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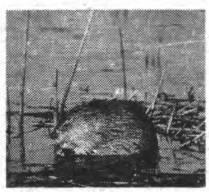
Northern River Basins Study



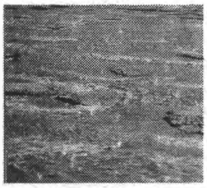




NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 130

ENVIRONMENTAL CONTAMINANTS IN WATER AND SEDIMENTS: PCDDs, PCDFs AND RESIN ACIDS, ATHABASCA RIVER BASIN FEBRUARY TO MAY, 1993





DATE DUE

Prepared for the
Northern River Basins Study
under Project 5313-E1

by

Robert W. Crosley
Environmental Conservation Branch
Environment Canada

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 130

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PREFACE:

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

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

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

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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
(Dr. Fred J. Wrona, Science Director)

16 May 96
(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. Larkin
(Dr. P. A. Larkin, Ph.D., Chair)

May 10/96
(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
(Lucille Partington, Co-chair)

May 9/96
(Date)

Robert McLeod.
(Robert McLeod, Co-chair)

May 21/96
(Date)

ENVIRONMENTAL CONTAMINANTS IN WATER AND SEDIMENTS: PCDDs, PCDFs AND RESIN ACIDS, ATHABASCA RIVER BASIN, FEBRUARY TO MAY, 1993

STUDY PERSPECTIVE

> ***Related Study Questions***
>
> *4a) 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?*
>
> *4b) Are toxins such as dioxins, furans, mercury, etc. increasing or decreasing and what is their rate of change?*
>
> *13b) What are the cumulative effects of man-made discharges on the water and aquatic environment?*

In response to water quality concerns due to expansion of the pulp and paper industry, Alberta Environmental Protection (AEP) has conducted annual winter synoptic surveys of water and sediment in the Athabasca River basin since 1988. River-borne sediments, in particular, have been found to transport and accumulate contaminant compounds, which in turn can be transferred through the food chain from bottom-dwelling invertebrates to larger predatory species of fish. In 1992, a 200 km reach of the Athabasca River between Hinton and Whitecourt was investigated intensively by the Northern River Basins Study to determine the levels of pulp mill related contaminants in water, sediments and biota. This initial survey documented detectable concentrations of several dioxins, furans and resin acids. The levels were many times higher in sediments than in water and, for some particular compounds, tended to persist with distance downstream. This report documents a follow-up investigation to gain a better understanding of contaminant concentrations and their distribution in the Athabasca River basin, by supplementing the data collected in the 1993 winter synoptic survey by AEP.

This project report presents the analytical results and spatial trends for polychlorinated dibenzo-*p*-dioxins, dibenzofurans and resin acids in water and sediment samples collected in 1993. Suspended sediments and water were collected at 23 mainstem, tributary and effluent (four pulp mills and three sewage effluents) sampling locations during winter low flow conditions; February to March. Depositional sediments were collected at eight mainstem Athabasca River locations in early May, shortly after ice-out.

Low concentrations of dioxins and furans (primarily lower chlorinated congeners) were detected in Athabasca River water, with some persisting for 230 km downstream of Hinton. Detectable concentrations of most dioxins and furans were reported in suspended and depositional sediment from the majority of effluent, mainstem and tributary locations. Although the spatial trends were very similar, levels of dioxins and furans remained higher in suspended than depositional sediments at all mainstem and tributary sites. Mass flux of most dioxins and furans shows an increased flux at sites immediately downstream of Hinton, followed by a complex variable trend due to a combination of slowly reducing concentration, tributary input, and changes in suspended sediment flux. Similarly, concentrations of resin acids were much higher in suspended sediments than in depositional sediments, with levels falling steadily in the mainstem river after the initial input at Hinton. Only for pimaric acid and total chlorinated resin acids was the observed mass flux in suspended sediments considerably more at the farthest downstream site than the upstream control site. Tributary inputs of resin acids remained lower than the values found at adjacent sites on the mainstem Athabasca River.

Similar to other studies, suspended sediments were found to be an important transport medium for dioxins, furans and resin acids. The data presented and described by this project will be incorporated into a synthesis report addressing the distribution of contaminants within these northern rivers. This document will provide the necessary interpretation and comparison with other studies dealing with contaminants in water and sediment downstream of pulp mills. In addition, results from this project will be incorporated into contaminant fate and food chain models being developed for these river systems.

REPORT SUMMARY

This report presents results for polychlorinated dibenzo-p-furans (PCDD), polychlorinated dibenzofurans (PCDF), and resin acids in water, suspended sediments, and depositional sediments collected from effluents, tributaries, and mainstem Athabasca River locations during February-March, 1993. The collections were commissioned by the Northern River Basins Study and conducted by Environment Canada, simultaneously with an Alberta Environmental Protection winter synoptic survey of the Athabasca River.

PCDD/F and resin acid concentrations and calculated contaminant mass loadings are presented. The contaminant loadings from seven effluent sources (one bleached kraft effluent, three chemical-thermomechanical pulp effluents, and three sewage treatment effluents) are compared. In-stream concentration-contaminant flux trends, and contaminant persistence are discussed.

ACKNOWLEDGEMENTS

The sample collections were carried out by Jim Syrgiannis, Heather Craig, and Robert Crosley of Ecological Research Division; Steve Smith and Ross Neureuther of Technical Operations, National Water Research Institute; and Scott Teed, Ecosystem Health Branch. Leigh Noton of Alberta Environmental Protection supervised the synoptic survey, and provided coordination between AEP and Environment Canada employees. Brian Brownlee (National Water Research Institute) provided technical assistance and equipment loans. Bill Gummer (Ecological Research Division) coordinated the work on behalf of the Northern River Basins Study. The analyses were supervised by George Duncan (National Water Research Institute) and Laurie Phillips (AXYS Analytical).

TABLE OF CONTENTS

REPORT SUMMARY I
ACKNOWLEDGEMENTS ii
TABLE OF CONTENTS iii
LIST OF TABLES iv
LIST OF FIGURES v

1.0 **INTRODUCTION** 1

2.0 **METHODS** 1
2.1 GENERAL 1
2.2 FIELD METHODS 3
2.2.1 Suspended Sediment Collection 3
2.2.2 Water Sample Collection and Field Extraction 3
2.2.3 Depositional Sediments 5
2.3 LABORATORY METHODS 6
2.3.1 Analytical Program 6
2.3.2 Particle Size and Carbon Analyses 6
2.3.3 PCDD/F Analyses 7
2.3.4 Resin Acid Analyses 7

3.0 **STUDY AREA** 7
3.1 GENERAL 7
3.2 EFFLUENTS 8

4.0 **RESULTS AND DISCUSSION** 9
4.1 SEDIMENT FLUX CALCULATIONS AND MASS BALANCES 9
4.2 QUALITY CONTROL 10
4.3 PARTICLE SIZE AND ORGANIC CARBON 11
4.4 POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 13
4.4.1 General 13
4.4.2 PCDD/Fs in Water 14
4.4.3 PCDD/Fs in Suspended Sediments and Depositional Sediments 17
4.5 RESIN ACIDS 30
4.5.1 General 30
4.5.2 Resin Acids in Suspended and Depositional Sediments 30

5.0 **REFERENCES** 42

APPENDIX A: TERMS OF REFERENCE 43
APPENDIX B: TABLES OF ANALYTICAL RESULTS 44

LIST OF TABLES

1. Suspended Sediment/Centrifugate Collection Sites, Winter 1993 Synoptic Survey 4
2. Depositional Sediment Collection Sites, Winter 1993 Synoptic Survey 6
3. Estimated Water and Sediment Dilution Factors for Effluents, Winter 1993 Synoptic Survey 9
4. Pressure Container Extraction Surrogate Recovery 11
5. Particle Size and Organic Carbon, Suspended and Depositional Sediments, February-March 1993 12
6. PCDD/F International Toxicity Equivalency Factors (I-TEFs) 13
7. Comparison of PCDD/F Results in Centrifugate from HCE (May 21, 1992 and February 11, 1993) 14
8. PCDD/F Congener Group Results in Centrifugate, CTMP and STP Effluents 15
9. PCDD/F Congener Group Results in Centrifugate, Mainstem Athabasca River 16
10. Suspended Sediment Mass Balance, February-March 1993 18
11. Mass Balance, D_2CDD in Suspended Sediment, February-March 1993 19
12. Total T_4CDD and 2,3,7,8-T_4CDD in Suspended Sediments, March-April 1992 and February-March 1993 21
13. Total T_4CDD and 2,3,7,8-T_4CDD in Depositional Sediments, March-April 1992 and February-March 1993 22
14. Mass Balance, T_4CDD in Suspended Sediment, February-March 1993 22
15. Mass Balance, O_8CDD in Suspended Sediment, February-March 1993 24
16. Mass Balance, D_2CDF in Suspended Sediment, February-March 1993 26
17. Mass Balance, T_4CDF in Suspended Sediment, February-March 1993 28
18. Mass Balance, Pimaric Acid in Suspended Sediment, Winter 1993 Synoptic Survey . . 31
19. Mass Balance, Isopimaric Acid in Suspended Sediment, February-March 1993 33
20. Mass Balance, Dehydroabietic Acid in Suspended Sediment, February-March 1993 . . . 35
21. Mass Balance, Abietic Acid in Suspended Sediment, February-March 1993 37
22. Mass Balance, Total Chlorinated Resin Acids in Suspended Sediment, February-March 1993 39
23. Percent Change in Resin Acid Concentration between Weldwood Haul Bridge and Windfall Bridge 41

LIST OF FIGURES

1. Sampling Locations for Suspended and Depositional Sediments, Winter 1993 Synoptic Survey 2
2. Observed Discharge during 1993 Winter Synoptic Survey (m^3/s) 8
3. Organic Carbon in Suspended and Depositional Sediments 12
4. Observed Mass Flux of Suspended Sediment 18
5. Observed Concentration of Total D_2CDD in Sediments 20
6. Observed Mass Flux of Total D_2CDD in Suspended Sediment 20
7. Observed Concentration of Total T_4CDD in Sediments 23
8. Observed Mass Flux of Total T_4CDD in Suspended Sediment 23
9. Observed Concentration of Total O_8CDD in Sediments 25
10. Observed Mass Flux of Total O_8CDD in Suspended Sediment 25
11. Observed Concentration of Total D_2CDF in Suspended Sediment 27
12. Observed Mass Flux of Total D_2CDF in Suspended Sediment 27
13. Observed Concentration of Total T_4CDF in Sediments 29
14. Observed Mass Flux of Total T_4CDF in Suspended Sediment 29
15. Observed Concentration of Pimaric Acid in Sediments 32
16. Observed Mass Flux of Pimaric Acid in Suspended Sediment 32
17. Observed Concentration of Isopimaric Acid in Sediments 34
18. Observed Mass Flux of Isopimaric Acid in Suspended Sediment 34
19. Observed Concentration of Dehydroabietic Acid in Sediments 36
20. Observed Mass Flux of Dehydroabietic Acid in Suspended Sediment 36
21. Observed Concentration of Abietic Acid in Sediments 38
22. Observed Mass Flux of Abietic Acid in Suspended Sediment 38
23. Observed Concentration of Total Chlorinated Resin Acids in Sediments 40
24. Observed Mass Flux of Total Chlorinated Resin Acids in Suspended Sediment 41

1.0 INTRODUCTION

The Northern River Basins Study (NRBS) initiated water quality investigations in a 200 kilometer reach of the Athabasca River (from Hinton to Whitecourt) in the spring of 1992. Following the initial survey, which included analyses of pulp-related contaminants in several media (water, suspended and depositional sediment, zoobenthos, fish, etc.), the NRBS contracted Environment Canada to collect water, suspended sediments, and depositional sediments throughout the Athabasca River system. Suspended sediments and water were collected at 23 mainstem, tributary, and effluent sampling locations in February-March 1993, as a supplement to the 1993 Alberta Environmental Protection (AEP) winter synoptic survey. Depositional bottom sediments at eight mainstem Athabasca River locations were collected in early May 1993, shortly after ice-out (bottom sediments from an additional remote mainstem site were collected during the synoptic survey).

AEP has undertaken winter synoptic surveys of the Athabasca River each year since 1988, in response to water quality concerns which arose due to expansion of the wood pulp industry. These surveys, focussing on the water phase and including an extensive list of water quality variables, have been carried out in the low-flow January to March period at approximately 60 mainstem, tributary, and effluent locations. Winter synoptics have been supplemented by surveillance and network monitoring, by applied studies of zoobenthos and sediment contaminants, and by oxygen modelling and calibration. AEP has produced a number of reports on the results of the synoptic surveys and supplemental work (e.g. Noton and Shaw, 1989; Casey and Noton, 1989; Macdonald and Hamilton, 1989; Andres *et al.*, 1989).

This report presents the 1993 results for polychlorinated dibenzodioxins-furans and resin acids in water, suspended sediments, and depositional sediments. AEP has published a detailed reports on additional results of the 1993 synoptic survey (Noton and Saffran, 1995).

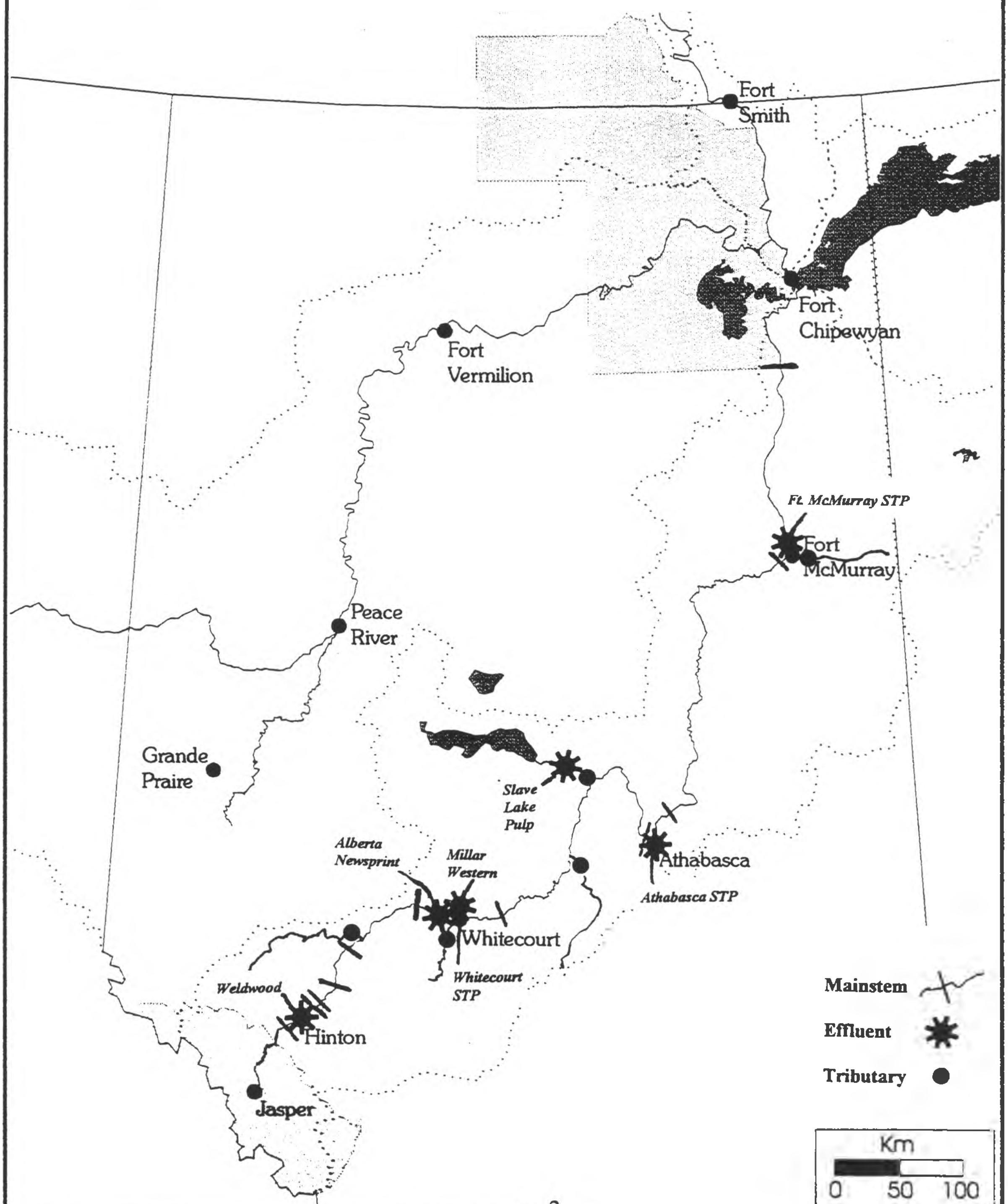
2.0 METHODS

2.1 GENERAL

Sampling began above Hinton on February 11, 1993, and advanced downstream. Sample collections were run-of-river, in an attempt to measure changes in a single parcel of water throughout the basin. The sampling schedule was derived from estimates of winter time of travel made through the use of dye-tracer work (Andres *et al.*, 1989; Van Der Vinne and Andres, 1992). The time of travel between Hinton and Lake Athabasca was estimated to be approximately 38 days.

Suspended sediments and centrifugate (clarified water) were usually sampled on the same day as AEP synoptic samples. Long centrifugation times required for collection of suspended sediments, however, led to variations of one or two days in reaches with closely-spaced sampling locations. A map showing sampling locations is presented in Figure 1.

Figure 1 Sampling Locations for Suspended and Depositional Sediments, Winter 1993 Synoptic Survey



2.2 FIELD METHODS

2.2.1 Suspended Sediment Collection

Alfa-Laval MB103 centrifuges were used for collection of suspended sediments. Two centrifuges operated simultaneously at each river site. River water was delivered to the centrifuges by submersible pump through stainless steel sheathed 1.25 cm teflon intake lines, at a rate of 4 liters/minute to each centrifuge. The centrifuges were housed in an ice-fishing hut which was heated with a 1500 watt heater and heat lamps. Power was provided by a 5000 watt generator.

Sample contact points, all constructed of stainless steel or teflon, were rinsed with acetone and hexane, and sample rinsed prior to use. Flow rates were checked at regular intervals to ensure maximum centrifugation efficiency. The centrifuges were operated for approximately 24 hours at mainstem and tributary locations (two centrifuges at 4 liters/minute = 11520 liters centrifuged). River sampling was done at locations in the cross-sections near maximum depth and velocity. A list of suspended sediment sampling locations, sampling times, and field notes is presented in Table 1.

Sufficient sample size was generated at effluent sites by operating a single centrifuge for approximately 4 hours (960 liters centrifuged). Separate centrifuges, bowls, pumps, and intake line were used at effluent and river locations. An attempt was made to collect pulp and sewage treatment effluent samples as near as possible to the final outlet points (see collection notes in Table 1).

Suspended sediments were transferred to pre-cleaned EPA protocol glass containers with teflon liners immediately after collection. Samples were labelled with a site label, centrifuge bowl number, and the collection date, and placed on dry ice. Sediments were subsequently transferred to an ultracold freezer for storage at -60 ° C.

Suspended sediment loads were extremely low at most mainstem and tributary sites during the winter of 1993. At a number of locations, total suspended sediment concentration was < 1 mg/L, leading to small sample sizes. Upper Athabasca River samples (from u/s Maskuta Creek to Emerson Lakes) were approximately 40-100 grams (wet), while lower Athabasca River and most tributary samples averaged 10-20 grams (wet). Pulp mill effluents generally provided larger samples (>100 grams wet), and sewage treatment plant samples were of variable size (40-100 grams wet). Small sample size limited the number of contaminant analyses possible for suspended sediments.

2.2.2 Water Sample Collection and Field Extraction

Duplicate 20-liter centrifugate samples were collected from teflon outlet lines attached to the centrifuge top assemblies at regular intervals throughout the centrifugation process, providing composite water samples reflecting the same time periods as suspended sediments. At mainstem and tributary locations, 2-liters of centrifugate was collected at two hour intervals throughout the sampling period (at effluent sites the sampling interval was approximately 15 minutes). Samples were collected in Millipore pressure containers, which were washed between samples with acetone, hexane, methylene chloride, and organic-free water.

Table 1 Suspended Sediment/Centrifugate Collection Sites, Winter 1993 Synoptic Survey

Mainstem Locations	Grid Reference	Start Centrifuges	Stop Centrifuges	Hrs.	Discharge m^3/sec (1)	N.F.R. (mg/L) (1)	km D/S HCE (2)	Field Notes
Ath R. u/s Maskuta Ck.	562146	93 02 11 1130	93 02 12 1130	24	28.7	20.7*	-7.6	300 meters u/s of Maskuta Ck. opposite rock face on left bank. Left-center in in channel.
Ath R. Weldwood Haul Br.	627196	93 02 11 1730	93 02 12 1730	24	29.0	11.0	1.1	75 meters off right bank, upstream of bridge near right bridge support.
Ath R. Obed Bridge	762306	93 02 12 1730	93 02 13 1800	24.5	29.9	8.0	21.0	150 meters u/s of bridge, right center. Majority of flow just left of sampling location. 40 cm depth under ice.
Ath R. Emerson Lakes	894500	93 02 13 1125	93 02 14 1125	24	30.2	4.0	47.7	40 meters u/s of bridge, 15 meters off right bank.
Ath R. u/s Berland River	103836	93 02 14 1430	93 02 15 1440	24.2	38.7	<1.0	101.9	220 meters u/s of Berland R. 50 meters from right bank. 2 meter depth, rocky bed.
Ath. R. at Windfall Bridge	613068	93 02 15 1830	93 02 16 1830	24	43.6	1.0	175.2	75 meters d/s of Windfall Bridge, 35 meters from right bank.
Ath R. near Blue Ridge	051021	93 02 18 1230	93 02 19 1210	23.7	49.6	1.0	234.3	Center left, approx. 80 meters above bridge.
Ath R. at Athabasca	526662	93 02 26 1625	93 02 27 1625	24	61.0	1.0	554.5	Right-center at hydrometric location 1 kilometer above bridge.
Ath R. u/s Alpac Site		93 02 28 0910	93 03 01 0910	24	62.0	<1.0	585.	Center stream 250 meters above Alpac bridge under construction. 3 km. NW of Alpac mill site.
Ath. R. u/s Ft. McMurray	753861	93 03 09 1600 93 03 10 1000	93 03 09 2200 93 03 11 1200	32	65.1	1.0	943.9	At hydrolab location left left-center 50 meters above water intake for Ft. McMurray WTP
Ath R. at 27 Baseline	785468	9303 16 1400	93 03 17 1300	23	139	2.3*	1130	Directly across from 27 Baseline cabin, right center in right (main) channel. 1.0 m ice, 1.2 meters water.
Tributary Streams								
Berland River near Mouth	103838	93 02 14 1620	93 02 15 1540	23.3	7.80	<1.0	102.3	80 meters above mouth, 0.7 meter depth, high velocity, low turbidity.
McLeod River near Mouth	852995	93 02 16 1930	93 02 17 1740	22.2	5.13	3.0	209.1	15 meters off right bank, 50 meters above RR bridge. Very low discharge, 0.4 meter depth.
Pembina River near Mouth	805610	93 02 23 1200	93 02 24 1330	25.5	1.56	1.0	391.9	Grid road 660, 3 miles SW of Flatbush. 25 meters above bridge left-center. 1.0 meter depth, slight amber colour.
Lesser Slave River nr Mouth	814237	93 02 25 1310	9302 26 1235	23.5	14.1	3.0	448.5	At AEP sampling site approx. 10 km. above mouth (2 km below Moose R.) Right center 300 meters above hydrolab.
Clearwater River nr Mouth	778874	93 03 11 1300	93 03 12 1400	25	41.7	4.0	948.7	100 meters above mouth of snye. Center stream 0.8 meters ice, 0.8 meters .
Effluents								
Hinton Combined Effluent		93 02 11 1040	93 02 11 1400	3.3	1.22	36*	0.0	Collected at sump adjacent to pump house above diffuser. 33 deg C. High foam, 45% ClO_2 substitution last 10 days.
Alberta Newsprint Effluent		93 02 16 1130	93 02 16 1600	4.5	0.181	38.5*	198.3	Sampled from sump in final clarifier pond near diffuser pipe outfall.
Millar Western Effluent		93 02 17 1000	93 02 17 1400	4.0	0.110	25.5*	209.6	Sampled directly from line pumping to diffuser.
Whitecourt Sewage Effluent		93 02 17 1500	93 02 17 1845	3.7	0.035	6.0	213.0	Sampled final effluent from sump before diffuser.
Slave Lake Pulp Effluent		93 02 24 1140	93 02 24 1515	3.5	0.048	168.5*	(448.5)	Floor tank fed by aerator ponds just before exiting to LSR.
Athabasca Sewage Effluent		93 02 27 1050	93 02 27 1550	5.0	0.013	6.0	555.5	Sampled at final effluent tap.
Ft. McMurray Sewage Eff.		93 03 10 1230	93 03 10 1630	4.0	0.161	11.0	950	In final chamber of east lagoon system, which had 2X flow of west system. Approx 5 km below highway bridge.

(1) Discharge and N.F.R. from Noton and Saffran (1995). * Average of two or more measurements.
(2) River kilometers below Hinton Combined Effluent. From Noton and Saffran (1995)

In-field methylene chloride extractions (at ambient pH) for polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) were done in the pressure containers within 24 hours of collection. A detailed review of the pressure container extraction method is available in Fox (1986). Field surrogates were added at the outset of extraction process to measure extraction efficiency. Surrogates for PCDD/Fs included ^{13}C-1,2,3,4-T_4CDD (1.0 ng in 100 mL. methanol) and ^{13}C-1,2,3,4,6,7,8 H_7CDF (2.0 ng in 100 mL. methanol). The duplicate 20-liter sample was extracted for organochlorines and polychlorinated biphenyls with Niagara Protocol extraction surrogates added (OC-PCB extracts were not subsequently analyzed). Both extracts were stored in glass containers pre-cleaned to EPA protocols, and labelled with the site code, date, and an analytical suffix (DF or OC).

2.2.3 Depositional Sediments

Mainstem Athabasca River depositional sediments were collected during the period May 5-7, 1993, in a low flow period very shortly after ice-out. Samples from the Athabasca River at 27 Baseline (boundary of Wood Buffalo National Park) were collected through the ice at the time of the synoptic collections, due to the remote nature of that site (Table 2).

Sampling was done in depositional areas in near proximity to the suspended collection sites (within 1-2 kilometers at all sites). The sampling locations were generally in small bays or in backwaters behind gravel bars or islands, typified by sandy beds overlain with varying thickness of silt-clay material commonly interspersed with layers of organic debris. Depositional areas with the finest material available were chosen at all sites. A stainless steel Ekman dredge (152 mm. X 152 mm. X 152 mm.) with operating handle was used for collection. Sites were accessed by wading, with the dredge pressed gently into the bottom sediment at each site to a depth of approximately 5-7 cm. Bottom sediments were taken from the top 1 cm. using a solvent washed stainless steel knife. Five replicates were collected at each site without compositing. Samples were placed in pre-washed 250 mL glass containers with teflon liners and frozen immediately on dry ice. Samples were labeled with the site label, a sequential number, and the date. Upon arrival at the field laboratory, samples were transferred to an ultracold freezer (-60° C) for storage.

Table 2 Depositional Sediment Collection Sites, Winter 1993 Synoptic Survey

Sampling Location	Grid Reference	Date/Time	Field Notes
Ath. R. u/s Maskuta Creek	566146	93 05 05 0900	Sampled right side 100 meters above Maskuta Ck. General backwater along right side, high bank left. Sandy silt over detritus.
Ath. R. Weldwood Haul Br.	637202	93 05 05 1200	Approx. 1 km. below Weldwood Haul Bridge right bank opposite Fish Ck. Small bay, sand overlain with brown silt-clay 1 cm thick. Worm burrows. Petroleum? leaching from mud banks in area.
Ath. R. Obed Bridge	767312	93 05 05 1600	Small rock bay 1 km. below Obed bridge right side. Near Baseline Ck. Small amount silt overlying sand.
Ath. R. Emerson Lakes	887522	93 05 05 1830	Approx. 2 km. below bridge left side. Small bay causing backwater. 2 cm. silt over sandy silt. Sandy beach.
Ath. R. u/s Berland River	095827	93 05 06 1100	Approx. 1 km. above Berland R. in splits area. In lee of large island, three channels in area. Thin layer silt overlaying sand. Some fines, silt-clay up to 4 cm thick.
Ath. R. Windfall Bridge	623060	93 05 06 1430	Approx 1 km. below bridge right side behind large bar. Mud beach, high sand with layer of silt.
Ath. R. near Blue Ridge	056024	93 05 06 1730	Approx. 500 meters below bridge right side behind gravel bar. Silty sand in backwater, ice remaining at edge.
Ath. R. at Athabasca	536685	93 05 07 1100	1.5 km below bridge left side in bay behind gravel bar. Silt layer over sand. Some organic debris.
Ath. R. at 27 Baseline		93 03 16 1700	Sampled five verticals in right channel directly across from 27 Baseline warden cabin. Sand with no fines. Used ponar.

2.3 LABORATORY METHODS

2.3.1 Analytical Program

Suspended and depositional sediments were analyzed for particle size and organic carbon at the National Water Research Institute Sedimentology Laboratory in Burlington, Ontario (small sample size for some suspended sediment samples made it impossible to analyze particle size and organic carbon on all samples). Depositional sediments were partitioned into sand and clay-silt fractions, with the clay-silt fraction undergoing subsequent analyses, with un-partitioned suspended sediments, of PCDD/Fs and resin acids at AXYS Analytical Services, in Sydney, B.C. Analyses of resin acids in effluent suspended sediments were done for pulp mill effluents only.

Centrifugate extracts from seven mainstem Athabasca River sites and six effluents were analyzed for PCDD/Fs (AXYS Analytical Services). Results for resin acids in whole water samples have been published by AEP (Noton and Saffran, 1995).

2.3.2 Particle Size and Carbon Analyses

Sediments (suspended and depositional) were freeze-dried, rolled, and sub-sampled by cone and quartering for particle size and organic carbon analyses. Depositional sediments were then seived through a stainless steel 63 micron (4 PHI) sieve. Material passing the sieve (the clay-silt fraction) was replaced in the original sample containers for contaminant analyses. All equipment contacting the samples during the rolling/partitioning procedures including sieves, spatulas, and sieve trays, were soap and water washed, Milli-Q water rinsed, rinsed with acetone and hexane, and dried prior to use. Aluminum foil used in the rolling procedure was fired at approximately 350° C for twelve hours and cooled prior to use.

Particle size analyses were done using the Sieve and Sedigraph method. Details of the methods are presented in Duncan and LaHaie (1979). Organic and inorganic carbon were analyzed on a LECO-12 Carbon Determinator using a two temperature dry combustion method.

2.3.3 PCDD/F Analyses

All samples were spiked with an aliquot of ^{13}C-labelled surrogate standards covering the D_2 to O_8 range. Sediment samples were soxhlet extracted. The water portion of the field extract was re-extracted, and this extract combined with the field methylene chloride portion. Extracts were subjected to a series of washing and chromatographic cleanup steps prior to analyses by high resolution mass spectrometric detection on an Ultima AutoSpec high resolution mass spectrometer/Hewlett Packard 5890 GC. Analysis and data interpretaion followed the protocols of the Environment Canada Reference Method (Environment Canada, 1992).

Batches of eight samples were analyzed for PCDD/Fs, with spiked samples, procedural blanks, duplicate or triplicate analyses included in each batch. Two duplicate and one triplicate analysis for PCDD/F were reported. Internal surrogates were reported as percent recovery, and results for the field surrogates were reported in total pG in 20 liters.

2.3.4 Resin Acid Analyses

Sediments were spiked with an aliquot of o-methyl podocarpic acid as internal standard for quantification of the target resin acids. Sediments were then sonicated prior to solvent extraction. The extracts were derivatized to methyl esters with diazomethane, and cleaned on silica gel prior to analysis by gas chromatography with mass spectrometric detection. GC/MS analyses were performed using a Finnigan INCOS 50 mass spectrometer/Varian 3400 GC.

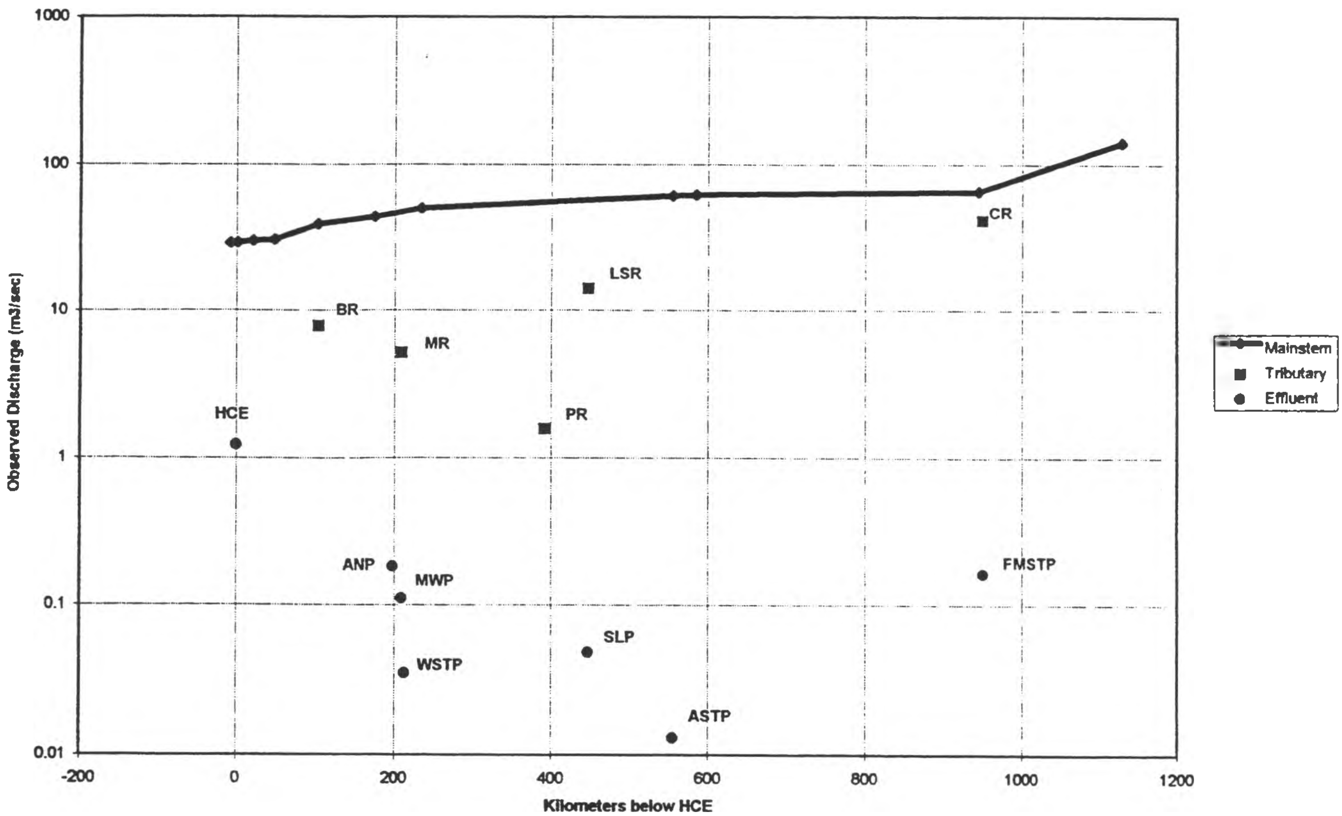
Resin acid analyses were done in four batches, each of seven samples, with one known matrix sample, one analytical duplicate, and one procedural blank in each batch.

3.0 STUDY AREA

3.1 GENERAL

The Athabasca River originates at Snowdome in Jasper National Park, and is unregulated as it flows in a generally northeasterly direction for 1400 kilometers to Lake Athabasca. River discharge during the 1993 winter synoptic survey ranged from approximately 30 m^3/s at Hinton, to approximately 140 m^3/s at the boundary of Wood Buffalo National Park. Discharges were near the long-term average yearly minima, as were river dilution factors for pulp mill and sewage treatment plant effluents. Observed discharges for mainstem sites, tributaries, and effluents at the time of the synoptic survey are presented in Figure 2 (data from Noton and Saffran, 1995).

Figure 2 Observed Discharge during 1993 Winter Synoptic Survey (m^3/s)



3.2 EFFLUENTS

Pulp effluent has entered the Athabasca River since 1957, with the opening of a bleached kraft mill at Hinton. This mill, currently operated by Weldwood of Canada, operated at 70% ClO_2 substitution during the winter of 1993, subsequently changing to 100% ClO_2 substitution in the summer of 1993 (Noton and Saffran, 1995). Mill effluent (combined with approximiately 5% Hinton municipal effluent) is treated in an aerated stabilization basin Effluent discharge at Hinton is the largest by volume of effluents on the Athabasca River, averaging 1.1 m^3/s. Effective dilution of the Hinton combined effluent during the synoptic survey were approximately 23.5:1 for water, and 13.5:1 for suspended sediment (Table 3).

The late 1980s and early 1990s saw rapid expansion of the pulp industry in the basin, with the opening of three non-chlorine bleaching chemical-thermomechanical (CTMP) mills, including Millar Western Pulp (Whitecourt) in August 1988, Alberta Newsprint Co. (Whitecourt) in August 1990, and Slave Lake Pulp Corp. (Slave Lake) in January 1991. Treatment at these mills is by activated sludge treatment, with much lower effluent discharges than at Hinton. Low effluent discharge is reflected in high water dilution factors for the three mills, though estimated sediment dilution factors during the winter of 1993 were similar to those at Hinton, due to low concentrations of suspended sediment in local receiving waters. The Alberta Pacific Forest Industries (Alpac) bleached kraft mill near Athabasca was not yet in operation at the time of this work (start-up September 1993).

Municipal sewage treatment plants at Whitecourt, Athabasca, and Fort McMurray all receive secondary treatment. Water and sediment dilution factors for the STP effluents (Table 3) were much higher than those for the pulp mills.

Table 3 Estimated Water and Sediment Dilution Factors for Effluents, Winter 1993 Synoptic Survey

Effluent	Km d/s HCE	Water Dilution			Sediment Dilution		
		Effluent Q (m3/s)	River Q (m3/s)	Dilution Factor	Effluent Load (tonne/day)	River Load (tonne/day)	Dilution Factor
Hinton Combined Effluent	0	1.22	28.7	23.5	3.79	51.33	13.5
Alberta Newsprint Pulp	198.3	0.181	43.6	241	0.60	3.77	6.3
Millar Western Pulp	209.6	0.11	48.9	445	0.24	5.70	23.8
Whitecourt STP	213.0	0.035	49.0	1400	0.02	5.94	297
Slave Lake Pulp	(448.5)	0.048	60.3	1254	0.70	7.37*	10.5*
Athabasca STP	555.5	0.013	61.0	4692	0.01	5.27	527
Ft. McMurray STP	950	0.161	106.8	663	0.15	20.03	134

*Dilution Factor for Slave Lake Pulp calculated for the Athabasca River below Lesser Slave River
Discharge data and background non-filterable residue data used in Table 3 from Noton and Saffran (1995)

4.0 RESULTS AND DISCUSSION

4.1 SEDIMENT FLUX CALCULATIONS AND MASS BALANCES

Mass flux (or loading) of sediment and contaminants on sediment were calculated using non-filterable residue data and discharges in Noton and Saffran (1995), and respective contaminant analytical results. Mass flux of suspended sediment was calculated:

non-filterable residue (mg/L) x discharge (m3/s) x .0864 = sediment flux (tonne/day)

Contaminant flux in suspended sediments was calculated as follows:

For PCDD/Fs: sediment flux (tonne/day) x pg/G = PCDD/F flux (ug/day)
For resin acids: sediment flux (tonne/day) x ng/G x .001 = resin acid flux (G/day)

The mass balance tables presented in the Results and Discussion contain suspended sediment contaminant flux results for all mainstem, tributary, and effluent locations where data were available, together with mass balance calculations, determined as apparent gain or apparent loss in sediment contaminant flux between mainstem Athabasca River locations. This has been done to facilitate the interpretation of deposition and/or degradation of PCDD/F and resin acids through the system.

4.2 QUALITY CONTROL

The results for procedural blanks showed non-detectable or very low background levels of PCDD/F target compounds. Procedural blanks for resin acids had non-detectable or low concentrations of all target compounds with the exception of dehydroabietic acid, which was detected in procedural blanks, but at much lower concentrations than in the samples.

Two sediment samples were analyzed in duplicate and one in triplicate for PCDD/F, with all showing agreement within ± 20%. Pressure container centrifugate extracts could not be analyzed in duplicate due to the detection limit effects which would be produced by splitting the extracts. Four sediment samples analyzed in duplicate showed agreement within ± 20%.

Internal laboratory surrogate recoveries were compared in the laboratory (AXYS Analytical) with recovery standards added just prior to injection, and analyses were repeated or extracts were re-injected based upon this comparison, or if surrogate recoveries were not within acceptable bounds (generally 70-100%). A total of 15 analyses for PCDD/Fs were repeated for recovery reasons. PCDD/F results for suspended sediment from the Athabasca River at Athabasca have not been reported, since inadequate sample was available for repeat analysis following initial low surrogate recovery. Analyses was repeated for 7 resin acid analyses due to initial recovery problems. The final analytical reports included low surrogate recovery for resin acids in two suspended sediment samples: Athabasca River at Obed Bridge (26%) and Alberta Newsprint Pulp Effluent (31%).

Recovery of field surrogates added at the time of field extraction for PCDD/Fs in centrifugate are presented in Table 4. As discussed in Section 2.2.2, 1.0 ng of ^{13}C-1,2,3,4-T4CDD and 2.0 ng of ^{13}C-1,2,3,4,6,7,8-H7CDF were added at the initial stages of the extraction. Surrogate recovery in mainstem extracts were generally within acceptable ranges (70-130%). Recoveries were more variable in effluent samples, with very low recovery reported for Hinton Combined Effluent (HCE), and unacceptably high recovery for Alberta Newsprint and Whitecourt STP. Low recoveries in large volume extracts can be caused by emulsion difficulties, and this may have been the cause of the HCE result. High recoveries are less common, and no likely explanation is offered for the high recoveries reported for Alberta Newsprint and Whitecourt STP.

Table 4 Pressure Container Extraction Surrogate Recovery

Location	^{13}C 1,2,3,4-T_4CDD		^{13}C 1,2,3,4,6,7,8-H_7CDF	
	Total pg	% Recovery	Total pg	% Recovery
Mainstem Sites:				
Ath. R. Obed Bridge	1080	108	2280	114
Ath. R. u/s Berland R.	1100	110	2100	105
Ath. R. Blue Ridge	940	94	1840	92
Ath. R. at Athabasca	720	72	1520	76
Ath. R. u/s Alpac Site	980	98	1940	97
Ath R. u/s Ft. McMurray	1040	104	2060	103
Ath. R. at 27 Baseline	660	66	1140	57
Effluents:				
Hinton Combined	15	1.5	94	4.7
Alberta Newsprint Pulp	3680	368	3760	188
Millar Western Pulp	980	98	1660	83
Whitecourt STP	1900	190	3800	190
Slave Lake Pulp	400	40	560	28

4.3 PARTICLE SIZE AND ORGANIC CARBON

Knowledge of particle size and organic carbon content of sediments is important in interpretation of contaminant concentrations. Hydrophobic and lipophilic contaminants partition preferentially to high carbon environonments and to small particles, due to the larger surface area available for adsorption. Particle size and organic carbon results from February-March 1993 are presented in Table 5. Note that small sample sizes made it impossible to analyze some suspended sediments for particle size and/or organic carbon.

Mainstem Athabasca River suspended sediments averaged >95% fines (clay + silt), with the degree of fineness (clay:silt ratio) tending to increase moving downstream. Suspended sediments from HCE and tributaries had particle size similar to mainstem Athabasca River sites. Mainstem depositional sediment particle size was more variable, with definitive longitudinal trends not apparent. In general, depositional sediments were coarser than suspended sediments. Depositional sediments were partitioned prior to analysis at the sand-silt boundary (63µ) to reduce contaminant concentration variability resulting from particle size variability. Some degree of size-related variability in concentration remains likely, however, both within and between sediment media, due to varying silt:clay ratios.

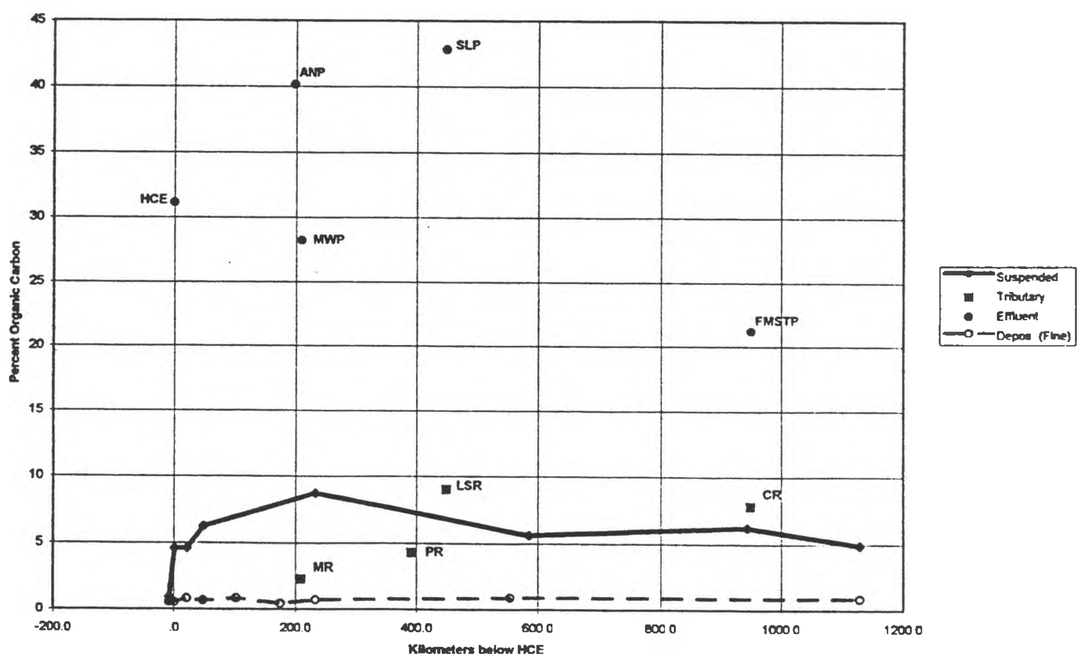
Organic carbon concentrations in depositional sediments were generally in a narrow range below one percent of total sediment weight. Concentrations in mainstem suspended sediment varied between 0.94% (control site u/s Maskuta Creek) and 8.7% (Ath. R. at Blue Ridge). Tributary suspended sediments had organic carbon from 2.3-9.0%. Higher organic carbon concentrations were reported

Table 5 Particle Size and Organic Carbon, Suspended and Depositional Sediments, February-March, 1993

Location	Km d/s HCE	Suspended Sediment				Depositional Sediment			
		% Sand	% Silt	% Clay	% Org C	% Sand	% Silt	% Clay	% Org C
AR u/s Maskuta Creek	-7.6	15.95	66.44	17.61	0.94	17.21	69.57	13.22	0.57
AR Weldwood Haul Br.	1.1	1.76	57.64	40.59	4.6	6.26	73.45	20.29	0.53
AR Obed Bridge	21.0	8.11	50.01	41.88	4.6	25.75	55.84	18.41	0.81
AR Emerson Lakes	47.7	0.39	31.39	68.21	6.2	27.43	56.18	16.39	0.68
AR u/s Berland River	101.9					40.61	36.27	23.12	0.86
AR Windfall Bridge	175.2					38.33	43.77	17.89	0.44
AR Blue Ridge	234.3	2.11	46.22	51.67	8.7	64.50	15.46	20.04	0.73
AR at Athabasca	554.5					32.97	36.38	30.66	0.90
AR u/s Alpac Site	585.				5.6				
AR u/s Ft. McMurray	943.9				6.2				
AR 27 Baseline	1130	0.88	21.99	77.13	4.9	98.05	1.00	0.85	0.87
McLeod River	209.1				2.3				
Pembina River	391.9				4.3				
Lesser Slave River	(448.5)	0.65	38.62	60.73	9.0				
Clearwater River	948.7	2.69	29.71	67.60	7.8				
Hinton Combined Effluent	0.0	0.24	66.89	32.87	31.1				
Alberta Newsprint	198.3				40.1				
Millar Western Pulp	209.6				28.2				
Slave Lake Pulp	448.5				42.8				
Ft. McMurray STP	950.0				21.2				

in effluent suspended sediments, with five effluents ranging from 21.2-42.8% organic carbon. Effluent inputs were sufficient to cause significant increases in mainstem concentrations of organic carbon (Figure 3). Based upon the sediment dilution ratios presented in Table 3, Hinton combined effluent produced an estimated 2.3% increase in mainstem organic carbon and Alberta Newsprint a 6.4% increase. Calculated mainstem organic carbon increases relating to other effluents include Millar Western (1.0%), Slave Lake Pulp (4.1%), and Ft. McMurray STP (0.2%). Concentrations in the Hinton-Whitecourt reach are in good general agreement with these estimates, while the effect of Slave Lake Pulp is not seen in the trend line in Figure 3.

Figure 3 Organic Carbon in Suspended and Depositional Sediments, February-March 1993



4.4 POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS

4.4.1 General

PCDDs and PCDFs are high molecular weight chlorinated tricyclic aromatic compounds comprising a total of 210 PCDD/F congeners, with distinctions between congeners based upon the distribution of chlorine molecules. They are produced in a number of industrial and natural processes, including bleached kraft pulp mills, chemical industry processes, incineration, and forest fires, and are generally hydrophobic, lipophilic-bioaccumulating, and persistent aquatic contaminants. Degradation can occur by photolysis and biodegradation. Concern over levels of PCDD/Fs in bleached kraft effluents has led to a number of improvements in pulp bleaching processes and effluent treatment, which have greatly decreased effluent concentrations.

The toxicity of different PCDD/F compounds vary. To facilitate interpretaion of complex mixtures of PCDD/Fs, international toxicity equivalency factors (I-TEFs) have been assigned to 17 individual PCDD/F congeners (Table 6). The most toxic PCDD/F is 2,3,7,8-T_4CDD, assigned an I-TEF of 1. The summation of all 17 I-TEF multiplied by the respective concentrations produces the TEQ or Toxicity Equivalence Quotient.

Table 6 PCDD/F International Toxicity Equivalency Factors (I-TEFs)

PCDD	I-TEF	PCDF	I-TEF
2,3,7,8-T_4CDD	1	2,3,7,8-T_4CDF	0.1
1,2,3,7,8-P_5CDD	0.5	2,3,4,7,8-T_4CDF	0.5
1,2,3,4,7,8-H_6CDD	0.1	1,2,3,7,8-T_4CDF	0.05
1,2,3,7,8,9-H_6CDD	0.1	1,2,3,4,7,8-H_6CDF	0.1
1,2,3,6,7,8-H_6CDD	0.1	1,2,3,7,8,9-H_6CDF	0.1
1,2,3,4,6,7,8-H_7CDD	0.01	1,2,3,6,7,8-H_6CDF	0.1
O_8CDD	0.001	2,3,4,6,7,8-H_6CDF	0.1
		1,2,3,4,6,7,8-H_7CDF	0.01
		1,2,3,4,7,8,9-H_7CDF	0.01
		O_8CDF	0.001

TEQ calculation: $TEQ = \Sigma\,(\text{I-TEF}_i \times [\text{compound}])_{n=1\text{ to }17}$ (Table from Trudel 1991)
I-TEFs of mono-, di-, and tri-substituted congeners assumed as zero

Until recently, analyses of ambient waters and effluents have included only the T_4-O_8 congeners, since these substitution groups include the compounds having highest PCDD/F toxicity and tendency to bioaccumulate. In recent years, analysis of M_1-T_3 congeners has become more common, and though these compounds have very low toxicity, they have been demonstrated to be persistent on sediments and are thought to be useful as markers of bleached kraft effluent (Pastershank and Muir, 1994).

Pastershank and Muir (1994) completed a review of PCDD/F concentrations in a number of biotic and abiotic media in the Hinton-Whitecourt reach of the Athabasca River. They reported that the most predominent PCDD/Fs in Hinton combined effluent were M_1, D_2, and T_3 congeners, though these congener groups were less commonly detected in fish than 2,3,7,8-T_4CDD or 2,3,7,8-T_4CDF.

Levels of PCDD/Fs in the reach were lower than Canadian Environmental Quality Guidelines for PCDD/Fs and Health Canada guidelines for fish tissue.

The 1993 results for PCDD/Fs in water, suspended sediments, and depositional sediments are presented in the Appendix. Total concentrations by degree of substitution are presented, though results for individual PCDD/F compounds are available from the NRBS upon request.

4.4.2 PCDD/Fs in Water

Effluents

2,3,7,8-T_4CDD (0.35 pg/L) and 2,3,7,8-T_4CDF (0.78 pg/L) were detectable in water from Hinton combined effluent. The 2,3,7,8-congener was the only T_4-dioxin detected at HCE, while five T_4-furans were detected, the major constituent being 2,4,6,8-T_4CDF (75 pg/L). The PCDD/F congeners at HCE in highest concentration were the M_1-T_3 furans, with major constituents being 2-M_1CDF (10 pg/L), 2,8-D_2CDF (73 pg/L), and 2,3,8-T_3CDF (12 pg/L). M_1-D_2 dioxins were non-detectable and T_3-dioxins were present in low concentration (Table 7). Other PCDD/Fs detected at HCE included total H_7CDD (0.16 pg/L), total O_8CDD (0.6 pg/L), and total P_5CDF (0.6 pg/L).

Table 7 presents a comparison of selected PCDD/F results with those from a 20-liter extract collected at HCE on May 21, 1992 during the Hinton-Whitecourt reach specific surveys. The two samples show similar results, and suggest that the 1993 extraction efficiency at HCE was much higher than indicated by the field surrogate recoveries (Section 4.2).

Table 7 Comparison of PCDD/F Results in Centrifugate from HCE (May 21, 1992 and February 11, 1993)

	PCDD/F in HCE Centrifugate (pg/L)	
	May 21, 1992	February 11, 1993
Total M_1CDD	nd	nd
Total D_2CDD	nd	nd
Total T_3CDD	0.38	0.38
Total T_4CDD	1.6	0.35
2,3,7,8-T_4CDD	0.47	0.35
Total P_5CDD	nd	nd
Total H_6CDD	nd	nd
Total H_7CDD	nd	0.16
Total O_8CDD	nd	0.6
Total M_1CDF	33	12
Total D_2CDF	180	94
Total T_3CDF	78	30
Total T_4CDF	48	76
2,3,7,8-T_4CDF	2.7	0.78
Total P_5CDF	nd	0.6
Total H_6CDF	nd	nd
Total H_7CDF	nd	nd
Total O_8CDF	nd	nd

nd = not detected

The water dilution factor for HCE on April 2, 1993 was 23.5:1 (from Table 3). Based upon this dilution factor, and with the detection limits provided by 20-liter extracts (approximately 0.1 pg/L), HCE-related detectable concentrations in Athabasca River receiving waters would be predicted for the M_1-T_4 furans only.

A comparison of PCDD/F congener group concentrations in water from CTMP and STP effluents is presented in Table 8. Concentrations of PCDD/Fs in CTMP effluents were low, with no detections reported in Millar Western effluent. Alberta Newsprint effluent had detectable concentrations of O_8CDD, total M_1CDF (2-M_1CDF 2.2 pg/L), total T_3CDF (2,3,8-T_3CDF 0.36 pg/L), and total T_4CDF (2,4,6,8-T_4CDF 0.36 pg/L). Total H_7CDD and total O_8CDD were detected in Slave Lake Pulp effluent.

Table 8 PCDD/F Congener Group Results in Centrifugate, CTMP and STP Effluents

	CTMP Effluents (pg/L)			STP Effluents (pg/L)	
	Alberta Newsprint	Millar Western	Slave Lake	Whitecourt	Ft. McMurray
Total M_1CDD	nd	nd	nd	nd	0.29
Total D_2CDD	nd	nd	nd	5.8	36
Total T_3CDD	nd	nd	nd	0.14	1.6
Total T_4CDD	nd	nd	nd	nd	nd
Total P_5CDD	nd	nd	nd	nd	nd
Total H_6CDD	nd	nd	nd	nd	nd
Total H_7CDD	nd	nd	0.15	0.87	1.1
Total O_8CDD	1.4	nd	0.38	3.0	4.0
Total M_1CDF	3.4	nd	nd	nd	2.4
Total D_2CDF	nd	nd	nd	nd	2.3
Total T_3CDF	0.83	nd	nd	nd	0.59
Total T_4CDF	0.39	nd	nd	nd	0.3
Total P_5CDF	nd	nd	nd	nd	0.5
Total H_6CDF	nd	nd	nd	0.31	0.24
Total H_7CDF	nd	nd	nd	nd	nd
Total O_8CDF	nd	nd	nd	nd	0.18

nd = not detected

In STP effluents, total D_2CDD (2,7/2,8-D_2CDD only) and O_8CDD were predominant at both Whitecourt and Ft. McMurray (note that D_2CDD had not been detected in HCE or the CTMP effluents. The Ft. McMurray effluent contained a complex mixture of furans, with most congener groups represented (2,3,7,8-T_4CDF was detected in Fort McMurray STP effluent at 0.15 pg/L), including P_5-, H_6-, and O_8-furans, which were not detected in HCE or CTMP effluents.

Of these CTMP and STP effluents, Ft. McMurray STP is the largest point source of PCDD/Fs to the Athabasca River, based upon PCDD/F concentration and discharge (Table 3). The water dilution factors during the winter of 1993, which ranged from 241:1 (Alberta Newsprint) to 1400:1 (Whitecourt STP), indicate that changes in Athabasca River water PCDD/F concentrations due to these effluents (either separately or cumulatively) would not be detectable.

Mainstem Athabasca River

PCDD/F concentrations in water at six mainstem Athabasca River locations are presented in Table 9. As discussed in the previous section, the water dilution factor (23.5 : 1) predicted that M_1-T_4 furans should be detectable in the receiving waters below HCE. D_2-furans were detectable at Kms. 21, 102, and 234, with apparent dilution at Obed of 21. : 1; T_3-furans were detected from Kms. 21, 102, and 234, with apparent dilution at Obed of 45 : 1; and T_4-furans were detected at Kms. 21 and 102, with apparent dilution at Obed of 200 : 1. M_1-furans were not detected in the Athabasca River and D_2-T_4 furans were not detected downstream of kilometer 234 (Blue Ridge). A comparison of the Obed 'apparent' dilution factors suggests differing rates of removal from the water column for the D_2-T_4 furans, with D_2-furans most persistent in water and T_4-furans least persistent. A number of mechanisms of removal from the water column probably occur simultaneously, including bio-degradation, photolysis (may be reduced under-ice), and partitioning to sediments and lipids.

Low concentrations of a number of dioxins were detected in water at some mainstem sites, including D_2-dioxins (Kms. 21, 234), H_7-dioxins (Kms. 21, 102), and O_8-dioxins (Kms 21, 102, and 944). These congener groups were not detected in HCE, but were present in low concentrations in STP effluents and one CTMP effluent. The low concentrations in the effluents combined with high water dilution factors eliminates considering them as potential causes of the river detections. It is likely, therefore, that the D_2, H_7, and O_8-dioxins detected at mainstem sites arose from diverse sources unrelated to the monitored effluents.

Table 9 PCDD/F Congener Group Results in Centrifugate, Mainstem Athabasca River

	PCDD/F Concentration (pg/L)					
	Obed Bridge	**u/s Berland River**	**Blue Ridge**	**u/s Alpac Site**	**u/s Ft. McMurray**	**27 Baseline**
Km. d/s HCE	21.0	101.9	234.3	585.	943.9	1130
Sample Date	1993 02 12	1993 02 14	1993 02 18	1993 02 28	1993 03 10	1993 03 16
Total M_1CDD	nd	nd	nd	nd	nd	nd
Total D_2CDD	0.59	nd	0.43	nd	nd	nd
Total T_3CDD	nd	nd	nd	nd	nd	nd
Total T_4CDD	nd	nd	nd	nd	nd	nd
Total P_5CDD	nd	nd	nd	nd	nd	nd
Total H_6CDD	nd	nd	nd	nd	nd	nd
Total H_7CDD	0.25	0.35	nd	nd	nd	nd
Total O_8CDD	0.7	1.4	nd	nd	0.7	nd
Total M_1CDF	nd	nd	nd	nd	nd	nd
Total D_2CDF	8.5	4.2	1.6	nd	nd	nd
Total T_3CDF	1.1	1.4	0.27	nd	nd	nd
Total T_4CDF	0.24	0.14	nd	nd	nd	nd
Total P_5CDF	nd	nd	nd	nd	nd	nd
Total H_6CDF	nd	nd	nd	nd	nd	nd
Total H_7CDF	nd	nd	nd	nd	nd	nd
Total O_8CDF	nd	nd	nd	nd	nd	nd

nd = not detected

4.4.3 PCDD/Fs in Suspended Sediments and Depositional Sediments

Analyses of PCDD/Fs were done on suspended sediments from 22 locations, including ten mainstem Athabasca River locations, five major tributaries, and seven effluents, and on depositional sediments from nine mainstem Athabasca River sites. Where duplicate or triplicate analyses were performed, the mean concentrations are presented and used in loading calculations. Detectable concentrations of most PCDD/F congeners were reported in suspended and depositional sediments from the majority of effluent, mainstem and tributary locations. Exceptions included suspended sediments in effluents Millar Western Pulp and Slave Lake Pulp, which had low or non-detectable concentrations of most PCDD/Fs. Where non-detectable concentrations were reported, concentrations equal to the detection limit were used in calculating contaminant flux.

The discussion of sediment PCDD/F results is limited to selected congener groups, including the T4 dioxins and T4 furans due to their presence and potential toxicity, and the D2-dioxins, O8-dioxins, D2-furans, based upon their presence in effluent sediments and/or ambient sediments. The complete PCDD/F congener group results for sediments are presented in the Appendix.

Mass Flux of Suspended Sediment

Table 10 presents suspended sediment mass flux calculations for the period of record. A review of Table 10 shows that suspended sediments arising from effluents had moderate (generally <<15%) effects on river flux, with the possible exception of the Whitecourt reach, where the cumulative addition of effluents from Alberta Newsprint, Millar Western, and Whitecourt STP added approximately 23% to the Athabasca River suspended sediment flux.. Tributary effects on mainstem suspended sediment flux were more significant, with the Clearwater River in particular adding large amounts of suspended sediment to the lower Athabasca River.

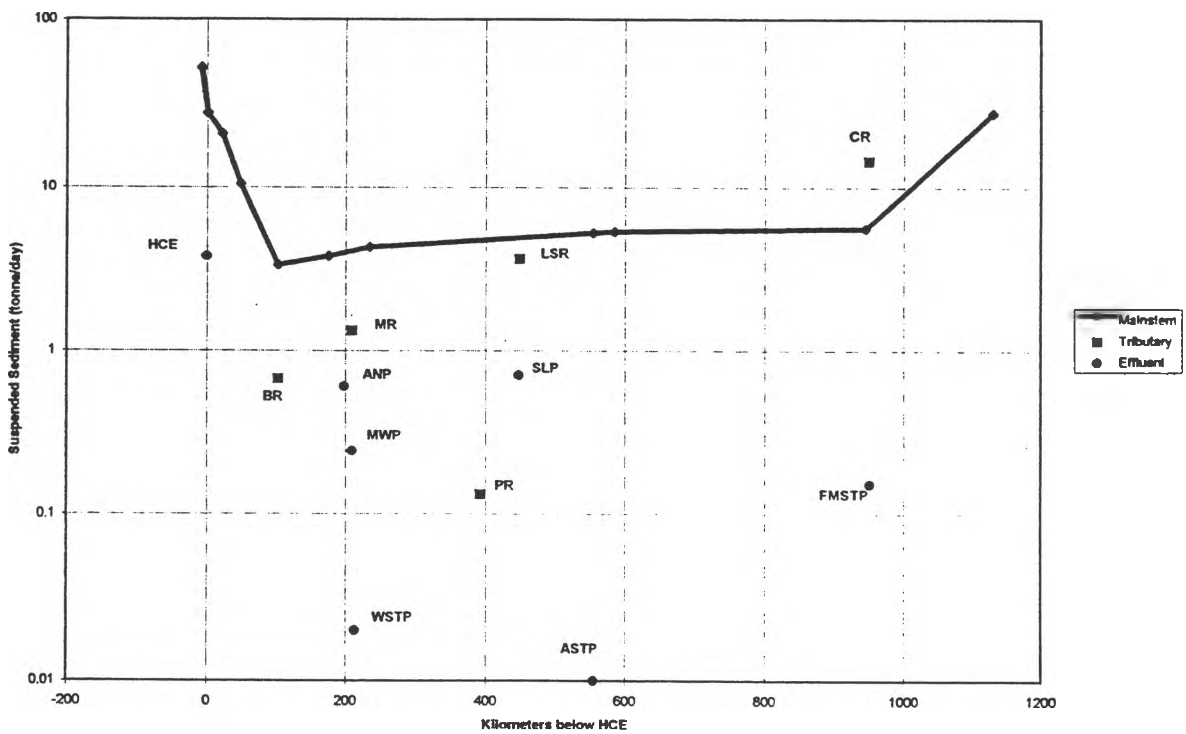
The gain/loss columns in Table 10 reflect the difference between the predicted flux at the next downstream site (previous site + effluents + tributaries) and the measured flux at that site. These columns thus reflect gain or loss through deposition and/or measurement error, including errors of ommission, such as potential un-monitored inputs. In subsequent mass balance tables for contaminants, these columns reflect degradation and partitioning to other media, together with measurement errors.

The mainstem trend line in Figure 4 indicates that Athabasca River sediment flux in February-March 1993 was highest in the Hinton area, fell rapidly in the Hinton-Whitecourt reach, rose very slowly between Whitecourt and Ft. McMurray, and rose more rapidly below Ft. McMurray, with addition of the Clearwater River and other tributaries between Ft. McMurray and Wood Buffalo National Park.

Table 10 Suspended Sediment Mass Balance, February-March 1993

Reach	Site	Km d/s HCE	Suspended Sediment Mass Flux (tonne/day)					Balance tonne/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	51.33						
	Hinton Combined Effluent	0			3.79				
	AR Weldwood Haul Br.	1.1		27.56					27.56
	AR Obed Bridge	21.0		20.67					6.89
	AR Emerson Lakes	47.7		10.44					10.23
	AR u/s Berland River	101.9		3.34					7.10
	Berland River	102.3				0.67			
	AR Windfall Bridge	175.2					3.77	0.24	
Whitecourt	AR Windfall Bridge	175.2	3.77						
	Alberta Newsprint Pulp	198.3			0.60				
	McLeod River	209.1			1.33				
	Millar Western Pulp	209.6			0.24				
	Whitecourt STP	213			0.02				
	AR Blue Ridge	234.3					4.29		1.67
Athabasca	AR Blue Ridge	234.3	4.29						
	Pembina River	391.9				0.13			
	Slave Lake Pulp	(448.5)			(0.70)				
	Lesser Slave River	448.5				3.65			
	AR Athabasca	554.5		5.27					2.80
	Athabasca STP	555.5			0.01				
	AR u/s Alpac Site	585.0					5.36	0.08	
Ft McMurray	AR u/s Alpac Site	585.0	5.36						
	AR u/s Ft. McMurray	943.9		5.62				0.26	
	Clearwater River	948.7				14.41			
	Ft McMurray STP	950			0.15				
	AR 27 Baseline	1130					27.62	7.44	

Figure 4 Observed Mass Flux of Suspended Sediment, February-March, 1993 (tonne/day)



D_2CDD in Sediment

Concentrations of D_2CDD in suspended and depositional sediment are shown graphically in Figure 5. Highest concentrations were measured in suspended sediments from the three STPs, with concentrations of 200 pg/G at Whitecourt, 1800 pg/G at Athabasca, and 1100 pg/G at Ft. McMurray. 2,7/2,8-D_2CDD were the congeners detected at all three locations. Concentrations of D_2CDD at HCE and the CTMP mills were lower than or similar to their respective receiving waters. Concentrations in depositional sediments (Figure 5) were 20-50% lower than those found in suspended sediments, but the longitudinal trend was very similar.

A review of Table 11 indicates that mass flux of D_2CDD from effluents was low compared to the mainstem flux, and little in the way of cause-effect relationship between effluent and mainstem flux is apparent. The influence of tributaries was more important, particularly the Clearwater River, which significantly affected the Athabasca River flux. The gain-loss columns show a large increase in D_2CDD suspended sediment flux between u/s Alpac (Km. 585) and u/s Ft. McMurray (Km. 944), and whether this is attributable to un-monitored tributary inputs or to diverse non-point sources is not known.

Figure 6 shows that mainstem sediment flux of D_2CDD decreased between Hinton and Athabasca, and then increased by greater than one order of magnitude between Athabasca and Wood Buffalo National Park. The unexplained increase between Kms 585-944 is clearly visible, as is the importance of the Clearwater River on the lower reaches.

Table 11 Mass Balance, D_2CDD in Suspended Sediment, February-March 1993

Reach	Site	Km d/s HCE	Mass Flux, D_2CDD in Suspended Sediment (ug/day)					Balance ug/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	395						
	Hinton Combined Effluent	0			49				
	AR Weldwood Haul Br.	1.1		524				80	
	AR Obed Bridge	21.0		413					111
	AR Emerson Lakes	47.7		313					100
	AR u/s Berland River	101.9		177					136
	Berland River	102.3				74			
	AR Windfall Bridge	175.2					263	12	
Whitecourt	AR Windfall Bridge	175.2	263						
	Alberta Newsprint Pulp	198.3			1.8				
	McLeod River	209.1				44			
	Millar Western Pulp	209.6			0.7				
	Whitecourt STP	213			3.6				
	AR Blue Ridge	234.3					146		167
Athabasca	AR Blue Ridge	234.3	146						
	Pembina River	391.9				7.6			
	Slave Lake Pulp	(448.5)			(5.3)				
	Lesser Slave River	448.5				87.7			
	Athabasca STP	555.5			12.1				
	AR u/s Alpac Site	585.0					129		124
Ft McMurray	AR u/s Alpac Site	585.0	129						
	AR u/s Ft. McMurray	943.9		1294				1165	
	Clearwater River	948.7				1354			
	Ft McMurray STP	950			168				
	AR 27 Baseline	1130					3038	222	

Figure 5 Observed Concentration of Total D_2CDD in Sediments, February-March, 1993 (pg/G)

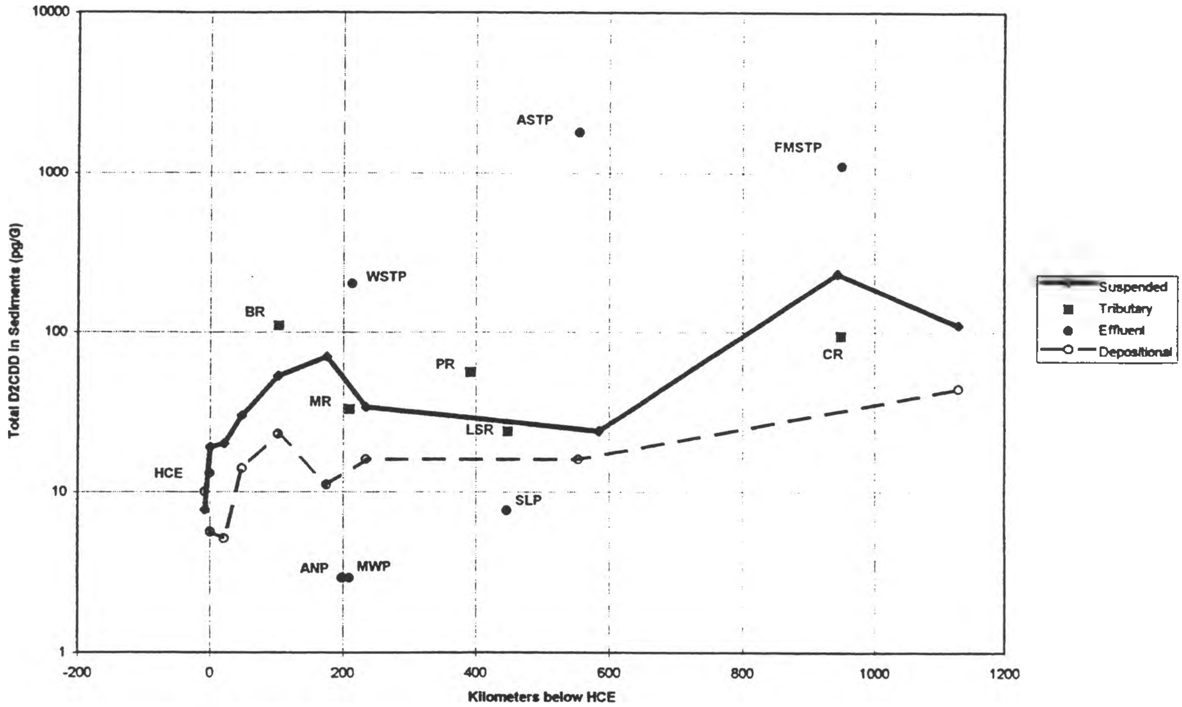
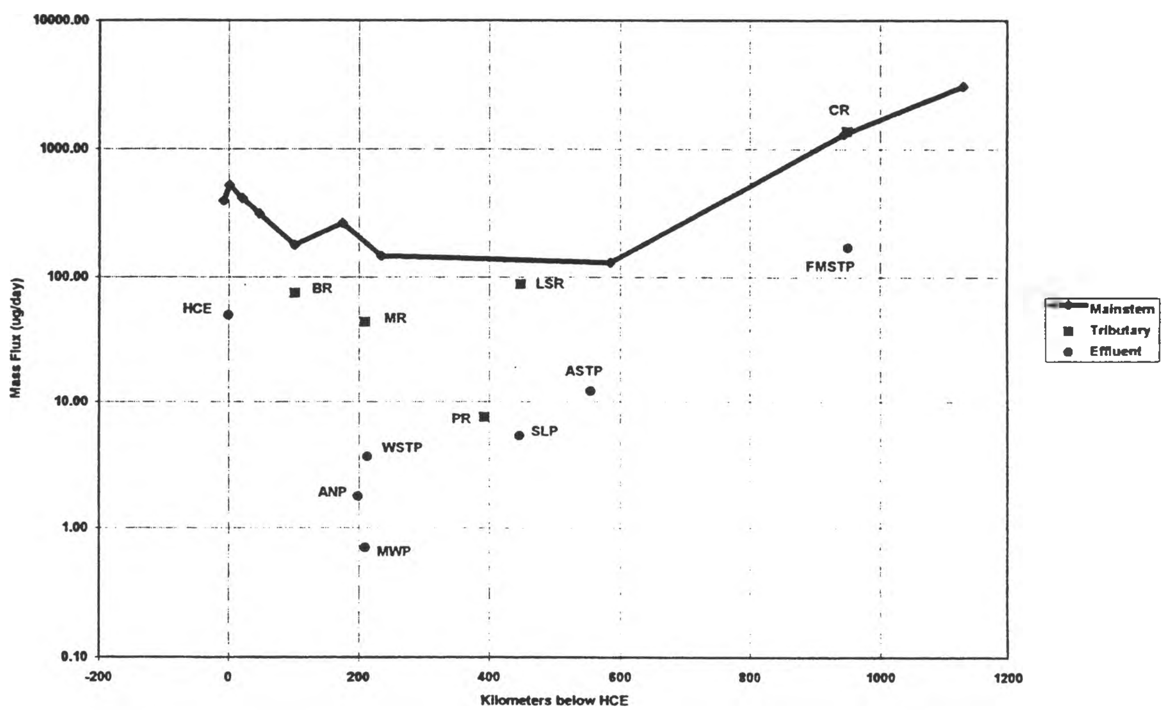


Figure 6 Observed Mass Flux of Total D_2CDD in Suspended Sediment, February-March, 1993 (ug/day)



T_4CDD in Sediment

Highest concentrations of T_4CDD in effluent suspended sediments were found at HCE (35 pg/G total T_4CDD, 24 pg/G 2,3,7,8-T_4CDD), Ft. McMurray STP (57 pg/G total T_4CDD, a complex mixture with non-detectable 2,3,7,8-T_4CDD), and Athabasca STP (30 pg/G total T_4CDD, a mixture with 27 pg/G 1,2,3,7/1,2,3,8-T_4CDD) (Figure 7). Most tributaries had T_4CDD concentrations similar or lower than those in the Athabasca River. The Lesser Slave River was slightly higher in concentration than the Athabasca River, with 13 pg/G total T_4CDD (non-detectable 2,3,7,8-T_4CDD). With one exception, 2,3,7,8-T_4CDD was detected in HCE and mainstem Athabasca River sites only. The surprising exception was the Berland River, which had 2,3,7,8-T_4CDD reported at 0.49 pg/G. PCDD/F results in suspended sediments from March-April 1992 and February-March 1993 are compared in Table 12. Concentrations in 1993 were somewhat higher than in 1992, but the longitudinal trends were similar.

Table 12 Total T_4CDD and 2,3,7,8-T_4CDD in Suspended Sediments March-April 1992 and February-March 1993

Sampling Location	Km d/s HCE	February-March 1993		March-April 1992	
		Total T_4CDD (pg/G)	2,3,7,8-T_4CDD (pg/G)	Total T_4CDD (pg/G)	2,3,7,8-T_4CDD (pg/G)
Upstream Maskuta Creek	-7.6	0.41	<0.1	0.2	0.2
Hinton Combined Effluent	0	35	24	31	11
Weldwood Haul Bridge	1.1	3.1	3.0	0.8 (2)	0.3 (2)
Obed Bridge	21.0	4.0 (3)	3.1 (3)	1.1	0.8
Emerson Lakes Bridge	47.7	6.4	3.7	2.0	1.0
Ustream Berland River	101.9	2.5	2.0	2.0	0.8
Windfall Bridge	175.2	2.4	1.5	1.8	0.6
Blue Ridge	234.3	4.8	0.94		
Upstream Alpac Site	585	6.1	0.45		
Upstream Ft. McMurray	943.9	2.7	<0.18		
At 27 Baseline (Wood Buffalo Park)	1130	3.0	<0.1		

Numbers in parenthesis indicate number of analyses

The sediment dilution factor for HCE in February 1993 was approximately 13.5 : 1 (Table 3). Total T_4CDD concentration at Obed Bridge (Km. 21.0), where mixing is generally assumed to be complete, are slightly higher than would be predicted from the HCE concentration. Total T_4CDD persistence in sediments is apparent, with concentrations detectable in mainstem Athabasca River suspended sediments throughout the synoptic reach. 2,3,7,8-T_4CDD was non-detectable by Ft. McMurray (Km. 944) (Figure 7).

Concentrations of total T_4CDD in depositional sediments were approximately one order of magnitude lower than in suspended sediments (Figure 7). Table 13 presents T_4CDD concentrations in depositional sediments from March-April 1992 and February-March 1993. Concentrations at Kms. 21 and 47 were somewhat higher during the 1992 survey, while concentrations at the remaining three sites were similar.

Table 13 Total T_4CDD and 2,3,7,8-T_4CDD in Depositional Sediments March-April 1992 and February-March 1993

Sampling Location	Km d/s HCE	February-March 1993		March-April 1992	
		Total T_4CDD (pg/G)	2,3,7,8-T_4CDD (pg/G)	Total T_4CDD (pg/G)	2,3,7,8-T_4CDD (pg/G)
Upstream Maskuta Creek	-7.6	<0.13	<0.13	<0.1	<0.1
Weldwood Haul Bridge	1.1	0.23	0.23	0.3	0.2
Obed Bridge	21.0	0.14	0.14	1.3 (2)	0.4 (2)
Emerson Lakes Bridge	47.7	0.22	0.22	1.9 (2)	0.4 (2)
Ustream Berland River	101.9	0.52	0.29		
Windfall Bridge	175.2	0.41 (2)	0.17 (2)	0.4	0.4
Blue Ridge	234.3	0.14	0.14		
Upstream Alpac Site	585	1.1	0.12		
Upstream Ft. McMurray	943.9	<0.25	<0.25		

Numbers in parenthesis indicate number of analyses

The mass balance (Table 14) shows that HCE (133 ug/day) and Ft. McMurray STP (8.7 ug/day) were the major effluent sources of total T_4CDD flux. Tributary additions ot T_4CDD were important, particularly from the Lesser Slave River (48 ug/day) and Clearwater River (22 ug/day). Mass flux of T_4CDD is shown graphically in Figure 8. The trend line is complex, with increased flux obvious at sites immediately below HCE, followed by a complex trend due a combination of slowly reducing T_4CDD concentration and changes in suspended sediment flux.

Table 14 Mass Balance, T_4CDD in Suspended Sediment, February-March 1993

Reach	Site	Km d/s HCE	Mass Flux, T_4CDD in Suspended Sediment (ug/day)					Balance ug/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	21						
	Hinton Combined Effluent	0			133				
	AR Weldwood Haul Br.	1.1		85					69
	AR Obed Bridge	21.0		82					3
	AR Emerson Lakes	47.7		67					15
	AR u/s Berland River	101.9		8.4					59
	Berland River	102.3				1.8			
	AR Windfall Bridge	175.2					9.0		1
Whitecourt	AR Windfall Bridge	175.2	9.0						
	Alberta Newsprint Pulp	198.3			0.1				
	McLeod River	209.1				6.1			
	Millar Western Pulp	209.6			0.1				
	Whitecourt STP	213			0.1				
	AR Blue Ridge	234.3					21		6
Athabasca	AR Blue Ridge	234.3	21						
	Pembina River	391.9				0.6			
	Slave Lake Pulp	(448.5)			(0.2)				
	Lesser Slave River	448.5				48			
	Athabasca STP	555.5			0.2				
	AR u/s Alpac Site	585.0					33		37
Ft McMurray	AR u/s Alpac Site	585.0	33						
	AR u/s Ft. McMurray	943.9		15					18
	Clearwater River	948.7				22			
	Ft McMurray STP	950			8.7				
	AR 27 Baseline	1130					83	37	

Figure 7 Observed Concentration of Total T_4CDD in Sediments, February-March, 1993 (pg/G)

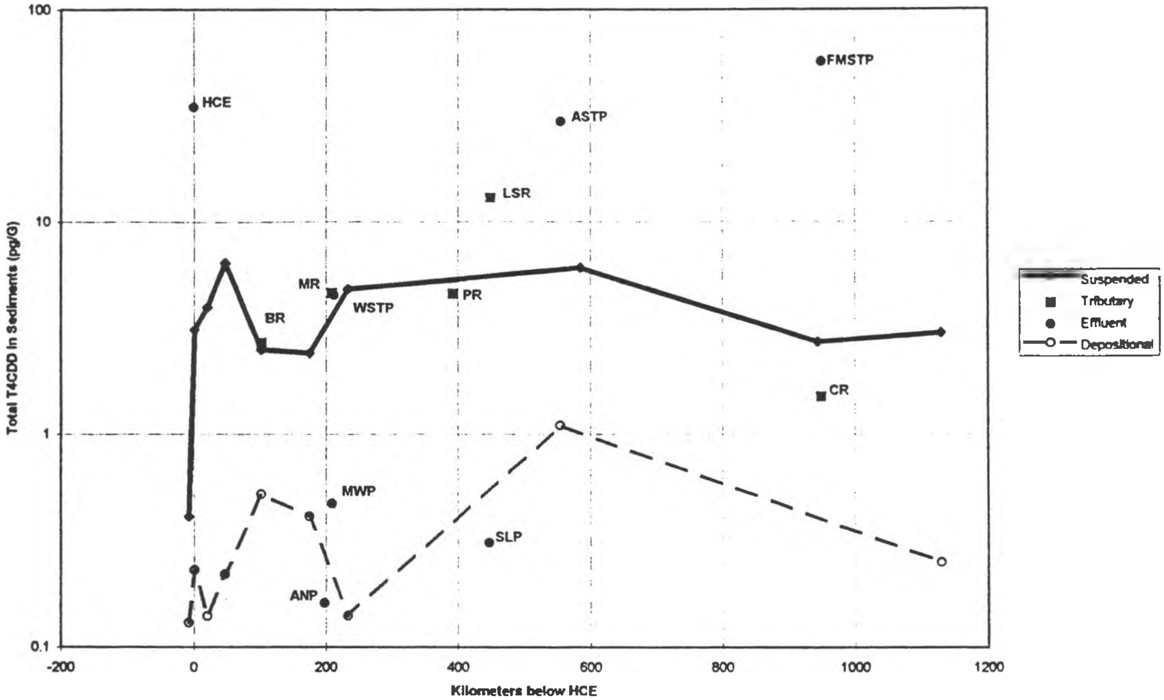
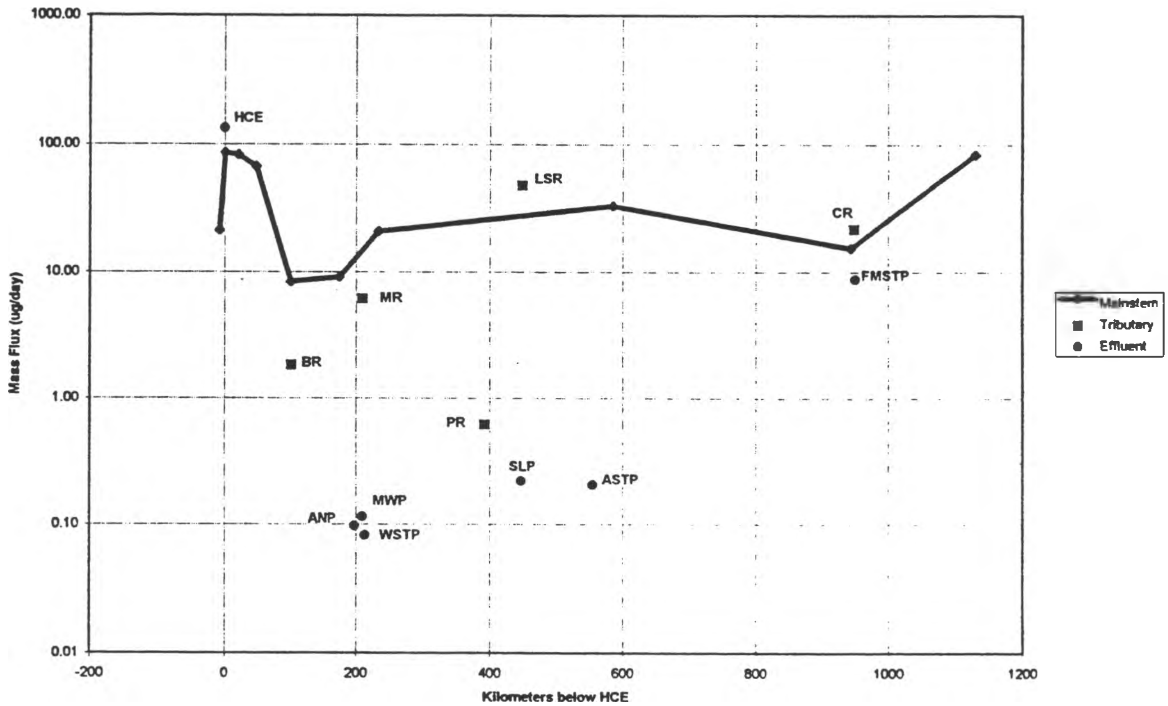


Figure 8 Observed Mass Flux of Total T_4CDD in Suspended Sediment, February-March, 1993 (ug/day)



O_8CDD in Sediment

Concentration of O_8CDD in suspended sediments is presented in Figure 9. Highest effluent concentrations were in sediments from the three sewage treatment plants at Whitecourt (1900 pg/G), Athabasca (3400 pg/G), and Ft. McMurray (1400 pg/G). Concentration in HCE suspended sediment was 130 pg/G (lower than the concentration in the Pembina River (160 pg/G). The concentration trend line for suspended sediments shows increased mainstem concentration below HCE, little change between Whitecourt and u/s of Alpac, increased concentration to u/s of Fort McMurray and lower concentrations in the reach below Ft. McMurray. Concentrations of O_8CDD in depositional sediments were approximately 20-50% of those in suspended sediments, with the exception of upstream of Hinton and 27 Baseline, where the concentrations were similar.

The mass balance data in Table 15 shows HCE (493 ug/day) and the Ft. McMurray STP (288 ug/day) to be of importance in adding sediment-bound O_8CDD to the Athabasca River. Tributary additions from the Lesser Slave River (168 ug/day) and Clearwater River (288 ug/day) were also sizeable. As was the case for D_2CDD flux, inputs of sediment-bound O_8CDD to the reach between Athabasca and Ft. McMurray of unknown source were significant (589 ug/day). The mass flux trend line (Figure 10) indicates that while effluent effects on O_8CDD mass flux are apparent, particularly below HCE, variability in flux appears to be largely controlled by other variables including tributary inputs and, probably, diverse non-point sources. Note that O_8CDD sediment flux at the control site (u/s Maskuta Creek) was similar or higher than at most downstream mainstem sites.

Table 15 Mass Balance, O_8CDD in Suspended Sediment, February-March 1993 Synoptic Survey

Reach	Site	Km d/s HCE	Mass Flux, O_8CDD in Suspended Sediment (ug/day)					Balance ug/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	616						
	Hinton Combined Effluent	0			493				
	AR Weldwood Haul Br.	1.1		1020					89
	AR Obed Bridge	21.0		909					111
	AR Emerson Lakes	47.7		720					189
	AR u/s Berland River	101.9		140					580
	Berland River	102.3				12			
	AR Windfall Bridge	175.2					215	63	
Whitecourt	AR Windfall Bridge	175.2	215						
	Alberta Newsprint Pulp	198.3			16				
	McLeod River	209.1				69			
	Millar Western Pulp	209.6			0.6				
	Whitecourt STP	213			34				
	AR Blue Ridge	234.3					133		202
Athabasca	AR Blue Ridge	234.3	133						
	Pembina River	391.9				22			
	Slave Lake Pulp	(448.5)			(2.0)				
	Lesser Slave River	448.5				168			
	Athabasca STP	555.5			23				
	AR u/s Alpac Site	585.0					198		148
Ft McMurray	AR u/s Alpac Site	585.0	198						
	AR u/s Ft. McMurray	943.9		787				589	
	Clearwater River	948.7				288			
	Ft McMurray STP	950			214				
	AR 27 Baseline	1130					718		571

Figure 9 Observed Concentration of Total O_8CDD in Sediments, February-March, 1993 (pg/G)

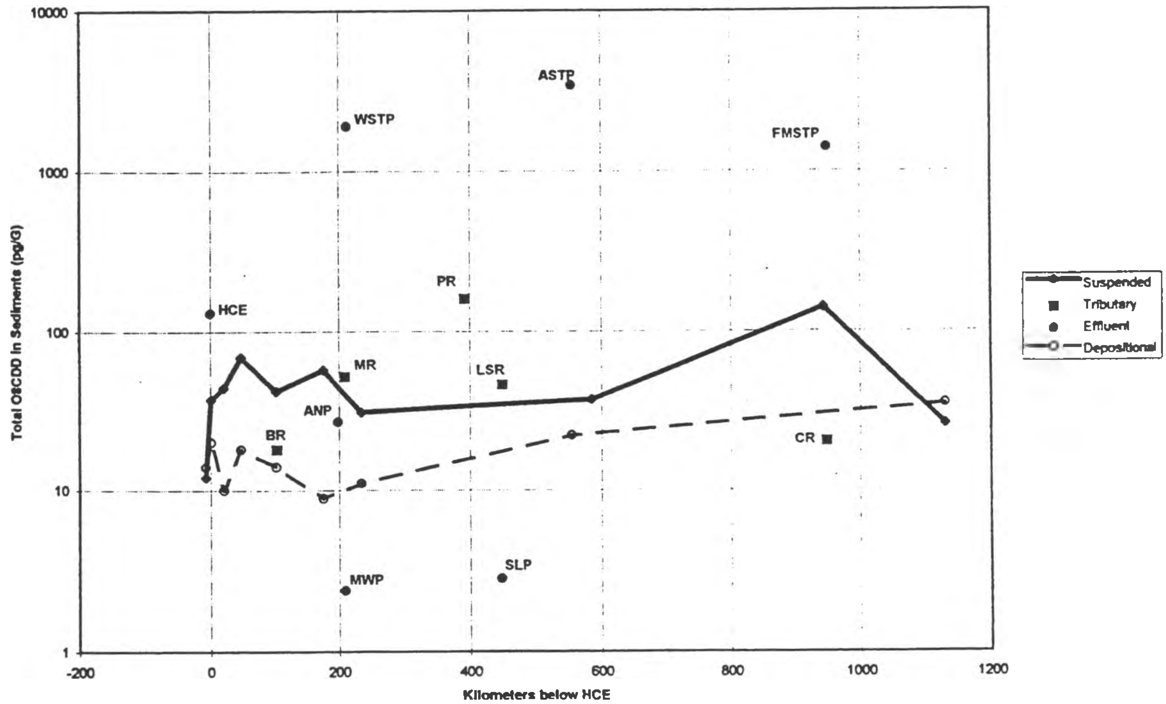
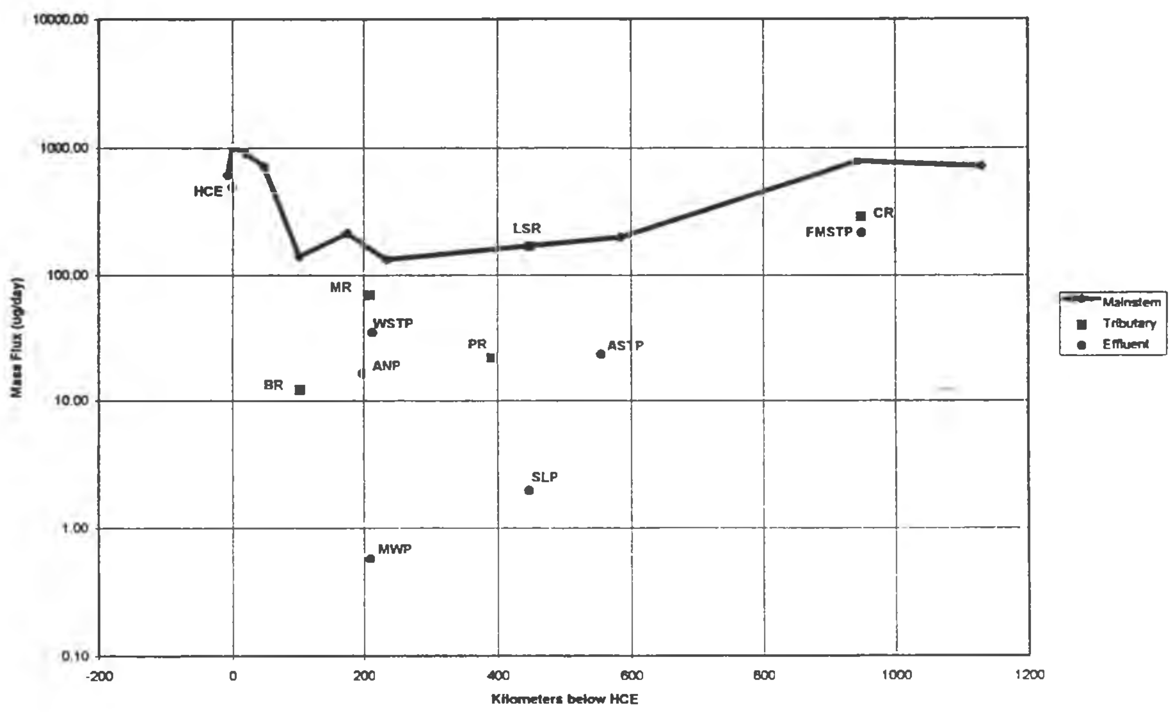


Figure 10 Observed Mass Flux of Total O_8CDD in Suspended Sediment, February-March, 1993 (ug/day)



D_2CDF in Sediment

D_2CDF concentrations in HCE suspended sediment (3600 ug/G with 2,8-T_2CDD at 3000 ug/G) were approximately three orders of magnitude higher than found at the control site, producing a dramatic increase in mainstem Athabasca River concentrations, which did not reduce to control levels until Km. 1130 (Wood Buffalo National Park) (Figure 11). The mass balance data (Table 16) shows HCE to be the only significant D_2CDF source in the basin, adding 13661 ug/day to the Athabasca River. Concentrations in depositional sediments followed a similar longitudinal trend, with concentrations about one order of magnitude lower than in suspended sediments.

The mass flux trend line (Figure 12) shows that D_2CDF flux decreased to control levels by Km. 585 (upstream of Alpac site). As suggested by Pastershank and Muir (1994), D_2CDF in suspended sediment appears to be an excellent tracer of bleached kraft effluent.

Table 16 Mass Balance, D_2CDF in Suspended Sediment, February-March 1993 Synoptic Survey

Reach	Site	Km d/s HCE	Mass Flux, D_2CDF in Suspended Sediment (ug/day)					Balance ug/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	287						
	Hinton Combined Effluent	0			13661				
	AR Weldwood Haul Br.	1.1		9922					4026
	AR Obed Bridge	21.0		10478				556	
	AR Emerson Lakes	47.7		5949					4529
	AR u/s Berland River	101.9		1170					4779
	Berland River	102.3				142			446
	AR Windfall Bridge	175.2					866		
Whitecourt	AR Windfall Bridge	175.2	866						
	Alberta Newsprint Pulp	198.3			10.8				
	McLeod River	209.1				52			
	Millar Western Pulp	209.6			0.3				
	Whitecourt STP	213			0.8				
	AR Blue Ridge	234.3					643		287
Athabasca	AR Blue Ridge	234.3	643						
	Pembina River	391.9				3.5			
	Slave Lake Pulp	(448.5)			(0.6)				
	Lesser Slave River	448.5				1.0			
	Athabasca STP	555.5			0.7				
	AR u/s Alpac Site	585.0					279		369
Ft McMurray	AR u/s Alpac Site	585.0	279						
	AR u/s Ft. McMurray	943.9		236					43
	Clearwater River	948.7				4.3			
	Ft McMurray STP	950			8.4				
	AR 27 Baseline	1130					331	82	

Figure 11 Observed Concentration of Total D_2CDF in Sediments, February-March, 1993 (pg/G)

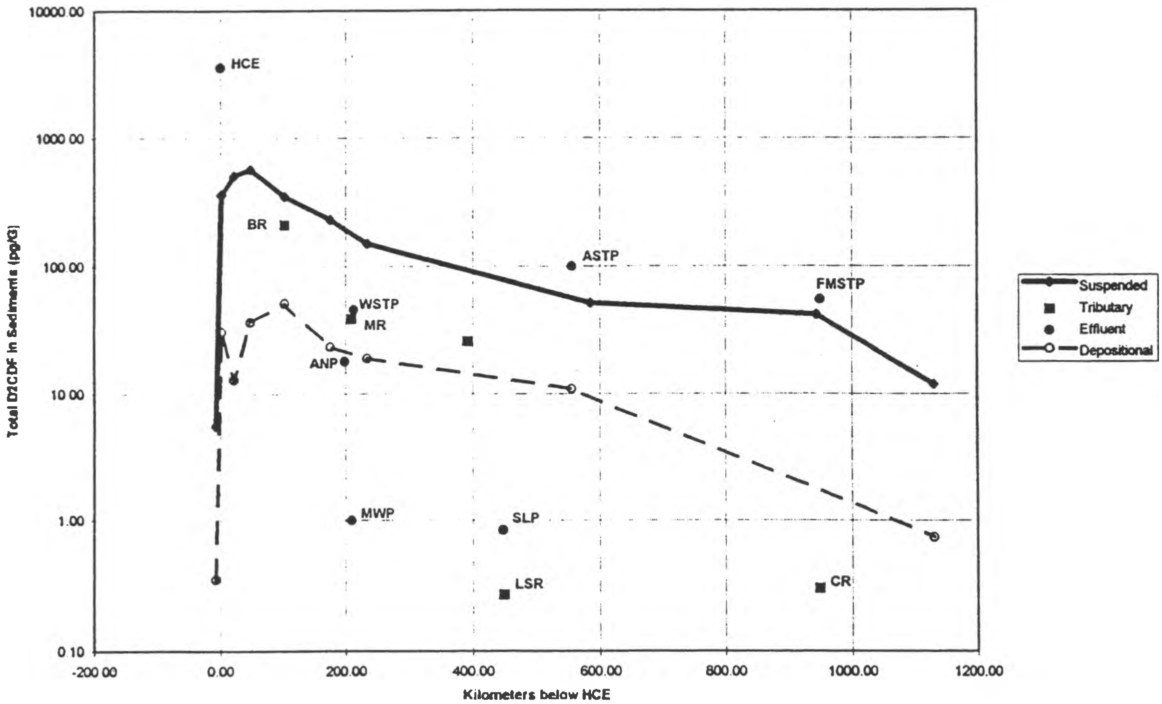
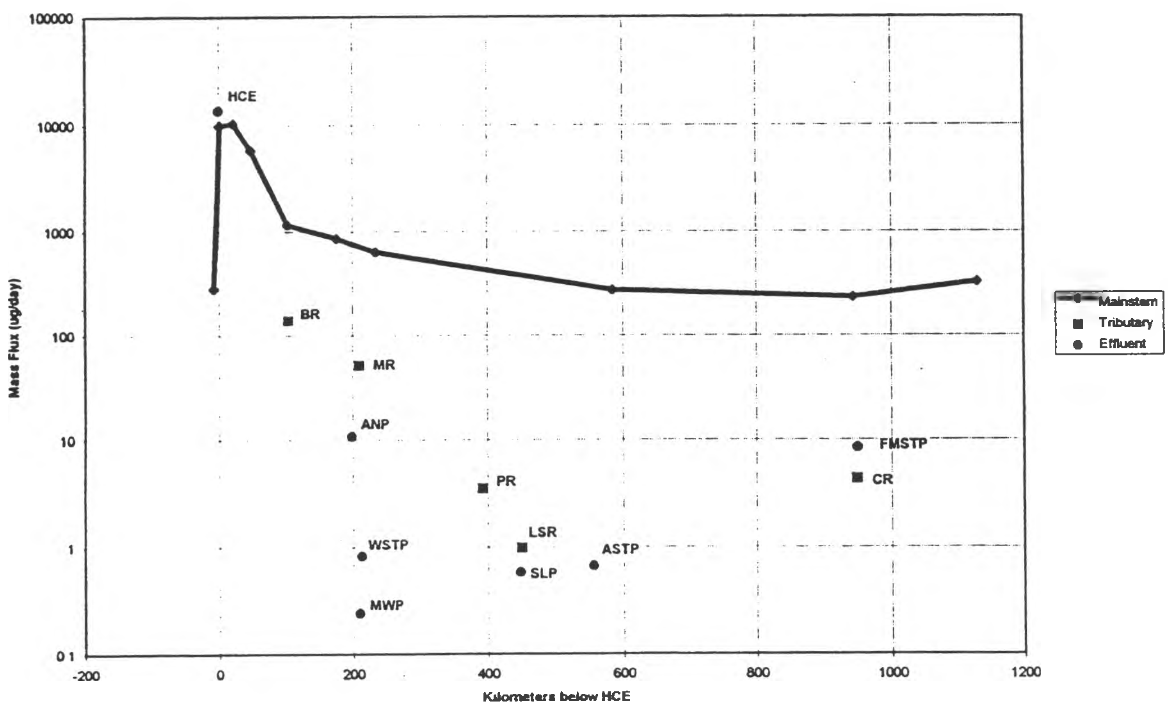


Figure 12 Observed Mass Flux of Total D_2CDF in Suspended Sediment, February-March, 1993 (ug/day)



T_4CDF in Sediments

The results for T_4CDF were very similar to those for D_2CDF, with HCE being the major basin source (250 pg/G total T_4CDF, 56 pg/G 2,3,7,8-T_4CDF, and 115 pg/G 2,4,6,8-T_4CDF). The effect of this input increased Athabasca River concentrations nearly two orders of magnitude, with concentrations remaining above control to Wood Buffalo National Park (Figure 13). Concentrations in the Athabasca River downstream of Hinton were near 30 pg/G, somewhat higher than predicted from the HCE sediment dilution ratio (19 pg/G). Concentrations in depositional sediments were about one order of magnitude lower than in suspended sediments at most mainstem sites, with the exception of u/s Maskuta Creek (control Km -7.6) and 27 Baseline (Km. 1130), where near-equilibrium in T_4CDF sediment concentrations existed.

Table 17 shows HCE input of sediment-bound T_4CDF totalled 949 ug/day, much larger than any other effluent or tributary source. The mass flux graphic (Figure 14) shows that T_4CDF mass flux did not return to control concentrations by the boundary of Wood Buffalo National Park. Similar to D_2CDF, T_4CDF in suspended sediment appears to be an excellent tracer of bleached kraft effluent.

Table 17 Mass Balance, T_4CDF in Suspended Sediment, February-March 1993

Reach	Site	Km d/s HCE	Mass Flux, T_4CDF in Suspended Sediment (ug/day)					Balance ug/day	
			In	Mainstem	Effluent	Tributary	Out	Gain	Loss
Hinton	AR u/s Maskuta Ck.	-7.6	26						
	Hinton Combined Effluent	0			949				
	AR Weldwood Haul Br.	1.1		772					203
	AR Obed Bridge	21.0		676					96
	AR Emerson Lakes	47.7		344					332
	AR u/s Berland River	101.9		97					247
	Berland River	102.3				6.2			16
	AR Windfall Bridge	175.2					87		
Whitecourt	AR Windfall Bridge	175.2	87						
	Alberta Newsprint Pulp	198.3			1.9				
	McLeod River	209.1				3.6			
	Millar Western Pulp	209.6			0.06				
	Whitecourt STP	213			0.3				
	AR Blue Ridge	234.3					86		7
Athabasca	AR Blue Ridge	234.3	86						
	Pembina River	391.9				0.2			
	Slave Lake Pulp	(448.5)			(0.1)				
	Lesser Slave River	448.5				10			
	Athabasca STP	555.5			0.2				
	AR u/s Alpac Site	585.0					38		58
Ft McMurray	AR u/s Alpac Site	585.0	38						
	AR u/s Ft. McMurray	943.9		43				5	
	Clearwater River	948.7				27			
	Ft McMurray STP	950			15				
	AR 27 Baseline	1130					52		33

Figure 13 Observed Concentration of Total T_4CDF in Sediments, February-March, 1993 (pg/G)

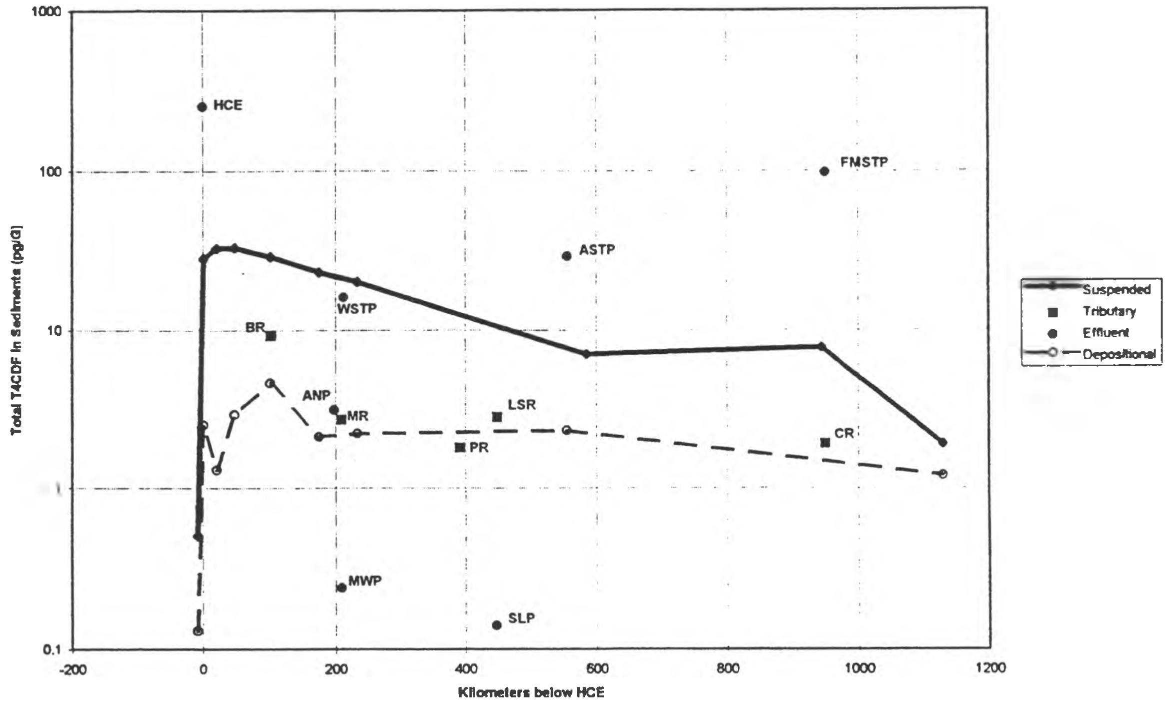
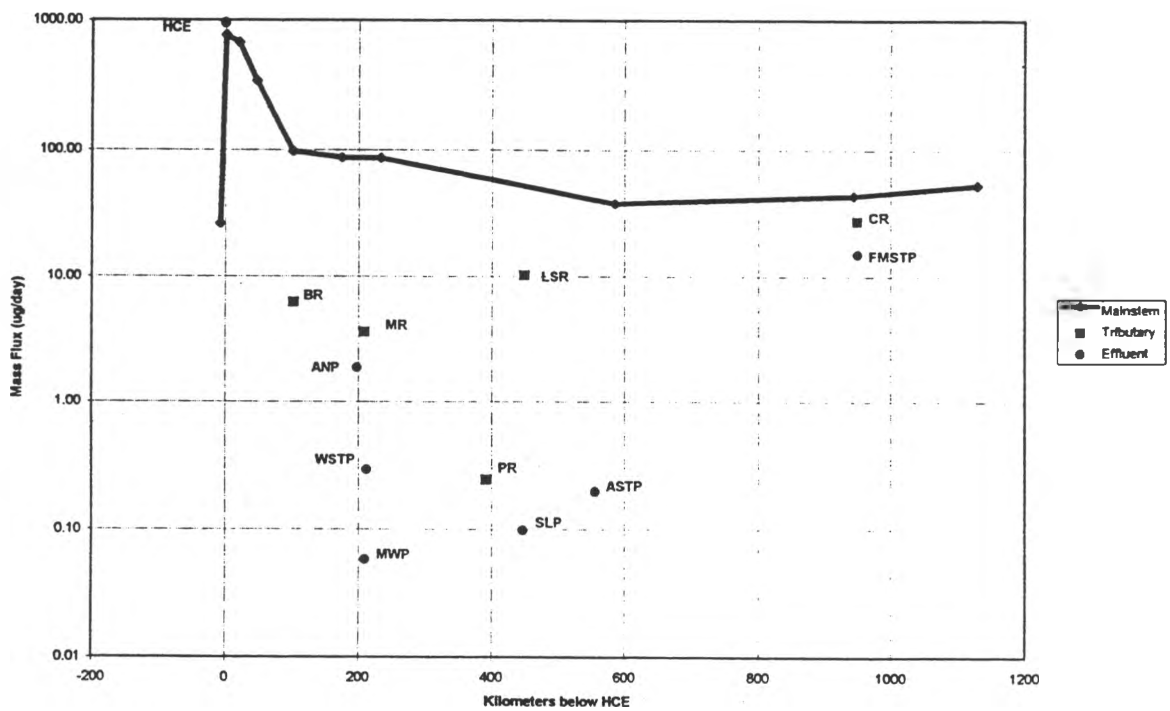


Figure 14 Observed Mass Flux of Total T_4CDF in Suspended Sediment, February-March, 1993 (ug/day)



4.5 RESIN ACIDS

4.5.1 General

Resin acid are natural products in tree bark and wood, with coniferous trees having concentrations as much as one order of magnitude higher than deciduous trees. Dependant upon the process used, resin acid concentrations in pulp mill effluent can vary greatly, with mechanical processes tending to produce resin acids in higher concentrations than chemical processes. Biological treatment is reported to reduce concentrations of non-chlorinated resin acids by approximately 90%, though chlorinated resin acids, which can be produced in bleached kraft mills, are somewhat more resistant to treatment. A significant percentage of the toxicity of pulp mill effluents is usually attributable to resin acids (McLeay *et al.*,1987).

Resin acids are hydrophobic and lipophilic compounds, with limited persistence in the water column. During the reach specific study on the upper Athabasca River, concentrations of resin acids in suspended sediment exceeded those in water by over three orders of magnitude, while transport on suspended sediments for distances exceeding 200 kilometers was reported (Crosley, 1996).

Resin acids were analyzed for February-March 1993 suspended sediments from five mainstem Athabasca River sites, two tributaries, and four pulp mill effluents, and for depositional sediments from nine mainstem Athabasca River sites. Resin acids in water were analyzed by AEP as part of the 1993 winter synoptic and have been reported in Noton and Saffran (1995).

4.5.2 Resin Acids in Suspended and Depositional Sediments

The discussion is limited to the predominent effluent resin acids found in sediments: pimaric acid, isopimaric acid, dehydroabietic acid, abietic acid, and total chlorinated resin acids. The same compounds were predominant in water (Noton and Saffran, 1995). The full analytical results for resin acids appear in the Appendix.

Pimaric Acid

Pimaric acid was predominant in HCE suspended sediments, at a concentration of 130000 ng/G (Figure 15). A similar concentration was reported for Alberta Newsprint (120000 ng/G). The remaining CTMP mills had much lower effluent sediment concentrations. It should be noted, as discussed in Section 4.2, that low recoveries of the analytical surrogate (o-methyl podocarpic acid) were reported for suspended sediments from Alberta Newsprint and the Athabasca River near Obed. Whether this low recovery reflects error in the results for samples from both locations is uncertain, though evidence exists that the results reported for Obed were high, as will discussed shortly.

HCE input produced an approximate four order of magnitude increase in Athabasca River pimaric acid. Pimaric acid was reported at 21000 ng/G at Km. 1.1 (Weldwood Haul Bridge), 95000 ng/G at Km. 21.0 (Obed Bridge), and 21000 ng/G at Km. 47.7 (Emerson Lakes). Concentration at the upstream control site was 4.8 ng/G. An HCE sediment dilution ratio of 13.5 : 1 produces a near-field mixed river concentration of approximately 9650 ng/G. This suggests that the concentration reported for pimaric acid in HCE may have been somewhat low, while the concentration reported for Obed was almost certainly high. Suspended sediments collected in April 1992 from HCE contained pimaric acid at 94000 ng/G, similar to the 1993 result.

Depositional sediments were generally one order of magnitude lower in pimaric acid concentration than suspended sediments (Figure 15). The increase in depositional sediment concentration of pimaric acid between Windfall Bridge and Blue Ridge (from 160 ng/G to 230 ng/G) may reflect inputs from Alberta Newsprint. Note that the suspended sediment trend line in Figure 15 has been interpolated between Kms. 47-1130. While this may be considered inappropriate due to the absence of intermediate sampling locations, the trend line has been left in to aid visual comparison with the depositional sediment results.

The probable over-estimated pimaric acid concentration at Obed is reflected in the mass balance (Table 18), which shows a large apparent flux gain-loss above and below Obed. Effluent mass flux of pimaric acid totalled 493 G/day from HCE, and 72.3 G/day from Alberta Newsprint. Inputs from other CTMP effluents and from the two tributaries were negligible. The mass flux of pimaric acid in Athabasca River mainstem suspended sediments remained above control levels at Km. 1130 (Figure 16).

Table 18 Mass Balance, Pimaric Acid in Suspended Sediment, Winter 1993 Synoptic Survey

Site	Km d/s HCE	Mass Flux, Pimaric Acid in Suspended Sediment (G/day)			Balance G/day	
		Mainstem	Effluent	Tributary	Gain	Loss
AR u/s Maskuta Ck.	-7.6	0.25				
Hinton Combined Effluent	0		493			
AR Weldwood Haul Br.	1.1	579			86	
AR Obed Bridge	21.0	1963			1384	
AR Emerson Lakes	47.7	219				1744
Alberta Newsprint Pulp	198.3		72.3			
Millar Western Pulp	209.6		0.5			
Slave Lake Pulp	(448.5)		0.1			
Lesser Slave River	448.5			0.03		
Clearwater River	948.7			0.07		
AR 27 Baseline	1130	3.6				

Figure 15 Observed Concentration of Pimaric Acid in Sediments, February-March, 1993 (ng/G)

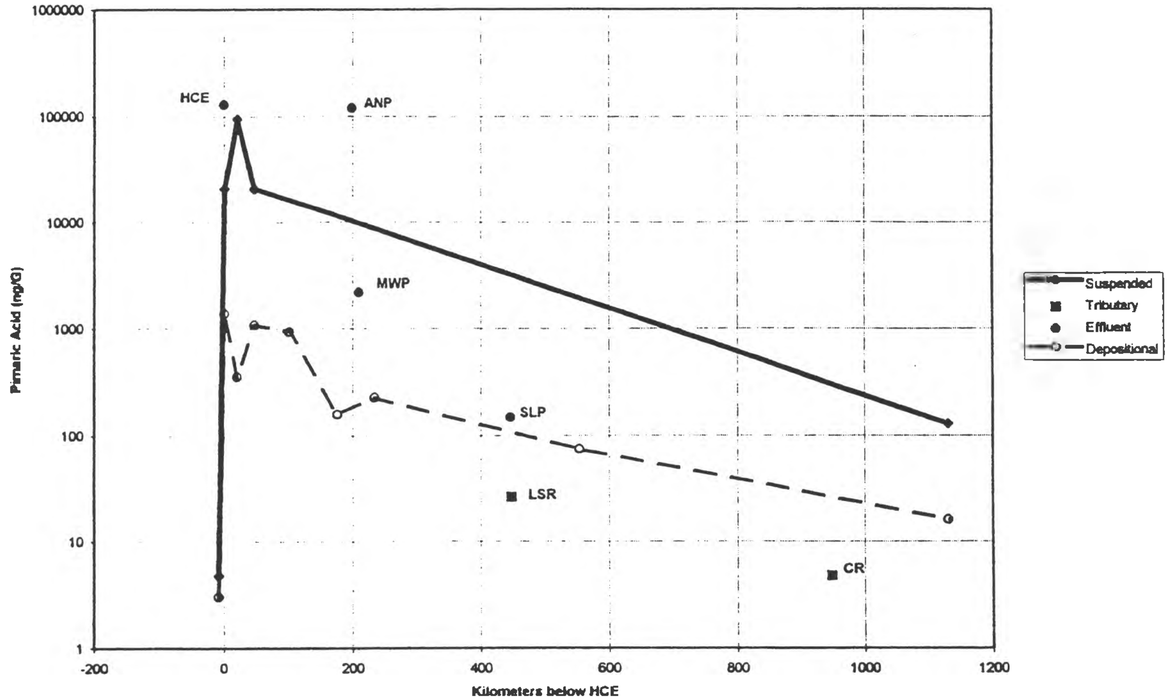
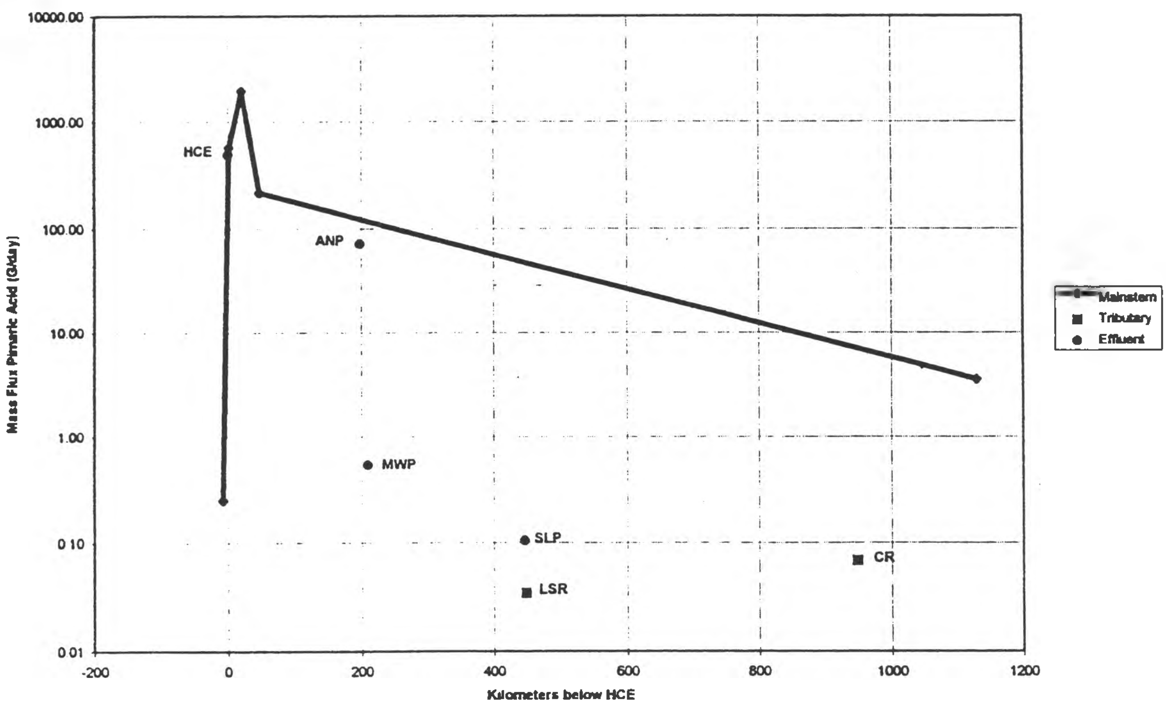


Figure 16 Observed Mass Flux of Pimaric Acid in Suspended Sediment, February-March, 1993 (G/day)



Isopimaric Acid in Sediments

The results for isopimaric acid were very similar to those for pimaric acid, with highest effluent concentrations in suspended sediments from HCE (68000 ng/G) and Alberta Newsprint (280000 ng/G). The two other CTMP effluents had much lower concentrations (Figure 17). Concentration of isopimaric acid at HCE was similar to that found in April, 1992 (67000 ng/G). The concentration trend lines show that concentrations of isopimaric acid in suspended sediments remained above control levels throughout the study reach. Concentrations of isopimaric acid in depositional sediments were approximately one order of magnitude lower than in suspended sediments at most sites, returning to near control concentration at 27 Baseline. As with isopimaric acid, a concentration increase in depositional sediment isopimaric acid between Windfall and Blue Ridge (from 120 ng/G to 210 ng/G) may reflect inputs from Alberta Newsprint.

Once again, overestimated isopimaric acid concentration at Obed is apparent in the mass balance data (Table 19) and in the mass flux graphic (Figure 18). Mass flux of isopimaric acid at 27 Baseline (2.7 G/day) was very near that for the upstream control site (2.0 G/day).

Table 19 Mass Balance, Isopimaric Acid in Suspended Sediment, February-March 1993

Site	Km d/s HCE	Mass Flux, Isopimaric Acid in Suspended Sediment (G/day)			Balance G/day	
		Mainstem	Effluent	Tributary	Gain	Loss
AR u/s Maskuta Ck.	-7.6	2.0				
Hinton Combined Effluent	0		258			
AR Weldwood Haul Br.	1.1	303			43	
AR Obed Bridge	21.0	1157			854	
AR Emerson Lakes	47.7	125				1032
Alberta Newsprint Pulp	198.3		169			
Millar Western Pulp	209.6		1.0			
Slave Lake Pulp	(448.5)		0.8			
Lesser Slave River	448.5			0.2		
Clearwater River	948.7			0.8		
AR 27 Baseline	1130	2.7				

Figure 17 Observed Concentration of Isopimaric Acid in Sediments, February-March, 1993 (ng/G)

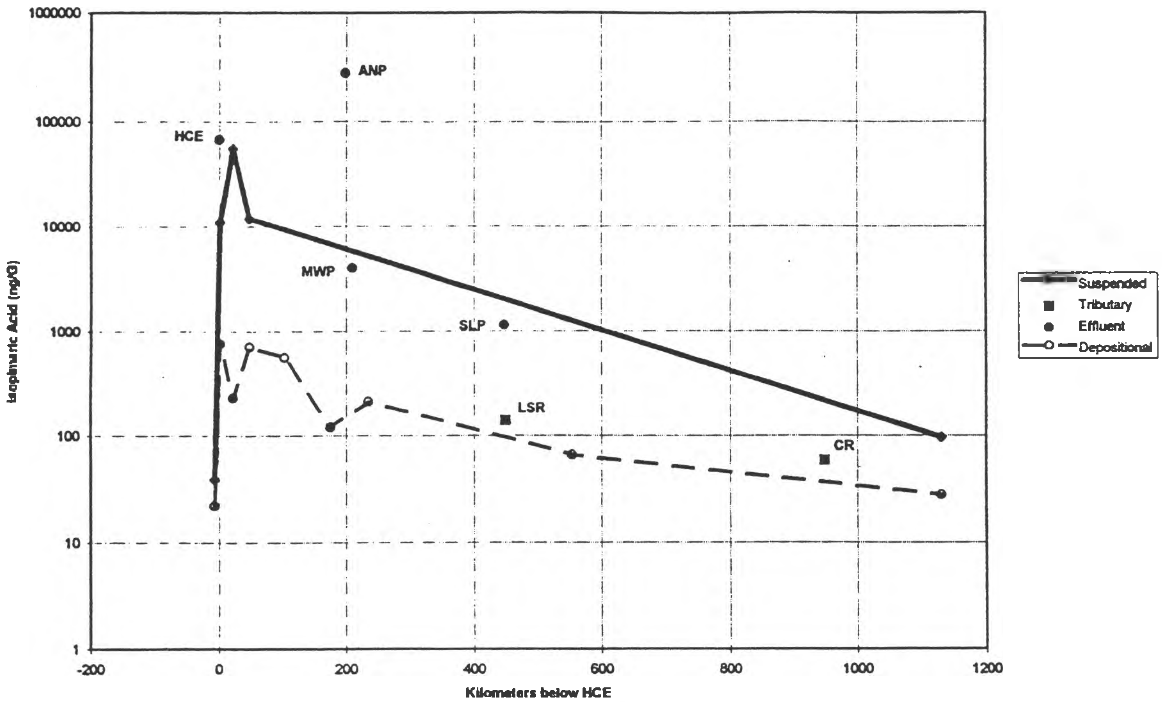
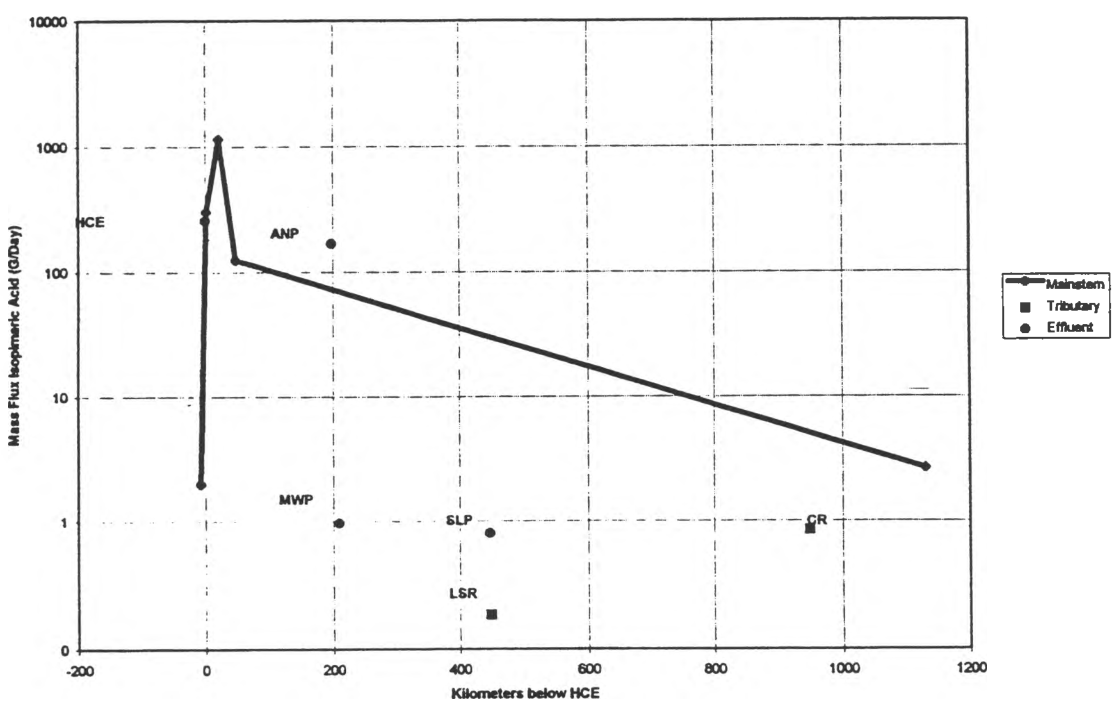


Figure 18 Observed Mass Flux of Isopimaric Acid in Suspended Sediment, February-March, 1993 (G/day)



Dehydroabietic Acid in Sediments

Dehydroabietic acid has been found to be the most persistent non-chlorinated resin acid in a number of contaminant studies (McLeay *et al.*, 1987). Highest concentrations in effluent were at Alberta Newsprint (700000 ng/G), followed by HCE (37000 ng/G), Millar Western (10000 ng/G), and Slave Lake Pulp (3450 ng/G). (The April 1992 dehydroabietic acid concentration in HCE was 36000 ng/G). Athabasca River concentration of dehydroabietic acid appears to be controlled by the large-volume Hinton combined effluent, though additional samples for resin acids would have been useful to better define concentration and mass flux patterns through the Whitecourt reach (Figures 19, 20). Dehydroabietic acid concentrations reported for Obed were again high, as can be seen in both the concentration and mass flux graphics.

The mass balance table (Table 20) shows that sediment flux of dehydroabietic acid was higher at Alberta Newsprint (421 G/day) than at HCE (140 G/day). Increased concentration in depositional sediment concentration at Blue Ridge (360 ng/G, up from 170 ng/G at Windfall Bridge) likely reflects Alberta Newsprint inputs.

Concentration of dehydroabietic acid remained above control (110 ng/G) at 27 Baseline (210 ng/G), though mass flux was nearly identical at the two locations (5.1 G/day, 5.2 G/day).

Table 20 Mass Balance, Dehydroabietic Acid in Suspended Sediment, February-March 1993

Site	Km d/s HCE	Mass Flux, Dehydroabietic Acid in Suspended Sediment (G/day)			Balance G/day	
		Mainstem	Effluent	Tributary	Gain	Loss
AR u/s Maskuta Ck.	-7.6	5.1				
Hinton Combined Effluent	0		140			
AR Weldwood Haul Br.	1.1	146			0.9	
AR Obed Bridge	21.0	641			495	
AR Emerson Lakes	47.7	67				574
Alberta Newsprint Pulp	198.3		421			
Millar Western Pulp	209.6		2.4			
Slave Lake Pulp	(448.5)		2.4			
Lesser Slave River	448.5			0.7		
Clearwater River	948.7			5.0		
AR 27 Baseline	1130	5.2				

Figure 19 Observed Concentration of Dehydroabietic Acid in Sediments, February-March, 1993 (ng/G)

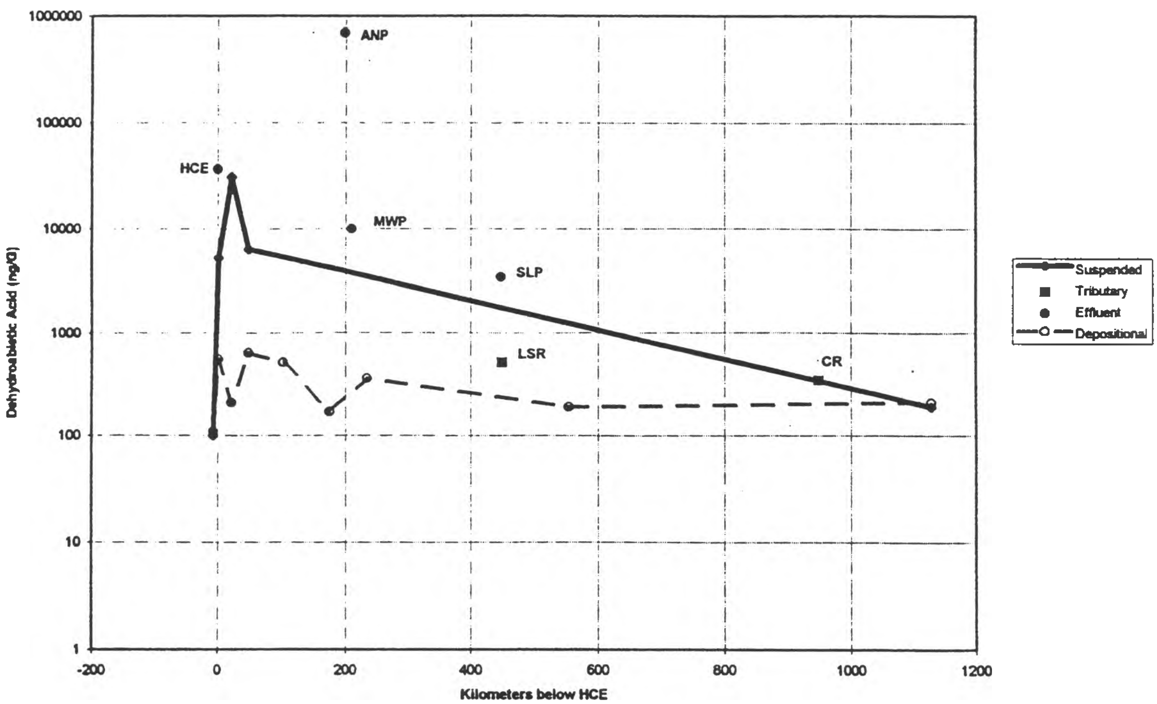
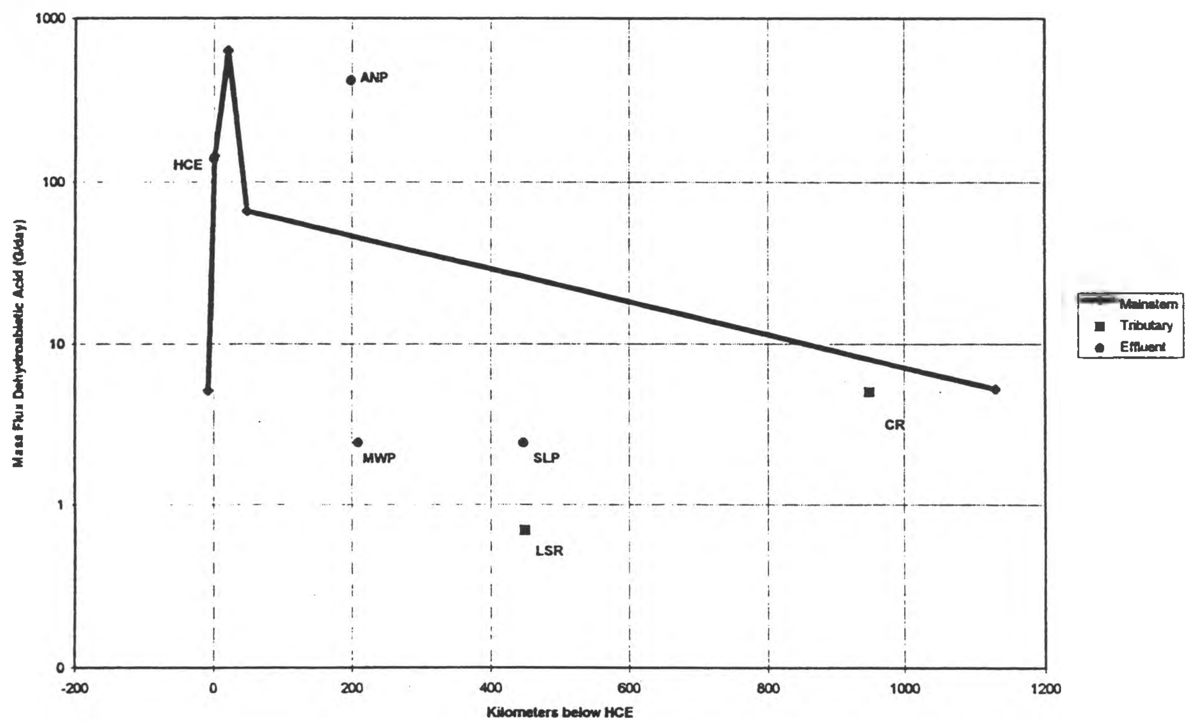


Figure 20 Observed Mass Flux of Dehydroabietic Acid in Suspended Sediment, February-March, 1993 (G/day)



Abietic Acid in Sediments

Effluent concentrations of abietic acid were as follows: Alberta Newsprint (760000 ng/G), HCE (28000 ng/G, compared to16000 ng/G in April 1992), Millar Western (6900 ng/G), and Slave Lake Pulp (1330 ng/G). Concentration and flux trends for abietic acid were virtually identical to dehydroabietic acid, with depositional sediments having abietic acid at concentrations 10% of those in suspended sediments, except at the upstream control and 27 Baseline locations, where concentrations were similar (Figure 21). Once again, an increase in depositional sediment abietic acid concentration observed between Windfall and Blue Ridge (53 ng/G and 180 ng/G, respectively). Mass flux of abietic acid at 27 Baseline (1.0 G/day) was slightly lower than at the upstream control (1.7 G/day) (Table 21, Figure 22).

Table 21 Mass Balance, Abietic Acid in Suspended Sediment, February-March 1993

Site	Km d/s HCE	Mass Flux, Abietic Acid in Suspended Sediment (G/day)			Balance G/day	
		Mainstem	Effluent	Tributary	Gain	Loss
AR u/s Maskuta Ck.	-7.6	1.7				
Hinton Combined Effluent	0		106			
AR Weldwood Haul Br.	1.1	176			68	
AR Obed Bridge	21.0	599			423	
AR Emerson Lakes	47.7	48				551
Alberta Newsprint Pulp	198.3		458			
Millar Western Pulp	209.6		1.7			
Slave Lake Pulp	(448.5)		0.9			
Lesser Slave River	448.5			0.1		
Clearwater River	948.7			0.8		
AR 27 Baseline	1130	1.0				

Figure 21 Observed Concentration of Abietic Acid in Sediments, February-March, 1993 (ng/G)

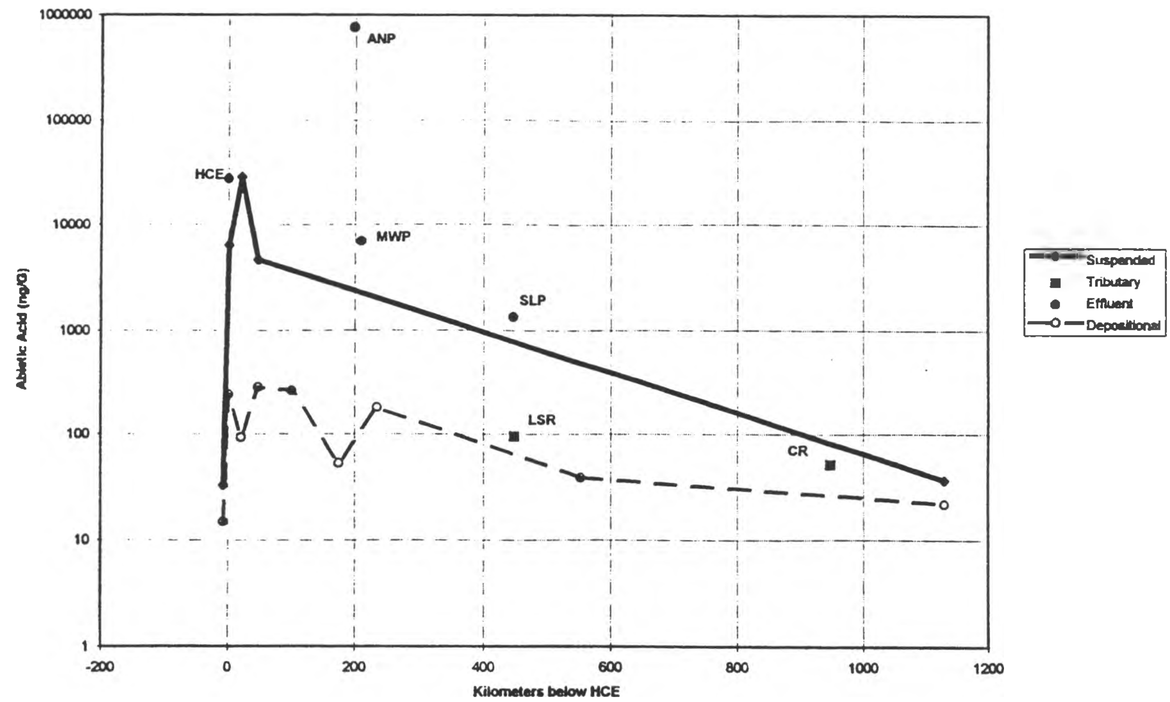
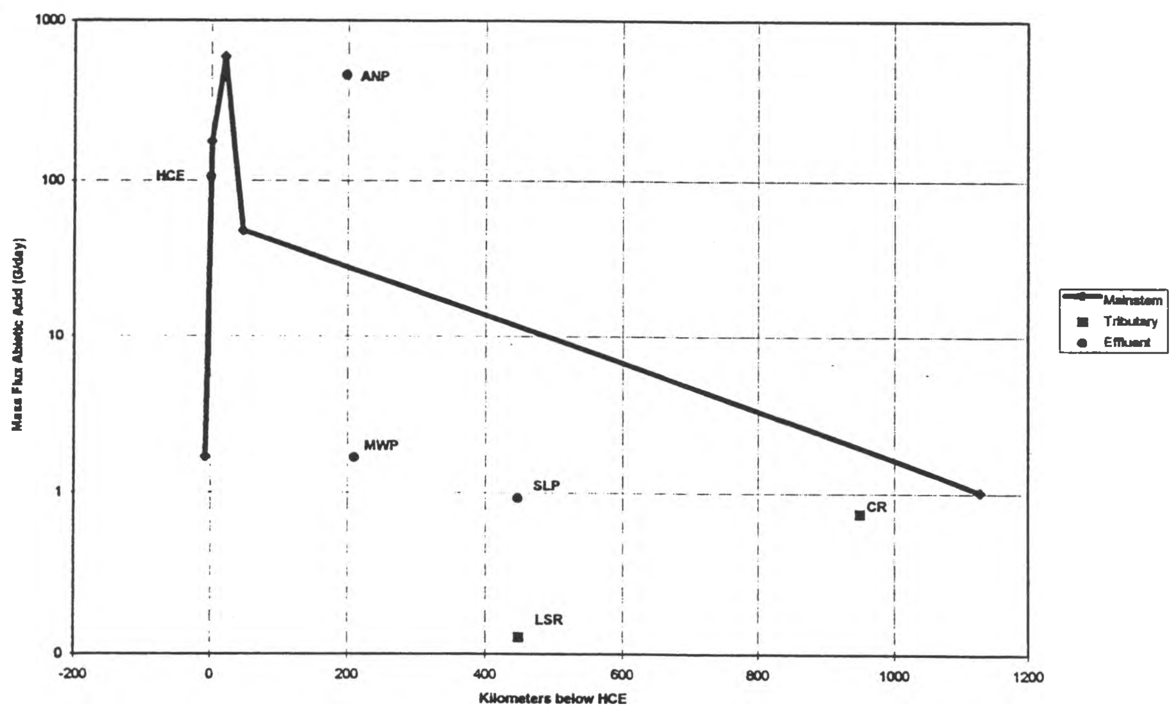


Figure 22 Observed Mass Flux of Abietic Acid in Suspended Sediment, February-March, 1993 (G/day)



Chlorinated Resin Acids in Sediments

The laboratory reported the concentrations of three chlorinated resin acids in sediment, including 12/14 chlorodehydroabietic acid (two congeners reported together) and 12,14 dichlorodehydroabietic acid. The analytical results for the three compounds have been summed for calculations and the discussion.

The only significant source of chlorinated resin acids was HCE, at a concentration of 8500 ng/G total (this compares with 12500 ng/G measured in April, 1992). Concentrations were non-detectable at CTMP mills and in tributaries with the exception of Alberta Newsprint (250 ng/G), though mass flux from Alberta Newsprint was low. No increase in depositional sediment concentration was found between Windfall and Blue Ridge, as had been seen for the non-chlorinated resin acids. Concentrations of chlorinated resin acids in both suspended and depositional sediments remained well above control concentrations at 27 Baseline (Figure 23). Mass flux of total chlorinated resin acids was 0.4 G/day at 27 Baseline, 8X higher than at the control site (0.05 G/day) (Table 22, Figure 24).

Table 22 Mass Balance, Total Chlorinated Resin Acids in Suspended Sediment, February-March 1993

Site	Km d/s HCE	Mass Flux, Σ Chlorinated Resin Acids in Suspended Sediment (G/day)			Balance G/day	
		Mainstem	Effluent	Tributary	Gain	Loss
AR u/s Maskuta Ck.	-7.6	0.05				
Hinton Combined Effluent	0		32			
AR Weldwood Haul Br.	1.1	20				12
AR Obed Bridge	21.0	105			85	
AR Emerson Lakes	47.7	8.0				97
Alberta Newsprint Pulp	198.3		0.2			
Millar Western Pulp	209.6		0.0			
Slave Lake Pulp	(448.5)		0.0			
Lesser Slave River	448.5			0.01		
Clearwater River	948.7			0.03		
AR 27 Baseline	1130	0.4				

Figure 23 Observed Concentration of Total Chlorinated Resin Acids in Sediments (ng/G) February-March, 1993

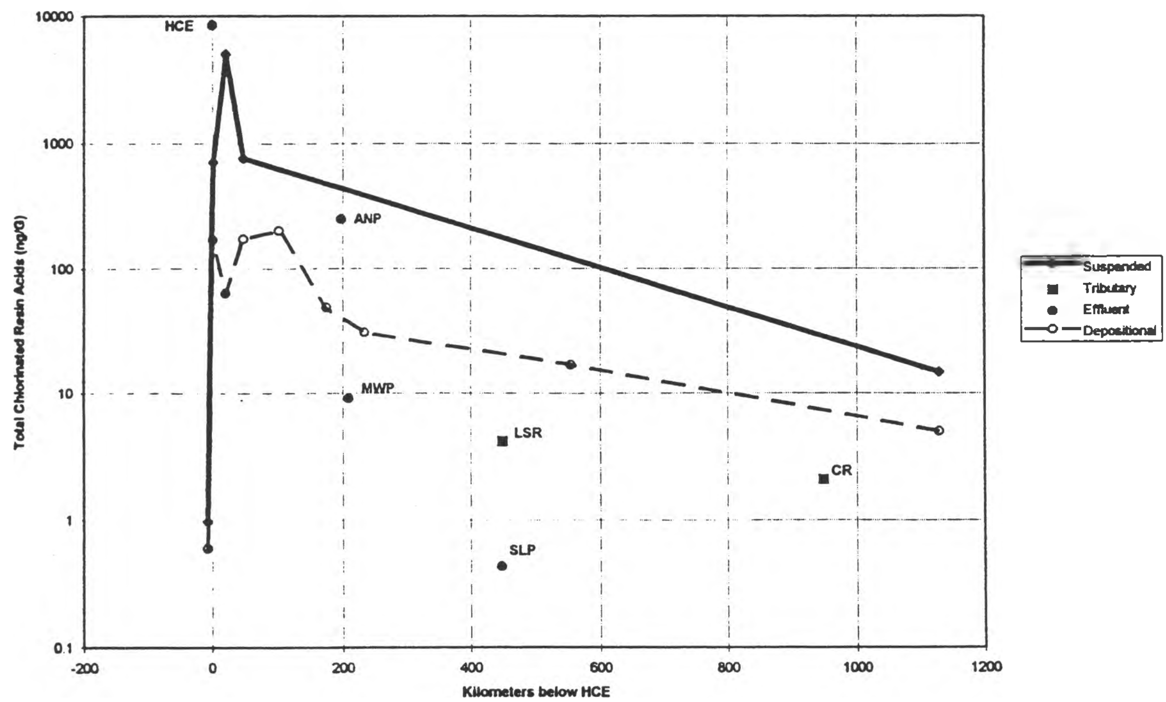
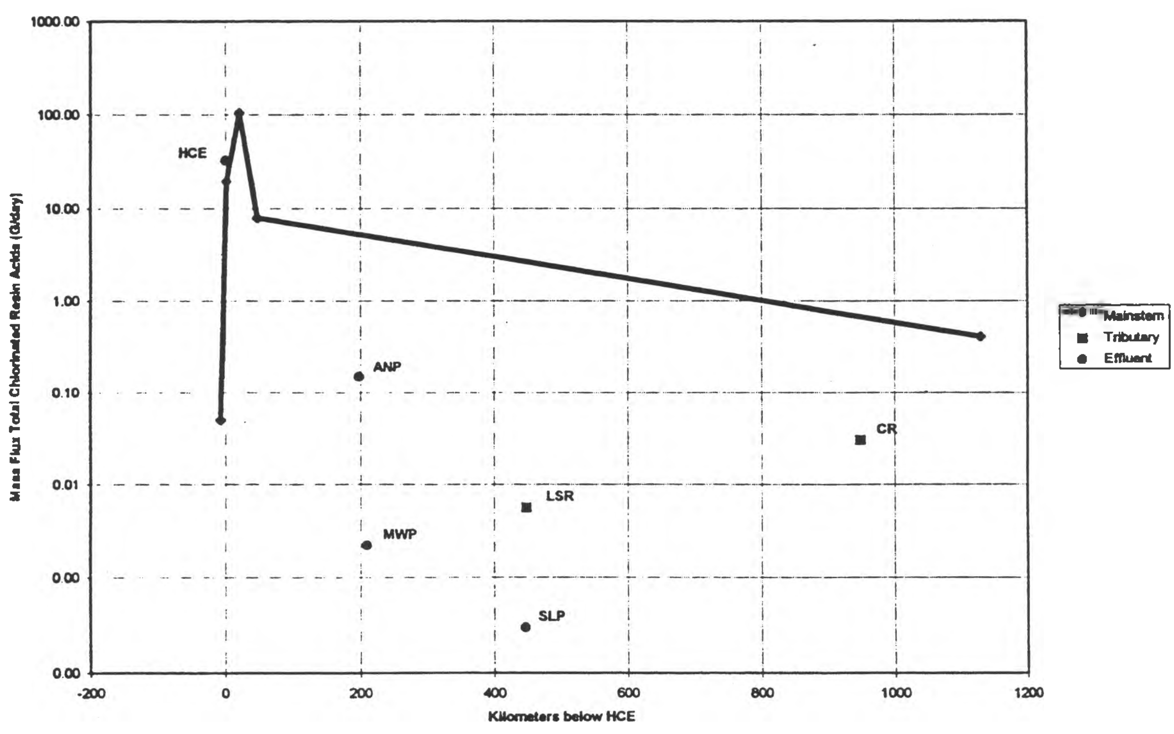


Figure 24 Observed Mass Flux of Total Chlorinated Resin Acids in Suspended Sediment (G/day) February-March, 1993



Relative Persistence of Resin Acids

Resin acid concentrations in depositional sediment in the reach below HCE, together with a calculation of percent change in concentration between Km. 1.1 and Km. 175.2, is presented in Table 23. A comparison of the percent change allows estimates to be made regarding transportability and persistence of resin acids. The analysis has been restricted to the Hinton-Whitecourt reach to reduce complications associated with multiple effluent sources. The percent change in concentrations through the reach were, in general, similar. Based upon this analysis, the order of resin acid persistence found during 1993, from most persistent to least persistent, was as follows: dehydroabietic acid > Σ chlorinated resin acids > abietic acid > isopimaric acid > pimaric acid.

Table 23 Percent Change in Resin Acid Concentration between Weldwood Haul Bridge and Windfall Bridge

Mainstem AR Location	**Km d/s HCE**	**Resin Acid Concentration in Depositional Sediments (ng/G)**				
		Pimaric Acid	Isopimaric Acid	Dehydroabietic Acid	Abietic Acid	Σ Chlorinated Resin Acids
Weldwood Haul Bridge	1.1	1400	760	560	240	170
Emerson Lakes	47.7	1090	705	640	280	172
u/s Berland River	101.9	940	560	520	260	202
Windfall Bridge	175.2	160	120	170	53	49
Percent Change Km. 1.1 to 175.2		**-88.6%**	**-84.2%**	**-69.6%**	**-77.9%**	**-71.2%**

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APPENDIX A: TERMS OF REFERENCE

No contractual Terms of Reference were prepared for the work documented in this report. The work was undertaken by the author as a contribution in kind from his employing agency and represents a part of his responsibilities to the working committee of the Contaminants Component of the Northern River Basins Study.

APPENDIX B: TABLES OF ANALYTICAL RESULTS

Table A1

Particle Size and Organic Carbon in Suspended and Depositional Sediments

	Km. d/s HCE	Date	Sand %	Silt %	Clay %	Org. C %	Org C.(Fine) %
Suspended Sediments							
AR u/s Maskuta Ck.	-7.6	93 02 11	15.95	66.44	17.61	0.94	
AR Weldwood Haul Br.	1.1	93 02 11	1.76	57.64	40.59	4.6	
AR Obed Bridge	21.0	93 02 12	8.11	50.01	41.88	4.6	
AR Emerson Lakes	47.7	93 02 13	0.39	31.39	68.21	6.2	
AR Blue Ridge	234.3	93 02 18	2.11	46.22	51.67	8.7	
AR u/s Alpac	585.0	93 02 28				5.6	
AR u/s Ft. McMurray	943.9	93 03 10				6.2	
AR 27 Baseline	1130	93 03 16	0.88	21.99	77.13	4.9	
McLeod River	209.1	93 02 16				2.3	
Pembina River	391.9	93 02 23				4.3	
Lesser Slave River	448.5	93 02 25	0.65	38.62	60.73	9.0	
Clearwater River	948.7	93 03 11	2.69	29.71	67.6	7.8	
Hinton Combined Eff.	0	93 02 11	0.24	66.89	32.87	31.1	
Alberta Newsprint Pulp	198.3	93 02 16				40.1	
Millar Western Pulp	209.6	93 02 17				28.2	
Slave Lake Pulp	448.5	93 02 24				42.8	
Ft. McMurray STP	950.0	93 03 10				21.2	
Depositional Sediments							
AR u/s Maskuta Ck.	-7.6	93 05 05	17.21	69.57	13.22	0.99	0.57
AR Weldwood Haul Br.	1.1	93 05 05	6.26	73.45	20.29	0.82	0.53
AR Obed Bridge	21.0	93 05 05	25.75	55.84	18.41	0.45	0.81
AR Emerson Lakes	47.7	93 05 05	27.43	56.18	16.39	0.72	0.68
AR u/s Berland River	101.9	93 05 06	40.61	36.27	23.12	0.82	0.86
AR Windfall Bridge	175.2	93 05 06	38.33	43.77	17.89	0.48	0.44
AR Blue Ridge	234.3	93 05 06	64.5	15.46	20.04	0.65	0.73
AR Athabasca	554.5	93 05 07	32.97	36.38	30.66	1.28	0.90
AR 27 Baseline	1130	03 03 16	98.05	1.00	0.85	0.36	0.87

Table A2

Dioxins-Furans in Clarified Water (20-liter Extracts)
Results in pg/L

Athabasca River Mainstem Locations:

	Obed Bridge 1993 02 12	Above Berland R. 1993 02 14	Blue Ridge 1993 02 18	Athabasca 1993 02 26	Above Alpac 1993 02 28	Above Ft. McMurray 1993 03 10	27 Baseline 1993 03 16
M1CDD	<0.1	<0.18	<0.1	<0.1	<0.12	<0.13	<0.14
D2CDD	0.59	<0.7	0.43	<0.53	<0.74	<0.78	<0.76
T3CDD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
T4CDD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
P5CDD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H6CDD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H7CDD	0.25	0.35	<0.2	<0.2	<0.2	<0.2	<0.2
O8CDD	0.7	1.4	<0.5	<0.5	<0.5	0.7	<0.5
M1CDF	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
D2CDF	8.5	4.2	1.6	<0.12	<0.22	<0.15	<0.13
T3CDF	1.1	1.4	0.27	<0.2	<0.2	<0.2	<0.2
T4CDF	0.24	0.14	<0.1	<0.1	<0.1	<0.1	<0.1
P5CDF	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H6CDF	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H7CDF	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
O8CDF	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Surrogates:							
1234-T4CDD (pg)	1080	1100	940	720	980	1040	660
1234678-H7CDF (pg)	2280	2100	1840	1520	1940	2060	1140

Table A3

Dioxins-Furans in Clarified Water (20-liter Extracts)
Results in pg/L

Effluents:

	Hinton Combined Effluent 1993 02 11	Alberta Newsprint Effluent 1993 02 16	Millar Western Effluent 1993 02 17	Whitecourt Sewage Effluent 1993 02 17	Slave Lake Pulp Effluent 1993 02 24	Fort McMurray Sewage Effluent 1993 03 10
M1CDD	<0.14	<0.39	<0.1	<0.12	<0.1	0.29
D2CDD	<0.91	<1.5	<0.52	5.8	<0.32	36
T3CDD	0.38	<0.18	<0.1	0.14	<0.1	1.6
T4CDD	0.35	<0.22	<0.11	<0.1	<0.1	<0.1
P5CDD	<0.1	<0.19	<0.1	<0.1	<0.1	<0.1
H6CDD	<0.1	<0.15	<0.1	<0.13	<0.1	<0.11
H7CDD	0.16	<0.42	<0.1	0.87	0.15	1.1
O8CDD	0.6	1.4	<0.3	3.0	0.38	4.0
M1CDF	12	3.4	<1.4	<1.4	<1.4	2.4
D2CDF	94	<0.48	<0.12	<0.18	<0.12	2.3
T3CDF	30	0.83	<0.2	<0.2	<0.2	0.59
T4CDF	76	0.39	<0.1	<0.1	<0.1	0.3
P5CDF	0.6	<0.1	<0.1	<0.1	<0.1	0.5
H6CDF	<0.1	<0.15	<0.1	0.31	<0.1	0.24
H7CDF	<0.1	<0.42	<0.12	<0.14	<0.11	<0.1
O8CDF	<0.1	<0.51	<0.18	<0.29	<0.26	0.18
Surrogates:						
1234-T4CDD (pg)	15	3680	980	1900	400	nr
1234678-H7CDF (pg)	94	3760	1660	3800	560	nr

Table A4

Dioxins-Furans in Suspended Sediments
Results in pg/G (dry)

Athabasca River Mainstem Locations:

	Above Maskuta Creek 93 02 11	Weldwood Haul Bridge 93 02 11	Obed Bridge 93 02 12	Obed Bridge Dup. 93 02 12	Obed Bridge Trip. 93 02 12	Emerson Lakes Bridge 93 02 13	Above Berland River 93 02 14	Windfall Bridge 93 02 15	At Blue Ridge 93 02 18	At Athabasca 93 02 26	Above Alpac 93 02 28	Above Fort McMurray 93 03 10	27 Baseline 93 03 16
M1CDD	<0.14	<0.16	<0.77	<1.0	<0.71	<0.45	<0.29	<0.42	<0.51	<0.49	0.96	<0.66	<0.62
D2CDD	7.7	19	18	21	21	30	53	70	34	58	24	230	110
T3CDD	0.37	2.3	3.5	6.2	4.7	4.9	3.1	3.5	5.6	170	8.2	9.2	5.7
T4CDD	0.41	3.1	3.8	4.2	3.9	6.4	2.5	2.4	4.8	140	6.1	2.7	3.0
P5CDD	<0.1	0.33	0.5	0.6	0.62	0.66	0.2	0.45	2.1	53	3.8	1.9	1.7
H6CDD	0.14	1.7	2.3	1.6	2.0	2.0	1.3	3.1	4.2	76	4.4	8.7	2.7
H7CDD	2.8	8.8	11	9.6	9.7	14	9.2	10	7.4	160	11	34	6.2
O8CDD	12	37	50	40	42	69	42	57	31	760	37	140	26
M1CDF	2.7	57	62	77	71	79	49	38	21	24	19	14	7.3
D2CDF	5.6	360	460	550	510	570	350	230	150	68	52	42	12
T3CDF	2.9	170	190	250	240	260	160	100	72	25	22	16	8.0
T4CDF	0.51	28	32	32	34	33	29	23	20	130	7.0	7.7	1.9
P5CDF	0.13	3.4	3.2	3.4	3.3	5.1	3.6	2.3	3.8	59	1.5	5.6	0.88
H6CDF	0.81	2.0	2.8	2.3	2.5	3.6	2.3	2.4	2.0	34	2.0	11	1.1
H7CDF	1.0	3.5	3.3	3.2	3.2	4.9	<0.17	3.7	1.8	46	1.7	6.6	2.4
O8CDF	1.1	3.4	4.4	4.0	3.6	5.9	3.7	4.0	2.4	51	1.9	11	1.7

Table A5

Dioxins-Furans in Suspended Sediments
Results in pg/G (dry)

Tributary Streams:

	Berland River	McLeod River	Pembina River	Lesser Slave River	Clearwater River
	1993 02 14	1993 02 16	1993 02 23	1993 02 25	1993 03 11
M1CDD	<0.92	0.93	1.2	<0.44	<0.44
D2CDD	110	33	56	24	94
T3CDD	2.2	5.1	3.2	9.0	4.8
T4CDD	2.7	4.6	4.6	13	1.5
P5CDD	<0.27	2.4	2.6	4.9	0.77
H6CDD	2.4	5.4	5.1	6.4	1.6
H7CDD	6.2	13	22	10	4.6
O8CDD	18	52	160	46	20
M1CDF	55	18	14	6.2	5.6
D2CDF	210	39	26	<0.27	<0.3
T3CDF	64	12	9.6	4.4	6.8
T4CDF	9.2	2.7	1.8	2.8	1.9
P5CDF	1.1	1.3	0.71	0.36	0.42
H6CDF	1.5	2.9	2.9	1.8	0.21
H7CDF	<0.4	3.0	17	1.8	0.68
O8CDF	2.6	3.6	10	2.0	0.8

Table A6

Dioxin-Furans in Suspended Sediments
Results in pg/G (dry)

Effluents:

	Hinton Combined Effluent	Alberta Newsprint Effluent	Millar Western Effluent	Millar Western Effluent Dup.	Whitecourt Sewage Effluent	Slave Lake Pulp Effluent	Athabasca Sewage Effluent	Fort McMurray Sewage Effluent
	1993 02 11	1993 02 16	1993 02 17	1993 02 17	1993 02 17	1993 02 24	1993 02 27	1993 03 10
M1CDD	<0.67	<0.52	<0.98	<0.82	<1.4	<0.52	<0.84	2.2
D2CDD	13	2.9	<4.0	<2.9	200	7.6	1800	1100
T3CDD	30	<0.72	<2.7	<2.3	29	<0.94	63	67
T4CDD	35	<0.16	<0.47	<0.48	4.5	<0.31	30	57
P5CDD	11	<0.4	<0.46	<0.26	6.0	<0.28	12	31
H6CDD	8.9	2.6	<0.3	<0.3	59	<0.27	86	88
H7CDD	24	3.1	<0.44	<0.48	280	<0.5	470	220
O8CDD	130	27	2.5	2.2	1900	2.8	3400	1400
M1CDF	430	4.5	1.3	1.3	5.5	0.5	22	13
D2CDF	3600	18	<1.0	<1.3	46	<0.84	100	55
T3CDF	1500	13	<1.0	<1.0	30	<1.0	48	67
T4CDF	250	3.1	<0.35	<0.24	16	<0.14	29	97
P5CDF	24	0.25	<0.26	<0.17	21	<0.15	29	140
H6CDF	9.2	0.67	<0.58	<0.47	38	<0.4	61	120
H7CDF	12	3.8	<0.74	<0.75	51	<1.2	130	24
O8CDF	15	2.1	<0.76	<0.76	86	<0.66	89	37

Table A7

Dioxin-Furans in Depositional Sediments
Results in pg/G (dry)

Athabasca River Mainstem Locations:

	Above Maskuta Creek 1993 05 05	Weldwood Haul Bridge 1993 05 05	Obed Bridge 1993 05 05	Emerson Lakes Bridge 1993 05 05	Above Berland River 1993 05 06	Windfall Bridge 1993 05 06	Windfall Bridge Dup. 1993 05 06	Blue Ridge 1993 05 06	Athabasca 1993 05 07	27 Baseline 1993 05 16
M1CDD	<0.25	<0.3	<0.26	<0.23	<0.4	<0.3	<0.3	<0.3	<0.3	<0.58
D2CDD	10	5.6	5.1	14	23	11	11	16	16	44
T3CDD	1.1	0.8	0.7	1.4	2.0	0.5	0.4	2.3	7.1	<2.0
T4CDD	<0.13	0.23	0.14	0.22	0.52	0.42	0.4	0.14	1.1	<0.25
P5CDD	<0.11	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.11	0.6	1.9
H6CDD	<0.2	0.52	0.29	0.38	0.72	0.17	0.29	0.45	1.5	0.99
H7CDD	1.4	4.5	2.9	3.7	4.6	2.3	2.7	3.6	9.7	5.7
O8CDD	14	20	10	18	14	8.9	8.8	11	22	35
M1CDF	1.9	6.8	3.6	6.7	9.0	5.1	4.3	5.0	3.9	10
D2CDF	<0.35	31	13	37	52	23	24	19	11	<0.74
T3CDF	1.5	16	7.1	17	23	14	12	11	9.8	4.2
T4CDF	<0.13	2.5	1.3	2.9	4.6	2.1	2.1	2.2	2.3	1.2
P5CDF	<0.12	0.11	<0.11	0.21	0.63	0.2	0.2	0.36	0.15	<0.3
H6CDF	0.66	1.1	0.54	1.0	0.77	0.46	0.36	0.53	0.94	<0.62
H7CDF	1.2	1.7	0.9	1.4	1.1	0.84	0.84	0.97	1.6	<1.9
O8CDF	1.1	1.6	0.77	1.2	0.82	0.72	0.69	0.9	1.1	<0.8

Table A8

Resin Acids in Suspended Sediments
Results in ng/G (dry)

Athabasca River and Tributaries:

	Above Maskuta Creek 93 02 11	Weldwood Haul Bridge 93 02 11	Obed Bridge 93 02 12	Emerson Lakes Bridge 93 02 13	Lesser Slave River 93 02 25	Clearwater River 93 03 11	27 Baseline 93 03 16	27 Baseline Dup. 93 03 16
Pimaric	4.8	21000	95000	21000	26	NDR(4.8)	130	130
Sandaracopimaric	NDR(4.6)	330	1300	380	NDR(89)	28	NDR(220)	NDR(220)
Isopimaric	39	11000	56000	12000	140	NDR(59)	100	93
Palustric	NDR(9.9)	1400	5700	NDR(140)	NDR(20)	NDR(36)	<36	<33
Dehydroisopimaric	<0.98	2100	10000	2000	NDR(9.9)	<2.4	<5.8	<5.8
Dehydroabietic	100	5300	31000	6400	520	350	190	190
Abietic	33	6400	29000	4600	96	52	<37	<39
Neoabietic	NDR(2.8)	820	3000	NDR(35)	NDR(18)	NDR(71)	<3.5	<3.5
12/14 Chlorodehydroabietic	<0.73	930	6600	1300	<2.7	<1.6	9.1	8.6
12,14 Dichlorodehydroabietic	<0.98	710	5100	770	<4.2	<2.1	NDR(12)	<7.8
o-Methyl Podocarpic (%)	65	98	26	130	67	63	110	130

Effluents:

	Hinton Combined Effluent 93 02 11	Alberta Newsprint Effluent 93 02 16	Millar Western Effluent 93 02 17	Slave Lake Pulp Effluent 93 02 24	Slave Lake Pulp Effluent 93 02 24 Duplicate
Pimaric	130000	120000	2200	170	130
Sandaracopimaric	2600	41000	DR(710	200	210
Isopimaric	68000	280000	4000	1300	990
Palustric	8900	55000	1400	510	490
Dehydroisopimaric	11000	680	<31	14	<11
Dehydroabietic	37000	700000	10000	3900	3000
Abietic	28000	760000	6900	1700	960
Neoabietic	6100	21000	950	420	460
12/14 Chlorodehydroabietic	5900	250	<4.4	<0.33	<5.0
12,14 Dichlorodehydroabietic	2600	<160	<9.1	<0.43	<8.6
o-Methyl Podocarpic (%)	94	31	70	85	93

Table A9

Resin Acids in Depositional Sediments
Results in ng/G (dry)

Athabasca River Mainstem:

	Above Maskuta Creek 93 05 05	Above Maskuta Creek 93 05 05 Duplicate	Weldwood Haul Bridge 93 05 05	Obed Bridge 93 05 05	Emerson Lakes Bridge 93 05 05	Emerson Lakes Bridge 93 05 05 Duplicate	Above Berland River 93 05 06	Windfall Bridge 93 05 06	Blue Ridge 93 05 06	Athabasca 93 05 07	27 Baseline 93 05 16
Pimaric	3.0	3.0	1400	360	980	1200	940	160	230	74	16
Sandaracopimaric	NDR(4.2)	NDR(8.0)	NDR(43)	NDR(8.7)	NDR(61)	NDR(73)	NDR(28)	NDR(6.1)	NDR(14)	NDR(4.9)	<2.6
Isopimaric	20	24	760	230	610	800	560	120	210	66	28
Palustric	NDR(13)	NDR(5.6)	NDR(67)	NDR(32)	NDR(35)	NDR(49)	NDR(32)	NDR(16)	NDR(14)	NDR(22)	<7.6
Dehydroisopimaric	<0.9	<1.5	150	58	140	180	130	40	37	12	<4.6
Dehydroabietic	110	110	560	210	580	700	520	170	360	190	210
Abietic	14	16	240	93	250	310	260	53	180	39	22
Neoabietic	<1.7	<1.2	13	5.0	NDR(8.5)	NDR(13)	NDR(4.6)	NDR(1.7)	NDR(2.4)	NDR(1.4)	<2.2
12/14 Chlorodehydroabietic	<0.41	<0.43	89	34	87	100	110	26	18	9.6	2.2
12,14 Dichlorodehydroabietic	<0.68	<0.58	81	30	73	84	92	23	13	7.4	2.8
o-Methyl Podocarpic (%)	72	70	84	66	67	55	58	66	84	92	160