Canada Alberta Northwest Territories

Northern River Basins Study

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 108

ENVIRONMENTAL CONTAMINANTS IN WATER AND SEDIMENTS,

UPPER ATHABASCA RIVER, APRIL, 1992

Prepared for the
Northern River Basins Study
under Project 5313-D1

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.

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.

NORTHERN RIVER BASINS STUDY
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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;
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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.A. 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, UPPER ATHABASCA RIVER, APRIL, 1992

STUDY PERSPECTIVE

In 1992, a 200 km reach of the Athabasca River between Hinton and Whitecourt was designated a Reach Specific Study (RSS) area by the Northern River Basins Study. This section of the river receives municipal effluent from the town of Hinton, and bleached kraft mill effluent from the Weldwood pulp mill. A number of aquatic media were sampled in this reach, including water, suspended sediment, bottom sediment, benthic invertebrates, biofilm and fish. The RSS was designed to examine the biomagnification of contaminants, such as dioxins and furans, from effluent and water to fish. 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.

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?*

This project report presents the analytical results for the water and sediment samples collected from the RSS in the spring of 1992. Samples were collected at the seven following sites: upstream of Hinton at Maskuta Creek, Hinton combined effluent (HCE), Weldwood Haul Bridge, Obed Mountain Coal Bridge, Emerson Lakes Bridge, Knight Bridge, and the Windfall Bridge downstream near Whitecourt. Water, suspended sediment, and bottom sediment samples were analyzed for a number of physical and contaminant parameters.

Samples of Athabasca River water generally showed low or non-detectable concentrations of contaminants. In contrast, suspended sediments were an important transport medium for most of the contaminants analyzed. Contaminant concentrations in suspended sediment were generally many times higher than in water, and higher than levels found in depositional sediments. The highest concentrations of dioxins and furans were found in suspended sediments, and in most cases the levels persisted for a short distance downstream of the HCE before falling to background levels. The lower chlorinated (di-, tri- and tetra-) dioxins and furans were found above detection limits in depositional sediments at most sites downstream Hinton. Overall dioxin and furan levels in the fine fraction of depositional sediments tended to increase with distance downstream of Hinton, although the toxicity level remained about 20% that carried by suspended sediments. Levels of chlorinated phenolics were highest in suspended sediments collected from the HCE itself, and many times lower in sediments collected from the river downstream. In general, depositional sediments had total resin acid concentrations from 20 to 50% of those found in suspended sediments, but levels tended to increase with distance downstream (48 km) to Emerson Lakes Bridge. Organochlorines were non-detectable in the few suspended sediment samples analyzed, but above-background levels of copper, cadmium and zinc were found in suspended sediments from the HCE.

Similar to other studies, suspended sediments were found to be an important transport medium for many types of contaminants. The data presented and described by this project will be incorporated into a Contaminants Component 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 form this project will be incorporated into contaminant fate and food chain models being developed for these river systems.

REPORT SUMMARY

In early 1992, a 200-kilometre reach of the Athabasca River between Hinton and Whitecourt was chosen as the NRBS reach-specific study area. The reach receives effluent from the Weldwood Canada pulp mill mixed with municipal effluent from the town of Hinton. Sampling in the reach for a number of aquatic media including water, suspended sediment, bottom sediment, benthic invertebrates, biofilm, and fish was initiated in late March 1992. The objective of the reach-specific study was to provide an intensive ecosystem database for a representative reach, with which to priorize subsequent basin-wide sampling.

This report presents the results from 1992 for contaminants in water, suspended sediments, and bottom sediments, and provides the following recommendations related to future contaminant analyses in these media:

Sample Replication and Analytical Duplication: Future NRBS surveys should include analyses of adequate numbers of field and laboratory replicates to allow complete statistical analyses of results, including the significance of spatial and temporal trends, the measurement of in-site spatial and temporal variability, and the determination of analytical precision.

Laboratory Selection: In determining place of analyses for future samples, care should be taken to ensure that analytical techniques are well-established, and that analytical detection limits are suitable for ambient environmental samples. Close cooperation between field and laboratory personnel should be maintained regarding sampling requirements, surrogate availability, etc., and guarantees of analytical turnaround times should be requested.

Future Analyses of Water Samples: Low or non-detectable concentrations of a number of contaminant groups were found in the water phase, including PCDD/Fs, polychlorinated biphenyls, organochlorine pesticides, and total mercury. Chlorinated phenolics and resin acids were generally detectable in water, but persistence in the water phase appears to be low. In general, analyses of water phase samples for basin-wide surveys is not recommended, with the possible exception of effluents.

Future Analyses of Suspended Sediments: As found by other workers, suspended sediments were found to be an important transporting medium for most of the contaminants analyzed. Contaminant concentrations in suspended sediment were generally several orders of magnitude higher than in water. The collection method (centrifugation) is labor-intensive, however, and collection of adequate sample size for a broad spectrum of analyses might be impractical during important low discharge periods. Interpretation of suspended sediment results is hindered by seasonal variability, and by a shortage of comparable datasets in the literature.

Future Analyses of Depositional Sediments: Concentrations of contaminants found in depositional sediments were generally lower than found in suspended sediments. A number of factors favor the use of depositional sediments in basin-wide surveys, however, including the relative ease of sampling, and

the ability to illustrate basin-wide contaminant presence/absence and long term temporal trend with less concern for seasonal variability than would be required for suspended sediments. Future surveys of depositional sediments should include data on intra-site variability and extremely precise documentation of sampling locations and sampling methods. Surveys should be timed for low-flow, ice-free periods when depositional areas are most readily accessible.

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1.0 INTRODUCTION AND BACKGROUND

The Northern River Basins Study (NRBS) was initiated in late 1991 by the governments of Canada, Alberta, and the Northwest Territories. The Study has a five-year mandate to examine the cumulative impacts of existing developments on the Athabasca, Peace, and Slave rivers. Study objectives include: to determine the effects of existing developments on aquatic ecosystems within the basins; to determine temporal trends; and to provide the information required to enable prediction of effects of future development.

The study is divided into eight issue areas including contaminants, food chain, nutrients, hydrology and hydraulics, synthesis/modelling, traditional knowledge, drinking water and other uses. Each issue area is governed by a list of sixteen study board questions which must be answered to enable the NRBS to fulfil its objectives. At the outset, the study was envisioned as having three distinct, though overlapping phases, including baseline description, assessment, and evaluation.

Due to the large size and complexity of the basins under study, it was determined that intensive study of a representative reach receiving bleach-kraft effluent, followed by carefully targeted sampling throughout the basins, would be the most effective way to undertake the baseline description phase of the study program. In early 1992, a 200-kilometre reach of the Athabasca River between Hinton and Whitecourt was chosen as the NRBS reach-specific survey (RSS) area. The reach receives effluent from the Weldwood Canada bleach-kraft pulp mill mixed with municipal effluent from the town of Hinton (Figure 1). Sampling in the reach for a number of aquatic media (water, suspended sediment, bottom sediment, benthic invertebrates, biofilm, and fish) was initiated in late March 1992.

Environment Canada was contracted by the NRBS to collect suspended sediments and water samples and R.L.&L. Environmental Services Ltd. were contracted for collection of depositional and erosional bottom sediments and benthos. The purpose of this report is to present the results from 1992 for contaminants in water, suspended sediments, and bottom sediments, and to provide recommendations related to future contaminant analyses in these media.

2.0 STUDY AREA

The study area and sampling locations are shown in Figure 1. Water and suspended sediments were collected from six mainstem Athabasca River locations and from the Weldwood-Hinton effluent (Hinton combined effluent or HCE) during the period March 31 to April 9, 1992. Depositional and erosional bottom sediments were collected at six mainstem sites from April 8 to April 14, 1992 (Table 1).

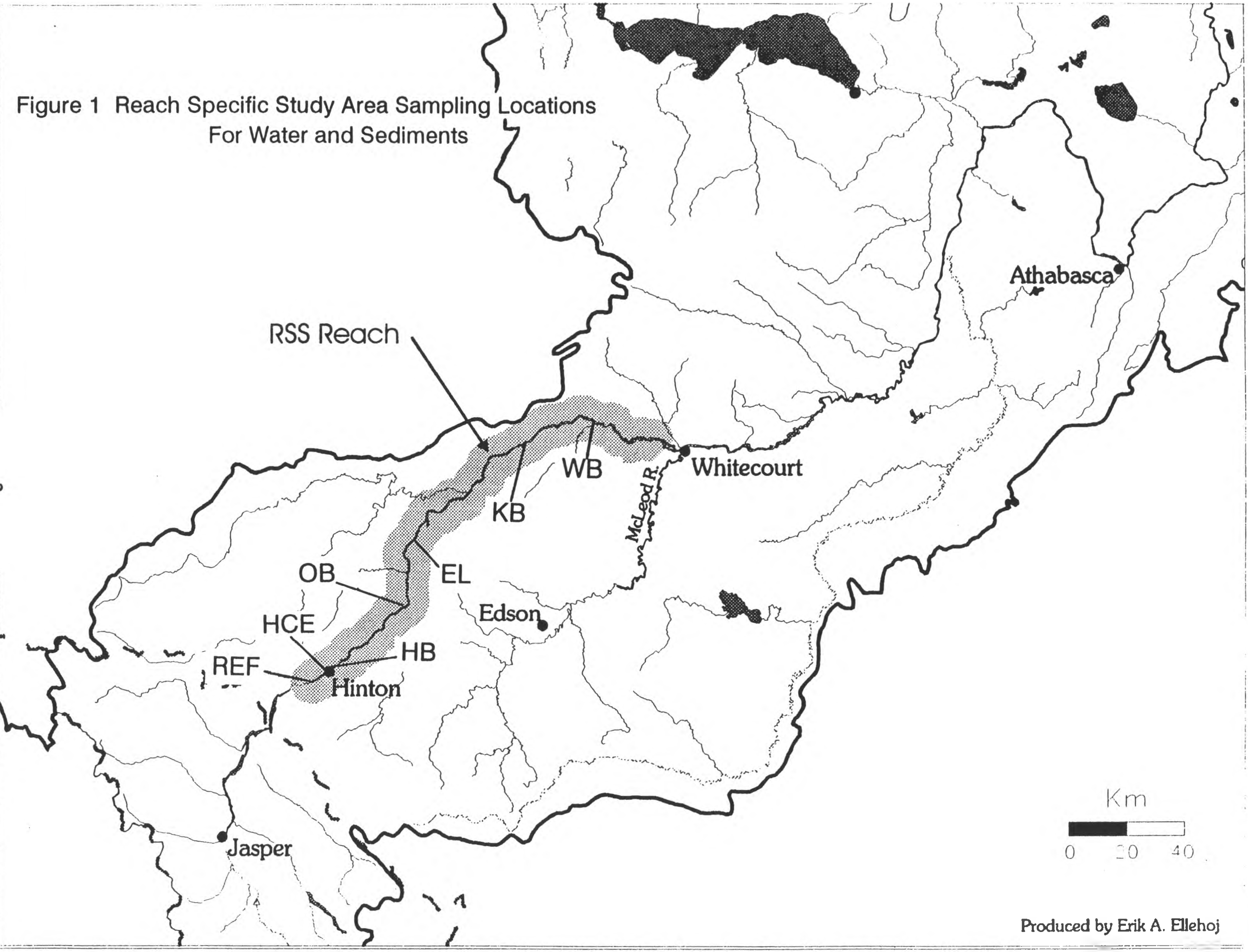


Figure 1 Reach Specific Study Area Sampling Locations For Water and Sediments

Produced by Erik A. Ellehoj

Table 1. RSS Sampling Locations for Water, Suspended Sediments, and Bottom Sediments

Sampling Location	Site Code	Kilometers Below HCE	Water	Suspended Sediment	Depositional Sediment
Above Maskuta Creek	REF	-7	√	√	√
Hinton Combined Effluent	HCE	0	√	√	
Weldwood Haul Bridge	HB	1	√	√	√
Obed Mountain Coal Bridge	OB	19	√	√	√
Emerson Lakes Bridge	EL	48	√	√	√
Knight Bridge	KB	116	√	√	√
Windfall Bridge	WB	176	√	√	√

Locations were sampled from upstream to downstream, with sample timing chosen to approximate Athabasca River time of travel. The survey followed ice-out very closely, with ice still prevalent along the banks at a number of locations. Discharge in the Athabasca River at Hinton varied from 39 to 54 m^3/sec during the sample collection period, typical of winter base flow and minimum dilution for the reach (Athabasca River discharge data from Water Survey of Canada). HCE discharge varied from 1.20 to1.28 m^3/sec during this period (HCE discharge data from Weldwood Canada), for an average river:effluent dilution ratio of approximately 36:1.

3.0 FIELD AND ANALYTICAL METHODS

3.1 METHODS FOR COLLECTION OF SUSPENDED SEDIMENTS AND WATER

3.1.1 Suspended Sediments

Alfa-Laval MB103 centrifuges were used for collection of suspended sediments and centrifugate (clarified water). The equipment used is known as the Sedisamp System, often referred to as Sedisampler. Water was delivered to the Sedisamplers by a Marsh magnetic drive submersible pump through stainless steel sheathed 1/2 inch teflon intake lines. A flow rate of 4 litres/minute was maintained to each of two Sedisamplers. The intake pump was suspended from a float with the pump intake placed between 0.5 and 1.0 meters below the water surface. The Sedisamplers were housed in an ice-fishing hut which was heated with a 1500 watt heater and heat lamp. The pump, centrifuges, heater, and lights were powered by a 5000 watt Honda generator.

Prior to the survey, the tubing, pumps, stainless-steel centrifuge top assembly, and stainless-steel centrifuge bowls were rinsed with organic-free water, acetone, and hexane (in that order). Between samples, the centrifuge bowls were again rinsed with organic-free water, and acetone and hexane. All other sample contact points (pump, tubing, and centrifuge top assembly) were flushed with large amounts of river water prior to sampling. A separate centrifuge bowl, pump, and intake lines were used to collect samples of Hinton combined effluent, as thorough cleaning in the field, especially of the intake lines, would have been difficult.

To meet anticipated analytical requirements, an attempt was made to collect at least 100 grams of wet suspended sediment from each sampling location. It was calculated prior to the survey that 48 centrifuge hours (2 centrifuges x 24 hours) should be sufficient to deliver this sample weight at the river locations, given Athabasca River suspended sediment concentrations near 10 mg/L. Adequate sample was collected at HCE in 7 hours using one centrifuge.

All river suspended sediments were collected from off the right bank to provide consistency through the reach, since it was known prior to the survey that effluent from HCE does not mix completely for at least 10 kilometres below HCE. Details of the suspended sediment collections are presented in Table 2.

Table 2 RSS Suspended Sediment Collections

Sampling Location	Kms. below HCE	Location Description	Start Centrifuges	Stop Centrifuges	Duration (hours)	Sediment Collected (gm wet)	Athabasca River at Hinton (m3/sec)
REF	(-7)	10 meters off right bank	31 Mar 92 1730	01 Apr 92 1810	24:40	225	38.7
HCE	0		02 Apr 92 0915	02 Apr 92 1615	7:00	580	40.3
HB	1	10 meters off right bank	02 Apr 92 1815	03 Apr 92 1700	23:15	530	40.3
OB	19	10 meters off right bank	04 Apr 92 0930	05 Apr 92 0730	22:00	332	51.1
EL	48	7 meters off right bank	05 Apr 92 1430	06 Apr 92 1000	19:30	163	54.3
KB	116	15 meters off right bank	07 Apr 92 1700	08 Apr 92 1600	23:00	141	50.1
WB	176	10 meters off right bank	08 Apr 92 1845	09 Apr 92 1750	23:00	110	47.2

Discharge data from Water Survey of Canada

Suspended sediments were removed from the centrifuge bowls using solvent-washed stainless-steel spatulas, and placed in pre-washed IChem glass sediment jars with teflon liners. Samples were weighed and frozen on dry ice immediately after removal from the bowls. Samples were subsequently transferred to an ultra-cold freezer for storage at -60 degrees C.

3.1.2 Whole Water and Clarified Water Samples

Whole water samples were collected by hand-dipping adjacent to the pump intake locations. The samples were composited throughout the centrifuge period (four 1/4 volume grabs were collected at regular intervals throughout the centrifugation process). Clarified water samples were composited in the same manner. Clarified water samples were taken from teflon outlet lines attached to the centrifuge top assembly. Large volume clarified water samples (20-litres for acid extractives and 40-litres for neutral extractives) were sampled 4-litres at a time, requiring 5 or 8 sample collections during the centrifugation period. All water samples were preserved, if required, immediately after collection of the first aliquot, and kept cool and dark until returned to the laboratory. Water samples for organic extraction and analyses were stored in pre-cleaned EPA protocol Eagle-Picher glass bottles.

3.2 METHODS FOR BOTTOM SEDIMENT COLLECTION

Field methods used by R.L.&L. Environmental Services Ltd. are fully described in a report to the NRBS titled Benthos and Bottom Sediment Field Collections, Upper Athabasca River, April to May, 1992 (R.L.&L. 1993). Bottom sediment samples were collected concurrently with samples for benthic invertebrates during the period April 7-14, 1992.

Bottom sediments were collected from undisturbed substrates in both erosional (cobble-gravel areas) and depositional zones (areas of fine-textured deposition). Sampling sites for erosional sediments were generally within a few hundred meters of the sites used for collection of suspended sediments and water. Depositional sediment collection sites were located, in some instances, a few kilometres above or below the erosional sediment collection locations. Preference in collection was given to finer-textured sediments. Each sample collected was a composite of 10 individual grabs distributed in a radius of 50-100 meters at each site, with only the top 5 cm of individual samples retained. Duplicate samples were collected at 3 of 6 depositional locations, and at 1 of 6 erosional locations.

Erosional sediments were collected with a large stainless steel spoon, with spoonfuls pooled in a stainless steel tray. Depositional sediments were collected with a stainless steel Ekman dredge, spoon and tray. Samples were stored on ice until delivered to NRBS officials. Samples were subsequently analyzed for particle size and carbon content, and fractionated by wet and dry seiving at the National Water Research Institute. Only the clay-silt fractions (<63 micron cutoff) were analyzed. The results for depositional bottom sediments only are presented in this report.

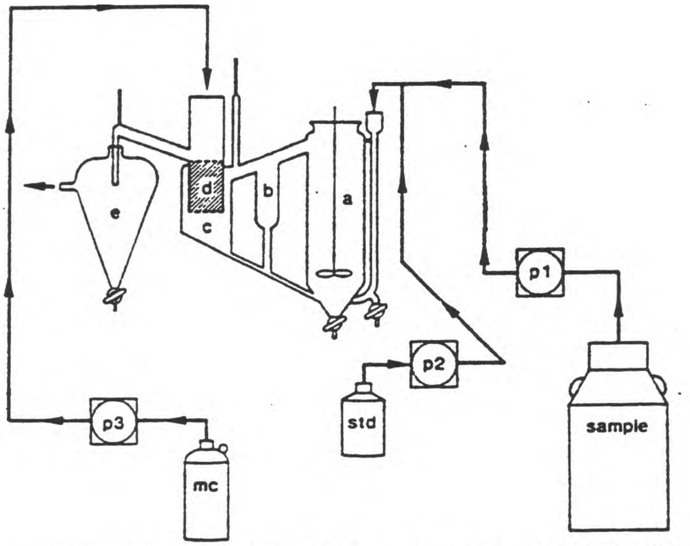
3.3 LARGE VOLUME EXTRACTION METHODS

Large volume Goulden extractions of clarified water were performed for dioxins-furans (PCDD/F), organochlorines-PCBs (OC-PCB), and chlorinated phenolics to provide the lowest possible detection limits in water for these parameter groups. Extractions were done in the Calgary field laboratory (Environment Canada) within 48 or 72 hours of the time of collection. A single methylene chloride extract for PCDD/F and OC-PCB was done on 40-litres of unpreserved clarified water. The 40-litre extract was subsequently split in the laboratory to provide 20-litre extracts for each analytical group. The chlorinated phenolic extract was done on a 20-litre sample of clarified water, which had been acidified to pH 2 with sulphuric and ascorbic acids at the time of collection. Recovery surrogates were metered into the extractor throughout the extraction process as indicated below:

PCDD/Fs: $^{13}C_6$*-1,2,3,4-TCDD (1.3 ng) and* $^{13}C_{12}$*-1,2,3,7,8,9-HCDD (2.5 ng)*
OC-PCBs: 1,3,5-tribromobenzene (10 ng), 1,2,4,5-tetrabromobenzene (10 ng), and delta-BHC (10 ng)
Chlorinated Phenolics: 2,4,6-tribromophenol (2500 nanograms)

A schematic of the Goulden continuous flow-through extractor is shown in Figure 3. The method used is described in Assembly, Set-Up, and Operation of the Goulden Large-Sample Extractor in Field and Laboratory Settings (Anthony 1990).

Figure 2 Schematic of Goulden Large Sample Extractor (from Foster and Rogerson 1990)



. Schematic representation of the Goulden large-sample extractor: (a) mixing chamber, (b) first and (c) second stage settling chambers, (d) packed column, and (e) third stage settling chamber; fluid metering systems including (p1) sample, (p2) standard (std), and (p3) methylene chloride (mc) make-up pumps.

3.4 CONTAMINANT ANALYSES

A number of analytical laboratories including Chemex Laboratories, AXYS Analytical Services, Enviro-Test Laboratories, Zenon Environmental Laboratories, and the National Water Research Institute, took part in analyses of RSS samples. As required in their contracts to the NRBS, each laboratory has provided detailed description of their analytical and quality assurance protocols to the NRBS, and these reports are available on request. The results of laboratory duplicates and blanks are discussed in Section 4.0 (Results and Discussion).

Table 3 outlines the analyses performed on RSS water and sediments and indicates the analyzing laboratory.

Table 3 List of Analyses, April 1992 Reach Specific Study

Parameter Group	Laboratory	Medium	Sampling Location (# of Analyses)						
			REF	HCE	HB	OB	EL	KB	WB
Non-Filterable Residue	Chemex	Whole Water	1	1	1		1		
		Clarified Water		1	1		1		
Particle Size and Carbon	NWRI	Suspended Sediment	1	1	1	1	1	1	1
		Bottom Sediment	1		1	1	1	1	1
Adsorbable Organic Halide	Zenon	Clarified Water (0.5 L)	1	1	1	1	1	1	1
		Whole Water (0.5 L)			5			5	
Extractable Organic Halide	Zenon	Suspended Sediment	1	2	1	1	1	1	1
		Clarified Water (4L)	1	2	1		1		
PCDD/F	AXYS	Suspended Sediment	1	1	2	1	1	1	1
		Bottom Sediment (Fine)	1		1	2	1		1
		Clarified Water (20L)	1		1	1	1	1	1
		Clarified Water (1L)		1					
Chlorinated Phenolics	Chemex	Suspended Sediment	1	1	1	1	1	1	1
		Bottom Sediment (Fine)	1			1			1
		Clarified Water (20L)	1	1	1	1	1	1	1
Resin Acids	AXYS	Suspended Sediment	1	1	1	1	1	1	1
		Bottom Sediment (Fine)	1		1	3	1		1
		Clarified Water (1L)	1	1	2	1	2	1	2
OC and PCB	Chemex	Suspended Sediment	1	1		1			
		Clarified Water (20L)	1	1	1		1		
Total Metals	Chemex	Suspended Sediment	1	1		1			
		Whole Water	1	1	1		1		

4.0 RESULTS AND DISCUSSION

All results are as reported by the analyzing laboratories and have not been corrected for laboratory or field surrogate recoveries. Where values of "less than detection limit" were reported, the value of the detection limit was used in graphical display of individual compounds, and a value of zero in most statistical calculations, including sums of constituents (to minimize difficulties associated with differing detection limits for different sampling locations). The results have been organized by analytical group rather than by aquatic medium, to facilitate inter-media comparison of results.

Due to a shortage of field splits and analytical replicates, the statistical analyses which can be applied to the RSS dataset, including the determination of significance of trend, and the measurement of in-site variability and of analytical precision, are limited. The reasons for the low number of field splits are two-fold: limited analytical budgets and, in the case of suspended sediments and large volume extracts, limited sample size. As seen in the gaps in Table 3, budget considerations made it necessary to analyze samples from selected sites only for some contaminants.

4.1 SUSPENDED SEDIMENT RECOVERY EFFICIENCY

Envirodata (1981) has published recovery data on the Sedisamp system. The report states that the Sedisampler provides >95% recovery of particles larger than 0.45 mm. Recovery will decrease proportionally with smaller grain size, though fine colloidals will be well-represented, since colloids centrifuge similarly to larger particles. Fine non-colloidals and organic particles will be under-represented since these materials may have specific gravities similar to that of water.

Non-filterable residue (NFR) results in centrifugate and whole water are available for three of the sites sampled. Based on the NFR results, suspended sediment recoveries were as follows: HCE 74.4%; HB 98.2%; and EL 78.1% (Table 4).

Table 4 Suspended Sediment Recovery Data

Sampling Location	Non-Filterable Residue Whole Water mg/L	Non-Filterable Residue Clarified water mg/L	% Recovery Suspended Sediment
Hinton Combined Effluent	50.0	12.8	74.4
Weldwood Haul Bridge	22.0	0.4	98.2
Emerson Lakes Bridge	6.4	1.4	78.1

4.2 LARGE VOLUME EXTRACTION RECOVERY EFFICIENCY

Recoveries of extraction surrogates for the PCDD/Fs (AXYS Analytical) and chlorinated phenolics (Chemex Laboratories) were generally within bounds considered acceptable for large volume extracts (Table 5). The recoveries for OC-PCBs (Chemex Laboratories) were more erratic. Only delta-BHC was quantified, since Chemex Laboratories did not have access to the appropriate standards for1,3,5-tribromobenzene or 1,2,4,5-tetrabromobenzene.

Extraction method blanks of organic-free water with recovery surrogates were performed for PCDD/Fs, OC-PCB, and chlorinated phenolics. No detections of analytes other than the surrogates were reported in any of the blanks.

Table 5 Goulden Extractor: Recovery of Extraction Surrogates

Sampling Site	**% Recovery**			
	$^{13}C_6$ 1,2,3,4-TCDD	**$^{13}C_{12}$ 1,2,3,7,8,9-HCDD**	**delta-BHC**	**2,4,6-tribromophenol**
REF	109	64	50	154
HCE	na	na	330*	164
HB	98	137	63	155
OB	102	46	na	98
EL	98	122	50	181
KB	100	128	na	90
WB	100	51	na	98
Method Blank	138	76	15	61

*laboratory reported severe interference with analysis; na: not analyzed by laboratory

4.3 PARTICLE SIZE AND ORGANIC CARBON

Analyses of particle size and carbon were done by the National Water Research Institute in Burlington. Particle size results are presented in Figures 3 and 4.

Suspended sediments (Figure 3) became progressively finer moving downstream, with percent silt decreasing from 60% to 24% in the reach between REF and WB, and percent clay increasing from 39% to 74%. Finer suspended sediments at the downstream sampling locations are to be expected, as the river slope and velocity generally reduces through the RSS reach. Hinton combined effluent suspended sediments were very fine, with 23% silt-size and 77% clay-size particles.

Figure 3 Suspended Sediment Particle Size RSS Reach, April 1992

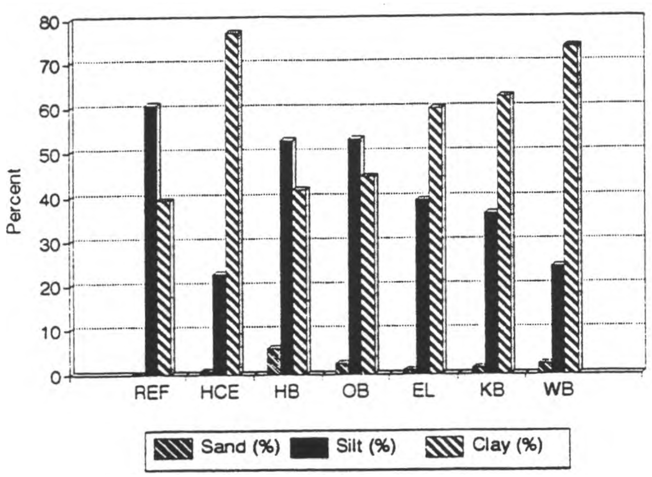
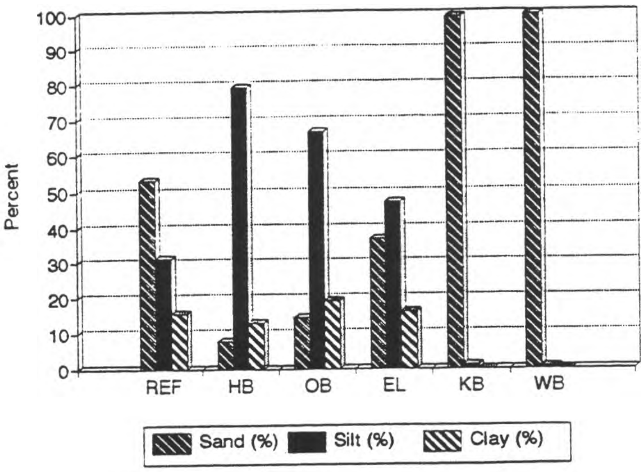


Figure 4 Depositional Sediment Particle Size RSS Reach, April 1992



Depositional sediments (Figure 4) became progressively more coarse moving downstream, with the samples from KB and WB being nearly 100% sand-size. This is surprising, and was not found to be the case in subsequent surveys of depositional sediments through the RSS reach. The field notes supplied by the collectors (R.L. &L. Environmental Services) indicate "brown-gray silt layer overlying sandy clay" for the KB depositional sediments, and 'gray-brown silt overlying black clay and organics" for WB sediments. This suggests the probability of either sample mis-labelling or an analytical mixup. It should be re-stated that the depositional sediments were fractionated at 63 µm (the sand-silt boundary) in the laboratory prior to contaminant analyses. Since clay-silt fraction sediments were available for subsequent analyses from both KB and WB, it is likely that the labelling and/or reporting problem was limited to the particle size and, perhaps, carbon analyses.

Suspended sediments at mainstem Athabasca River sites had similar total organic carbon throughout the reach, with total carbon near 7% (of total sediment weight) and organic carbon near 3% (Figure 5). Much higher carbon content was present in the HCE sample, with total carbon at 29%. The majority of the carbon in HCE suspended sediments (93%) was organic carbon. On visual inspection, the suspended sediments from HCE appeared as fine, fibrous mats with a woody-appearance.

Total and organic carbon were more variable in the depositional bottom sediments. Carbon concentrations were highest (6-7% total and 4-5% organic carbon) in the finer samples (HB, OB, and EL). Lower total carbon concentrations (near 2%) were reported for bottom sediments from KB and WB, respectively.

Figure 5 Carbon in Suspended Sediment
RSS Reach, April 1992

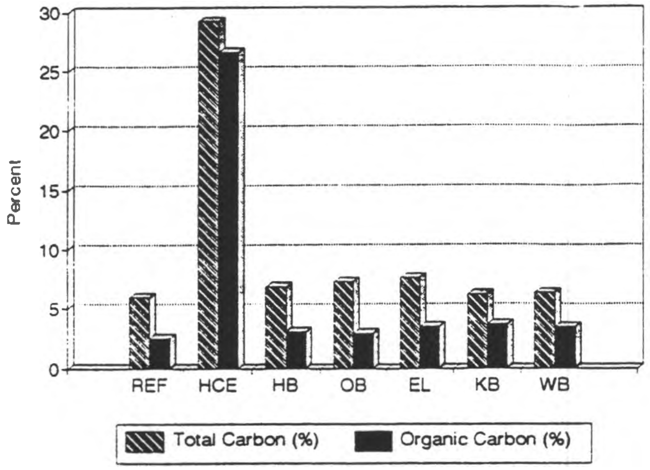
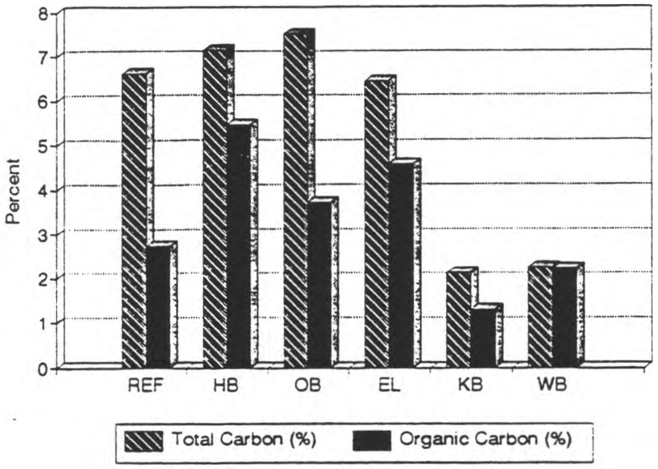


Figure 6 Carbon in Depositional Sediment
RSS Reach, April 1992



4.4 ADSORBABLE ORGANIC HALOGENS AND EXTRACTABLE ORGANIC HALOGENS

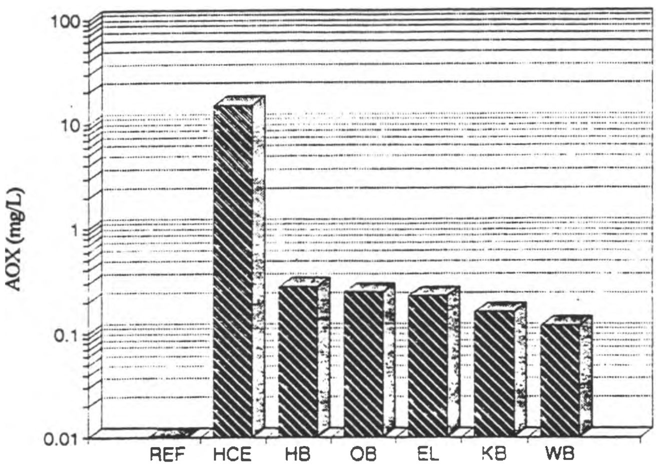
Adsorbable organic halogen (AOX) was analyzed to provide an estimate of the total organic chlorine (TOCl) in water. AOX includes all halogenated organics, but since chlorine is the only halogen used in significant quantities in BKMs, AOX results for BKM reaches are often interpreted as a direct measure of organic chlorine. AOX was analyzed on clarified water from all RSS sites. As well, AOX was analyzed for cross-sectional whole water samples from HB and KB to provide information on mixing at those locations.

Extractable organic halide (EOX) measures halogenated organics that can be extracted by non-polar solvents, and is considered to be an indicator of halogenated compounds likely to accumulate in lipid pools (Swanson et al. 1993). EOX:AOX ratios tend to be very small, in the range of 0.1 to 4% (Barry et al. 1991 in Swanson et al. 1993). EOX was analyzed on clarified water and suspended sediments. AOX and EOX were analyzed by Zenon Environmental Laboratories.

Duplicate AOX analyses were done on two samples and indicate good reproducibility (OB 0.25 mg/L and 0.23 mg/L; HB 0.38 mg/L and 0.34 mg/L). The AOX method blank was non-detectable at 0.01 mg/L.

HCE effluent had an AOX concentration of 15 mg/L on April 2, 1992. AOX concentration in the Athabasca River concurrently increased from <0.01 mg/L at REF to 0.28 mg/L at HB, located 1 kilometer below HCE (Figure 7). Through the remainder of the RSS reach, AOX concentrations decreased to 0.12 mg/L at WB. This concentration decrease may have been more to dilution effects than to AOX degradation, since AOX is considered to be a highly persistent constituent.

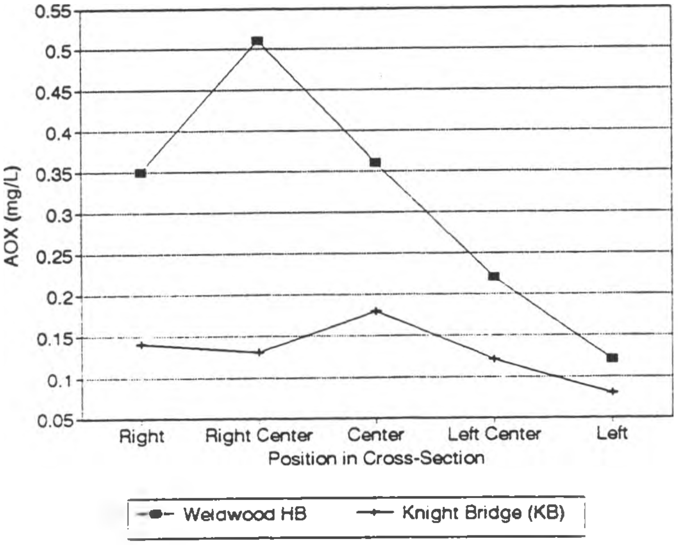
Figure 7 AOX in Water, RSS Reach, April 1992



Mean daily discharge (April 2, 1992) of the Athabasca River at Hinton averaged 40.3 m^3/sec (data from Water Survey of Canada), while HCE discharged at 1.22 m3/sec (data from Weldwood Canada), for a dilution ratio of 33:1. Mass-balancing effluent AOX of 15 mg/L, the near-field Athabasca River concentration would be predicted to be 0.45 mg/L AOX, somewhat higher than the AOX result for HB (0.28 mg/L). The difference between measured and predicted is likely due to incomplete mixing in the reach.

Cross-sectional AOX in whole water from HB and KB are shown in Figure 8. AOX concentrations at HB were found to be highest at river right-center, probably due to the proximity to the HCE outfall and the stream dynamics in the 1 kilometre reach. The AOX measured at right-center in whole water (0.51 mg/L) was very close to the mass balance prediction. Note that suspended sediments and clarified water at HB were collected at the vertical marked 'right'. More homogenous mixing was found at KB, located 116 kilometres below HCE.

Figure 8 AOX Cross-Sections at Weldwood Haul Bridge and Knight Bridge, April 1992

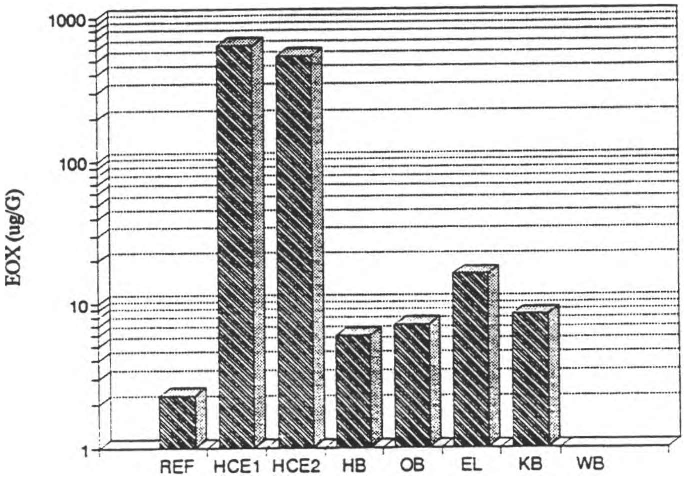


AOX concentrations in HCE during April 1992 were somewhat lower than those recorded in Weyerhaeuser effluent in 1990-91 while that mill was operating at 70% ClO_2-substitution (Swanson et al. 1993). Five samples collected of Weyerhaeuser effluent from 1990-1991 contained AOX concentrations of between 18 mg/L and 28 mg/L (values estimated from report graphics). The same report showed that AOX output from the Weyerhaeuser BKM decreased as the percentage of chlorine dioxide substitution was increased.

Clarified water from HCE had an EOX concentration of 0.05 mg/L (0.043 mg/L in a duplicate). EOX concentrations were below analytical detection limits (<0.01 mg/L) in clarified water from REF, HB, and EL, as would be expected considering the 33:1 dilution ratio. The ratio of EOX:AOX in HCE clarified water was 0.3%, within the range found by earlier workers (Barry et al. 1991 in Swanson et al. 1993).

Suspended sediment EOX results are shown graphically in Figure 9. Duplicate samples from HCE had EOX concentrations of 632 ug/G and 533 ug/G (mean 583 ug/G). Main stem concentrations increased from 2.3 ug/G at REF, to a range of 5.9 - 16 ug/G in the RSS reach, with the highest concentration recorded at EL (kilometer 48 below HCE). Suspended sediment loading on April 2 from HCE totalled 4020 kg/day (data from Weldwood Canada). The sediment loading at REF for April 2 is estimated to be approximately 30,600 kg/day, based upon river discharge for April 2 (40.3 m^3/sec), and non-filterable residue measured on April 1 at REF (8.8 mg/L). Using the resulting sediment dilution ratio (7.6:1), the concentration in near-field suspended sediments would be predicted to be approximately 75 ug/G EOX, from 5X to an order of magnitude higher than the concentrations measured in the RSS reach. The reasons for this discrepancy are uncertain.

Figure 9 EOX in Suspended Sediment, RSS Reach, April 1992



4.5 POLYCHLORINATED DIBENZODIOXINS (PCDD) AND DIBENZOFURANS (PCDF)

PCDD/Fs are high molecular weight tricyclic aromatic molecules comprising a total of 210 PCDD/F congeners, with distinctions between congeners based upon the distribution of chlorine atoms on the ring structures. These compounds are produced as bi-products of a number of industrial and natural processes including BKMs, chemical production, incineration, automobile combustion, and forest fires.

As a class, PCDD/Fs are hydrophobic, lipophilic, and persistent aquatic contaminants. Pathways of degradation in aquatic environments include photolysis and biodegradation (Pastershank and Muir 1994). PCDD/F display greatly differing toxicity, and to aid interpretation International Toxic Equivalent Factors (I-TEFs) have been assigned to 17 PCDD/F congeners based upon their relative toxicity. The most toxic congener is 2,3,7,8-T_4CDD, assigned an I-TEF of 1.0. Examples of other I-TEFs are as follows: 2,3,7,8-T_4CDF 0.1; 1,2,3,7,8-P_5CDD 0.5; 1,2,3,7,8,9-H_6CDD 0.1; 1,2,3,4,6,7,8-H_7CDD 0.01; and O_8CDD 0.001. The summation of the 17 congener-specific I-TEFs produces the Toxicity Equivalent Quotient, or TEQ.

The primary PCDD/F congeners formed in softwood BKMs using chlorine gas include 2,3,7,8-T_4CDD, 2,3,7,8-T_4CDF, and 1,2,7,8-T_4CDD (Swanson et al. 1993). With increased use of chlorine dioxide substitution in BKMs during the early 1990s, BKM effluent concentrations of the higher substituted and more toxic PCDD/Fs, including 2,3,7,8-T_4CDD, have decreased significantly (Swanson et al. 1993).

Di- and tri-substituted PCDD/Fs are also formed in softwood bleaching, but due to their low toxicity (I-TEF for di-substituted TCDDs is 0) and limited tendency to bioaccumulate, they have seldom been included to date in analytical programs. Di- and tri-substituted TCDD/Fs are good markers of ClO_2-substituted BKM effluent, however, and were analyzed for the RSS. The di- and tri-substituted TCDD/F results are not included in this report, but have been fully discussed in Pastershank and Muir's 1994 report to the NRBS on PCDD/Fs in various RSS aquatic media.

Analyses of PCDD/Fs in water, suspended sediments, and depositional sediments were performed at AXYS Analytical Laboratories. Duplicate samples of depositional sediments were analyzed by Enviro-Test Laboratories (ETL). The ETL results are not discussed in this report, but are included in Pastershank and Muir (1994).

4.5.1 PCDD/Fs in Water

Analyses of clarified water were performed on 20-liter methylene chloride extracts from all sites with the exception of HCE, which was analyzed using a backup four-liter sample submitted following a laboratory mishap. Extraction surrogate recoveries were generally in acceptable ranges (Table 5, Section 4.2). The laboratory reported detection limits <1.0 pg/L for the 20-liter extracts, and in the 1-5 pg/L range for HCE.

Concentrations of most PCDD/Fs in clarified water were below analytical detection limits in both the Hinton combined effluent and Athabasca River receiving waters. 2,3,7,8-T_4CDF was detected at trace concentration at two locations: HB (0.1 pg/L) and EL (0.09 pg/L). 2,3,7,8-T_4CDF was reported at <1.5 pg/L in HCE clarified water, though the same sample had total-T_4CDF of 6.6 pg/L. The only other congener detected in water was O_8CDD, present at four sites as follows: HCE (9.0 pg/L), HB (0.8 pg/L), EL (0.6 pg/L), and KB (0.3 pg/L).

4.5.2 PCDD/Fs in Suspended Sediments

Duplicate analyses for PCDD/F was performed on suspended sediments from HB. The results showed a high level of analytical reproducibility, with differences between duplicates generally below ten percent. The procedural blank was detection-free and surrogate recoveries in the 62-97 percent range. Analytical detection limits for most congeners was <0.5 pg/G. The results for the P_5-O_8 PCDD/Fs are presented graphically in the Appendix (Figures A1-A5).

Trace concentrations of several congeners were reported in REF suspended sediment, including 2,3,7,8-T_4CDD (0.2 pg/G) and 2,3,7,8-T_4CDF (0.3 pg/G). Whether these results reflect near detection limit noise or real sources is uncertain.

The three most toxic PCDD/Fs were detected in HCE suspended sediment: 2,3,7,8-T_4CDD was detected at 11 pg/G, 1,2,3,7,8-P_5CDD at 1.4 pg/G, and 2,3,4,7,8-T_5CDF at 2.7 pg/G. 2,3,7,8-T_4CDD remained measureable throughout the RSS reach at concentrations near 1.0 pg/G (Figure 10), a 5-fold increase from REF. 2,3,7,8-T_4CDF concentrations increased approximately 8-fold below HCE (HCE 2,3,7,8-T_4CDF concentration was 40 pg/G), from 0.3 pg/G at REF to near 2.5 pg/G in the reach below. Concentrations of 2,3,7,8-T_4CDD and 2,3,7,8-T_4CDF below HCE were approximately 70% and 50% (respectively) of the concentrations predicted using a sediment dilution ratio of 7.6:1. The TEQ for Hinton combined effluent was 22 pg TEQ/G on April 2, 1992. The effluent had the effect of doubling the Athabasca River TEQ from 0.9 pg TEQ/G at REF to 1.4-2.0 pg TEQ/G downstream (TEQs from Pastershank and Muir 1994).

Figure 10 T_4CDD/F in Suspended Sediment RSS Reach, April 1992

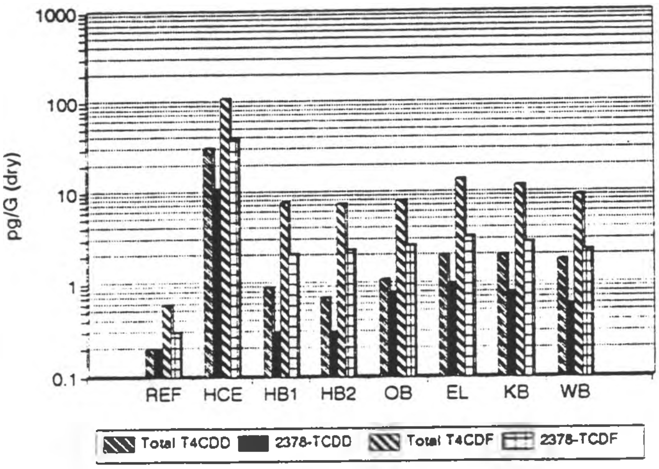
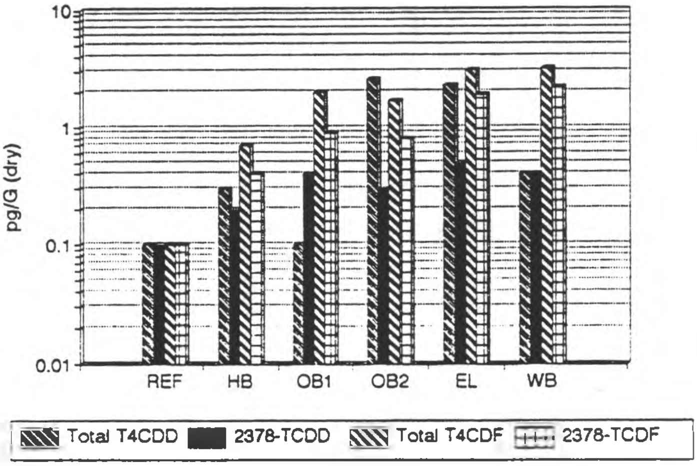


Figure 11 T_4CDD/F in Depositional Sediment RSS Reach, April 1992



For a number of lower toxicity PCDD/F congeners, concentrations in suspended sediments from HB were equal to or higher than those from HCE (see Graphs A1-A5, Appendix). These included total H_7CDD, O_8CDD, total H_6CDF, total H_7CDF, and O_8CDF. The reason(s) for this apparently anomalous result is uncertain.

4.5.3 PCDD/Fs in Depositional Sediments

Analyses of PCDD/Fs in depositional sediments were performed on samples from five locations: REF, HB, OB (duplicated), EL, and WB (Figure 11) . Analyses were performed on the clay-silt fraction (<63 μm) of the sediments collected.

Detectable concentrations of 2,3,7,8-T_4CDD were reported in depositional sediments from the four locations below HCE, in a range from 0.2-0.5 pg/G.. Total T_4CDD at the four downstream locations ranged from 0.3-2.6 pg/G. 2,3,7,8-T_4CDF was in the range from 0.4-2.2 pg/G below HCE. The control location (REF) was non-detectable for T_4-substituted congeners at a detection limit of 0.1 pg/G. P_5- and H_6- substituted CDD/Fs were not detected in bottom sediments, though H_7- and O_8- substituted CDD/Fs were present in trace concentrations at most sites, including REF.

The PCDD/F TEQs for depositional sediments downstream of HCE ranged from 0.21 pg TEQ/G at HB to 0.55 TEQ/G at EL, significantly below the draft Canadian Environmental Quality Guidelines for bottom sediment of 79 pg TEQ/G (Environment Canada 1993). Based on a comparison of PCDD/F TEQs in the reach below HCE during April 1992, depositional sediments had approximately 20% of the toxicity carried by suspended sediments.

4.6 CHLORINATED PHENOLICS

Chlorinated phenolics are a family of compounds with a large number of industrial, medical, preservative, and other uses. They are commonly found in Canadian aquatic environments below urban and industrial areas (CCREM 1987). The toxicity of individual chlorinated phenolics, and of associated substituted phenolics such as the guaiacols and catechols, varies substantially. Generally, the higher the number of chlorines, the higher the acute and chronic toxicity to aquatic organisms (CCREM 1987). Chlorinated phenolics can cause odour and taste tainting of fish muscle at concentrations lower than those which would produce toxicity.

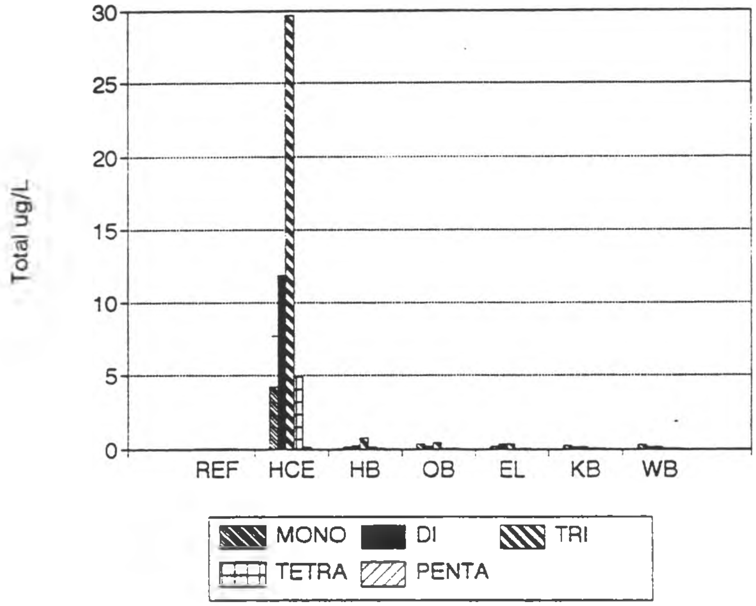
Bleach-kraft pulp mills have been known for some time to produce chlorinated phenolics in the pulping process. In recent years, with increased ClO_2 -substitution, chlorinated phenolics in pulp effluents have been reduced substantially. When the Weyerhaeuser Pulp Mill (Grande Prairie, Alberta) went from 70% to 100% ClO_2-substitution, chlorinated phenolics in the effluent were reduced by 98% (Swanson et al. 1993).

4.6.1 Chlorinated Phenolics in Water

Analysis of chlorinated phenolics were performed on methylene chloride extracts of 20-litre samples of acidified clarified water. Each 20-liter sample was collected, as discussed earlier, through the entire centrifugation process (approximately 24 hours at river sites), to provide comparability with the results for suspended sediments. Difficulties in establishing the analytical technique at the analyzing laboratory (Chemex Laboratories), followed by a change in analytical technique between analytical batches, has reduced the interpretability of the water results. Graphs of individual chlorinated phenolics detected in water are found in the Appendix (Figures A6-A9)

The results for chlorinated phenolics in clarified water (summations by degree of chlorine substitution) are presented in Figure 12. Chlorinated phenolics were not detected at the upstream control site REF. Results for HCE were as follows: Σmono- 4.2 ug/L; Σdi- 11.9 ug/L; Σtri-29.7 ug/L;Σtetra- 4.9 ug/L; and Σpenta- 0.08 ug/L. The chlorinated phenolic 'fingerprint' for HCE is similar to that found in 1991 at Weyerhaeuser (Swanson et al. 1993), with regard to the relative proportions of Cl-substitution fractions. Concentrations in HCE were approximately 30-50% of those found in Weyerhaeuser effluent during 1991, when Weyerhaeuser was operating at 70% ClO_2-substitution.

Figure 12 Chlorinated Phenolics in Water, RSS Reach, April 1992



Ten chlorinated phenolic compounds were detected in HCE clarified water at concentrations exceeding 1 ug/L. Table 6 presents a comparison of concentrations at HCE and HB for these predominant compounds. The concentrations at HB are in good general agreement with mass balance predictions using a 33:1 dilution ratio.

Table 6 Predominant Chlorinated Phenolics in Clarified Water

Chlorinated Phenolic	HCE (ug/L)	HB (ug/L)	Ratio HCE:HB
3,4,5-trichloroguaiacol	16.5	0.42	39:1
4,6-dichloroguaiacol	6.2	0.14	44:1
2,4,6-trichlorophenol;	6.1	0.14	44:1
4,5,6-trichloroguaiacol	5.7	0.15	38:1
6-chlorovanillin	4.2	0.10	42:1
tetrachlorocatechol	2.4	<0.05	>48:1
5,6-dichlorovanillin	2.35	0.07	34:1
tetrachloroguaiacol	2.35	0.07	34:1
4,5-dichloroguaiacol	1.3	<0.05	>26:1
2,4-dichlorophenol	1.03	0.03	34:1

The Canadian Water Quality Guidelines have recommended guidelines for chlorinated phenolics in water for the protection of freshwater aquatic life (CCREM 1987). These objectives, applicable to the sum of all constituents and based upon the degree of chlorine substitution, are as follows: monochlorophenols 7 ug/L; dichlorophenols 0.2 ug/L; trichlorophenols 18 ug/L; tetrachlorophenols 1 ug/L; and pentachlorophenols 0.5 ug/L. At downstream RSS locations, the maximum concentration present at any location for each chlorinated phenolic substitution group were as follows:

mono-Cl	0.3 ug/L	OB
di-Cl	0.3 ug/L	EL
tri-Cl	0.7 ug/L	HB
tetra-Cl	0.07 ug/L	HB
penta-Cl	0.003 ug/L	HB

The RSS results for chlorinated phenolics in water exceeded the CCREM (1987) guideline for di-substituted constituents (0.2 ug/L) at HB and EL. The predominant di-chlorinated compounds causing the exceedences included 4,6-dichloroguaiacol and 5,6-dichlorovanillin.

Concentrations of chlorinated phenolics in water decreased rapidly between HB (kilometre 1) and WB (kilometre 176), though 15 compounds were still detectable at WB at concentrations >0.001 ug/L. The compounds present at highest concentration at WB were 6-chlorovanillin (0.3 ug/L) and 3,4-dichloroguaiacol (0.07 ug/L).

4.6.2 Chlorinated Phenolics in Suspended Sediments

Variation in detection limits resulting from differing available sample sizes and probable (though unspecified) in-laboratory technique difficulties, have limited the degree of interpretation possible for chlorinated phenolics in suspended sediments.

Chlorinated phenolic concentrations in suspended sediments (summation by degree of substitution) are presented in Figure 13. This graphic is quite similar to that for water, especially regarding the proportions in the HCE 'fingerprint', with tri-substituted compounds predominant. Concentrations of predominant chlorinated phenolics in HCE suspended sediments were approximately two orders of magnitude (w/w) higher than in clarified water.

Figure 13 Chlorinated Phenolics in Suspended Sediment RSS Reach, April 1992

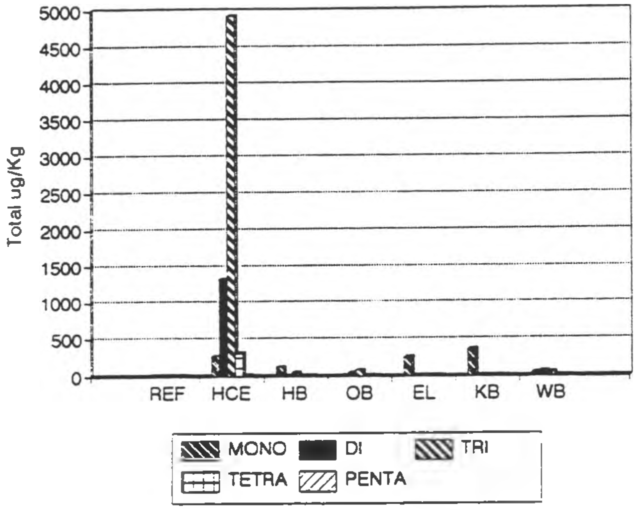
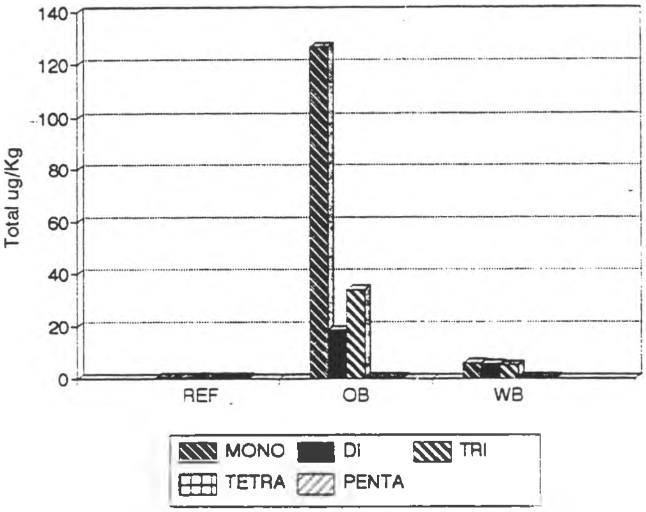


Figure 14 Chlorinated Phenolics in Depositional Sediment RSS Reach, April 1992



The guaiacols were the major chlorinated phenolic group present in HCE suspended sediments, notably 3,4,5-trichloroguaiacol (3600 ug/Kg), 4,5,6-trichloroguaiacol (980 ug/Kg), and 3,4-dichloroguaiacol (700 ug/Kg). Downstream persistence of chlorinated phenolics in suspended sediment appears to be low, though detection limit differences mask spatial trends.

Attempts to mass balance HCE concentrations with downstream sites using the sediment dilution ratio were unsuccessful. As well, a number of compounds, including 3,4,5-trichlorocatechol, 4-chlorocatechol, and 6-chlorovanillin were reported at higher concentration in downstream samples than in HCE (see Appendix Figures A10-A13), casting doubt as to the reliability of the suspended sediment results.

4.6.3 Chlorinated Phenolics in Depositional Sediments

Chlorinated phenolics were analyzed in depositional sediments (clay-silt fraction) from REF, OB, and WB only. No detections of chlorinated phenolics were reported for depositional sediments from REF (Figure 14). Total concentration (all reported compounds) in depositional sediments was 179 ug/Kg at OB, and 16 ug/Kg at WB. Mono-Cl substituted compounds were predominant at OB.

The predominant constituents included 6-chlorovanillin at OB (79.5 ug/Kg), and a number of catechols at both OB and WB, including 3,4,5-trichlorocatechol, 4,5-dichlorocatechol, and 4-chlorocatechol. Guaiacols were present in only trace quantities in the depositional sediments. Tetra- and penta-substituted chlorinated phenols were not detected (see Appendix Figures A14, A15).

Total chlorinated phenolic concentrations in depositional sediments from OB exceeded those in suspended sediments by approximately by 25%. At WB, depositional sediment concentrations were approximately 10% of the concentrations in suspended sediments. As was considered to be the case with with suspended sediments, the results for chlorinated phenolics in depositional sediments should be viewed as potentially unreliable.

4.7 RESIN ACIDS

Resin acids are naturally occurring constituents of tree bark and wood, with concentrations in coniferous trees exceeding those in deciduous trees by as much as 8:1. Dependant upon the pulping process used, mill effluents can vary greatly in resin acid concentration. Mechanical processes tend to produce higher effluent concentrations than chemical processes. Biological treatment reduces effluent concentrations of non-chlorinated resin acids by approximately 90%. Chlorinated resin acids are somewhat more resistant to biological treatment (Leach et al. 1977 and Chung et al. 1979 in McLeay et al. 1987). The concentrations of resin acids in pulp effluents depend, therefore, upon three major factors: the wood furnish, the pulping process, and the degree of biological treatment.

A major percentage of the toxicity of pulp mill effluents is attributable to resin acids (McLeay et al. 1987). Resin acids are acutely toxic to rainbow trout in concentrations ranging between 400 and 1700 ug/L (various sources quoted in McLeay et al. 1987).

Resin acids are hydrophobic and lipophilic organic compounds. Persistence in the water column is reported to be limited, with most resin acids returning to non-detectable concentrations within a few kilometres of outfalls. Dehydroabietic acid (DHA) has been reported to be the most persistent resin acid, with concentrations measurable at 'significant' distance from sources (Fox 1976 in McLeay et al. 1987).

Resin acid persistence on sediments is reported to be somewhat greater than in water. DHA has been found at 10 times background concentrations 10 kilometres below an Ontario mill discharging into

Lake Superior (Fox 1976 in McLeay 1987). Resin acids have been shown to bioaccumulate in fish and other biota (numerous references in McLeay et al. 1987).

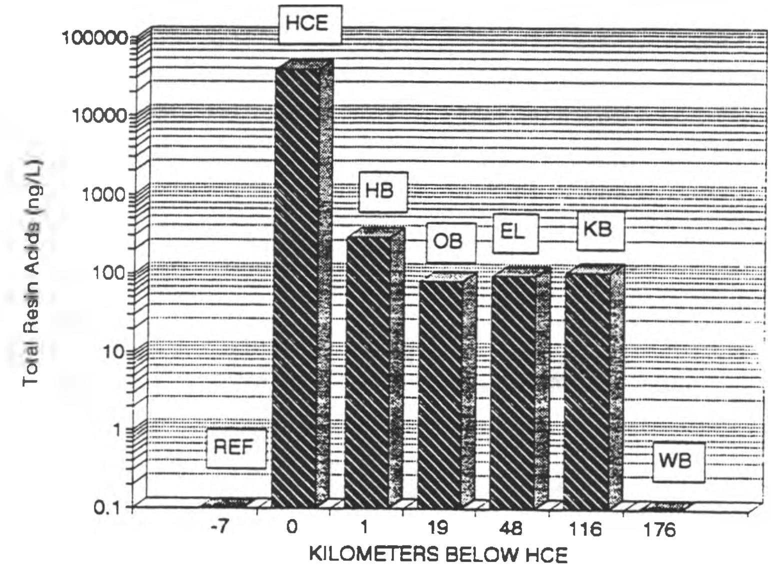
Analyses of resin acids on water and sediments were performed by AXYS Analytical Services. Detection limits reported were in the 1-100 ng/L and sub-ng/G ranges, respectively. The results for individual resin acids are presented in the Appendix (Figures A16-A21).

4.7.1 Resin Acids in Clarified Water

One-liter samples of clarified water were composited throughout the centrifugation process, preserved with NaOH, and refrigerated until analyses of resin acids. The laboratory did duplicate analyses on samples from HB, EL, and WB, with the results showing generally good reproducibility, though some duplicate results for individual resin acids differed by in excess of 50 percent. Differing analytical detection limits achieved for separate laboratory batches has reduced the interpretation possible.

The concentration in HCE centrifugate of total resin acids (sum of all resin acid analytes) was 38.6 ug/L on April 2, 1994 (Figure 15). The relative order of resin acid predominance in HCE was as follows: pimaric acid (18 ug/L) > isopimaric acid (9 ug/L) > DHA (8 ug/L) > abietic acid (1.5 ug/L). All other resin acids were present in HCE at concentrations below 1 ug/L.

Figure 15 Resin Acids in Water, RSS Reach, April 1992



Resin acids were not detected at the control site (REF) or at WB, located at kilometer 176 (note that the results for WB had unusually high detection limits). Total resin acids at the four locations downstream of HCE ranged from 0.3-0.1 ug/L. The mass balance prediction (using 33:1 dilution ratio) for total resin acids at HB was 1.2 ug/L, compared to the measured 0.3 ug/L. The four-fold differential between predicted and measured exceeds that to be expected from incomplete mixing, and may reflect rapid in-stream degradation. The most persistent resin acid in water was dehydroabietic acid (DHA). DHA was detected at KB (kilometre 116) at a concentration of 0.08 ug/L.

The results for total chlorinated resin acids in water (12/14 chlorodehydroabietic acid(s) and 12,14 dichlorodehydroabietic acid) are presented in Table 7. Again, variability in detection limits hinders interpretation of spatial trend. The mass balance prediction for total chlorinated resin acid concentration at HB (33:1 dilution) equalled 21.5 ng/L, approximately twice the measured concentration at the site.

Table 7 Total Chlorinated Resin Acids in Clarified Water, RSS Sites, April 1992

Sampling Location	Total Chlorinated Resin Acids (ng/L)
REF	<36
HCE	710
HB	10.3
OB	<69
EL	7.1
KB	2.8
WB	<83

The concentrations of resin acids in HCE water were on the low end of the range from other BKMEs (McLeay et al. 1987). Receiving water concentrations of resin acids were several orders of magnitude lower than published LC_{50}s (96 hour rainbow trout).

4.7.2 Resin Acids in Suspended Sediments

The laboratory performed duplicate analyses on suspended sediments from HB, and the results indicate good reproducibility (<5% differential). A standard sediment blank was free of detections.

HCE suspended sediments had the following order of resin acid predominance: pimaric acid (94 ug/G) > isopimaric acid (67 ug/G) > dehydroabietic acid (36 ug/G) > abietic acid (16 ug/G), the same relative order of predominance seen in the water phase. Total resin acid concentration on HCE suspended sediments was 253 ug/G (Figure 16). Concentrations of resin acids in HCE suspended sediment exceeded those in HCE clarified water by 6600:1 (w/w).

Figure 16 Resin Acids in Suspended Sediment RSS Reach, April 1992

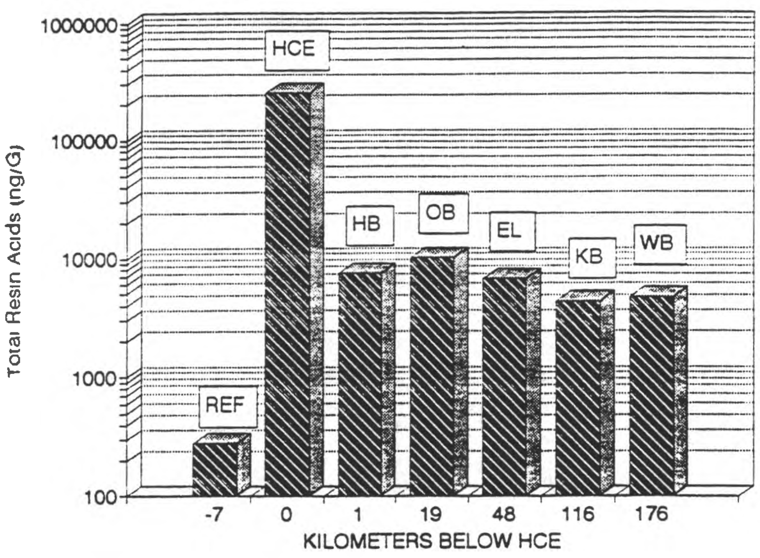
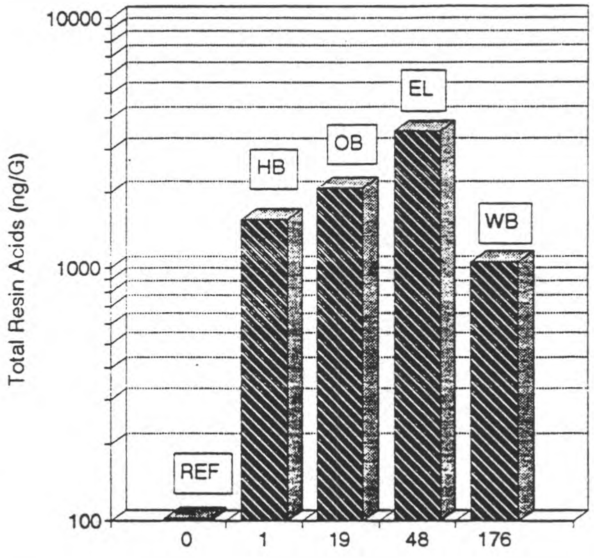


Figure 17 Resin Acids in Depositional Sediment RSS Reach, April 1992



Total resin acid concentration in REF suspended sediment was 0.28 ug/G. Below HCE, total resin acid concentrations increased to 7.4 ug/G at HB and 10 ug/G at OB. Concentration in suspended sediments decreased approximately 50 percent through the remainder of the RSS reach, to 4.7 ug/G at WB. Pimaric acid remained the predominant resin acid detected at WB (1.6 ug/G), followed by DHA (0.98 ug/G) and isopimaric acid (0.83 ug/G).

Rapid initial degradation in suspended sediment resin acids is indicated by sediment mass balance calculations. The predicted concentration at HB, using a 7.6:1 sediment dilution ratio, 33.3 ug/G total resin acids, was four-fold higher than the measured concentration (7.4 ug/G), similar to the finding in water.

Results for total chlorinated resin acids in suspended sediments are presented in Table 8. Mass balance calculations for chlorinated resin acids indicate a similar four-fold differential seen for total resin acids (1640 ng/G predicted for HB). The spatial trend for chlorinated resin acids is similar to that seen in Figure 17 for total resin acids in depositional sediments, with highest concentrations measured at EL.

Table 8 Total Chlorinated Resin Acids in Suspended Sediments, RSS Sites, April 1992

Sampling Location	Total Chlorinated Resin Acids (ng/G)
REF	<0.7
HCE	12,500
HB	430
OB	530
EL	670
KB	440
WB	287

4.7.3 Resin Acids in Depositional Sediments

Analyses of depositional sediments were done on samples from 5 RSS sites. Triplication of analyses for OB, and duplication of analyses for WB, indicated reproducibility in the 10 percent range.

Total resin acid concentration of 0.1 ug/G was reported for REF. Concentrations below HCE were in the range from 1.0 to 3.5 ug/G total resin acids, with highest concentrations found at EL (Figure 17). The apparent spatial trend likely relates to a combination of hydrologic (river slope and velocity) and degradation factors. In general, depositional sediments had total resin acid concentrations from 20 to 50% of those found in suspended sediments. The relative order of predominance of resin acids in depositional sediments was: pimaric acid > dehydroabietic acid > isopimaric acid > abietic acid. Dehydroabietic acid was predominant in sediments from WB, the downstream RSS location.

Total chlorinated resin acid results in depositional sediment are presented in Table 9. Concentrations of chlorinated resin acids in depositional sediments were from 23% (WB) to 60% (EL) of concentrations found in suspended sediments.

Table 9 Total Chlorinated Resin Acids in Depositional Sediments, RSS Sites, April 1992

Sampling Location	Total Chlorinated Resin Acids (ng/G)
REF	<0.1
HB	131
OB	207
EL	400
WB	65

4.8 ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS

Clarified water (20-liter) extracts from REF, HCE, HB, and EL were analyzed for a suite of 19 organochlorine pesticides and toxaphene, for polychlorinated biphenyls (PCBs) as arochlors, and for 17 coplanar PCBs. Suspended sediments from REF, HCE, and OB were analyzed for the same list of organochlorines, but not for arochlors or coplanar PCBs. Analyses were done by Chemex Laboratories.

Organochlorine pesticides were not detected in clarified water from RSS river sites at detection limits of 0.01 ug/L. Dieldrin was reported present in HCE water, at 0.16 ug/L. Arochlors and coplanar PCBs were not detected in water in either HCE or receiving waters at detection limits of 0.01 ug/L and 0.2 ug/L, respectively.

The three suspended sediment samples submitted for organochlorine analyses were non-detectable for all analytes at detection limits of 5 ug/Kg. Toxaphene was non-detectable in suspended sediments at a detection limit of 100 ug/Kg.

4.9 METALS

Whole water (REF, HCE, HB, EL) and suspended sediments (REF, HCE, OB) were analyzed for metals by Chemex Laboratories. Ten total metals (including mercury and methyl-mercury) were analyzed on water samples, and seven metals were analyzed in suspended sediment. Graphs of the metals results appear in the Appendix (Figures A22-A24).

4.9.1 Metals in Water

Total metals detected in HCE water at concentrations above river background included total aluminum (0.77 mg/L), total manganese (0.75 mg/L), and total zinc (0.058 mg/L). HCE inputs produced subtle downstream concentration increases in all three metals. Aluminum concentrations at HB and EL exceeded the CCREM (1987) guideline for the protection of freshwater aquatic life (0.1 mg/L) (note that the total aluminum concentration at REF was very near this guideline as well, at 0.09 mg/L). Manganese and zinc concentrations below HCE remained below the respective CCREM (1987) guidelines. Methyl-mercury and total mercury were not detected in HCE or the receiving waters at detection limits of 0.05 ug/L. Concentrations of metals in HCE water were similar to those reported for the Whitecourt CTMP mill during 1989 (Noton and Shaw 1989).

4.9.2 Metals in Suspended Sediment

Above-background concentrations of copper (30.5 ug/G), cadmium (6.5 ug/G), and zinc (354 ug/G) were found in suspended sediments from HCE. Arsenic, chromium, and vanadium were at lower concentration in HCE suspended sediments than in REF. Analyses of mercury and methyl-mercury were requested, but insufficient sample was available to complete the analyses.

5.0 RECOMMENDATIONS FOR FUTURE SURVEYS OF WATER AND SEDIMENTS

Following are a list of recommendations for future NRBS undertakings, based upon experience gained through the Reach Specific Study:

Sample Replication and Analytical Duplication: Future NRBS surveys should include analyses of adequate numbers of field and laboratory replicates to allow complete statistical analyses of results, including the significance of spatial and temporal trends, the measurement of in-site spatial and temporal variability, and the determination of analytical precision.

Laboratory Selection: In determining place of analyses for future samples, care should be taken to ensure that analytical techniques are well-established, and that analytical detection limits are suitable for ambient environmental samples. Close cooperation between field and laboratory personnel should be maintained regarding sampling requirements, surrogate availability, etc., and guarantees of analytical turnaround times should be requested. Analytical results for polycyclic aromatic hydrocarbons have not been presented with the RSS results, since the analyses were performed at unacceptably high detection limits.

Future Analyses of Water Samples: Low or non-detectable concentrations of a number of contaminant groups were found in the water phase, including PCDD/Fs, polychlorinated biphenyls, organochlorine pesticides, and total mercury. Chlorinated phenolics and resin acids were generally detectable in water, but persistence in the water phase appears to be low. In general, analyses of water phase samples for basin-wide surveys is not recommended, with the possible exception of effluents.

Future Analyses of Suspended Sediments: As found by other workers, suspended sediments were found to be an important transporting medium for most of the contaminants analyzed. Contaminant concentrations in suspended sediment were generally several orders of magnitude higher than in water. The collection method (centrifugation) is labor-intensive, however, and collection of adequate sample size for a broad spectrum of analyses might be impractical during important low discharge periods. Interpretation of suspended sediment results is hindered by seasonal variability, and by a shortage of comparable datasets in the literature.

Future Analyses of Depositional Sediments: Concentrations of contaminants found in depositional sediments were generally lower than found in suspended sediments. A number of factors favor the use of depositional sediments in basin-wide surveys, however, including the relative ease of sampling, and the ability to illustrate basin-wide contaminant presence/absence and long term temporal trend with less concern for seasonal variability than would be required for suspended sediments. Future surveys of depositional sediments should include data on intra-site variability and extremely precise documentation of sampling locations and sampling methods. Surveys should be timed for low-flow, ice-free periods when depositional areas are most readily accessible.

6.0 REFERENCES

Anthony, D.H.J. 1990. Assembly, Set-Up, and Operation of the Goulden Large-Sample Extractor (G.L.S.E.) in Field and Laboratory Settings. Research and Applications Branch, National Water Research Institute, Burlington, Ontario. Internal document.

Barry, R.M., C.E. Luthe, R.H. Voss, P.E. Wrist, P. Axelgard, G. Gellerstedt, P.O. Lindbald and I. Popke. 1991. The effects of recent changes in bleached softwood kraft mill technology on organochlorine emissions: an international perspective. Pulp and Paper Canada 92: 43-54. Cited in Swanson et al. 1993.

Canadian Council of Resources and Environment Ministers (CCREM). 1987. Canadian Water Quality Guidelines. Environment Canada, Ottawa.

Chung, L.T.K., H.P. Meier and J.M. Leach. 1979. Can pulp mill effluent toxicity be estimated from chemical analyses? TAPPI 62: 71-74. Cited in McLeay et al., 1987.

Envirodata Limited. 1981. Sedisamp system: operator's manual: Envirodata Ltd., Winnipeg, Manitoba. Revised 03/85. 16 pp.

Environment Canada. 1993. Draft Canadian Environmental Quality Guidelines for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. Prepared by D.D. MacDonald. MacDonald Environmental Services Ltd., B.C. 149 pp. Cited in Pastershank and Muir, 1993.

Foster, G.D. and P.F. Rogerson. 1990. Enhanced preconcentration of pesticides from water using the Goulden large-sample extractor. International Journal of Environmental and Analytical Chemistry. Vol 41. pp 105-117.

Fox, M.E. 1976. Fate of selected organic compounds in the discharge of kraft paper mills into Lake Superior, p. 641-659. In L.H. Keith, Ed. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science Publishers Inc. Ann Arbor, MI.

Leach, J.M., J.C. Mueller and C.C. Walden. 1977. Biodegradability of toxic compounds in pulp mill effluents. Trans. Tech. Section Can. Pulp Paper Assoc. 3:126-130.

McLeay, D. and Associates Ltd. 1987. Aquatic Toxicity of Pulp and Paper Mill Effluents: A Review. Report prepared for Environment Canada, Fisheries and Oceans Canada, Canadian Pulp and Paper Association, Ontario Ministry of the Environment. Report EPS 4/PF/1. Ottawa, Ontario. 191 pp.

Noton, L.R. and R.D. Shaw. 1989. Winter Water Quality in the Athabasca River System. 1988 and 1989. Environmental Assessment Division, Alberta Environment, Edmonton, Alberta.

Pagenkopf, G.K. 1978. Introduction to Natural Water Chemistry. Marcel Dekker Inc., New York. 272 pp. Cited in CCREM 1987.

Pastershank, G.M. and D.C.G. Muir. 1994. Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Fish and Other Environmental Samples Collected Downstream from Kraft Pulp and Paper Mills. Results from the NRBS reach specific study, general fish collection, and burbot special collection, April to June 1992. Northern River Basins Study, Edmonton, Alberta. June 30, 1994. Draft Report.

R.L.&L. Environmental Services Ltd. 1993. Benthos and Bottom Sediment Field Collections, Upper Athabasca River, April to May 1992. Northern River Basins Study Project Report #2. Northern River Basins Study, Edmonton, Alberta. February, 1993.

Swanson, Stella M. and Sentar Consultants. 1993. Wapiti/Smoky River Ecosystem Study. Report under contract to Weyerhaeuser Canada Limited, Grande Prairie, Alberta. 176 pp.

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: GRAPHS OF CONTAMINANTS IN WATER AND SEDIMENTS, REACH SPECIFIC STUDY, APRIL 1992

Figure A1 RSS Suspended Sediments, P_5CDD and P_5CDF

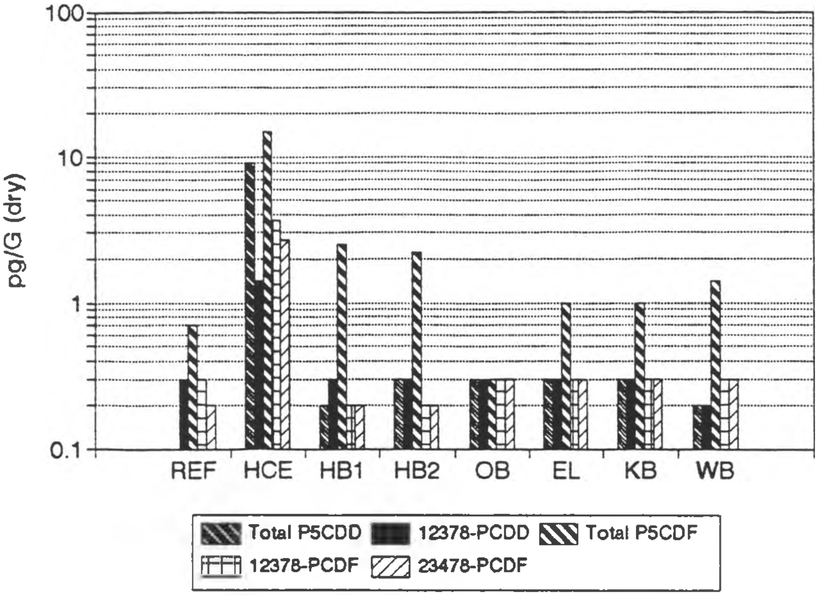


Figure A2 RSS Suspended Sediments, H_6CDD

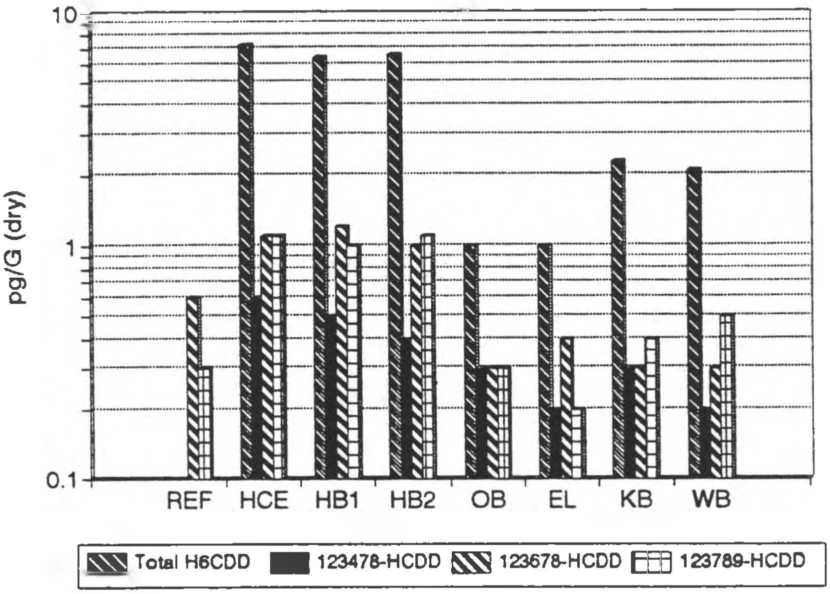


Figure A3 RSS Suspended Sediments, H_6CDF

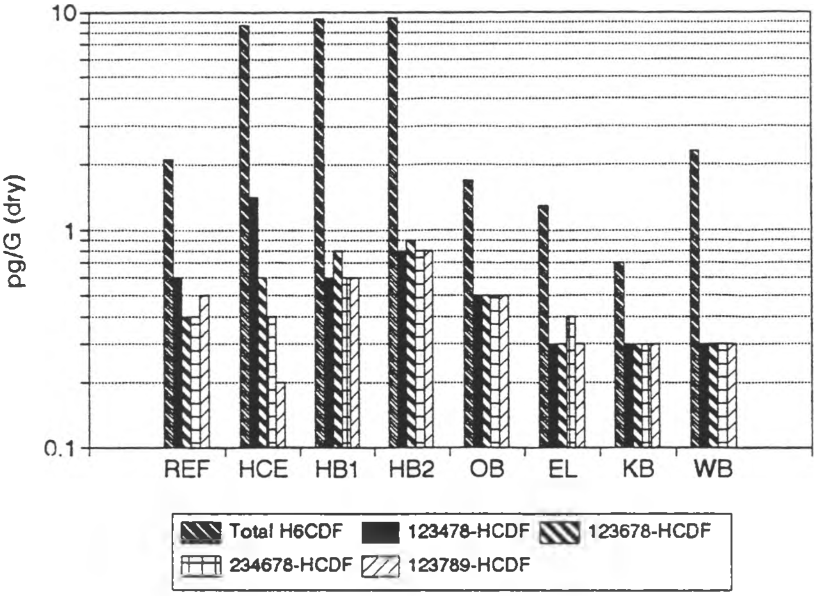


Figure A4 RSS Suspended Sediments, H_7CDD and O_8CDD

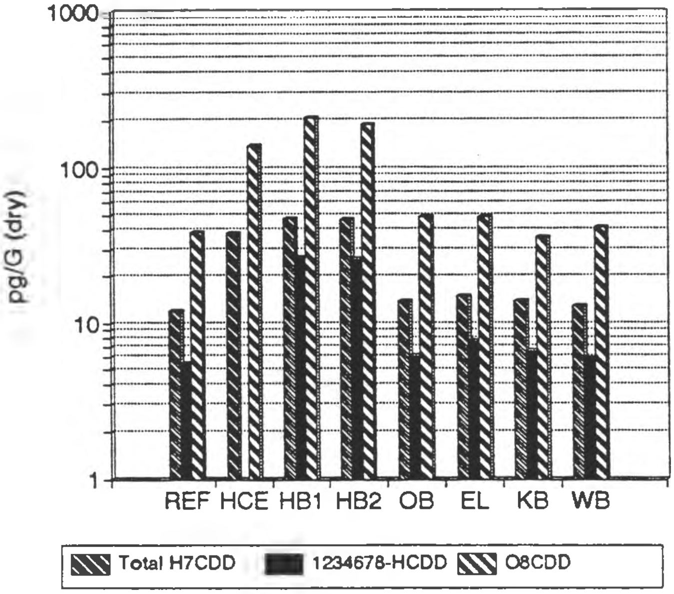


Figure A5 RSS Suspended Sediments, H_7CDF and O_8CDF

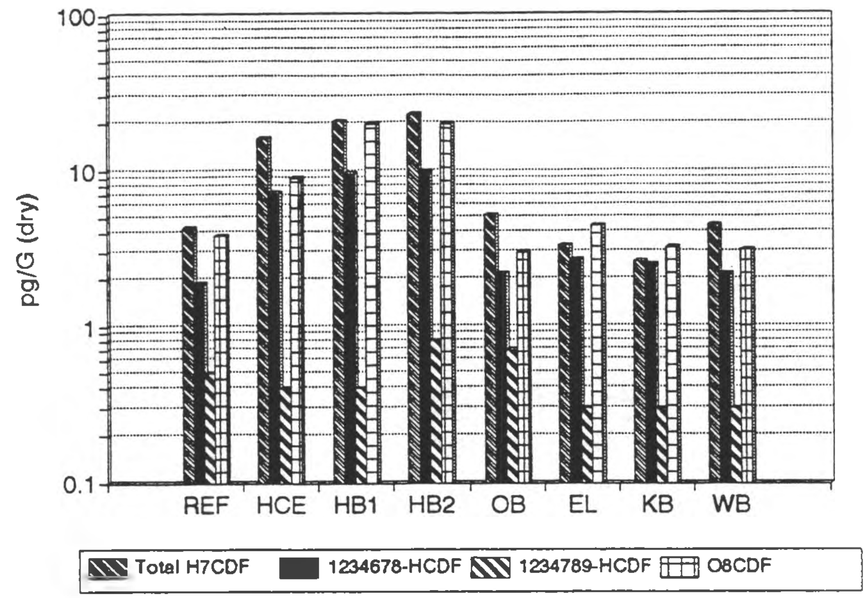


Figure A6 RSS Clarified Water, Chlorinated Phenolics

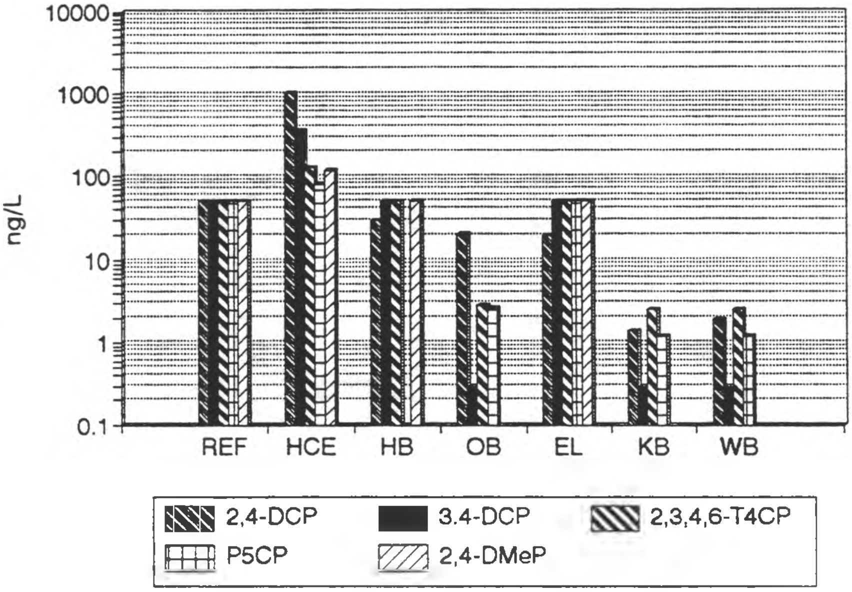


Figure A7 RSS Clarified Water, Chlorinated Phenolics (cont.)

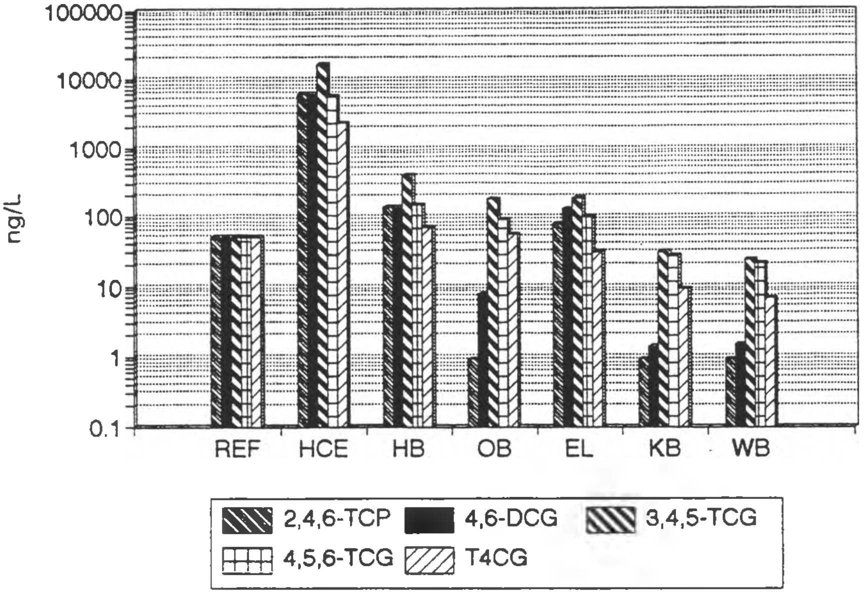


Figure A8 RSS Clarified Water, Chlorinated Phenolics (cont.)

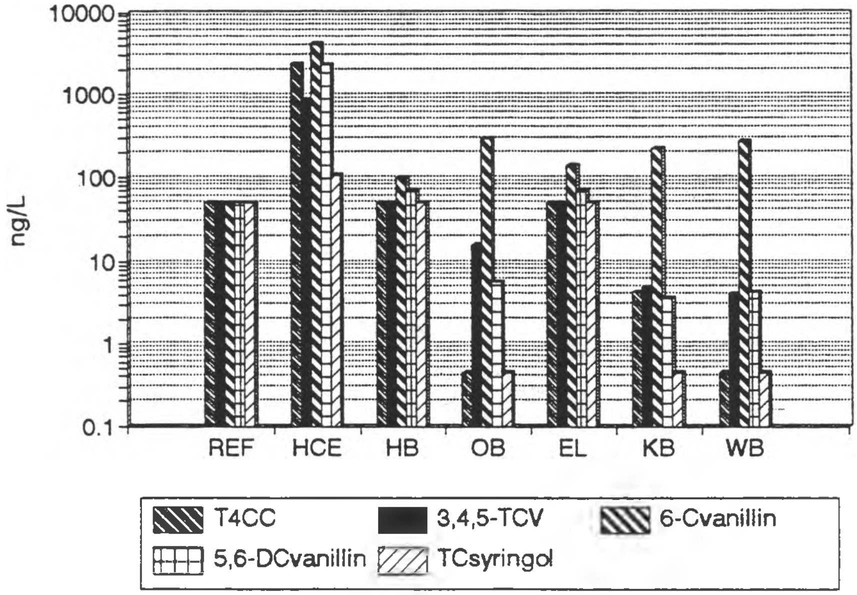


Figure A9 RSS Clarified Water, Chlorinated Phenolics (cont.)

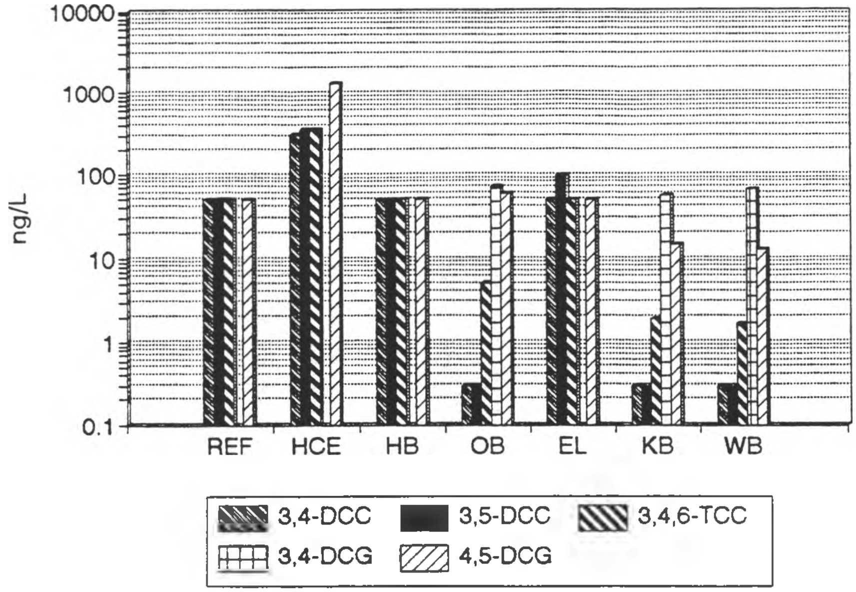


Figure A10 RSS Suspended Sediments, Chlorinated Phenolics

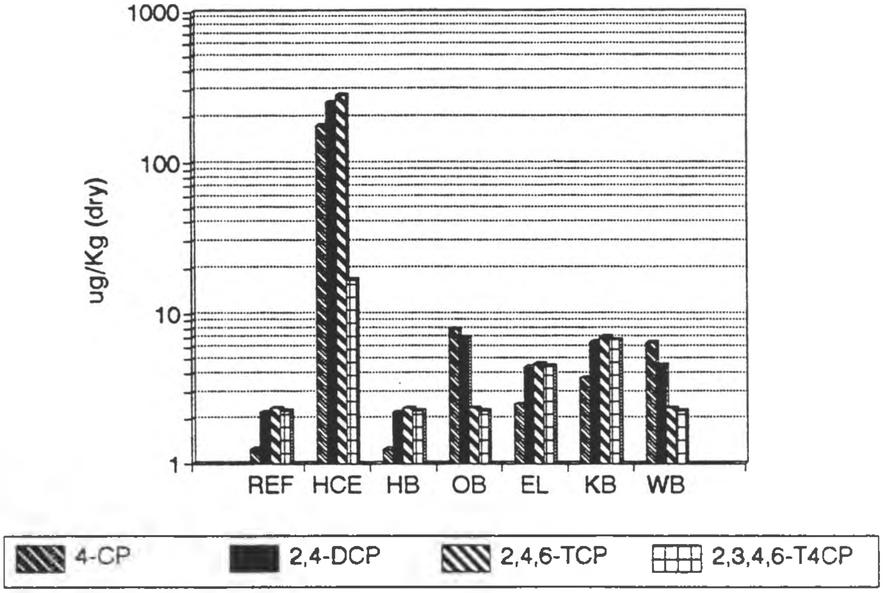


Figure A11 RSS Suspended Sediments, Chlorinated Phenolics (cont.)

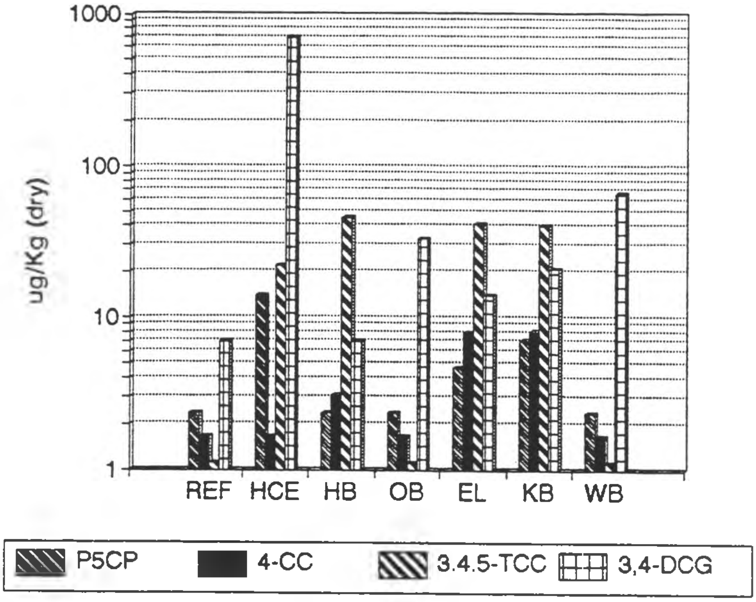


Figure A12 RSS Suspended Sediments, Chlorinated Phenolics (cont.)

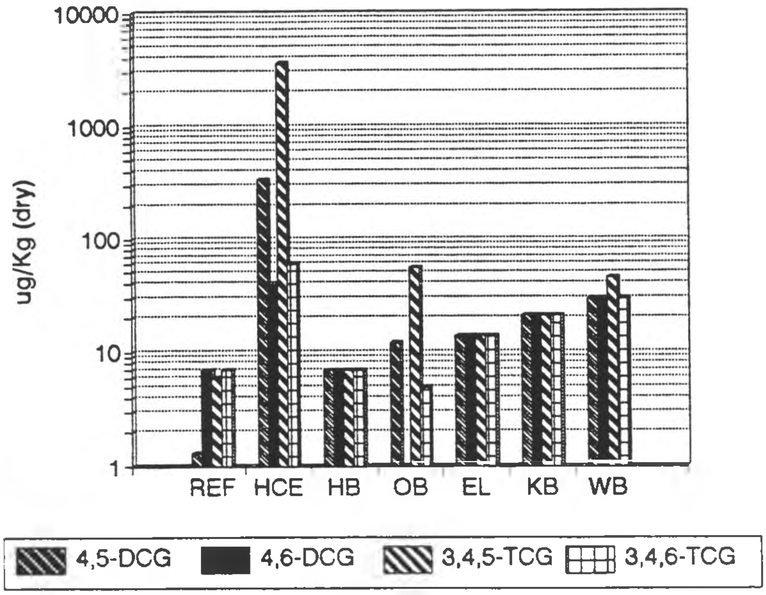


Figure A13 RSS Suspended Sediments, Chlorinated Phenolics (cont.)

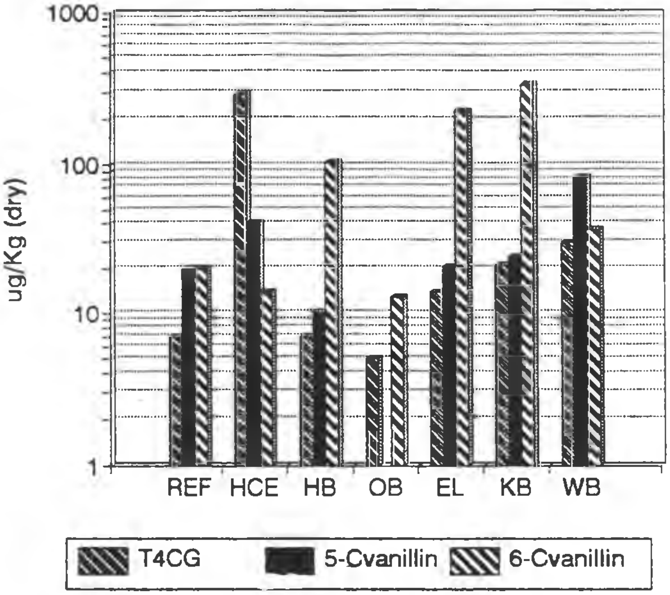


Figure A14 RSS Depositional Sediments, Chlorinated Phenolics

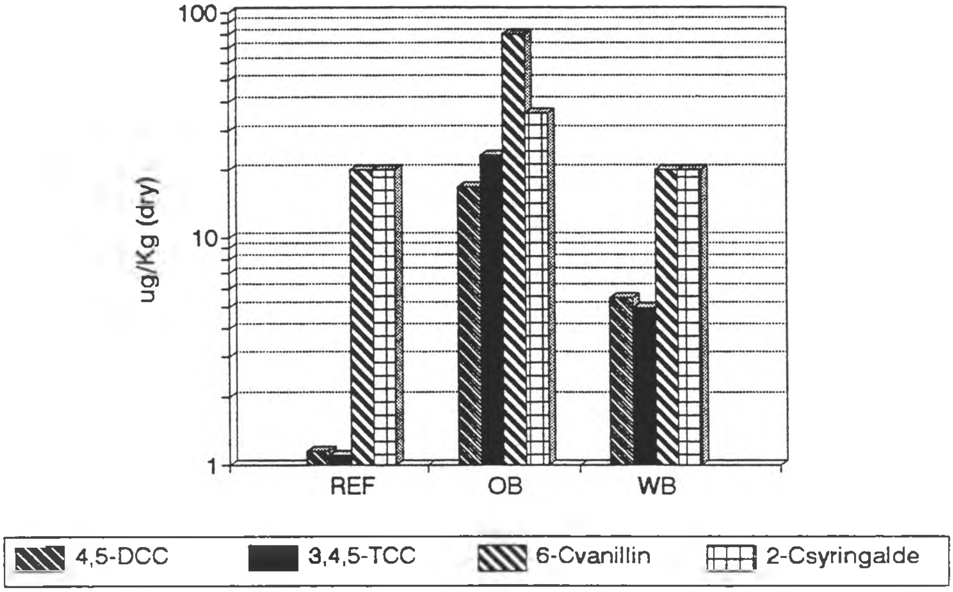


Figure A15 RSS Depositional Sediments, Chlorinated Phenolics (cont.)

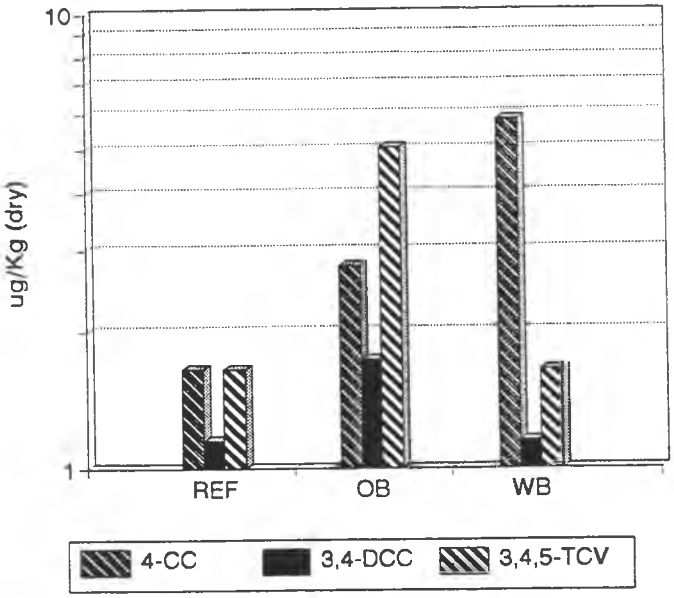


Figure A16 RSS Clarified Water, Resin Acids

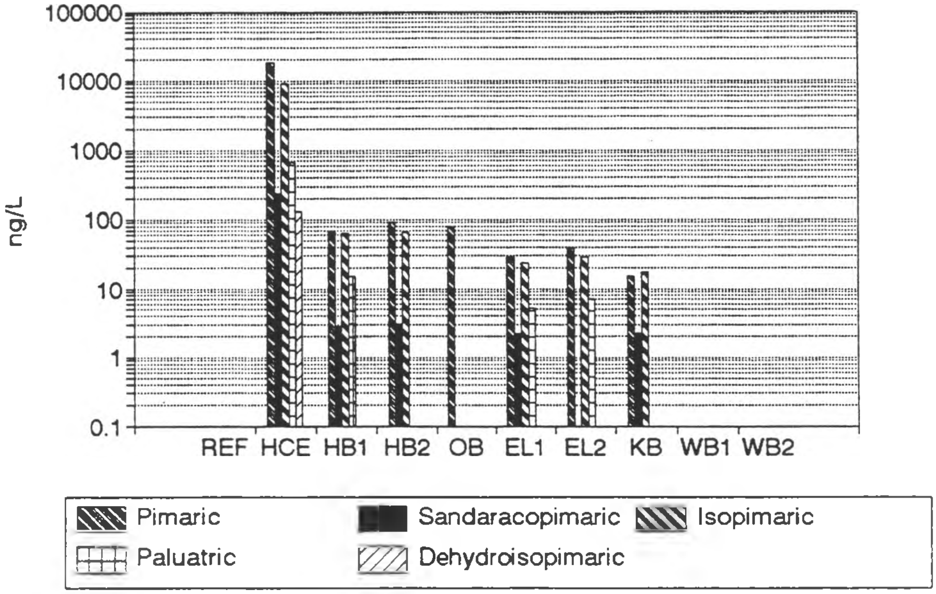


Figure A17 RSS Clarified Water, Resin Acids (cont.)

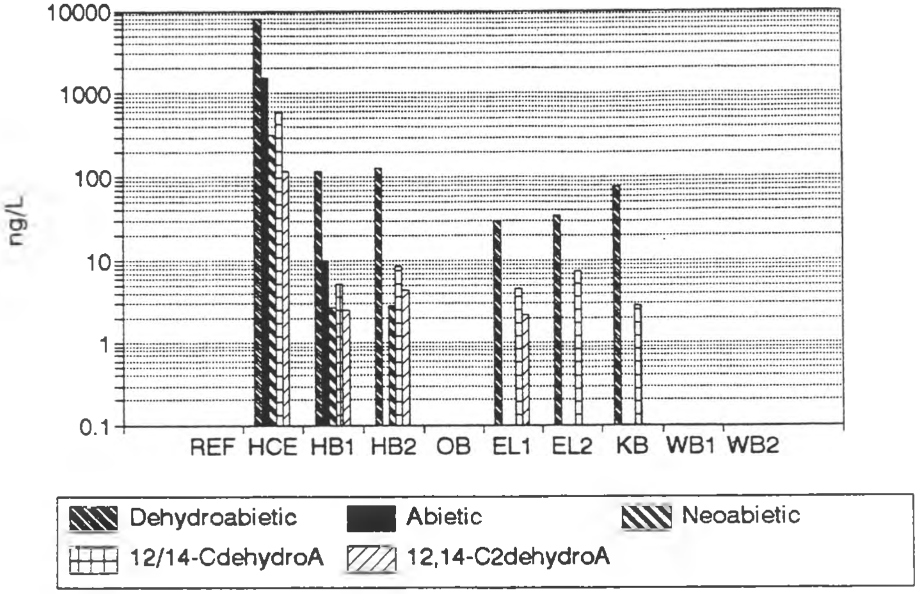


Figure A18 RSS Suspended Sediments, Resin Acids (cont.)

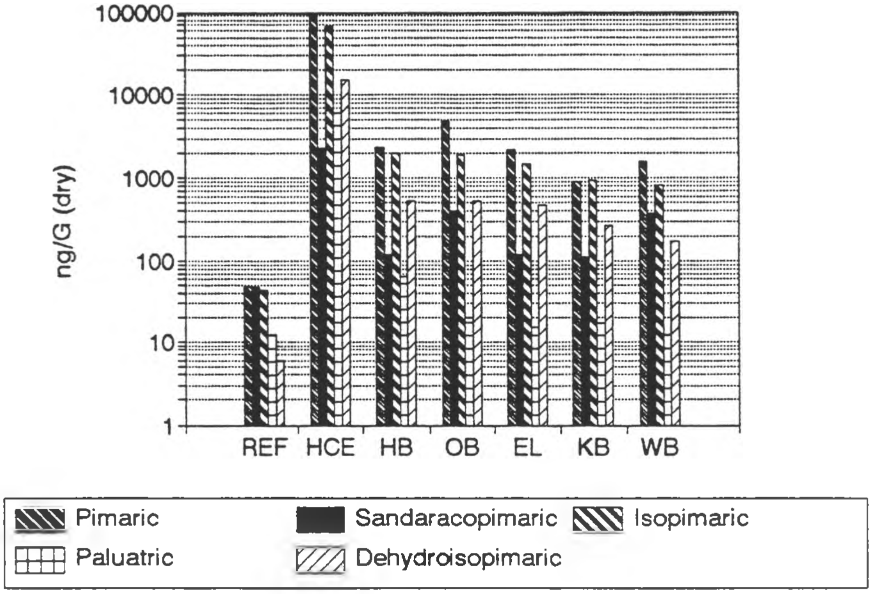


Figure A19 RSS Suspended Sediments, Resin Acids (cont.)

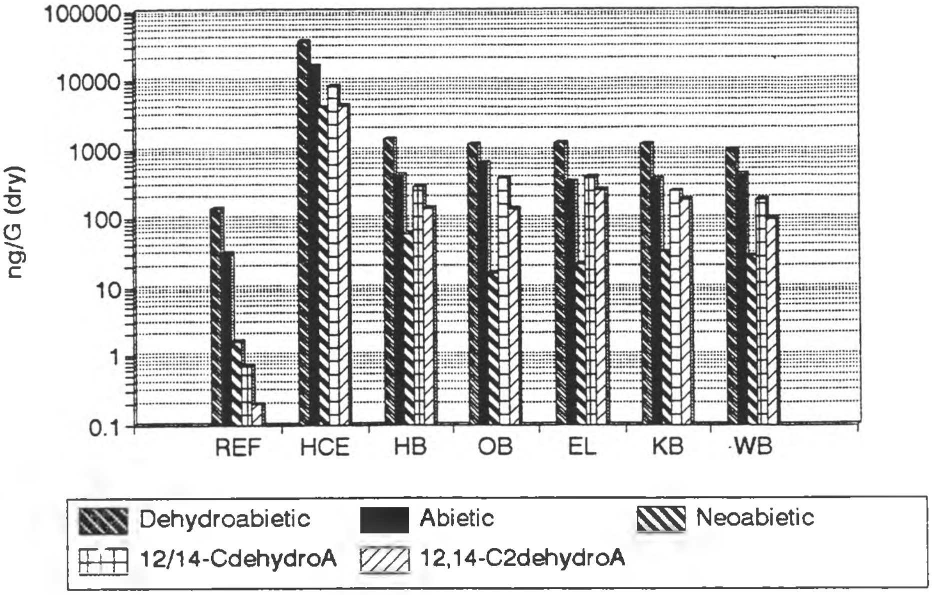


Figure A20 RSS Depositional Sediments, Resin Acids

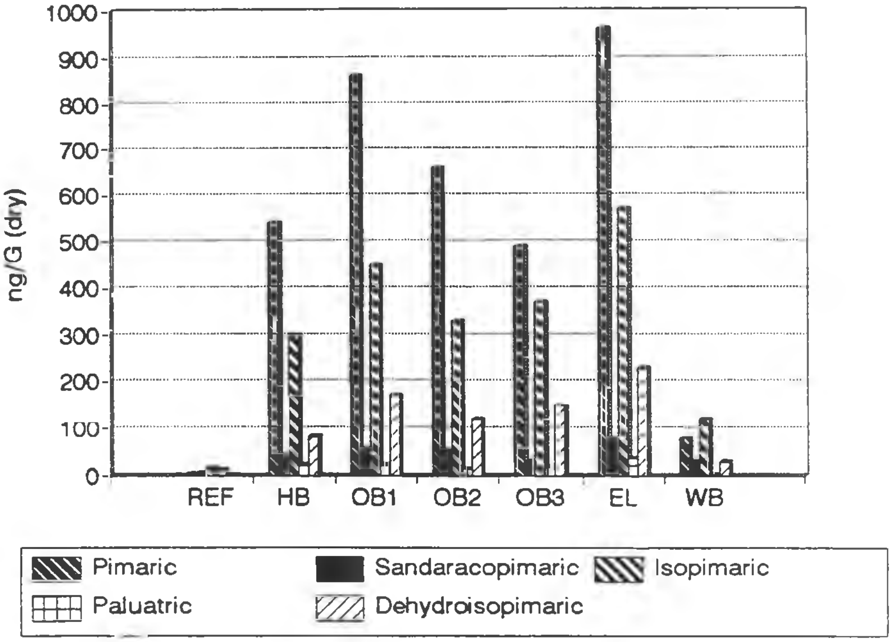


Figure A21 RSS Depositional Sediments, Resin Acids (cont.)

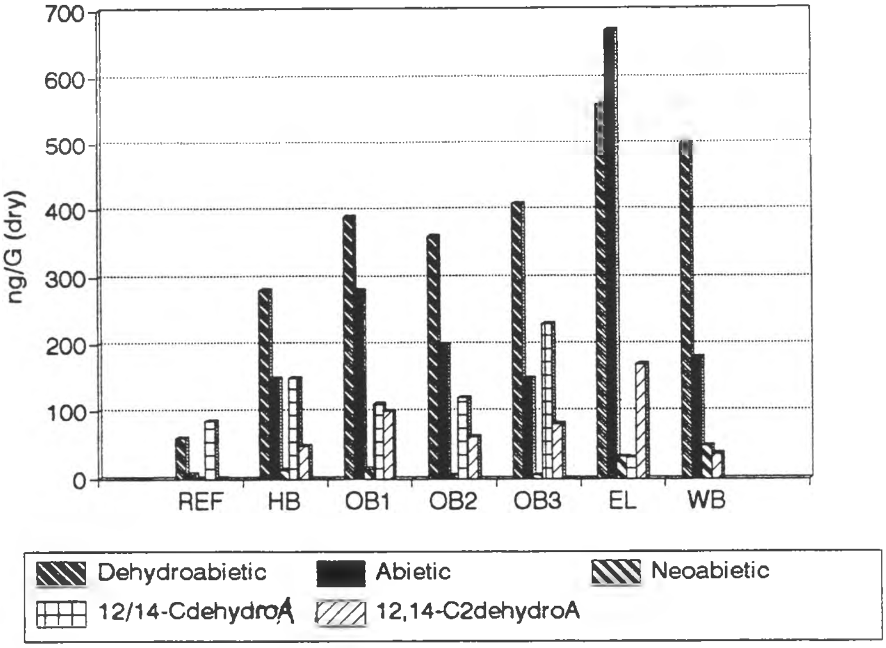


Figure A22 RSS Whole Water, Total Metals

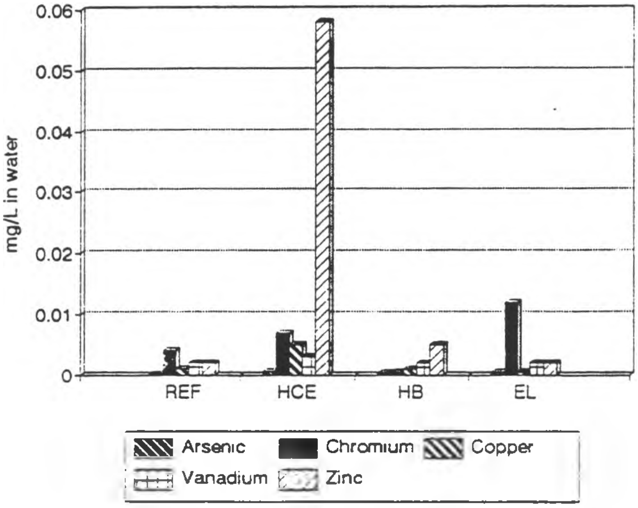


Figure A23 RSS Whole Water, Total Metals (cont.)

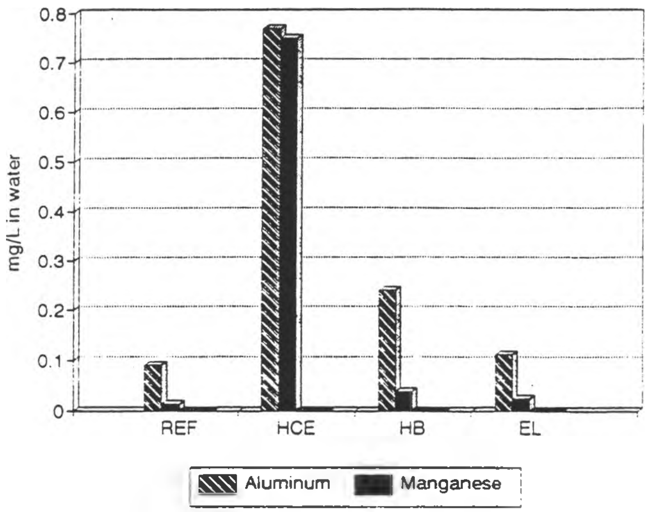


Figure A24 RSS Suspended Sediments, Metals