on of Contaminants in the Water, Sediment and Biota in the Peace, Athabasca and Slave River Basins: Present Levels and Predicted Future Trends

3

Synthesis Report

Canada Alberta Northwest Territories

Northern River Basins Study

NORTHERN RIVER BASINS STUDY
SYNTHESIS REPORT NO. 3

DISTRIBUTION OF CONTAMINANTS IN THE WATER, SEDIMENT AND BIOTA IN THE PEACE, ATHABASCA AND SLAVE RIVER BASINS: PRESENT LEVELS AND PREDICTED FUTURE TRENDS

by

J.H. Carey
Leader, Contaminants Component
Northern River Basins Study and
National Water Research Institute,
Environment Canada

O.T.R. Cordeiro
Consultant

B.G. Brownlee
Co-Leader, Contaminants Component,
Northern River Basins Study and
National Water Research Institute,
Environment Canada

Published by the
Northern River Basins Study
Edmonton, Alberta
November, 1997

CANADIAN CATALOGUING IN PUBLICATION DATA

Carey, John H.

Distribution of contaminants in the water, sediment and biota in the Peace, Athabasca and Slave River Basins: present levels and predicted future trends

(Northern River Basins Study synthesis report,
ISSN 1205-1616; no. 3)
Includes bibliographical references.
ISBN 0-662-25369-8
Cat. no. R71-49/4-3E

1. Water — Pollution — Alberta — Athabasca River Watershed.
2. Water — Pollution — Peace River Watershed (B.C. and Alta.)
3. Water — Pollution — Slave River Watershed (Alta. And N.W.T.)

I. Cordeiro, O. T. R.
II. Brownlee, B. G.
III. Northern River Basins Study (Canada)
IV. Title.
V. Series.

TD387.A43C27 1997 363.739'4971231 C97-980019-6

If you would like:

- additional copies of this report, or
- other information regarding the Northern River Basins Study

please contact:

Alberta Environmental Protection
Information Centre
9920 - 108 Street
Edmonton, Alberta T5K 2M4

Telephone: (403) 422-2079
Fax: (403) 427-4407

SUMMARY

Several approaches were employed by NRBS to characterize the organochlorines and other contaminants entering the NRBS river systems from municipal, industrial (pulp mill and non-pulp mill) sources and from long-range atmospheric transport. These included literature reviews, compilations of information available in historical governmental records on municipal and industrial discharges of liquid effluent to the NRBS area (SENTAR 1996 and McCubbin *et al.* 1996), field studies in the Hinton to Whitecourt reach of the Athabasca River in 1992 and 1993 (Crosley 1996a,c), and broad spectrum analyses for non-routine contaminants in industrial and municipal effluent samples (Johnson *et al.* 1996). Additional information from the scientific literature was used to characterize the long-range atmospheric transport of contaminants and to develop source-specific contaminant profiles.

The location, treatment technology and waste disposal methods of all licenced municipal and non-pulp mill effluent dischargers in the Peace, Athabasca and Slave River basins were summarized for the NRBS by SENTAR (1996). Existing information from government and industry sources was compiled into a database, and covered the chemistry, microbiology, ecotoxicology, timing, nature, duration, loadings, quality assurance/quality control, licencing details, compliance data, data gaps, and an assessment of the relative importance of various effluents with respect to nutrient, contaminant and microbial loading.

The literature on characteristics of pulp and paper mill effluents of relevance to the NRBS was reviewed by McCubbin and Folke (1993). In addition to documenting the pulp and paper mills in the basins, McCubbin and Folke provide a generalized description of pulping processes and describe the differences between the pulping processes used by mills in the basins. This report is supplemented by NORTHDAT, a database assembled from monitoring data for Alberta pulp mills for the years 1990, 1991 and 1992 (McCubbin *et al.* 1996)

As a result of the various source reviews, five families of contaminants were chosen as the main targets of interest. They are: polychlorinated dioxins and furans (PCDDs and PCDFs); polychlorinated phenolics (PCPs); polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs); resin acids (RAs) and polycyclic aromatic hydrocarbons (PAHs).

The contaminants identified through the various reviews as associated with sources within the basins were compiled into a list of target compounds for further investigation. Samples of water, effluent, sediment, fish and benthic invertebrates were then collected from various locations within the basins and analysed for the target compounds. These analyses were for the specific contaminants only, however, and yield no information regarding other contaminants that may have been present. To obtain information concerning the nature and concentrations of non-target contaminants, a broad spectrum analytical approach was implemented, based on interpretation of mass spectra generated by full scan gas chromatography-mass spectrometric (GC-MS) analysis of the samples.

The results of broad spectrum analysis (BSA) demonstrated that at the time of the study the most prevalent non-routine contaminants in effluents within the basin were phthalate acid esters. Both naturally-occurring and apparently-anthropogenic carboxylic acids were also present, in

some cases at high concentrations. Elongated fatty acids (>C20) were observed in several effluents. In addition, high concentrations of organic phosphate were present in all sewage treatment plant effluents. Dialkyl polysulphides and alkylated thiophenes were also observed in the Grande Prairie sewage treatment plant effluent. The Suncor process effluent contained a mixture of PAHs and alkylated PAHs in addition to naphthenic acids.

Considerable effort was directed to determining the geographical distribution of contaminants in the northern river basins. Since it was not possible to study all contaminants everywhere, the major effort focussed on those contaminant families identified in the characterization studies as arising from several sources within the basin or as being of greatest toxicological significance. These were resin acids, PCDDs, PCDFs, PCBs, CPs and PAHs. In addition, to avoid placing all the emphasis on these six contaminant families, a receiving water survey was conducted examining waters upstream and downstream from major effluent discharges for the contaminants identified in the broad spectrum analysis part of the characterization studies. The first stage of the program comprised a series of preliminary studies of limited geographical range or of limited study design to provide an information base from which the selection of an abiotic compartment and a biological indicator species suitable for basin-wide surveys could be made.

For the abiotic compartments, the phases considered were ambient water, suspended sediment and bottom sediment. Low or non-detectable concentrations of a number of contaminant groups were found in the ambient water phase including chlorinated phenolics, some chlorinated dioxins and furans and some resin acids. These were detectable in water at some sites but over most of the river reaches sampled, concentrations were near or below detection limits. The BSA of receiving waters did not identify any new, widely-distributed compounds that should be added to the list of target compounds in future distribution studies. In general, concentrations in water were orders of magnitude lower than concentrations in sediment, as discussed below. We concluded that water was not a desirable abiotic compartment for the basin-wide survey, and, with the possible exception of effluents, analyses of water phase samples should not be part of the basin-wide surveys to determine contaminant distributions.

Results of the preliminary sediment surveys indicated that suspended sediments were an important transport medium for most of the contaminants analysed, with concentrations in suspended sediment generally several orders of magnitude higher than in water. However, the collection method is labour-intensive and collection of adequate sample size throughout the basin was considered impractical during important low discharge periods. Concentrations of contaminants found in depositional sediments were generally lower than those found in suspended sediments, making analysis problematic; however, 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 that required for suspended sediments were convincing factors. As a result, we concluded that the most appropriate abiotic compartment for a basin-wide survey of contaminant distribution was the fine silt-clay fraction of bottom sediments.

The basin-wide sediment survey was conducted in 1994-95. The results did not indicate widespread contamination of the northern river basins by significant levels of anthropogenic contaminants. Bleached kraft mills in the system contributed detectable concentrations of chlorinated resin acids and chlorophenols, but not PAHs. Diffuse, presumably natural sources of PAHs and resin acids contributed detectable levels of these compounds throughout the systems, suggesting that attention should be paid to the upstream reaches of the Peace River to identify the sources of PCBs, PAHs and resin acids.

Sediments from two downstream lakes were also analysed during the study. The contaminants in Lake Athabasca sediments revealed a much lower pulp mill signature than expected and the data suggested that atmospheric sources of contaminants were the main contaminant sources to this part of the northern river basins. While there were indications that the rivers carried significant percentages of total loadings of contaminants to the lake, there was minimal indication that Great Slave Lake receives significant loading of effluent-related contaminants via the northern river basins, although there was a clear effluent-related signal for some compounds like TCDF and chloroveratroles in the west basin. Long-range transport of atmospheric pollutants was found to be a more significant contaminant source than anticipated at the start of the study.

To provide preliminary information on which to base a choice of biological indicator species, three related preliminary studies were conducted with the general objective of determining spatial and, in some cases, temporal contaminant trends in fish. The most intensive was the Reach Specific Study (RSS) of 1992-93 in the Hinton to Whitecourt reach of the Athabasca River. In addition to the RSS, the General Fish Collection provided samples of fish from the Athabasca River in 1992, and an additional survey in 1992 sampled for burbot on the Peace, Wapiti and Smoky Rivers. Contaminants were detectable in fish from most sites on the upper reaches of the two river systems. Concentrations were lower in fish from the lower reaches, particularly the lower Athabasca River. However, the results of the fish surveys indicated that a particular fish species was often not available at many sites. There appeared to be a change in fish community between the upper and the lower reaches of the Athabasca River, and the fish species available in the Peace River appeared to be different from either the upper or lower Athabasca River. We decided the species most closely meeting the bioindicator criteria was the burbot. Several species were identified as potential alternates: namely northern pike, longnose sucker and flathead chub. These species had more restricted ranges or other characteristics that made them less suitable as a basin-wide bioindicator than burbot, but were available in some areas where burbot had not been reported.

The basin-wide fish bioindicator fish survey was conducted in late 1994. Burbot, northern pike, longnose sucker, and flathead chub were collected from 23 sites in the basins. In total, 535 fish were caught consisting of 222 burbot, 50 northern pike, 88 longnose sucker, and 24 flathead chub. Contaminants were detectable in fish from most of the sites. Results of the basin-wide fish survey indicated there were at least two types of contaminant distribution evident in the northern river basins. For the contaminants showing the first distribution, concentrations were broadly comparable throughout the basin, although some site differences were evident. Since there was little relationship with known effluent discharges and the examples of contaminants with this distribution, e.g. p, p'-DDE (dichlorodiphenyl dichloroethylene) and *cis*-chlordane, are known to be atmospherically-transported, it is presumed that this distribution is mostly representative of long-range transport of air pollutants. In the second distribution pattern, contaminant concentrations were higher at sites downstream from municipal/industrial discharges in the upper sections of both the Peace and the Athabasca River systems. Contaminants showing the second distribution, including total PCBs, TCDD and TCDF, have all been associated with either municipal or bleached kraft mill discharges. This distribution is presumed, therefore, to be representative of point source discharges in the system.

Four approaches were employed to identify trends in contaminants within the basins: broad spectrum analysis of data on the chemical character of effluents discharging into the basins during the period of 1989 to 1994; comparison of data obtained on contaminants in NRBS sediment samples with results of comparable analyses on historical sediments obtained from the Alberta Environment surveys; comparison of data on contaminants in biota from analysis of NRBS samples obtained during the study; and analysis of contaminant distribution on sediment cores from permanent deposition areas in Lake Athabasca and Great Slave Lake.

In general, the BSA for the period 1989-1994 indicated current levels of contaminants discharged by the seven mills are lower than at any time over the period of record. Evidently, the use of state-of- the-art technology in the newer mills and the process modifications implemented in the other mills since 1989 positively affected the character of the effluents. Better washing and oxygen delignification of pulp prior to bleaching reduce the organic material carried over to the bleach plant, resulting in dramatic decreases in hydrocarbon, terpenes and sulphur-containing compounds in effluents. Replacement of chlorine with chlorine dioxide in the Hinton and Grande Prairie mills, and use of hydrogen peroxide in extraction stages have resulted in large reductions in chlorinated terpenes and chlorinated aromatic compounds. Similar effects are expected in the Peace River effluent where chlorine use has been eliminated since 1994. Concentrations of 1,1-dichlorodimethylsulphone remain detectable at the bleached kraft mills.

Temporal trends were not evident for the five main chlorinated pesticides detected in sediment cores from Lake Athabasca and from Weekes and Legend lakes. Comparisons of concentrations indicated that the atmosphere, not the river systems, was the major source. The PCDD/PCDFs were dominated by higher chlorinated congeners, also apparently originating from atmospheric sources, except for TCDF which likely had a BKME origin. A contribution of higher chlorinated PCDD from chlorophenol use within the basin could also have occurred. Riverine transport and a pulp mill source were suggested for chlorinated resin acids whose input to Lake Athabasca began about 20 to 30 years before the time of sampling. Although increases in chlorinated resin acids appear to have ceased in 1975, there was no strong evidence for a decrease to date, likely indicating a lag while sediment is transported down river. There was no indication from the sediment record of significant increases in contaminant loadings occurring at this time.

Fish samples were also examined for trends. Although there was only a small set of comparable data, comparisons of concentrations in fish tissue collected during the study indicated a significant decline in PCDD/PCDF concentrations in fish in both the Wapiti and Athabasca rivers downstream from bleached kraft pulp mills. Depending on the sites used in the comparison, the declines varied from 3 to 17-fold. There was no evidence for changes in atmospherically transported substances or in total PCBs.

For the sediments, results supported the substantial declines observed in the BSA analysis of effluent samples over the same time period. Concentrations of total chlorinated resin acids in Athabasca River sediments downstream from Hinton were 75% lower in the 1995 sample than in the 1992 sample, while concentrations of total resin acids on Wapiti River sediments collected near the confluence with the Smoky River declined from 69 ng/g to 22 ng/g to 5 ng/g in the 1989, 1994 and 1995 samples, respectively. Similar apparent declines were observed for pulp mill-related PCDDs/PCDFs. For example, concentrations of 2,3,7,8-TCDF on sediment from the Athabasca River downstream from Hinton decreased from 7 pg/g in 1988 to 2 pg/g in 1992 to <1 pg/g in 1995. Similarly, in the Wapiti River near the Smoky River confluence, concentrations of 2,3,7,8-TCDF on sediment decreased from 36 ng/g in 1988 to <2 pg/g in 1994 and 1995. There were no apparent temporal trends in the data for PAHs and PCBs. Other OCs and mercury were not detected on sediments in the surveys. For the Peace River upstream from the Smoky River confluence, concentrations of several contaminants increased between 1989 and 1995. The data pointed to non-kraft mill sources but did not allow a discrimination between non-point sources or sources in British Columbia. At most other sites in the basin, sediment contaminants, with the exception of non-chlorinated resin acids, are approaching or are at detection limits. Further extensive surveys are likely not warranted.

Apart from mercury, where the existing consumption advisory was supported by NRBS data, preliminary analysis of the contaminant results did not indicate a significant risk to fish eaters. In view of the recent dramatic declines in TCDD/TCDF levels in fish tissue, existing consumption advisories in the northern river basins based on these compounds should probably be re-evaluated.

Studies were also conducted on in-site variability in sediment sampling and on the importance of flocculation of suspended sediment in the northern river basins. Overall, a high degree of in-site variability of sediments was observed, highlighting the need to sample intensively within a reach to produce a composite sample that accurately reflects the average conditions in that reach. In addition, in light of the finding that unexpectedly significant concentrations of contaminants were found on the sand fractions, it was recommended that future sediment surveys focus on unpartitioned sediment.

Flocculation studies produced interesting new information concerning the importance of this process in controlling the seasonal transport and distribution of contaminated sediment in these systems. Results suggested that the deposition of effluent solids and ambient sediment could persist over a period of almost eight months in a year when the flow rate is lower than the fall survey value. The deposited sediment could become resuspended during the high flows that normally start in June in the Athabasca River. At freshet, it is possible that the bed-shear stress will exceed the critical shear stress for erosion and resuspension of the deposited material will occur, resulting in transport of the material further downstream. When the flow rate decreases, the deposition cycle repeats. A new algorithm for the transport of fine sediment in this system was developed that can now be implemented in water quality models for predicting the transport of contaminants in the Athabasca River.

ACKNOWLEDGEMENTS

This report is possible due to the work of the many researchers who investigated contaminants issues on behalf of the Northern River Basins Study. The Contaminants Working Group would like to acknowledge the contributions of the following Project Leaders:

Richard Bourbonniere, B.G. Krishnappan and Derek Muir, NWRI, Burlington

Robert Crosley, Ecological Research Division, Calgary

David Donald, Ecological Research Division, Regina

Mark Wayland, Ecological Research Division, Saskatoon

Marlene Evans, NHRI, Saskatoon

Ian Johnson, Alberta Environmental Centre, Vegreville;

We would also like to thank the NRBS Study Board, the NRBS Science Advisory Committee, and the other NRBS working groups for their contribution to the body of knowledge upon which this synthesis report is built. Thanks also are owed to the NRBS Science Office for their support and co-ordination of the activities of the Contaminants Component.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

The Northern River Basins Study (NRBS) was established in 1991 by the governments of Canada, Alberta and the Northwest Territories to gather and assess information on water and ecosystem quality, fish and fish habitat, vegetation, wildlife, hydrology and use of aquatic resources in the Peace, Athabasca and Slave river basins. The goal of this study is to assess the cumulative effects of industrial, municipal, agricultural and other development on the northern river basins and to provide recommendations to the governments on their future management.

Eight scientific component groups were established to design and carry out the Study's science program. To provide guidance for the design of the scientific program, the Northern River Basins Study Board developed a vision statement identifying 16 guiding questions. This report summarizes the activities of the Contaminants Component of the study addressing the following questions:

> ***Question #4a.*** *Describe the content and nature of contaminants entering the system and describe their distribution in the aquatic ecosystem with particular reference to water, sediment and biota; and*
>
> ***Question #4b.*** *Are toxins such as dioxins, furans, mercury, (and other contaminants) increasing or decreasing and what is their rate of change?*

The work plan designed by the Contaminants Component to address these questions consisted of several objectives. These objectives were:

1. to identify the contaminants entering the basins and their sources,
2. to determine the distribution of contaminants within the basins through surveys of water, sediment and biota,
3. to determine the trends of contaminant concentrations,
4. to assess the extent of contamination of biota in the basin relative to existing standards,
5. to identify important processes controlling contaminant transport and fate within the basins, and
6. to develop suitable models of contaminant transport and fate within the basins.

This document provides a summary of the research undertaken to address these objectives.

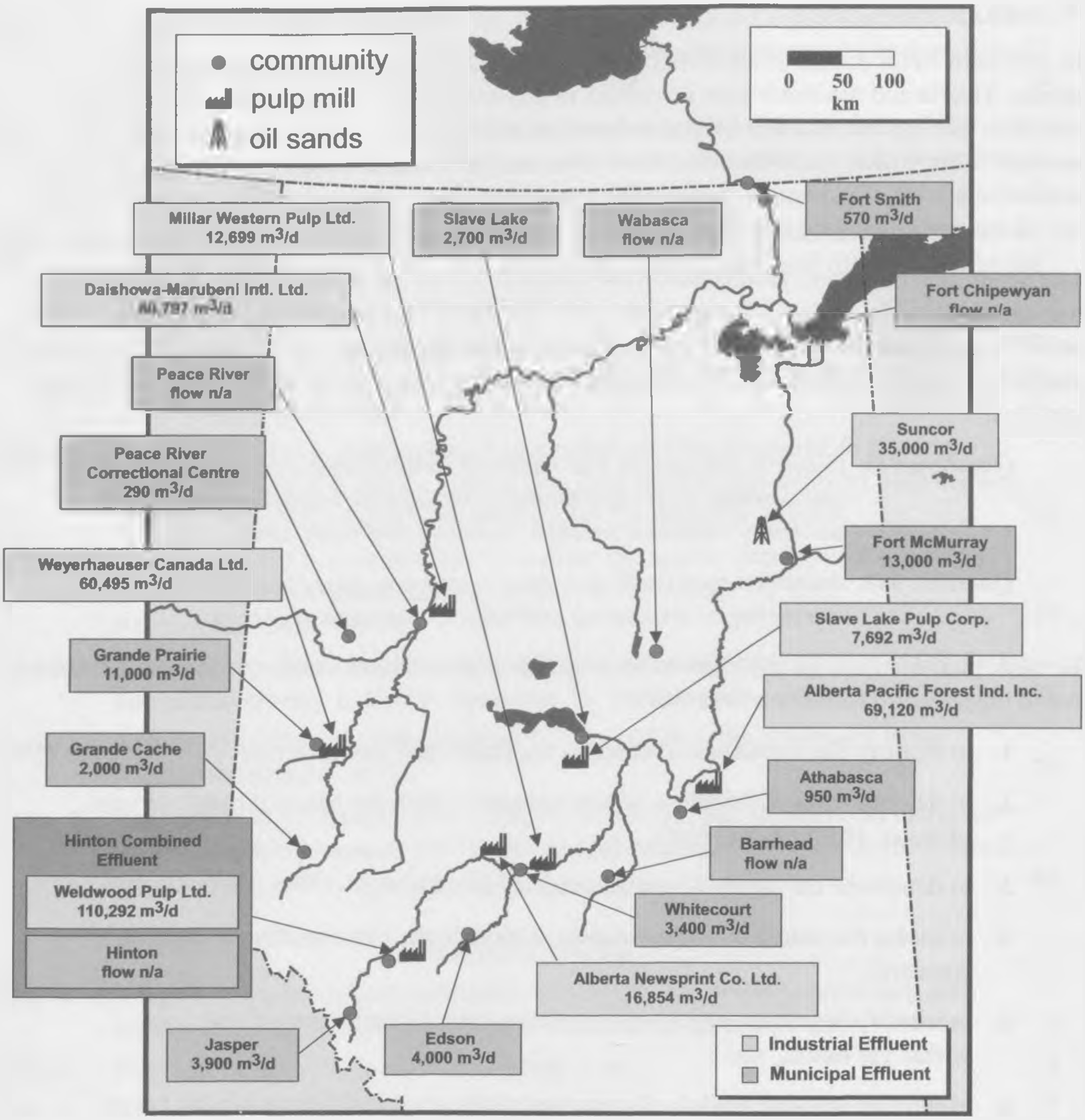

Figure 1. Map of the Northern River Basins Study area showing the locations of major point source dischargers of effluents.

2.0 CHARACTERIZATION OF CONTAMINANTS AND CONTAMINANT SOURCES

Two approaches were employed by the NRBS to characterize the organochlorines and other contaminants entering northern river systems from municipal, industrial and diffuse sources. The first was to review the scientific literature for information on contaminants from various sources and compile information available in historical governmental records on municipal and industrial point source discharges of liquid effluent to the NRBS area. The resulting information on the identity of contaminants likely entering the system from point and non-point sources was used to select representative families of contaminants for study in field surveys of contaminant concentrations in water, sediment and biota. Additional information from the scientific literature on source-specific contaminant profiles was used in combination with results from field sampling to help identify the most important contaminant sources to various parts of the basins. The second approach was to conduct broad spectrum analysis of effluents and receiving waters to investigate the identities and concentrations of contaminants not routinely analysed in monitoring programs. These activities are summarized in the following sections of this chapter.

2.1 POINT SOURCE EFFLUENT DISCHARGERS

The location, treatment technology and waste disposal methods of all licenced municipal and non-pulp mill effluent dischargers in the Peace, Athabasca and Slave River basins were summarized for the NRBS by SENTAR (1996). Existing information from government and industry sources was compiled into a database. The scope of the information covered the chemistry, microbiology, ecotoxicology, timing, nature, duration, loadings, quality assurance/quality control, licencing details, compliance data, data gaps, and an assessment of the relative importance of various effluents with respect to nutrient, contaminant and microbial loading.

The literature on characteristics of pulp and paper mill effluents of relevance to the NRBS was reviewed by McCubbin and Folke (1993). In addition to documenting the pulp and paper mills in the basins, McCubbin and Folke provide a generalized description of pulping processes and describe the differences among the pulping processes used by mills in the basins. This report is supplemented by NORTHDAT, a database assembled from monitoring data for Alberta pulp mills for the years 1990, 1991 and 1992 (McCubbin *et al.* 1996).

2.1.1 Municipal Sources

A total of 123 intermittent and 16 continuous dischargers of domestic wastewater were identified in the NRBS area (SENTAR 1996). The continuous dischargers were clearly the most important. Total annual discharges from 12 of the 16 continuous dischargers are 15,970,210 m^3 as compared to 4,474,828 m^3 for intermittent ones. The locations of continuous sewage discharges are shown in Figure 1. Some of the larger municipalities such as Grande Prairie and Fort McMurray emit BOD_5 (biological oxygen demand over 5 days) and TSS loadings comparable to loading from some mechanical pulp mills in the basin (SENTAR 1996).

The review of government and industry records uncovered very little information on the concentrations of organochlorines and other contaminants from which contaminant loading from municipal sources in the NRBS study area could be estimated (SENTAR 1996). To characterize possible contaminant inputs, therefore, it was necessary to use published information for municipal effluents in other regions. The most complete data set available was produced by the Ontario Ministry of the Environment in the Municipal and Industrial Strategy for Abatement (MISA) program. In that program, data were collected on contaminants in 37 municipal dischargers in Ontario. The data from the MISA program were assumed to be comparable to the ranges of raw sewage, primary municipal effluent, lagoon effluent, and secondary and tertiary municipal effluents from wastewater treatment plants in the NRBS study area. The major families of chlorinated compounds in municipal wastewater identified in the MISA program were polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzo-*p*-furans (PCDFs), chlorophenols (CPs), volatile organic compounds (VOCs), and polychlorinated biphenyls (PCBs). A summary of the MISA data is presented in Table 1.

Table 1. Range of contaminant concentrations in raw sewage, primary, secondary and tertiary effluent for the 37 municipal wastewater treatment plants in Ontario.

	Raw Sewage	Primary Effluent	Secondary Effluent	Tertiary Effluent
Chlorodibenzodioxins (ng/L)	0.73 - 28.0	0.08 - 1.4	0.1 - 11.0	no data
Chlorodibenzofurans (ng/L)	3.0 - 4.8	0.1 - 0.1	0.33 - 0.5	no data
Chlorophenols (µg/L)	29.6 - 120.8	no data	6.8 - 58.7	9.9 - 21.5
Volatile Organics (µg/L)	12 - 9800	6.4 - 420	2.0 - 84.0	2.70 - 75.0
PCBs (tot) (µg/L)	0.08 - 4.5	0.05 - 0.45	0.04 - 0.19	no data
Hg, unfiltered (µg/L)	0.02 - 1.6	0.01 - 0.36	0.01 - 0.36	0.07 - 0.39

Information on the individual components of several organochlorine families in Canadian municipal wastewater is reported by Coulston and Kolbye (1994). Typical chlorinated substances identified in the VOC fraction include chloroform, carbon tetrachloride, dichloroethane, dichloromethane, trichloroethylene and tetrachloroethylene. Typical chlorinated dioxins and furans were tetrachloro isomers from both families and octa and heptachlorodioxins. Typical members of the chlorinated phenol family in municipal wastewater include 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, arising primarily from the disinfection of final-treated municipal effluent with chlorine; and tetrachlorophenol and pentachlorophenol, likely occurring due to their use as fungicides for wood protection and preservation. Other chlorinated contaminants included the 1,2 and 1,3 and 1,4 isomers of dichlorobenzene, 1,2,4-trichlorobenzene and hexachlorobenzene.

2.1.2 Pulp Mill Dischargers

In total, there are ten pulp or pulp and paper mills discharging effluent into the Peace and Athabasca River systems. Seven of the mills are in Alberta (Figure 1): Weldwood of Canada Ltd. at Hinton; Weyerhaeuser Co. at Grande Prairie; Daishowa Canada Ltd. at Peace River; Alberta Pacific Forest Products Ltd. near Athabasca; Millar Western Pulp Ltd. and Alberta Newsprint Co. Ltd. at Whitecourt; and Slave Lake Pulp Corp. at Slave Lake. The first four produce bleached kraft pulp, while Millar Western Pulp Ltd. and Slave Lake Pulp Corporation mills are bleached chemi-thermomechanical pulp (CTMP) mills and Alberta Newsprint Co. Ltd. produces newsprint. The three pulp and paper mills in British Columbia are Fletcher Challenge Canada Ltd. and Finlay Forest Industries Ltd. at Mackenzie, a bleached kraft pulp mill, a bleached chemi-thermomechanical pulp mill respectively, and Fibreco Pulp Inc. at Taylor, a newsprint producer. A summary of these mills is given in Table 2. Table 3 contains a list of common abbreviations used to describe pulp and paper processes.

The identities and quantities of substances discharged by a pulp and paper mill depend on the processes employed at that mill. These processes are described in some detail by McCubbin and Folke (1993). A brief description is given here. There are three basic stages in the paper making process that may be employed at a given site. First the raw material is *pulped* to produce usable fibres. Second, when the required product is white, the pulp is bleached or brightened. Finally, at some mills, the pulp is made into paper.

Table 2. Pulp and Paper Mills in the NRBS Study Area.

Company, Location	Bleaching Sequence	Mill Type/ Product	Production (Adt/d)	Discharge (m^3/d)	Effluent Treatment	History (Start-Up, Wastewater Treatment)
Alberta Newsprint Co. Ltd. Whitecourt, AB	1% sodium hydrosulphite	CTMP, NEW	655	16,854	Extended Aeration AST	Start-up 1990. Phosphorus reduced in 1992 and discontinued in 1993.
Alberta Pacific Forest Ind. Inc. Athabasca, AB	-	BKP	1,500	69,120	Extended Aeration AST	Start-up in 1993.
Daishowa-Marubeni Intl. Ltd. Peace River, AB	O_2-D/CE$_O$(DN)D	BKP	1,035	60,797	ASB	Start-up in 1990. Back-up ASB added in 1991.
Millar Western Pulp Ltd. Whitecourt, AB	alkaline P	BCTMP	800	12,699	Extended Aeration AST	Start-up in 1988. ASB changed to AST in 1989.
Slave Lake Pulp Corp. Slave Lake, AB	P	BCTMP	365	7,692	Extended Aeration AST	Start-up 1990. Added 2nd 2° clarifier in 1992.
Weldwood Pulp Ltd. Hinton, AB	D/CE$_O$(DESD)	BKP	1,035	110,292	ASB	Start-up in 1957. Chlorine substitution began in 1993.
Weyerhaeuser Canada Ltd. Grande Prairie, AB	D$_C$EHDED	BKP	861	60,495	ASB	Start-up in 1973. Improved aeration and increased retention time.
Fibreco Pulp Inc. Taylor, BC	P,P	BCTMP	*481	*11,352	Extended Aeration AST	Started in 1988. In 1994, changed ASB to AST.
Finlay Forest Ind. Ltd. Mackenzie, BC	-	RFP, NEW	*463	*11,144	Aeration Ponds	Sawmill and pulp mill started 1964 and 1969, respectively.
Fletcher Challenge Can. Ltd. Mackenzie, BC	D$_O$E$_O$DED	BKP	*581	*55,260	ASB	In 1993, ECF bleaching initiated.

BKP=Bleached Kraft Pulp; BCTMP=Bleached Chemithermomechanical Pulp; RFP=Refiner Mechanical Pulp; NEW=Newsprint; ASB=Aerated Stabilization Basin; AST= Activated Sludge Treatment, *=measured in 1993

There are two classes of *pulping* processes, mechanical and chemical, shown schematically in Figure 2. In mechanical pulping (Figure 2(a)), fibres are physically separated from the wood by some form of mechanical action. Mechanical pulping is known as *high-yield* when more than 80% of the wood used in the process is converted into pulp. Mechanical pulps have short stiff fibres that produce a smooth printing surface but they are weaker than pulps produced by chemical pulping processes and they may be subject to yellowing with age because they contain more lignin than chemical pulps. They are most often used in newsprint and other printing paper and are usually considered unsuitable for applications like packaging where strength is a concern. There are several mechanical pulp mills in the NRBS system, including one that produces newsprint.

In chemical pulping (Figure 2(b)), chemical reactions occurring under a combination of chemical reactants, heat and pressure break down the lignin so that it can be separated from the fibres. Of the two common chemical pulping processes, kraft and sulfite, only the kraft process

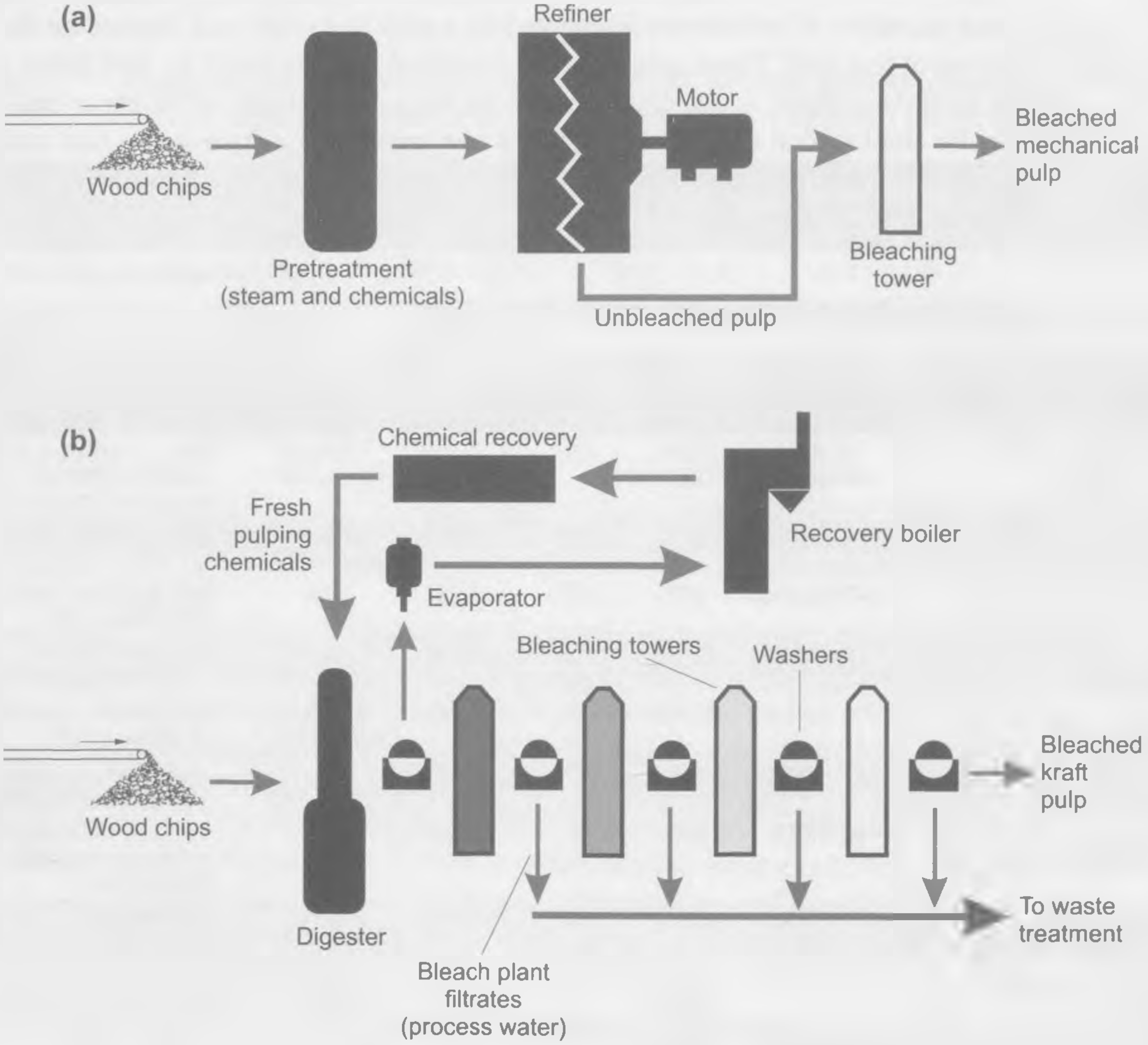

Figure 2. **Schematic representation of pulping processes in use in the Northern River Basins Study area: (a) bleached CTMP and (b) bleached kraft.**

is used in the NRBS area. In the kraft process, wood chips are cooked with chemicals in a vessel called a digester. The cooking dissolves most of the lignin and converts the wood into pulp. The pulp is separated from the cooking liquor, washed and either used, sold or sent to the bleach plant. The waste cooking liquor, called *weak black liquor*, is sent to the chemical recovery system. The chemical recovery system is an important part of the kraft process. In the recovery system, water is removed from the black liquor in a series of evaporators and the resulting concentrated black liquor is burned in a recovery boiler. Energy is recovered from burning the organic extractives and wood residues in the black liquor and cooking chemicals are recovered from the inorganic residue. Most chemical recovery systems recover about 99% of the cooking chemicals. From an environmental standpoint, the recovery process is important because it prevents a large portion of the chemicals extracted from the wood during cooking from being discharged as liquid effluent. Thus, although the yields of pulp in kraft processes are lower than mechanical processes and a much higher proportion of the wood is converted into dissolved form, the actual quantities of material discharged in effluents can be lower than mechanical pulp mills, depending on the actual percentages diverted to the recovery system.

Table 3. Abbreviations for bleaching unit operations.

Abbreviation	Unit Operation
C	Chlorination stage, where pulp is treated with gaseous, molecular chlorine, primarily to chlorinate the residual lignin, so that it can be later be solubilised.
E	Caustic Extraction. Dissolution of reaction products with sodium hydroxide.
E_O	As “E” above, with the addition of about 5 kg/tonne elemental oxygen. 1980s technology which has rapidly become universal in Canada and popular elsewhere.
O	Treatment of pulp with elemental oxygen, in alkaline conditions.
Z	Treatment of pulp with ozone, under acid conditions.
D	Reaction with chlorine dioxide, applied as an aqueous solution.
C/D	Chlorination stage with chlorine dioxide. Most mills use chlorine dioxide in the C stage, and the abbreviation “C” is often loosely used to refer to a C/D stage.
C_d	Chlorination stage with chlorine dioxide addition after Cl_2.
D_c	Sequential addition of chlorine dioxide followed by chlorine.
H	Reaction with hypochlorite (normally sodium).
P	Reaction with hydrogen peroxide.
Q	Chelating agents such as EDTA.
Y	Reaction with dithionite (also known as hydrosulphite).
W	Wash stage. (Indicated only where a washer would not normally be expected, eg. WW where two stage washing is installed.)
n or N	No-wash (Indicated only where a washer would normally be expected).
Subscript	Used to indicate percentage substitution of molecular chlorine where relevant, eg. CD_{70} would imply 70% substitution of molecular chlorine with chlorine dioxide.

From: McCubbin and Folke (1993).

One significant difference between kraft and CTMP processes employed in Alberta is the species of wood used as feedstock. With the exception of AlPac, the kraft mills use coniferous woods like lodge-pole pine while the CTMP mills use aspen. This results in considerable differences in the profile of extractives observed in untreated effluents.

When the final desired product is white pulp, the pulp undergoes several additional stages of chemical treatment with bleaching agents to remove more lignin and brighten the pulp. Mechanical pulps can be bleached or brightened with hydrogen peroxide whereas chemical pulps are usually bleached with stronger bleaching agents. Until the early 1990s, elemental chlorine was the bleaching agent of choice for kraft pulps. More recently, there has been a major shift in bleaching agent from elemental chlorine to chlorine dioxide (ClO_2) to prevent the formation of chlorinated substances during bleaching (Berry *et al.* 1991; Earl and Reeve 1990). For two of the Alberta bleached kraft mills, these bleaching changes occurred during the NRBS study. The results of these changes on effluent and environmental quality will be discussed in later sections. The other kraft mills in the NRBS system were newer and had a significant degree of ClO_2 substitution from the start of production.

One noteworthy feature of the Alberta bleached kraft mills discussed by McCubbin and Folke is the extent of use of *oxygen delignification*. In this process, some of the residual lignin is removed from the pulp by oxidation prior to bleaching. The organic material removed from the pulp in oxygen delignification is burned in the chemical recovery system. Since this process produces a pulp that has a lower lignin content and is less brown, it reduces the organics that must be removed from the pulp in bleaching and therefore significantly reduces both the BOD and concentration of chlorinated materials in the bleach plant effluents. By the end of the NRBS study period, more than 80% of the bleached kraft pulp production in Alberta involved oxygen delignification compared to around 25% or less in other parts of North America.

As described in McCubbin and Folke (1993), the general parameters used to quantify discharges of pollutants from pulp mills in the NRBS area include BOD_5, chemical oxygen demand (COD), Dissolved Organic Carbon (DOC), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Specific Conductance, Total Kjeldahl Nitrogen (TKN), Ammonia plus Ammonium ion, Nitrate + Nitrite, Phosphorus, Sulphide and Adsorbable Organic Halogen (AOX). The variables of interest to the chemi-thermomechanical pulp and newsprint mills include all of the above with the exception of Sulphide and AOX. Most of these parameters fall in the realm of the Nutrients Study Group and will not be discussed in depth in this report. In general, effluent quality for the mills in the northern river basins ranges from very good to equaling the best in the world (McCubbin and Folke 1993).

Metals commonly measured in kraft pulp mill effluent include aluminum, chromium, copper, molybdenum, nickel, zinc and mercury, while common metals in chemi-thermomechanical pulp and newsprint effluent are aluminum, cadmium, chromium, copper, lead, molybdenum, nickel, and zinc. Generally, metal levels in pulp mill effluents are low and pulp mill effluents are not usually regarded as point sources of pollution by metals. One exception is mercury. Prior to 1970, toxic mercury compounds were used as slimicides in white water systems in the industry. However, mercury is not used in Northern River Basins Study mills, nor is it found in Alberta mill effluents.

Effluents from pulp mills can contain complex mixtures of chlorinated and non-chlorinated organic compounds whose composition is greatly influenced by the type of wood used, the pulp digestion sequence and procedures, bleaching process and effluent treatment used. From a toxicological viewpoint, the most significant are naturally-occurring toxic substances released from the wood during pulping. Of these, the resin acid family is likely the most important. In addition, effluents from pulp mills using chlorine bleaching can contain other chlorinated resin and fatty acids, phenols, guaiacols, catechols, alcohols, aldehydes, ketones, sugars, and aliphatic and aromatic hydrocarbons. Based on the review by McCubbin and Folke (1993) and data in NORTHDAT (McCubbin *et al.* 1996), the following groups of contaminants are of interest and can be quantified in the effluents from pulp and paper mill effluents: chlorinated dioxins and furans; chlorinated phenolics; and, resin and fatty acids.

2.1.3 Chlorinated Dioxins and Furans

Chlorinated dioxins and furans often detected in pulp mill effluents include: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), 2,3,7,8-tetrachlorodibenzofuran (TCDF), and octachlorodibenzo-*p*-dioxin (OCDD) (Clement *et al.* 1989; Kuehl *et al.* 1987). Within the mill, most of the 2,3,7,8-substituted chlorinated dioxins and furans were found in the first extraction stage and to a lesser extent the first chlorination stage in bleaching processes that used elemental chlorine. The 2,3,7,8-TCDD and 2,3,7,8-TCDF predominated with the chlorinated furan isomer detected at greater concentrations than chlorinated dioxin isomer (Coulston and Kolbye 1994).

In reviewing the data in the NORTHDAT database, McCubbin and Folke reported ranges of dioxins and furans discharged from three Alberta pulp mills to be 1.8-7.3 pg/L for 2,3,7,8-TCDD and 4.5-28.4 pg/L for 2,3,7,8-TCDF. This corresponds to production rate ranges of 0.4-1.3 µg/tonne for 2,3,7,8-TCDD and 0.9-2.2 µg/tonne for 2,3,7,8-TCDF. These compare very favourably with U.S. mills surveyed in 1988-1989 that ranged from 1 to 500 µg/tonne for TCDD. According to McCubbin and Folke, concentrations of TCDD and TCDF in final effluent in a 104 mill survey of U.S. mills in 1988 ranged from the detection limit of 10 pg/L to 320 pg/L for TCDD and 4000 pg/L TCDF. Many of the mills in this survey had not implemented process modifications to control dioxins at the time they were sampled. Consequently, values should be much lower now. According to Joshi and Hillaby (1991), increasing the substitution of chlorine dioxide for chlorine from 25% to 70% at the Grande Prairie mill in 1990 resulted in a reduction in 2,3,7,8-TCDD concentration in the effluent from 7-8 pg/L to below the detection limit of 2-3 pg/L.

2.1.4 Chlorinated Phenolics

Phenolics such as phenol, guaiacol, syringol and others are common constituents of waste cooking liquors in kraft mills and may also be produced in the oxidation of residual lignin during pulp bleaching. These phenolics may become chlorinated during bleaching with elemental chlorine. Chlorinated phenolics that have been observed in pulp mill effluents include: 2,4-dichlorophenol; 2,4,6-trichlorophenol; 2,5-, 3,4-, 4,6-, and 4,5-dichloroguaiacols

(DCG) and catechols (DCC); 3,4,6-, 3,4,5-, and 4,5,6-trichloroguaiacol (TCG) and catechols(TCC); tetrachloroguaiacol (TeCG) and tertachlorocatechol (TeCC). Chlorinated syringols and chlorinated vanillins may also be formed.

The chlorophenolics are dependent on the type of wood used. Generally, it has been found that the pulping of softwood produces more chloroguaiacols, chlorocatecols and chlorovanillins while the pulping of hardwoods produces chlorinated syringols and chlorinated syringaldehydes that do not appear to be produced from softwoods. In the past, the main chlorophenolics in treated bleached kraft mill effluent were the tri- and tetrachloroguaiacols.

The total chlorophenol concentrations in the NORTHDAT database ranged from 0.01-0.07 mg/L for the Peace River mill, 0.01-0.08 mg/L for the Hinton mill and 0.01-0.140 mg/L for the Grande Prairie mill. According to Joshi and Hillaby (1991), the process change at the Grande Prairie mill in 1990 involving the move to 70% ClO_2 substitution resulted in a decrease of 15-82% in polysubstituted chlorophenols depending on extent of chlorine substitution. Pryke *et al.* report a further reduction after the move to 100% substitution in 1992. After the switch to 100% substitution, most chlorophenolics were near the detection limit of 0.0001 mg/L with the exception of 6-chlorovanillin.

2.1.5 Resin and Fatty Acids

Resins and fatty acids are natural components of wood liberated during pulping and present in cooking liquors. The prominent resin acids in kraft pulp mill effluent include: abietic acid, chlorodehydroabietic acid, dehydroabietic acid, isopimaric acid, levopimaric acid, neoabietic acid, pimaric acid, oleic acid, and dichlorodehydroabietic acid. In mills without chlorine-based bleaching all of the above are found with the exception of chlorodehydroabietic acid and dichlorodehydroabietic acid. The resin acids are an important family of compounds since they are significant contributors to acute toxicity if cooking liquors are lost to the effluent.

Resin acid concentrations in NORTHDAT were summarised by McCubbin and Folke (1993). Concentrations of total resin acids ranged from 184-794 μg/L for the kraft mills and 57 to 1,048 μg/L for the non-kraft mills.

2.1.6 Adsorbable Organic Halogen (AOX)

Adsorbable organic halogen (AOX) is a measurement of the halogen (chlorine, bromine, iodine) content of a sample that can be adsorbed on charcoal and detected by a variety of instrumental methods. AOX is generally taken as an indication of the total amount of organochlorines in a sample. Thus the AOX measurement includes both toxic and non-toxic organochlorines. The composition of the AOX and the ratio of toxic to non-toxic organochlorines varies from sample to sample and from site to site. AOX is a useful process parameter because it gives an indication of the extent to which the bleaching process is operating under conditions that can produce polychlorinated aromatic compounds like chlorinated dioxins, furans and phenols. These latter substances are generally produced at detectable levels in mills with AOX production rates above 2 kg/tonne pulp. At low AOX production rates, the organic matter discharged has similar carbon to chlorine ratios to naturally occurring dissolved organic material in natural waters and has not been associated with toxic effects. This means that despite its utility as a production parameter, AOX is not a good predictor of toxicity and its value as an environmental parameter is questionable.

By the end of the study, all four bleached kraft mills in the NRBS system were discharging less than 2 kg/tonne AOX. Two of the mills, Daishowa and AlPac employed more modern bleaching processes from the start of operation. The advanced processes employed at AlPac gave this mill one of the lowest rates of AOX discharge from bleached kraft mills in the world. For the other two mills, changes to bleaching and other processes at the Grande Prairie and Hinton mills substantially reduced their AOX discharge during the course of the study. For example, the changes made at Grande Prairie in 1990 decreased average AOX in their discharge from 1.9 to 1.5 kg/tonne (Joshi and Hillaby 1991). Additional process changes at this mill in 1992 further reduced average AOX discharge to 0.5 kg/tonne (Pryke *et al.*, pers comm).

2.1.7 Non-Pulp Mill Industrial Sources

Industrial sources of contaminants are related to regional natural resources which include forests, coal, tar sands, oil, gas and gravel. Among the non-pulp mill industrial sources found in the NRBS compilation were 37 gas plants and 62 other industrial sites (SENTAR 1996). Tar sands and oil resource-based industries such as Suncor Inc. discharge 35,000 m^3/d of effluent. The only non-pulp mill industry that is required to submit extensive monitoring data is Suncor Inc. The other industries, although licensed, are apparently not discharging effluent of a quantity or quality requiring monitoring. The SENTAR report (1996) provides statistical summaries of the monitoring data from January 3, 1988 to January 1, 1993. During this period, Suncor Inc.'s effluent did not exceed the licensed limits in TSS, BOD_5 and similar parameters. However, the value of this information in determining contamination to the NRBS study area was questioned since some negative values were found in the Suncor database (SENTAR 1996). No specific organic contaminants were identified in the review that could be used as markers of Suncor effluent. However, in companion studies conducted by Environment Canada and funded by the Panel on Energy Research and Development (PERD), polycyclic aromatic hydrocarbons (PAH) were suggested as useful contaminant indicators for this effluent (Brownlee, pers comm).

2.2 NON-POINT SOURCES OF CONTAMINANTS

Natural and human-induced pollutants can be introduced to the environment through what is often referred to as diffuse or non-point sources: that is, sources that are not confined and not readily controllable. Potential non-point sources of contaminants to the NRBS system include agriculture, forestry, natural petroleum deposits and long-range atmospheric transport and deposition.

2.2.1 Agriculture

Both agriculture and forestry employ pesticides as part of the management strategy to optimize production and product quality. At the time NRBS was conducted, another initiative, the

Canada-Alberta Environment-Agriculture Sustainability Agreement (CAESA), under Canada's Green Plan, was undertaken to examine the impacts of agriculture on water quality. We did not conduct studies within NRBS that would duplicate this work. Instead, it has been our intention to draw upon the results from CAESA as they become available. Cotton and Bytrus (1995), as part of CAESA, conducted a review of pesticide sales data and have reported trends in sales across the Province of Alberta. Although this information by itself does not indicate residue levels of pesticides in the aquatic ecosystem, this report and a report by Cotton (1995) that examines the environmental significance of various pesticides, can together provide a useful primer for residents in the northern river basins. It is probably still safe to say that agricultural pesticide use in the northern river basins has not reached a level of significant basin-wide concern. However, there is insufficient data to comment on the situation at local or regional scales. Furthermore, the CAESA reports provide compelling evidence that pesticide monitoring is virtually absent in the northern river basins and that existing government pesticide monitoring programs are not relevant with respect to the pesticides of highest use or environmental concern (Anderson 1995, Cotton 1995). According to the Cotton and Bytrus (1995) review, the pesticides most used in the province of Alberta are glyphosate, 2,4-D, triallate, trifluralin, MCPA, bromoxynil, ethalfluralin and imazamethabenz.

2.2.2 Forestry

About 382,000 km^2 of forested land lies within the NRBS area (Lyons 1995) and according to Hebert (1995) timber harvesting accounts for about 0.25 percent of the land base each year. This involves the alteration of large tracts of land by deforestation. Aquatic quality issues associated with land clearing generally relate to the hydrologic cycle and include reduced evapotranspiration, moisture loss in soil, temperature increases, changes in local precipitation patterns, decreased snow pack, increased runoff rates and increased surface runoff, disappearing wetlands, and depth to ground water table. With increased runoff and erosional material (suspended sediment), increased loading fluxes of nutrients, organic carbon, pesticides and dissolved salts are common (Alke 1995). The effects of forestry are seldom controllable by point source strategies, and require instead approaches that apply erosion control techniques, buffer zones near water bodies, small cut blocks spaced through the landscape, and so forth. Hebert (1995) provides a brief overview of these forestry management trends in the northern river basins.

NRBS conducted a workshop to examine the effects of land clearing on aquatic ecosystems (Alke 1995). The workshop participants identified several major areas of deficiency in our knowledge about how deforestation contributes to non-point source pollution. Factors such as turbidity, pH, temperature, nitrogen and phosphorus compounds, dissolved salts, and organic carbon can change in receiving aquatic environments as a result of land clearing. Our ability to predict these changes is poor and depends on site-specific characteristics that are often unknown. Our understanding of the bio-physical-chemical and ecological processes that lead to increased non-point source pollution is still wanting. Our ability to study non-point source pollution from deforestation at a level where we can detect ecological effects on individuals, populations or communities is far behind our analytical ability to detect low levels of pollutants.

The effects of forestry management on aquatic ecosystems has been the subject of considerable research across North America (Westworth 1992, Alke 1995, Corns 1994) and was considered by the NRBS workshop (Alke 1995). However, there is very little information specific to northern Alberta although several research initiatives are currently underway. The Natural Sciences and Engineering Research Council's Centre of Excellence Program has recently established a Sustainable Forest Centre of Excellence at the University of Alberta. As part of its mandate, this Centre will investigate the effect of forestry management on the quality and ecology of surface waters. As well, the Model Forest initiative under Canada's Green Plan is expected to provide improved understanding of the ecosystem impacts of forestry practices.

With respect to contaminants, pesticides and herbicides are used in forest management. Since they will be considered in the major studies mentioned above, these substances were not targeted in the NRBS studies. However, it may be of interest to point out that if the trend nationally is reflective of the trend in the northern river basins area, the forest industry is now using *Bacillus thuringiensis* (B.t.), a biological control agent for many insect infestations. B.t. is significantly less harmful than chemicals to non-target species (Environment Canada 1991).

2.2.3 Long Range Transport of Contaminants

Long-range transport and deposition of contaminants, particularly persistent chlorinated organic chemicals, is responsible for the widespread low level contamination of most of the northern hemisphere (Ballschmitter 1991). There were no data on the analysis of wet and dryfall deposition of contaminants in the NRBS area. However, atmospheric deposition has been well documented as a significant contaminant source to Canadian surface waters in the Great Lakes (Swackhamer and Hites 1988; Muir *et al.* 1993; Hoff 1994) and the Arctic (Cotham and Bidleman 1991; Barrie *et al.* 1992; Muir *et al.* 1992; Lockhart *et al.* 1992). Contaminant inputs to terrestrial ecosystems have also been documented in Canada (Strachan *et al.* 1993), Europe (Calamari *et al.* 1994) and the Arctic (Thomas *et al.* 1992). Therefore, literature data from elsewhere in Canada were used to characterize contaminants entering the basin from long-range sources. The most complete data set close to the NRBS area was published by Hoff *et al.* (1992). They determined concentrations and fluxes in the gas, particulate and rain phases for a range of contaminants in Lake Superior. A summary is shown in Table 4. Compared to the contaminant profile of pulp mill effluents, long-range atmospheric transport includes the deposition of metals such as lead (Pb), arsenic (As), selenium (Se), and cadmium (Cd) and a greater amount of PAHs and PCBs. Based on the data presented in Table 4, the persistent anthropogenic organic contaminants most likely to be deposited within the northern river basins and useful as indicators of long-range transport of air pollutants (LRTAP) include several families already discussed above. These are the PCDDs, PCDFs, PCBs and PAHs.

> *As a result of the various source reviews, five families of contaminants were chosen as the main target contaminants of interest. They are: polychlorinated dioxins and furans (PCDDs and PCDFs); polychlorinated phenolics (PCPs); polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs); resin acids (RAs) and polycyclic aromatic hydrocarbons (PAHs).*

Table 4. **Long range transport and atmospheric deposition of toxic chemicals to Lake Superior for 1992.**

	GAS		PARTICULATE		RAIN	
Contaminant	Conc. (pg/m^3)	Flux (net) (ng/m^2/y)	Conc. (pg/m^3)	Flux (net) (ng/m^2/y)	Conc. (pg/m^3)	Flux (net) (ng/m^2/y)
Alpha -HCH	110	4500	0.2	13	1.4	950
Gamma-HCH	32	1700	0.1	7.3	1.2	750
Dieldrin	14	-9500	1.5	90	0.4	250
DDE	2.5	120	0.08	4.9	0.06	32
DDT	3.9	460	0.3	19	0.2	76
DDD	1.5	220	1.2	74	0.0	0.0
HCB	98	3500	0.2	8.5	0.1	65
Σ-PCB (Total)	90	-20700	5.60	330	1.2	700
Phenanthrene	860	-41500	19	1220	3.7	3170
Pyrene	190	19500	22	1460	2.7	1950
B(K)F	19	2440	22	630	2.7	1460
B(A)P	9.3	1060	11	707	2.9	1700
Toxaphene	NO	NO	<0.1-56 (GLE90)*	59	<0.1-1.2 (ELAK8991)*	152
TCDD	NO	NO	1.70e-03	NO	0.0096-0.100 (GL8890)*	0.2
OCDD	NO	NO	8.46e-01	NO	0.030-0.084 (GL8890)*	41
Total PCDD's	NO	NO	1.34e+00	NO	0.030-0.084 (GL8890)*	
TCDF	NO	NO	2.60e-02	NO	0.0096-0.100 (GL8890)*	4.6
OCDF	NO	NO	2.20e-02	NO	0.0096-0.100 (GL8890)*	0.5
Total PCDF's	NO	NO	3.88e-01	NO	0.0096-0.100 (GL8890)*	

Ref.: R. Hoff. *et al.* 1996; and (*) Eisenreich and Strachan, 1992.
Abbreviations: NO=Not Obtained; GL8890=Great Lakes, 1988-1990;
ELAK=ELA-Kenora, 1989-91; GLE90=Great Lakes, ELA-Kenora, 1990.

2.3 SOURCE-SPECIFIC CONTAMINANT PROFILES

Various individual members of the five families selected above may be source specific, eg. chlorinated resin acids from pulp mills. However, in the case of families of compounds with members that can come from a variety of sources, the relationship among different members of the family can provide important additional information. Of the families listed here, the one likely to be most useful with respect to source-specific congener profiles is the PCDD/PCDF family. Relationships between congeners have been used to discriminate sources in several studies (Broman *et al.* 1989; Evers *et al.* 1989; Rappe *et al.* 1991).

Chlorinated dioxins and furans enter the environment due to their formation in trace amounts in industrial processes, particularly processes involving chlorination of organic substances; their formation in combustion processes, particularly incineration; and indirectly in leachates and sewage (Fiedler *et al.* 1990). Industrial processes producing TCDDs and TCDFs include manufacture of chlorinated pesticides, metallurgy, reactivation of activated carbon, and manufacture of certain plastics. With respect to these industrial process sources, the ones most likely to be relevant to the NRBS are the bleaching of wood pulp and the use of wood products treated with chlorophenol fungicides. Clement *et al.* (1989) and Kuehl *et al.* (1987) reported the distribution of PCDD and PCDF in suspended solids and sludges from pulp and paper mill treatment systems. They report significant differences between mechanical pulp mills and bleached kraft mills. Tetrachloro congeners predominated at bleached kraft mills while higher chlorinated congeners were most abundant at the non-bleach kraft mills. Similar profiles were reported by Rappe *et al.* (1990) for Swedish pulp mills. The congener pattern found at the CTMP mills was very similar to that reported by Rappe *et al.* (1991) associated with penta- and tetrachlorophenol fungicides. A representative distribution by homologue group for each of these sources is shown in Figure 3.

The main pathway for entry of PCDDs and PCDFs into the environment is via combustion processes (Fiedler *et al.* 1990). Combustion sources of TCDDs and TCDFs include municipal and other waste incinerators, combustion of sewage sludge and recycling of scrap metal, particularly polyvinyl chloride (PVC) coated wire. There are also a variety of diffuse combustion sources including automobile exhausts, fossil fuel combustion for home heating, forest fires and cigarette smoking. Accidental fires involving PCB and PVC containing materials have also contributed TCDD/TCDFs to the environment. Polychlorinated biphenyls (PCBs) can be converted to polychlorinated dibenzofurans (PCDFs) and other products but not PCDDs in fires (Erikson 1989). TCDDs may be formed in combustion of PCBs containing chlorobenzene impurities. PCDD/PCDF congener profiles from combustion of hard PVC were reported by Theisen *et al.* (1989). The congener profile was similar to that of house fires and other accidental fires where this material was present as coatings on wires, etc. The pattern from combustion of PVC was dominated by higher chlorinated furans. According to Dickson *et al.* (1989), catalysed formation from chlorophenol precursors rather than *de novo* synthesis is the most likely route of formation of chlorinated dioxins in municipal incinerators. Particulate carbon catalyses the formation of octachlorodioxin from pentachlorophenol and also the dechlorination of octachlorodioxin to heptachloro- and hexachlorodioxins. These processes explain the patterns of

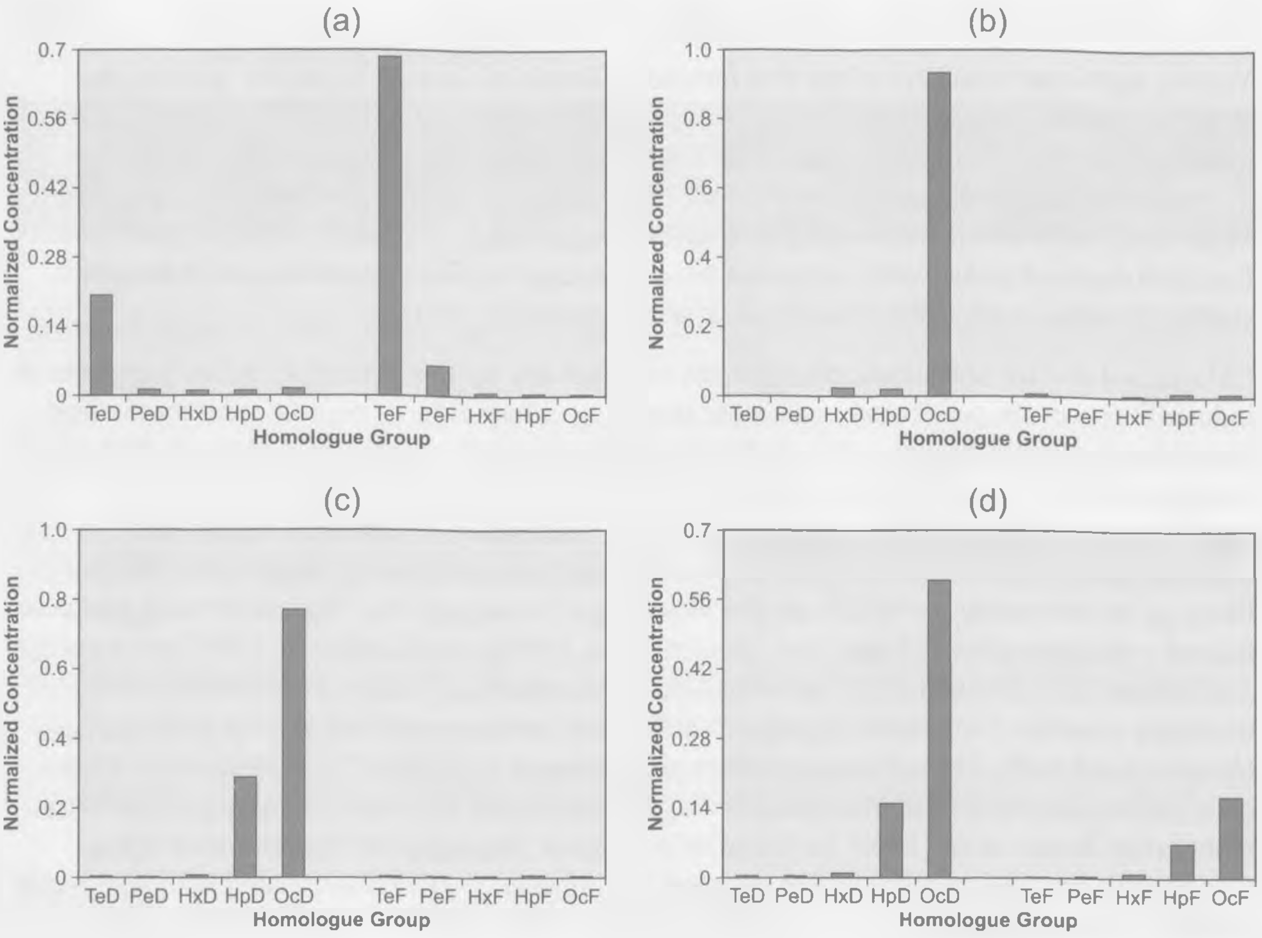

Figure 3. **Comparison of representative congener profiles for PCDD/PCDFs produced in: (a) bleached kraft pulp mill effluent; (b) CTMP pulp mill effluent; (c) municipal wastewater treatment plant effluent; and (d) pentachlorophenol fungicide.**

congener distribution observed in gaseous and particulate discharges from municipal and other waste incineration. Congener profiles from several combustion sources are presented in Figure 4.

The congener profiles presented in Figures 3 and 4 form a collection of base profiles against which profiles from analysis of field samples from the Northern River Basins could be compared in order to characterize the major sources of TCDDs and TCDFs to various parts of the basins.

2.4 BROAD SPECTRUM ANALYSES

Under the Northern River Basins Study, the contaminants identified through the various reviews as associated with sources within the basins were compiled into a list of target compounds for further investigation. Samples of water, effluent, sediment, fish and benthic invertebrates were then collected from various locations within the basins and analysed for these target compounds. However, these analyses were for the specific contaminants only and yielded no information regarding other contaminants that may have been present. To obtain information concerning the

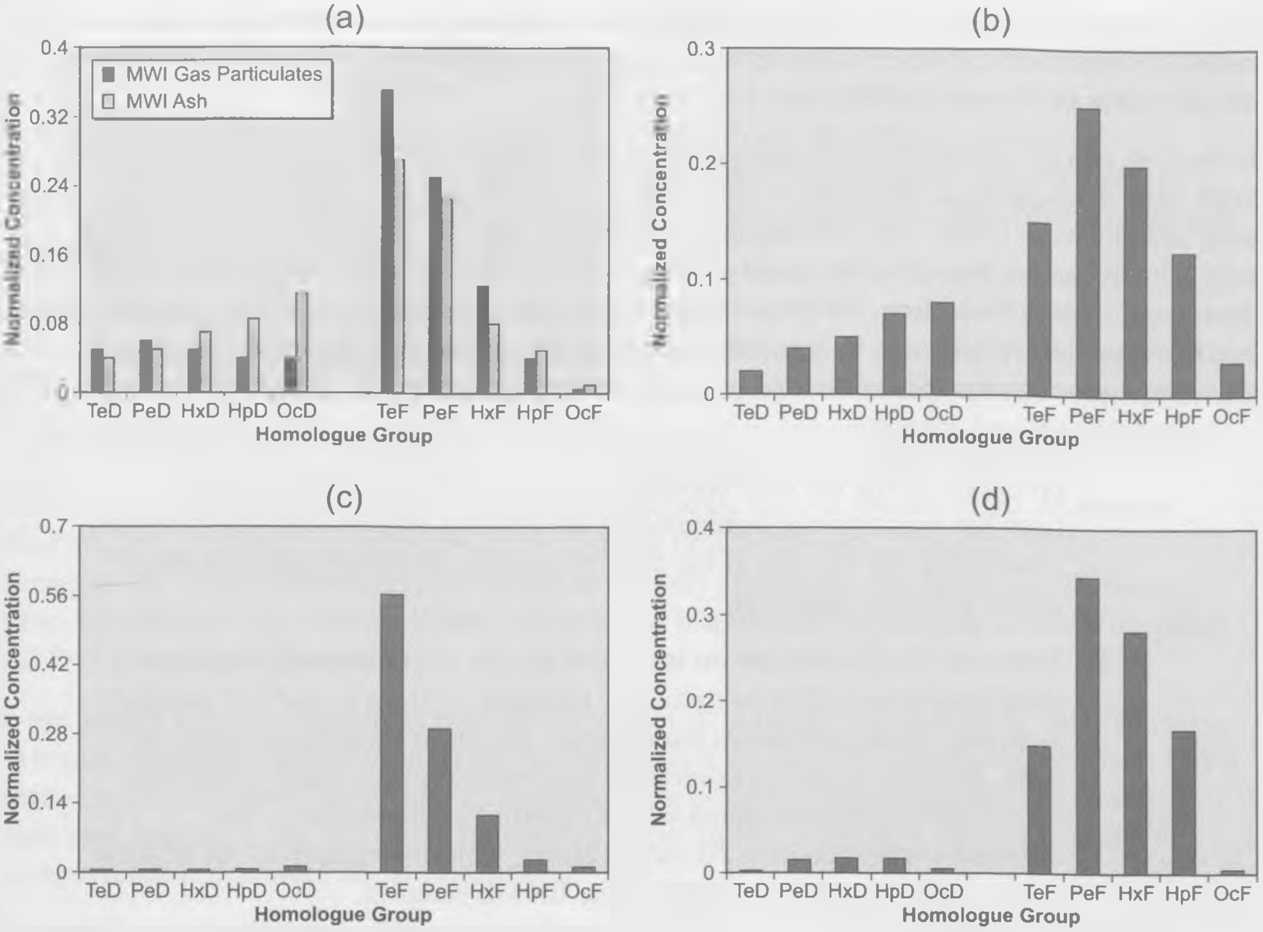

Figure 4. Comparison of representative congener profiles for PCDD/PCDFs produced in: (a) incineration of municipal waste; (b) incineration of hospital waste; (c) PCB combustion; and (d) PVC combustion.

nature and concentrations of non-target contaminants, a broad spectrum analytical approach was also implemented. This approach was based on interpretation of mass spectra generated by full scan gas chromatography-mass spectrometric (GC-MS) analysis of the samples.

In the first phase of the broad spectrum analysis (BSA), the archived data produced in the analysis of effluents discharging into the Northern Basins during the period of 1989 to 1994 as part of numerous surveys and monitoring programs of Alberta Environmental Protection was reviewed. This data had been produced using a full scan GC-MS method that yielded spectra that could be used to identify or characterize the compounds present. These spectra were compiled to build searchable mass spectral libraries used in later phases of the project. The results of this characterization phase are described in Johnson (1996).

The data in the database were divided into the following groups: i) bleached kraft pulp mill effluents (BKME), ii) high yield pulp mill effluents, comprising both thermomechanical and chemi- thermomechanical pulp mill effluents (CTMP), iii) municipal sewage treatment plant effluents (STP), and iv) Suncor effluent. Separate searchable libraries were created for each group. Since no standards were available to be run during this phase of the study, the concentrations were estimated using surrogate standards and making several assumptions that are discussed in Johnson (1996).

In the first part of characterization phase of the BSA, data for effluent from all four bleached kraft mills discharging to the rivers in the Northern Basins between 1989 and 1994 were analysed (Johnson 1996). Very few organic compounds were detected in the AlPac effluent; only a hydrocarbon, identified as dimethylcyclohexane, dichloromethyl-methylsulphone and two diterpenes. This differed from the other three mills whose effluents had many more compounds and were qualitatively similar to each other. Compounds observed in the remaining three bleached kraft effluents can be divided into four broad groups:

1. **Hydrocarbons**. This group includes hydrolysis products of polysaccharides produced during the pulp cooking process, aromatic compounds resulting from the hydrolysis of lignin during the cooking process, and nonylphenols observed in the effluent of the Weldwood mill, presumably present due to use as a process chemical.
2. **Terpenes**. Terpenoids are an important family of compounds present at significant concentrations (max. tot. terpenes ~450 µg/L) and not routinely analysed. These substances are naturally produced compounds found in trees. Terpenoids can be subdivided into monoterpenes which contain 10 carbon atoms, sesquiterpenes which contain 15 carbon atoms, and diterpenes which contain 20 carbon atoms. Chlorinated derivatives of these compounds were also observed in the BKME samples.
3. **Chlorinated compounds**. These compounds result from the chlorination of compounds carried over from the cooking process to the bleach plant or from the oxidative degradation/chlorination of residual lignin in the pulp during the chlorination in the bleach plant. The most prominent chlorinated compound was 1,3-dichlorodimethylsulfone. This compound comprised from 70 to 90% of the total chlorinated compounds detected.
4. **Sulphur-containing compounds** produced during cooking process. This group consisted mostly of alkylsulfones/sulfides and polysulfides, substituted thiophenes and unidentified compounds containing sulfur.

Data for effluents from the three CTMP mills discharging effluents to the northern river basins during the 1989 to 1994 interval were also analysed in the characterization phase of the BSA (Johnson 1996). There were differences in effluent quality between mills that appeared to be related to effluent treatment and not process technology. The compounds observed in CTMP effluents can be separated into two groups:

1. Natural wood products such as terpenoids, naturally produced aromatic compounds and naturally produced organic acids.
2. Anthropogenic compounds, principally phthalates.

Very little organic material was observed in Alberta Newsprint Company mill effluents. Compared to the kraft mills, the discharge of organics from the CTMP mills was more episodic in nature. These were likely due to problems in the effluent treatment systems. Such episodes were not observed in the Alberta Newsprint Company effluent. In addition, several anthropogenic compounds were observed in the Slave Lake Pulp Company mill effluents in high concentrations. These compounds are not generally associated with the CTMP process and we can give no reason for their presence in the effluent.

Data on effluents from four municipal STPs over the 1989 to 1994 period were also examined in the first characterization phase of the BSA (Johnson 1996). Most compounds observed in the STP effluents were present at low concentrations (<1.0 µg/L). Notable exceptions were caffeine, some phosphates and some phthalates, all usually present in concentrations less than 10 µg/L. There were differences in the composition of effluents. Caffeine was present in high concentrations in Athabasca and Fort McMurray effluents but not present in the Whitecourt effluents, and in lower concentrations in the Grande Prairie effluents. The other major contaminants were 2-butoxyethyl phosphate in the Fort McMurray and Athabasca effluents, tributylphosphate in the Grande Prairie effluent, and bis(ethylhexyl)phthalate in the Whitecourt and Fort McMurray effluents.

In the Suncor effluent chromatograms, the only resolvable peaks were due to the internal and surrogate standards that had been added during analysis. In the 1992 chromatogram, there was a large unresolved "hump" composed of hydrocarbons, probably naphthenic acids and other associated hydrocarbons. Given the unresolved nature of this material it was not possible to produce reliable estimates of contamination.

Total numbers of compounds characterized for use in later phases of the BSA were 149 compounds in kraft mill effluents; 119 compounds in CTMP effluents; and 91 compounds in sewage treatment plant effluents (Johnson 1996). A summary of these compounds is given in Table 5.

In the second phase of the BSA, fresh samples of effluents were collected, extracted by solid phase extraction, fractionated and analysed by GC-MS. Using the mass spectral libraries compiled in the first phase of the BSA, contaminants previously observed were quantified. The results of this project are summarized by Johnson *et al.* (1996). As in the first phase of the BSA, effluents were assorted into four groups: i) bleached kraft mill effluents; ii) chemi-thermomechanical pulp mill effluents; iii) municipal sewage treatment plant effluents; and iv) Suncor effluent. The compounds present in the effluent samples were characterized and described by i) tentative identification based on interpretation of mass spectra, mass spectral library search results, and elution order when possible, ii) class of type of compound, i.e. chlorinated terpene, alkylated benzene, alkylated thiophene etc., and iii) substructure such as carboxylic acid or incorporation of special elements such as chlorine or sulphur as determined from the molecular ion cluster, characteristic losses or characteristic ions. Full mass spectra of the identified compounds are given in Johnson *et al.* (1996).

The concentrations of compounds in BKMEs are reported for each mill in Johnson *et al.* (1996). In comparison to the effluents from the 1989-1994 period analysed in the earlier phase of the BSA, it was evident that the character of the BKME effluents had changed considerably.

Table 5. Summary of NRBS BSA Results.

Compound Category	BKME	CTMP	Municipal STP	Suncor
Hydrocarbons produced during pulp cooking, aromatic compounds from hydrolysis of lignin, and process chemicals e.g. nonyl phenols	■	■	■	
Hydrocarbons from process effluent, e.g. naphthenic acids				■
Caffeine			■	
Organophosphates (e.g. tributylphosphate in the Grande Prairie effluent, 2-butoxyethyl phosphate in Fort McMurray and Athabasca effluents)			■	
Other anthropogenic compounds, e.g. phthalates		■		
Terpenes, natural products in wood released during pulp cooking	■	■	■	
Chlorinated compounds from pulping compounds carried over to the bleach plant or from the oxidation/chlorination of lignin during bleaching	■		■	
Sulphur-containing compounds produced during pulp cooking	■		■	

Specifically, no monoterpenes, sesquiterpenes, alkylated sulphides or polysulphides, thiophenes, or chlorinated compounds were observed in any of the current effluents. In addition, nonylphenols previously observed in Weldwood-Hinton mill effluent were not in the current effluent. Instead, phthalate esters were present at significant concentrations. Phthalate esters were also present at the other mills, but at lower levels. In all BKME samples in this phase of the BSA, the most abundant compounds were either carboxylic acids or phthalate acid esters. The most prevalent carboxylic acids were generally palmitic (hexadecanoic), stearic (octadecanoic) and oleic (octadecenoic) acids. These naturally occurring acids are the most prevalent fatty acids found in the lipids of organisms. Both mono- and dicarboxylic acids were present in all effluents but in much lower amounts in the AlPac effluent. Although no monoterpenes and sesquiterpenes were observed, diterpenes and triterpenoids (C27 to C30) were observed in some effluents, particularly in the Weyerhaeuser-Grande Prairie effluent in which 3 diterpene acids were also observed. However, the compounds observed in highest concentrations were the phthalate esters with some esters occurring in the 20 to 50 µg/L range.

Phthalate esters and mono- and dicarboxylic acids were also observed at significant (20 - 50 µg/L) concentrations in CTMP effluents (Johnson *et al.* 1996). Mono-, sesqui-, and diterpenes were not observed although triterpenoids were present in the effluent from Slave Lake Pulp. The anomalous contaminants previously observed in high concentrations in the Slave Lake mill effluent in the first phase of the BSA (Johnson 1996) were not observed in this phase.

In STP effluents, as with the pulp mill effluents, both phthalates and carboxylic acids were the dominant components (Johnson *et al.* 1996). The carboxylic acid characteristic traces were again dominated by the fatty acids of lipid origin, i.e. palmitic, stearic and oleic acids. The

Grande Prairie STP effluent differed from the others, containing an additional fatty acid homologue series extending up to octacosanoic acid (C28:0). A shorter fatty acid homologue series was also seen in the Fort McMurray effluent, but only extending to pentacosanoic acid (C25:0). The source and variability of these compounds in the effluents are unknown. However, the absence of a preference for even numbers of carbons suggests that the source is unlikely to be natural.

There were several compounds observed in the STP effluents that were not present in the pulp mill effluents (Johnson *et al.* 1996). These include: 2-butoxyethanol phosphate, observed in all effluents in significant concentrations (4.1 to 7.6 µg/L); triphenyl phosphate, observed in concentrations which ranged from 128 µg/L in the Whitecourt STP effluent to 0.4 µg/L in the Fort McMurray STP effluent; and caffeine, which was observed in previous work, was observed only at low concentration (1.1 µg/L) in the Athabasca STP effluent. Another class of compounds were sterol derivatives, i.e. sterols, sterones, stanols and stanones. These derivatives are commonly observed in sewage effluents and are related to the transformation of cholesterol and other sterols. They were most prominent in the Grande Prairie STP effluent but were present in all STP effluents. Nonyl phenols were observed in all STP effluents surveyed. In view of the recent suggestions that nonyl phenols may be endocrine- disruptors, these compounds may be the most significant of all those identified from a toxicological viewpoint.

Paradoxically, dialkyl polysulphides and substituted thiophenes, previously only observed in kraft mill effluents, were observed in the Grande Prairie STP effluent but not in the BKMEs analysed.

As observed in the first phase of the BSA, the organic component of the Suncor effluent consisted primarily of naphthenic acids, a very complex mixture of alicyclic carboxylic acids (Johnson *et al.* 1996). Naphthenic acids are not resolvable by simple gas chromatography, making their quantification impossible. In addition, their presence masked the presence of PAHs, which were also present in the same fraction in the 0.1 to 1 µg/L concentration range. Alkylated and heterocyclic PAHs were likely also present in the same concentration range.

The BSA results demonstrated that the most prevalent non-routine contaminants in effluents within the basin were phthalate acid esters. Both naturally-occurring and apparently-anthropogenic carboxylic acids are also present, in some cases at high concentrations. Elongated fatty acids (>C20) were observed in several effluents. In addition, high concentrations of organic phosphate were present in all sewage treatment plant effluents. Dialkyl polysulphides and alkylated thiophenes were also observed in the Grande Prairie sewage treatment plant effluent. The Suncor process effluent contained a mixture of PAHs and alkylated PAHs in addition to naphthenic acids.

3.0 DISTRIBUTION OF CONTAMINANTS IN THE NORTHERN RIVER BASINS

Obtaining a detailed picture of contaminant distribution in a system as large and complex as that covered by the NRBS is a task far beyond the means of the Contaminant Component. Therefore, some simplifying decisions were required. The first of these simplifications concerned the identity of the contaminants whose distributions would be determined since it was clearly not possible to analyse for everything everywhere. We decided that the major effort would be directed towards those contaminant families identified in the characterization studies as arising from several sources within the basin or of greatest toxicological significance. As discussed above, these were resin acids, PCDDs, PCDFs, PCBs, CPs and PAHs. In addition, to avoid placing all the emphasis on these six contaminant families, a receiving water survey was conducted examining waters upstream and downstream from major effluent discharges for the contaminants identified in the broad spectrum analysis part of the characterization studies.

A second simplification involved determining which environmental compartments would be analysed for which contaminants, again recognizing that it was not possible or practical to measure all six of the target families of contaminants in all possible compartments. The compartments considered were water, sediment and biota. Each had its advantages and disadvantages. The water phase is important from a contaminant transport standpoint and, in principle, is very easy to sample. Water samples provide a snapshot of the conditions at the time sampled. However, river water is not an integrative medium and water samples can give no indication of conditions existing prior to the time of sampling. In addition, five of the six target contaminant families are sparingly soluble in water and there was a risk their levels would be below analytical detection limits in the water from many parts of the basin. The limitations to the use of water samples in distribution studies have caused some authors to suggest that sediment is a more relevant compartment (Ongley *et al.* 1988).

Sediment has the potential to be useful in distribution studies since contaminants that are sparingly soluble in water tend to partition into the organic phase of the sediment and therefore can usually be detected in sediment at sites where they cannot be detected in the water phase. Suspended sediment in rivers is an important transport medium for contaminants but more needs to be known about processes affecting its in-stream fate, such as flocculation, before suspended sediment can be used in basin-wide surveys. Contaminants can accumulate in depositional sediments but, unfortunately, bottom sediment distribution in rivers is not homogeneous. It depends strongly on discharge conditions that vary from reach to reach and season to season. Since sediment composition can vary considerably within a basin and even within a specific reach, considerable information about intra-site variability in sediment composition and about partitioning of contaminants in different sediment components is required to avoid affecting the data with sampling artifacts.

Many contaminant distribution studies are based on biological samples since the bioconcentration and/or bioaccumulation of contaminants in organisms can lead to analytically significant concentrations, and detecting the presence of contaminants in organisms is evidence that the contaminants in a system are bioavailable. Fish are generally considered the most suitable aquatic biomonitors, although invertebrates may also be used. The key criteria regarding choice of contaminant biomonitor species are usually sensitivity, availability, distribution, and mobility. There are differences between species in the degree to which they bioconcentrate contaminants. Therefore, it is important to chose a biomonitor that responds strongly to exposure. The species should be widely available at most times of the year and readily captured. Invertebrates with annual life cycles are only available in specific life stages once per year. This tends to limit their value as biomonitors. Biomonitor species should be non-mobile so that the samples will be representative of the area in which they are captured and the species should be widely distributed within the ecosystem under study to allow the geographical distributions of the contaminants to be determined.

There was not enough information available to us at the start of the NRBS to allow these questions to be considered and the choice of monitoring compartment made. Therefore, we conducted several preliminary studies at reduced geographical scales to provide information on what compartments would be most useful in basin-wide studies. The most detailed was a set of multi-compartment surveys known within the NRBS as the Reach Specific Survey (RSS). The RSS was centred on the Hinton to Whitecourt reach of the Athabasca River and was conducted in the spring of 1992. 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 with additional sampling performed in 1993. An additional preliminary study on a broader geographical scale but a narrower compartmental focus than the RSS occurred in the spring of 1993, when a survey focusing on bottom sediment of the Athabasca River basin was conducted. Several of the preliminary surveys examined contaminant levels in various species of fish and other biota. In the RSS study, contaminants in mountain whitefish and northern pike muscle were examined. Additional samples for preliminary analysis of contaminant distributions were provided by the NRBS General Fish surveys on Athabasca River. These surveys provided mountain whitefish and longnose sucker collected from two sites downstream from Hinton, and walleye and goldeye collected further downstream at five sites. In addition, samples of burbot tissue were obtained from nine sites on the Peace/Wapiti/Smoky system during the fall of 1992. The objective of these preliminary studies was to provide a database that could be used as a basis to design subsequent basin-wide sampling in an internally-consistent manner. Following these preliminary studies, a primary abiotic compartment, bottom sediment, and a primary biotic compartment, burbot liver, were selected and basin-wide sampling and analysis of fish and sediment were conducted. The results of the preliminary and basin- wide surveys to determine contaminant distribution are discussed by environmental compartment (i.e. water, sediment and biota) in the following sections.

3.1 WATER

The results of the water analyses for the 1992 RSS conducted in March-April are reported by Crosley (1996a). Water was collected from six sites along the 200-kilometre reach of the Athabasca River between Hinton and Whitecourt. The reach receives effluent from the Weldwood Canada pulp mill mixed with municipal effluent from the town of Hinton. The Hinton combined effluent (HCE) was also sampled. Water and effluent samples were analysed for AOX, EOX (extractable organic halides), PCDDs, PCDFs, CPs, resin acids, PCBs and other organochlorines, and total metals.

The concentration of AOX in the HCE was 15 mg/L of which about 0.05 mg/L or about 0.3% was extractable as EOX (Crosley 1996a). These values were within the range found in other studies at mills using similar technologies. AOX in river water 1 km downstream from the mill was 0.28 mg/L, a significant increase over the <0.01 mg/L found upstream from the mill. EOX was below detection limits in all river samples. AOX concentration decreased to 0.12 mg/L at the farthest downstream site, presumably due to a combination of dilution and degradation. Ten chlorophenolics were detected in HCE at concentrations ranging from 1.3 to 16.5 μg/L. The most prominent were the tri- and dichloroguaiacols and 6-chlorovanillin. The concentrations of these compounds in the Athabasca River ranged from <0.05 to 0.42 μg/L, as expected from average dilution calculations. Concentrations decreased rapidly over the 200 km reach although they were still detectable at concentrations >0.001 μg/L at the furthest downstream site. Resin acid analysis was hampered by analytical variability but the sum of total resin acids in HCE was 38.6 μg/L, dominated by pimaric, isopimaric and dehydroabietic acids. Downstream concentrations were in the 0.1-0.3 μg/L range. Dehydroabietic acid was the most persistent. Chlorinated resin acids were detected in HCE at a total concentration of 0.71 μg/L. Their concentrations in river water downstream from the mill ranged from 0.003 to 0.01 μg/L. PCBs and a suite of 19 organochlorine pesticides (OCs) were not detected in river water at detection limits of about 0.01 μg/L. In the HCE, only one organochlorine pesticide, dieldrin, was reported at a concentration of 0.16 μg/L while PCBs were not detected. Of the metals, aluminum, manganese and zinc were sufficiently above natural background levels in HCE to give rise to subtle decreases downstream from the mill.

The concentrations of PCDDs and PCDFs in the RSS samples are discussed in detail by Pastershank and Muir (1995). Lower chlorinated PCDFs but not PCDDs were detectable in the dissolved phase of the HCE. Concentrations of total mono-, di-, and tri-CDF congeners in the dissolved phase of HCE were 33, 180, and 78 pg/L respectively. Both TCDDs and TCDFs were detected in the HCE centrifugate. The total concentration of TCDDs was 2.1 pg/L of which 0.47 pg/L was the 2,3,7,8- congener while the total concentration of TCDFs was 51 pg/L of which 2.7 pg/L was 2,3,7,8-TCDF. The di- and tri-CDFs were present at low but detectable levels in centrifugate water at RSS sites downstream from Hinton.

A second study focusing on PCDD/PCDFs and resin acids in water and sediment was conducted in the Athabasca River basin under low flow conditions in February-May, 1993. For the dissolved phase, the focus was limited to the PCDD/PCDF families. The results of this study are reported by Crosley (1996c). Results of the HCE effluent analyses were similar to the 1992 RSS. Lower chlorinated PCDFs dominated the dioxin/furan family, with concentrations of total mono-, di- tri- and tetrachloro- congeners in HCE of 12, 94, 30 and 76 pg/L respectively. Although after dilution in the river, concentrations of these lower chlorinated furans were very low, ranging from non-detect to 8.5 pg/L, lower chlorinated furan congeners remained detectable in the Athabasca River above background for up to approximately 250 km downstream from Hinton. Effluents from the three CTMP mills on the Athabasca and the Whitecourt and Fort McMurray STPs were also analysed. In addition to low (<5 pg/L) but detectable levels of octachlorodioxin in both STPs and two of the three pulp mills, a suite of chlorinated dibenzofuran congeners was detected in Ft. McMurray STP effluent over a 0.3-2.5 pg/L range.

Surface water analysis was also conducted as part of the broad spectrum analysis (BSA) project. The results are reported by Johnson and Urso (1996). As previously described, the second phase of the BSA involved the GC-MS characterisation of effluents currently discharging into the northern river basins. The compounds detected were separated into major classes, characteristic chromatograms representative of each class were constructed, and searchable libraries of spectra containing a total of 260 compounds were compiled. The third phase of the BSA involved analysis of surface waters for the compounds in the libraries. None of the compounds observed in Phase II BSA of current effluents or in the Phase I characterization of past effluents were observed in surface waters at significant concentrations. A potentially more sensitive approach based on constructing chromatograms that were the sums of single ion mass chromatograms of ions characteristic for specific classes of compounds was also attempted. Characteristic traces for methyl esters, phthalate esters, nonylphenols and a group of unidentified acids specific to STP effluents were obtained. A few compounds, including linear alkanes, phthalate esters and methyl esters of fatty acids were observed at low concentrations. However, these compounds can arise from a number of sources and analytical blanks usually contain detectable amounts due to their ubiquitous distributions.

Low or non-detectable concentrations of a number of contaminant groups were found in the water phase including chlorinated phenolics, some chlorinated dioxins and furans and some resin acids. These were detectable in water at some sites but over most of the river reaches sampled, concentrations were near or below detection limits. The BSA of receiving waters did not identify any new widely distributed compounds that should be added to the list of target compounds in future distribution studies. In general, concentrations in water were orders of magnitude lower than concentrations in sediment discussed in the next section. We concluded that water was not a desired abiotic compartment for the basin-wide survey and that, with the possible exception of effluents, analyses of water phase samples should not be part of the basin-wide surveys to determine contaminant distributions.

3.2 RIVER SEDIMENT

3.2.1 Preliminary Studies of River Sediment

Sediment samples were collected in both the 1992 RSS and in the subsequent 1993 study in the Athabasca River basin. Both depositional sediments from the river bottom and suspended sediments were collected in these surveys. The RSS sediments were analysed for TCDD/TCDFs, resin acids, CPs and PCBs/OCs while the 1993 Athabasca River samples were analysed for TCDD/TCDFs and resin acids only. In addition, analyses were conducted on a set of depositional sediment grab samples collected by Alberta Environmental Protection (AEP) from 1988 to 1990 at 26 sites throughout the northern river basins. The results of the analysis of the 1992 RSS are described by Crosley (1996a), Brownlee *et al.* (1996) and Pastershank and Muir (1995), while Crosley (1996c) describes the results of the 1993 Athabasca River basin study. The results of the analysis of the AEP archived samples are reported by Brownlee *et al.* (1996).

Crosley (1996a) compared results for depositional and suspended sediment collected during the 1992 RSS. PCDD/PCDFs detected in sediments included 2,3,7,8-TCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PCDD and 2,3,4,7,8-PCDF. These compounds were present in suspended sediment from HCE at concentrations of 40, 11, 1.4 and 2.7 pg/g respectively. Concentration of 2,3,7,8-TCDF in river suspended sediment increased from 0.3 pg/g upstream from the mill to 2.5 pg/g downstream. Calculated as Toxic Equivalents (TEQ), the HCE carried a total of 22 pg TEQ/g while the upstream and downstream suspended sediment samples were 0.9 and 1.4 - 2.0 pg TEQ/g respectively. There was no apparent effluent-related increase in concentrations of the higher chlorinated dioxin and furan congeners like octa- and heptachlorodioxin and furan. Analysis of the clay-silt fraction of the depositional sediments revealed lower but still detectable concentrations of 2,3,7,8-TCDD and TCDF at most downstream sites.

Brownlee *et al.* (1996) discussed both the RSS depositional sediment results and the results of analysis of the AEP archived sediments. The congeners most frequently detected were 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDD and OCDD. Concentrations of 2,3,7,8-TCDF were elevated downstream from the bleach kraft mills and were suggested as good markers for geographical extent of bleach kraft mill effluent impacts. Interestingly, in the Athabasca River, the highest concentrations were observed at sites more than 100 km downstream from the mill. Concentrations in the Peace River system were higher downstream from the Peace-Smoky confluence than they were in the Wapiti River near the mill. The reasons for this distribution are not clear. It is tempting to speculate that this distribution is indicative of seasonally-related sediment deposition and resuspension down the river. If that were the case, the lower concentrations near the mill would be the result of the recent changes to the bleaching process and the downstream maxima would be related to historical discharges. Alternately, this distribution could be the result of in-stream sediment processing producing enriched fractions downstream.

Concentrations of OCDD showed a broad distribution and no mill related increase in the Peace River system. In the Athabasca River system, concentrations of OCDD were highest in the 200 km reach downstream from the town of Hinton but persisted throughout the system, unlike TCDF which eventually returned to upstream levels. Based on these results, Brownlee *et al.* (1996) concluded that TCDF was a better sediment marker of bleach kraft mill inputs than OCDD. Pastershank and Muir (1995) reported levels of lower chlorinated dioxins and furans in suspended and depositional sediments from the RSS. Concentrations of lower chlorinated dioxins were low compared to the chlorinated furans. Total mono-, di- and trichlorodibenzofurans concentrations were 39, 110 and 39 pg/g (dry weight), respectively, compared to not detected (nd), 22 and 1.5 pg/g for the corresponding dioxin congener groups. This was considerably higher than the total tetrachlorodibenzofurans and dioxins that were 10 and 1 pg/g dry weight respectively.

Congener profiles for three sediment samples are presented in Figure 5. The profile for HCE demonstrates the profile expected for a combination of bleached kraft mill effluent and municipal effluent profiles shown in Figure 3. The river profile from Obed, downstream form

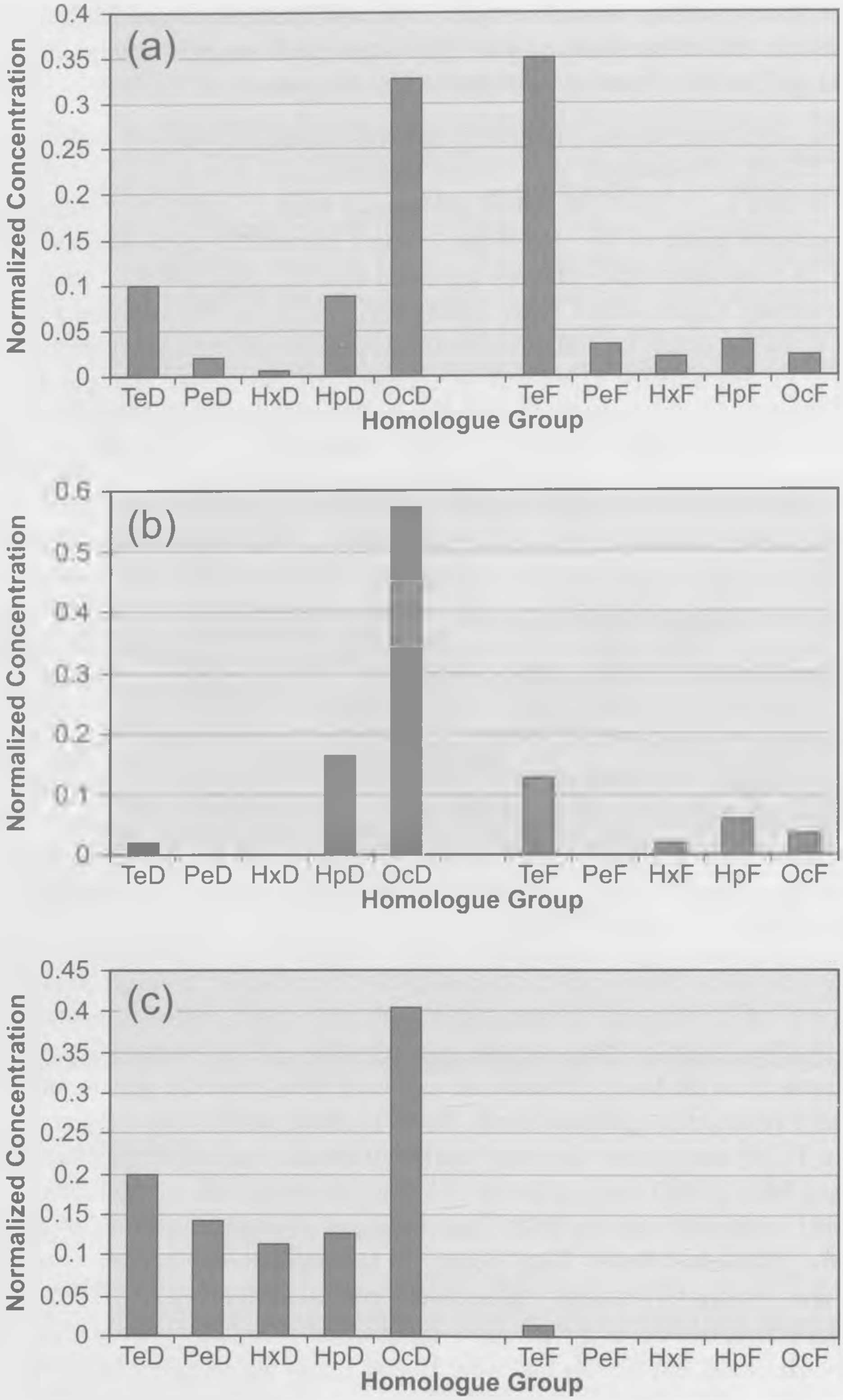

Figure 5. TCDD/TCDF congener profiles for: (a) suspended solids in Hinton Combined effluent; (b) bottom sediment from the Athabasca River near Obed; and (c) surface sediment from Lake Athabasca.

Hinton, and the Lake Athabasca profile are more indicative of PCP-related sources since TeCDF and PeCDF, which are the main contributors to the BKME and combustion profiles, are minor contributors to the dioxin profiles at these sites.

In general, chlorophenolics were not widespread sediment contaminants in either of the sediment surveys. This is not surprising since most chlorophenolics are very water soluble and most are ionised at ambient pH. These properties do not favour partitioning to sediments. Non-detectable results were also obtained for organochlorine pesticides on suspended sediments.

Resin acids were present at significant concentrations in both suspended sediment and depositional sediment from the RSS (Crosley 1996a). The highest concentrations of total resin acids were 10 μg/g for suspended sediments and 3.5 μg/g for depositional sediments and occurred from 19 to 50 km downstream from the mill. These concentrations were approximately 50x higher than the reference sites. Pimaric acid and dehydroabietic acid were predominant in both sediments. Concentrations of chlorinated resin acids at the sites downstream from the mill were approximately 400x higher than at the upstream reference site. Distributions of resin acids were generally similar, peaking within 50 km downstream from the mills. The results of the analyses of archived basin-wide sediments from 1988-1990 were in good agreement with these results (Brownlee *et al.*1996b). Chlorinated resin acids appeared to be excellent markers to determine the geographical extent of sediment contamination by kraft mill effluent.

The reason sediment-bound chlorinated resin acids peaked in concentration much closer to the mills than chlorinated dibenzofurans when both are present in the mill discharge on suspended solids is not obvious. Brownlee *et al.* (1996) conducted correlation analyses to determine if the concentrations of chlorinated dioxins/furans and those of resin acids were related. Although there was a correlation between the chlorinated and non-chlorinated resin acids, suggesting they all originated at the pulp mills, there was not correlation between the TCDF and the resin acid families. This was surprising since the principal source of both TCDF and chlorinated resin acids in the system appeared to be bleached kraft pulp mills, but it was consistent with the geographical distributions. The TCDF concentrations peaked 200-300 km below the kraft pulp mill discharges whereas the resin acid concentrations peaked maximum of 50 km downstream. Possible explanations for this lack of correlation include rapid degradation of the resin acids or some sort of physical separation based on sediment dynamics. The latter explanation could only be valid if the resin acids and the TCDF were bound to different types of particles.

The results of the preliminary sediment surveys indicated that sediment contamination by pulp mill-related contaminants persisted as much as 300 km downstream from the mills. In addition, there were some unknown factors controlling geographical distributions of sediment-associated pulp mill-related contaminants. With respect to choice of suspended or depositional sediment for a subsequent basin-wide survey, there were pros and cons for either choice. Suspended sediments were an important transporting medium for most of the contaminants analysed with concentrations in suspended sediment generally several orders of magnitude higher than in water. However, the collection method is labour-intensive, the centrifuges are heavy, making them difficult to maneuver at remote sites away from roads, 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 lack of knowledge of the effects of seasonally-dependent flows. Although concentrations of contaminants found in depositional sediments were generally lower than found in suspended sediments possibly making analysis problematic, a number of factors favor the use of depositional sediments in basin-wide surveys. These include 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. However, attention must be paid to 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.

The results of the preliminary sediment surveys indicated that suspended sediments were an important transporting medium for most of the contaminants analysed with concentrations in suspended sediment generally several orders of magnitude higher than in water. However, the collection method is labour-intensive and collection of adequate sample size throughout the basin was likely impractical during important low discharge periods. Concentrations of contaminants found in depositional sediments were generally lower than found in suspended sediments possibly making analysis problematic, but 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 were convincing factors. As a result of the preliminary surveys, we concluded that the most appropriate abiotic compartment for a basin-wide survey of contaminant distribution was the fine silt-clay fraction of bottom sediments.

3.2.2 Basin-Wide Survey of River Bottom Sediments

After we concluded that the most appropriate abiotic compartment for a basin-wide survey of contaminant distribution was the fine fraction of bottom sediments, a basin-wide bottom sediment survey was designed and carried out in 1994 and 1995. The sampling design, analytical protocols and results of the 1994-95 sediment surveys are reported by Crosley (1996b). Sampling locations were chosen to provide broad geographical coverage of both the Athabasca and Peace River basins, especially the mixing zones below the four bleached kraft pulp mills, and also to coincide with sites sampled previously. In 1994, composite sediment samples were obtained from ten depositional areas in the basins comprising one site on the Wapiti River near its confluence with the Smoky River, one site on the Smoky River, and four sites each on the Peace and Athabasca River mainstems. One of these sites, the Peace River downstream from the Daishowa pulp mill, was intensively sampled. In 1995, five sites were intensively sampled, one each on the Wapiti and Peace rivers and three on the Athabasca River. The sampling locations and type of samples collected are listed in Table 6.

Table 6. **Sampling locations and sample types for the 1994-95 basin-wide bottom sediment survey (Crosley 1996b).**

Sampling Location	Year	Number and Type of Samples
Peace River Basin		
Wapiti River near mouth	1994	3 replicate composites
	1995	10 discrete areas
Smoky River near mouth	1994	3 replicate composites
Peace River u/s Smoky River	1994	3 replicate composites
Peace River d/s Daishowa	1994	10 discrete areas
Peace River u/s Notikewan River	1994	3 replicate composites
Peace River d/s Fort Vermilion	1994	3 replicate composites
	1995	10 discrete areas
Athabasca River Basin		
Athabasca River u/s Hinton	1995	10 discrete areas
Athabasca River near Emerson Lakes	1995	10 discrete areas
Athabasca River u/s Lesser Slave River	1994	3 replicate composites
Athabasca River d/s AlPac	1994	3 replicate composites
	1995	10 discrete areas
Athabasca River u/s Horse River	1994	3 replicate composites
Athabasca River u/s Fort McKay	1994	3 replicate composites

After the sediment composition was characterized and resin acids were analysed as a screening parameter to select representative samples from each site for contaminant analysis, selected samples were analysed for PAHs, CPs, PCDDs/PCDFs, PCBs, OCs, extractable organic chlorine (EOCl) and mercury. Concentrations, geographical distributions and within-site variability of contaminants found in the 1994-95 basin-wide sediment survey are reported in Crosley (1996b).

Resin acids were found at detectable levels throughout the basins. The geographical distribution of total resin acids is shown in Figure 6 (Crosley 1996b). In the Athabasca River samples, the highest resin acid concentrations were found in the Emerson lakes sample, the closest downstream sample to Hinton. Concentration of total resin acids at this site were 1,818 ng/g, a significant increase from the concentration of total resin acids in the upstream control of about 100 ng/g. Total resin acid concentrations at the five sites downstream from Emerson Lakes ranged from 255 to 529 ng/g.

In the Peace River system, the highest concentrations were found at the furthest upstream site on the Peace River. At this site, upstream from the Smoky River confluence, concentrations of total resin acids were 3,175 ng/g. Concentrations along the Peace River decreased steadily from this site to Fort Vermilion where they were about 800 ng/g, approximately twice the

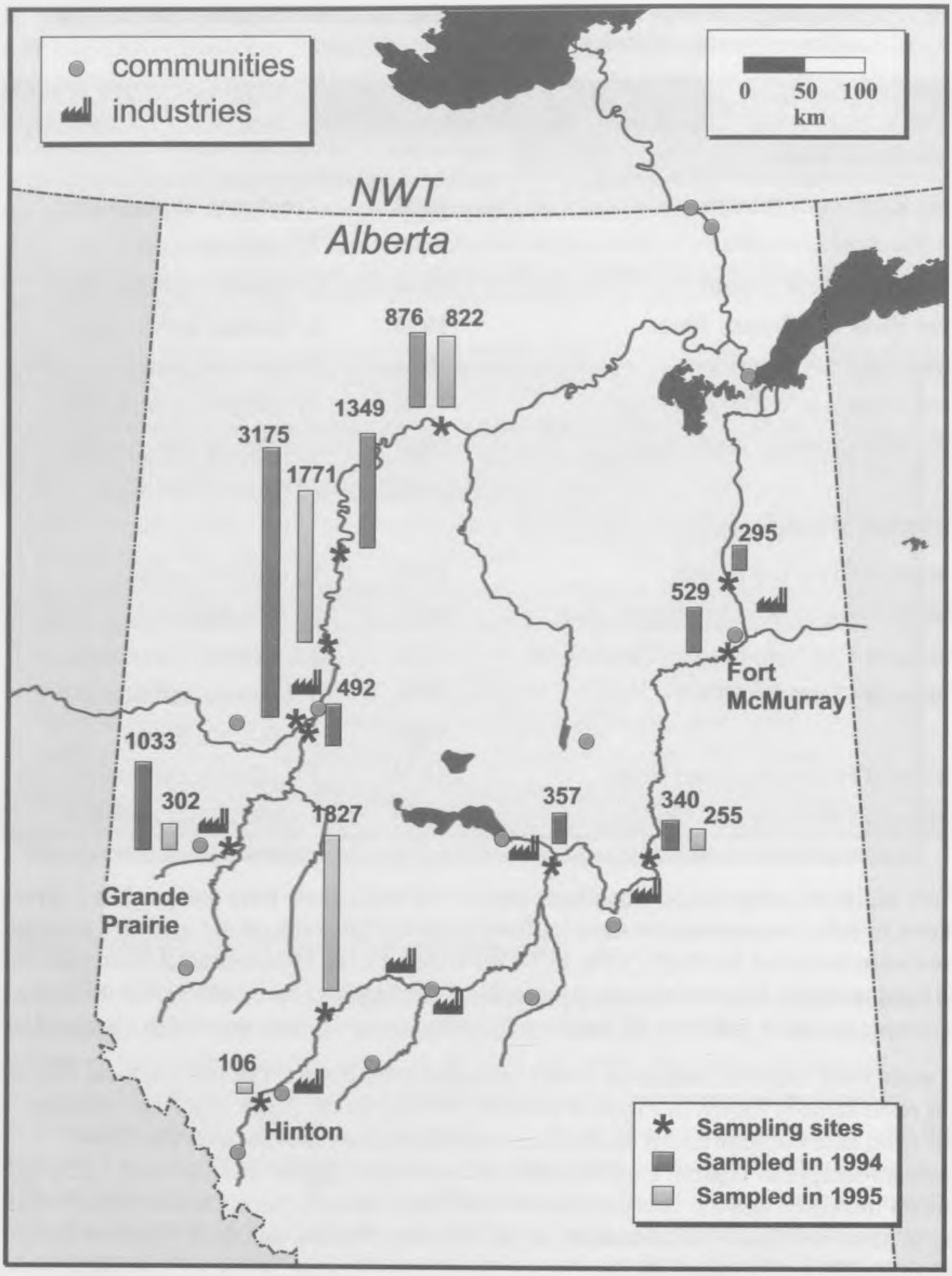

Figure 6. Geographical distribution of total resin acids (ng/g dw) in the fine sediment fraction of depositional sediment from the 1994-95 basin-wide sediment survey (Crosley 1996b).

concentration found in the lower Athabasca River. Along the Smoky River, concentrations were highest in 1994 at the Wapiti River-Smoky River confluence. This was the downstream site closest to Grande Prairie. However, concentrations in the Smoky River at its confluence with the Peace were the lowest in the survey, suggesting that the Grande Prairie mill is not as significant a source of resin acids as the source upstream on the Peace. The identity of this source is not known. Although resin acids can be found in pulp mill effluents, they are naturally occurring compounds that can be released from trees when they decompose. Unlike non-chlorinated resin acids, chlorinated resin acids do not occur naturally in significant concentrations and are often considered markers of effluents from mills using chlorine bleaching. The geographical distribution of total chlorinated resin acids in the system differed from that of the non-chlorinated resin acids (Crosley 1996b). In contrast to the non-chlorinated resin acids, the chlorinated resin acids were present at highest concentrations in the Athabasca River system (Figure 7). The highest concentration was observed downstream from Hinton, suggesting that this mill is the main source. Interestingly, increases in chlorinated resin acids were not seen in the sediments downstream from AlPac and Daishowa and were present at significant levels downstream from Grande Prairie in 1995 but not 1996. In addition, chlorinated resin acids were not detected in the sample from the Peace River upstream from the Smoky River that had the highest concentrations of non-chlorinated resin acids. This suggests that the source of resin acids upstream on the Peace River is not a bleached kraft mill.

PAHs were also widely distributed in both river systems (Crosley 1996b). The geographical distribution of total PAHs is shown in Figure 8. In the Athabasca River, PAHs occurred at similar levels from the control site upstream from Hinton to the reach below AlPac, suggesting that the pulp mills along the Athabasca are not sources of these compounds. Concentrations of PAHs increased at the two sites furthest downstream, with higher concentrations found above Fort McMurray. This suggests that there are natural sources of PAHs in the lower Athabasca River, and indicates and that these sources are more significant than the oil extraction industries in that part of the river. In contrast, the upstream sites on the Peace system had higher concentrations than the downstream sites. The concentrations at the downstream sites, from the Smoky River mouth to downstream from Fort Vermilion, were similar and were comparable to the downstream concentrations on the Athabasca River. Common PAHs were perylene, retene, phenanthrene and alkyl-substituted phenanthrenes, all of which are naturally occurring.

The concentrations of PCDD/PCDFs in these sediments were very low (Crosley 1996b). Total PCDD/PCDFs on the Athabasca River ranged from a low of 34.2 to a high of 64.4 pg/g among the sites, including the upstream control. On the Peace River system, concentrations of total PCDD/PCDFs ranged from 17.6 to 38.6 pg/g. The most commonly detected congeners were octachloroDD/DF, a heptachlorodioxin and 2,3,7,8-TCDF. The results suggest that 2,3,7,8-TCDF was mainly from BKM sources. However, OCDD results may indicate a significant atmospheric component given its widespread detection at sites far from BKM and STP emissions.

Concentrations of chlorophenolics were very low but detectable at most sites in the basin-wide sediment survey (Crosley 1996b). The highest concentrations were in the Athabasca River sediment from the site downstream of Hinton (44 ng/g) while the second highest in the survey were found at the Wapiti River mouth (35 ng/g). Concentrations in the lower parts of both rivers mostly ranged from about 5 to 20 ng/g. Mono- and dichlorinated chlorophenolics predominated in

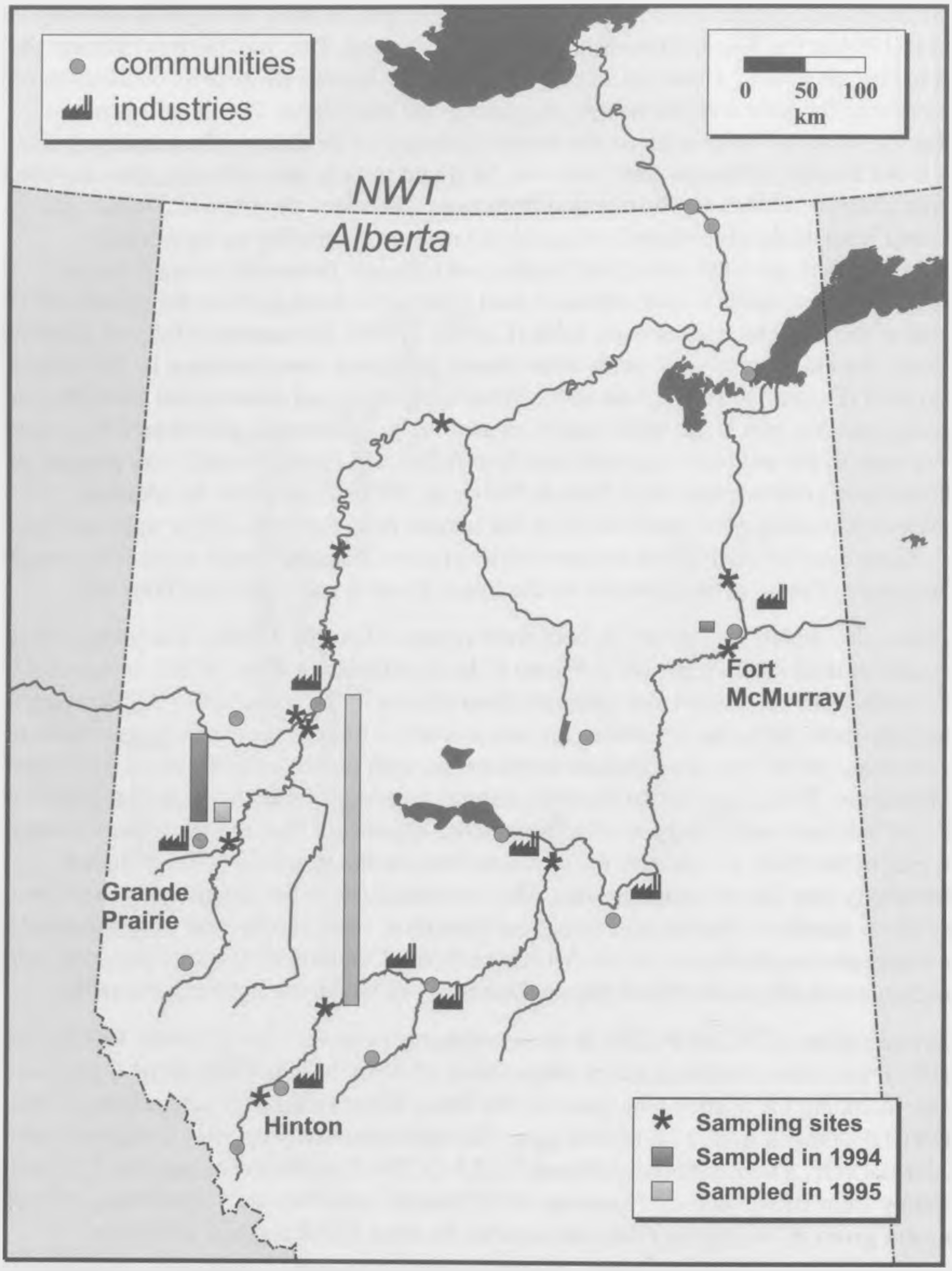

Figure 7. Geographical distribution of total chlorinated resin acids (ng/g dw) in the fine sediment fraction of depositional sediment from the 1994-95 basin-wide sediment survey (Crosley 1996b).

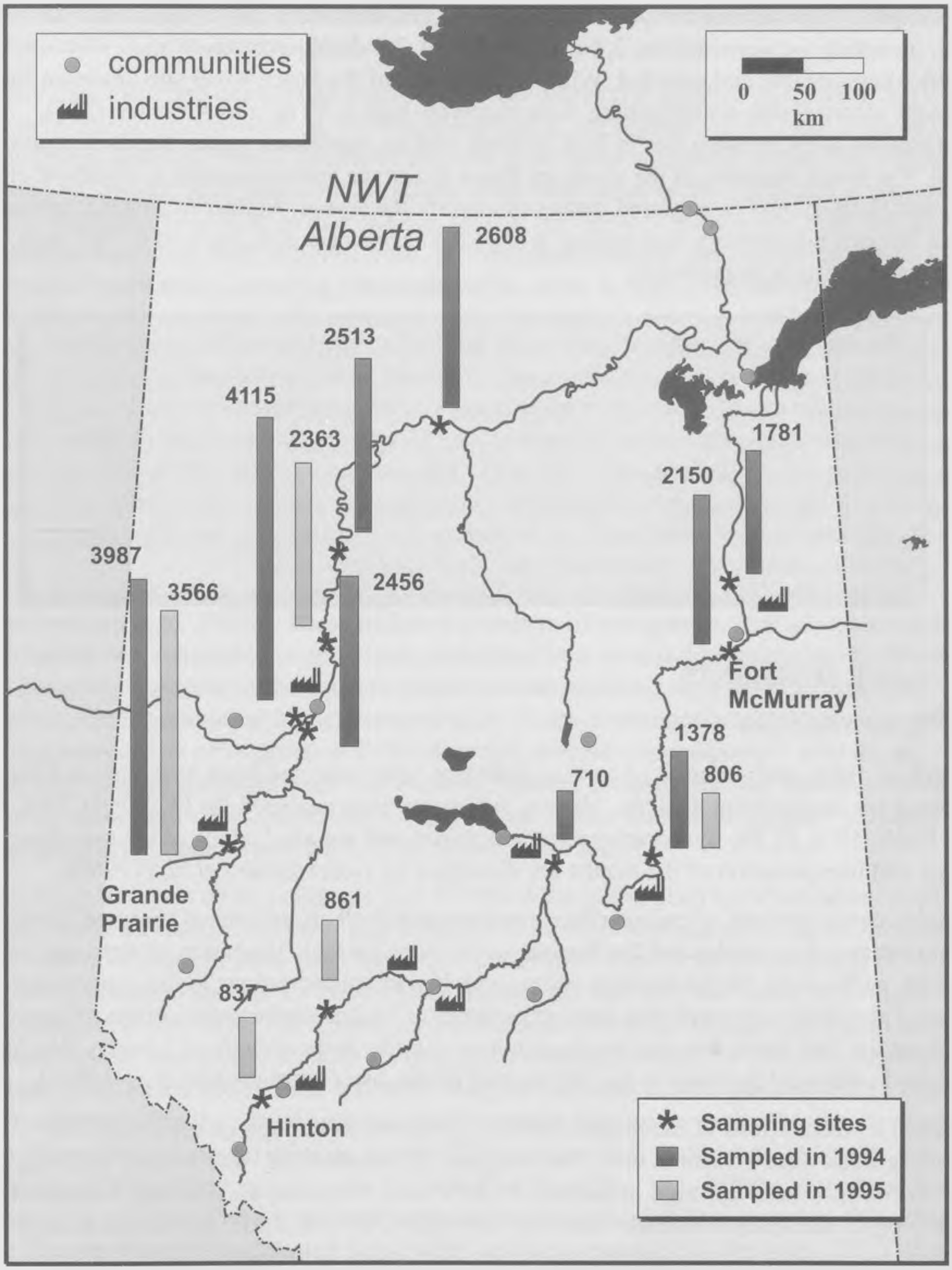

Figure 8. Geographical distribution of total PAH (ng/g dw) in the fine sediment fraction of depositional sediment from the 1994-95 basin-wide sediment survey (Crosley 1996b).

these samples. Predominant compounds included several consistent with a bleached kraft mill source, including 6-chlorovanillin, 2,4-dichlorophenol, 3,4-dichlorocatechol, and 3,4,5-trichloroguaiacol and catechol. With the exception of the Peace River site upstream from the Smoky River where concentrations were relatively high (~50 ng/g as Arochlor 1254), concentrations of PCBs were low in both systems with no significant spatial trends (Crosley 1996b). The levels observed at the upstream Peace River site are comparable to threshold effects levels and likely should be explored further to identify the source. Neither toxaphene, extractable organic halogen nor mercury was present at any sites above detection limits of 0.1-0.7 ng/g, 1.5 µg/g and 0.1 µg/g respectively.

The results of the sediment survey did not indicate widespread contamination of the northern river basins by significant levels of anthropogenic contaminants. Bleached kraft mills in the system contributed detectable concentrations of chlorinated resin acids, chlorophenols, and TCDD/TCDFs. Diffuse, presumably natural sources of PAHs and resin acids contributed detectable levels of these compounds throughout the systems. The results suggested that attention needs to be paid to the upstream reaches of the Peace River to identify the sources of PCBs, PAHs and resin acids.

3.3 LAKE SEDIMENTS

3.3.1 Lake Athabasca

In March of 1992, grab samples of surface sediment were collected from nine sites in Lake Athabasca for contaminant analysis. Various sediments were analysed for PCDDs/PCDFs, resin acids, PAHs, OCs, PCBs, hydrocarbons, radionuclides and metals. Details of the sampling, analysis and interpretation of the results are described by Bourbonniere *et al.* (1996b).

Detectable concentrations of radionuclides were present in all six sediments analysed. Both the uranium series radionuclides and the thorium series were present. There was an apparent west to east trend, particularly for the uranium series, with higher concentrations in the easternmost samples. The results suggested that there are sources of background uranium series radionuclides throughout the lake basin, but that uranium mining activity in the vicinity of Langley Bay had contributed additional loadings to the eastern part of the lake (Bourbonniere *et al.* 1996b).

Detectable concentrations of members of all five of the tetra- through octachloro PCDD congener groups were present at each site analysed. Concentrations were in the 1 to 25 pg/g range. In contrast, tetra- through octachloro PCDFs were present at much lower concentrations (ND to 2 pg/g) and many congeners were not detected at several sites. OCDD was present at highest concentrations. There was no noticeable relationship between PCDD/PCDF concentrations and proximity to the Athabasca River since differences between sites were not readily apparent. The distribution among congener groups was also relatively constant. As shown in Figure 5, the congener pattern did not have a prominent bleached kraft mill signature; the pattern most closely resembled that seen for pentachlorophenol with a probable smaller contribution from combustion sources. The PCDD/PCDF results did not support the suggestion that the bleached kraft pulp mills in the upper Athabasca River were major contributors of contaminants to Lake Athabasca.

Resin acids, including chlorinated resin acids, were detected at all sites analysed along the west-east transect (Bourbonniere *et al.* 1996b). Surprisingly, the highest values were observed at the westernmost and easternmost sites with the sites in between noticeably lower. The westernmost site had the highest resin acid concentrations. High resin acids at the westernmost site are readily explained as indicative of a riverine source, but the easternmost site is an area of permanent deposition well removed from the immediate effect of the Athabasca River. The presence of resin acids, including chlorinated resin acids, at high levels at this site is unexplained. Some sort of sediment fractionation involving a fraction enriched in resin acids relative to the other unenriched fractions is one potential explanation. Nevertheless, the high levels of resin acids at the site most susceptible to riverine influence is highly suggestive that pulp mill contaminants from this family are reaching the lake. This suggestion is supported by the detectable levels of chlorinated resin acids since these compounds do not occur naturally at high levels but are produced in pulp bleaching with chlorine. Their presence likely indicates that bleached kraft mill contaminants from the mills on the upper Athabasca River do contribute some contaminants to Lake Athabasca.

Eleven PAHs were observed in Lake Athabasca sediments along the west-east transect (Bourbonniere *et al.* 1996b). These included members of two groups. One group, comprising naphthalene and substituted naphthalenes, exhibited west to east decreasing trends. These PAHs are commonly observed in the aqueous phase in areas receiving significant hydrocarbon pollution. Their presence at higher concentrations in the westernmost samples is suggestive of a riverine source. The other group of PAHs detected, comprising compounds with higher molecular weights and more rings like fluorene, pyrene, benzopyrene and benzofluoranthenes, are often associated with combustion sources. These higher molecular weight PAHs exhibited no geographical trends, consistent with an atmospheric source.

Long-range transport of air pollutants (or LRTAP) is the mechanism by which atmospheric contaminants are transported very long distances to be deposited and affect the environment thousands of kilometres away from the source of the emissions. From investigation of lake sediments, chemical species are known to be transported into the river basins of northern Alberta via atmospheric pathways. The Atmospheric Environment Service (AES) Lagrangian back trajectory model was used to identify the potential atmospheric routes for airborne contaminants to the basin (McDonald 1996). Back trajectory analysis indicates that the possible source areas are more wide-spread in the closed water season than in the open-water season as may be expected from climatology. Although there are subtle differences between the seasons, generally, the greatest frequency of air passages are from the northern Pacific Ocean (30 to 40%) and western North America (50 to 65%). There is no direct transport from Mexico or South America, little transport from Europe (0 to 1 %) and central Asia (0.5 to 0.7%) or eastern North America (2 to 3%), but more transport from eastern Asia (3 to 4%) including Japan, China and northern Russia.

The suggestion that the most frequent air passage was from western North America is consistent with the observation that the major PCDD/PCDF congeners were PCP related. This compound was widely used as a fungicide for short-term wood protection in Canada, particularly in western British Columbia. It is known that formulations of this fungicide used in the 1970s and early 1980s contained significant quantities of chlorophenoxy-phenols, sometimes called pre-dioxins. These substances can readily form dioxins during low temperature combustion such as occured in teepee burners in former times.

3.3.2 Great Slave Lake

The watershed of Great Slave Lake includes the entire Northern River Basins Study area. Although the distances are very great between the lake and developments in the south, Great Slave Lake receives nearly 90% of its annual inflow from the Peace/Athabasca/Slave River systems. In addition, the lake is very deep and permanent sedimentation certainly occurs there. This means that even a contaminant present at a very low concentration could still be significant to the lake ecosystem. We wished to obtain information on organic contaminants in Great Slave Lake that might be related to river inflow and to evaluate the potential role of the riverine system as a source of organic contaminants to the lake. Therefore, a study of contaminants in Great Slave Lake was carried out in partnership with the Arctic Environmental Strategy Program of the federal government.

In August, 1993, surficial sediments were collected at a series of 10 sites in the west basin of Great Slave Lake in the vicinity of the Slave River outflow. The system was resampled in 1994 and again in 1995 (Evans *et al.* 1996). Sediments were analysed for 130 individual organochlorines, including 90 individual PCB congeners, and PAHs. Results of these analyses are reported by Evans *et al.* (1996). Concentrations of organochlorines detected in this study were very low and comparable to other arctic and subarctic lakes not influenced by anthropogenic discharges. PCBs were the predominant organochlorine followed by chlorobenzenes, DDT, hexachlorocyclohexanes and dieldrin. Since there was no apparent spatial relationship to the Slave River discharge, it is presumed that the source of these substances to the lake was atmospheric. The compounds detected are all common atmospheric pollutants throughout the northern hemisphere and are known to be deposited in aquatic systems via LRTAP. PAHs were very abundant and dominated by combustion-related compounds also known to be atmospherically transported. Extremely low concentrations of PCDD/PCDFs were detected, dominated by OCDD along with dichloro-dioxins and di- and trichloro-furans. The only compounds detected suggestive of a potential pulp mill source were tri and tetrachloroveratroles. These compounds are known to be produced in sediments from methylation of chloroguaiacols, the most common chlorophenolic discharged from bleached kraft mills in the days when chlorine was used in the bleaching process.

The contaminants in Lake Athabasca sediments revealed a much lower pulp mill signature than expected and the data suggested that atmospheric sources of contaminants could be the main contaminant sources to this part of the Northern River Basins. Although there were indications that the rivers carried significant percentages of total contaminant loadings to the lake, there was minimal indication that Great Slave Lake receives significant loading of effluent-related contaminants via the Northern River Basins. Long-range transport of atmospheric pollutants was a more significant contaminant source than anticipated at the start of the study.

3.4 RIVER BIOTA

Just as there was not enough information available at the start of the study about contaminant levels in abiotic compartments to choose a compartment for the basin-wide survey, the same was true of biotic compartments. There was not enough information available to us at the start of the study on availability and distribution of potential bioindicator fish species and their mobility, nor was there enough information on contaminant concentrations in these species to allow us to assess their bioaccumulation potential for contaminants. There was even less known about the distribution and contaminant concentrations of aquatic invertebrates and other biota. To provide preliminary information upon which we could base a choice of biomonitor, a number of preliminary studies were conducted to generate an information base that would permit us to chose a suitable bioindicator species.

Three related studies were conducted with the general objective of determining spatial and, in some cases, temporal contaminant trends in fish. The most intensive was the Reach Specific Survey (RSS). Fish samples for the RSS were collected in the spring and fall of 1992 from the upper Athabasca River between Jasper National Park and the Windfall Bridge upstream from Whitecourt. There were six sites for the collections, one site upstream and five sites downstream from Hinton. Details of the collections are presented in Barton *et al.* (1993a and b).

In the spring collection, the original plan to collect 10 fish of the largest size class for each species was thwarted by low fish numbers throughout the system (Barton *et al.* 1993a). Therefore, sampling focused on collecting mature adults. For the most numerous benthivorous fish species, the mountain whitefish (*Prosopium williamsoni*), 10 adult fish were collected at each site. For the most numerous piscivore, northern pike (*Esox lucius*), the desired number was obtained at only the two most downstream sites. Numbers at the other sites varied from 0 to 2 for the downstream sites to 6 at the upstream site. Extra effort to obtain more fish was unsuccessful. At least part of this nonhomogeneous distribution may have been due to differences in habitat. In the fall of 1992, fish were collected from the same sites as the spring survey, i.e. one site upstream and five sites downstream from Hinton (Barton *et al.* 1993b). The results paralleled the spring survey. Fish were not sufficiently numerous at any of the sites to follow the original plan to obtain 10 samples of the largest size or age class. Sampling again focused on collecting 10 samples of adult fish of each species. Sufficient numbers of mountain whitefish were collected at all six sites but sufficient numbers of northern pike were caught only at the sites farthest downstream. Additional mountain whitefish were collected in 1993 from the upstream site and three sites downstream between Hinton and the Emerson Lakes Road bridge.

The analytical results for contaminants in fish collected in the RSS surveys are summarised by Pastershank and Muir (1996). Mountain whitefish and northern pike from the spring 1992 RSS collection were analysed for PCBs, chlorinated phenolics and organochlorine pesticides, while in the fish from the fall collection, only PCBs and OCs were analysed. Mountain whitefish collected in 1993 were analysed for PCDD/PCDFs only. On a wet weight basis, PCBs were the major organochlorines detected followed by OCs and then CPs. Relative to the concentration of total PCBs in fish from the upstream site (11 ± 7.3 ng/g), concentrations of total PCBs in the reach between Hinton and Windfall were elevated by a factor of about 2 to 3 fold. There was a high variance among the results that made it difficult to detect statistically significant differences and spatial trends in these small sample sizes. There was a difference between species, with mountain whitefish accumulating approximately twice the PCB concentrations as northern pike at both the upstream reference site (11.7 ± 7.3 vs 4.5 ± 2.8 ng/g) and the downstream sites. Organochlorine pesticides were detected in both species at the upstream and downstream sites at low concentrations. The spatial distribution was not consistent with a pulp mill source. For example, the highest concentrations of total chlordane, DDT and related compounds, and toxaphene in both species in the spring collection were seen at the upstream site. There was also no significant difference between sites for PCP concentrations. Apart from two mountain whitefish with detectable concentrations of 3,4,5-trichloroguaiacol, chloroguaiacols and lower chlorinated phenols were not detected. The major chlorophenolics detected were tetrachloroveratrole (TCV) and pentachloroanisole. Of all compounds analysed in the fish from the RSS, TCV was the one with the clearest indication of a pulp mill source. Average concentrations of this compound in mountain whitefish muscle ranged from 3.6 to 7 ng/g in samples from the three nearest downstream sites to the mill compared to <0.4 ng/g at the upstream site.

The main PCDD/PCDFs detected in mountain whitefish and northern pike muscle from the RSS were 2,3,7,8-TCDD and 2,3,7,8-TCDF (Pastershank and Muir 1995). With a few exceptions, neither the di- and trichloro- congeners that were prevalent in the abiotic samples nor the penta- through octa- congeners were detected in these fish. Concentrations were generally higher in mountain whitefish than northern pike. In mountain whitefish, concentrations of TCDD increased from an average of 0.4 ng/g at the upstream site to from 3 to 8.5 ng/g at the downstream sites while for TCDF, concentrations increased from 0.9 upstream to a range of 3.7 to 14 ng/g at the downstream sites.

In addition to the RSS, the General Fish Collection on the Athabasca River in 1992 provided samples of walleye and goldeye collected at five sites in the lower Athabasca, from 300 to 630 km downstream from Hinton. These fish had the lowest concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF of all fish species from the Athabasca River sampled in spring or fall 1992. The lowest levels of organochlorines were found in the muscle samples of the goldeye and walleye collected near the Athabasca River delta. Concentrations of all major groups of CPs, PCB homologues and OC pesticides were all <1 ng/g.

To evaluate suitability of another fish species as a potential bioindicator, an additional survey, sampling at nine sites for burbot was carried out during October and November 1992 on the Peace, Wapiti and Smoky Rivers (Hvenegaard and Boag 1993). The concentrations of PCBS, CPs and OC pesticides observed in liver from these burbot are reported by Pastershank and Muir (1996). Concentrations were much higher than in muscle of pike, mountain whitefish and other species. This may be the result of the higher lipid content of the burbot liver relative to the other species or their trophic position as piscivores. The most commonly detected chlorophenolics in burbot liver were PCP and TCV. Similar to the spatial distribution in mountain whitefish from the Athabasca River, there was a clear indication of pulp mill source to the TCV with the highest levels seen at sites closest to the Grande Prairie and Daishowa pulp mills. The main OCs detected in these burbot livers were p,p′-DDE (dichlorodiphenyl dichloroethylene), chlordanes, toxaphene and hexachlorobenzene (HCB). Average concentrations of p,p′-DDE ranged from <0.5 to 60 ng/g and were highest at sites downstream from pulp mill/municipal effluent discharges. Average total chlordane in these fish ranged from 0.5 to 27 ng/g.

3.4.1 Basin-wide Survey of Contaminant Concentrations in Bioindicator Fish

In designing the basin wide survey, the group were faced with a problem common to many of the NRBS components, too large an area to permit intensive sampling with many replicates. While large sample numbers may have detected subtle differences in contaminant concentrations between sites, contaminant analyses can be very expensive. To conduct a basin-wide study at that level of detail would have required many more years and resources than were available for the NRBS. The group decided that since much of the public concern centred around pulp mills and their impact on the river, the study design should focus on determining whether contaminant inputs from pulp mills could be observed in aquatic biota. We grouped sites in the Peace-Athabasca-Slave system into three regional classes. These were: reference sites on tributaries or on the main stems upstream from any known sources; near-field sites, within 100 km of pulp mill discharges; and, far-field sites, more than 100 km from a pulp mill discharge. In carrying out the collections, we found that fish of the right species and size were not available at all these sites and three sites had to be resampled after the initial collections were complete. A limited number of other sites were eventually dropped for logistical reasons. The sites where fish were collected and their designations in the regional scheme are given in Table 7.

The difficulties in obtaining large enough samples experienced during the RSS fish survey had a direct bearing on the choice of fish species targeted as biomonitor species in the basin-wide survey. Ideally, a fish species used in a monitoring program should have certain characteristics that permit its use as biomonitor. Individuals of that species should be available at all sites in the study area in appropriate ages and sexes. They should be non-mobile and therefore representative of local conditions. They should be readily captured, preferably with a selective capture technique that would not also capture large numbers of unwanted and in some cases rare species. They should be a species that is known to bioaccumulate contaminants but should not be so sensitive that they are unavailable in areas receiving low or moderate levels of anthropogenic stress.

The results of the fish surveys described above indicated that for the Athabasca River, a selected fish species was often not available at many sites. There appeared to be a change in fish community between the upper and the lower reaches of the river. Adding to that complexity, the mix of species available in the Peace River appeared to be different from either the upper or lower Athabasca River. After extensive discussion, we decided that the species most closely meeting the criteria described above was the burbot. This species was relatively widely distributed and relatively easy to catch in the NRBS surveys (Hvenegaard and Boag 1993; R.L. & L. 1994a,b). The preferred method of capture, set lines, was reasonably selective for burbot; not many other fish species were inadvertently captured. Although they were known to have spawning runs in midwinter, there was no indication of high mobility so they were expected to be reasonably indicative of local or, at worst, regional conditions. They could be found in some upstream and tributary locations, so they offered the possibility of a choice of reference locations. The preliminary studies indicated that burbot feeding at the top of the food

Table 7. **Location of fish collection sites in the NRBS Basin-wide Survey indicating fields used in the statistical analysis and possible discharge sources for each site.**

Drainage/ Delta	River	Site	Field	General Location	Potential Effluent Exposure
Athabasca	Athabasca	A1a	NEAR	near highway 947 crossing	d/s from Hinton pulp mill
		A1b		near Berland River	
		A2	REF	u/s Hinton	d/s from Jasper
		A3	NEAR	near Fort Assiniboine	d/s Whitecourt pulp mills
		A4	NEAR	near the Calling River	d/s from ALPAC pulp mill
		A5	FAR	near Fort Mackay	d/s from Suncor
	McLeod	MR	REF	near Whitecourt	d/s from town of Edson
		MR2	REF	u/s from town of Edson	tributary reference, d/s from coal mines
	Pembina	P	REF	near town of Jarvie	d/s town of Barrhead, tributary reference
	Lesser Slave	LSV	NEAR	near town of Slave Lake	d/s Slave Lake Pulp
	Clearwater	CW	REF	u/s from Fort McMurray	tributary reference
Peace	Peace	PR1	FAR	near Many Islands Prov. Park	d/s from B.C. pulp mills & old refinery at Taylor
		PR2	NEAR	near the Notikewan River	d/s from Daishowa mill and Smoky River confluence
		PR3	FAR	u/s from Fort Vermilion	further d/s from Daishowa mill and Smoky River confluence
	Wapiti	WR1	REF	near Pipestone Creek Prov. Park	20 km u/s from Grande Prairie mill
		WR2	REF	near O'Brian Prov. Park	5 km u/s from Grande Prairie mill
	Smoky	SR1	NEAR	near Watino	d/s Grande Prairie mill
		SR2	REF	near Grande Cache	u/s reference, nearby coal mine & power plant
		SR3	REF	u/s from Wapati confluence	u/s reference
	Little Smoky	LSR1	REF	near highway 744 crossing	Tributary reference
		LSR2		3 km d/s LSR1	
	Wabasca	WB	REF	near highway 67 crossing	Tributary reference
Peace-Athabasca	Delta	JV1	FAR	near Jackfish Lake village	
		JV2		near Big Eddy	
Slave	Delta	SRD1	FAR	u/s from Nagle Channel	d/s from Fort Smith
		SRD2		at mouth of Nagle Channel	

chain were good general indicators of contaminant bioaccumulation. Their large fatty livers tend to accumulate high concentrations of nonpolar contaminants like certain chlorinated organics (Muir *et al.* 1990), so they offer good sensitivity for detecting contaminants. Finally, their contaminant burdens had some social significance, because both the flesh and livers are consumed by people in local communities (Balagus *et al.* 1993).

Based on these characteristics, burbot were chosen as the primary biomonitor species for the subsequent basin-wide fish survey conducted in 1994. Several alternate species were identified as potential back-ups. They were northern pike, longnose sucker and flathead chub. These species had more restricted ranges or other characteristics that made them less suitable as a basin-wide bioindicator than burbot, but were available in some areas where burbot had not been reported.

Burbot, northern pike, longnose sucker, and flathead chub were collected from mid-September to late October 1994 and in mid-December from 23 sites in the NRBS study area (Jacobson and Boag 1995). Fishing techniques included baited setlines, electrofishing, gill nets, and angling. There were nine sampling sites in the Peace River drainage visited during the fall. These included sites on the Peace, Smoky, Little Smoky, Wapiti, and Wabasca rivers. Two sites were resampled in mid-December, one on the Smoky River and one on the Little Smoky River, to try to increase the sample size. Nine sites were sampled in the Athabasca River drainage: five Athabasca River sites, the McLeod, Pembina, Lesser Slave, and Clearwater rivers. The McLeod River also was sampled in December. Fish were also collected from the Peace-Athabasca Delta and the Slave River Delta.

In total, 535 fish were caught consisting of 222 burbot, 50 northern pike, 88 longnose sucker, and 24 flathead chub. Burbot were caught at all sites sampled except the Smoky River near Grande Cache and the Peace-Athabasca Delta near Jackfish Village. Northern pike were not collected at the Wabasca, McLeod, and Lesser Slave rivers, and four of the five Athabasca River sites and were relatively scarce at the other sites sampled. Most longnose sucker were caught in the Peace, Smoky, Little Smoky, and Wapiti rivers. In the Athabasca River basin, the set line fishing method produced longnose suckers at only one site on the Athabasca River and in the McLeod River. Flathead chub were found in the Peace, Smoky, Little Smoky, and Wapiti rivers.

The results for the OC and PCB analyses of these fish are discussed in Pastershank and Muir (1996) while the PCDD/PCDF results are reported in Muir and Pastershank (1996). A summary of ranges of these compounds arranged by site group is given in Table 8. One interesting feature of the data presented in Pastershank and Muir (1996) and Muir and Pastershank (1996) is that

Table 8. Mean concentrations and ranges of selected contaminants in burbot liver from the basin-wide survey arranged by site grouping (Pastershank and Muir 1996: Muir and Pastershank 1996).

Compound	Reference Sites		Near-field Sites		Far-field Sites	
	Mean conc.	Range	Mean conc.	Range	Mean conc.	Range
PCBs*	123 (35)	7-420 (7-54)	197	88-390	118	48-180
DDE*	18 (7.5)	4-57 (4-9.5)	26	14-49	27	9-38
cis-chlordane*	3.2 (1.3)	.8-11 (.8-1.8)	7	2.3-13	7.4	1-13
dieldrin*	3.4 (2.6)	1-5.3 (1-5)	5.6	1.5-11	3.7	1-11
HCB*	2.4 (1.8)	1-3.8 (1-2.4)	6.8	4.8-13	5.7	.4-13
2,3,7,8-TCDD†	1.7 (~1)	ND-2.7 (ND-1.1)	3	1.1-10	1.4	.5-2.4
2,3,7,8-TCDF†	12.8 (2.9)	1-25.2 (1-5.2)	25	4.5-64	3.5	1.6-6.2

concentrations in * ng/g and † pg/g (non-mainstem reference sites in parentheses) for many contaminants, there appeared to be a clear difference in concentrations between fish collected at upstream reference sites and those collected on tributaries. For all contaminants listed in Table 8, the highest concentrations among the sites in the reference group were observed at mainstem Athabasca and Wapiti River sites, upstream from known discharges. In the case of total PCBs, DDE, *cis*-chlordane and 2,3,7,8-TCDF, means calculated for non-mainstem reference sites (presented in parentheses in Table 8) were significantly lower than means for the group as a whole. The concentrations of these substances observed in fish from the mainstem upstream reference sites were comparable to the downstream near-field sites. Pastershank and Muir (1996) discuss possible reasons for this difference between mainstem and tributary reference sites. The most obvious explanation is that the burbot were more mobile than expected on the main stems and that fish caught at mainstem reference sites had spent part of their lives downstream where they were exposed to contaminants. Another explanation could be related to nutrition if mainstem fish have more food choices and are generally in better condition. More lipid would mean higher contaminant concentrations on a wet weight basis.

There were two main patterns of contaminant distribution evident in the results of the basin-wide fish survey. In the first pattern, contaminants were distributed throughout the river systems in broadly comparable concentrations, although there was variability between individual sites, whereas in the second pattern, contaminant concentrations were highest at sites downstream from municipal/industrial discharges in the upper sections of both the Peace and the Athabasca River systems. DDE and chlordane are among the contaminants showing the former pattern. The range in p,p′-DDE concentrations in the 1994 burbot samples was similar to the results of the preliminary studies in 1992 where the sites were coincident. Average concentrations ranged from a low of 4 ng/g on the Clearwater River to a high of 54 ng/g on the Wapiti River. Geographical distribution of p,p′-DDE in samples of burbot liver from the basin-wide survey is shown in Figure 9. A similar geographical distribution was seen for average total chlordane (Figure 10) except that the highest concentrations were seen in fish from the Slave River delta. Average concentrations of total chlordanes ranged from 3.5 ng/g in the Clearwater to 81 ng/g in the Slave River delta samples.

Total PCBs, 2,3,7,8-TCDD and 2,3,7,8-TCDF are examples of contaminants demonstrating the second pattern of contaminant distribution. For these contaminants, concentrations were highest in fish from the upper sections of both the Peace and the Athabasca River systems. The geographical distribution of these contaminants in burbot liver is shown in Figures 11, 12, and 13. The PCB distribution (Figure 11) differs from the other two examples in that significant concentrations were found in fish from the farthest upstream sites, ie. sites upstream from all known point sources. The highest total PCB concentrations in the survey were observed in fish from the Wapiti River, upstream from Grande Prairie. In the cases of 2,3,7,8-TCDD (Figure 12) and 2,3,7,8-TCDF (Figure 13), a relationship to the BKME discharges at Hinton and Grande Prairie was indicated. In addition, TCDF concentrations in fish from the upstream site on the Wapiti River were comparable to those in fish from the site on the Smoky River, downstream from the Wapiti River confluence. This suggests that the Wapiti River fish at the upstream site had been exposed to BKME and therefore, that these fish may be too mobile to be considered representative of local conditions in some cases.

The results of the basin-wide fish survey indicated that there were at least two types of contaminant distribution evident in the northern river basins. For the contaminants showing the first distribution, concentrations were broadly comparable throughout the basin, although some site differences were evident. Since there was little relationship between known effluent discharges and the contaminants with this distribution (e.g. p,p′-DDE and cis-chlordane, are known to be atmospherically-transported) it is presumed that this distribution is mostly representative of LRTAP sources. In the second distribution pattern, contaminant concentrations were higher at sites downstream from municipal/industrial discharges in the upper sections of both the Peace and the Athabasca River systems. Contaminants showing the second distribution, including total PCBs, TCDD and TCDF, have all been associated with either municipal or bleached kraft mill discharges. Therefore, this distribution is presumed to be representative of point source discharges in the system.

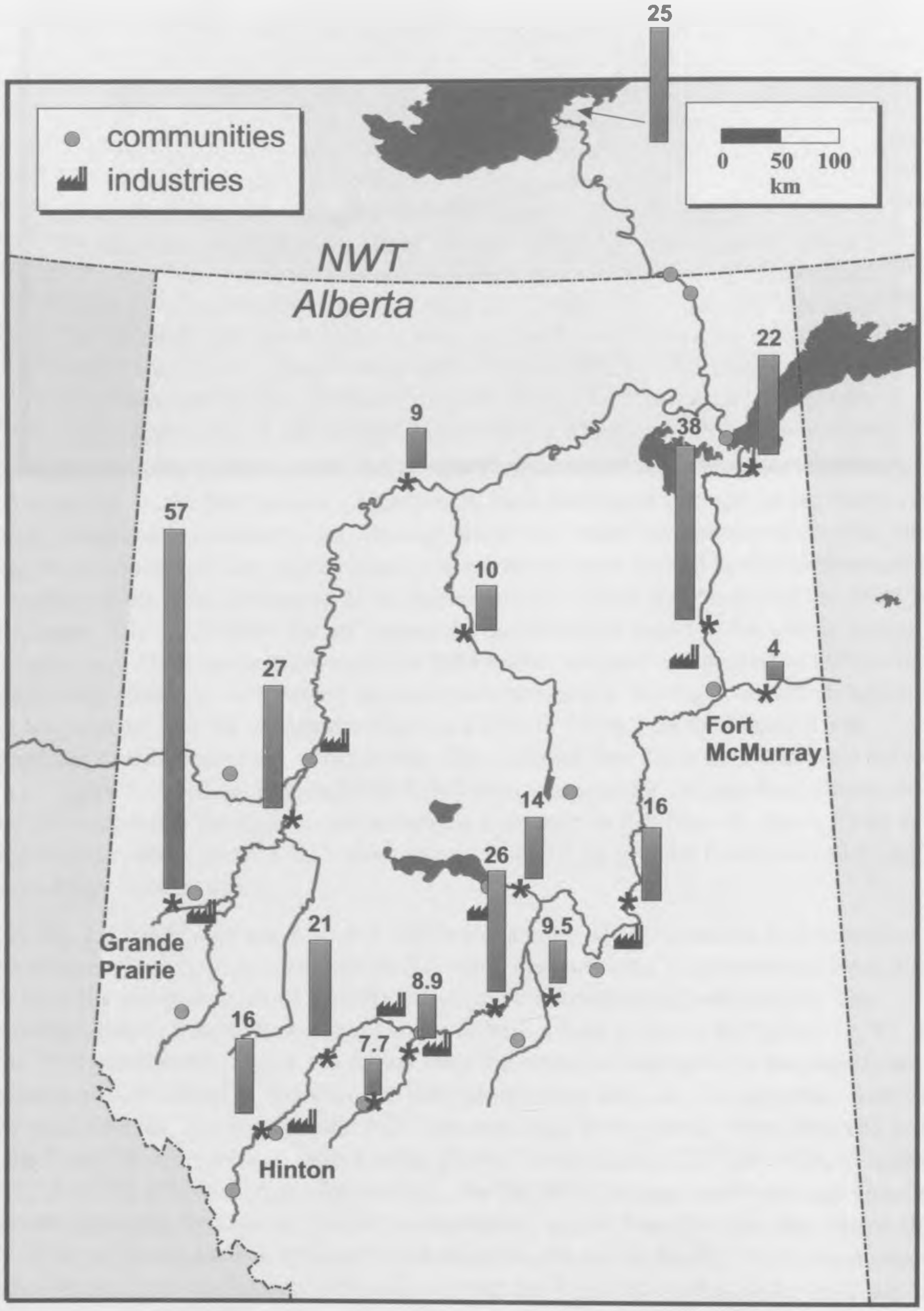

Figure 9. Geographical distribution of average p,p'-DDE concentration (ng/g ww) in samples of burbot liver from the basin-wide fish survey (Pastershank and Muir 1996).

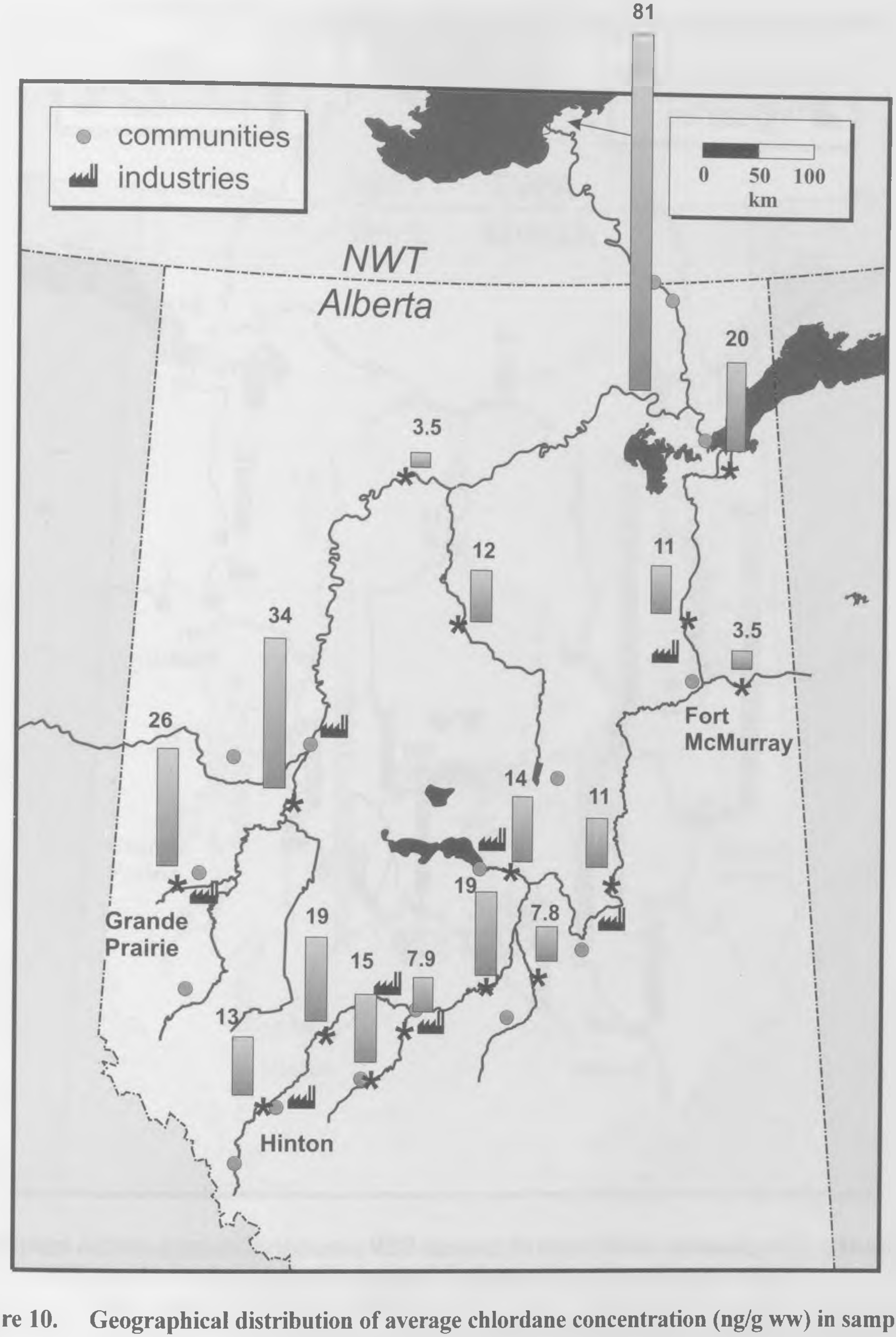

Figure 10. Geographical distribution of average chlordane concentration (ng/g ww) in samples of burbot liver from the basin-wide fish survey (Pastershank and Muir 1996).

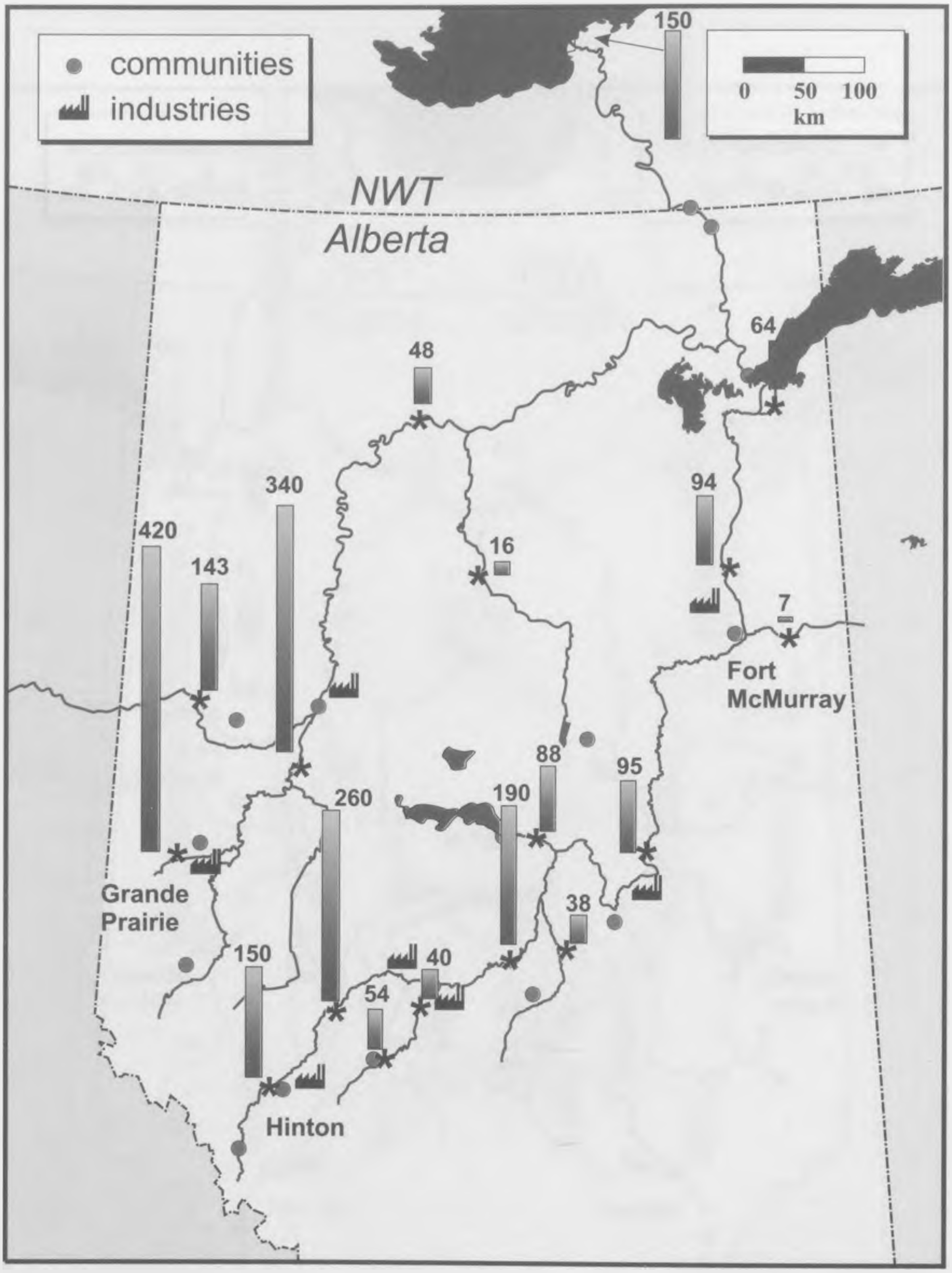

Figure 11. Geographical distribution of average PCB concentration (ng/g ww) in samples of burbot liver from the basin-wide fish survey (Pastershank and Muir 1996).

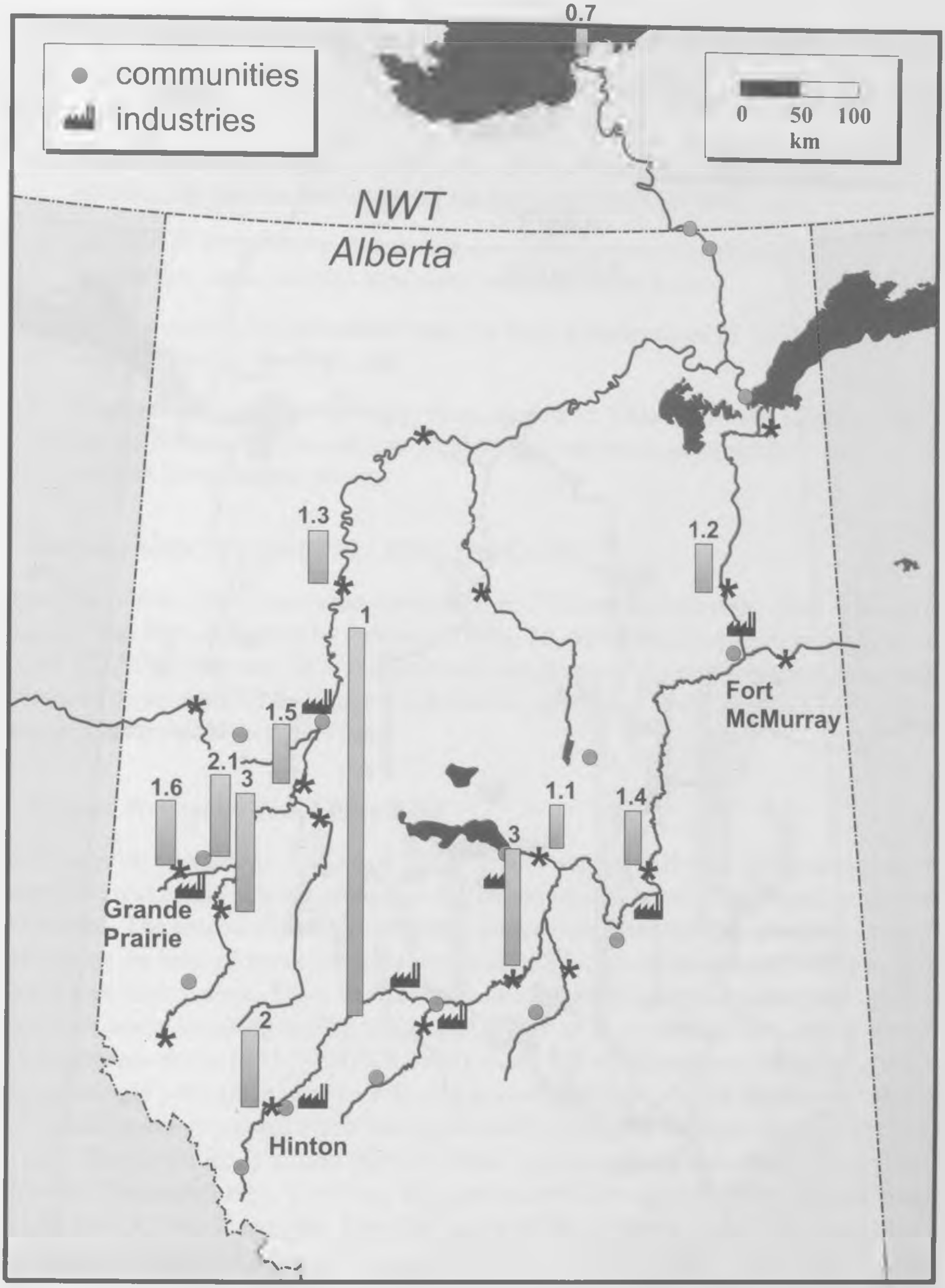

Figure 12. Geographical distribution of average 2,3,7,8-TCDD concentration (pg/g ww) in samples of burbot liver from the basin-wide fish survey (Muir and Pastershank 1996).

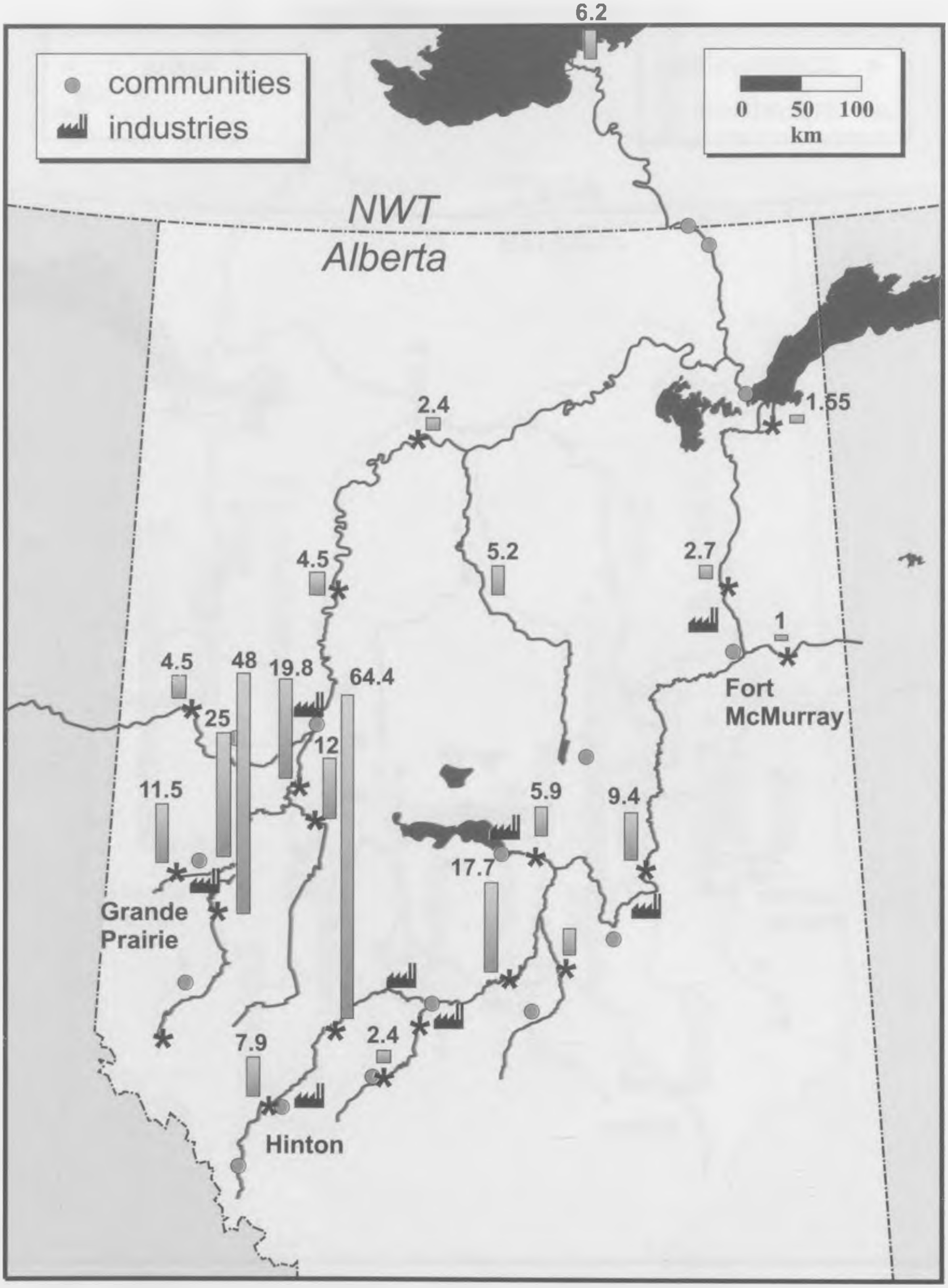

Figure 13. Geographical distribution of average 2,3,7,8-TCDF concentration (pg/g ww) in samples of burbot liver from the basin-wide fish survey (Muir and Pastershank 1996).

4.0 CONTAMINANT TRENDS IN THE NORTHERN RIVER BASINS

The Contaminants Component employed four approaches to identify trends in contaminants within the basins. These included:

- broad spectrum analysis of data on the chemical character of effluents discharging into the basins during the period of 1989 to 1994
- analysis of contaminant distribution on sediment cores from permanent desposition areas in Lake Athabasca and Great Slave Lake
- comparison of data on contaminants in biota from analysis of NRBS samples obtained during the study, and
- comparison of data obtained on contaminants in NRBS sediment samples with results of comparable analyses on historical sediments obtained from the Alberta Environment surveys.

4.1 BROAD SPECTRUM EFFLUENT ANALYSIS

The historical picture of contaminants discharged in effluents summarised below is based on the first phase of the BSA described by Johnson (1996). To aid in the interpretation of the historical picture, an historical summary of mill operations was prepared from information presented in the reviews of direct effluent dischargers (McCubbin and Folke 1993; SENTAR 1996). Results are presented on an individual mill basis.

4.1.1 Alberta Newsprint Co., Whitecourt

Alberta Newsprint operates an integrated CTMP and newsprint mill near Whitecourt, Alberta. No significant changes to the pulping process or the treatment system have been implemented since the mill started. The extended aeration activated sludge treatment (AST) system has a total hydraulic retention time of about 5 days, comprised of 2.5 days in an aeration pond and another 2.5 days in a polishing pond. There have been some changes in operations since startup. These include a pilot scale de-inking facility that began operation in November 1992 and an end to the use of polyphosphorus in 1993 (SENTAR 1995). Since the sole product of the pulping process at this mill is a single pulp grade used specifically as newsprint furnish, the degree and conditions of the chemical pulping process employed at Alberta Newsprint are milder than a conventional CTMP mill. This is the likely reason that very little organic material was observed in effluents from this mill (Johnson 1996). There was no apparent trend in the low level of organic material discharged from Alberta Newsprint. Episodic upsets of the treatment system that were observed at the two other CTMP mills were not apparent in the samples analysed for this mill.

4.1.2 Alberta Pacific Forest Industries Inc., Athabasca

Alberta Pacific commenced operations in September of 1993. Mill features include oxygen delignification and 100% substitution of chlorine dioxide. Effluent treatment includes neutralisation, primary treatment by two clarifiers which remove suspended solids and secondary treatment by an AST system and secondary clarifiers. The state-of-the-art AST system with extended aeration has two bioreactors and a hydraulic retention time of 38 hours. The effluent treatment system also contains an emergency spill pond, an equalisation/cooling pond and cooling tower. This mill was state-of-the-art when it was built during the study and it remains one of the lowest dischargers of chlorinated and non- chlorinated organics of the world's kraft mills. Only low concentrations of organics were observed in the effluent from this mill. There were no apparent trends.

4.1.3 Weldwood Pulp Ltd., Hinton

The Weldwood bleached kraft pulp mill at Hinton has been in operation since 1957 producing softwood pulp. Both the mill's production and the extent of its pollution abatement practices have changed over the years. The effluent system at start-up consisted of a 3-4 day settling basin. A diffuser was installed on the river bottom in 1966. In 1967, a mechanical primary clarifier was installed and the original settling basin was converted to an aerated stabilisation basin (ASB) with 5-day retention time. In 1975, the ASB was expanded by deepening to a 6.3 day design retention time and aeration capacity was increased. In 1978, a low-rate steam stripper was installed and, in 1979, a low odour recovery boiler was installed which improved brownstock washing and lowered liquor losses. Further process improvements during 1987 to 1989 included installation of pulp cleaners, a new brownstock screening system and reductions in chlorine use.

An expansion and modernisation project in 1989 and 1990 included installation of oxygen delignification, a new high-rate steam stripper, in-house spill recovery systems, a non-contact cooling water bypass around the ASB, and upgrading of ASB aeration. Other changes have occurred more recently. In 1993, the quiescent zone of the ASB was doubled as a means of reducing TSS discharges, which also increased BOD removal. The Hinton mill also began using 100% chlorine dioxide substitution in June 1993, eliminating the use of elemental chlorine in their bleaching process. In 1994, recycling of approximately 40% of mill contaminated condensates commenced. Although the production capacity of the mill doubled after 1990, the 1994 BOD discharge is less than half the 1986 level according to SENTAR Consultants (May, 1995).

The results from the analysis of effluent data for this mill conducted in the first phase of the BSA are shown in Figure 14 (Johnson 1996). Comparing the results for 1989 through 1994, it is apparent that quantities of all four groups of contaminants analysed in the BSA have decreased substantially over the years. There has been an approximately 90% decrease in chlorinated organics discharged. In the 1994 sample, the only analytically significant chlorinated organic at this mill was 1,3-dichloromethylsulfone. Discharge of terpenes, miscellaneous hydrocarbons and sulfur-containing contaminants also declined by approximately 90% over the 1989-1994 period. Nonyl phenols, that had been significant contaminants in the hydrocarbon group in 1989 were present at very low levels in the 1994 sample.

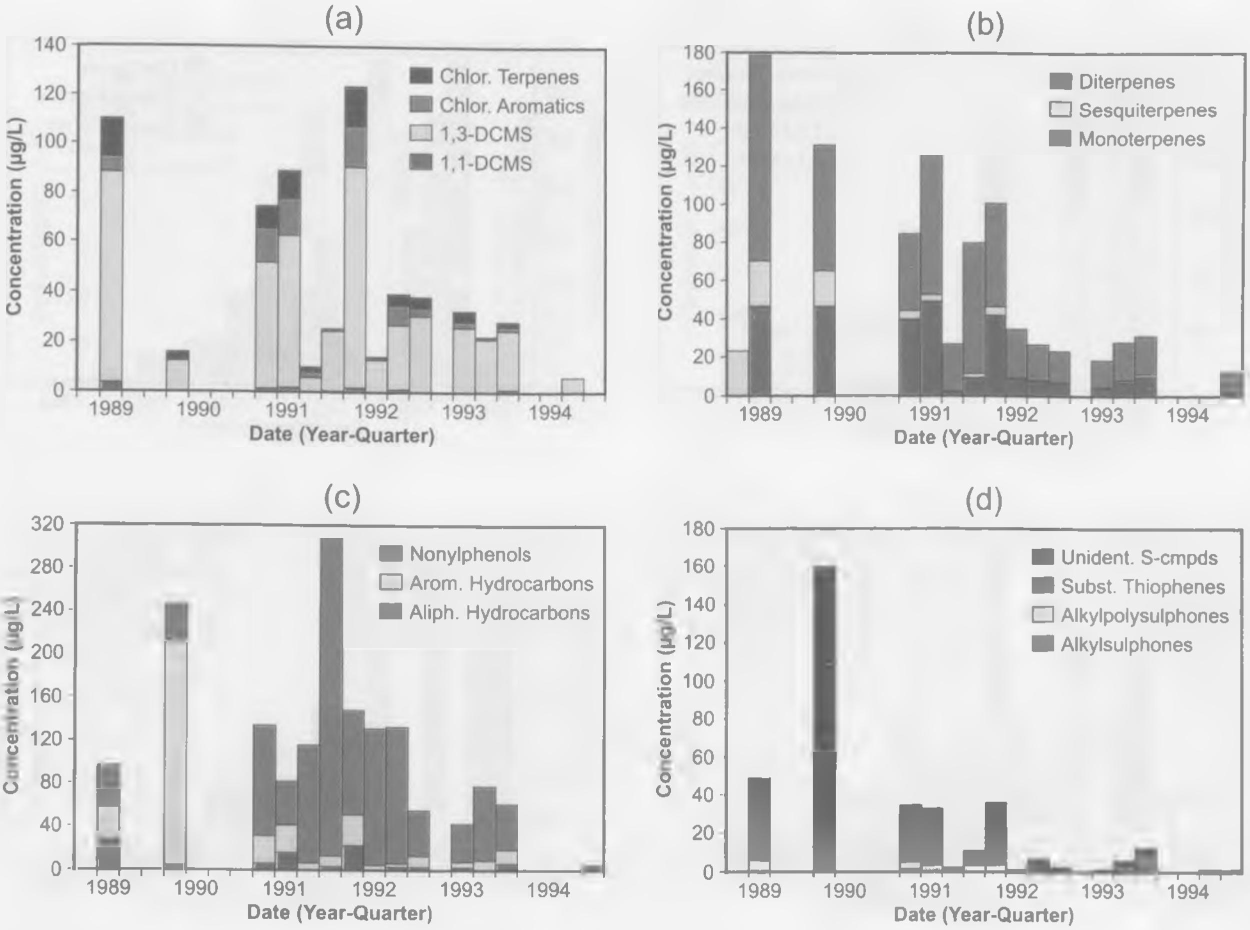

Figure 14. **BSA analysis of effluent data for the Weldwood mill at Hinton (1989-1994) for contaminant groups: (a) chlorinated substances; (b) terpenes; (c) hydrocarbons; (d) sulfur containing compounds (Johnson 1996).**

4.1.4 Weyerhaeuser Pulp Ltd., Grande Prairie

The Weyerhaeuser bleached kraft softwood pulp mill at Grande Prairie commenced operations in 1973. The mill has been upgrading since beginning operations, and the following mill process changes include: peroxide reinforced extraction stage, pressure diffuser, "closed" screen room, and digester washing improvements. The first stage of the bleach plant was significantly altered in the fall of 1990, which resulted in 70% chlorine dioxide substitution. A 100% chlorine dioxide substitution for molecular chlorine was completed in July 1992. An odour reduction project was completed in September 1993. The effluent is treated in a primary clarifier and aerated lagoons prior to discharge. Recent effluent treatment improvements include additional aeration and increased hydraulic retention time in the treatment ponds (SENTAR 1995).

As documented in the BSA Phase I (Johnson 1996) report, substantial declines in discharge of contaminants occurred at the Grande Prairie mill over the period 1989-1994 (Figure 15).

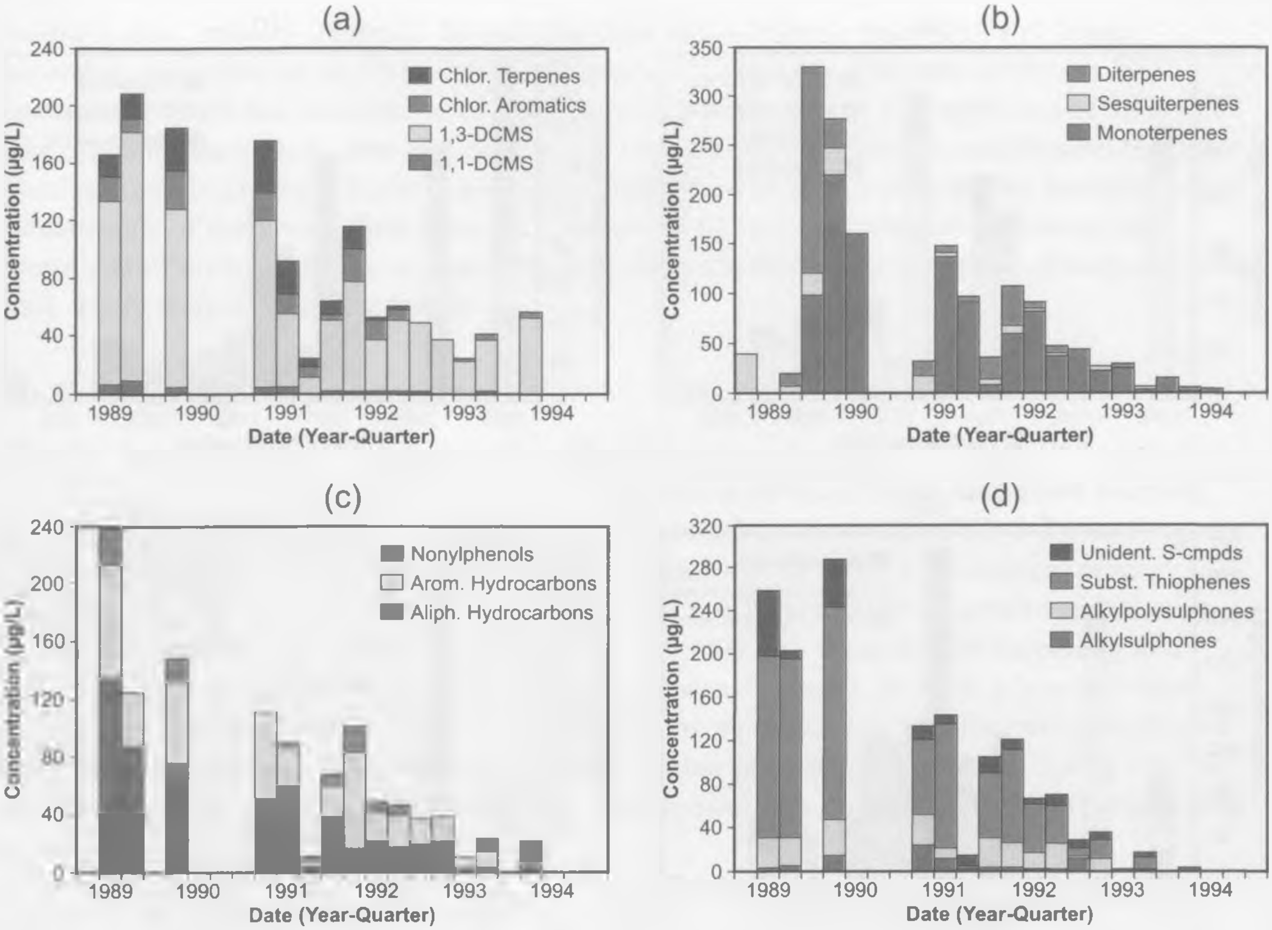

Figure 15. **BSA analysis of effluent data for the Weyerhaeuser mill at Grande Prairie (1989-1994) for contaminant groups: (a) chlorinated substances; (b) terpenes; (c) hydrocarbons; (d) sulfur containing compounds (Johnson 1996).**

Declines in discharge of terpenes, sulfur-containing compounds and hydrocarbons were in excess of 90%, while there was an approximately 75% decline in chlorinated substances discharged. The remaining chlorinated substances in the discharge were dominated by 1,3-dichloromethylsulfone, similar to the situation for the mill at Hinton.

4.1.5 Daishowa, Peace River

Daishowa's Peace River Pulp Division is a bleached kraft pulp mill that was designed as a single-line operation that alternately processes hardwood and softwood pulps in runs lasting several weeks each. Mill features include an oxygen delignification system, both a primary clarifier and a secondary (ASB) effluent treatment system with a ten-day retention time, an emergency spill pond and a collection system for recycling discharges from process upsets. To enhance biological treatment, nutrients are added to the effluent. The mill began operations in

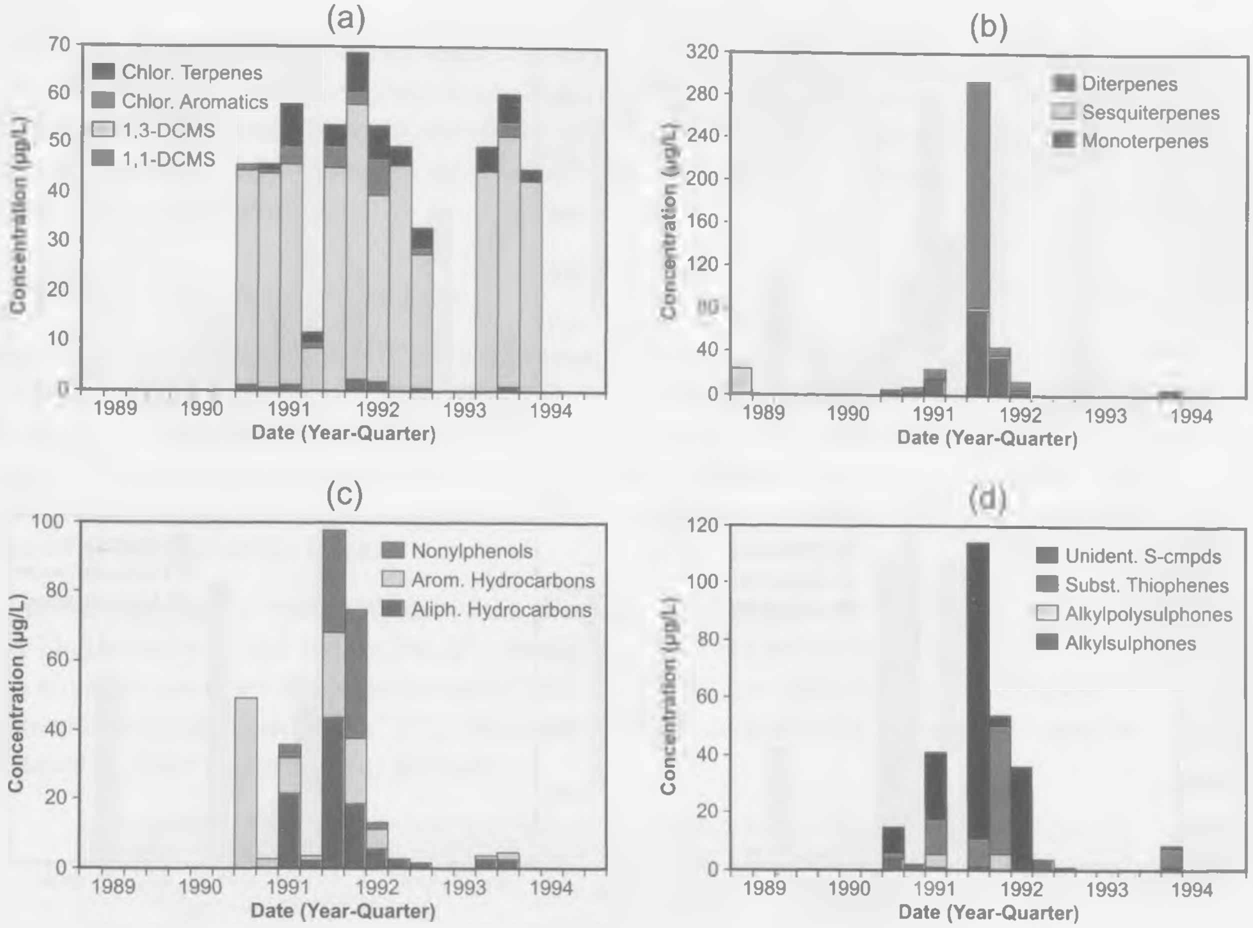

Figure 16. **BSA analysis of effluent data for Daishowa's Peace River Pulp Division (1989-1994) for contaminant groups: (a) chlorinated substances; (b) terpenes; (c) hydrocarbons; (d) sulfur containing compounds (Johnson 1996).**

July 1990 and there have been no notable physical changes to the wastewater treatment process since start-up (SENTAR 1995).

At the Peace River mill, there has not been a declining trend in contaminants discharged (Figure 16), but in general contaminant levels are low at this mill (Johnson 1996). Chlorinated substances have remained relatively constant. They are dominated by one substance, 1,3-dichloromethylsulfone, although there were also detectable levels of chlorinated terpenes and chlorinated aromatics. This may be because the mill did not employ 100% ClO_2 substitution over the time period sampled. Levels of other contaminants were generally low, except for a period in late 1992 to early 1993 when concentrations of terpenes, sulfur- containing compounds and hydrocarbons were high. This likely originated from process upsets related to cooking liquor losses since there was no matching large increase in chlorinated substances from the bleaching process.

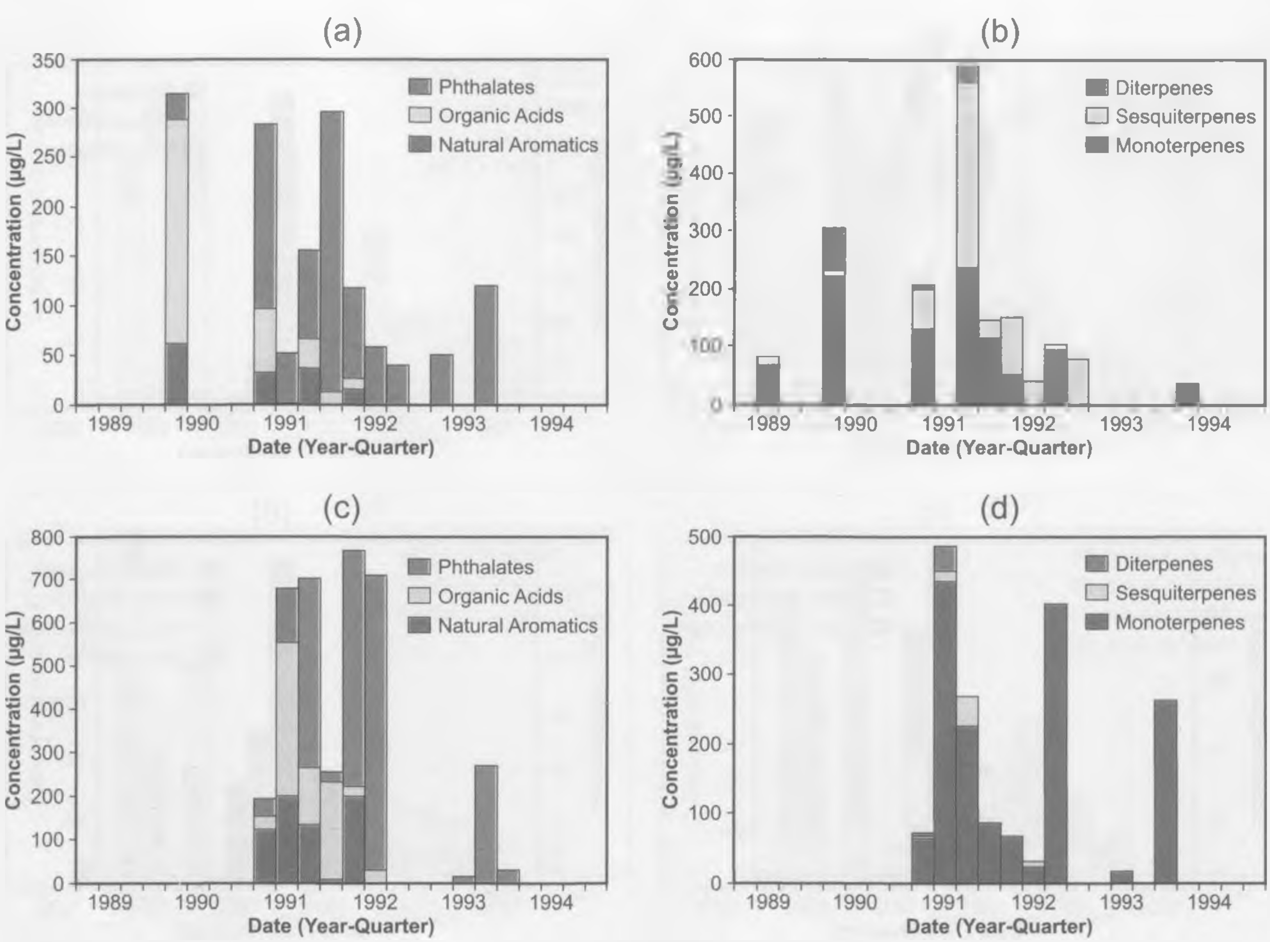

Figure 17. BSA analysis of effluent data (1989-1994) for: (a) non-terpenes and (b) terpenes for the Millar Western mill at Whitecourt; and (c) non-terpenes and (d) terpenes for the Slave Lake Pulp Corporation (Johnson 1996).

4.1.6 Millar Western Pulp Ltd., Whitecourt

Millar Western operates a two-line alkaline-peroxide pulp (APP) mill at Whitecourt about 10 km downstream from the Alberta Newsprint mill. The mill began operating in July 1988, but treated effluent volumes were less than capacity during the fall of 1988. The effluent treatment system of the Millar Western mill was originally designed and built as an ASB, but it was changed to an activated sludge treatment (AST) process with extended aeration in the fall of 1989. Wastewater treatment currently comprises three steps: pretreatment, primary treatment and AST secondary treatment. Wastewater streams collected in the floor trench system receive treatment in the primary clarifier, a 15,000 m^3/d, 6-hour retention time solids reactor clarifier. The primary clarifier discharge combines with two other streams that do not require clarification to form the influent to the extended aeration AST. The retention time in the 150,000 m^3 biobasin of the AST is approximately 10 days (SENTAR 1995). Discharges of contaminants from the Millar Western mill have stabilised in recent years and are now a fraction of those detected in past samples (Figure 17 (a) and (b); Johnson 1996). This is likely due to more stable operating conditions since past samples exhibited considerable variation on levels of contaminants discharged suggestive of episodic upsets to the treatment system. The recent samples indicated that the discharge of terpenes from this mill is currently the lowest over the period of record. Among the non- terpenoids, only phthalates have been detected at analytically significant levels since early 1992. The presence of these compounds is unexplained, but they were not detected in the most recent samples.

4.1.7 Slave Lake Pulp, Slave Lake

Construction of the bleached CTMP mill owned by the Slave Lake Pulp Corporation was completed in December 1990. Pulp bleaching is performed in a two-stage high consistency alkaline peroxide process. Water use for pulp production is very low at only 18 m^3/ADt. The Slave Lake mill has an extended aeration AST system which has been modified since 1990 to improve effluent quality. In the summer of 1992, a second secondary clarifier was added to control suspended solids losses.

As in the case for the Millar Western mill, discharge of contaminants from the Slave Lake mill was highly variable and suggestive of episodic upsets of the treatment system (Johnson 1996). The situation has been more stable since 1992. Very high unexplained concentrations of phthalates were evident before 1992, but these declined considerably in 1993 and were not detected in 1994 (Figure 17 (c) and (d)).

In general, the results of the BSA of effluents indicated that current levels of contaminants discharged by the seven mills are lower than at any time over the period of record. Evidently, the use of state-of-the-art technology in the newer mills and the process modifications implemented in the other mills since 1989 positively affected the character of the effluents. Better washing and oxygen delignification of pulp prior to bleaching reduces the organic material carried over to the bleach plant, resulting in dramatic decreases in hydrocarbon, terpenes and sulphur containing compounds in effluents. Replacement of chlorine with chlorine dioxide in the Hinton and Grande Prairie mills, and use of hydrogen peroxide in extraction stages, have resulted in large reductions in chlorinated terpenes and chlorinated aromatic compounds. Similar effects are expected in the Peace River effluent where chlorine use has been eliminated since 1994. Concentrations of 1,1-dichlorodimethylsulphone remain detectable at the bleached kraft mills.

4.2 LAKE SEDIMENT CORES

The history of both natural changes and pollution-related changes of a water body is recorded in its sediments. Although sediment desposition occurs in rivers, permanent sedimentary records are rare due to erosion and mixing of the sediment deposits during seasonal and episodic high flow events. This episodic nature makes sediment records in rivers difficult to decipher.

However, many lakes have zones that are deep enough that resuspension and mixing of sediments does not occur. In such cases, sediment deposition is permanent, producing an historical record of conditions in the water body. In river fed lakes where much of the sediment originates upstream, the sedimentary record will also reflect conditions in the watershed.

4.2.1 Lake Athabasca

Lake Athabasca is a large depositional basin significantly influenced by the Athabasca River and possibly also by the Peace River. Sediment cores from Lake Athabasca offer the possibility that historical patterns in contaminant inputs and ecological processes occurring within the Athabasca River basin can be identified and quantified. Therefore, a sampling and analytical program was designed to obtain suitable sediment cores from Lake Athabasca, determine the age-depth relationships for these sediment cores, analyse slices of the cores for contaminants, and integrate the data to construct historical profiles of contaminant inputs and other processes over the last 100 years.

In March of 1992, sediment cores were obtained from three sites along an east-west transect in Lake Athabasca. Slices from these cores were analysed for PCDDs/PCDFs, resin acids, PAHs, OCs, PCBs, hydrocarbons and metals. The sampling, analysis and initial interpretation of these cores for the NRBS is discussed by Bourbonniere *et al.* (1996a).

Similar to the Lake Athabasca surface sediment samples, detectable concentrations of members of all five of the tetra- through octachloro-PCDD congener groups were present in the core samples. In contrast, TCDF and OCDF were the only chlorinated furan congener groups broadly detected. Among the PCDDs/PCDFs, OCDD was present at highest concentrations. A marked increasing trend in concentration of several congener groups was evident, beginning in the mid-1970's. At the mid-lake site, this recent increase involved the penta- through octachloro-congener groups, while for the furans, it involved all the tetra- through octachloro- groups. As shown in Figure 5, the congener pattern did not have a prominent bleached kraft mill signature. The pattern most closely resembled that seen for pentachlorophenol with a probable smaller contribution from combustion sources.

A variety of PAHs were observed in most sections of the cores (Bourbonniere *et al.* 1996a). These included members of two groups. One group, comprising naphthalenes and substituted naphthalenes, are commonly observed in the aqueous phase in areas receiving significant hydrocarbon pollution. The other group, comprising compounds with higher molecular weights and more rings like fluorene, pyrene, benzopyrene and benzofluoranthenes are often associated with combustion sources. Concentrations of these substances with depth in the core were highly variable indicating that there has been no consistent increase or decrease in concentration over the last 100 years. The higher variability in their concentrations over time relative to the PCDD/PCDF family is suggestive of a more episodic source. One possible explanation for this variability is that forest fires and other fires were major sources of these compounds to the system. There was a slight west to east gradient in concentrations of the lower molecular weight PAHs consistent with a riverine source. In contrast, the higher molecular weight PAHs exhibited no geographical trends, consistent with an atmospheric source.

In dating one of the three deep sediment cores from the permanent depositional areas of the Lake Athabasca using radioisotopes, an unexpected subsurface maximum in radioactivity was noted indicating radionuclide interference. To investigate ths source of this interference, additional studies on both the surficial sediments and deep sediment cores were conducted. Samples were analysed for the uranium and thorium series radionuclides, radioisotopes often associated with uranium ores and uranium mining. A comparison was made between the radionuclide results from this survey and those from a previous investigation in 1983 (Wagner and Gummer, in prep).

Six of the surficial sediments collected in March 1992 and the top 5 cm of the three cores were analysed for radionuclides. Values were compared with results from 1983 for an uncontaminated control site and a site contaminated by uranium mining in the Uranium City area. Analysis of the dated cores indicated an increased deposition of radionuclides in the sediments beginning at about 3 cm depth. This corresponds approximately to the time period between 1955 and 1980, the period of uranium mining in the Uranium City region. In more recent sediments, radionuclide concentrations have been returning to background levels. Complementary studies of radionuclide levels in fish from Lake Athabasca discussed elsewhere in this report indicated that these buried radionuclides do not currently impact the aquatic system.

4.2.2 Weekes and Legend Lakes

Overall, the Lake Athabasca coring revealed a much lower pulp mill signature than expected and the data suggested that atmospheric sources of contaminants could be the main contaminant sources to this part of the Northern River Basins. To further test these conclusions, we decided to conduct sampling of lakes isolated from the influence of mainstem riverine contaminants. Two reference lakes were selected for this purpose. These were Weekes Lake in the Birch Mountains to the southwest of Lake Athabasca, and Legend Lake on the Canadian Shield to the northeast of Lake Athabasca. Bourbonnierre *et al.* (1996a) describe the sampling, dating and character of these cores. These analyses indicated that while the depositional environment in Weekes Lake had been stable for the last 100 years but that Legend Lake experienced a change in sedimentation rate in the early 1980s. Thus the depositional history of sediment-associated contaminants can be more confidently inferred for Weekes Lake than for Legend Lake.

Bourbonniere (1996) compared the organochlorines in the cores from Lake Athabasca and Weekes Lake along with a surficial sediment sample from Legend Lake. Contaminants involved in the comparison were PCDD/PCDFs, resin acids, OCs, and PCBs. Many of the organochlorine contaminants were present at higher concentrations in sediments from Weekes and Legend lakes than in Lake Athabasca. These include tetra- through octa-PCDD/PCDFs, PCBs and OCs. This distribution is not consistent with an effluent related source along the Athabasca River and most likely arises due to atmospheric deposition as the main source of these substances. Chlorinated resin acids were unique to Lake Athabasca and not detected at the other two lakes. They were considered by Bourbonniere (1996) as the most promising markers of bleached kraft mill inputs. Their input to Lake Athabasca began about 20 to 30 years ago. This suggested that the time of travel of these sediment-bound substances from Hinton to the lake was 10 to 15 years. This may explain why the decrease in chlorinated resin acids that was so evident in the recent sediments collected in the basin-wide survey and described by Crosley (1996b) are not yet evident in the Lake Athabasca sediments. Di- and trichlorodioxins were also more concentrated in Lake Athabasca sediment than in sediment from the reference lakes suggesting an unexplained riverine source for these substances (Bourbonniere *et al.* 1996b).

Five chlorinated pesticides were detected in sediment cores from Lake Athabasca and from Weekes and Legend lakes. Comparisons of concentrations indicated that the atmosphere, not the river systems, was the major source. Temporal trends were not evident. The PCDD/PCDFs were dominated by higher chlorinated congeners, also apparently originating from atmospheric sources. Riverine transport and a pulp mill source was suggested for chlorinated resin acids whose input to Lake Athabasca began about 20 to 30 years before the time of sampling. Although increases in chlorinated resin acids appears to have ceased in 1975, there was no strong evidence for a decrease to date, likely indicating a lag while sediment is transported down river. There was no indication from the sediment record of significant increases in contaminant loadings occurring at this time.

4.3 TRENDS IN CONTAMINANTS IN BIOTA

Pastershank and Muir (1996) examined the data for OCs and PCBs in various fish collected during the NRBS for evidence of temporal changes. Temporal trends in lipid normalised concentrations of PCB and OCs in burbot liver were examined at two sites on the Wapiti/Smoky system at which samples were collected in 1992 and in 1994. No significant differences were seen over the two year period.

Muir and Pastershank (1996) summarised the levels of PCDDs and PCDFs in fish from various studies and assessed temporal trends of 2,3,7,8-TCDD and 2,3,7,8-TCDF by comparison with previously published data. Temporal trends in 2,3,7,8-TCDD and 2,3,7,8-TCDF in mountain whitefish from the Athabasca River were examined over a four year period by combining the three sampling times in the upper Athabasca River with data from previous studies (DFO National Dioxin Program 1989). The data were consistent with a decline in 2,3,7,8-TCDD and TCDF concentrations in mountain whitefish downstream of Hinton in the period 1989 to 1992, although the extent of the decline depends to a large extent on the sites used for comparison. If the data for the Weldwood and Obed sites from the basin-wide survey are used, the decline is about five-fold for both TCDD and TCDF over four years. However, if fish from the Emerson Lake site are included the decline is about 3-fold.

Declines were also evident at some sites in the Peace River system. Concentrations of 2,3,7,8-TCDD and -TCDF in burbot liver from the fall 1994 basin-wide collection were lower than in the fall 1992 preliminary survey at four sites; downstream from the Grande Prairie pulp mill discharge, on the Peace River near the mouth of the Notikewin River and also at a site upstream from Fort Vermilion. Although the sampling sites were not in the same locations each year, the results for the Wapiti River downstream from the pulp mill at Grande Prairie show a decline of 4 to 17-times in the case of 2,3,7,8-TCDF. There was no evident decline in TCDD or TCDF concentrations in burbot livers from the Peace River upstream from the Smoky River confluence, suggesting that the source upstream , perhaps in British Columbia, has not decreased. When expressed as TCDD TEQ'S, the Wapiti River burbot liver results agreed well with those of Swanson *et al.* (1996) who found a 5-fold decline in TEQs downstream of the Grande Prairie BKM between summer 1991 and spring 1994.

Although there was only a small set of comparable data, comparisons of concentrations in fish tissue collected during the study indicated a significant decline in PCDD/PCDF concentrations in fish in both the Wapiti and Athabasca Rivers downstream from bleached kraft pulp mills. Depending on the sites used in the comparison, the declines varied from 3 to 17 fold. There was no evidence for changes in atmospherically transported substances or in total PCBs.

4.4 TRENDS IN CONTAMINANTS IN SEDIMENT

Two datasets on contaminants in sediments were obtained during the NRBS that allow some temporal comparison to determine contaminant trends in sediments. As described above, one of the initial sediment surveys undertaken by the NRBS involved the analysis of AEP archived sediment from 26 sites throughout the basin for PAHs, CPs, PCDDs/PCDFs, PCBs, OCs, EOCl and mercury. These samples represented the period 1988-1992 but most were from 1989. Additional bottom sediment surveys were conducted in 1994 and 1995 for the NRBS. In 1994, nine composite sediment samples were obtained from depositional areas in the basins and at one additional site, a more intensive composite sample was obtained. One of these sites was in the Wapiti River near its confluence with the Smoky River, four sites each were in the Peace and Athabasca River mainstems. In 1995, an additional five sites, one each on theWapiti and the Peace Rivers and three on the Athabasca, were sampled using the discrete area approach. The contaminant results of the sediment surveys are compared by Crosley (1996b).

The sediment results supported the substantial declines observed in the BSA analysis of effluent samples over the same time period. For example, concentrations of total chlorinated resin acids in sediments downstream from Hinton were 75% lower in the 1995 sample than in the 1992 sample. Similarly, concentrations of total resin acids on Wapiti River sediments collected near the confluence with the Smoky River declined from 69 ng/g to 22 ng/g to 5 ng/g in the 1989, 1994 and 1995 samples, respectively. As discussed above, the geographical distribution of chlorinated resin acids on sediments suggested that these compounds were distinctive chemical markers for bleached kraft pulp mill effluent discharges. Similar apparent declines were observed for pulp mill-related PCDDs/PCDFs. For example concentrations of 2,3,7,8-TCDF on sediment from the Athabasca River downstream from Hinton decreased from

7 pg/g in 1988 to 2 pg/g in 1992 to <1 pg/g in 1995. Similarly, in the Wapiti river near the Smoky River confluence, concentrations of 2,3,7,8-TCDF in sediment decreased from 36 ng/g in 1988 to <2 pg/g in 1994 and 1995. There were no apparent temporal trends in the data for PAHs and PCBs. Other OCs and mercury were not detected on sediments in the surveys.

At one site in the survey, the Peace River upstream from the Smoky River confluence, concentrations of several contaminants increased between 1989 and 1995. The data pointed towards non-kraft mill sources but did not allow a discrimination between non-point sources or sources in British Columbia. It is likely worth monitoring the upper Peace River to determine if this increasing trend continues. At most other sites in the basin, sediment contaminants, with the exception of non-chlorinated resin acids, are approaching or are at detection limits. Further extensive surveys are likely not warranted.

The sediment results supported the substantial declines observed in the BSA analysis of effluent samples over the same time period. Concentrations of total chlorinated resin acids in Athabasca River sediments downstream from Hinton were 75% lower in the 1995 sample than in the 1992 sample while concentrations of total resin acids on Wapiti River sediments collected near the confluence with the Smoky River declined from 69 ng/g to 22 ng/g to 5 ng/g in the 1989, 1994 and 1995 samples, respectively. Similar apparent declines were observed for pulp mill-related PCDDs/PCDFs. For example concentrations of 2,3,7,8-TCDF on sediment from the Athabasca River downstream from Hinton decreased from 7 pg/g in 1988 to 2 pg/g in 1992 to <1 pg/g in 1995. Similarly, in the Wapiti river near the Smoky River confluence, concentrations of 2,3,7,8-TCDF on sediment decreased from 36 ng/g in 1988 to <2 pg/g in 1994 and 1995. There were no apparent temporal trends in the data for PAHs and PCBs. Other OCs and mercury were not detected on sediments in the surveys. For the Peace River upstream from the Smoky River confluence, concentrations of several contaminants increased between 1989 and 1995. The data pointed towards non-kraft mill sources but did not allow a discrimination between non-point sources or sources in British Columbia. At most other sites in the basin, sediment contaminants, with the exception of non-chlorinated resin acids, are approaching or are at detection limits. Further extensive surveys are likely not warranted.

5.0 CONTAMINATION OF BIOTA IN THE NORTHERN RIVER BASINS

5.1 FISH

5.1.1 OCs, PCBs and PCDD/PCDFs

Pastershank and Muir (1996) attempted a preliminary assessment of the PCB and OC pesticide concentrations in fish muscle and liver using Health Canada's tolerable daily intake (TDI) values and US EPA non-cancer hazard levels. The preliminary conclusion was that the organochlorine levels in fish muscle (mountain whitefish, pike, goldeye, walleye, longnose suckers) did not represent a human health hazard. Although higher levels of most contaminants were found in burbot liver, they concluded that a 60 kg individual would have to consume 150 g burbot liver per day to exceed the TDI for PCBs, assuming the worst case concentration of 400 ng/g. However, these criteria may not take into account all fish related tissues that may be consumed as part of the traditional diet (e.g., fish eggs, liver, fat).

The concentrations in fish muscle should also be evaluated for possible risks to fish-eating wildlife. Concentrations of PCBs and DDT in muscle of all fish sampled were also well below US EPA criteria for protection of fish-eating wildlife by a factor of at least 5 to >10-fold. However, mountain whitefish and northern pike muscle samples from the upper Athabasca River collected during the RSS in 1992 exceeded draft Canadian Environmental Quality guidelines for PCBs although they did not exceed the criteria for p,p′-DDE. Other species in the lower Athabasca had lower levels and did not exceed the draft guidelines.

5.1.2 Mercury in Fish

Data on concentrations of mercury in water, sediment, fish and invertebrates from the Athabasca and Slave River basins were reviewed for NRBS by Donald *et al.* (1996). Elevated levels of mercury have not commonly been detected in samples of abiotic compartments from the basins. The sediment sampling conducted for the NRBS found mercury concentrations similar to the concentrations found in soils across Canada. There was no indication of increases related to industrial or municipal discharge. Among the biotic compartments, mercury has been detected in some aquatic invertebrates from the lower Athabasca River sampled in the early 1980s and but it is generally detected in fish from throughout the basin. Although it is present in all species, concentrations are highest in predatory fish like pike, walleye, burbot and bull trout. Older, larger individuals within a species contain the highest concentrations. For the Athabasca River basin, Donald *et al.* (1996) found that the decreasing order of concentration of mercury in fish was walleye > goldeye > northern pike > longnose sucker > mountain whitefish. In the lower Athabasca River, from the town of Athabasca to Lake Athabasca, 25% of the walleye analysed had mercury concentrations in excess of the Health Canada limit of 500 µg/kg. Because of these high levels, consumption guidelines have been established for walleye from the Athabasca River and for several lakes within the basin.

High concentrations of mercury were also evident in fish caught upstream on the Peace River in the Williston reservoir in British Columbia. Downstream from the reservoir, concentrations were lower. Apart from the reservoir, the highest fish mercury concentrations in the Peace River system occurred downstream from the Smoky River-Peace River confluence. However, fish from the Smoky River system had lower concentrations, suggesting that the source of the mercury is not within the Smoky River system.

There was no apparent relationship between industrial/municipal discharges and mercury concentrations. This implies that the source of mercury in these fish is either natural or diffuse. In view of the continuing high levels in the lower Athabasca River, more studies on the sources and pathways of mercury in this part of the northern river basins is likely warranted.

5.1.3 Fort Chipewyan Domestic Fishery

To obtain contaminant data directly relevant to fish consumed by people eating country foods, fish collected in 1994 in the traditional domestic fishery in the Peace-Athabasca delta region were analysed for contaminants. The survey involved five species; burbot, northern pike, lake whitefish, goldeye and walleye. Composites muscle samples from 8 to 10 individuals of each species from each of three sites were analysed for PCBs, OCs and PCDD/PCDFs. The results of these analyses are reported by Pastershank and Muir (1996) and Muir and Pastershank (1996).

Concentrations of contaminants in these samples were very low. Total PCBs ranged from 1.1 to 9.9 ng/g while organochlorine pesticides ranged from 0.1 to 2.2 ng/g (Pastershank and Muir 1996). PCDD/PCDF congeners in these composite samples were at or near detection limits of from <0.1 to <0.8 pg/g (Muir and Pastershank 1996). 2,3,7,8-TCDF was detectable in most samples in the range <0.1 to 0.5 pg/g. Concentrations in burbot liver composites were higher, from 1.7 to 2.9 pg/g. These concentrations were comparable to levels in fish from isolated tributary sites with no known anthropogenic contaminant inputs. In general, therefore, there was no indication of contamination of these fish from development upstream in the basins. A preliminary risk assessment showed that tolerable daily intakes based (TDI) on TCDD TEQs would be unlikely to be exceeded. A 60 kg person would have had to consume 1.2 kg/day of these samples to exceed the TDI (Muir and Pastershank 1996). Consumption would have to be even greater to exceed TDIs based on PCBs and selected OCs (Pastershank and Muir 1996).

5.1.4 Lake Athabasca Radionuclides

In February 1993, the NRBS collected fish from traditional winter harvest areas in the Peace-Athabasca Delta and the western end of Lake Athabasca. These collections were made to determine the levels of chemical contaminants in fish species commonly consumed by area residents. To determine whether past mine-mill operations in the Uranium City area of Lake Athabasca had led to unacceptably high levels of radionuclides in fish, fish from two Lake Athabasca sites were analysed for radionuclides (Smithson 1993).

Bone and muscle tissue from twenty northern pike, twenty lake whitefish, eleven white sucker and one longnose sucker were analysed for polonium-210, lead-210, radium-226, three thorium isotopes and uranium. Mean concentrations for all radionuclides except uranium were below detection limits. The mean values for uranium in whitefish were significantly above detection limits. These results are comparable to or lower than radionuclide levels found in fish from other parts of northern Saskatchewan that are not exposed to uranium mine-mill operations. There were also no apparent abnormal gross pathological effects in these fish.

The results of this study indicate that fish from traditional winter harvest sites at the west end of Lake Athabasca are not contaminated with radionuclides. Further testing of fish for radionuclide contamination in the Peace-Athabasca Delta is therefore not recommended.

> *Apart from mercury where the existing consumption advisory was supported by NRBS data, preliminary analysis of the contaminant results did not indicate a significant risk to fish eaters. In view of the recent dramatic declines in TCDD/TCDF levels in fish tissue, existing consumption advisories in the northern river basins based on these compounds should likely be re-evaluated.*

5.2 BIRDS

5.2.1 Mergansers

Fish eating birds have been used as bioindicator species in a number of contaminant monitoring programs. Among the fish eating birds of the Peace-Athabasca River systems, mergansers (*Mergus merganser*) are a widely distributed species. They reside along lakes, streams and rivers where they raise broods of precocial young. The young feed mainly on small fish. Prefledged young were considered as a possible bioindicator for the northern river basins since they have not had the opportunity to pick up contaminants in wintering areas or at off-river sites and their use of aquatic prey make them a candidate for bioaccumulation of lipophilic contaminants like PCBs and PCDDs/PCDFs. To determine their suitability as bioindicators, a preliminary study was conducted near the Weyerhaeuser mill site at Grande Prairie. Collection of prefledged mergansers for the NRBS was described by Court (1993). Six mergansers were collected along the Wapiti River upstream from the mill and four were collected downstream from the mill. Liver samples from individual birds were analysed for PCBs, OCs and metals, while composite samples were analysed for PCDDs/PCDFs and CPs. The results of these analyses are reported by Wayland (1995b). Of the 25 chlorinated dioxin and furan congeners analysed, only 2,3,7,8-TCDF was detected, at concentrations less than 2 pg/g. It was present at both upstream and downstream sties with levels twice as high downstream from the mill. CPs were not detected in the upstream composite but PCP, tetrachlorophenols and 4,5,6-trichloroguaiacol were reported in the downsteram sample. However, the CPs present at highest concentrations were PCP and tetrachlorophenols. These are not common pulp mill contaminants. They usually enter the environment due to their use for wood protection and are common constituents in sewage effluents. Thus their presence here may be due to the town sewage discharge rather than the pulp mill. This suggestion is reinforced by the fact that the two most common chloroguaiacols associated with pulp mill effluent, 3,4,5-trichloroguaiacol and tetrachloroguaiacol were not detected in these samples. Levels of PCBs and metals were not noticably elevated downstream from the mill relative to upstream.

Mergansers in this study exhibited lower contaminant burdens than a variety of birds in other locations, including mergansers from pulp mill sites elsewhere in Canada. Possible reasons for these low contaminant results were discussed by Wayland (1995b). It was concluded that although prefledged mergansers may have been abundant enough to serve as bioindictaor species, they may not have had enough time to accumulate significant body burdens of contaminants. Alternately, they may have exhibited lower concentrations because they were exposured to lower concentrations of contaminants than birds from other sites. In view of these unpromising results, further sampling of mergansers was not conducted during the NRBS.

5.2.2 Canvasback

Canvasback (*Aythya valisneria*) are a species of waterfowl common on the Peace-Athabasca delta that has traditionally been hunted by delta inhabitants. Canvasbacks live in wetland areas eating primarily aquatic vegetation although aquatic insect larvae form a significant part of the diet of ducklings and breeding females. Liver tissues from six juvenile canvasbacks collected in the Peace-Athabasca delta were analysed for PCDDs/PCDFs, CPs, PCBs, OCs, PAHs and metals. Results are reported by Wayland (1995c). PCDD/PCDF congeners were detected in four of the six samples. The most common was 2,3,7,8-TCDF while 1,2,3,7,8- and 2,3,4,7,8-PeCDF (pentachlorinated dibenzo-*p*-furan) were also detected. These congeners are suggestive of either a pulpmill or a PCB combustion source. Concentrations were low. On a wet weight basis, TEQs were less than 1 pg/g in both sexes. Chlorophenolics were detected in five of six livers. The most common were tetrachloroguaiacol and 4,5,6-trichloroguaiacol while 3,4,5-trichloroguaiacol and 3,4,5-trichlorocatechol were also detected. As discussed above, these chlorophenolics are generally associated with pulp bleaching. Combustion related PAHs like fluoranthene, and benzo(b+k)fluoranthene were infrequently detected at low levels while PCBs and OCs were not detected.

The results suggest that canvasbacks in the Peace-Athabasca delta in 1992 were exposed to low levels of pulp mill-related contaminants and some individuals may have bioaccumulated low levels of these contaminants. The concentrations observed were substantially lower than concentrations in other bird species exposed to pulp mill effluents in other areas, suggesting that the Peace-Athabasca delta is far less contaminated that known contaminated areas (Wayland 1995c). A Health Canada evaluation of these data concluded that comsumption of these canvasbacks would not pose a hazard to human beings.

5.3 MAMMALS

5.3.1 Mink

Mink (*Mustela vison*) were considered a possible indicator of contaminants because their use of aquatic and riparian prey as food make them a prime candidate for bioaccumulation of persistent lipophilic contaminants like PCBs and PCDDs/PCDFs. Mink collected by trappers with traplines in the Peace- Athabasca delta and along the Wapiti, Smoky, Peace and Athabasca Rivers were obtained for analysis (Horstman and Code 1994). Composite samples each representing three sampling sites were prepared from the livers of a total of thirteen mink. The composites were analysed for PCDDs/PCDFs, CPs, PCBs, OCs, PAHs and metals. The results of these analyses were reported by Wayland (1995a). Contaminant concentrations were very low in the mink liver homogenates, with most of the analysed contaminants not detected. PCBs and DDE were highest in the Wapiti River composite but the concentrations were very low at <0.05µg/g and 0.014 µg/g respectively. 2,3,7,8-TCDD was higher in the Athabasca River composite (0.6 pg/g) than in the Wapiti River composite (0.2 pg/g) and was not detected in the composite from the Peace-Athabasca delta. 2,3,7,8-TCDF, the most prominent of the higher chlorinated PCDDs/PCDFs in pulp mill effluent, was not detected in any of the samples. Total and methyl mercury were higher at both river sites compared to the delta sample, but the concentrations were low compared to samples from other locations.

In retrospect, mink may not be a suitable bioindicator species for riverborne contaminants. Although they feed on aquatic species, their preferred habitat is in upland areas along small creeks, streams and ponds. The mink sampled in this study were trapped within 5 km of the river and it is debatable whether they spent much time on the mainstems to be exposed to river-borne contaminants. Because of this uncertainty and the low levels of contaminants observed in the composite samples, no further analysis of contaminants in mink was carried out.

5.3.2 Muskrats

Muskrat (*Ondatra zibethicus*) are an important species of mammal to the inhabitants of the Peace- Athabasca delta who trap this species for its fur. Muskrats live in wetlands eating emergent aquatic vegetation and occasional aquatic bivalves. In 1992, muskrats were collected from two perched basin lakes in the delta (Green 1994). Adipose tissue from 12 juvenile muskrats collected in the Peace- Athabasca delta were analysed for TCDDs/TCDFs, CPs, PCBs, OCs, PAHs and metals. Results are reported by Wayland (1995c). Apart from several dichlorodioxins detected in one of the twelve samples, PCDDs and PCDFs were not detected in any of the muskrat samples in this study. Among the chlorophenolics, 2,4,6-TCP (trichlorophenol) was detected in three of the animals at very low levels (max 0.0009 µg/g) while four other CPs were detected once each. Several PAHs were also detected in three of the animals at low levels (max. 0.06 µg/g) while PCBs were detected in only one individual. Generally, concentrations found in this study were far below toxicologically relevant levels and were not indicative of significant contaminant pollution.

6.0 SEDIMENT TRANSPORT AND DEPOSITION PROCESSES

The results of the Reach Specific Survey (RSS) and the basin-wide surveys indicated that sediments were likely playing an important role in the transport and storage of contaminants within the Northern River Basins. This suggested that sampling of sediment could be an important component of any long-term monitoring program established after the completion of the NRBS. Therefore, studies were conducted to address several questions concerning sediment that arose during the study.

6.1 SEDIMENT DEPOSITION

In both of the preliminary sediment surveys undertaken by the NRBS, the analysis of AEP archived sediment from 26 sites throughout the basin, and the RSS sediment survey, several factors were less than ideal. In an effort to address a broad geographical range, the two surveys did not address internal site variability in sediment composition or provide enough analytical replication to assess site variability in contaminant concentrations. This information is required to confidently determine the significance of between-site concentration differences. In addition, some of the analytical methods employed in the preliminary surveys were not sensitive enough to detect the low levels of contaminants encountered.

Another factor not adequately addressed in the initial surveys was the influence of particle size on contaminant concentrations. In both of the preliminary sediment surveys undertaken by the NRBS, contaminant analysis focused on the fine sediment fraction. This was done in an attempt to standardise the analysis of samples with varying sand-silt-clay ratios. Although this method of standardisation focused on the fraction generally considered to be the major carrier of contaminants, several reviewers suggested that ignoring the sand fraction may not be justified. It was suggested that in cases where the sand fraction was particularly high, the larger mass of that fraction could compensate for the lower concentration of contaminants in this fraction than in the fine fraction, and could make the sand fraction the major storage and transport compartment for contaminants.

In consideration of these factors, the additional bottom sediment surveys conducted in 1994 and 1995, attempted to assess the within-site variability at a number of locations by conducting more extensive sampling and by using more sensitive analytical methods.

The results of the 1994-95 sediment surveys are reported by Crosley (1996b). In 1994, nine composite sediment samples were obtained from depositional areas in the basins. One of these sites was in the Wapiti River near its confluence with the Smoky River, four sites each were in the Peace and Athabasca River mainstems. The composites were integrated from ten dredge samplings from a total of four depositional areas throughout the depositional reach. At one site, the Peace River downstream from the Daishowa pulp mill, a total of 10 discrete samples were collected from five dredges each at ten depositional areas. In 1995, an additional five sites were sampled using the 10 discrete area approach. Sediment composition was characterised and analyses were performed on most of these samples for PAHs, CPs, PCDDs/PCDFs, PCBs, OCs, EOCl and mercury.

Coefficients of variation on triplicate split samples were calculated to provide an indication of errors involved in mixing and splitting the samples in the field and in subsampling and analysis in the laboratory (Crosley 1996b). For some parameters at some sites, coefficients of variation in the split samples were large. For example, the range of coefficients of variation in percent sand content over the nine sites was 3.6-86.6%. A comparison of variations within and among samples revealed that the variability between sites exceeded the variability within a site for all three size fractions. The magnitude of the within-site variability confirmed that sampling one depositional area, regardless of the degree of compositing, is likely insufficient to confidently describe that depositional reach. The methods used in this study, compositing 10 sub-samples from at least four depositional areas within a reach were likely sufficiently rigorous to provide reasonable estimates of representative means.

A further complication was also uncovered in this survey (Crosley 1996b). A comparison of the October and May samples indicated that there may have been considerable seasonality in some parameters. The sediments were slightly coarser in May but had increased organic and inorganic carbon. For most of the contaminants analysed, coefficients of variation were much higher for the sand fraction than for the silt clay fraction. With respect to the relative contributions of the sand and the silt-clay fractions, the results indicated that significant contaminant concentrations occurred in the sand fraction. These were correlated with organic carbon content. For some contaminants like PAHs, concentrations on sand were higher than on silt-clay although the total loads were comparable due to higher fraction of total mass in the silt-clay fraction.

Overall, the in-site variability observed in the sediment survey highlighted the need to sample intensively within a reach to produce a composite sample that accurately reflects the average conditions in that reach. In addition, in light of the finding that unexpectedly significant concentrations of contaminants were found on the sand fractions, it was recommended that future sediment surveys focus analysis on unpartitioned sediment (Crosley 1996b).

6.2 SEDIMENT TRANSPORT

In view of the importance of suspended sediment in contaminant transport in the northern river basins, a project was undertaken by NRBS to characterise the size distribution of the suspended load in the upper reaches of the Athabasca river and to examine the possible impacts of the pulp mill effluent on the transport characteristics of the ambient sediments. The results of this project are reported by Krishnappan *et al.* (1995). The project consisted of two field surveys: one, during the winter of 1993 when the flow was low and the river was ice-covered and the other during the fall of the same year under open-water conditions. In both surveys, the river reach covered was between Entrance and Windfall on the Athabasca river and the measurements consisted of flow field, size distribution of *in situ* and primary particles, and concentration of suspended particles.

The sediment transport rates in metric tones per day observed at various river segments in the two surveys are summarized in Figure 18. In the winter survey, 74% of the incoming sediment

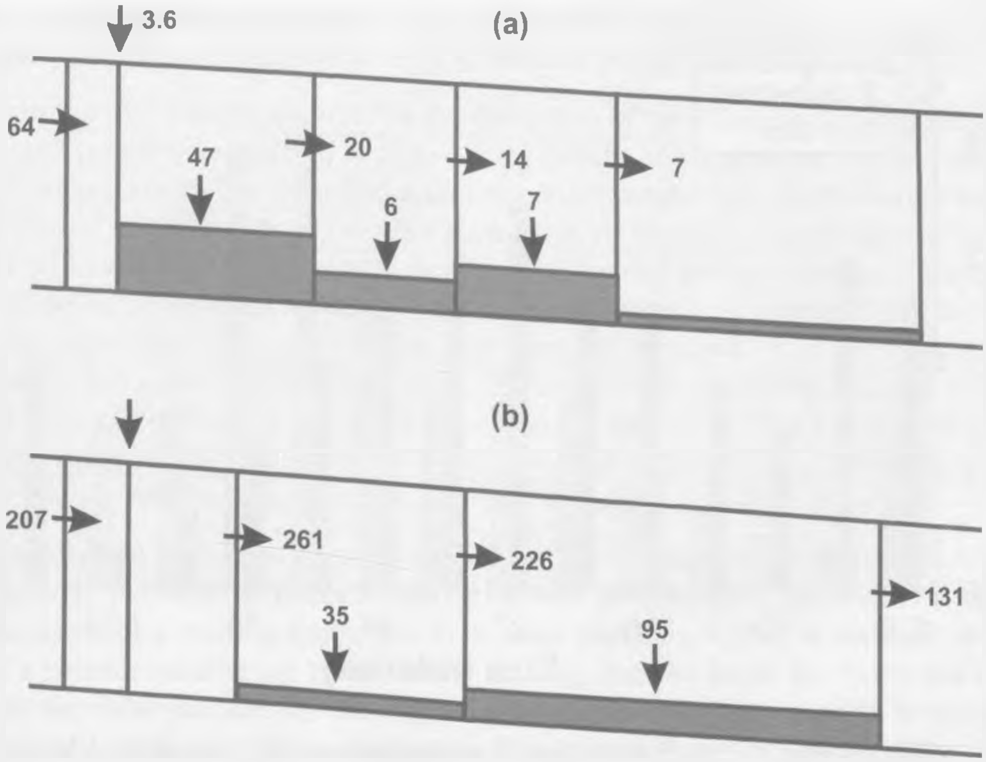

Figure 18. **The sediment transport and deposition load (metric tons per day) for several reaches of the Athabasca River from Hinton to Obed observed in the winter and fall surveys (Krishnappan *et al* 1995).**

deposited in the reach between the outfall and Obed. The deposition continued in the reach between Obed and Emerson, but at a slower rate. In this reach, 30% of the material entering the Obed transect deposited. Overall, only 20% of the material entering the reach at Entrance left at the Emerson transect under base flow conditions. The fall survey demonstrated that even during moderate flows (e.g., flows in the order of five times the base flow), there was still evidence of enhanced sediment deposition, although the deposition rate was slower and the deposition zone shifted further downstream. Even under these conditions, there was approximately 50% deposition in the Hinton to Windfall reach.

From the consideration of flow hydrodynamics and sediment transport alone it was not possible to explain this deposition of suspended particles. The flow velocity and the stream energy to transport sediment were higher at the downstream reach (i.e. the reach containing the sampling transects) than the upstream reach so that unless there was a change in sediment properties (size, density or settling velocity) during transport, the sediment delivered to the downstream reach from upstream should not have been deposited in the sampled reach. Since deposition occurred, it was concluded that the properties of the suspended sediment must have been altered. The pulp mill discharge located at the beginning of the zone of enhanced deposition was considered the most likely cause of the change in properties of the suspended sediment. Colloidal material, fibres or bacteria present in the effluent could all have acted as sites of aggregation, causing the sediment particles to become attached and form larger units that settle.

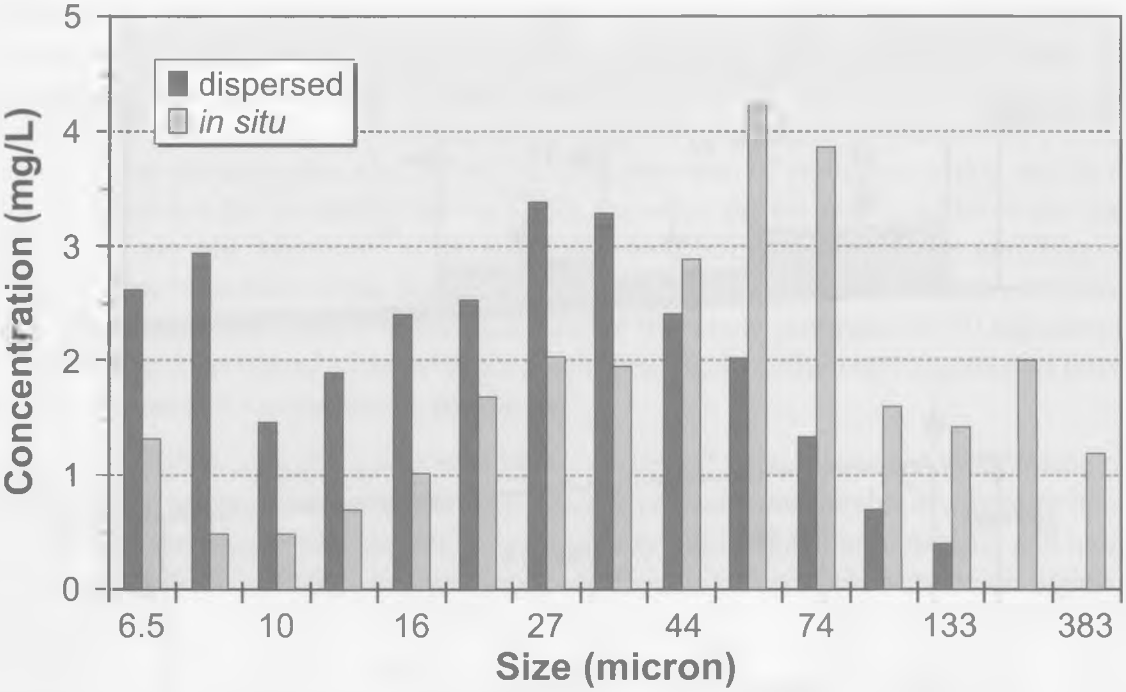

Figure 19. Comparison of size distribution of suspended particles measured *in situ* in the Athabasca River at Entrance using a new laser particle size analyser with the size distribution measured in the laboratory after the dispersal of flocs.

The size distribution of the suspended particles was measured using a new submersible laser particle size analyser developed by Environment Canada. A representative size distribution is shown in Figure 19. The figure compares the *in situ* particle size distribution with the size distribution after dispersal of the flocculated particles (flocs) to their primary particles. From the figure, it can be seen that the suspended particles are transported in a flocculated form at this transect. The *in situ* distribution contains particles in size classes as large as 204 and 383 microns whereas the primary particles are finer and do not contain any particles in these size classes. In other experiments, it was shown that the concentration of particles in every size class diminished during their transport from Entrance to Obed. This implied a dynamic process in which the smaller particles were involved in floc formation.

The data from the two surveys showed that the pulp mill effluents have affected the physical transport characteristics of the ambient sediment in the Athabasca River downstream from the Weldwood Pulp Mill at Hinton. The effluents appear to have promoted the flocculation of the incoming sediment and increased their deposition rate. The effects are most pronounced during low-flow periods when the ratio of the effluent discharge to the flow discharge is the highest (about 4%, during this study). During low flow periods, 74% of the incoming sediment deposited within 20 km from the effluent discharge location. Deposition can continue up to 100 km, but at a slower rate. During moderate flows (i.e., flows in the order of five times the winter flow) the deposition continued at a slower rate further downstream from the outfall. *In situ* measurement of size distribution of suspended particles during the winter survey showed that the suspended particles are transported in the reach in a flocculated form. The deposition of the incoming sediment and the solid fraction of the pulp mill effluent is likely to continue during low-flow periods.

The results of the two surveys suggest that the deposition of the effluent solids and the ambient sediment could persist over a period of almost eight months in a year when the flow rate is lower than the fall survey value. The deposited sediment could become resuspended during the high flows that normally start in June in the Athabasca River. At freshet, it is possible that the bed-shear stress will exceed the critical shear stress for erosion and the resuspension of the deposited material will occur, resulting in transport of the material further downstream. When the flow rate decreases, the deposition cycle repeats. The results pointed to a need for an improved sediment transport model that considers the flocculation mechanism of the incoming sediment in the presence of pulp mill effluent. Models in existence at the start of the NRBS would not predict sediment deposition downstream from the Weldwood Pulp Mill outfall and therefore were not suitable for making realistic predictions of pulp mill impacts in the Athabasca River.

Follow-up studies on sediments from the Athabasca River near Hinton were conducted in the rotating flume of the National Water Research Institute in Burlington, Ontario. This unique apparatus consists of a rotating flume (5.0 m in mean diameter, 0.30 m in width, 0.30 m in depth) and a counter-rotating top cover, called the ring, that fits inside the flume and makes contact with the water surface. By rotating the platform and the ring assembly in opposite directions, it is possible to generate nearly two dimensional shear flows and to study the behaviour of the sediment under different flow conditions. The flume is equipped to measure the flow field, the bed shear stress, the *in situ* particle size distribution in the flow and the suspended sediment concentration.

Sediment and water samples from the Athabasca River near Hinton were brought to the rotating flume and were tested for erosion and deposition characteristics. In the deposition tests, a sediment-water mixture was thoroughly mixed in the flume and then subjected to different bed shear stresses. There was deposition of sediment under all shear stresses tested. The time to reach steady state and the magnitude of steady state concentration depended on the bed shear stress. The time to reach steady state decreased as the shear stress increased whereas the magnitude of the steady state concentration increased with the shear stress indicating that the amount of deposition was decreasing as shear stress increased. At the lowest shear stress tested, the concentration of the sediment in suspension dropped to about 30 mg/L from the initial concentration of 200 mg/L. If the shear stress had been reduced further, all of the sediment would have deposited. The shear stress at which this occurs is called the critical shear stress for deposition. For the Athabasca River sediment this value is slightly lower than 0.121 N/m^2, the lowest shear stress tested in these experiments.

Deposition tests were also carried out studying the effect of additions of pulp mill effluent. Size distribution tests indicated that the suspended flocs in the presence of pulp mill effluent were larger and had higher deposition rates. These experiments confirmed hypotheses raised in the earlier *in situ* studies (Krishnappan *et al.* 1995) that pulp mill effluent enhanced deposition of particles in the Athabasca River. The size distribution data also showed that the particles flocculated as they were deposited and the equilibrium size distribution of the sediment flocs was a function of bed shear stress.

The erosion characteristics were studied by allowing the sediment to deposit completely on the flume bed and then applying bed shear stresses in steps. As in deposition tests, concentration and size distribution of the eroded sediment were measured at different shear stresses. From these measurements, it was possible to determine the critical shear stress for erosion and the erosion rate function for different shear stress steps. The results for all bed erosion tests were similar. The sediment deposit was completely stable until the bed shear stress reached a value of 0.169 N/m^2, which can be considered as the critical shear stress for erosion. After that, the sediment bed started to erode and the concentration of sediment in suspension increased. At each shear stress step, sediment concentration increased gradually and showed a tendency to attain a steady state. The appearance of a steady state in these erosion experiments was informative. Evidently, there was an increased shear strength in the interior of the bed that required an increased shear stress to further erode the material. At the maximum shear stress of 0.520 N/m^2, not all of the deposited sediment was re-suspended. The maximum concentration reached was only about sixty percent of the total concentration that would have resulted from complete resuspension. The maximum concentration that was attained at the shear stress of 0.520 N/m^2 was about the same as the steady state concentration that resulted in a deposition test at a much lower shear stress of 0.324 N/m^2. The critical shear stress for erosion was therefore higher than the critical shear stress for deposition.

The size distribution of the re-suspended sediment measured during the erosion tests indicated that the sediment bed was peeled off during the erosion process and the re-suspension contained a large percentage of larger flocs. As the bed shear stress increased, the larger flocs were broken up and the distribution became finer.

The results from the present investigation were used to develop a new algorithm for the transport of fine sediment in the Athabasca River (Krishnappan 1996). The algorithm can now be implemented in water quality models for predicting the transport of contaminants in the Athabasca River. For extrapolating the laboratory data to the field conditions, a scale relationship for the bed shear stress was developed to account for the difference in the flow characteristics near the bed in the laboratory channel and in the natural river. The shear stress values obtained covered a wide range of flow conditions that exist in the Athabasca River.

The results of the flocculation surveys suggested that the deposition of the effluent solids and the ambient sediment could persist over a period of almost eight months in a year when the flow rate is lower than the fall survey value. The deposited sediment could become resuspended during the high flows that normally start in June in the Athabasca River. At freshet, it is possible that the bed-shear stress will exceed the critical shear stress for erosion and the resuspension of the deposited material will occur, resulting in transport of the material further downstream. When the flow rate decreases, the deposition cycle repeats. A new algorithm for the transport of fine sediment in the Athabasca River was developed and can now be implemented in water quality models for this system.

7.0 PREDICTIONS - CONTAMINANT MODELLING

7.1 INTRODUCTION

The purpose of contaminant modelling for NRBS is to make predictions about the distribution and fate of contaminants in response to new or changed loadings to the northern rivers basins. These predictions can be made for the abiotic (water and sediment) and biotic (invertebrates and fish) components of the rivers. Two current questions which the modelling work attempts to address are: (1) At what rate do we predict that persistent contaminants in river sediments are being transported down river and through the system? and (2) At what rate do we predict that concentrations of persistent contaminants such as chlorinated dibenzofurans will decline in fish in response to declining loadings?

Contaminant modelling in river systems of this size (1000 km or more) presents problems of scale and is rarely attempted. Prior to NRBS, very little contaminant modelling work had been done on these rivers. Accordingly, our effort was concentrated on those areas where the most information was available and with the highest probability of success, i.e., the Athabasca River and the Wapiti/Smoky system. The mainstem of the Peace River was not attempted because of scale and contaminant dilution by the high flows found in the Peace.

The basic steps in model work are model selection, setup, calibration, validation and, finally, application. A modelling workshop was held in April, 1993 to consider model selection and the consequences for setup and calibration of fate and food chain models (Brownlee and Muir 1994). For fate modelling, the WASP (Water Quality Analysis Simulation Program) developed by the USEPA was recommended. For food chain modelling, the Thomann-Connolly model was recommended.

The fate modelling required a time series of loading data to generate a simulation and point or synoptic data for calibration. The food chain modelling required information about food webs and bioenergetics for invertebrates and fish in the rivers as well as environmental concentrations from point data or time series generated from fate model output.

A Modelling Sub-Committee was established with members from Environment Canada, Fisheries and Oceans Canada, Alberta Environmental Protection (AEP) and Syncrude Canada. The Sub-Committee was responsible for guiding the work, especially the selection of compounds to be modelled, the assembly of field data sets, selection of environmental properties of the modelled compounds and the review, testing and application of the models. The modelling work was done by private sector consulting firms with established expertise in fate and food chain modelling. Fate modelling was carried out by Golder Associates Ltd. (Golder 1997a,b) and the food chain modelling was carried out by CanTox Inc. (Starodub and Ferguson 1997a,b).

Loading data were available from the NRBS Northdat database. Calibration data were available from AEP winter synoptic surveys of the Athabasca River (Noton and Saffran 1995), and from NRBS field surveys conducted in April and May, 1992 (R.L.&L. 1993, Crosley 1996a, Pastershank and Muir 1995) and February-March, 1993 (Crosley 1996c). The 1993 NRBS survey was carried out in conjunction with the AEP winter synoptic survey. Information on fish diet, feeding patterns and movement was available from the Food Chain Component of NRBS. For the Wapiti/Smoky River, an industry data set was used (SENTAR 1993).

7.2 CONTAMINANT FATE MODEL

Prior to model calibration for organic compounds, two separate but parallel activities were initiated: choosing the compounds to be modelled and selection of environmental fate properties for them; and setting up the hydraulic regime for the rivers, calibration of the model for a conservative substance (sodium ion), and calibration for total suspended solids. Discussions were held between the Modelling Sub-Committee and the consultants to decide on points of model setup such as bottom sediment type, biofilm, and sediment transport.

The following organic compounds were selected for modelling:

- 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF)
- Dehydroabietic acid
- 12,14-Dichlorodehydroabietic acid
- 3,4,5-Trichlorocatechol
- 3,4,5-Trichloroguaiacol
- 3,4,5-Trichloroveratrole, and
- Phenanthrene

These compounds represent four classes of compounds with a fairly wide range of environmental properties. The first six had the most extensive loading information and field data for calibration. Phenanthrene was included because it is a widely distributed polycyclic aromatic hydrocarbon (PAH) and was most likely to have loading and survey data available. As it turned out, only limited data were available for phenanthrene.

Another possibility was to model a range of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs). A limited amount of survey data were available for PCDFs from dichloro- to octachloro-, but loading information was limited or not available. The decision was made to leave modelling of this group of compounds (except for 2,3,7,8-TCDF) to the model testing and application stage.

The following environmental fate properties were required for chemical fate modelling in WASP:

- Water solubility
- Octanol-water partition coefficient, log K_{ow}
- Sediment-water partition coefficient, log K_{oc}
- Henry's Law constant
- Photolysis and biodegradation rates

The first stage was a literature search carried out by the consultants (Golder Associates and CanTox). The Modelling Sub-Committee critically reviewed these values, added further information from the literature, field results and property estimation software (Brownlee 1996), and made the final selection of environmental fate properties to be used in initial model calibration for the compounds.

The time period for the simulation is January 1, 1992 to December 31, 1993. Figure 20 shows the Athabasca River calibration for sodium ion against three synoptic surveys (AEP). The model was able to simulate the hydraulic component reasonably well.

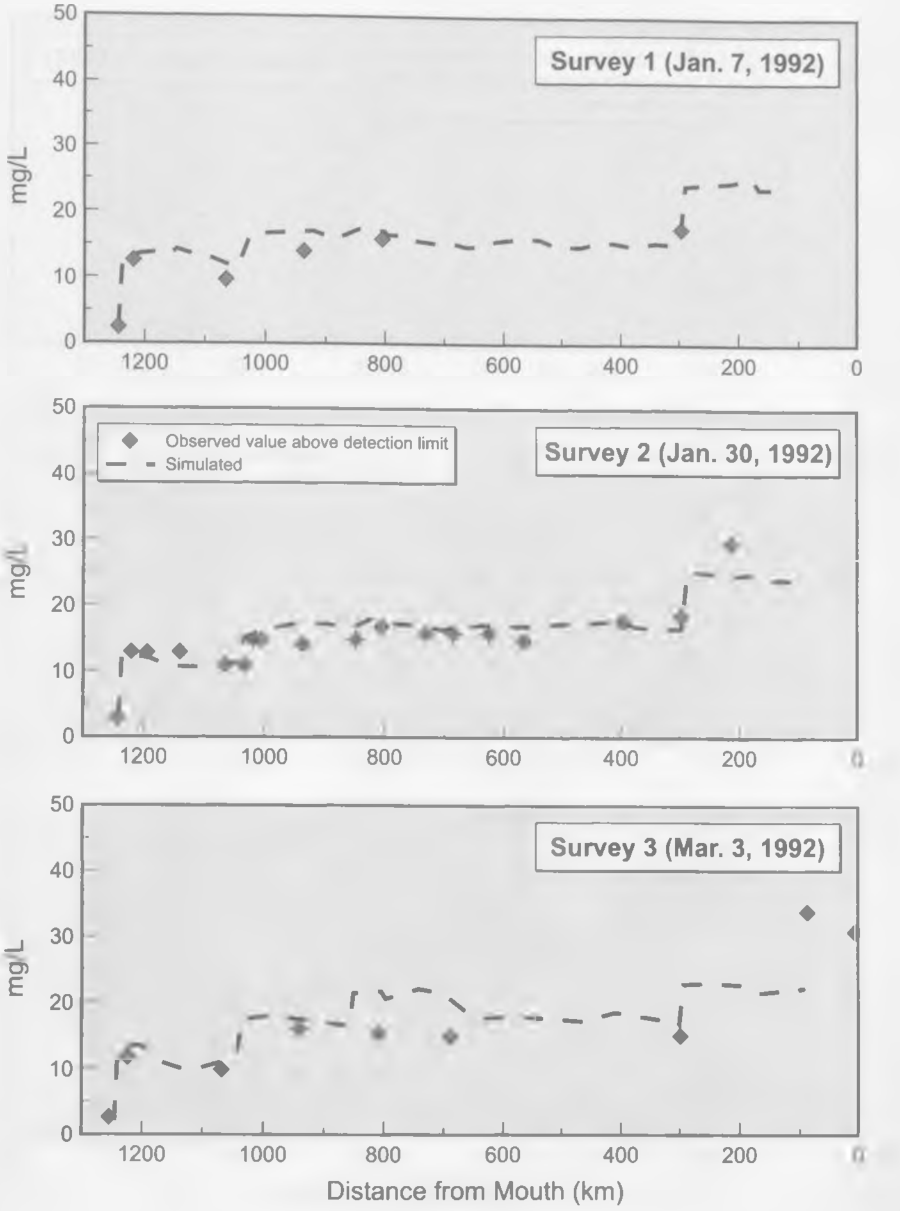

Figure 20. **The Athabasca River calibration for sodium ion against three synoptic surveys (AEP) for the time period January 1, 1992 to December 31, 1993 (Golder Associates 1997a).**

There were insufficient data for total suspended solids (TSS) upstream from Hinton, so a time series was generated from a turbidity-TSS relationship between turbidity measurements at the Hinton intake and TSS. This and other loadings of TSS are described in Golder (1995). The results of the TSS calibration against three synoptic surveys are shown in Figure 21.

The next step involved the Phase I calibration for organic compounds. Only results for 2,3,7,8-TCDF in the Athabasca and Wapiti/Smoky rivers are presented here (Figures 22 a and b). Results for all compounds in both systems are given in Golder (1995). Calibration was

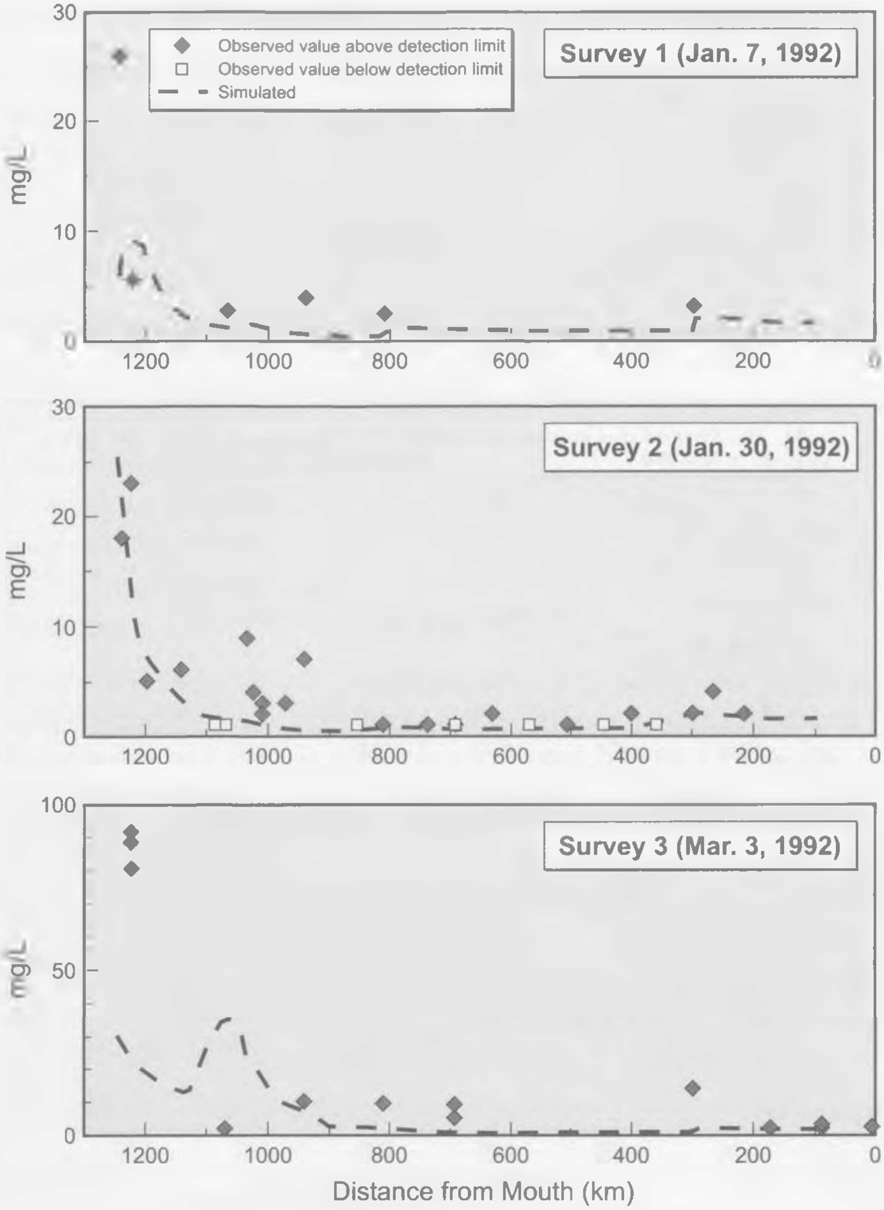

Figure 21. The Athabasca River calibration for TSS against three synoptic surveys (AEP) for the time period January 1, 1992 to December 31, 1993 (Golder Associates 1997a).

"successful" for only some compounds in some compartments (water, suspended sediment or bottom sediment). This was not unexpected given the shortage of loading information and point data in the rivers in some cases such as 12,14-dichlorodehydroabietic acid, dehydroabietic acid and phenanthrene. In general, calibration was most successful for those compounds with the most information. A quantitative measure of the "success" of the calibrations was not attempted, rather it was based on a subjective evaluation of the fit of the simulated concentrations to the observed values. There were insufficient data sets to validate the model since all of the available data were required for calibration.

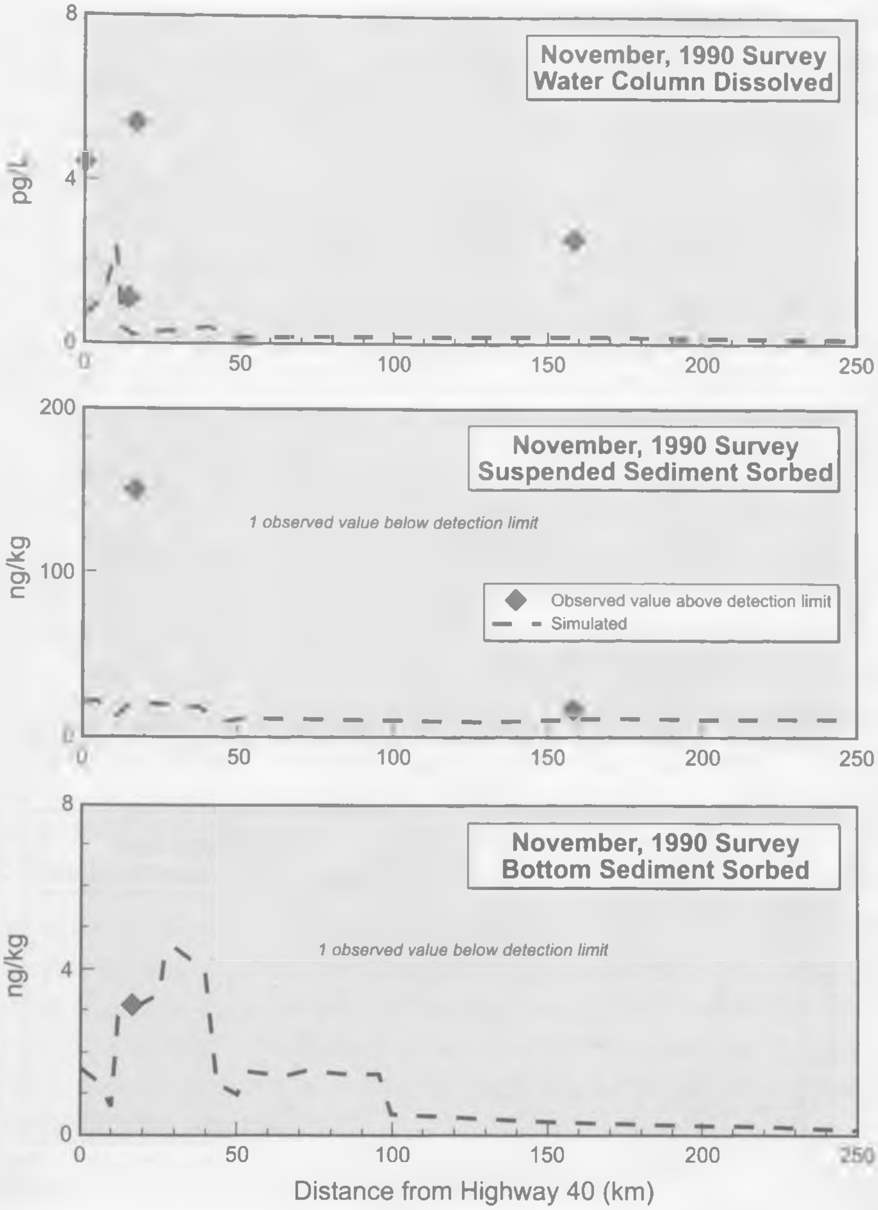

Figure 22. Results of the Phase I calibration for 2,3,7,8-TCDF in the Athabasca River (Golder Associates 1997a).

The calibration results for bottom sediments showed the need for a better understanding of sediment transport processes. The model predicted slowly increasing bottom sediment contaminant concentrations as sediment settled onto the river bed. Accordingly, a second phase of modelling was undertaken to refine the algorithms used for sediment transport by prediction of sediment deposition and resuspension based on critical shear stress (Krishnappan 1996; Golder 1997b).

In the Phase I work, descriptive sediment transport was used in WASP4 whereby sediment settling and resuspension velocities was specified in a user-defined time series. Sufficient data

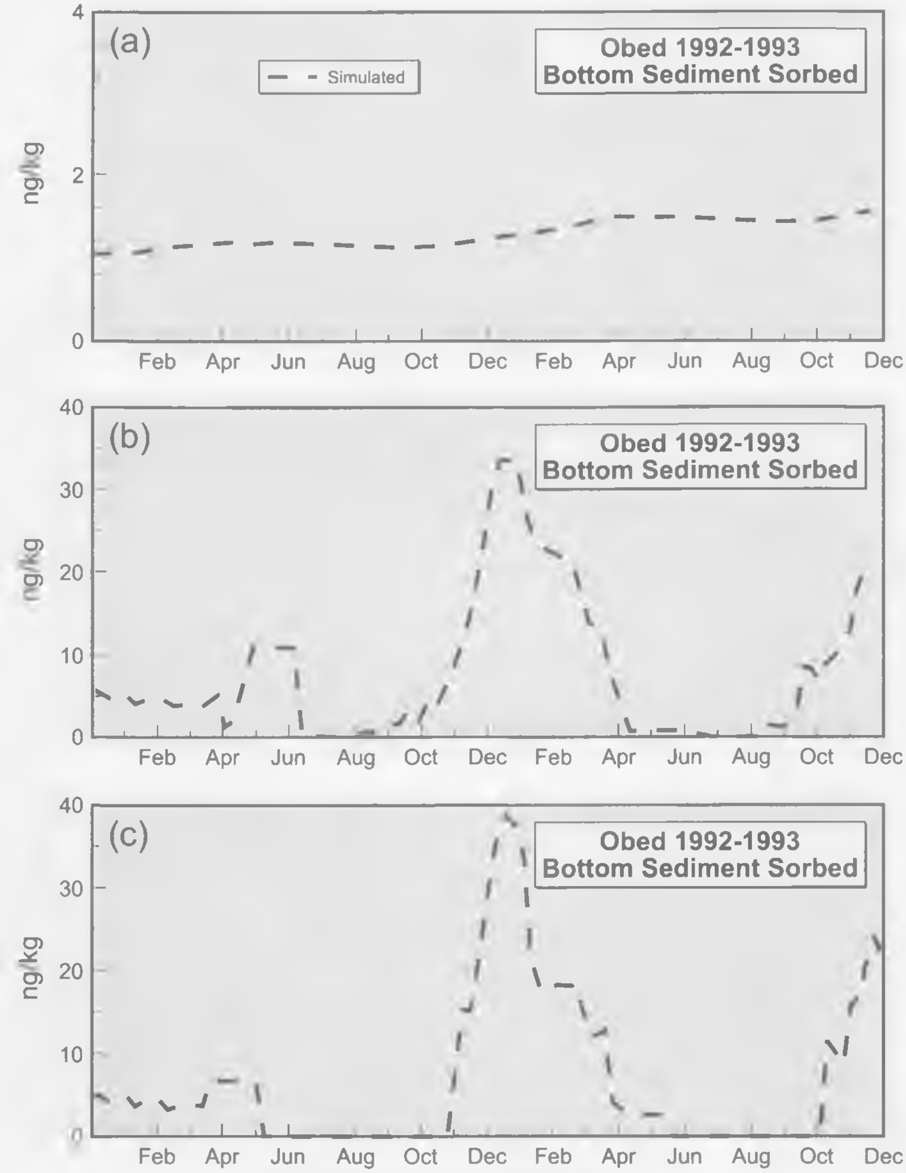

Figure 23. **The simulated concentration of 2,3,7,8-TCDF in the bed sediment (a) increased slowly (Golder Associates 1997a); (b) and (c) seasonally dynamic in the Phase II simulations (Golder Associates 1997b).**

existed to define net settling rates, but not resuspension. The model simulated a continual accumulation of bed sediment and no net downstream movement of bed sediment. In Phase II, a totally new predictive sediment transport routine was written. The underlying science for this is based on field and laboratory studies of Krishnappan and Stephens (1996) for Athabasca River sediments, which uses critical shear stress to predict sediment settling and resuspension. This algorithm incorporates parameters for bed roughness (D65), critical shear stress for deposition (Tcd), and the ratio of open water to ice-covered bed shear stress. As well, the ratio of fine/coarse sediment was varied. The first simulation series (Part B in Figure 23) used

D65=0.002 m, Tcd=0.50 N/m², SEDICEFC=0.50 and a fine to coarse sediment ratio of 15:85 for the upper river and 85:15 for the lower river. The second simulation series (Part C in Figure 23) used D65=0.02 m, Tcd=0.50 N/m², SEDICEFC=1.0 and a fine to coarse sediment ratio of 15:85 for the entire river.

The original calibration of Phase I was rerun with this new algorithm using two sets of parameter values for Phase II. There are some differences between water column dissolved and suspended sediment concentrations of contaminants from the Phase I calibration, but the biggest differences are in the bed sediment. Originally, the simulated contaminant concentrations in the bed sediments increased slowly (Part A in Figure 23). In the Phase II simulations, contaminant concentrations are seasonally dynamic (Parts B and C in Figure 23). There is an accumulation of fine sediment during winter, ice-covered months with higher concentrations of BKME-related contaminants. This fine sediment is almost completely removed during the spring freshet and there is no significant net accumulation of fine sediment during the late spring to late fall period.

All of the NRBS sediment collections were carried out in spring or fall months so no winter results are available to test these predictions. From the RSS results, contaminant (e.g., 2,3,7,8-TCDF) and organic carbon concentrations in suspended sediments collected in the winter (Crosley 1996a,c) are higher than in the fine (< 62 µm) fraction of bed sediments collected in open water months (Crosley 1996b). Accumulation of this settled material on the bed would result in elevated concentrations of contaminants and organic carbon in bed sediment during winter months. This could be tested by collection of bed sediments during the winter from depositional zones that are now well characterised (Crosley 1996b). The indications are that the model may be qualitatively but not quantitatively correct.

Future work can examine the original question posed in Section 7.1, namely at what rate are persistent contaminants in river sediments being transported down river? This can be done with a simulation run in which all background and loadings are set to zero and the first bed sediment cell is given an artificially high contaminant concentration. By examining the time series at downstream sites it may be possible to predict through simulation the downstream movement of this "plug" of contaminated bed sediment.

Further possibilities for model testing and application are:

- vary photolysis and biodegradation rates seasonally
- model other PCDF and PCDD congeners; most of these loadings can only be estimated by their ratio to 2,3,7,8-TCDF as determined on two sampling occasions by NRBS, and
- test the robustness of the model, i.e., what is the likelihood that a calibration "success" is fortuitous?

7.3 CONTAMINANT FOOD CHAIN MODEL

Information on fish diet and contaminant levels for the Athabasca River came from NRBS sources (Crosley 1996a; Pastershank and Muir 1995) and for the Wapiti/Smoky from SENTAR (1993). Information on invertebrate and fish energetics came from literature sources (cited in

Starodub and Ferguson 1997b). The same suite of compounds was used for food chain and fate modelling, except that phenanthrene was not used in the food chain modelling.

The following environmental properties were required for food chain modelling:

- Octanol-water partition coefficient, log K_{ow}
- Sediment-water partition coefficient, log K_{oc}
- Bioconcentration factor, BCF

The first two were already available from the exercise carried out for the fate modelling and the third was added specifically for food chain modelling. The selection process is described in Brownlee (1996).

The Phase I food chain modelling concentrated on the bioenergetic Thomann-Connolly model. As a comparison, 2,3,7,8-TCDF was also modelled for mountain whitefish and longnose sucker using the Gobas partitioning model (Starodub and Ferguson 1997b).

For both models, one of the primary requirements was a quantitative description of the food web based on gut content analysis of fish. This was established for the upper Athabasca River using NRBS data. Two distinct exposure pathways were considered by including both bottom-feeding and filter-feeding invertebrates. Initial values for octanol-water partition coefficient, gill membrane permeability ratio, dietary chemical assimilation efficiency, and chemical excretion rate were based on literature values. Exposure concentrations for the upper Athabasca River came from NRBS 1992 RSS results (Crosley 1996a). For model calibration, concentrations from NRBS collections were used (Pastershank and Muir 1995). Data were available for three species of fish (mountain whitefish, longnose sucker and northern pike) and three different orders of invertebrates.

In our application of the Thomann-Connolly Model, calibration for the resin acids (dehydroabietic and 12,14-dichlorodehydroabietic acids) and for the chlorophenolic compounds (3,4,5-trichlorcatechol, 3,4,5-trichloroguaiacol and 3,4,5-trichloroveratrole) were complicated by the limited kinetic data available for them in the literature and also by the limited field data available for levels in biota. Accordingly, calibration efforts concentrated on 2,3,7,8-TCDF at the site about 1 km downstream from the Weldwood mill.

For all fish species modelled with the Thomann-Connolly model, agreement of predicted with observed values was considerably closer when an explicit excretion rate was used for 2,3,7,8-TCDF rather than using a bioconcentration factor (BCF) calculated from the octanol-water partition coefficient and percent lipid.

For mountain whitefish, the best calibration for 2,3,7,8-TCDF overestimated observed concentrations by a factor of about three. The diet was 61% filter-feeding invertebrates and 39% bottom-feeding invertebrates. For longnose sucker, the best calibration overestimated observed concentrations by a factor of about two. The diet was 45% detritus, 6% filter-feeding invertebrates and 49% bottom-feeding invertebrates. For northern pike, the best calibration overestimated field concentrations at the Weldwood site by a factor of about ten, but agreement was better with sites further downstream. The diet for this calibration was 34% mountain whitefish, 42% longnose sucker and 24% small foraging fish.

The Gobas model, on the other hand, underpredicted observed concentrations for 2,3,7,8-TCDF in fish, and predicted concentrations were very sensitive to dietary composition for mountain whitefish. For mountain whitefish at the Weldwood site, the best calibration underpredicted observed concentrations by a factor of more than two with a diet of 100% filter-feeding invertebrates. For longnose sucker at the Weldwood site, the best calibration underpredicted observed concentrations by a factor of about five with a diet of 100% benthic invertebrates.

Using a steady state, bioenergetic model, the Phase I modelling succeeded in establishing a credible food web configuration for invertebrates and three species of fish in the upper Athabasca River. Using literature values for bioenergetic and pharmacokinetic parameters, the calibration for 2,3,7,8-TCDF in fish was within a factor of two to ten, depending on the species. The model predicted 2,3,7,8-TCDF concentration in mountain whitefish > longnose sucker > northern pike at the Weldwood site. The model also provided some support for the theory that consumption of filter-feeding invertebrates and suspended solids represent the primary exposure pathway for mountain whitefish.

This modelling approach has some limitations, however. Because it is steady state it cannot easily be used to predict trends over time. Because point values of environmental concentrations are used as input it cannot be used to simulate a range of exposure concentrations and therefore a range of predicted concentrations in the species being modelled. To overcome these limitations, a second phase was undertaken in which the basic Thomann-Connolly model was modified to provide a stochastic, time variable model.

For initial calibration of the stochastic, time variable model in Phase II (Starodub and Ferguson 1997a), the model was run with the same dietary composition and bioenergetic and pharmacokinetic parameters as used in the Phase I model. Two sets of stochastic environmental exposure concentrations were calculated from the same values as used in Phase I using the variability of 2,3,7,8-TCDF loading from the Weldwood mill. These sets simulated the periods of January to June, 1992 and July to December, 1992. The model predicted well the 2,3,7,8-TCDF concentrations in both bottom-feeding and filter-feeding invertebrates at the Weldwood site, but underpredicted the 2,3,7,8-TCDF concentrations in the three species of fish by a factor of five to ten.

In view of this result some initial testing has been carried out and has shown that initial contaminant concentration and temperature had minimal effect on predicted contaminant levels in invertebrates and fish (Brownlee *et al.,* in prep.). As expected, environmental concentrations do have an effect on predicted contaminant levels in fish and invertebrates. Further work is needed to generate time series of several years of contaminant (2,3,7,8-TCDF) concentrations in water, suspended sediment, porewater and bottom sediment. This can draw upon the NRBS data set of measured field values as well as simulated values from the chemical fate model. One time series has been generated (Brownlee *et al.,* in prep.) taking a “reach average” approach (Hinton to Windfall) and using the Phase I fate model, NRBS data and historical data. When used as input to the model, this time series resulted in predictions of 2,3,7,8-TCDF that track the declining environmental concentrations but differ from observed values in fish by a factor of three to five, lower or higher depending on species, and overpredict concentrations in invertebrates by a much larger factor.

The stochastic, time variable model has the capability to address the question posed in Section 7.1 about predicting how concentrations of contaminants such as 2,3,7,8-TCDF will change in response to declining loadings. However, further calibration and testing are required to provide better predictions of actual concentrations in fish and especially in invertebrates.

7.4 MODELLING CONCLUSIONS

Future monitoring should strive to provide actual numbers and not a lot of Non-Detect values. This will require larger sample sizes and more sensitive analytical methods than were employed in the NRBS.

For Contaminant Fate Modelling, winter sampling of bed sediments should be carried out to test the Phase II model predictions of higher contaminant and organic carbon concentrations in bed sediments during winter months. Laboratory studies are necessary to give better estimates of chemical fate properties where our knowledge is weak, e.g., biodegradation rates.

For Food Chain Modelling, refinements in the following areas may contribute to better model calibration:

- Fish movement (further analysis of NRBS data plus new data);
- The structure of food webs in these rivers;
- Excretion rates (literature/laboratory studies).

8.0 RECOMMENDATIONS

Monitoring and Reporting

1) Given the low levels of organochlorines in water, sediment and biota by the end of the study period, it is recommended that the design and purpose of existing water quality monitoring programs be reviewed based on the NRBS findings. There appears to be no need for intensive basin-wide monitoring for these contaminants. Periodic monitoring, on a two or three year cycle, for contaminants in relevant compartments only, for example PCBs and chlorinated dioxins/furans in fish and PAHs and resin acids in sediment, should be sufficient to detect changes in the basin.

2) Mercury levels in certain areas of the basin, for example the lower reaches of the Athabasca River, are high and likely exceed human health consumption guidelines. It is recommended that mercury levels continue to be monitored regularly, particularly in the lower Athabasca River and western Lake Athabasca.

3) Burbot or, failing that, one of the sucker species are likely the most suitable large fish for use as an indicator species for biological monitoring. It is recommended that whitefish not be used for biological monitoring in this system.

4) It is recommended that a combination of the NRBS results from the broad spectrum analysis and selected target compound analysis be used to establish a baseline finger-print pattern of contaminants in effluents and ambient waters against which future changes can be assessed through the use of pattern recognition techniques.

5) It is recommended that a data management system be established to allow storage and access of all contaminant data collected by governments, industry etc.

6) In view of the unique character of the NRBS samples and their potential value to future generations, it is recommended that government agencies undertake to ensure that the NRBS samples are adequately stored so that they can be made available as a baseline reference for future studies.

Fish Consumption/Water Quality Guidelines

7) In light of the dramatic decreases in chlorinated dioxin and furan concentrations in fish observed by the NRBS after bleaching changes by the pulp mills, it is recommended that these bleaching changes be permanent for the mills and that fish consumption advisories based on chlorinated dioxin/furan concentrations be reviewed.

8) It is recommended that better dietary intake information for subsistence fish eaters be obtained to improve the risk assessment.

9.0 REFERENCES

Alke, E.E. 1995. Executive summary of a workshop on the impacts of land clearing on the hydrologic and aquatic resources of boreal forests in Alberta, November 18 and 19, 1994. Northern River Basins Study Project Report No. 63.

Anderson, A-M. 1995. Overview of Pesticide Data for Alberta Surface Waters. Prepared for the Canada/Alberta Environmentally Sustainable Agriculture Agreement.

Balagus, P., A. De Vries and J.E. Green. 1993. Collection of fish from the traditional winter fishery on the Peace-Athabasca Delta, 1993. Northern River Basins Study Project Report No. 20.

Ballschmiter, K. 1991. Global distribution of organic compounds. Environ. Carcin. Ecotox. Revs. C9, 1-46.

Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, D. Muir, R. Shearer, T. Tracey, T. Bidleman. 1992. Arctic contaminants: sources, occurrence and pathways. Sci. Tot. Environ. 22, 1-74.

Barton, B.A., C.P. Bjornson and K.L. Egan. 1993a. Special Fish Collections, Upper Athabasca River, May, 1992. Northern River Basins Study Project Report No. 8.

Barton, B.A., D.J. Patan and L. Seeley. 1993b. Special Fish Collections, Upper Athabasca River, September and October, 1992. Northern River Basins Study Project Report No. 10.

Berry, R.M., C.E. Luthe, R.H. Voss, P.E. Wrist, P. Axegard, G. Gellerstedt, P.-O. Lindblad and I. Pöpke. 1991. The effects of recent changes in bleached softwood kraft mill technology on organochlorine emissions: an international perspective. Pulp Pap. Can. 92(6): T155-165.

Bourbonniere, R.A., S.L. Telford and J.B. Kemper. 1996a. Depositional history of sediments in Legend and Weekes Lakes: Geochronology and bulk parameters. Northern River Basins Study Project Report No. 71.

Bourbonniere, R.A., S.L. Telford and J.B. Kemper. 1996b. Depositional history of sediment in Lake Athabasca: Geochronology, bulk parameters, contaminants and biogeochemical markers. Northern River Basins Study Project Report No. 72.

Broman, D., Näf, Y. Zebür and K. Lexen. 1989. The composition, distribution and flux of PCDDs and PCDFs in settling particulate matter (SPM) - a sediment trap study in the northern Baltic. Chemosphere 19: 445-450.

Brownlee, B.G. and D.C.G. Muir. 1994. Notes of the Contaminant Fate and Food Chain Modelling Workshop, April 20 and 21, 1993. Report for Northern River Basins Study Project 2381-C8.

Brownlee, B. 1996. Selection of Environmental Fate Properties for a Suite of Organic Compounds Employed in Northern River Basins Study Contaminant Fate and Food Chain Modelling. Technical Note AEPB-TN-96-04. National Water Research Institute, Burlington, Ontario.

Brownlee, B.G., S.L. Telford, R.W. Crosley and L.R. Noton. 1996. Distribution of organic contaminants in bottom sediments, Peace and Athabasca River Basins, 1988-1992. Northern River Basins Study Project Report No. 134.

Calamari, D., P. Tremolada, A. DiGuardo and M. Vighi. 1994. Chlorinated hydrocarbons in pine needles in Eurpoe: Fingerprint for the past and recent use. Environmental Science and Technology 28, 429-434.

Clement, R.E., S.A. Suter, E. Reiner, D. McCurvin and D. Hollinger. 1989. Concentrations of chlorinated dibenzo-*p*-dioxins and dibenzofurans in effluents and centrifuged particulates from Ontario pulp and paper mills. Chemosphere 19: 649-654.

Corns, I.G.W. 1994. An Annotated Bibliography on Boreal Mixed Wood Literature of the Prairie Provinces. Canada Forestry Center. Edmonton, Alberta.

Cotham, W.E. and T.F. Bidleman. 1991. Estimating the atmospheric deposition of organic compounds to the Arctic. Chemosphere 22: 165-188.

Cotton, M.M. 1995. Pesticide Characteristics and a Preliminary Assessment of the Potential Environmental Significance of Pesticides to Surface Water. Prepared for the Canada/Alberta Environmentally Sustainable Agriculture Agreement.

Cotton, M.M. and G. Bytrus. 1995. Pesticide Sales Trends in Alberta. Prepared for the Canada/Alberta Environmentally Sustainable Agriculture Agreement.

Court, G. 1993. Collection of young-of-the-year mergansers, Wapiti and Athabasca Rivers, August, 1992. Northern River Basins Study Project Report No. 4.

Crosley, R. 1996a. Environmental contaminants in water and sediments, upper Athabasca River, April 1992. Northern River Basins Study Project Report No. 108.

Crosley, R. 1996b. Environmental contaminants in bottom sediments, Peace and Athabasca River Basins, October 1994 and May 1995. Northern River Basins Study Project Report No. 106.

Crosley, R.W. 1996c. Environmental contaminants in water and sediments; PCDDs, PCDFs and resin acids, Athabasca River basin, February-May, 1993. Northern River Basins Study Project Report No. 130.

Dickson, L.C., D. Lenoir and O. Hutzinger. 1989. Surface-catalyzed formation of chlorinated dibenzodioxins and dibenzofurans during incineration. Chemosphere 19: 277-282.

Donald, D.B., H.L. Craig and J. Syrginnis. 1996. Contaminants in environmental samples: Mercury in the Peace, Athabasca and Slave River basins. Northern River Basins Study Project Report No. 105.

Earl, P.F. and D.W. Reeve. 1990. Chlorinated organic matter in bleached chemical pulp production. Part 6: Chlorinated compounds in effluents. Tappi J. 73(1): 179-184.

Eisenreich, S.J. and W.M.J. Strachan. 1992. Estimating atmospheric deposition of toxic substances to the Great Lakes - An update. Environment Canada, Burlington, ON. 59 pp.

Environment Canada. 1991. The State of Canada's Environment. Ottawa, Ontario.

Evans, M.S., R.A. Bourbonniere, D.G.C. Muir, W.L. Lockhart, P. Wilkinson and B.N. Billeck. 1996. Depositional history of sediments in Great Slave Lake: Spatial and temporal patterns in geochronology, bulk parameters, PAHs and chlorinated contaminants. Northern River Basins Study Project Report No. 99.

Evers, E.G.H., J.W. Van Berghem and K. Olie. 1989. Exploratory data analysis of PCDD and PCDF measurements in sediments from industrialised areas. Chemosphere 19: 459-466.

Fiedler, H., O. Hutzinger and C.W. Timms. 1990. Dioxins: Sources of environmental load and human exposure. Toxicol. and Environ. Chem. 29: 157-234.

Golder Associates Ltd. 1997a. Contaminant fate modeling, Athabasca, Wapiti and Smoky Rivers (Volume I). Northern River Basins Study Project Report No. 112.

Golder Associates Ltd. 1997b. Contaminant fate modelling for the Athabasca River: Implementation of new sediment flux routines. Northern River Basins Study Project Report No. 136.

Green, J.E. 1994. Delta basins contaminant survey: muskrat collections in the Athabasca River Delta, December, 1992. Northern River Basins Study Project Report No. 30.

Hebert, D. 1995. Overview of Forest Impacts and the Extent of Harvesting in Northern Alberta. Section 2.3 in "Executive Summary of a workshop on The Impacts of Land Clearing on the Hydrologic and Aquatic Resources of Boreal Forests in Albert," Northern River Basins Study Project Report No. 63.

Hoff, R.M. 1994. An error budget for the determination of atmospheric mass loading of toxic chemicals in the Great Lakes. Journal of Great Lakes Research 20: 229-239.

Hoff, R.M., D.G.C. Muir and N.P. Grift. 1992. Annual cycle of polychlorinated biphenyls and organohalogenated pesticides in air in southern Ontario. I. Air concentration data. Environmental Science and Technology 26: 266-275.

Hoff, R.M., W.M.J. Strachan, C.W. Sweet, C.H. Chan, M. Shackelton, T.F. Bidleman, K.A. Brice, D.A. Burniston, S. Cuisson, D.F. Gatz, K. Harlin and W.H. Schroeder. 1996. Atmospheric deposition of toxic chemicals to the Great Lakes. Atmospheric Environment 30: 3505-3527.

Horstman, L.P. and T.E. Code. 1994. Mink Contaminants, Field Component, January to March, 1992. Northern River Basins Study Project Report No. 1.

Hvenegaard, P.J. and T.D. Boag. 1993. Burbot collections, Smoky, Wapiti and Peace Rivers, October and November, 1992. Northern River Basins Study Project Report No. 12.

Jacobson, T.L. and T.D. Boag. 1995. Fish collections, Peace, Athabasca and Slave River Basins - September to December 1994. Northern River Basins Study Project Report No. 61.

Johnson, I., A. Urson and L. Geleta. 1996. Broad spectrum analysis of municipal and industrial effluents discharged into the Northern River Basins, 1989-1994. Northern River Basins Study Project Report No. 138.

Johnson, I. and A. Urso. 1996. Analysis of northern river surface waters for contaminant identified in the broad spectrum analysis of municipal and industrial effluents. Northern River Basins Study Project Report No. 121.

Johnson, I. 1996. Review of GC-MS data produced in analysis of municipal and industrial effluents discharged into the northern river basins between 1989 and 1994. Northern River Basins Study Project Report No. 111.

Joshi, B.K. and B.J. Hillaby. 1991. Effects of process improvements on pulp mill effluent characteristics. In *Environmental fate and effects of bleached pulp mill effleunts,* A. Södergren (Ed.), Swedish Environmental Protection Agency Report 4031, pp. 101-109.

Krishnappan, B.G. 1996. A New Algorithm for Fine Sediment Transport. National Water Research Institute, Burlington, Ontario, NWRI Contribution No. 96-160.

Krishnappan, B.G. and R. Stephens. 1996. Critical shear stresses for erosion and deposition of fine suspended sediment from the Athabasca River. Northern River Basins Study Project No. 85.

Krishnappan, B.G., R. Stephens, J.A. Kraft and B.H. Moore. 1995. Size distribution and transport of suspended particles, Athabasca River, February and September, 1993. Northern River Basins Study Project report No. 51.

Kuehl, D.W., B.C. Butterworth, W.M. DeVita and C.P. Sauer. 1987. Environmental contamination by polychlorinated dibenzo-*p*-dioxins and dibenzofurans associated with pulp and paper mill discharge. Biomed. Environ. Mass. Spectrom. 14: 443-447.

Lockhart, W.L., R. Wagemann, B. Tracey, D. Sutherland and D.J. Thomas. (1992): Presence and implications of chemical contaminants in fresh waters of the Canadian Arctic. Sci. Tot. Environ. 122: 165-245.

Lyons, B. 1995. Environmental Overview of the Northern River Basins. NRBS Synthesis Report No.8.

McCubbin, N. And J. Folke. 1993. A review of Literature on pulp and paper mill effluent characteristics in the Peace and Athabasca River basins. Northern River Basins Study Project Report No. 15.

McCubbin, N., P. Labrosse and AGRA Earth and Environmental Ltd. 1996. NORTHDAT, an effluent database management system, application description. Northern River Basins Study Project Report No. 16.

McDonald, K. 1996. Probable pathways for long-range transport of air pollutants to Lake Athabasca: Analysis using a Lagrangian back trajectory model. Northern River Basins Study Project Report No. 109.

Muir, D.C.G., C.A. Ford, N.P. Grift, D.A. Metner and W.L. Lockhart. 1990. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. Arch. Environ. Contam. Toxicol. 19: 530-542.

Muir, D.C.G., R. Wagemann, B.T. Hargrave, D.J. Thomas, D.B. Peakall and R.J. Norstrom. 1992. Arctic marine ecosystem contamination. Sci. Tot. Environ. 122: 75-134.

Muir, D.C.G., M. Segstro, P.M. Welbourne, D. Toom, S.J. Eisenreich, C.R. Macdonald and D. Whelpdale. 1993. Patterns of accumulation of airborne organochlorine contaminants in lichens from the upper Great Lakes region of Ontario. Environmental Science and Technology 27: 1201- 1210.

Muir, D.C.G. and G.M. Pastershank. 1996. Environmental contaminants in fish: Spatial and temporal trends of polychlorinated dibenz-*p*-dioxins and dibenzofurans, Peace, Athabasca and Slave River basins, 1992-1994. Northern River Basins Study Project Report No. 129.

Noton, L.R. and K.A. Saffran. 1995. Water Quality in the Athabasca River System 1990-93. Alberta Environmental Protection, Edmonton, Alberta.

Ongley, E.D., D.A. Birkholz, J.H. Carey and M.R. Samoiloff. 1988. Is water a relevant sampling medium for toxic chemicals? An alternative environmental sensing strategy. J. Environ. Qual. 17: 391-401.

Pastershank, G.M. and D.G.C. Muir. 1995. Contaminants in environmental samples: PCDDs and PCDFs downstream of bleached kraft mills, Peace and Athabasca Rivers, 1992. Northern River Basins Study Project Report No. 44.

Pastershank, G.M. and D.G.C. Muir. 1996. Environmental contaminants in fish: Polychlorinated biphenyls, organochlorine pesticides and chlorinated phenols, Peace and Athabasca Rivers, 1992 to 1994. Northern River Basins Study Project Report No. 101.

R.L.&L. 1993. Benthos and Bottom Sediment Field Collections Upper Athabasca River April to May, 1992. Northern River Basins Study Report No. 2.

R.L.&L. 1994. A General Fish and Riverine Habitat Inventory, Athabasca River, April to May, 1992. Northern River Basins Study Report No. 32.

R.L.&L. 1994. A General Fish and Riverine Habitat Inventory, Athabasca River, October, 1993. Northern River Basins Study Report No. 40.

SENTAR Consultants Ltd. 1996. A synthesis of information on effluent characteristics of municipal and non-pulp mill industrial sources in the Peace, Athabasca and Slave River basins. Northern River Basins Study Project Report No. 79.

SENTAR. 1993. Wapiti/Smoky River Ecosystem Study. SENTAR Consultants Ltd.

Smithson, G. 1993. Radionuclide levels in fish from Lake Athabasca, February, 1993. Northern River Basins Study Project Report No. 26.

Starodub, M.E. and G. Ferguson. 1997a. A Bioenergetic Model of Food Chain Uptake and Accumulation of Organic Chemicals in the Athabasca River: Stochastic and Time Variable Version. Northern River Basins Study Project Report No. 113.

Starodub, M.E. and G. Ferguson. 1997b. A Bioenergetic Model of Food Chain Uptake and Accumulation of Organic Chemicals, Athabasca River Northern River Basins Study Project Report No. 137.

Strachan, W.M.J., G. Eriksson, H. Kylin and S. Jensen. (1993): Organochlorine compounds in pine needles: Methods and trends. Env. Toxicol. Chem 13: 443-451.

Swackhamer, D.L. and R.A. Hites. (1988): Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior. Environmental Science and Technology 22: 543-548.

Thomas, D.J., B. Tracey, H. Marshall and R.J. Norstrom. (1992): Arctic terrestrial ecosystem contamination. Sci. Tot. Environ. 122: 135-164.

Theisen, J., W. Funcke, E. Balfanz and J. König. 1989. Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials. Chemosphere 19: 423-428

Wayland, M. 1995a. Environmental contaminants in pre-fledged common mergansers, Wapiti River, August 1992. Northern River Basins Study Project Report No. 48.

Wayland, M. 1995b. Environmental contaminants in mink, Peace and Athabasca Rivers, December 1991 and January 1992. Northern River Basins Study Project Report No. 47.

Wayland, M. 1995c. Environmental contaminants in muskrats and canvasbacks, Peace-Athabasca Delta, 1992. Northern River Basins Study Project Report No. 64.

Westworth, D.A. and Associates. 1992. An Overview of Potential Forest Harvesting Impacts on Fish and Fish Habitat in the Northern Boreal Forests of Canada's Prairie Provinces. Prepared for the Department of Fisheries and Oceans.

The Northern River Basins Study was established to examine the relationship between industrial, municipal, agricultural and other development and the Peace, Athabasca and Slave river basins.

Over four and one half years, about 150 projects, or "mini studies" were contracted by the Study under eight component categories including contaminants, drinking water, nutrients, traditional knowledge, hydrology/hydraulics, synthesis and modelling, food chain and other river uses. The results of these projects, and other work and analyses conducted by the Study are provided in a series of synthesis reports.

This Synthesis Report documents the scientific findings and scientific recommendations of one of these components groups. This Synthesis Report is one of a series of documents which make up the Northern River Basins Study's final report. A separate document, the Final Report, provides further discussion on a number of scientific and river management issues, and outlines the Study Board's recommendations to the Ministers. Project reports, synthesis reports, the Final Report and other NRBS documents are available to the public and to other interested parties.

Synthesis Report