









NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 134 DISTRIBUTION OF ORGANIC CONTAMINANTS IN BOTTOM SEDIMENTS, PEACE AND ATHABASCA RIVER BASINS, 1988 TO 1992













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by

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PREFACE:

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

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been 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.

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May 29/96 ate)

(Robert McLeod, Co-chair)

DISTRIBUTION OF ORGANIC CONTAMINANTS IN BOTTOM SEDIMENTS, PEACE AND ATHABASCA RIVER BASINS, 1988 TO 1992

STUDY PERSPECTIVE

A major area of interest for the Northern River Basins Study (NRBS) was determination of the effects of contaminants from industrial and municipal sources on the aquatic ecosystem of the Peace, Athabasca and Slave rivers. Contaminant information for these basins was lacking and additional research needed to be done to describe the nature and distribution of chemical contaminants entering the rivers.

Environments are constantly changing; that the aguatic environments contained within the Northern River Basins Study area (NRBS) were being changed as a result of development was not challenged. Typically, the change that occurs within the environment like those found in the Peace, Athabasca and Slave rivers, takes place over an extended period of time. Although not as evident or dramatic, the change and its effects can be just as substantive as those occurring within a shorter time frame; the changes are so subtle as to go unnoticed. A major difficulty for aquatic scientists working with these large aquatic systems is the lack of documented information covering a long period of time. The monitoring that was underway or done prior to the onset of the NRBS Study was disparate and information gaps existed.

Related Study Questions

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

Many contaminants released to the aquatic environment do not remain in solution but attach themselves to fine particles suspended in the water column. Knowledge of sediment - contaminant interaction, combined with an understanding of sediment transport dynamics better enables researchers to simulate the transport and uptake of contaminants within the aquatic environment.

Analysis of deposited river bottom sediments offers researchers the opportunity to explore trends contaminant transport and likelihood of bioaccumulation within the aquatic environment. This report describes some initial work undertaken by NRBS to investigate contaminants associated with sediments collected by Alberta Environmental Protection three years prior to the onset of the Study as well as recently collected samples gathered under NRBS in 1992. Assessment of the results indicates that there is minimal correlation between the organic content of the samples and the concentration of contaminants. Contaminant concentrations within the sediments was low throughout the river basins.

Information gathered under this project was used to support follow-up contaminant fate modelling work described in NRBS Project Report No. 137 (*A Bioenergetic Model of Food Chain Uptake and Accumulation of Organic Chemicals, Athabasca River*), No. 112 (*Contaminant Fate Modelling, Athabasca, Wapiti, and Smoky Rivers*), and No. 113 (*A Bioenergetic Model of Food Chain Uptake and Accumulation of Organic Chemicals, Athabasca River*); Stochastic and Time Variable Version).



REPORT SUMMARY

Results of contaminant analyses are presented for bottom sediments collected from the Peace and Athabasca River basins from 1988-90 by Alberta Environmental Protection and in 1992 by the Northern River Basins Study. Contaminant groups represented are the polychlorinated dibenzo-*p*-dioxins and dibenzofurans, resin acids, chlorophenolic compounds and polycyclic aromatic hydrocarbons.

Contaminant concentrations were correlated with percent organic carbon of the fine fraction (the fraction on which contaminant analyses were performed). There was no significant correlation. Organic carbon content of the sediments was a poor predictor of contaminant concentration.

Correlations between concentrations of bleached kraft mill-related contaminants were also investigated. Correlations between 2,3,7,8-tetrachlorodibenzofuran and chlorinated dehydroabietic acid concentrations were not significant at the 20% level, but correlations between dehydroabietic acid and chlorinated resin acids were significant at the 1% level.

ACKNOWLEDGEMENTS

We would like to thank John Carey, National Water Research Institute, Burlington, ON and Ian Johnson, Alberta Environmental Centre, Vegreville, AB for helpful discussions regarding the organic carbon vs. compound and compound vs. compound correlations. Erik Ellehoj, GIS Coordinator for NRBS prepared the compound distribution maps.

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1.0 INTRODUCTION AND HISTORY

Question 4 of the Northern River Basins Study (NRBS) fundamental questions deals with the distribution (4a) and rate of change (4b) for contaminants in the Peace, Athabsca and Slave River basins. Analysis of river bottom sediments for contaminants can be used to establish trends in concentrations through space and over time, and provide information for contaminant fate and food chain modelling since sediments can "store" contaminants and then serve as sources of these contaminants to the food chain.

In 1992 sediment samples from the Alberta Environmental Protection archive and samples newly collected by NRBS during the 1992 Reach Specific Survey (Hinton to Whitecourt) were processed and submitted for analysis for several groups of contaminants. This sample set was to establish baseline concentrations for the pre-NRBS and early NRBS period. This report summarizes the results for four of these contaminant groups as well as the physical properties of thes sediment samples. Terms of Reference for this report are given in Appendix A.

2.0 <u>THE SAMPLE SET</u>

Bottom sediment grab samples were taken from twenty-six sites throughout the Peace-Athabasca River Basins. The majority of these samples were collected and archived by Alberta Environmental Protection (AEP) in 1989, though some samples were taken in 1988 and 1990. They were provided to NRBS by AEP for contaminant analysis. In 1992, R.L.&L. Environmental Services Ltd. collected sediment samples for NRBS at six sites along the Athabasca River (R.L.&L 1993). Figure 1 shows the locations of these sites in the basin. Their collection dates, NRBS refence numbers and a list of latitudes and longitudes for these sites are given in Table 1. In the text, A.R.=Athabasca River, W.R.=Wapiti River, S.R.=Smoky River and P.R.=Peace River.

This report provides the results for polychlorinated dioxin and furan (DF), resin acid (RA), chlorophenolic compounds (CP) and polycyclic aromatic hydrocarbon (PAH) analyses. Conventional parameters such as percent Organic Carbon (OC) and particle size analysis (PSA) have also been completed. During the process of data analysis, it was discovered that a few sample results were unavailable. These are footnoted in Table 1.

3.0 SAMPLE PREPARATION AND ANALYTICAL METHODS

Analysis of the sediment samples were carried out by three different laboratories depending upon which parameters were being analysed. Details regarding sample preparation and analytical methods for each of the extraction/analysis procedures undertaken are summarized in their respective laboratory reports. Percent OC and particle size analysis was completed by the Research and Applications Branch of the National Water Research Institute (NWRI) in Burlington, Ontario. After

Site ^a	NRBS #	Date	Latitude	Longitude
A.R. above Maskuta Ck.	1	Oct/89	53°23 N	117º41 W
A.R. @ Obed Br.	6	Oct/89	53°36 N	117°13 W
A.R. above ANC	4	Oct/89	54°12 N	116° 0 0 W
A.R. @ Blue Ridge Br.	7	Oct/89	54°09 N	115°24 W
A.R. above Smith	2	Oct/89	55°04 N	114°05 W
A.R. above Horse R.	3	Oct/89	56°43 N	111°26 W
A.R. above Firebag R.	8	Oct/89	57°45 N	111°22 W
A.R. @ Big Pt.Ch. @ mth	5	Oct/89	58°36 N	110º48 W
Richardson L.	19	Apr/90	58°24 N	111°04 W
McLeod R. @ mth	15	Oct/89	54°09 N	115º41 W
W.R. @ Hwy 40	26	Oct/89	55°05 N	118°48 W
W.R. d/s P&G Haul Br.	25	Oct/89	55°04 N	118°42 W
W.R. @ RR Br., 1/c ^b	23	Oct/89	55°04 N	118°36 W
W.R. u/s Bear R.	22	Oct/89	55°06 N	118°28 W
W.R. 0.5 km u/s mth ^b	24	Oct/89	55⁰07 N	118°18 W
S.R. u/s Puskwaskau R.	21	Oct/89	55°29 N	118°09 W
S.R. @ mth	20	Oct/89	56°10 N	117°19 W
P.R. u/s S.R.	17	Sep/88	56°10 N	117°23 W
P.R. u/s Notikewin R.	18	Sep/88	57°16 N	117°06 W
P.R. above W.B.N.P.	16	Sep/88	58°38 N	114°10 W
A.R. u/s Hinton	9	Apr/92	53°23 N	117°41 W
A.R. @ Weldwood Br.	10	Apr/92	53°28 N	117°27 W
A.R. @ Obed Br.	11	Apr/92	53°33 N	117°13 W
A.R. @ Emerson L.	12	Apr/92	53°42 N	117°09 W
A.R. @ Knight Br.	13	Apr/92	54°08 N	116°45 W
A.R. @ Windfall Br. ^c	14	Apr/92	54°12 N	116°03 W
-				

 Table 1. Northern Rivers Sample Site Identifications and Latitudes and Longitudes.

^a Abbreviations are as follows: Athabasca River (A.R.), creek (Ck.), bridge (Br.), Alberta, Newsprint Company (ANC), mouth (mth), lake (L.), upstream (u/s), downstream (d/s), Wapiti River (W.R.), left-centre (l/c), Smoky River (S.R.), Peace River (P.R.), railroad (RR), Procter and Gamble (P&G).

^b Missing particle size results.

^c Results for PAH and CP were not included due to discrepancy in the sample name.



freeze-drying of the sediment, subsamples were removed for TOC (Total and Organic Carbon) and particle size analysis and the remainder of the sample was dry-sieved at the sand-silt boundary (ca. 60 μ m). The fine fraction was used for contaminant analysis. Procedural information can be found in <u>NWRI Report No. RAB-91-25U: Particle Size Report</u> by G. Duncan (1992).

Dioxin and furan analyses were carried out by Axys Analytical Services Ltd. in Sidney, British Columbia. Dioxin and furan procedures are detailed in <u>Analytical Results for the Analysis of Sediment and Water Extract Samples for PCDDs and PCDFs</u> (Axys Analytical Services Ltd., 1993). Resin acid procedures are found in <u>Analytical Results for the Analysis of Sediment and Water Extract Samples for Resin Acids</u> (Axys Analytical Services Ltd., 1993). Analysis of chlorophenolic compounds and PAHs was completed by CHEMEX Labs Alberta Inc., Calgary, Alberta using USEPA method #8270 in Test Methods for Evaluating Solid Waste SW-846.

4.0 DATA ANALYSIS METHODS AND CONVENTIONS

4.1 ABBREVIATIONS USED FOR COMPOUND NAMES

The convention used for naming of "dioxins" and "furans" is as follows. For example 2,3,7,8-tetrachlorodibenzo-p-dioxin is abbreviated 2378TCDD, and 2,3,7,8-tetrachlorodibenzofuran is abbreviated 2378TCDF, i.e., the numbers in the abbreviation refer to the position of the chlorine atoms and the letter following the numbers designates that they are "tetra" chlorinated congeners. For higher chlorinated congeners, Pe=pentachloro, Hx=hexachloro, Hp=heptachloro, and O=octachloro.

The abbreviation for dehydroabietic acid used in this report is DHA. For the chlorinated dehydroabietic acids, the 12/14CDHA is a mixture of 12- and 14-chlorodehydroabietic acid and 12,14DCDHA is 12,14-dichlorodehydroabietic acid. The nonchlorinated resin acids, chlorinated phenolic compounds and PAHs are referred to by their full names.

4.2 BLANKS: QA/QC

The blanks for each of the compounds analysed appear to be free from contamination. Blank corrections were not carried out on these samples in order to be consistent with the data processing of other NRBS contaminants data.

For the dioxins and furans, the only notable peak in the blanks was found in DX-SBLK 647 for OCDD. This blank corresponds to the A.R. samples from 1992. However, the area of this peak in the samples themselves is not noticeably different than in the other samples implying that only the blank had OCDD contamination.

In the resin acids analyses, peak detections in the blanks were generally negligible. In some sample blanks, NDR (see below for definition) isopimaric peaks were detected.

The blanks for the chlorophenolic compounds and PAHs were free from detectable contamination.

4.3 DUPLICATES

Results for duplicate analyses are available only for dioxins, furans and resin acids. There were no replicates done for chlorophenolic compounds and PAHs. Replicate dioxin and furan analyses were carried out on the A.R. @ Big Pt. Ch. @ mth, S.R. @ mth, P.R. above W.B.N.P., A.R. @ Obed Br. and A.R. @ Emerson L. The results are, on the whole, similar to those of the initial sample. For the resin acids, of the four duplicates and one triplicate completed, consistency varied. The A.R. above Maskuta Ck. and P.R. u/s S.R. duplicates are excellent. Agreement between the A.R. @ Big Pt. Ch. @ mth, A.R. @ Obed Br. and A.R. @ Windfall Br. replicate results are not as good.

4.4 CORRECTION FOR RECOVERY

All sample results have been corrected for the recovery of their corresponding internal surrogate. The formula by which this was accomplished varied depending upon which laboratory the samples were analysed in. Axys Analytical Services Ltd. corrects for surrogate recovery when they first calculate compound concentrations. Sample peaks are referenced to an internal standard rather than an injection or recovery standard. This internal standard undergoes the same extraction procedure as the sample and thus, any loss of sample compound is accounted for (assuming a similar loss of the internal standard). Surrogate recoveries are summarized in Tabel 2. There is a confusing error in the laboratory write-up for the resin acids, <u>Analytical Results for the Analysis of Sediment and Water Extract Samples for Resin Acids</u>, (Axys, 1993), which should be noted. In the write-up, the internal standard -- O-methyl modocarpic Acid -- is erroneously referred to as a "labelled" surrogate. The O-methyl podocarpic acid is not labelled but is a basic internal standard.

CHEMEX Labs does not correct for recovery in their concentration calculations. Rather, concentrations are calculated using the injection/recovery standard peaks. Hence, there is no correction for losses which occurred during the extraction procedure. To account for these, the chlorophenolic compounds and the PAHs are recovery corrected by dividing the uncorrected concentration value by ((percent recovery)/100) of the relevant surrogate. For example, if the uncorrected concentration value was 5 and the percent recovery of the relevant surrogate was 50 percent then: 5/.5 = 10, therefore the corrected concentration value is 10.

Since CHEMEX uses more than one surrogate in its methods, a choice had to be made as to which surrogate a given compound would be referenced to. The decision was made based on structural similarities between the compound and the surrogate and on chromatographic retention time similarities. For the chlorophenolic compounds, the "mono" and "di" compounds were corrected according to the percent recovery of 4-bromophenol. The "tri" and "tetra" chlorophenolics were

DIOXINS	% RECOVERY RANGE	FURANS	% RECOVERY RANGE
13C-TCDD	32-110	13C-TCDF	39-96
13C-PeCDD	24-117	13C-PeCDF	26-99
13C-HxCDD	37-119	13C-HxCDF	35-94
13C-HpCDD	23-96	13C-HpCDF	22-87
13C-OCDD	12-104		

 Table 2.
 Percent Recovery of Dioxin and Furan Surrogates.

corrected according to the percent recovery of 2,4,6-tribromophenol. For the PAHs, two and three ring PAH structures were corrected according to the percent recovery of 2-fluorobiphenyl. PAHs with larger ring structures were corrected according to the percent recovery of *p*-terphenyl- d_{14} .

4.5 TREATMENT OF "ND" AND "NDR" VALUES

Values which were recorded as ND (not detected) or NDR (peak detected but does not meet quantification criteria) are included in all tables and maps. NDR values are given when a peak is detected but fails to meet one or more of the quantification criteria. Quantification criteria include: (1) the detected peak must have a retention time within three seconds of the corresponding compound retention time in the calibration standard, (2) the peak must have a height equal to or greater than three times the maximum "noise" peak height of a blank run, and (3) the peak maxima for the characteristic ions must coincide within two seconds and the area ratios must be within $\pm 20\%$ of the calibration standard value.

When a peak is not detected, the detection limit is indicated and the value is labelled as "L" for less than this detection limit value. For Axys Analytical Services Ltd., the detection limit is referred to as the Sample Detection Limit (SDL). The SDL is calculated as the concentration corresponding to the area of a peak with a height three times the maximum noise level. CHEMEX Labs Alberta, Inc. distinguishes between a Method Detection Limit (MDL), and a Practical Quantification Limit (PQL). The MDL is essentially the same as Axys' maximum noise level and the PQL is equivalent to Axys' SDL. CHEMEX refers to any value between the MDL and the PQL values as "trace." Finally, the values for NDR results are simply included "as is" and labelled "NDR."

5.0 DATA TABLES AND DISTRIBUTION MAPS

Contaminant concentrations are given for each of the compound groups (DFs, RAs, CP, PAHs) in Tables 4-7. Geographical distribution for 10 selected compounds is shown by maps 1-10 in Appendix C.

5.1 PHYSICAL PROPERTIES

Physical parameters such as OC and particle size are useful both in a qualitative manner (they describe the sediment samples and indicate something of the nature of the site) and as a factor in interpreting results. The physical properties of a sample may affect the resulting concentration values for a given compound. Generally, hydrophobic compounds are expected to adsorb to particulate matter. This adsorption will be a function of surface area and organic carbon content. Since adsorption is a surface phenomenon, higher compound concentrations are more likely to be found in silt or clay samples than in coarser, sandy sediments. Concentration should also correlate positively with OC because of hydrophobic partitioning.

Given the above, the physical properties of the sediment samples were determined and are listed in Table 3. Organic carbon in the fine fraction and particle size (%silt+clay) were only weakly correlated with r=0.18 (n=21).

In a national dioxin and furan survey, Trudel (1991) found no significant correlation between sediment characteristics (organic carbon content, particle size, etc.) and dioxin/furan contaminant sorption but rather concluded that geographical factors (site locations, hydrological and ambient conditions) and contaminant sources were more important when interpreting and explaining results.

5.2 DIOXINS AND FURANS

Dioxin and furan results are given in Table 4. In the <u>Wapiti/Smoky River Ecosystem Study</u> (SENTAR, 1993), dioxins and furans were always at or below detection limits with detectable concentrations usually occurring during periods of low flow. Our results likewise showed that, for most of the dioxin and furan congeners, concentrations were at or below detection. However, the NRBS sample set is limited in temporal coverage. The only area where there are results for more than one season is the Hinton to Whitecourt reach of the Athabasca River.

The congeners most frequently above detection were 2378TCDF, 1234678HpCDD, and OCDD. The congeners selected for mapping were 2378TCDD, 2378TCDF, and OCDD. 2378TCDD concentrations were not sufficiently above detection to draw any conclusions. 2378TCDF concentrations are somewhat elevated in sediments downstream from the two bleached kraft mills in operation at the time of sampling. This compound is a good marker for effluent from bleached kraft mills using molecular chlorine for bleaching. OCDD showed a broad distribution pattern

Site	% OC _b ^a	% OC _f ^b	% Sand	% Silt	% Clay
A.R. above Maskuta Ck.	4.22	0.158	7.3	81.4	11.3
A.R. @ Obed Br.	4.14	0.414	30.0	52.3	17.7
A.R. above ANC	2.45	0.540	71.4	15.2	13.4
A.R. @ Blue Ridge Br.	2.98	0.561	54.7	18.6	26.7
A.R. above Smith	3.22	0.700	17.0	46.0	36.9
A.R. above Horse R.	2.65	0.348	56.3	19.8	23.9
A.R. above Firebag R.	3.19	0.739	4.7	61.5	33.8
A.R. @ Big Pt.Ch. @ mth	3.87	0.712	16.7	47.8	35.6
Richardson L.°	3.69	1.341	6.7	34.9	58.4
McLeod R. @ mth	4.97	NA	95.3	4.55°	
W.R. @ Hwy 40	1.72	0.379	63.2	16.1	20.8
W.R. d/s P&G Haul Br.	2.05	0.297	30.5	38.0	31.5
W.R. @ RR Br., 1/c	2.90	0.585	NA	NA	NA
W.R. u/s Bear R.	4.03	NA	98.3	1.7 ^d	
W.R. 0.5 km u/s mth	2.93	0.673	NA	NA	NA
S.R. u/s Puskwaskau R.	2.00	0.231	61.6	18.3	20.0
S.R. @ mth	2.02	0.279	22.2	44.0	33.8
P.R. u/s S.R.	1.77	0.360	0.0	67.0	33.0
P.R. u/s Notikewin R.	1.21	0.277	79.4	9.2	11.4
P.R. above W.B.N.P.	0.81	0.394	95.8	4.21 ^d	
A.R. u/s Hinton	2.74	0.235	53.2	31.3	15.5
A.R. @ Weldwood Br.	5.46	0.288	7.8	79.3	12.9
A.R. @ Obed Br.	3.72	0.390	14.3	66.7	19.1
A.R. @ Emerson L.	4.58	0.436	36.9	47.1	16.0
A.R. @ Knight Br.	1.30	0.674	99.0	0.98 ^d	
A.R. @ Windfall Br.	2.24	NA	99.7	0.26 ^d	
-					

Table 3: Organic Carbon (OC) and Particle Size of Sediment Samples. Percent OC and particle size -- sand, silt and/or clay.

^a Percent organic carbon for bulk sediment from Duncan (1992).

^b Percent organic carbon for fine fraction (< ca. 60 μ m) from Gauthier (1994).

• Richardson L. sample composed of top 5 cm of several cores.

^d Silt and clay values combined.

NA Not Analyzed.

consistent with diffuse sources. Interestingly, concentrations of OCDD in the Athabasca River basin are higher than in the Peace River basin.

5.3 **RESIN ACIDS**

Resin acid results are summarized in Table 5. The resin acids are consistently detectable throughout the basin with concentrations generally being higher in the southwestern stretch of the Athabasca River (sampled in 1992) than in the northern end of the Athabasca River and in the Wapiti-Smoky-Peace sites (variously sampled between September 1988 and April 1990). The results of this study for the W-S-P section are similar to those reported in the <u>Wapiti/Smoky River Ecosystem Study</u>.

The predominant resin acids are dehydroabietic acid (DHA), abietic acid, isopimaric acid and pimaric acid. These results are not unusual. According to Mahood and Rogers (1975), dehydroabietic and isopimaric acids are expected from western Canada pulp mills which pulp Spruce, Douglas Fir and other coniferous trees besides pine.

Dehydroabietic acid has an aromatic "C" ring and hence is quite stable. Abietic acid on the other hand, has a conjugated double bond which lends itself to isomerization relatively easily (Morales *et al.*, 1992). The high concentrations of abietic acid may, in part, be due to the isomerization of palustric and neoabietic acids which can "change into" abietic acid. During the acidification stage of resin acid extraction conditions are ideal for such isomerization processes. Thus, the concentration of abietic acid in a given sample after acidification may be elevated compared to its original state, while concentrations for palustric and neoabietic acid may have decreased. Mahood and Rogers (1975) and Morales *et al.* (1992) recommend a lower pH limit of 5 to minimize isomerization. This is the pH level used by AXYS during resin acid extraction. Finally, although isopimaric and pimaric acids also have double bonds, these are not conjugated and so isomerization is not much of a concern.

Four resins acids were selected for mapping: isopimaric acid, dehydroabietic acid, 12/14CDHA, and 12,14DCDHA. All four show elevated concentrations downstream from the bleached kraft mills. Isopimaric and dehydroabietic acids at about 5-10 times background and the chlorinated dehydroabietic acids at 100-2300 times background. The chlorinated dehydroabietic acids are produced by reaction of dehydroabietic acid with chlorine and appear to be excellent markers for bleached kraft mill effluent from mills using molecular chlorine for bleaching.

5.4 CHLORINATED PHENOLIC COMPOUNDS

The only site with a notable range of chlorophenolic compounds is the A.R. @ Obed Br. site (Table 6). Half of these compounds were detected only in trace amounts and in five instances, the A.R. @ Obed Br. site is the only site where these compounds were detected.

Site	Tolal TCDD (a) pg/g		Total PeCDD Pg/g		Total HxCDD pg/g		Total HpCDD pg/g	Tolal TCDF pg/g		Total PeCDF pg/g		Total HxCDF pgrg	
		1				Ī			Ī		Ī		
A.R. above Mastruta Ck.	+	0.2	1	0.3	L	0.3	e	0.1	2.0	_	0.1	_	0.3
A R. above ANC	_	0.2	Ţ	03		0.8	e	5	2.9		0.2	ر	02
A R. @ Blue Ridge Br.	L	0.2	7	0.1		0.9	ŝ	5	10	_	0.1	_	0.2
A R. above Smith	,r	0.2	4	0.1		1.7	4	1.2	19	-	0.1	_	02
A.R. above Horse R.	A.	0.1		0.8		0.7	-	1	1.4	_	0.1	4	0 1
A R. above Firebag R.		0.8		1.0		1.8	£	8	12		0.6		0.8
A.R. @ Big Pt.Ch. @ mth	1	0.2		1.3		1.0	2	2	0.4	_	0.2	-	04
A.R. @ Big Pt.Ch. @ mth-r	÷	0.1		1.1		1.1	e	.1	0.5	a)	0.1	T	0.2
Richardson L.	-	3.4		1.7		1,4	1	8	6.0	à	0.1	4	0.2
McLeod R. @ mth		0.4		1,6		1.8	2	S.	1.1	4	0.1	4	0.3
W.R. @ Hwy 40		0.5	1	0.04		0.2	0	8	0.7		0.04	-	0,06
W.R. d/s P&G Haul Br.		0.6	1	0.03		0.3	0	7.0	0.2	4	0.04	_	0.07
W.R. @RRBL. I/c		0.8		04		0.6	5	1.31	2.7	4	0.05	3	0.06
W.R. u/s Bear R.		0.3	1	0.1		0.6		1.7	3,8		0.1		03
W.R. 0.5 km u/s mlh		1.4		0.04		0.7	1	2	2.0	1	0.03	4	0 05
S.R. u/s Puskwaskau R.		1.3		0.6		0.7	-	2	1.0		0.04	4	0.08
S.R. @ mth		5.4		16		2,1	- 1	8	8.0		0.06		0_1
S.R. @ mth-r		6.4		3.3		3.1	-	8	8.0	_	10.0		0 1
P.R. u/s S.R.		3.6		22		1.6	Ł	3	0.2	1	0.03	1	60.0
P.R. u/s Notikewin R.		2.9		1.2		1.5	(4	53	6.2		0.2		0 2
P.R. above W.B.N.P.		3.8		3.1		2.1	-	0	1.4		0.2	-	0 0 7
P.R. above W.B.N.P.		3,2		2.7		1.8		3	12		0.07	4	0 05
A.R. u/s Hinton	-	0.1		0.2	Ļ	0.2	4	1.3 L	0.1	r	0.2	L.	0.2
A.R. @ Weldwood Br.		0.3	_	0.2	-	0.1	10	8	0.7	7	0.1	4	0.2
A R. @ Obed Br.	1	0.1	L	0.3	-	0.3		2	2	4	0.2	1	0.3
A.R. @ Obed Br -r		2.6	-	0.2	4	0.5	Ω,	5.8	1.7	-	0.1	L	0.4
A.R. @ Emerson L.		2.3	_	0.1	_	0.3	-	7.4	3.1	F	0.1	4	0.4
A.R. @ Emerson Lr		1.6	_	0.2	Ļ	0.6	e	6	4.2	-	0.1	1	0.3
A.R. @ Windfall Br.		0.4	_	0.2	_	0.6	£1	5.4	3.2		0.1	1	0_1
		7				_		_					

Table 4. Dioxins and Furans Detected in the Peace/Athabasca River Basin.

continued...

Site	Total HpCDF		23.	80	123 -Pe	178 CDD	123 Hx	678 CDD	123 -Hx	789 CDD	1234 -HpC	678 DD	OCDD
	6/6d		bd	5)6d		hgq	0	böd		6/6d		5/5d
A.R. above Maskuta CK	۲	0.3		0.2	-	0.3		0.3	_	0.3		16	9.2
A.R. above ANC		0.6	NDR	0.3	-	0.3	-	0.2	4	0.2		1.5	14
A.R. @ Blue Ridge Br.	٦	0.2	_	0.2	4	0.1	4	0.2	-	0.2		1.2	7,9
A.R. above Smith		0.6	_	0.2	7	0.1	3	0.2	-	0.2		2.0	12
A.R. above Horse R.		0.2	NDR	0.2	1	0.1	1	0.1	L	0.1	NDR	0.8	53
A.R. above Finebag R.		0.3	NDR	0.4	4	0.1	NDR	0.1	1	0.1		1.6	8.5
A.R. @ Big Pt.Ch. @ mth	L	0.3	_	0.2	4	0,3	_	03	-	03		1.2	5,9
A.R. @ Big Pt.Ch. @ mth-r	-	0 2	_	01	4	0.1	1	0.2	à	0.2		1.4	9.3
Richardson L.	-	01		0.2	1	0,1	-	0,1	2	0.1		6.0	5,0
McLeod R. @ mth	4	0.2		0.1	Ļ	0.2	-	0.2	L	0.2		22	15
W.R. @ Hwy 40	7	0.04	NDR	0.04	-	0.04	_	0.03	Г	0.03		0.3	2.7
W.R. d/s P&G Haul Br.		0.1	ر	0.06	2	0.03		0.03	1	0.03		0.4	22
W.R. @RRBr., Ic	7	0.05	NDR	0.1	-	0.09		0.06	_	0.05		0.5	2,9
W.R. u/s Bear R		0.4		0.1	r	0.1	NDR	0.1	NDR	0.1		0.8	4.2
W.R. 0.5 km u/s mth	2	0.07		0.09	-	0.04	-	0.08	_	0.08		9.0	3,8
S.R. u/s Puskwaskau R.	٦	0,08	NDR	0.07	1	0.05	_	0.06	_	0.06		9.0	3.0
S.R. @mth	1	0.08		0.2	2	0.06		0.07	_	0.05		6.0	4,8
S.R. @ mth-r	1	0.1		0.3	-	0.05		0.09		0.1		0.9	50
P.R. u/s S.R.		0.2	4	0.04	4	0.05	_	0.05	_	0.05		0.6	4.5
P.R. u/s Notikewin R.		06		0.3	NDR	0.07		0,1	NDR	60 0		EF.	7.2
P.R. above W.B.N.P.		0.3	NDR	0.1	7	0.07	NDR	0.1		0.06		0.9	5.1
P.R. above W.B.N.Pr		0.3	NDR	0.08	۲	0.05	NDR	0.07		0.06		0.6	4.3
A.R. u/s Hinton		2	-	0.1		0.2	-	0 2	٦	0.2		19	13
A.R. @ Weldwood Br.		2.3	NDR	0.2	1	0.2	4	0.1	_	0.1		3.6	20
A.R. @ Obed Br		1.6	NDR	0.4	ب	0.3	_	0.3	1	03		2	17
A.R. @ Obed Brr		2.1		0.3	-	0.2	_	0.5	-	0.5		2.8	19
A.R. @ Emerson L.		2.1		0.5	4	0.1	4	0.3	1	0.3		3.4	25
A.R. @ Emerson Lr		2 2		0.4	1	0.2	_	06	_	06		34	20
A.R. @ Windfall Br.		1 2		0.4	4	0.2		06	L	0.6		23	13

continued..

Table 4 continued

Site	2378 -TCDF pg/g		2378 PeCDF ig/g	234 -Pe pg/	78 CDF	123 -Hx pg(478 CDF g	1236 -HxC pg/g	578 CDF	123. -Hp(pg/g	1678 CDF	00 d	ЧБ
A R above Maskinta Ck	0.8		0.1	_	0.1	L _	0.3	_	0.3	NDR	0.5		1.1
A.R. above ANC	1.4		0.2	-	0.2	-	0.2	Г	0.2	NDR	0.2	NDR	0.8
A.R. @ Blue Ridge Br.	0.6	-	0.1	٦	0.1	-	0.2	-	0.2	NDR	0.3	NDR	0.8
A.R. above Smith	1.0	L	0.1	L	0.1	L	0.2	L	0.2	NDR	0.3	NDR	-
A.R. above Horse R.	0.8	L	0.1	Ч	0.1	L	0.1	L	0.1	NDR	0.2		0.4
A.R. above Firebag R.	0.6	NDR	0.1	L	0.1	NDR	0.2	NDR	0.2	NDR	0.5		0.5
A.R. @ Big Pt.Ch. @ mth	0.4	L	0.2	-	0.2	-	0.4	L	0.4	L	0.3	NDR	0.8
A.R. @ Big Pt.Ch. @ mth-r	0.5	L	0.1	L	0.1	Г	0.2	-	0.2	L	0.2	NDR	0.5
Richardson L.	0.4	L	0.1	-	0.1	-	0.2	-	0.2	NDR	0.2	NDR	0.2
McLeod R. @ mth	0.5	NDR	0.2	Г	0.1	L	0.3	L	0.3	NDR	0.7	NDR	1.4
W.R. @ Hwv 40	0.4	-	0.04	-	0.04	-	0.06	Ļ	0.06	L	0.1		0.2
W.R. d/s P&G Haul Br.	0.1	-	0.04	_	0.04	٦	0.07	L	0.07		0.1		0.1
W.R. @RR Br. I/c	0.8	-	0.05	-	0.05	L	0.06	-	0.06	NDR	0.3	NDR	0.2
W.R. u/s Bear R.	1.5	-	0.07	٦	0.07	NDR	0.1	-	0.08		0.3		0.4
W.R. 0.5 km u/s mth	0.8	-	0.03	-	0.03	-	0.05	L	0.05	NDR	0.2		0.2
S.R. u/s Puskwaskau R.	0.5	7	0.04	-	0.04	Г	0.08	Г	0.08	NDR	0.2		0.2
S.R. @ mth	3.8	-	0.06	٦	0.06	٦	0.09	-	0.09	NDR	0.2		0.5
S.R. @ mth-r	3.8	-	0.07	L	0.07	L	0.06	L	0.06	NDR	0.3		0.4
P.R. u/s S.R.	0.1	Г	0.03	-	0.03	L	0.09	L	0.09	NDR	0.2		0.3
P.R. u/s Notikewin R.	2.7	NDR	0.06	NDR	0.08	٢	0.1	L	0.1		0.2		0.5
P.R. above W.B.N.P.	0.6	-	0.06	-	0.06	NDR	0.1	L	0.07	NDR	0.4		0.4
P.R. above W.B.N.Pr	0.6	-	0.05	L	0.05	NDR	0.08	L	0.05	NDR	0.3		0.4
A.R. u/s Hinton	L 0.1	-	0.2	L	0.2	L	0.2	L	0.2		0.9	NDR	1.1
A.R. @ Weldwood Br.	0.4	Г	0.1	٦	0.1	٢	0.2	L	0.2		0.9		1.7
A.R. @ Obed Br.	0.9	-	0.2	L	0.2	-	0.3	-	0.3	NDR	0.7	NDR	1.1
A.R. @ Obed Brr	0.8	-	0.1	-	0.1	۲	0.4	_	0.4		0.8		5.
A.R. @ Emerson L.	1.9	-	0.1	-	0.1	-	0.4	-	0.4		0.8		1.8
A.R. @ Emerson Lr	2	-	0.1	L	0.1	L	0.3	-	0.3		0.8		1.4
A.R. @ Windfall Br.	2.2	-	0.1	٦	0.1	٦	0.1	-	0.1	NDR	0.8		-
)													

(a) NDR = Peak detected but does not meet quantification criteria
 L = Less than the Sample Detection Limit value (used when sample peak is not detected)
 -r = Replicate.

Table 4. Concluded

	Pimaric	San	dara-	Isopimario		Palustric	0 2	Jehyrdro- topimaric		ehydro- bietic	Abletic		Neoabietic		12/14 Chloro Dehydroablet		12,14 Dichloro- Dehydroabletic	% 0	Recovery +methyh
Cito	Acid (a)	cop	imaric	Acid		Acid		Acid		Acid	Acid		Acid		Acid		Acid	a -	odocarpic Acid
80	6/6u	2	6	6/6u		6,6u		6/6u		6/6u	6/6u		5/6u		6,6u		6/6u	s	urrogate
A P shove Maskida Ck			IDR 1	17	27	NDR	8	L	0.3	73		25	NDR	0.9	د	0.2	ر	0.3	69
A.R. above Maskuta Ckr	8	4	4DR 9	5	27	NDR	8.2	٦	0.3	73	-	24	NDR	0.8	٦	0.1	-	0.2	68
A.R. above ANC	2	76	+	18	83	NDR	6.8		8.8	220	-	130	NDR	2.3		56		11	15
A.R. @ Blue Ridge Br.	2	50	1	14	71	NDR	7.4		2.8	180	6	88	NDR	1.7		18		24	78
A.R. above Smith	7	11		48	250	NDR	6.4		4.1	370	6	210	NDR	1.6		35		46	69
A.R. above Horse R.	6	30	7	8.	31	NDR	5.8	NOR	0.8	26	-	40	NDR	0.9		12		14	88
A.R. above Firebag R.	2	22	NDR 8	11	45	NDR	11		1.6	140	0	53	٦	0.1		11		14	87
A.R. @ Big Pt.Ch. @ mth	-	17 1	NDR 8	8.	35		3		+	100	0	42	NDR	0.8		7.3	NDR	8.8	50
A.R. @ Big Pt.Ch. @ mth-r	-	18 1	NDR 8	8.8	36	NDR	16		1.1	110	0	47	NDR	1.1		8.1	NOR	10	92
Richardson L.	-	12 1	NDR 1	.2	11	NDR	8.8		1.5	36	0	6.4	-	14.7		1.2	NDR	1.5	58
McLeod R. @ mth	-	12	NDR	11	34	NDR	7.5	NDR	0.4	14(0	37	NDR	2.7	NDR	0.2	NDR	0.4	74
W.R. @ Hwy 40	4	*	1 ADK	80	10	NDR	22	Ļ	0.8	58	•	5.1	٦	0.5	-	0.3	L	0.5	54
W.R. d/s P&G Haul Br.	7.	4	VDR 5	.3	28	NDR	0.7	L	0.6	12(0	18	-	0.7	-	0.2	٢	0.3	69
W.R. @ RR Br., Vc	14	40		26	180	NDR	28		15	41(0	240		12		110		40	73
W.R. u/s Bear R.	11	10		18	130	NDR	19		10	27(C	170		5.8		80		30	73
W.R. 0.5 km u/s mth	40	85		19	120	NDR	21		9.2	30(0	110		3.5		53		16	15
S.R. u/s Puskwaskau R.		15 1	NDR 4	1.1	22	NDR	12		1.7	12	8	18	NDR	0.5		8.8		3.6	72
S.R. @ mth	2	51	8	3.6	61	NDR	14		3.3	13(0	73		1.8		28		24	78
P.R. u/s S.R.	2	4	NDR 1	8.1	7.7	NDR	11	٦	0.3	ē	*	4.8	-	0.2	۲	0.2	-	0.2	75
P.R. u/s S.Rr	2	2.3	NDR 1	8.	7.6	NDR	11	٦	0.3	3(8	4.7	-	0.2	٦	0.2	L	0.2	74
P.R. u/s Notikewin R.	6	38	NOR 7	1.	44	NDR	11		4	121	0	38	-	0.1		18		21	87
P.R. above W.B.N.P.	8	3.6	NDR	2.5	12	NDR	12		0.8	Ŧ	89	8.3	NDR	-		4.7		4	98
A.R. ws Hinton	3.	1.0	NDR 4	9.1	16	NDR	12	٢	0.3	91	0	6.4	NDR	0.2	٢	0.1	L	0.1	85
A.R. @ Weldwood Br.	54	40		41	300		22		83	281	0	150		12		88		48	83
A.R. @ Obed Br.	88	80	-	54	450		23		170	391	0	280		14		150		100	54
A.R. @ Obed Brr	86	80	NDR	50	330	NDR	14		120	36	0	200	NDR	4.9		110		61	63
A.R. @ Obed Br2r	49	80	NDR	28	370	NDR	17		150	41	0	150	NDR	4.6		120		81	84
A.R. @ Emerson L.	96	80	-	80	570		38		230	58	0	870		32		230		170	84
A.R. @ Windfall Br.	80	80	NDR	29	120	-	5	NDR	28	NDR 50	0	180	NDR	48		30		36	46
A.R. @ Windfall Brr	3	1 08	NDR	29	110	٦	1	NDR	24	NDR 47	0	120	NDR	36		28		36	82

Table 5: Resin Acids Detected in the Peace/Athabasca River Basin.

(a) NDR = Peak detected but does not meet quantification criteria
 L = Less than Sample Detection Limit value (used when sample peak is not detected)
 -r = Replicate

5.4.1 Phenols and Anisoles

None were detected.

5.4.2 <u>Catechols. Guaiacols and Veratroles</u>

Of the various chlorophenolic compounds, catechols were the most widely detected, though their presence is by no means widespread nor highly concentrated in the basin. The following catechols were detected in at least one of the sample sites: 4-chlorocatechol, 3,4-dichlorocatechol, 4,5-dichlorocatechol, 3,4,5-trichlorocatechol (and possibly 3,4,6-trichlorocatechol though this is suspect as it may in fact be 3,4,5-trichlorocatechol misidentified) and finally, tetrachlorocatechol.

3,4,5-Trichloroguaiacol, 3,4,5-trichloroveratrole (345TCV) and chlorosyringaldehyde were detected at the A.R. @ Obed Br. site. Effluent can contain trace amounts of 345TCV (Noton and Shaw 1989, Neilson <u>et al.</u> 1989, Noton 1992) which is probably produced by the biological methylation of the parent phenol, guaiacol or catechol rather than directly from the chlorination of lignin (Neilson <u>et al.</u> 1989). However, chlorinated veratroles do not generally accumulate in aquatic sediments, likely due to de-O-methylation and dechlorination reactions (Neilson <u>et al.</u> 1989, Rosemarin <u>et al.</u> 1990, de Sousa <u>et al.</u> 1988).

Distributions of 4,5-dichlorocatechol and 3,4,5-trichlorocatechol were mapped. Elevated levels were found downstream of the two bleached kraft mills, although only a few sites had concentrations above detection.

5.4.3 <u>Vanillins</u>

5-Chlorovanillin was detected in trace amounts at the A.R. @ Obed Br. site only. The distribution map for 6-chlorovanillin shows indications of elevated concentrations downstream from the bleached kraft mills, although all but one of the values is a "trace" concentration.

5.5 PAH

The most predominant PAH is phenanthrene which is found at all but three of the sites and generally in higher concentrations than the other PAHs. Generally though, it was the PAHs with 4+ ring structures which were detected in the basin. Chrysene, benzo[ghi]perylene and benzo[b]fluoranthene in particular were found, though trace amounts of fluoranthene and benzo[a]pyrene were also detected. These PAHs were detected in the Wapiti, Smoky and Peace River sites more frequently than in the Athabasca River sites. It is usually accepted that higher % OC values correspond to higher PAH concentrations (Varanasi, 1989). However, there is no evidence for such a relationship here.

Site	4-Chloro- catechol {a},{b} ng/g		3,4-Dichloro- catechol ng/g		4,5-Dichloro- catechol ng/g		3,4,5- Trichloro- catechol ng/g		3,4,6- Trichloro- catechol ng/g		Tetrachloro- catechol ng/g	
A R above Maskuta Ck	_	4.6	-	3.2	-	3.2	L	1.2	_	2.1	-	1.6
A.R. @ Obed Br. (1989)		22		3.8	Trace	9.7		11.1	L	2.5	Trace	4.3
A.R. above ANC	L 1	1.0	-	7.7	۲	7.7	L	2.3	Г	4.0	L	3.1
A.R. @ Blue Ridge Br.	L K	9.7	L	6.8	L	6.9	L	2.8	L	4.9	L	3.7
A.R. above Smith	L 1	1.0	L	7.7	L	7.7	L	2.4	L	4.2	Г	3.2
A.R. above Horse R.	L	5.5	L	3.8	L	3.8	Trace	1.6	L	2.8	L	2.2
A.R. above Firebag R.	L (6.9	-	4.8	-	4.8	L	1.8	L	3.1	L	2.3
A.R. @ Big Pt.Ch. @ mth	L (6.6	L	4.6	L	4.6	L	2.3	L	4.0	-	3.0
Richardson L.	L	5.7	L	20.9	-	20.9	L	10.5	-	18.1	L	13.8
McLeod R. @ mth	L 1	5.7	-	11.0	L	11.0	_	2.9	Ļ	5.1	-	3.9
W.R. @ Hwv 40		3.2	Ļ	2.2	L	2.2	-	1.2	L	2.1	٦	1.6
W.R. d/s P&G Haul Br.		6.9	_	4.8	L	4.8	Ļ	1.2	L	2.0	L	1.6
W.R. @ RR Br. I/c	L 1	5.0	_	10.5		57.3	-	2.6		26.3	Trace	6.2
W.R. u/s Bear R.	L	8.1	_	13.8	L	13.8		16.6	L	4.8	-	3.9
W.R. 0.5 km u/s mth	_	7.2	_	5.0	-	5.0	L	1.6	L	2.7	-	2.1
S.R. u/s Puskwaskau R.	-	5.0	-	3.5	L	3.5	L	1.0	L	1.8	_	1.4
S.R. @ mth	-	6.1	-	4.3	L	4.3	L	1.7	L	3.0	-	2.3
P.R. u/s S.R.	L 1	6.5	L	11.5	L	11.5	L	3.1	Ļ	5.4	L	4.1
P.R. u/s Notikewin R.	L 1	1.8	-	8.2	L	8.2	L	3.2	L	5.6	-	4.3
P.R. above W.B.N.P.	-	9.2	٦	6.4	L	6.4	L	2.2	Ļ	3.7	-	2.8
Method Blank 1	-	2.9	L	2.0	L	2.0	L	1.3	L	2.3	L	1.7
A.R. u/s Hinton	L	3.3	-	2.4		2.3	L	2.3	L	4.0	-	3.0
A.R. @ Obed Br.	Trace	8.7	Trace	3.8		52.2		64.7	L	5.3	L	4.0
A.R. @ Windfall Br.		9.6		2.0		8.9		4.6	L	1.8	-	1.3
Method Blank 1	_	4.0	L	2.9		2.8	L	1.2	L	2.1	-	1.6
Method Blank 2	г Г	3.5	L	2.6		2.4	L	2.2	L	3.8	-	2.9
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Table 6. Chlorophenolic Compounds Detected in the Peace/Athabasca River Basin.

continued...

Table 6. Concluded

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Site	5-Chloro- vanillin {c} ng/g		6-Chloro- vanillin {c} ng/g		3,4,5- Trichloro- guaiacol {c} ng/g		3,4,5- Trichloro- veratrole ng/g		2-Chloro- syring- aldehyde {c ng/g	÷	% Recovery 4-Bromo Phenol surrogate	% Recovery 2,4,6-Tri- bromophenol surrogate
A.R. above Maskuta Ck.		18.5		18.5	L -	2.6	L	1.9		18.5	36	89
A.R. @ Obed Br. (1989)		22.2	Trace	21.0	-	3.1	L	2.2	-	22.2	30	76
A.R. above ANC	-	44.4	-	44.4	۲	5.0	-	3.5	L	44.4	15	5 47
A.R. @ Blue Ridge Br.	L	39.2	-	39.2	L	6.0	L	4.2	L	39.2	17	36
A.R. above Smith	-	44.4	-	44.4	L	5.2	L	3.7	L	44.4	15	45
A.R. above Horse R.	L	22.2	-	22.2	٦	3.5	L	2.5	L	22.2	30	0 67
A.R. above Firebag R.	Г	27.8	-	27.8	٢	3.8	L	2.7	L	27.8	24	4 62
A.R. @ Big Pt.Ch. @ mth	L	26.7	L	26.7	L	4.9	L	3.4	L	26.7	25	48
Richardson L.	Г	60.6	-	60.6	۲	11.1	L	15.7	Ļ	60.6	11	1 21
McLeod R. @ mth	L	31.7	-	31.7	L	3.1	Г	4.4	L	31.7	2	1 75
W.R. @ Hwy 40	-	12.8	L	12.8	ب	2.6	-	1.9	Г	12.8	5	2 85
W.R. d/s P&G Haul Br.	L	27.8	L	27.8	-	2.5	۲	1.8	L	27.8	24	93
W.R. @ RR Br., I/c	-	60.6	Trace	116.4	L	5.4	L	3.8	Г	60.6	1	43
W.R. u/s Bear R.	L	26.7	Trace	90.06	L	2.0	L	4.2	L	26.7	25	119
W.R. 0.5 km u/s mth	-	29.0	Trace	80.0	L	3.3	L	2.4	L	29.0	23	3 70
S.R. u/s Puskwaskau R.	L	20.2	L	20.2	-	2.2	L	1.5	Г	20.2	ж	3 107
S.R. @ mth	-	24.7	Trace	28.5	-	3.6	L	2.6	L	24.7	2	2 64
P.R. u/s S.R.	-	66.7	L	66.7	L	6.7	L	4.7	Г	66.7	10	36
P.R. u/s Notikewin R.	-	47.6	-	47.6	L	6.9	-	4.9	L	47.6	1	4 34
P.R. above W.B.N.P.	٦	37.0	-	37.0	L	4.6	-	3.2	-	37.0	18	51
Method Blank 1	-	11.7	-	11.7	L	2.8	L	2.0	L	11.7	2	7 84
A.R. u/s Hinton	L	13.3	L	13.3	L	4.9	Г	3.4	L	13.3	5(46
A.R. @ Obed Br.	Trace	27.8		248.4	Trace	15.6		14.1		110.8	3	36
A.R. @ Windfall Br.	L	10.9	L	10.9	L	2.2	L	1.5	L	10.9	9	1 105
Method Blank 1	L	16.3	Г	16.3	L	2.6	-	1.9	L	16.3	4	1 86
Method Blank 2	L	14.2	Г	14.2	L	4.7	L	3.3	L	14.2	4	7 50

(a) All results have been corrected for percent recovery of the 4-Bromophenol ("mono" and "di" chlorophenols) and the 2,4,6-Tribromophenol ("tri" and "tetra" chlorophenols) surrogates

(b) Trace = Peak detected at a value between the Method Detection Limit (MDL) and the Practical Quantification Limit (PQL)

L = Less than the MDL value (used when no sample peak is detected)

(c) No exact MDL was established therefore L = less than PQL3 (here, PQL = 3 X the average MDL rounded to a whole number)

Site	Benzo(a)- anthracene {a},{t ng/g	íq	Benzo(b)- fluoranthene ng/g		Benzo(a)- pyrene ng/g		Benzo(ghi)- perylene ng/g		Chrysene ng/g		Dibenzo(a,h)- anthracene ng/g	
A.R. above Maskuta Ck.		4.6		14.6	Trace	6.5	Trace	7.4		18.9	Г	4.6
A.R. @ Obed Br. (1989)	-	4.6	Trace	13.4	Trace	6.8	Trace	7.4		17.8	Trace	9.7
A.R. above ANC	L	7.7	Trace	18.6	L	7.7	L	7.7	Trace	14.0	L	7.7
A.R. @ Blue Ridge Br.	-	7.7	Trace	18.6	Trace	10.9	L	7.7	Trace	12.0	L	7.7
A.R. above Smith	L	4.6		17.4	Trace	5.4	Trace	10.5	Trace	9.8	Ļ	4.6
A.R. above Horse R.	-	4.3		14.9	L	4.3	L	4.3	Trace	10.7	L	4.3
A.R. above Firebag R.	-	4.3		16.9	L	4.3	Trace	0.0	Trace	13.3	L	4.3
A.R. @ Big Pt.Ch. @ mth	Г	4.6		17.5	L	4.6	L	4.6		15.2	L	4.6
Richardson L.	L	8.0	٦	8.0	Г	8.0	L	8.0	Trace	8.4	L	8.0
McLeod R. @ mth	L	7.7	Trace	21.7	Trace	13.2	L	7.7	Trace	12.0	L	7.7
Method Blank 1	L	5.5	L	5.5	-	5.5	L	5.2	-	5.5	L	5.5
	ŀ			0.00	Traco	15.4		0 00		28.6	1	7.1
W.K. @ Hwy 40	Irace	1		0.00	1909			23.7		37 5	Trace	13.0
W.R. d/s P&G Haul Br.		15.5		34.3	,	0.0		1.04		0.00	Trace	0.01
W.R. @ RR Br., I/c	-	4.3		29.0	Trace	9.7		19.7	-	79.0	Irace	9.01
W.R. u/s Bear R.	L	12.9	Trace	36.9	Trace	21.3	Trace	27.1	Trace	23.3	-	12.9
W.R. 0.5 km u/s mth		18.2		39.8	Trace	13.3		28.3		47.0	Trace	13.3
S.R. u/s Puskwaskau R.	Trace	11.0		29.0	Trace	15.1	Trace	19.4	Trace	20.7	L	8.6
S.R. @ mth		32.6	NA	0.0	Trace	11.3		17.6	L	4.3	L	4.3
P.R. u/s S.R.	L	4.3		26.1	Trace	12.0		28.3		19.1	Trace	10.6
P.R. u/s Notikewin R.	L	6.2		32.2	Trace	15.5		34.3		30.3	Trace	14.6
P.R. above W.B.N.P.	L	8.3		25.8	Trace	14.2	Trace	23.3	Trace	15.5	Trace	16.8
Method Blank 2	Г	4.3	-	4.3	L	4.3	L	4.3	Г	4.3	-	4.3
A R. u/s Hinton	_	3.2		11.1	_	3.2	-	3.2		23.9	Ļ	3.2
A.R. @ Obed Br.	L	2.9	-	2.9	Trace	5.4	Г	2.9		20.7	T	2.9
A.R. @ Windfall Br.	L	3.2	-	3.2	Г	3.2	L	3.2		13.8	Г	3.2
Method Blank 3	-	2.9	L	2.9	-	2.9	L	2.9	L	2.9	L	2.9
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continued..

Table 7: PAHs Detected in the Peace/Athabasca River Basin.

Site	Fluoranthen ng/g	æ	Indeno(1,2,3-0 pyrene ng/g	-(p:	Naphthalene ng/g		Phenanthrer ng/g	g	Pyrane ng/g		% Recovery 2-Fluoro- biphenyl	% Racovery p-Terphenyl -d14
A R above Maskuta Ck	Trace	9 21	-	4.6	Tace	8.4		78.2	Trace	88	45	65
A.R. @ Obed Br. (1989)	Trace	82	-	4.6	L	6.7		77.3	Trace	12.6	45	65
A.R. above ANC	Trace	10.5	1	1.7	L	11,9		67.1	Trace	10.5	42	65
A.R. @ Blue Ridge Br	Trace	9.8	-	7.7	1	11.9		47.6	Trace	10.9	42	65
A.R. above Smith	Trace	8.3	1	46		32.7		30.7	Trace	10.5	45	65
A.R. above Horse R	Trace	7.0	-	4.3	-	6.4		24.3	Trace	11.3	47	70
A R. above Firebag R	Trace	7.0	Trace	6.6	L.	7.0		25.1	Trace	9.9	43	20
AR. @ Bg Pt Ch @ mh	Trace	7.5	T	4.6		6.7		20.9	Trace	11.4	45	65
Richardson L.	Trace	9.6	a.	8.0		12.0	Trace	32.8		8.0	50	75
McLeod R. @ mth	Trace	12.0	Trace	12,0	-	11.1		38.0	Trace	15.5	45	65
Method Blank 1		5.5	-	5,5	-	10.0	_	10.01	-	5.5	30	55
W.R. @ Hwy 40	Trace	15.4	Trace	154	Trace	14.1		91,2		22 0	49	20
W.R. d/s P&G Haul Br.		17.2	Trace	13.8	Trace	14.9		107.4		27.8	43	60
W.R. @ RR Br. I/c		143	Trace	12.0	Trace	11.0		30.2		249	50	02
W.R. u/s Bear R.	Trace	21.3	-	12.9	Trace	19.0		97.8	Trace	27.1	50	70
W.R. 0.5 km u/s mth		20.7		151	Trace	13.3		142.2		35.5	46	60
S.R. u/s Puskwaskau R.	Trace	13.7	Trace	15.1	Trace	14.0		74,6	Trace	18.0	48	20
S.R. @ mih	Trace	10.6	Trace	12.7	-	5.9		56 3		16.3	51	02
P.R. u/s S.R.	Trace	12.0	Trace	13.4	_	6.8		63.0		19.7	44	02
P.R. u/s Notikewin R	Trace	16.6	Trace	16.6		85		81.3		22.5	47	65
P.R. above W.B.N.P.	Trace	13.0	Trace	15.5	-	11,4		40.5	Trace	15.5	44	60
Method Blank 2	-	4.3	-	4.3	-	6.3	L	6.3	-	4.3	48	02
A.R. u/s Hinton	Trace	4.8	L	3.2	Trace	7.8		84.3	Trace	4,8	65	96
A.R. @ Obed Br.		8.9	Trace	3.5		14.5		72.9		11.2	80	105
AR @Windfall Br.	Trace	6.6		3,2	_	4.7		58.8	Trace	9.9	85	125
Method Blank 3		29		29	L	3.8	Ч	3.8	-	2.9	80	105
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Table 7. Concluded.

(a) All results have been corrected for percent recovery of the 2-Fluorobiphenyl (2-ring PAHs) and p-Terphenyl-d14 (3+-ring PAHs) surrogates

(b) L = Less than the Method Detection Limit (MDL) value Trace = Greater than the MDL but less than the Practical Quantification Limit (PQL = approximately 3 X MDL) NDR = Peak detected but does not meet quantification criteria NA = Not available

6.0 CORRELATIONS

The purpose of correlation analysis is to test for a relationship between an independent variable and a certain dependent variable (i.e., to illustrate a correlation between two variables). The selection of independent and dependent variables is arbitrary when comparing concentrations of two compounds in a set of samples. This is less arbitrary when comparing OC or particle size and compound concentrations since the assumption is made that OC and particle size may, to varying degrees, determine the concentration of the organic compound in the sediment, but not *vice versa*.

Correlation between contaminant concentration and physical properties may be overidden by distance downstream from an input (location) where that input represents a major loading of the compound to the river. Where two compounds have a common source, such as BKME, there is more likely to be a correlation between their concentrations than with physical properties of the sediment.

Accordingly, concentrations of four compounds (2378TCDF, dehydroabietic acid, 12/14CDHA and 12,14DCDHA) were correlated against percent OC of the fine fraction. Values of the correlation coefficient, r, for contaminant concentration vs. OC were: -0.212 (n=20), 0.084 (n=21), -0.209 (n=16) and -0.200 (n=16), espectively. These are all insignificant at the 20% level. No attempt was made to correlate contaminant concentrations with percent silt+clay since the chemical analyses were performed on the silt/clay fraction of the sediment rather than on bulk sediment.

To test whether the dioxin/furan group and the chlorinated resin acids are associated, correlation anlaysis was carried out on 2378TCDF vs. 12/14CDHA and 12,14DCDHA. Correlations were insignificant at the 20% level, with r values of 0.161 (n=19) and 0.253 (n=19), respectively. This is consistent with the pattern from the distribution maps where 2378TCDF concentrations appear to peak 100-300 km downstream from the mills, especially on the Peace system, whereas concentrations of the chlorinated resin acids reach a maximum of 50 km downstream of the mills and decline steadily with distance downstream.

Good correlations were found between concentrations of dehydroabietic acid and concentrations of 12/14CDHA and 12,14DCDHA, with r values of 0.788 (n=19) and 0.761 (n=19), respectively, both significant at the 1% level. This indicates that the parent dehydroabietic acid and the chlorinated dehydroabietic acids are associated with the same particle sources in mill effluents. As well, the intercepts from these correlations (estimated DHA concentration at zero concentration of 12/14CDHA or 12,14DCDHA) indicate a background level for dehydroabietic acid of about 50 ng/g.

7.0 DISCUSSION

In general, concentrations of compounds from the groups analyzed were low throughout the river basins. These results indicate that the two bleached kraft mills were sources of some members of the dioxin/furan group, most notably 2378TCDF, and of the chlorophenolic group (6-chlorovanillin, 4,5-dichlorocatechol, and 3,4,5-trichlorocatechol) as evidenced by somewhat elevated concentrations

downstream from the mills. This pattern was more pronounced for several of the resin acids and and the two chlorinated resin acids, 12/14CDHA and 12,14DCDHA.

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APPENDICES

APPENDIX A: TERMS OF REFERENCE

Project 2321-D1: Interpretation of Contaminant Data for Basin-wide Sediments

I. BACKGROUND AND OBJECTIVES

River bottom sediments from the Athabasca River and Wapiti-Smoky-Peace River systems were sampled and analyzed for selected contaminants and related variables in fiscal year 1992-93. These sediment samples were collected to provide important data for use by other projects addressing aquatic fate and food web accumulation of contaminants. These analyses will also be used as input data for the ToxiWasp model. The specific objectives of this study interpret and synthesize the lab analysis data for selected contaminants collected under these NRBS projects: 2321-B1 and 2325-B1,C1.

II. GENERAL REQUIREMENTS

The contractor is required to analyze and interpret contaminant data collected under the following NRBS projects:

2321-B1: Archived basin-wide bottom sediment samples collected for contaminant analysis by Alberta Environmental Protection (20 samples);

2325-B1,C1: Bottom sediment samples collected during 1992 RSS (6 samples).

Specific lab data to be analyzed include those existing for the following compounds:

- dioxins/furans (PCDD/Fs)
- resin acids
- polycyclic aromatic hydrocarbons (PAHs)
- chlorophenolic compounds

Note: PCBs will not be analyzed further because of detection limit problems.

The required lab approvals from project 2321-B1 are: 029 and 030. The required lab approvals from project 2325-B1,C1 are: 019, 037, 047, 048 and 049.

III. DELIVERABLES

1. A synthesis report that incorporates the assembling tabulating and mapping of contaminant results from the sediment data sets indicated above.

A-1

2. Six to ten 35 mm slides that can be used at public meetings to summarize the purpose, methods and key findings of the project.

APPENDIX B: LIST OF COMPOUNDS ANALYSED IN SEDIMENT SAMPLES

The sediment samples were analysed for the presence of a wide range of compounds under the primary categories of: Dioxins and Furans; Resin Acids; Chlorophenolic Compounds and; PAHs. Only those compounds which were detected were reported in the body of this report. The following is a complete list of all such compounds analysed for in this study.

Table B-1:	List of Al	Compounds	Analysed in	Sediment	Samples.
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DIOXINS AND FURANS	RESIN ACIDS	CHLOROPHENOLIC COMPOUNDS	PAHs
TCDD - Total 2,3,7,8	Pimaric Acid	Chloroanisoles 2 3 4	Acenaphthene
PeCDD - Total 1,2,3,7,8	Sandaracopimaric Acid	DiCl-Anisole 2,3 2,4 2,5 2,6 3,4 3,5	Acenaphthylene
HxCDD - Total 1,2,3,4,7,8 1,2,3,6,7,8 1,2,3,7,8,9	Isopimaric Acid	TriCl-Anisole 2,3,4 2,3,5 2,3,6 2,4,5 2,4,6 3,4,5	Benzo[a] anthracene
HpCDD - Total 1,2,3,4,6,7,8	Palustric Acid	TetraCl-Anisole 2,3,4,5 2,3,4,6 2,3,5,6	Benzo[b] fluoranthene
OCDD	Dehydroisopimaric Acid	PentaCl-Anisole Chlorophenol 2 3 4	Benzo[k] fluoranthene

DIOXINS AND FURANS	RESIN ACIDS	CHLOROPHENOLIC COMPOUNDS	PAHs
TCDF - Total 2,3,7,8	Dehydroabietic Acid	DiCl-Phenol 2,3 2,4 2,5 2,6 3,4 3,5	Benzo[a]pyrene
PeCDF - Total 1,2,3,7,8 2,3,4,7,8	Abietic Acid	TriCl-Phenol 2,3,4 2,3,5 2,3,6 2,4,5 2,4,6 3,4,5	Benzo[ghi] perylene
HxCDF - Total 1,2,3,4,7,8 1,2,3,6,7,8 2,3,4,6,7,8 1,2,3,7,8,9	Neoabietic Acid	TetraCl-Phenol 2,3,4,5 2,3,4,6 2,3,5,6	Chrysene
	12/14 Chloro dehydroabietic Acid	PentaCl-Phenol Chlorocatechol 4	Dibenzo[a,h] anthracene
HpCDF - Total 1,2,3,4,6,7,8 1,2,3,4,7,8,9	12,14 Dichloro dehydroabietic Acid	DiCl-Catechol 3,4 3,5 4,5	Fluoranthene
OCDF		TriCl-Catechol 3,4,5 3,4,6	Fluorene
		TetraCl-Catechol	Indeno [1,2,3-cd] pyrene

continued

Table B-1

DIOXINS AND FURANS	RESIN ACIDS	CHLOROPHENOLIC COMPOUNDS	PAHs
		DiCl-Guaiacol 3,4 4,5 4,6	Napthalene
		TriCl-Guaiacol 3,4,5 3,4,6 4,5,6	Phenanthrenene
		TetraCl-Guaiacol	
		DiCl-Veratrole 4,5	
		TriCl-Veratrole 3,4,5	
		TetraCl-Veratrole	
		TriCl-TriMeth- oxybenzene	
		Chlorovanillin 5 6	
		DiCl-Vanillin 5,6	
		TriClSyringol	
		Cl-Syringaldehyde 2	
		DiCl-Syringaldehyde 2,6	

APPENDIX C: CONTAMINANT DISTRIBUTION MAPS

LIST OF COMPOUNDS MAPPED

- 2,3,7,8-Tetrachlorodibenzofuran
- 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin
- Octachlorodibenzo-p-dioxin
- Isopimaric Acid
- Dehydroabietic Acid
- 12/14-Chlorodehydroabietic Acid
- 12,14-Dichlorodehydroabietic Acid
- 6-Chlorovanillin
- 4,5-Dichlorocatechol
- 3,4,5-Trichlorocatechol



10.0