_d} \qquad \text{(Equation 3)}$$

where K_{POC} = equilibrium constant for partitioning of the chemical between water and POC (C_{POC}/C_T in centrifugate) and K_{DOC} = equilibrium constant for partitioning of the chemical between water and DOC

Figure 4: PCDD/F (TEQs) in Water (Centrifugate (pg/L)) from the Athabasca River, Spring, 1992.



Note - Most of the PCDD/F congeners were below the detection limits (assumed to be equal to K_{POC}) and f_d = fraction of chemical freely dissolved. Where particles have been removed by centrifugation the term $POC \cdot K_{POC}$ in equation 3 can be omitted and f_d determined by Equation 4:

$$f_d = 1/(1 + DOC \cdot K_{POC}) \qquad \text{(Equation 4)}$$

Centrifugate water samples from all sites had 2,3,7,8-TCDD levels below the analytical detection limits (0.020 to 0.050 pg L^{-1}). To determine the f_d concentration of 2,3,7,8-TCDD, the detection limits were exchanged for the non-detect values. The f_d concentrations for 2,3,7,8-TCDD were used later to determine Bioconcentration Factors (BCFs) for northern pike and mountain whitefish, but are of limited value because dissolved concentrations are overestimated. The levels of 2,3,7,8-TCDF were detected the centrifugate water samples at Weldwood (0.10 pg L^{-1}) and Emerson Lake (0.090 pg L^{-1}). The Obed Coal, Knight Bridge, and Windfall Bridge sites had 2,3,7,8-TCDF concentrations below the AXYS analytical detection limits. For TCDF, it can be reasonably assumed that the detection limit is close to actual concentrations. The estimated dissolved fraction of 2,3,7,8-TCDF in the river water at the Weldwood Haul Road site was 35% while at the Emerson Lake site it was 28% (Table 10).

Table 10: Concentrations of 2,3,7,8-TCDF (pg L^{-1}) in Water (Centrifugate) and Freely Dissolved, and the Water-POC Partition Coefficient.

Sampling Site	Centrifugate C_T[a]	Fraction Freely Dissolved in Centrifugate f_d[b]	Estimated Freely Dissolved Concentration C_{fd}[c]	K_{POC}[d] x 10^6
Weldwood Haul Road	0.10	0.35	0.035	2.2
Obed Coal Bridge[e]	< 0.40	0.65	0.26	0.35
Emerson Lake	0.090	0.28	0.025	3.6
Knight Bridge[e]	< 0.020	0.083	0.0020	47
Windfall Bridge[e]	< 0.40	0.59	0.24	0.29

[a] Total 2,3,7,8-TCDF concentration detected in centrifugate water (includes DOC bound fraction).
[b] $f_d = 1/(1 + DOC \cdot K_{POC})$ - assumes $K_{DOC} = K_{POC}$.
[c] Estimated $C_{fd} = C_T \cdot f_d$
[d] $K_{POC} = C_{POC}/C_{fd}$
[e] Note: analytical detection limits were substituted in for C_T at these sites.

4.1.3 Biofilm

Only three higher chlorinated PCDD/F congeners exceeded the detection limits for biofilm samples: OCDD at the upstream site (1.0 pg g^{-1}), and 1,2,3,4,6,7,8-HpCDD (1.8 pg g^{-1}) and 2,3,7,8-TCDF (0.38 pg g^{-1}) at the Obed Coal site (Appendix A: Table A6). The highest OCDD in biofilm was found at the upstream site. Detection limits were relatively high (compared to invertebrates) because of small sample size.

4.1.4 Sediments

The lower chlorinated 2,7-/2,8-CDD, 2,3-CDD, 2,3,7-CDD, 2,8-CDF, 2,3,8-CDF and 2,3,7,8-TCDF were found above the detection limits in depositional sediments at most of the sampling sites downstream from the Weldwood of Canada Ltd. Pulp and Paper Mill (Appendix A: Tables A7 to A8). Generally the concentrations (dry wt basis) of PCDDs were low. For example, at the Obed Coal Site, < 3.0 pg g^{-1} for 2,7/2,8-CDD, < 2.1 pg g^{-1} for 2,3-CDD, and $\leq$ 0.3 pg g^{-1} for 2,3,7-CDD. Higher levels of the lower chlorinated PCDFs were found in the sediments; 2-MCDF (8.31 pg g^{-1}), 2,8-DCDF (36 pg g^{-1}) and 2,3,8-CDF (5.2 pg g^{-1}).

Both 2,3,7,8-TCDD and 2,3,7,8-TCDF were above the detection limits in depositional sediment at the Weldwood Haul Road, Obed Coal Bridge, Emerson Lake, and Windfall Bridge sites. No samples were analyzed from the Knight Bridge site. Other tetra-CDFs were also identified in the sediments, 1,2,7,8-TCDF at both the Obed Coal and Windfall Bridge site (0.50 and 1.1 pg g^{-1}, respectively) and 2,4,6,8-TCDF (1.0 pg g^{-1}) at the Windfall Bridge Site (Appendix A: Table A9). All penta-, and hexa-CDD/Fs were below the detection limits in the sediment samples (Appendix A: Table A10). The higher chlorinated hepta-, and octa-CDD/Fs were also found in the sediments. Further details on PCDD/Fs in sediment can be found in Crosley (1994) and Brownlee et al. (1994).

The fraction of OC in depositional sediment (bulk) varied from 0.029 at the Obed Coal Bridge site to 0.036 at the Knight Bridge site (Appendix A: Table A11) and did not show a consitent trend downstream. Further details on the sediment characterisitics are given in Dalton (1992).

PCDD/F (TEQs) in sediments increased from the Weldwood Haul Road site (0.21 pg TEQ g^{-1}) to the Emerson Lake site (1.4 pg TEQ g^{-1}) (Figure 5). At Emerson Lake these values exceed the interim draft Environmental Quality Guideline for sediments of 0.25 ng TEQ kg^{-1} for TCDD TEQs for the protection of aquatic life (CCME 1995).

4.1.4.1 Temporal trends in sediments (1987 to 1992). Results for PCDD/Fs in depositional sediments collected downstream of Hinton in 1987/88 and in 1989 were available for comparison with those analyzed in 1992. However, 2,3,7,8-TCDD and -TCDF were below the detection limits in sediment samples collected downstream of the Weldwood of Canada Ltd. pulp and paper mill in 1987. The detection limits varied from 0.2 to 1.9 pg g^{-1} and 0.2 to 1.1 pg g^{-1}, respectively (Alberta Environment 1988). Environment Canada (Trudel 1991) also conducted sediment sampling in 1988 in the same vicinity. The only congener above the detection limit at that time was OCDD ($\leq$ 225 pg g^{-1}). Trudel (1991) reported PCDD/F (TEQ) values of 16 pg g^{-1}, which is about 16 times higher than those obtained in 1992, due to the substitution of the higher detection limit values for 2,3,7,8-TCDD (i.e., 7.5 ng kg^{-1}) when calculating the TEQs. The best comparison is with samples collected in 1989 and analysed in 1992 as part of basin-wide sediment analyses (Brownlee et al. 1994). TCDD TEQs in sediments at Windfall in 1989 (1.4 pg g^{-1}) were similar to those found at Emerson Lake in 1992.

4.1.5 Erosional Sediments

The levels of lower and higher chlorinated PCDD/Fs found in erosional sediments are summarized respectively in Tables A12 and A13 in Appendix A. Similar congener patterns to the depositional sediments were seen. The hepta-, and octa-CDD/Fs were seen in upstream samples suggesting another source such as background atmospheric deposition of combustion-related PCDD/Fs. In the downstream sites, the 2,3,7,8-TCDD/F congeners were also detected in the depositional and erosional sediments.

4.1.6 Suspended Sediments

A wide range of PCDD/Fs (di- to octachloro-) were found in suspended sediments downstream of the Hinton combined effluent (summarized in Appendix A: Table A1, A2, and A14). 2,8-DCDF was the most prominent di/tri- PCDD/F congener while OCDD was the most prominent congener with > 4 chlorines. The PCDD/F profile was identical in the SPM associated with the BKME and in the river water at the downstream sites. The PCDD/Fs TEQ (dry wts) for suspended sediments doubled from the control site (0.90 pg TEQ g^{-1}) to the downstream sites ($\approx$ 1.9 pg TEQ g^{-1}) (Figure 6). On a dry wt basis, the PCDD/Fs TEQs for SPM were higher than for river bottom depositional sediments.

Other physical attributes (i.e., percent total carbon, OC, sand, silt, and clay) are summarized in Appendix A (Table A15). Organic carbon levels in SPM varied < 0.5% downstream of the effluent and were only slightly elevated (+0.4 to 1.1%) compared to the upstream site.

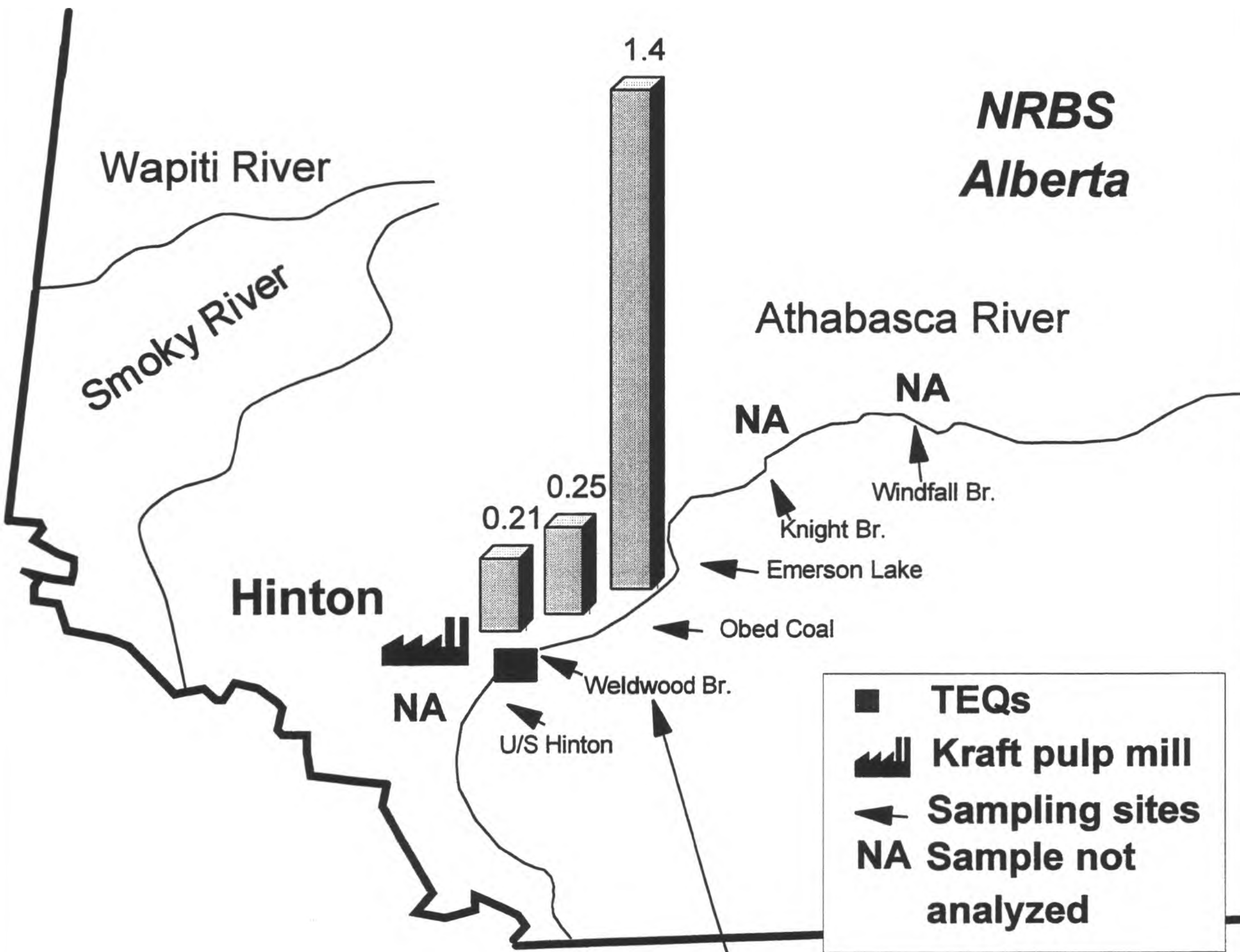
4.2 CONCENTRATION OF PCDD/Fs IN BIOTA

4.2.1 Invertebrates

2,3,7,8-TCDD and -TCDF were the major congeners detected in aquatic invertebrates from the RSS Study (Appendix A: Table A16). Other congeners which were infrequently detected in invertebrates were 1,2,3,4,6,7,8-HpCDD, OCDD, and non-2,3,7,8-substitutedTCDD/Fs. The mono-, di-, and tri-CDD/Fs were not determined for invertebrates.

Figure 7 summarizes the 2,3,7,8-TCDD/F TEQs (pg g^{-1} wet wt) for invertebrates. TEQ values increase from the control site (lowest) to Emerson Lake site (highest). At the Windfall Bridge site (176 km downstream from the Weldwood Pulp and Paper Mill), the TEQ levels for all three invertebrate groups were at control levels. A Canadian Environmental Guideline value of 1.1 pg g^{-1} TEQ for PCDD/Fs has been recommended for aquatic biota (CCME 1995). The Trichoptera composite obtained from the Weldwood Bridge site (8.0 pg TEQ g^{-1} ,wet wt) and Ephemeroptera from Emerson Lake (7.1 pg TEQ g^{-1}, wet wt) exceed this value. One invertebrate composite taken in 1987 downstream of Hinton by Alberta Environment (1988) had a similar TEQ value to that found in 1992.

Figure 5: PCDD/F (TEQs) for the Fine Fraction of Depositional Sediment (pg/g (dry wt)) from the Athabasca River, Spring, 1992.



Historical Trends

1987 - 2,3,7,8-TCDD/F (TEQs) ranged from 0.22 to 2.0 (detection limits) (Alberta Environment 1988)

1988 - 2,3,7,8-PCDD/F (TEQs) ranged from 16.3 to 16.4 (detection limits) (Trudel 1991)

Figure 6: PCDD/F (TEQs) in Suspended Sediment (pg/g (dry wt)) from the Athabasca River and Hinton Combined Effluent, Spring, 1992.

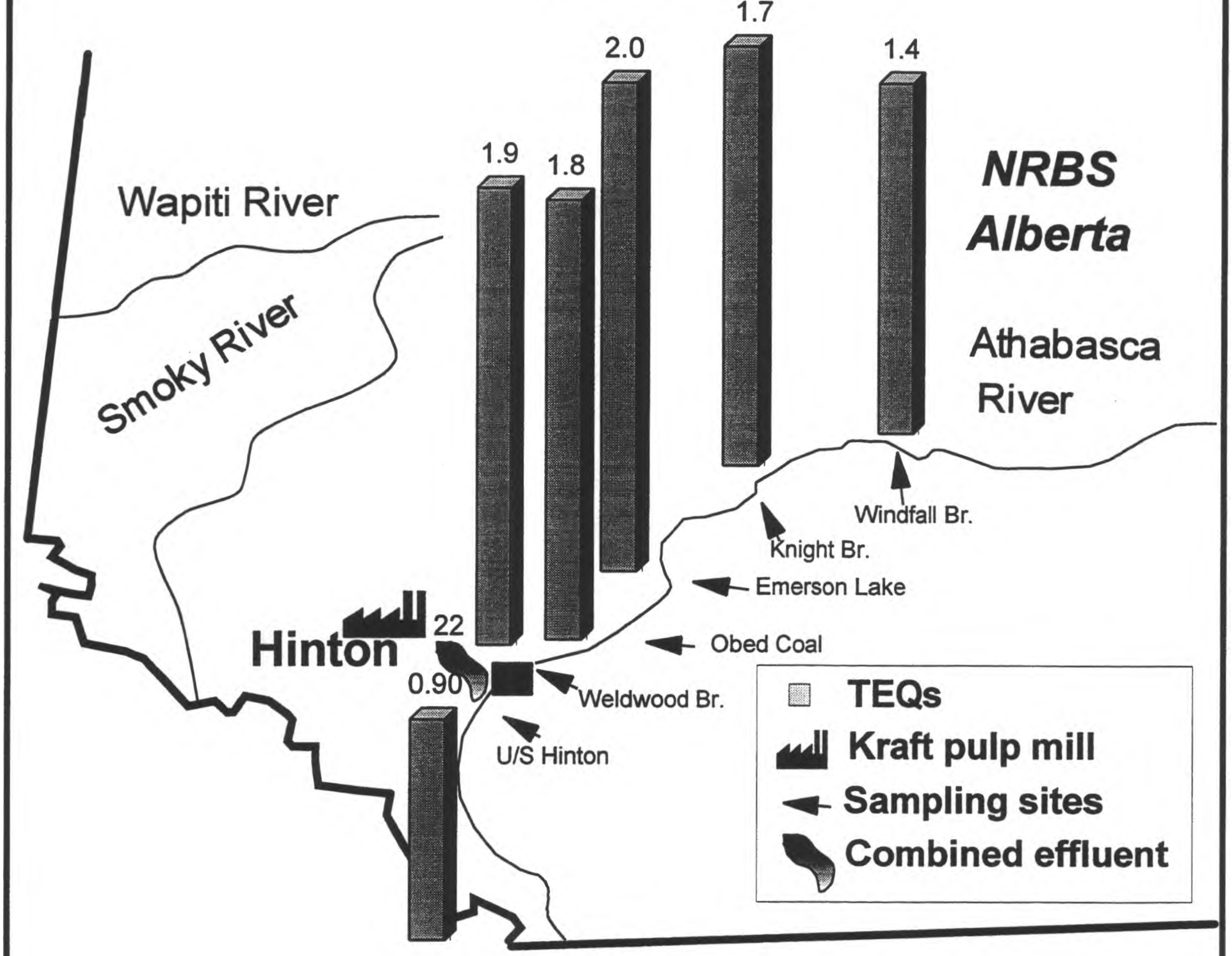
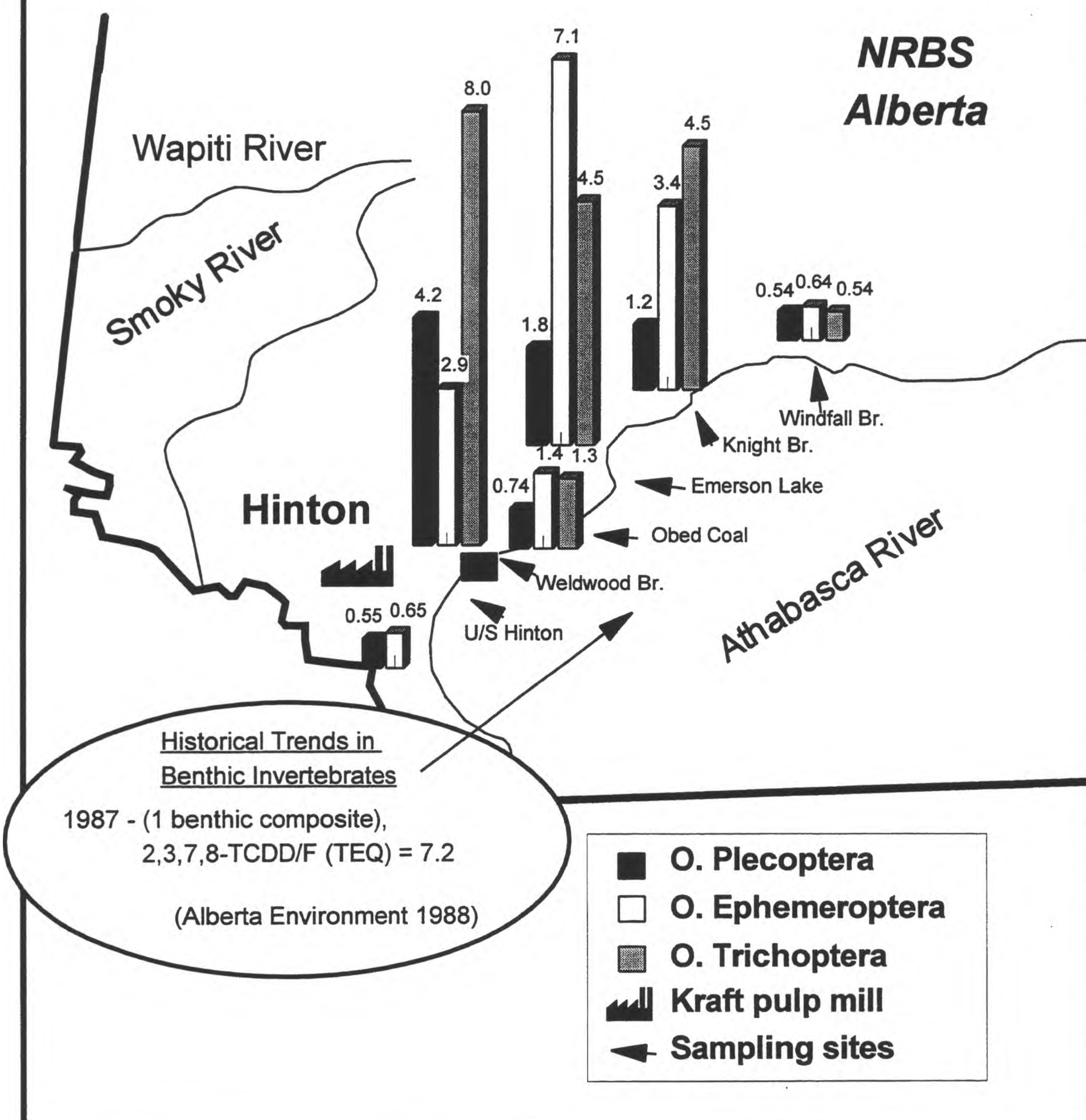


Figure 7: 2,3,7,8-TCDD/F (TEQs) in Invertebrates (pg/g (wet wt)) from the Athabasca River, Spring, 1992.



4.2.2 Fish

2,3,7,8-TCDD and -TCDF were the major PCDD/F congeners in muscle (skinless fillet) of mountain whitefish and northern pike collected downstream of Hinton in the RSS. Mean wet weight and lipid normalized concentrations are given in Tables 6 to 9. TCDD TEQs ranged from 3.4 to 9.9 in mountain whitefish and from 0.36 to 2.7 in northern pike (Figure. 8). These concentrations exceed the draft guideline for protection of fish-eating wildlife (1.1 pg g^{-1}) and on a lipid weight basis (Table 7 and 9) they exceed the guideline for protection of aquatic life (50 pg g^{-1} lipid).

Many lower chlorinated mono-, di-, and tri-CDD/Fs were detected in the abiotic samples, but not in the fish. The only di-, and tri-CDD/Fs exceeding the detection limits in mountain whitefish and northern pike were 2,7/2,8-DiCDD, 2,3,8-TriCDF, and co-eluting tri-CDFs (Appendix A: Table A17 and A18). This suggests that many lower chlorinated dioxins and furans may be readily eliminated or metabolized by mountain whitefish and northern pike. With a few exceptions, penta-, hexa-, hepta-, and octa-congeners were not detected in fishes. 2,3,7,8-TCDD TEQs were determined for three mountain whitefish fillets sampled in 1989 as part of the DFO National Dioxin program (M. Whittle, Dept. of Fisheries and Oceans, Burlington, ON, pers. comm. with D.C.G. Muir) and are summarized in the footnote in Figure 8. The 2,3,7,8-TCDD TEQ values obtained for mountain whitefish in the fall of 1989 are about two times higher than the spring values of 1992, suggesting a decline in PCDD/F levels. The reason for the decline, as noted above, is the BKM's substitution of molecular chlorine with chlorine dioxide.

4.2.2.1 Variation with fish species. On a wet wt basis, mountain whitefish had significantly higher levels (NPAR1WAY, $p > 0.05$) of 2,3,7,8-TCDD than northern pike at the Weldwood Haul Road and Windfall Bridge sites (Table 6) and higher levels of 2,3,7,8-TCDF only at the Weldwood Haul Road Site (Table 7). On a lipid corrected basis, northern pike had significantly higher levels of 2,3,7,8-TCDD than mountain whitefish at two sites; Weldwood Haul Road (NPAR1WAY, $p < 0.05$) and Knight Bridge (NPAR1WAY, $p < 0.01$) (Table 8). Lipid normalized 2,3,7,8-TCDF was significantly higher (NPAR1WAY, $p < 0.01$) for northern pike sampled at Knight Bridge than for mountain whitefish (Table 9). These observations may be explained by the significantly lower (NPAR1WAY, $p < 0.05$) percent fraction of lipids (arc-sine transformed) in northern pike than mountain whitefish.

Higher 2,3,7,8-TCDD/F TEQs (wet wts) were seen in mountain whitefish ($\leq$ 9.9 pg TEQ g^{-1}) than for northern pike ($\leq$ 3.6 pg TEQ g^{-1}) (Figure 8). Unlike invertebrates, the 2,3,7,8-TCDD/F TEQs for both northern pike and mountain whitefish did not return to upstream levels at the Windfall Bridge site. This may be due to the fact that both these fish species can move and feed over a great distance in river reach.

4.2.2.2 Effects of Lipid. The percent fraction of lipid (arc-sine transformed) for 62 mountain whitefish (5.2 ± 1.8%) was significantly higher (NPAR1WAY, $p < 0.05$) than for 29 northern pike (0.82 ± 0.30%). No significant differences (Student's t-test, $p > 0.05$) was seen in the percent fraction of lipid (arc-sine transformed) between the 39 female mountain whitefish (5.4 ± 2.0%) and 13 male mountain whitefish (5.3 ± 1.2%). No differences (NPAR1WAY, $p > 0.05$) in the percent fraction of lipid (arc-sine transformed) were found between 14 female northern pike (0.89 ± 0.38%) and 14 male northern pike (0.77 ± 0.17%).

Table 6: Concentrations of 2,3,7,8-TCDD (± SD) in Northern Pike and Mountain Whitefish Muscle from the Athabasca River, Spring 1992[a].

Location	Northern pike Conc. pg g^{-1} (wet wt)	Northern pike Sample Size	Mountain whitefish Conc. pg g^{-1} (wet wt)	Mountain whitefish Sample Size	NPAR1WAY[b,c] (p = 0.05)
U/S Hinton (-10 km)	0.17 ± 0.12	6	0.4 ± 0.43	10	NS[c]
Weldwood Haul Bridge (1 km)	0.3 ± 0.28	2	7.7 ± 5.6[d]	12	*[c]
Obed Coal Bridge (19 km)	ND[c]	ND	8.0 ± 5.5[d]	10	N/A[c]
Emerson Lake (48 km)	2.8	1	8.5 ± 8.4[d]	10	NS
Knight Bridge (116 km)	2.1 ± 1.4[e]	10	3.0 ± 3.2[d]	10	NS
Windfall Bridge (176 km)	0.70 ± 1.0[e]	10	3.8 ± 4.0[d]	10	*

[a] Data obtained from ETL laboratories

[b] This column tests significant differences between the levels of TCDD in mountain whitefish and northern pike.

[c] Symbols: NS = Not Significant; ND = No Data; * = significant at the $p < 0.05$ level; ** = highly significant at the $p < 0.01$ level; N/A = Not Applicable.

[d] Levels of 2,3,7,8-TCDD were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for mountain whitefish.

[e] Levels of 2,3,7,8-TCDD were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for northern pike.

Table 7: Concentrations of 2,3,7,8-TCDF (± SD) in Northern Pike and Mountain Whitefish Muscle from the Athabasca River, Spring 1992[a].

Location	Northern pike Conc. pg g^{-1} (wet wt)	Northern pike Sample Size	Mountain whitefish Conc. pg g^{-1} (wet wt)	Mountain whitefish Sample Size	NPAR1WAY[b,c] (p = 0.05)
U/S Hinton (-10 km)	0.49 ± 0.31	6	0.86 ± 1.2	10	NS[c]
Weldwood Haul Bridge (1 km)	0.60 ± 0.42	2	13 ± 12[d]	12	*[c]
Obed Coal Bridge (19 km)	ND[c]	ND	12 ± 8.5[d]	10	N/A[c]
Emerson Lake (48 km)	7.9	1	14 ± 11[d]	10	NS
Knight Bridge (116 km)	6.2 ± 6.8[e]	10	3.7 ± 4.2[d]	10	NS
Windfall Bridge (176 km)	2.6 ± 4.7[e]	10	8.6 ± 11[d]	10	NS

[a] Data obtained from ETL laboratories.

[b] This column tests significant differences between the levels of TCDF in mountain whitefish and northern pike.

[c] Symbols: NS = Not Significant; ND = No Data; * = significant at the $p < 0.05$ level; N/A = Not Applicable.

[d] Levels of 2,3,7,8-TCDF were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for mountain whitefish.

[e] Levels of 2,3,7,8-TCDF were significantly higher (NPAR1WAY, $p = 0.05$) than the upstream value for northern pike.

Table 8: Lipid Normalized 2,3,7,8-TCDD Concentrations (± SD) in Northern Pike and Mountain Whitefish Muscle from the Athabasca River, Spring 1992[a].

	Northern pike		Mountain whitefish		
Location	Conc. pg g^{-1} (lipid wt)	Sample Size	Conc. pg g^{-1} (lipid wt)	Sample Size	NPAR1WAY[b,c] (p = 0.05)
U/S Hinton (-10 km)	28 ± 26	6	15 ± 25	10	NS[c]
Weldwood Haul Bridge (1 km)	41 ± 35	2	120 ± 48[d]	12	*[c]
Obed Coal Bridge (19 km)	ND[c]	ND	170 ± 140[d]	10	N/A[c]
Emerson Lake (48 km)	160	1	120 ± 100[d]	10	NS
Knight Bridge (116 km)	220 ± 120[e]	10	63 ± 540[d]	10	**[cc]
Windfall Bridge (176 km)	91 ± 130[e]	10	67 ± 690[d]	10	NS

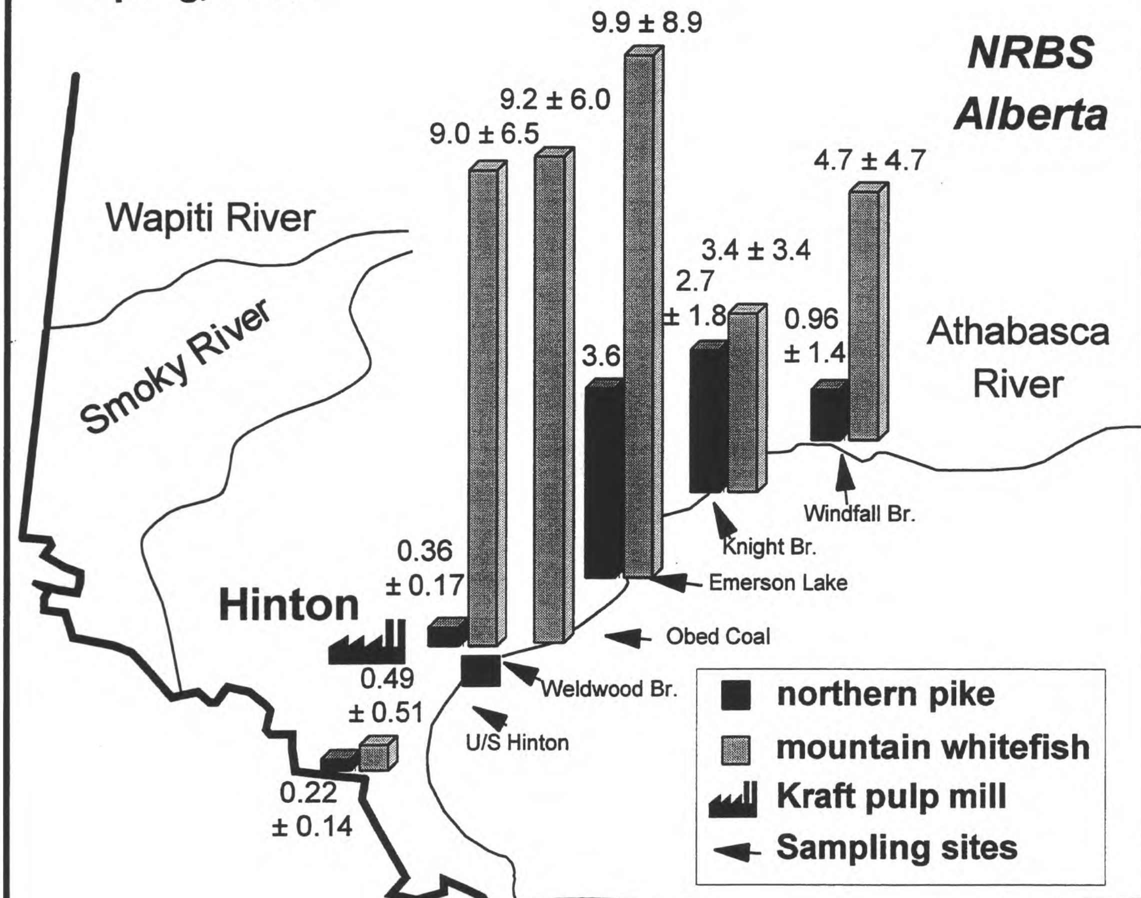
[a] Data obtained from ETL laboratories.
[b] This column tests significant differences between the levels of TCDD in mountain whitefish and northern pike.
[c] Symbols: NS = Not Significant; ND = No Data; * = significant at the $p < 0.05$ level; ** = highly significant at the $p < 0.01$ level; N/A = Not Applicable.
[d] Levels of 2,3,7,8-TCDD were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for mountain whitefish.
[e] Levels of 2,3,7,8-TCDD were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for northern pike.

Table 9: Lipid Normalized 2,3,7,8-TCDF concentrations (± SD) in Northern Pike and Mountain Whitefish Muscle from the Athabasca River, Spring 1992[a].

	Northern pike		Mountain whitefish		
Location	Conc. pg g^{-1} (lipid wt)	Sample Size	Conc. pg g^{-1} (lipid wt)	Sample Size	NPAR1WAY[b,c] (p = 0.05)
U/S Hinton (-10 km)	78 ± 59	6	35 ± 71	10	NS[c]
Weldwood Haul Bridge (1 km)	95 ± 78	2	200 ± 110[d]	12	NS
Obed Coal Bridge (19 km)	ND[c]	ND	250 ± 180[d]	10	N/A[c]
Emerson Lake (48 km)	440	1	190 ± 130[d]	10	NS
Knight Bridge (116 km)	600 ± 490[e]	10	86 ± 75[d]	10	**[c]
Windfall Bridge (176 km)	340 ± 620[e]	10	150 ± 150[d]	10	NS

[a] Data obtained from ETL laboratories.
[b] This column tests significant differences between the levels of TCDF in mountain whitefish and northern pike.
[c] Symbols: NS = Not Significant; ND = No Data; ** = highly significant at the $p < 0.01$ level; N/A = Not Applicable.
[d] Levels of 2,3,7,8-TCDF were significantly higher (NPAR1WAY, $p < 0.05$) than the upstream value for mountain whitefish.
[e] Levels of 2,3,7,8-TCDF were significantly higher (NPAR1WAY, $p = 0.05$) than the upstream value for northern pike.

Figure 8: 2,3,7,8-TCDD/F (TEQs) ± SD in Northern Pike and Mountain Whitefish (pg/g (wet wt)) from the Athabasca River, Spring, 1992.



Historical Trends

Fall 1989- 2,3,7,8-TCDD/F (TEQs) = 26.8 for two mountain whitefish caught between the Weldwood Bridge and Obed Coal sties.

Fall 1989-2,3,7,8-TCDD/F (TEQs) = 21.0 for one mountain whitefish caught at the Emerson Lake site (Data obtained from Whittle (pers. comm. 1992))

4.2.2.3 Effects of location. When compared to the upstream site (10 km upstream of Hinton), significantly higher levels (NPAR1WAY, $p < 0.05$) of 2,3,7,8-TCDD and 2,3,7,8-TCDF (wet wt and lipid normalized basis) were seen in mountain whitefish at all five sampling sites downstream from the Weldwood pulp and paper mill: Weldwood Haul Road (1 km), Obed Coal Bridge (19 km), and Emerson Lake (48 km), Knight Bridge (116 km) and Windfall Bridge (176 km) (see Tables 6 to 9).

There were no significant increases in 2,3,7,8-TCDD and 2,3,7,8-TCDF levels (NPAR1WAY, $p > 0.05$) in northern pike caught at Weldwood Haul Road (n=2), Obed Coal (n=0), and Emerson Lake (n=1) when compared to the upstream site(n=6) (see Tables 6 to 9). Ten northern pike were caught each at the Knight Bridge and Windfall Bridge sites. Levels of 2,3,7,8-TCDD/F in northern pike on both a wet wt and lipid normalized were significantly higher (NPAR1WAY, $p < 0.05$) at the Knight Bridge site than the upstream site. The same holds true for northern pike caught at the Windfall Bridge site, except for the levels TCDD (lipid normalized) which were not significantly different (NPAR1WAY, $p > 0.05$) than the upstream site.

4.2.2.4 Effects of sex. The sex of the mountain whitefish had no influence on the levels of 2,3,7,8-TCDD/F on a wet wt or lipid normalized basis for five out of six sites sampled. At the Windfall Bridge site, female mountain whitefish contained significantly higher NPAR1WAY, $p = 0.05$) TCDD/F on a wet wt and lipid normalized basis (Table 10). There were no significant differences (Student t-test, $p > 0.05$) in the percent fraction of lipid (arc-sine transformed) between males and females at this site (Table 10).

Table 10: Comparison of TCDD and TCDF ($pg\ g^{-1}$) Concentrations in Female and Male Mountain Whitefish at the Windfall Bridge Site.

	Female (n=6)	Male (n=4)	NPAR1WAY[a] (p = 0.05)
Fraction of lipid (arc-sine transformation)	4.7 ± 1.9	5.7 ± 1.3	NS
Concentration of TCDF (wet wt)	2.2 ± 2.2	18 ± 12	*
Concentration of TCDD (wet wt)	1.1 ± 0.84	8.0 ± 3.0	*
Concentration of TCDF (lipid normalized)	55 ± 49	300 ± 130	*
Concentration of TCDD (lipid normalized)	21 ± 49	140 ± 50	*

[a] Symbols: NS = Non Significant; * = Significant ($p < 0.05$)

4.2.2.5 Effects of age. weight and length. Generally, the levels of TCDD and TCDF, on both a wet wt. and lipid normalized basis, were positively correlated ($p < 0.01$) with the age, weight, and length of the northern pike caught at the Knight Bridge and Windfall Bridge sites (Table 11). The only exception was seen at the Knight Bridge site, where the levels of lipid normalized TCDF were not correlated with the weight of the fish. The correlation coefficients for northern pike were not higher with lipid normalized data.

Table 11. Pearson Correlation Coefficients (r) for Levels of TCDD and TCDF (Wet wt and Lipid Normalized) in Northern Pike with Age, Length, Weight.

	N	Age	Length	Weight
Site: Knight Bridge				
TCDD (wet wt)	10	0.842**[a]	0.894**	0.861**
TCDF (wet wt)	10	0.768**	0.858**	0.971**
TCDD (lipid normalized)	10	0.780**	0.732*	0.491 (NS)
TCDF (lipid normalized)	10	0.818**	0.896**	0.865**
Site: Windfall Bridge				
TCDD (wet wt)	10	0.937**	0.946**	0.979**
TCDF (wet wt)	10	0.938**	0.901**	0.944**
TCDD (lipid normalized)	10	0.941**	0.927**	0.968**
TCDF (lipid normalized)	10	0.929**	0.884**	0.931**

[a] Symbols: NS = Non Significant; * = Significant ($p < 0.05$); ** = Highly Significant ($p < 0.01$)

These strong correlations between the levels of contaminants and physical attributes of northern pike were not seen in the mountain whitefish. At the Weldwood Haul Road, Obed Coal, and the Knight Bridge sites, no significant correlations ($p > 0.05$) were detected between TCDD or TCDF with the age, weight, or length of the mountain whitefish (Table 12). At the Emerson Lake site, only the levels of TCDF (on a wet wt and lipid normalized basis) were positively correlated ($p < 0.01$) with the weight of the mountain whitefish. At the Windfall Bridge site, the levels of TCDF were positively correlated ($p < 0.05$) with the length and weight of the mountain whitefish.

4.3 STABLE ISOTOPES

Stable isotope work conducted concurrently by Hesslein and Ramlal (1993) (NRBS Food Chain Component), helped define the trophic positions (nitrogen isotopes) and food sources (sulphur isotopes for river biota collected in the Reach Specific Study Area. Their study has clearly identified four trophic levels (Figure 9) through the use of nitrogen isotopes. At the Weldwood Haul Road site, mountain whitefish (occupying the top trophic level #4) had higher TCDD TEQs than invertebrates from the Order Plecoptera (occupying trophic level #2) and Ephemeroptera (occupying trophic level #1). This correlation of trophic position with higher concentrations of TCDD TEQs was found in other food webs (Broman et al. 1991). However this trend was not detected for northern pike (also occupying the top trophic level #4) and long-nosed suckers (trophic level #3). They had lower TCDD TEQs at the

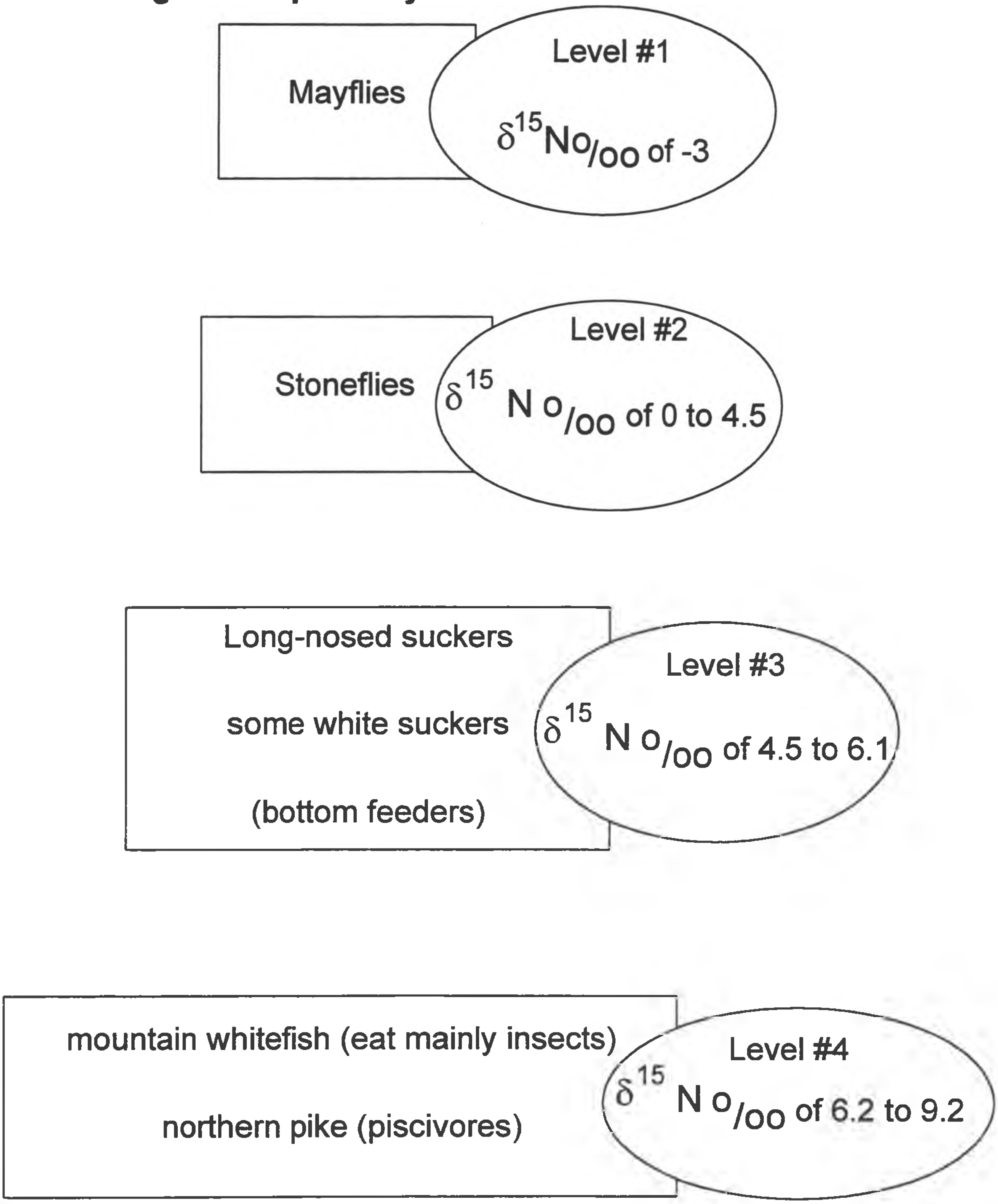
Table 12. Pearson Correlation Coefficients (r) for Levels of TCDD and TCDF (Wet Wt and Lipid Normalized) in Mountain Whitefish with Age, Length, Weight.

	N	Age[a]	Length	Weight
Site: Weldwood Haul Road				
TCDD (wet wt)	12	0.240 (NS[a])	0.0569 (NS)	0.0201 (NS)
TCDF (wet wt)	12	0.00361 (NS)	-0.0497 (NS)	-0.0586 (NS)
TCDD (lipid normalized)	12	0.0801 (NS)	-0.00578 (NS)	-0.00542 (NS)
TCDF (lipid normalized)	12	-0.268 (NS)	-0.129 (NS)	-0.0851 (NS)
Site: Obed Coal				
TCDD (wet wt)	10	-0.165 (NS)	0.392 (NS)	0.623 (NS)
TCDF (wet wt)	10	-0.140 (NS)	0.318 (NS)	0.531 (NS)
TCDD (lipid normalized)	10	-0.143 (NS)	0.437 (NS)	0.522 (NS)
TCDF (lipid normalized)	10	-0.110 (NS)	0.412 (NS)	0.513 (NS)
Site: Emerson Lake				
TCDD (wet wt)	10	0.301 (NS)	0.207 (NS)	0.846**
TCDF (wet wt)	10	0.241 (NS)	0.0965 (NS)	0.493 (NS)
TCDD (lipid normalized)	10	0.494 (NS)	0.134 (NS)	0.847 **
TCDF (lipid normalized)	10	0.434 (NS)	-0.0422 (NS)	0.361 (NS)
Site: Knight Bridge				
TCDD (wet wt)	10	-0.595 (NS)	-0.225 (NS)	-0.196 (NS)
TCDF (wet wt)	10	-0.299 (NS)	0.0669 (NS)	0.0436 (NS)
TCDD (lipid normalized)	10	-0.518 (NS)	-0.217 (NS)	-0.172 (NS)
TCDF (lipid normalized)	10	-0.0444 (NS)	0.0318 (NS)	0.284 (NS)
Site: Windfall Bridge				
TCDD (wet wt)	10	0.103 (NS)	0.573 (NS)	0.598 (NS)
TCDF (wet wt)	10	0.426 (NS)	0.643*	0.690*
TCDD (lipid normalized)	10	-0.0478 (NS)	0.557 (NS)	0.564 (NS)
TCDF (lipid normalized)	10	0.310 (NS)	0.677*	0.697*

[a] At the Weldwood site, there were only ages for 10 mountain whitefish

[a] Symbols: NS = Non Significant; * = Significant ($p < 0.05$); ** = Highly Significant ($p < 0.01$)

Figure 9: Trophic Levels Identified in the Athabasca River by Nitrogen Isotope Analysis*



* Nitrogen isotope and trophic levels defined by Hesslein and Ramlal (1993)

Weldwood Haul Road site than the invertebrates occupying the lower trophic levels. The different composition of the diet of northern pike, long-nosed suckers, and mountain whitefish may be responsible for the different TCDD TEQs.

A report by R.L. & L Environmental Services (1993) analyzed the stomach contents of northern pike and mountain whitefish caught during the spring of 1992. Northern pike gut contents were empty or contained one fish species (sculpin, rainbow or bull trout, white sucker, fathead minnows, and mountain whitefish). The gut contents of approximately 20% of the northern pike contained small quantities of benthic invertebrates. The stomach contents of mountain whitefish indicated that they rarely preyed on other fish species. Their gut contents showed a diet of primarily aquatic insects. Species from the Order Trichoptera. (i.e., Brachycentridae and Hydropsychidae) made up the majority of the invertebrate diet, however, a few mountain whitefish guts contained more species from the Order Plecoptera. Most mountain whitefish has small quantities of Ephemeroptera sp. A large portion of the gut content of mountain whitefish consisted of undifferentiated matter: inorganic (i.e., caddisfly cases) and organic matter. Although the gut contents of long-nosed suckers was not conducted, they are known to be non-discrimatory benthic foragers.

The sulphur isotope data help to explain intraspecies variability in the PCDD/F levels in mountain whitefish at the Knight and Windfall Bridge sites (Figures 10-11). The results suggest that there are mainstream, tributary and mixed feeders. The highest levels of PCDD/Fs were seen in the Athabasca River main stem feeders ($\delta^{34}S$ range of 7.5 ‰ to 11.5 ‰). The lowest PCDD/F levels were seen in the tributary feeders ($\delta^{34}S$ of < 1‰). Mixed feeders had sulphur and PCDD/F values inbetween tributary and main stem feeders.

For unknown reasons, at the Weldwood Haul Road site, the one mountain whitefish with the highest levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF also had the lowest nitrogen signal (Figure 12). This mountain whitefish occupies a lower trophic status ($\delta^{15}N$ ‰ of 4.34) than the remaining fish ($\delta^{15}N$ ‰ of 6.07 to 7.33) with lower 2,3,7,8-TCDD/F concentrations.

4.4 PREDICTED BIOCONCENTRATION FACTORS (BCFs)

BCFs are useful estimates of bioaccumulation potentials and can be determined from Equation 5. At equilibrium lipid normalized BCFs for persistent organochlorine chemicals may equal their K_{OW} values (US EPA 1993). The observed BCFs for 2,3,7,8-TCDD and 2,3,7,8-TCDF in mountain whitefish and northern pike agree well with their K_{OW} values (Table 13).

BCF = Concentration in fish (lipid normalized)/estimated C_{FD} in H_2O (Equation 5)

Accurate BCFs are generally difficult to calculate for hydrophobic compounds due to the difficulty in measuring the low fraction "freely dissolved". The age, size, and lipid content of fish species may also affect their ability to bioconcentrate hydrophobic compounds.

Figure 10: Concentration of 2,3,7,8-TCDD and 2,3,7,8-TCDF and Sulphur Isotopes in Mountain Whitefish from the Windfall Bridge Site, Spring 1992.

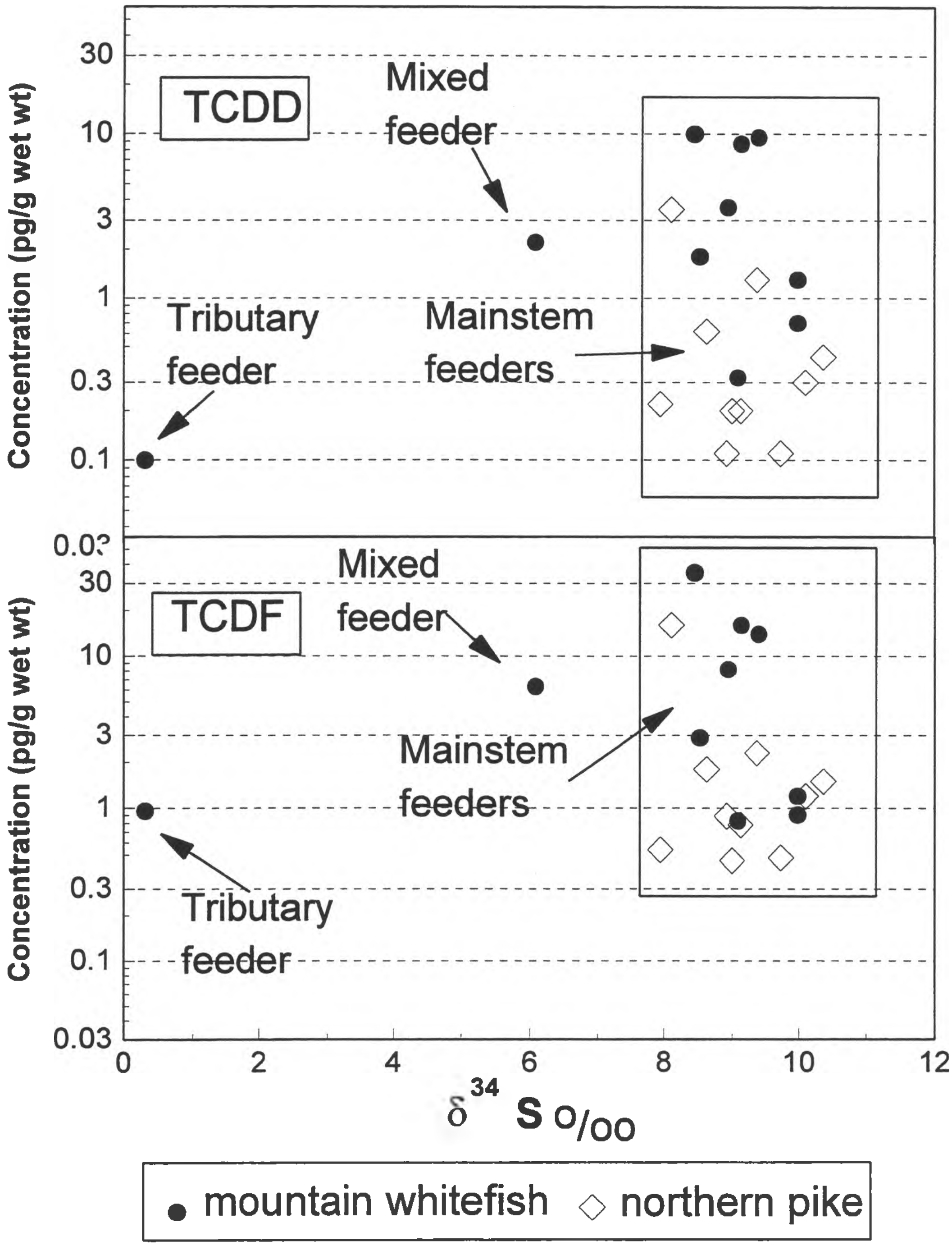


Figure 11. Concentration of 2,3,7,8-TCDD and 2,3,7,8-TCDF and Sulfur Isotopes in Mountain Whitefish from the Knight Bridge Site, Spring 1992.

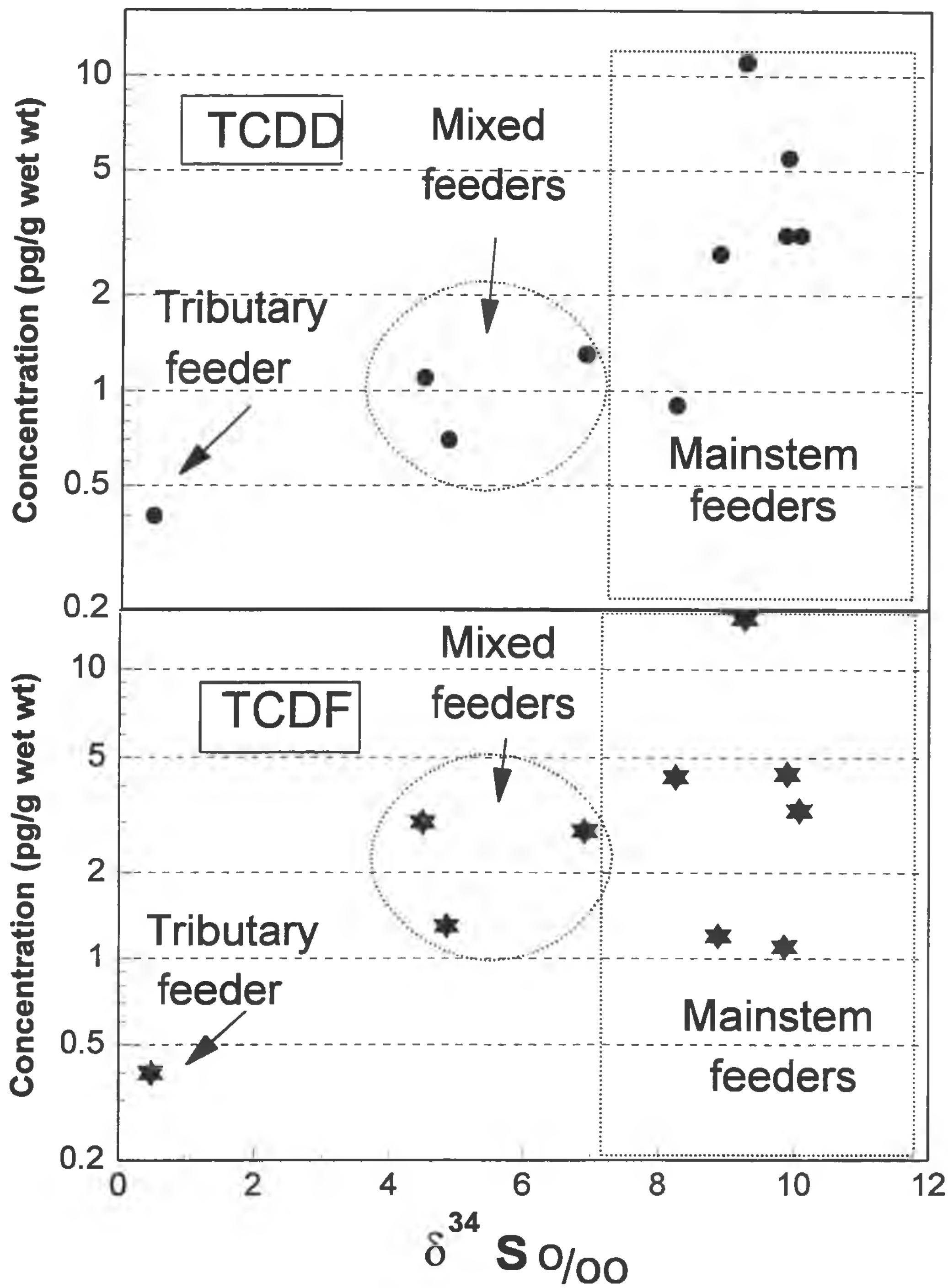
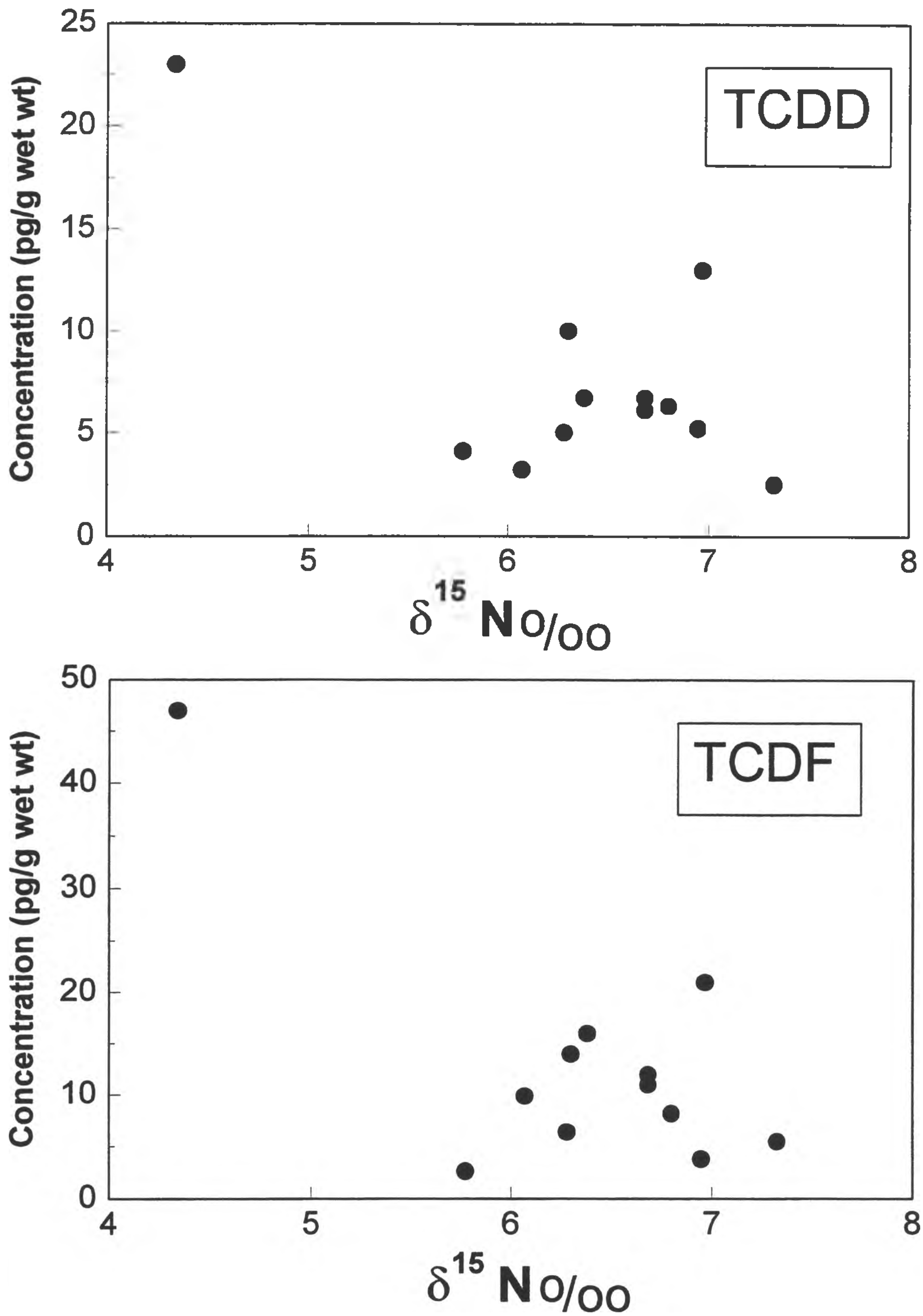


Figure 12: Concentration of 2,3,7,8-TCDD and 2,3,7,8-TCDF and Nitrogen Isotopes in Mountain Whitefish from the Weldwood Haul Road Site, Spring, 1992.



At the Weldwood Haul Road site, mountain whitefish had higher BCFs for the 2,3,7,8-substituted congeners than northern pike. However, at the three sites sampled further downstream, Emerson Lake, Knight Bridge, and Windfall Bridge, the BCFs for northern pike were higher by an order of magnitude (see Table 13).

Table 13: Predicted BCFs[a] for TCDD for Mountain Whitefish and Northern Pike Sampled Downstream From the Weldwood Pulp and Paper Mill.

	BCF x 10^6 for TCDD[b] (lipid basis)		BCF x 10^6 for TCDF (lipid basis)	
Sample Site	mountain whitefish	northern pike	mountain whitefish	northern pike
Weldwood Haul Road	5.33	1.73	6.53	2.48
Obed Coal Bridge	16.6	ND[c]	0.96	ND
Emerson Lake	6.21	7.49	8.26	17.5
Knight Bridge	18.4	52.5	54.2	375
Windfall Bridge	10.2	13.6	0.717	1.58

[a] BCF (lipid normalized) is determined as the concentration in fish ÷ estimated dissolved concentration in water

[b] The levels of TCDD measured in water were below the detection limits at all the samples sites and were assumed to be the detection limits.

[c] Symbol: ND = No Data

The BCFs obtained for mountain whitefish and northern pike were similar to those obtained by Schmieder et al. (1992) for medaka (Oryzias latipes) of 4.3 x 10^6 where TCDD was added in by a generator column in a freely dissolved state. Other experiments that added TCDD in a cosolvent, or where the content of binding to organic carbon is unknown, have BCFs for fish species an order of magnitude lower, i.e., rainbow trout (7.8 x 10^5) and carp (7.3 x 10^5) (Mehrle et al. 1988, Cook et al. 1991).

4.5 BIOTA-SEDIMENT/SUSPENDED SEDIMENT ACCUMULATION FACTORS

Calculations of the BSAFs (Equation 6) and BSSAFs (Equation 7) were calculated for 2,3,7,8-TCDD and 2,3,7,8-TCDF in mountain whitefish and northern pike and are summarized in Tables 14 and 15, respectively.

BSAF = concentration in fish (lipid basis) ÷ concentration in sediment (OC basis) (Equation 6)

BSSAF = concentration in fish (lipid basis) ÷ concentration in SPM (OC basis) (Equation 7)

Table 14: Predicted BSAFs[a] for 2,3,7,8-TCDD and 2,3,7,8-TCDF for Mountain Whitefish and Northern Pike Sampled Downstream From the Weldwood Pulp and Paper Mill.

	BSAF for TCDD		BSAF for TCDF	
Sample Site	mountain whitefish	northern pike	mountain whitefish	northern pike
Weldwood Haul Road	13.6	11.8	31.1	11.8
Obed Coal Bridge	18.7	ND[b]	10.8	ND
Emerson Lake	12.0	14.5	5.08	10.7

[a] BSAF is determined as the concentration in fish (lipid basis) ÷ bottom sediment (OC basis)
[b] Symbol: ND = No Data

Table 15. Predicted BSSAFs[a] for 2,3,7,8-TCDD and 2,3,7,8-TCDF for Mountain Whitefish and Northern Pike Sampled Downstream from the Weldwood Pulp and Paper Mill.

	BSSAF for TCDD		BSSAF for TCDF	
Sample Site	mountain whitefish	northern pike	mountain whitefish	northern pike
Weldwood Haul Road	13.6	4.43	3.04	1.16
Obed Coal Bridge	5.5	ND[b]	2.61	ND
Emerson Lake	4.57	5.51	2.3	4.85
Knight Bridge	3.27	9.32	1.15	7.97
Windfall Bridge	4.24	5.67	2.49	5.49

[a] BSSAF is determined as the concentration in fish (lipid) ÷ suspended sediment (OC basis)
[b] Symbol: ND = No Data

Ideally, the BSAFs and BSSAFs allow comparisons to be made with other data sets because they normalize results for varying lipid content in biota and sediment organic carbon (US EPA 1993; Ankley et al. 1992). At equilibrium BSAFs should equal the K_{OW} divided by the K_{OC} value assuming octanol is a surrogate for lipids (Equation 8):

$$\textbf{BSAF (or BSSAF)} \approx K_{OW}/K_{OC} \approx \frac{C_{oct}/C_{fd}}{C_{OC}/C_{fd}} \approx C_{lipid}/C_{OC} \qquad \text{(Equation 8)}$$

Because K_{OW} is of similar magnitude to K_{OC} the BSAF should approach one (USEPA 1993). The limited information available for PCDD/Fs has shown BSAF values for 2,3,7,8-TCDD ranging from 0.03 to 0.3 for fish from different lake ecosystems (Batterman et al. 1989, Carey et al. 1990) and river ecosystems (Keuhl et al. 1986). Higher BSAFs for 2,3,7,8-TCDD have been observed for sediment-dwelling invertebrates (0.48-0.93; USEPA 1993; Muir et al. 1992a). BSAFs are not entirely independent of the ecosystem type and the fish's habitat and feeding niches.

In the RSS study the BSAFs for 2,3,7,8-TCDD (Table 30) obtained for mountain whitefish (12.0 to 18.7) were similar to those obtained for northern pike (11.8 to 14.5). BSAFs for 2,3,7,8-TCDF (see Table 14) varied from 5.08 to 31.1 in mountain whitefish to 10.7 to 11.8 in northern pike. The differences in feeding behavior between mountain whitefish and northern pike may help to explain the elevated BSAFs seen for 2,3,7,8-TCDF in mountain whitefish. Mountain whitefish consume a diet predominately of invertebrates permitting them to be in more intimate contact with the depositional sediments than the piscivorous northern pike. BSAFs for 2,3,7,8-TCDD in mountain whitefish and long-nosed suckers collected downstream from Hinton in the fall of 1989 were also similar to those obtained in this study ranging from 1.50 to 8.50 in whitefish and from 0.37 to 0.61 in suckers (Muir et al. 1992a).

The slightly higher BSAFs seen for mountain whitefish caught in the spring (1992) samples (12.0 to 36.3) compared to the fall (1989) samples (1.50 to 8.50) could be due to the substitution of detection limit values for 2,3,7,8-TCDD. Higher detection limits were used in the 1988 study by Trudel (1991) from which the BSAFs were calculated.

The BSSAFs for both 2,3,7,8-TCDD and 2,3,7,8-TCDF were generally lower than BSAFs (see Table 14 and 15). The BSAFs and BSSAFs greater than one indicates an disequilibrium between water, sediment, and biota. This may be due to selective feeding by invertebrates on organic rich particles rather than on the bulk sediment, selective feeding by fish on these invertebrates, or non-equilibrium between effluent (SPM and dissolved phases) and river water and particulate phases. BSSAFs were less variable than BSAFs over the 176 km reach and therefore a better tool for predicting bioaccumulation of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

5.0 RESULTS AND DISCUSSION: GENERAL FISH COLLECTION (RSS)

5.1 FISH MUSCLE SAMPLES

Concentrations of PCDD/Fs (wet wt) in mountain whitefish and long-nosed suckers captured downstream from Hinton in the spring 1992 are summarized in Tables 16 and 17. Levels of PCDD/Fs in walleye and goldeye also collected during the General Fish survey in the spring of 1992, are condensed into Tables B1 and B2 in Appendix B.

5.1.1 Mountain Whitefish and Long-nosed Suckers

TCDD/F TEQs in mountain whitefish ranged from 12 ± 9.6 pg TEQs g^{-1} (wet wt) at the Weldwood Haul Road Site to 1.3 ± 0.91 pg g^{-1} to Whitecourt 214 km downstream (Figure 13). Long-nosed suckers had noticeably lower 2,3,7,8-TCDD/F TEQs on a wet wt basis (Weldwood Haul Road site: 0.75 ± 0.43 pg TEQ g^{-1}, and Whitecourt site: 0.35 ± 0.22 pg TEQ g^{-1}) than mountain whitefish. The total TEQs measured for mountain whitefish and long-nosed suckers are lower than Health and Welfare guidelines for human consumption of 20 pg TEQ g^{-1}.

5.1.1.1 Effects of location. Levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF (on a wet wt and lipid normalized basis) in mountain whitefish sampled were significantly higher (NPAR1WAY, $p < 0.05$) at the Weldwood Haul Road site than the Whitecourt site. Only levels of 2,3,7,8-TCDD (on a wet wt and lipid normalized basis) were significantly higher (NPAR1WAY, $p < 0.05$) for long-nosed suckers sampled at the Weldwood Haul Road site than the Whitecourt site. Sample location did not significantly (NPAR1WAY, $p > 0.05$) affect the levels of 2,3,7,8-TCDF (on a wet wt and lipid normalized basis) long-nosed suckers.

5.1.1.2 Effects of fish species. Mountain whitefish contained significantly higher (NPAR1WAY, $p < 0.05$) levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF (on a wet wt and lipid normalized basis) than for long-nosed suckers at the Weldwood Road site (see Table 16 and 17). These differences were not as noticeable at the Whitecourt site. A significant difference (NPAR1WAY, $p < 0.05$) was only seen for 2,3,7,8-TCDD on a wet wt basis (see Tables 16 and 17).

5.1.1.3 Effects of sex of fish and the percent of lipid. The perecent fraction of lipid (arc-sine transformed) in mountain whitefish (6.4 ± 2.2%) was significantly higher (NPAR1WAY, $p < 0.05$) than for long-nosed suckers (3.4 ± 1.3%). No significant differences (NPAR1WAY, $p > 0.05$) in the percent fraction of lipids (arc-sine transformed) was seen between the male and female mountain whitefish or long-nosed suckers at each sample site. No significant differences (NPAR1WAY, $p > 0.05$) in the levels of 2,3,7,8-TCDD/F (on a wet wt and lipid normalized basis) was attributed to the sex of the mountain whitefish or long-nosed sucker at either site.

Table 16: Concentrations of 2,3,7,8-TCDD (± SD) in Mountain Whitefish and Long-Nosed Sucker Muscle from the Athabasca River, Spring 1992[a].

	Mountain whitefish		Long-nosed sucker		
Location	Conc. pg g^{-1}	Sample Size	Conc. pg g^{-1}	Sample Size	NPAR1WAY[b,c] ($p = 0.05$)
1. Wet Weight					
Weldwood Haul Road	11 ± 8.9	10	0.51 ± 0.32	10	**[b]
Whitecourt	0.86 ± 0.59	10	0.22 ± 0.22	10	**
2. Lipid Weight					
Weldwood Haul Road	180 ± 140	10	15 ± 11	10	**
Whitecourt	13 ± 8.7	10	8.0 ± 9.8	10	NS[b]

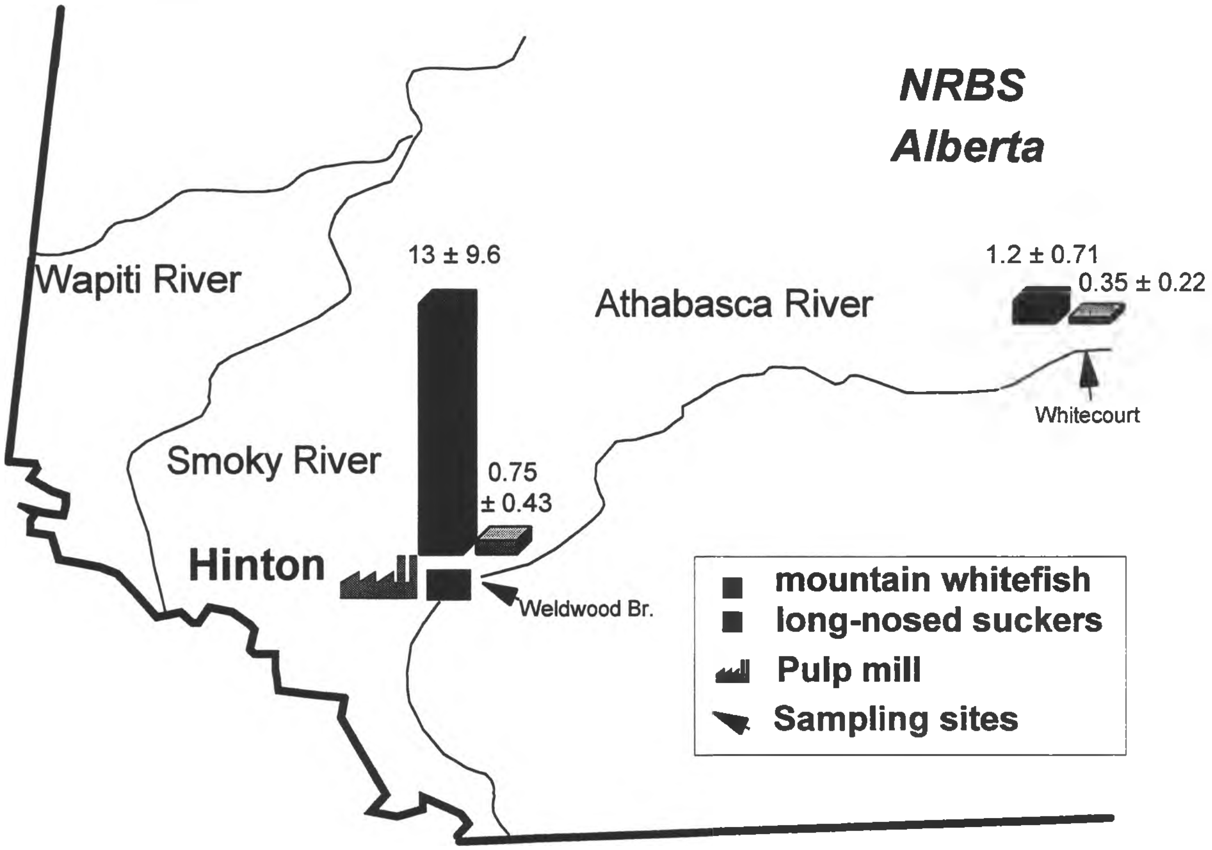
[a] Data obtained from ETL
[b] Symbols: NS = not significant ($p > 0.05$); ** = highly significant at the $p < 0.01$ level.
[c] This column tests significant differences between the levels of TCDD in mountain whitefish and long-nosed suckers.

Table 17: Concentrations of 2,3,7,8-TCDF (± SD) in Mountain Whitefish and Long-Nosed Sucker Muscle from the Athabasca River, Spring 1992[a].

	Mountain whitefish		Long-nosed sucker		
Location	Conc. pg g^{-1}	Sample Size	Conc. pg g^{-1}	Sample Size	NPAR1WAY[b,c] ($p = 0.05$)
1. Wet Weight					
Weldwood Haul Road	15 ± 13	10	2.4 ± 1.5	10	**[b]
Whitecourt	3.2 ± 3.2	10	1.3 ± 0.92	10	NS[b]
2. Lipid Weight					
Weldwood Haul Road	250 ± 200	10	73 ± 49	10	*[b]
White Court	42 ± 39	10	53 ± 43	10	NS

[a] Data obtained from ETL
[b] Symbols: NS = not significant ($p > 0.05$); * = significant at the $p < 0.05$ level; ** = highly significant at the $p < 0.01$ level.
[c] This column tests significant differences between the levels of TCDF in mountain whitefish and long-nosed suckers.

Figure 13: 2,3,7,8-TCDD/F (TEQs) ± SD in Mountain Whitefish and Long-Nosed Suckers (pg/g wet wts) from Two Sites on the Athabasca River, Spring, 1992



5.1.1.4 BCFs, BSAFs, and BSSAFs for mountain whitefish and long-nosed suckers. Calculated BCFs, BSAFs, and BSSAFs for TCDD and TCDF for mountain whitefish and long-nosed suckers caught at the Weldwood Haul Road Bridge site are summarized in Table 18. The BSAFs for 2,3,7,8-TCDD and 2,3,7,8-TCDF for mountain whitefish were three times higher than those calculated for mountain whitefish caught at the Weldwood Haul Road site in the RSS study (see Table 14). The BCFs and BSSAFs obtained for mountain whitefish at the Weldwood Haul Road site, however, were very close to those obtained in the RSS study (Tables 13, and 15, respectively). BSAFs and BSSAFs could not be made for the fish sampled at the Whitecourt site, because no sediment or suspended sediment samples were taken.

Table 18. Predicted BCFs, BSAFs, and BSSAFs for Mountain Whitefish and Long-Nosed Suckers at the Weldwood Haul Road Site.

	mountain whitefish		long-nose suckers	
	TCDD	TCDF	TCDD	TCDF
BCF(a)	7.71×10^6	7.52×10^6	0.594×10^6	2.00×10^6
BSAF(b)	52.4	35.7	1.81	9.51
BSSAF(c)	19.7	3.5	1.52	0.932

[a] BCF (lipid normalized) = concentration in fish ÷ estimated dissolved concentration in water
[b] BSAF = concentration in fish (lipid basis) ÷ bottom sediment (OC basis)
[c] BSSAF = concentration in fish (lipid) ÷ suspended sediment (OC basis)

5.2 WALLEYE AND GOLDEYE MUSCLE

Walleye and goldeye had the lowest 2,3,7,8-TCDD/F TEQs of all fish species sampled on the Athabasca River (spring 1992). The lower accumulation of 2,3,7,8-TCDD/F could be explained by such factors as different food webs and contaminant uptake parameters, and because of their location downstream from the BKM (299.8 to 633.8 km) than northern pike, mountain whitefish and long-nosed suckers (< 200 km). Slightly higher TEQs were detected in walleye sampled at Jackfish Lake and Goose Island Lake: 0.27 and 0.40 pg TEQ g^{-1}, respectively. Goldeye sampled at Jackfish Lake also contained higher level of TEQ, 0.32 pg TEQ g^{-1} (wet wt) than the Athabasca mainstem goldeyes. The reason for this is unknown. These levels are well below fish consumption guidelines of Health Canada, the guideline of 1.1 pg g^{-1} for protection of fish-eating wildlife or the interim 50 pg g^{-1} (lipid) guideline for the protection of aquatic life (CCME 1995).

6.0 CHAPTER III. RESULTS AND DISCUSSION. SPECIAL BURBOT COLLECTION. FALL - 1992

6.1 CONCENTRATION OF PCDD/Fs IN BURBOT LIVER

The levels of PCDD/Fs (pg g^{-1} (wet wt)) are summarized in Appendix C: Tables C1 to C3. The PCDD/F congeners detected and used to calculate the TEQs were 2,3,7,8-TCDD (TEF = 1), 2,3,7,8-(TEF= 0.1), 1,2,3,7,8- PeCDF (TEF = 0.05), 2,3,4,7,8-PeCDF (TEF = 0.5), 1,2,3,7,8- PeCDD (TEF = 0.5), 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9- HxCDD (TEF = 0.1), 1,2,3,4,6,7,8-HpCDD (TEF = 0.01), and OCDD (TEF = 0.001). The highest PCDD/F (TEQs) and concentrations (pg g^{-1} wet wt) were seen in the burbot livers sampled nearest to the BKMs at the confluences of Smoky/Wapiti Rivers (40 ± 27 pg TEQ g^{-1}) and Wapiti/Peace Rivers (53 ± 87 pg TEQ g^{-1}) (Figure 14). At these two locations the Health Canada guideline limits of 20 pg TEQ kg^{-1} were exceeded. Caution should be used when interpreting these results because burbot fillets have been shown to contain lower 2,3,7,8-TCDD/F (TEQs) than liver tissues. At one site downstream from the Grande Prairie BKM, burbot livers contained a mean 2,3,7,8-TCDD/TCDF (TEQ) of 42 pg g^{-1} whereas the levels in fillets were 0.36 pg g^{-1} (Swanson et al. 1992).

6.1.1 Di-. and Tri-CDD/Fs

The burbot livers generally did not contain di- and tri-CDD/Fs, unlike the mountain whitefish and northern pike muscle samples from the Athabasca River near Hinton. Trichlorofurans were detectable (4.3 ± 4.8 pg g^{-1} (wet wt)) only in samples collected at the Smoky/Peace confluence. The specific tri-CDF isomers were not identified. The low levels of di- and tri-CDD/Fs in the burbot livers suggest that these compounds are more easily metabolized and/or eliminated by burbot livers compared with the muscle tissues mountain whitefish and northern pike.

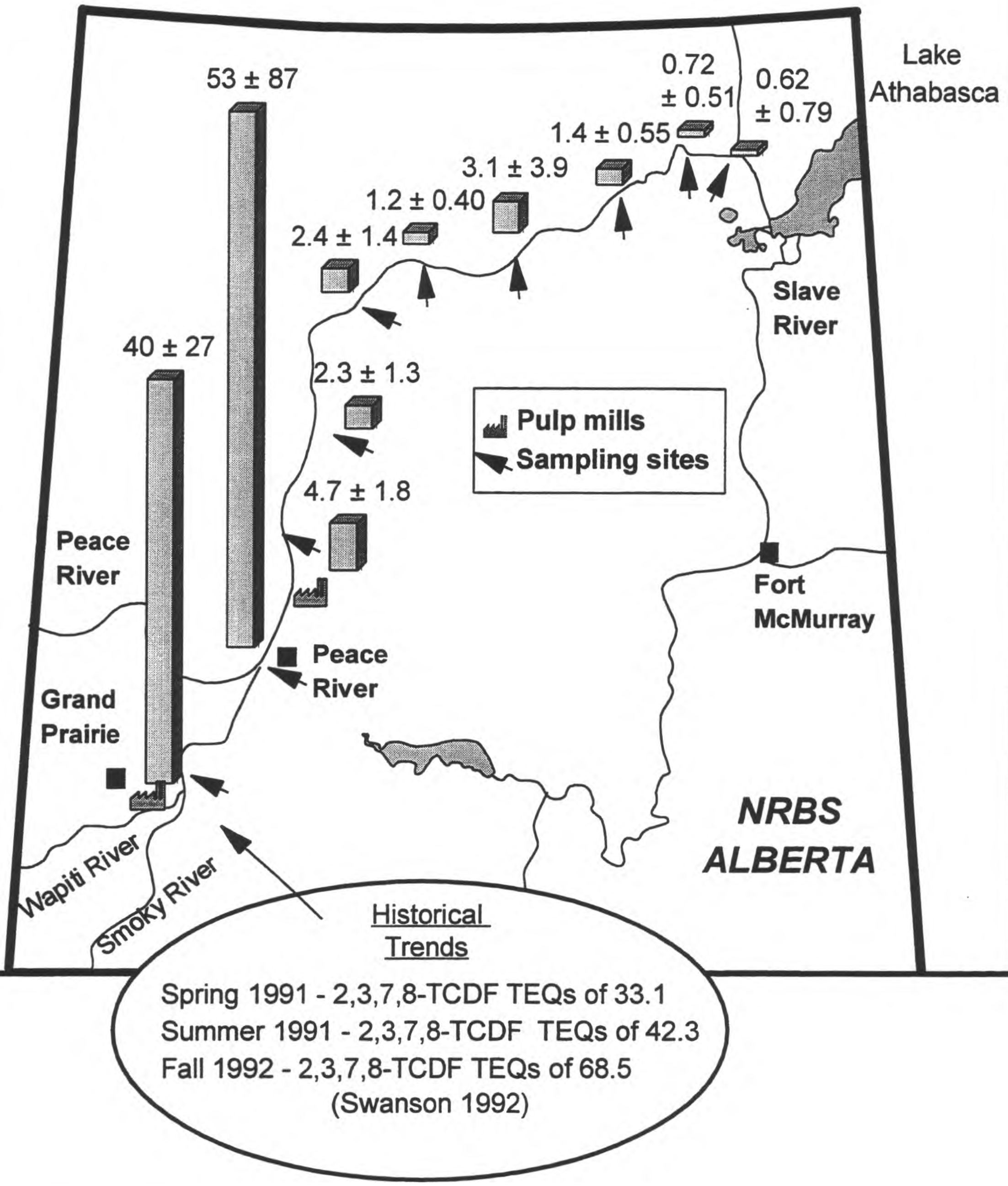
6.1.2 Tetra CDD/Fs - Octa CDD/Fs

The major PCDD/F isomers found in the burbot livers were 2,3,7,8-TCDD and 2,3,7,8-TCDF. These two congeners accounted for 41.6 to 95.7% of the TEQs for PCDD/Fs. No other tetra-CDD/Fs were detected in the burbot livers. Highest concentrations of tetra-, to octa-CDD/Fs were found in the burbot livers at sampling sites closest to the BKMs.

The only penta-CDD congener identified in burbot livers was 1,2,3,7,8-PeCDD. The two penta-CDF congeners identified (1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF) were slightly above the detection limits. Other, unidentified non-2,3,7,8-substituted pentachlorofurans were detected at a concentration greater than those obtained for either the 1,2,3,7,8-PeCDF or 2,3,4,7,8-PeCDF individually.

The only two hexa-CDD congeners detected were 1,2,3,6,7,8- and 1,2,3,7,8,9-HxCDD. No other hexa-CDD/Fs were detected. No HpCDFs or OCDFs were found in the burbot livers. Higher levels of hepta- and octa- CDD(s) were found on a wet wt basis than the tetra-, penta-, and hexa-CDDs.

Figure 14: Mean PCDD/F (TEQs) ± SD in Burbot Liver (pg/g (wet wt)) from the Peace River, Fall1992.



7.0 CONCLUSION

The Reach Specific Study on the Athabasca River downstream of Hinton has documented similar spatial trends of contamination by PCDD/Fs to those observed by Swanson et al. (1992) near the BKM at Grande Prairie on the Wapiti/Smoky systems. Highest levels of all PCDD/Fs were found in environmental samples (i.e., sediment, water, suspended sediments, invertebrates, and fish) within 50 km downstream from the town of Hinton and Weldwood of Canada Ltd. effluent. The PCDD/F levels returned to control levels in fish at the sampling sites more than 116 km downstream from the mill effluent source. The most prominent PCDD/Fs in the effluent were mono-, di- and trichlorodibenzofurans. These compounds proved to be excellent markers of BKM effluent downstream of the mill because they were present in all abiotic samples. Recent studies of surface sediments in Great Slave Lake and in Lake Athabasca have also shown the presence of 2,8-di- and 2,3,8-trichlorodibenzofuran (M. Evans, NHRI, Saskatoon, unpublished data) indicating that they are transported long distances in particle and dissolved phases. The mono-, di- and tri- PCDD/Fs were not detected in significant concentrations in fishes. Bioaccumulation studies have shown di- and trichloro-PCDD/Fs were eliminated rapidly by fish (Sijm and Opperhuizen 1988; Muir et al. 1992c). Emissions from the Hinton Combined Effluent contained 2,3,7,8-TCDD and 2,3,7,8-TCDF mainly in the particulate phase. The bioaccumulation potential of 2,3,7,8-TCDD and 2,3,7,8-TCDF is apparent from the high BCFs (1.70 to 52.5 x 10^6 for TCDD; 1.00 to 375 x 10^6 for TCDF) relative to the di- and trichlorofurans ($<10^4$).

The results from the RSS represent a "snapshot" of the environmental distribution of PCDD/Fs prevailing in the spring of 1992, prior to high water flows in the Athabasca River that occur in May and June as a result of snow melt in the Rockies. During 1993, the Weldwood of Canada BKM went to complete substitution of molecular chlorine with chlorine dioxide. This is expected to further reduce emissions of all chlorinated organics including the PCDD/Fs. Samples collected during the spring 1993 at the same locations as the 1992 RSS will provide some temporal trend information on PCDD/Fs in various environmental matrices. Samples from the spring 1993 survey have been analyzed but results are not yet available for interpretation.

2,3,7,8-TCDD/F TEQs levels in mountain whitefish and northern pike fish muscle (skinless fillet) samples monitored downstream from Hinton were lower than the Health Canada guideline limits of 20 pg g^{-1} but exceeded draft Canadian Environmental Quality guidelines proposed by CCME (1995)for protection of aquatic life (50 pg g^{-1} lipid) and for protection of fish eating wildlife (1.1 pg g^{-1}). PCDD/F TEQ concentrations in depositional and suspended sediments also exceeded CCME guidelines for sediment (0.25 pg g^{-1}). Two invertebrate samples, from the Order Trichoptera (1 km downstream of Hinton) and Order Ephemeroptera (48 km downstream of Hinton) had TCDD TEQs exceeding the Environmental Quality Guideline value for aquatic biota. PCDD/F TEQs in burbot livers at the two sampling locations nearest to the Grande Prairie BKM exceeded Health Canada guidelines for fish consumption.

Significantly higher concentrations of 2,3,7,8-TCDD and -TCDF (on a wet wt and lipid normalized basis) were seen in mountain whitefish than long-nosed suckers (one trophic level lower). It is unusual not to see a consistent relationship between trophic levels and concentrations of persistent organochlorines. Comparison with previous analyses of mountain whitefish and long-nosed suckers by Alberta Environment and the DFO National Dioxin program indicated that concentrations of TCDD and

TCDF had declined by about 2.5 fold. However, previous work was based on a very limited number of samples.

Burbot livers appear to be good indicators of the spectrum of tetra- to octa-chlorodioxins and -chlorofurans emitted to the aquatic environment. The NRBS study has demonstrated that sulphur and nitrogen isotopes (^{34}S and ^{15}N) helped to characterize mountain whitefish with unusually low PCDD/Fs by identifying mainstem and tributary feeders. Further stable isotope work on environmental samples in the Peace River may also help to explain the variability seen in PCDD/F levels in burbot livers. Measurement of the PCDD/F levels in burbot muscle would allow a comparison to be made with the levels in burbot liver (containing higher concentrations of contaminants) and with the muscle tissues of different fish species in the RSS study area collected at the same time. Results reported by Swanson et al (1992) showed very similar TEQs (33 to 69 pg g^{-1}) during 1991 and 1992 to those in the special burbot collection from 1992 (40 to 53 pg g^{-1}).

The RSS study has yielded valuable information for use in fate and food chain modelling of PCDD/Fs in the Athabasca River. The estimates of dissolved and particulate bound levels of PCDD/Fs which are essential for predicting food chain contamination in the models of Thomann et al. (1992) will be particularly useful for modelling which is now underway by the Contaminants Component. Data from the 1993 survey will also be valuable for modelling because of the anticipated decline in PCDD/F loadings to the Athabasca and Wapiti/Smoky systems as a result of process changes at the mills.

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APPENDIX A: RESULTS FROM THE RSS STUDY - SPRING - 1992

Table A1: Concentration of Mono-, Di-, Tri-CDD/Fs in Suspended Sediments (pg g^{-1} (dry wt)[a].

Congener	HCE	Obed Coal	Windfall Bridge
MCDD - Total	0.80	<0.90	0.60
2-MCDD	0.80	< 0.90	0.60
1-MCDD	< 0.40	< 0.90	< 0.40
DCDD - Total	24	22	34
27/28-DCDD	20	22	34
2,3-DCDD	2.5	1.2	1.8
TriCDD - Total	5.0	1.5	3.1
1,2,4-TriCDD	< 0.10	< 0.40	< 0.090
2,3,7-TriCDD	4.4	0.9	2.0
1,2,3-TriCDD	0.70	< 2.4	0.40
MCDF - Total	210	39	110
2-MCDF	190	30	95
4-MCDF	12	2.3	6.1
DCDF - Total	1400	110	700
2,4-DCDF	< 0.10	2.8	5.1
2,8-DCDF	1000	96	510
2,6-DCDF	90	13	45
TriCDF - Total	570	39	156
2,4,6/2,4,8-TriCDF	56	5.6	26
2,3,8-TriCDF	280	17	130

[a] Data obtained from AXYS laboratories

Table A2: Concentration of Tetra-, Penta-, Hexa-, Hepta-, and Octa-CDD/Fs in Suspended Sediments (pg g^{-1} (dry wt))[a].

Congener	HCE	Control	Weldwood Road[b]	Obed Coal[b]	Emerson Lake	Knight Bridge	Windfall Bridge
TCDD (non-2,3,7,8-)	31	0.20	0.80	1.1	2.0	2.0	1.8
2,3,7,8-TCDD	11	0.20	0.30	0.80	1.0	0.80	0.60
PeCDD	9.0	< 0.10	< 0.25	< 0.30	< 0.30	< 0.30	< 0.20
1,2,3,7,8-PeCDD	1.4	< 0.30	0.30	< 0.30	0.30	0.30	< 0.20
1,2,3,4,7,8-HxCDD	0.60	< 0.10	0.45	< 0.30	0.20	0.30	0.20
1,2,3,6,7,8-HxCDD	1.1	0.60	1.1	< 0.30	0.40	0.30	0.30
1,2,3,7,8,9-HxCDD	1.1	0.30	1.1	< 0.30	0.20	0.40	0.50
HpCDD - Total	38	12	48	14	15	14	13
1,2,3,4,6,7,8-HpCDD	18	5.5	27	6.1	7.6	6.6	5.9
OCDD	140	39	200	49	49	36	42
TCDF (non-2,3,7,8-)	110	0.60	7.7	8.1	14	12	9.2
2,3,7,8-TCDF	40	0.30	2.2	2.6	3.2	2.8	2.3
PeCDF	15	0.70	2.4	< 0.30	1.0	1.0	1.4
1,2,3,7,8-PeCDF	3.6	0.30	0.20	< 0.30	0.30	0.30	< 0.30
2,3,4,7,8-PeCDF	2.7	0.20	< 0.20	< 0.30	0.30	0.30	< 0.30
HxCDF - Total	8.6	2.1	9.3	1.7	1.3	0.70	2.3
1,2,3,4,7,8-HxCDF	1.4	0.60	< 0.70	< 0.50	< 0.30	< 0.30	< 0.30
1,2,3,6,7,8-HxCDF	0.60	0.40	<0.90	< 0.50	< 0.30	< 0.30	< 0.30
2,3,4,6,7,8-HxCDF	0.40	0.40	< 0.70	< 0.50	0.40	< 0.30	< 0.30
1,2,3,7,8,9-HxCDF	< 0.20	0.50	< 0.70	< 0.50	< 0.30	< 0.30	< 0.30
HpCDF - Total	16	4.3	22	5.2	3.3	2.6	4.5
1,2,3,4,6,7,8-HpCDF	7.3	1.9	9.8	2.2	2.7	2.5	2.2
1,2,3,4,7,8,9-HpCDF	0.40	0.50	< 0.60	< 0.70	< 0.30	< 0.30	< 0.30
OCDF	9.1	3.8	20	3.0	4.4	5.2	3.1

[a] Data obtained from Axys Laboratories [b] Mean from two samples

Table A3: Concentration of Mono-, Di-, and Tri-CDD/Fs identified in 20 L Centrifugate Water Samples (pg L^{-1})[a].

Congener	HCE	Weldwood Road	Emerson Lake	Knight Bridge[b]
MCDD - Total	<0.32	< 0.10	< 0.10	< 0.10
2-MCDD	< 0.32	< 0.10	< 0.10	< 0.10
1-MCDD	< 0.32	< 0.10	< 0.10	< 0.10
DCDD - Total	<1.6	< 0.20	< 0.20	0.80
27/28-DCDD	<1.6	0.50	1.1	0.80
2,3-DCDD	<1.6	< 0.20	< 0.20	< 0.10
TriCDD - Total	<0.38	< 0.10	< 0.10	< 0.10
1,2,4-TriCDD	<0.12	< 0.10	< 0.10	< 0.10
2,3,7-TriCDD	0.56	< 0.10	< 0.10	< 0.10
1,2,3-TriCDD	< 0.20	< 0.10	< 0.10	< 0.10
MCDF - Total	33	< 2.1	< 2.1	< 2.1
2-MCDF	31	< 2.1	< 2.1	< 2.1
4-MCDF	1.6	< 2.1	< 2.1	< 2.1
DCDF	180	2.6	1.6	0.60
2,4-DCDF	61	0.40	0.50	0.30
2,8-DCDF	150	2.6	1.6	0.60
2,6-DCDF	22	0.80	0.50	0.10
TriCDF - Total	78	1.1	0.70	0.40
2,4,6/2,4,8-TriCDF	10	0.30	0.20	0.10
2,3,8-TriCDF	36	0.50	0.30	0.20

[a] Data obtained from AXYS laboratories
[b] Sample volume was 40 L

Table A4: Concentration of Tetra-, Penta-, Hexa-, Hepta-, and Octa-CDD/Fs in 20 L Centrifuged Water Samples (pg L^{-1})[a].

Congener	HCE	Control	Weldwood Road	Obed Coal	Emerson Lake	Knight Bridge	Windfall Bridge
2,3,7,8-TCDD	0.47	< 0.020	< 0.040	< 0.020	< 0.050	< 0.020	< 0.030
1,2,3,7,8-PeCDD	< 0.11	< 0.020	< 0.090	< 0.020	< 0.090	< 0.030	< 0.030
1,2,3,4,7,8-HxCDD	< 0.15	< 0.080	< 0.10	< 0.050	< 0.070	< 0.030	< 0.050
1,2,3,6,7,8-HxCDD	< 0.15	< 0.080	< 0.10	< 0.050	< 0.070	< 0.030	< 0.050
1,2,3,7,8,9-HxCDD	< 0.15	< 0.080	< 0.10	< 0.050	< 0.070	< 0.030	< 0.050
1,2,3,4,6,7,8-HpCDD	< 0.10	< 0.10	< 0.30	< 0.20	< 0.20	< 0.080	< 0.30
OCDD	< 0.14	< 0.40	0.80	< 0.30	0.60	0.30	< 1.00
2,3,7,8-TCDF	2.7	< 0.40	0.10	< 0.4 0	0.090	< 0.020	< 0.40
1,2,3,7,8-PeCDF	< 0.10	< 0.20	< 0.070	< 0.30	< 0.070	< 0.020	< 0.20
2,3,4,7,8-PeCDF	< 0.10	< 0.20	< 0.070	< 0.30	< 0.070	< 0.020	< 0.20
1,2,3,4,7,8-HxCDF	< 0.10	< 0.20	< 0.20	< 0.30	< 0.08	< 0.020	< 0.20
1,2,3,6,7,8-HxCDF	< 0.10	< 0.20	< 0.2 0	< 0.30	< 0.080	< 0.020	< 0.20
2,3,4,6,7,8-HxCDF	< 0.10	< 0.20	< 0.20	< 0.30	< 0.080	< 0.020	< 0.20
1,2,3,7,8,9-HxCDF	< 0.10	< 0.20	< 0.20	< 0.30	< 0.080	< 0.020	< 0.20
1,2,3,4,6,7,8-HpCDF	< 0.10	< 0.20	< 0.30	< 0.20	< 0.30	< 0.070	< 0.20
1,2,3,4,7,8,9-HpCDF	< 0.10	< 0.20	< 0.30	< 0.20	< 0.30	< 0.070	< 0.20
OCDF	< 0.12	< 0.10	< 0.30	< 0.20	< 0.30	< 0.10	< 0.20
Total PCDD/F TEQs (pg L^{-1})[b]		0.28	0.33	0.37	0.20	0.060	0.29

[a] Data obtained from AXYS laboratories; [b] These TEQs calculated using detection limits for non-detect values.

Table A5: Concentration of total non-2,3,7,8-substituted Tetra-, Penta-, Hexa-, and Hepta- CDD/Fs in 20 L Centrifuged Water Samples (pg L^{-1})[a].

Congener	HCE	Control	Weldwood Road	Obed Coal	Emerson Lake	Knight Bridge	Windfall Bridge
TCDD	1.6	< 0.020	< 0.040	< 0.020	< 0.050	< 0.020	< 0.030
PeCDD	< 0.11	< 0.020	< 0.090	< 0.020	< 0.090	< 0.030	< 0.030
HxCDD	< 0.15	< 0.080	< 0.10	< 0.050	< 0.070	< 0.030	< 0.050
HpCDD	< 0.10	< 0.10	< 0.30	< 0.20	< 0.20	< 0.080	< 0.30
TCDF	48	< 0.40	0.20	< 0.4 0	0.20	< 0.020	< 0.40
PeCDF	< 0.10	< 0.20	< 0.070	< 0.30	< 0.070	< 0.020	< 0.20
HxCDF	< 0.10	< 0.20	< 0.20	< 0.30	< 0.080	< 0.020	< 0.20
HpCDF	< 0.10	< 0.20	< 0.30	< 0.20	< 0.30	< 0.070	< 0.20

[a] Data obtained from AXYS laboratories

Table A6: Concentration of Tetra-, Penta-, Hexa-, Hepta-, and Octa-CDD/Fs in Biofilm Samples ($pg\ g^{-1}$)[a].

Congener	Control	Weldwood Road	Obed Coal	Emerson Lake	Emerson Lake [b]	Knight Bridge	Windfall Bridge
2,3,7,8-TCDD	< 0.010	< 2.1	< 0.20	< 2.3	< 2.7	<3.8	< 0.30
1,2,3,7,8-PeCDD	< 0.010	< 1.1	< 0.20	< 3.3	< 4.4	< 5.5	< 0.30
1,2,3,4,7,8-HxCDD	< 0.040	< 6.6	< 0.50	< 9.5	< 11	< 15	< 0.40
1,2,3,6,7,8-HxCDD	< 0.040	< 6.3	< 0.50	< 9.8	< 12	< 15	< 0.40
1,2,3,7,8,9-HxCDD	< 0.040	< 6.5	< 0.50	< 9.6	< 12	< 15	< 0.40
1,2,3,4,6,7,8-HpCDD	< 1.4	< 10	1.8	< 21	< 42	< 47	< 1.2
OCDD	10	< 110	< 4.1	< 82	< 250	< 100	< 3.4
2,3,7,8-TCDF	< 0.10	< 0.90	0.38	<1.9	<1.9	< 3.2	< 0.10
1,2,3,7,8-PeCDF	< 0.10	< 0.70	< 0.10	< 1.9	< 2.6	< 4.2	< 0.20
2,3,4,7,8-PeCDF	< 0.10	< 1.0	< 0.10	< 2.3	< 3.3	< 4.3	< 0.20
1,2,3,4,7,8-HxCDF	< 0.40	< 2.7	< 0.30	< 4.6	< 4.3	< 8.1	< 0.30
1,2,3,6,7,8-HxCDF	< 0.30	< 2.4	< 0.30	< 2.5	< 4.6	< 6.2	< 0.30
2,3,4,6,7,8-HxCDF	< 0.50	< 5.5	< 0.30	< 7.2	< 80	< 9.7	< 0.40
1,2,3,7,8,9-HxCDF	< 0.70	< 8.5	< 0.50	< 9.5	< 13	< 22	< 0.50
1,2,3,4,6,7,8-HpCDF	< 0.50	< 8.0	< 0.60	< 12	< 19	< 26	< 0.50
1,2,3,4,7,8,9-HpCDF	< 1.6	< 14	< 0.90	< 18	< 42	< 48	< 0.90
OCDF	< 2.4	< 16	< 2.1	< 75	< 190	< 100	< 1.7
Percent lipid	0.056	0.020	0.13	0.16	0.16	0.10	0.14
Percent moisture	48	83	73	87	87	89	62

[a] Data obtained from AXYS laboratories [b] Duplicate sample

Table A7: Concentration of Mono-, Di-, Tri-CDD/Fs in Depositional Sediments (pg g^{-1} (dry wt))[a].

Congener	Control	Obed Coal
2-MCDD	< 0.60	< 0.90
1-MCDD	< 0.60	< 0.90
27/28-DCDD	3.0	3.0
2,3-DCDD	< 0.60	< 2.1
TriCDD	0.40	0.50
1,2,4-TriCDD	< 0.20	< 0.30
2,3,7-TriCDD	< 0.20	< 0.30
1,2,3-TriCDD	< 0.20	< 0.30
MCDF	2.3	11
2-MCDF	0.90	8.3
4-MCDF	0.30	1.0
2,4-DCDF	< 0.10	< 0.10
2,8-DCDF	1.9	36
2,6-DCDF	< 0.10	< 0.10
TriCDF	< 0.10	12
2,4,6/2,4,8-TriCDF	0.30	1.7
2,3,8-TriCDF	0.60	5.2

[a] Data obtained from AXYS laboratories

Table A8: Concentrations of Di-, Tri-CDD/CDFS (pg g^{-1} (dry wt)) in Depositional Sediments[a].

Sampling Sites	2,7-CDD	2,8-CDD	2,3,7,-CDD	TriCDD[b]	2,8-CDF	2,3,8-CDF	TriCDF[c]
Weldwood Haul Road	1.8	< 0.10	< 0.10	< 0.10	16	6.3	2.9
Obed Coal Bridge	2.2	< 0.10	< 0.10	< 0.10	26	8.9	4.8
Emerson Lake	3.2	< 0.10	< 0.10	< 0.10	55	25	7.0

[a] Data obtained from ETL laboratories
[b] Total TriCDDs
[c] Total TriCDFs

Table A9: Congener Profile of Tetra- and Hepta-CDD/Fs in Depositional Sediments (pg g^{-1} (dry wt))[a].

Congener	Control	Obed Coal	Windfall Bridge
T_4CDD	< 0.10	< 0.10	< 0.10
1,2,3,4,6,7,9-HpCDD	2.4	< 0.60	3.1
2,4,6,8-TCDF	< 0.1	0.60	< 0.10
1,2,7,8-TCDF	< 0.1	0.50	1.1
1,2,8,9-TCDF	< 0.1	< 0.10	1.0
1,2,3,4,6,8,9-HpCDF	1.1	1.6	1.4
1,2,3,4,6,7,9-HpCDF	< 0.2	< 0.5	< 0.20

[a] Data obtained from AXYS laboratories

Table A10: Concentration of Tetra-, Penta-, Hexa-, Hepta-, and Octa-CDD/Fs in Depositional Sediments (pg g^{-1} (dry wt))[a].

Congener (AXYS lab #)	Control 2815-15	Weldwood Road 2815-34	Obed Coal 2815-35	Obed Coal[b] 2815-16	Emerson Lake 2815-47	Windfall Bridge 2815-19
T_4CDD	<0.10	0.30	2.6	<0.10	2.3	0.40
2,3,7,8-TCDD	< 0.10	0.20	0.30	0.40	0.50	0.40
1,2,3,7,8-PeCDD	< 0.20	<0.20	< 0.20	< 0.30	< 0.10	< 0.20
1,2,3,4,7,8-HxCDD	< 0.20	< 0.10	< 0.50	< 0.30	< 0.30	< 0.60
1,2,3,6,7,8-HxCDD	< 0.20	< 0.10	< 0.50	< 0.30	< 0.30	< 0.60
1,2,3,7,8,9-HxCDD	< 0.20	< 0.10	< 0.50	< 0.30	< 0.30	< 0.60
HpCDD	4.3	7.8	5.8	2.0	3.4	5.4
1,2,3,4,6,7,8-HpCDD	1.9	3.6	2.8	2.0	25	2.3
OCDD	13	20	19	17	25	13
T_4CDF	<0.10	0.70	1.7	2.0	3.1	3.2
2,3,7,8-TCDF	< 0.10	0.40	0.80	0.90	1.9	2.2
1,2,3,7,8-PeCDF	< 0.20	< 0.10	< 0.10	< 0.20	< 0.10	< 0.10
2,3,4,7,8-PeCDF	< 0.20	< 0.10	< 0.10	< 0.20	< 0.10	< 0.10
1,2,3,4,7,8-HxCDF	< 0.20	< 0.20	< 0.40	< 0.30	< 0.40	< 0.10
1,2,3,6,7,8-HxCDF	< 0.20	< 0.20	< 0.40	< 0.30	< 0.40	< 0.10
2,3,4,6,7,8-HxCDF	< 0.20	< 0.20	< 0.40	< 0.30	< 0.40	< 0.10
1,2,3,7,8,9-HxCDF	< 0.20	< 0.20	< 0.40	< 0.30	< 0.40	< 0.10
HpCDF	2.0	2.3	2.1	1.6	2.1	1.2
1,2,3,4,6,7,8-HpCDF	0.90	0.90	0.80	0.70	0.80	0.80
1,2,3,4,7,8,9-HpCDF	< 0.20	< 0.20	< 0.20	< 0.50	< 0.20	<0.20
OCDF	1.1	1.7	1.5	1.1	1.8	1.8

[a] Data obtained from AXYS laboratories [b] Duplicate Sample

Table A11: Levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF (pg g^{-1} (dry wt)) and Fraction of Organic Carbon in Depositional Sediments.

Sampling Sites	Concentration of 2,3,7,8-TCDD pg/g (dry wt)		Concentration of 2,3,7,8-TCDF pg/g (dry wt)		Fraction of Organic Carbon[c]
	[a]	[b]	[a]	[b]	
U/S (Control)	< 0.10	ND[d]	< 0.10	ND	0.027
Weldwood Haul Rd.	0.20	< 0.30	0.40	< 0.20	0.055
Obed Coal Bridge	0.35	0.30	0.85	1.0	0.037
Emerson Lake	0.50	0.50	1.9	2.1	0.046
Knight Bridge	ND	ND	ND	ND	0.013
Windfall Bridge	0.4	ND	3.2	ND	0.022

[a] Data obtained from AXYS
[b] Data obtained from ETL
[c] Data obtained from Duncan (1992)
[d] Symbol: ND = No Data

Table A12: Concentration of Lower Chlorinated PCDD/Fs Detected in Erosional Sediments (pg g^{-1}, dry wt)[a].

Congener	Control	Obed Coal	Windfall Bridge
2,8,9-TCDD	< 0.10	2.2	< 0.10
1,2,3,7/1,2,3,8-TCDD	< 0.10	0.18	< 0.10
Total MCDF	5.3	41	35
2-MCDF	2.2	31	1.6
4-MCDF	0.80	3.0	18
Total DCDF	< 0.10	110	28
2,4-DCDF	< 0.10	2.6	2.6
2,8-DCDF	1.9	9.3	28
2,6-DCDF	< 0.10	21	< 0.05
Total tri-CDF	0.80	51	35
2,4,6/2,4,8-TriCDF	0.50	4.6	1.6
2,3,8-TriCDF	1.5	24	18
2,4,6,8-TCDF	< 0.10	1.7	< 0.10
1,2,7,8-TCDF	< 0.10	2.1	1.1

[a] Data obtained from AXYS laboratories. Only congeners which were detected in one or more samples are reported.

Table A13: Concentration of Higher Chlorinated PCDD/Fs Detected in Erosional Sediments (pg g^{-1} (dry wt))[a].

Congener	Control	Obed Coal	Windfall Bridge
T_4CDD	< 0.10	3.7	0.50
2,3,7,8-TCDD	< 0.10	1.3	0.50
PeCDD - Total	< 0.20	< 0.20	< 0.20
1,2,3,7,8-PeCDD	< 0.20	< 0.02	< 0.20
HxCDD- Total	< 0.20	0.20	< 0.30
1,2,3,4,7,8-HxCDD	< 0.20	< 0.20	< 0.30
1,2,3,6,7,8-HxCDD	< 0.20	0.30	< 0.30
1,2,3,7,8,9-HxCDD	< 0.20	< 0.20	< 0.30
HpCDD - Total	5.8	7.7	7.9
1,2,3,4,6,7,8-HpCDD	2.4	3.6	2.5
OCDD	18	27	15
T_4CDF	< 0.10	7.5	3.7
2,3,7,8-TCDF	< 0.10	3.7	2.0
PeCDF - Total	< 0.20	0.50	< 0.20
1,2,3,7,8-PeCDF	< 0.20	0.20	< 0.20
2,3,4,7,8-PeCDF	< 0.20	< 0.20	< 0.20
HxCDF - Total	< 0.20	0.70	< 0.30
1,2,3,4,7,8-HxCDF	< 0.20	0.20	< 0.30
1,2,3,6,7,8-HxCDF	< 0.20	< 0.20	< 0.30
2,3,4,6,7,8-HxCDF	< 0.20	< 0.20	< 0.30
1,2,3,7,8,9-HxCDF	< 0.20	< 0.20	< 0.30
HpCDF - Total	0.70	3.3	2.5
1,2,3,4,6,7,8-HpCDF	0.70	1.4	1.1
1,2,3,4,7,8,9-HpCDF	< 0.30	< 0.20	< 0.30
OCDF	1.7	3.0	1.3

[a] Data obtained from AXYS

Table A14: Concentration of 2,3,7,8-TCDD and 2,3,7,8-TCDF in Suspended Sediments at Five Sampling Sites Downstream from the Weldwood Pulp and Paper Mill[a].

Sampling Sites	Concentration of 2,3,7,8-TCDD pg/g (dry wt)	Concentration of 2,3,7,8-TCDF pg/g (dry wt)	Fraction of Organic Carbon[c]
U/S (Control)	[b]	[b]	0.025
Weldwood Haul Road	0.30	2.2	0.031
Obed Coal Bridge	0.80	2.6	0.029
Emerson Lake	1.0	3.2	0.035
Knight Bridge	0.80	2.8	0.036
Windfall Bridge	0.60	2.3	0.034

[a] Data obtained from ETL
[b] Symbol: ND = No Data.
[c] Data obtained from Dalton (1992)

Table A15. Physical Attributes of Suspended Sediment [a].

Site	Percent Total Carbon	Percent Organic Carbon	Percent Sand	Percent Silt	Percent Clay
Control	5.9	2.5	0.00	61	39
HCE	29	27	0.53	23	77
Weldwood Haul Bridge	6.9	3.1	5.8	53	42
Obed Coal Br.	7.3	2.9	2.3	53	45
Emerson Lake Br.	7.6	3.5	0.87	39	60
Knight Br.	6.2	3.6	1.4	36	62
Windfall Br.	6.3	3.4	2.2	24	74

[a] Data obtained from a report by Dalton (1992).

Table A16: Concentration of 2,3,7,8-TCDD/F pg g^{-1} (wet wt) for Three Orders of Invertebrates: O. Plecoptera, O. Ephemeroptera, and O. Trichoptera[a].

	O. Plecoptera		O. Ephemeroptera		O. Trichoptera	
Sample Site	TCDD	TCDF	TCDD	TCDF	TCDD	TCDF
U/S of Hinton	<0.50	< 0.50	< 0.60[c]	< 0.50[c]	(d)	(d)
Weldwood Haul Road	3.6	6.0	2.2	6.8	6.7	13
Obed Coal Bridge	0.60[1]	1.4[1]	1.0[c]	3.6[c]	< 1.2[e]	< 0.9[e]
Emerson Lake	< 0.95	< 8.0	5.8	13	< 4.0	4.8
Knight Bridge	< 1.0	< 1.8	< 2.4	< 9.5	3.6	9.0
Windfall Bridge	0.50[b]	< 0.40[b]	< 0.50[c]	1.4[c]	0.50[e]	< 0.40[e]

[a] Data obtained from ETL laboratories
[b] Stoneflies
[c] Mayflies
[d] Symbol: ND = No Data
[e] Caddisflies

Table A17: Concentrations of Di-, Tri-CDD/Fs (pg g^{-1} (wet wts)) in Mountain Whitefish Muscle from Six Sites on the Athabasca River, Spring 1992[a].

Location	Number in Sample	2,7/2,8-DiCDD	2,3,8-TriCDF	TriCDF[b]
Upstream	4	5.5 ± 4.9	0.83 ± 0.050	0.83 ± 0.050
Weldwood Haul Rd.	10	1.8 ± 1.2	1.8 ± 0.65	1.3 ± 0.70
Obed Coal Bridge	1	1.1	0.9	0.9
Emerson Lake	10	0.87 ± 0.41	2.1 ± 1.2	1.3 ± 0.49
Knight Bridge	9	0.90 ± 0.19	0.80 ± 0.39	0.54 ± 0.26
Windfall Bridge	3	0.47 ± 0.058	0.40 ± 0.20	0.23 ± 0.058

[a] Data obtained from ETL laboratories
[a] Total TriCDFs

Table A18: Concentrations of Di-, Tri-CDD/Fs (pg g^{-1} (wet wts)) in Northern Pike Muscle from Three Sites on the Athabasca River, Spring 1992[a].

Location	Number in Sample	2,7/2,8-DiCDD	2,3,8-TriCDF	TriCDF[a]
Weldwood Haul Rd.	2	1.1 ± 0.71	0.60 ± 0.14	0.50 ± 0.28
Emerson Lake	1	1.2	0.50	0.50
Knight Bridge	10	2.8 ± 3.9	0.61 ± 0.17	0.61 ± 0.17

[a] Data obtained from ETL laboratories
[a] Total TriCDFs

APPENDIX B: RESULTS FROM THE LOWER ATHABASCA RIVER - SRING - 1992

Table B1: Concentrations of 2,3,7,8-TCDD (± SD) in Walleye and Goldeye Muscle from the Athabasca River, Spring 1992.

	Walleye		Goldeye	
Location[a]	Conc. pg/g (wet wt)	Sample Size	Conc. pg/g (wet wt)	Sample Size
km 633.8	0.20	1	0.10	2
km 630	0.10 ± 0.00	2	0.071 ± 0.10	2
km 627	0.12 ± 0.041	6	0.15 ± 0.071	2
km 299.9	0.10 ± 0.00	10	0.13 ± 0.049	7
km 230.4	0.13 ± 0.058	3	0.19 ± 0.12	7
Jackfish Lake	0.21 ± 0.15	9	0.22 ± 0.13	13
Goose Island	0.38 ± 0.096	4	ND	ND

[a] km U/S river mouth

Table B2. Concentrations of 2,3,7,8-TCDF (± SD) in Walleye and Goldeye Muscle from the Athabasca River, Spring 1992.

	Walleye		Goldeye	
Location[a]	Conc. pg/g (wet wt)	Sample Size	Conc. pg/g (wet wt)	Sample Size
km 633.8	0.10	1	0.10 ± 0.00	2
km 630	0.30 ± 0.00	2	0.071 ± 0.10	2
km 627	0.13 ± 0.052	6	0.15 ± 0.071	2
km 299.9	0.11 ± 0.032	10	0.19 ± 0.11	7
km 230.4	0.30 ± 0.26	3	0.16 ± 0.11	7
Jackfish Lake	1.1 ± 2.0	9	0.51 ± 0.13	13
Goose Island	0.15 ± 0.058	4	--	--

[a] km U/S river mouth

APPENDIX C: SPECIAL BURBOT COLLECTION RESULTS - FALL - 1992

Table C1: Concentration of PCDDs (pg g^{-1} (wet wts)) in burbot livers, Peace River, Spring 1992.

Km	Sample Size	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD
Slave River	1	< 0.20	< 0.50	< 0.60	< 0.60	< 2.0	< 3.4
0	2	< 0.20	< 0.25	< 0.40	< 0.35	< 0.40	< 2.7
17	2	< 0.25	< 0.35	< 0.65	< 0.55	< 1.1	< 1.25
312	3	0.53 ± 0.57	0.20 ± 0.0	0.90 ± 0.56	0.50 ± 0.10	1.5 ± 0.56	4.6 ± 0.20
348	10	1.2 ± 1.5	1.5 ± 2.0	2.4 ± 3.2	2.6 ± 3.5	4.0 ± 0.44	9.7 ± 9.6
396	10	0.32 ± 0.14	0.41 ± 0.19	1.2 ± 0.82	0.54 ± 0.20	1.4 ± 0.48	5.2 ± 3.5
587	10	0.79 ± 0.74	0.42 ± 0.18	0.84 ± 0.21	0.83 ± 0.30	1.5 ± 0.30	5.0 ± 2.9
674	10	0.53 ± 0.27	0.62 ± 0.35	1.1 ± 0.56	0.86 ± 0.28	2.6 ± 1.2	6.3 ±3.2
812	10	0.96 ± 0.33	0.56 ± 0.36	1.9 ± 1.1	0.81 ± 0.42	2.2 ± 1.3	11 ± 10
915 (Wapiti)	10	28 ± 44	1.1 ± 0.82	6.1 ± 7.4	1.5 ± 1.4	4.0 ± 3.3	8.9 ± 17
982 (Smoky)	10	16 ± 12	1.0 ± 0.65	13 ± 11	1.9 ± 1.3	5.4 ± 3.5	6.9 ± 6.2

Table C2. Concentration of PCDFs (pg g^{-1} (wet wts)) in Burbot Livers, Peace River, Spring 1992.

Km	Sample Size	2,3,7,8-TCDF	Homologue TCDF	1,2,3,7,8-PeCDD	2,3,4,7,8-PeCDD	Homologue PeCDD
Slave	1	2.2	< 0.10	< 0.30	< 0.30	< 0.30
0	2	1.20	< 0.10	< 0.15	< 0.15	< 0.15
17	2	0.45	< 0.10	< 0.20	< 0.20	< 0.20
312	3	6.80 ± 4.6	2.7 ± 1.0	0.23 ± 0.58	0.23 ± 0.058	0.87 ± 1.1
348	10	0.93 ± 0.58	1.0 ± 0.98	0.91 ± 1.2	0.92 ± 1.2	1.0 ± 1.2
396	10	3.3 ± 2.4	0.60 ± 0.54	0.28 ± 0.10	0.28 ± 0.092	0.56 ± 0.57
587	10	9.8 ± 8.7	1.3 ± 1.1	0.43 ± 0.23	0.41 ± 0.21	0.52 ± 0.34
674	10	7.3 ± 10	0.88 ± 1.4	0.88 ± 0.51	0.89 ± 0.51	0.97 ± 0.50
812	10	27 ± 18	4.0 ± 2.4	0.64 ± 0.36	0.68 ± 0.40	1.3 ± 1.3
915 (Wapiti)	10	240 ± 420	4.1 ± 6.6	1.4 ± 2.0	1.7 ± 2.5	2.4 ± 5.2
982 (Smoky)	10	210 ± 180	0.51 ± 0.68	3.8 ± 3.4	1.2 ± 0.80	0.94 ± 0.60

Table C3: Burbot liver TEQs (pg g^{-1} (wet wts)) from the Peace River, Spring 1992.

Congener	I-TEQ	km 0	km 17	km 312	km 348	km 396	km 587	km 674	km 812	Km 915	Km 982
2,3,7,8-TCDD	1	0.2	0.25	0.53	1.18	0.32	0.79	0.53	0.96	28	16
2,3,7,8-TCDF	0.1	0.12	0.045	0.68	0.09	0.33	0.98	0.73	2.74	23	21
1,2,3,7,8-PeCDF	0.05	0.0075	0.01	0.10	0.73	0.21	0.21	0.31	0.28	0.55	0.52
2,3,4,7,8-PeCDF	0.5	0.075	0.1	0.011	0.046	0.014	0.022	0.044	0.032	0.07	0.19
1,2,3,7,8-PeCDD	0.5	0.13	0.18	0.12	0.46	0.14	0.21	0.45	0.34	0.86	0.61
1,2,3,6,7,8-HxCDD	0.1	0.35	0.065	0.090	0.24	0.12	0.084	0.11	0.19	0.61	1.3
1,2,3,7,8,9-HxCDD	0.1	0.04	0.55	0.050	0.26	0.054	0.083	0.086	0.081	0.15	0.19
1,2,3,4,6,7,8-HpCDD	0.01	0.06	0.011	0.015	0.040	0.014	0.015	0.026	0.022	0.040	0.054
OCDD	0.001	0.0027	0.0013	0.0046	0.0097	0.0052	0.0050	0.0063	0.0011	0.0089	0.0069
Total TEQ[a]		0.62	0.72	1.4	3.1	1.2	2.4	2.3	4.7	53	40
% 2,3,7,8-TCDD/F		52	41	76	42	54	74	55	80	96	93
% non 2,3,7,8-tetra		48	59	24	58	46	26	45	20	4.3	7.2

[a] These TEQs calculated using detection limits for non-detect values.

APPENDIX D: TERMS OF REFERENCE

NORTHERN RIVER BASINS STUDY

TERMS OF REFERENCE

Project 2602-B1: Regulatory Requirements for Nutrient Effluent Discharges

I. Objective

The purpose of this project is to prepare a report that reviews effluent and instream nutrient guidelines/objectives, both in Canada and internationally.

II. Requirements

1) Compile and review information from Alberta, Canada and other jurisdictions on effluent and instream nutrient quality objectives/guidelines as well as the critieria (case/method, etc.) for selecting these objectives/guidelines. Regulatory requirements for nutrient loading from pulp mills should be examined where possible.

2) Based on the information assembled in 1, above, prepare a comprehensive synthesis report on criteria for the setting of nutrient quality objectives from various jurisdictions. The report should clearly state the criteria upon which the regulatory requirements are based and the parameters measured by regulatory agencies for monitoring nutrient loads. The report is also to include a brief summary of the general effects of nutrient loading on aquatic (river) ecosystems. The report should also clearly state the regulatory requirements imposed on nutrient loads from licensed discharges in the Peace, Athabasca and Slave river systems.

III. Reporting Requirements

1) Prepare a comprehensive synthesis report on the regulatory requirements of various jurisdictions for the setting of nutrient quality objectives. The report should contain tables that compare and contrast regulatory requirements in various jurisdictions.

2) Ten copies of the draft report are to be submitted to the Project Liaison Officer (Greg Wagner, Office of the Science Director, Northern River Basins Study: phone (403) 427-1742, fax (403) 422-3055) by April 23rd, 1993.

3) Three weeks after the receipt of review comments the Consultant is to submit ten cerlox bound copies and two camera-ready originals of the final report to the Project Liaison Officer. An electronic copy of the report, in Word Perfect 5.1 format, is to be submitted to the Project Liaison Officer along with the final report. The final report is to contain a table of contents, list of figures (if appropriate), list of tables (if appropriate), acknowledgements, executive summary and an appendix containing the Terms of Reference for this contract.