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# SLAVE RIVER ENVIRONMENTAL QUALITY MONITORING PROGRAM SUMMARY REPORT

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**SLAVE RIVER ENVIRONMENTAL QUALITY MONITORING  
PROGRAM  
SUMMARY REPORT**

**TABLE OF CONTENTS**

TABLE OF CONTENTS .....	iii
LIST OF TABLES .....	v
LIST OF FIGURES .....	vi
<b>MAJOR CONCLUSIONS</b> .....	vii
Water .....	viii
Sediment .....	viii
Fish .....	ix
<b>RECOMMENDATIONS</b> .....	ix
Further Monitoring	
Water .....	ix
Sediment .....	x
Fish .....	x
Other General Recommendations .....	xi

**THE SLAVE RIVER ENVIRONMENTAL QUALITY MONITORING PROGRAM**

INTRODUCTION .....	1
OBJECTIVES .....	1
WHY THE STUDY WAS DONE .....	1
WHAT WAS STUDIED: THE ECOSYSTEM APPROACH .....	5
WHAT WAS LOOKED FOR: ANALYTICAL PARAMETERS .....	5
WHERE WERE THEY LOOKED FOR: SAMPLING MEDIA .....	7
Water .....	7
Suspended Sediment .....	7
Fish .....	8

WHERE AND HOW THE SAMPLES WERE COLLECTED: SAMPLING METHODS . .	11
General . . . . .	11
Water and Sediment . . . . .	11
Fish . . . . .	12
Control Sites . . . . .	12
WHAT WAS FOUND: RESULTS AND DISCUSSION . . . . .	23
Water Summary . . . . .	23
Physicals and Metals . . . . .	23
Organic Parameters . . . . .	30
Overall . . . . .	30
Suspended Sediment Summary . . . . .	30
Particle Size Distribution . . . . .	31
Metals . . . . .	31
Organic Parameters . . . . .	33
Chlorophenols . . . . .	33
Dioxins and Furans . . . . .	33
PAHs . . . . .	33
Overall . . . . .	34
Fish Summary . . . . .	35
Biological . . . . .	35
Metals . . . . .	35
Mercury . . . . .	36
Organic Parameters . . . . .	37
Chlorinated Phenolics . . . . .	38
Dioxins and Furans- General . . . . .	38
Dioxins and Furans- Detailed . . . . .	39
Toxaphene . . . . .	50
PAHs . . . . .	52
HEALTH ASSESSMENT . . . . .	52
REFERENCES . . . . .	53

## LIST OF TABLES

Table 2.1 Summary of Analytical Parameters and Sampling Media . . . . .	5.
Table 3.1 Centrifugate Water and Suspended Sediment Sampling Dates . . . . .	11
Table 5.1, 5.2, 5.4 Grab Water Samples - Mean Seasonal Concentrations . . . . .	24
Table 5.5 Comparison of Concentrations ( $\mu\text{g/L}$ ) in Grab vs Centrifugate Samples . . . . .	29
Table 5.7 Comparison of Metal Concentrations in Suspended Sediment Samples (n =18) to Draft Interim FSQ Guidelines ( $\mu\text{g/g}$ ) . . . . .	32
Table 5.18 Mercury Concentrations - Mean and Range ( $\mu\text{g/g}$ ) in Fish Tissues (n) . . . . .	36
Table 5.30 Toxaphene Concentration ( $\mu\text{g/g}$ ; % detection) in Fish. . . . .	50
Table 5.31 Toxaphene Concentrations ( $\mu\text{g/g}$ ) in Burbot Liver Samples . . . . .	51

## LIST OF FIGURES

Figure 1-1	Mackenzie River Basin - Upstream Industrial Activity (Source, NRBS Report to the Ministers, 1996). . . . .	3
Figure 2-7	The water collected after centrifuging (centrifugate) did not contain any appreciable amount of sediment. . . . .	9
Figure 3-30	Bile was collected with a sterile syringe taking care not to break the gall bladder, in order to avoid contamination of the liver. . . . .	9
Figure 2-3	SREQMP - Fort Smith, NWT Sampling Sites . . . . .	13
Figure 2-5	Slave River, Rapids of the Drowned at Fort Smith - Winter: The river does not freeze completely due to the turbulence caused by the rapids. . . . .	15
Figure 3-15	The sediment was scraped from the sides and bottom of the centrifuge bowl with clean Teflon-covered stainless steel spatulas and mixed thoroughly. . . . .	15
Figure 2-2	SREQMP - Pre- and Post-Dam Mean Annual Hydrographs - Slave River at Fitzgerald . . . . .	17
Figure 5-2	Average Percentage of Particle Size Distribution by Season . . . . .	27
Figure 3-20	During the open water season, fish were captured using 89mm and 114mm stretched mesh nets. . . . .	19
Figure 3-21	Fish samples collected from the Slave River were taken to the DIAND Fort Smith District warehouse, where a temporary lab was set up for processing . . .	19
Figure 3-31	Otoliths were collected from the cranial cavity . . . . .	21
Figure 5-1	SREQMP - Grab and Centrifugate Water Sampling Dates (Fort Smith) vs Mean Daily Discharge (Fitzgerald) . . . . .	25
Figure 5-2	Average Percentage of Particle Size Distribution by Season . . . . .	27
Figure 5-3	SREQMP TCDD Levels in Walleye Wholefish - Slave River and Control Site .	41
Figure 5-4	SREQMP TCDF Levels in Walleye Wholefish - Slave River and Control Site .	43
Figure 5-5	SREQMP TCDD Levels in Burbot Liver - Slave River and Control Site . . . . .	45
Figure 5-6	SREQMP TCDF Levels in Burbot Liver - Slave River and Control Site . . . . .	47

The numbering of Tables and Figures is not consecutive because they are copies of the same items in the full report (Sanderson *et al.*, 1997). The reader will be able to easily refer to the full report for further details.

# **The Slave River Environmental Quality Monitoring Program**

The Slave River Environmental Quality Monitoring Program (SREQMP) was a five year multimedia sampling program operating from 1990 to 1995, to characterize baseline conditions of the aquatic ecosystem in the Slave River at Fort Smith, Northwest Territories (NWT), Canada.

This report provides a summary of the Slave River Environmental Quality Monitoring Program Final Five Year Report (Sanderson *et al.*, 1997). Further details on the study design, field and analytical methods, and interpretation of results are included in the full report, which is available from the Water Resources Division of the Department of Indian Affairs and Northern Development in Yellowknife.

The SREQMP was a successful project that met the objectives of determining contaminant levels, developing a baseline and providing information for transboundary negotiations.

The comprehensive sampling program developed a solid baseline for the aquatic ecosystem of the Slave River in the NWT, against which future changes can be measured. The data set can be considered representative of the current conditions of the aquatic ecosystem. By taking an ecosystem approach, the most appropriate indicator for each type of contaminant was established which will allow future monitoring to be more focussed. The vast database compiled will be invaluable in developing ecosystem objectives to protect this northern environment and is essential for transboundary negotiations. This will allow the NWT to enter into agreements with their neighbours which will ensure the continued use of this resource for many generations.

## **MAJOR CONCLUSIONS**

In general, the results of the study indicate that many parameters were present at extremely low levels or were not detected even with state of the art analytical techniques. Of those compounds which were found, metals and polycyclic aromatic hydrocarbons (PAHs) are most likely from natural sources, while pesticides and polychlorinated biphenyls (PCBs) indicate atmospheric transport. The detection of chlorinated phenolics, dioxins and furans, although at low levels, could be a result of downstream transport. While some findings may warrant further study, overall the levels of contaminants measured in the aquatic environment at Fort Smith are not likely to cause adverse effects. All results are currently undergoing a human health assessment by Health Canada.

## **Water**

A review of sampling dates and daily discharge rates reveals that samples were collected at representative times and flows. This fact, along with the comparability to historical data, indicates that the SREQMP water data can be considered representative of the current conditions. It can be expected, therefore, that the sediment and fish data are also representative of the aquatic system.

A comparison between grab and centrifugate results shows that levels of metals were lower after centrifugation. This suggests that the metals detected in the Slave River are primarily associated with suspended sediments.

## **Sediment**

The results indicate that suspended sediment is a good medium for monitoring organic and inorganic contaminants. Since historic suspended sediment quality data for the Slave River are not available, values collected from the SREQMP are the baseline for future comparisons. Future results can be compared to this database to verify the occurrence of downstream transport or detect a change in contaminant levels.

Those metals found in high concentrations in the grab water samples were also detected at elevated levels in the suspended sediment samples, which supports the conclusion that metals are associated with suspended particulates.

Results of the *Daphnia magna* and Microtox bioassays indicated that the suspended sediment samples collected were not acutely toxic.

## **Fish**

The Slave River Environmental Quality Monitoring Program focussed on sampling those fish which were most likely to be consumed by local people. Comparison of K factors (plumpness) to other NWT fish indicate that walleye, northern pike, lake whitefish and burbot collected from the Slave River and control lakes were robust.

Future monitoring should focus on burbot liver as it fulfills both public health and scientific criteria. In the wholefish samples, walleye had higher values and a wider range of contaminants than lake whitefish and northern pike and therefore could also serve as a good indicator of



environmental pollution.

For metals, the percentages of detection and the range of values were generally comparable between the Slave River and the control lakes. This suggests similar sources of metals, either geological or airborne.

The presence of chlorinated phenolics, organochlorine pesticides, PCBs, toxaphene, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in fish from both the Slave River and the control sites suggests that the contaminants are being transported to these sites via the atmosphere.

The MFO liver enzyme data set determined that the Slave River fish had low levels of induction, suggesting a pristine environment.

## **RECOMMENDATIONS**

### **Further Monitoring**

#### **Water**

Some metal levels in water samples were above the Canadian Guidelines for the Protection of Freshwater Aquatic Life (CPFAL). However these levels were within the range of historical values, which are considered to be the result of natural weathering of rocks. While it is unlikely then that these concentrations would cause any adverse impacts to aquatic life, further research may be warranted, since toxicity of metals tends to increase in softer waters such as those observed at the Fort Smith site.

#### **Sediment**

Follow up studies on the toxicity and natural variability of the metals in the suspended sediments in the Slave River at Fort Smith could be warranted.

Since the concentrations of some PAHs in suspended sediment were above bottom sediment guidelines, further monitoring of these compounds may be warranted to determine if the source is natural or anthropogenic.

Presence of chlorinated phenolics and dioxin and furan isomers could indicate downstream transport of these contaminants from developments and therefore may warrant further study.

A comparison of the SREQMP data to the bottom sediment data collected in the depositional areas of the Slave River Delta and results from sediment cores from Great Slave Lake, would be useful in studying the fate and transport of contaminants.

## **Fish**

The presence of elevated levels of some metals may justify further study to ascertain their source and impact on the aquatic system. Since accumulation of metals is influenced by biological factors such as species and age, further analysis of the data may also be warranted to highlight species specific trends.

For chlorinated phenolics and PCCD/Fs, levels are higher in the Slave River than the control sites, which suggests that these fish are exposed to an additional source of organochlorines, most likely associated with upstream development. Further monitoring may be warranted.

Several factors point to a natural source of PAHs in the Slave River. Concentrations of PAHs were not similar to patterns seen at sites downstream of oil spills. Therefore further study may be warranted to verify if the source is natural and determine impacts.

## **Other General Recommendations**

An ecosystem approach should be considered in future studies when developing a baseline. The use of this approach provides a complete database and allows the most appropriate medium for each parameter to be monitored. This ensures that specific bioindicators can be determined. With a comprehensive monitoring program, important results are less likely to be missed.

When designing a sampling program, local people should be involved in all aspects of the project from identification of concerns to choice of sampling locations and presentation of results.

When dealing with large multimedia sampling programs, there should be a continual review of results to ensure that objectives are being met.

With long term monitoring programs, both methods and detection limits may change over the

years. These changes should be well documented.

When developing a baseline for a relatively pristine environment, state of the art analytical techniques with low detection limits should be employed despite the costs.

When results involve trace levels of contaminants, special attention should be paid to the handling of less-than-detection values. It is essential to the analysis of the results and an important factor to consider.



# **The Slave River Environmental Quality Monitoring Program**

## **INTRODUCTION**

The Slave River Environmental Quality Monitoring Program (SREQMP) was a five year multimedia sampling program operating from 1990 to 1995, to characterize baseline conditions of the aquatic ecosystem in the Slave River at Fort Smith, Northwest Territories (NWT), Canada. The comprehensive nature of the program made it the first of its kind in the Northwest Territories.

The SREQMP was a cooperative program among the Water Resources Division of the Department of Indian Affairs and Northern Development (DIAND), the Government of the Northwest Territories' Department of Renewable Resources (GNWT), the Department of Fisheries and Oceans (DFO) and Environment Canada (DOE).

## **OBJECTIVES**

In general terms, the objectives of the Slave River Environmental Quality Monitoring Program were to:

- i) address concerns of northerners regarding possible contamination of fish, water and suspended sediment from pulp mill, hydrocarbon and agricultural developments upstream; and
- ii) provide baseline data on contaminant levels in fish, water and suspended sediment at the NWT boundary to support transboundary water negotiations between Alberta and the NWT.

## **WHY THE STUDY WAS DONE**

With a mean annual discharge of 3400 m<sup>3</sup>/s, the Slave River is the largest tributary of the Mackenzie River (Reid, pers. comm., 1997; Figure 1-1). The river draws its flow from a catchment area of approximately 600,000 km<sup>2</sup>, nearly all of which is located in the provinces of Alberta, British Columbia and Saskatchewan (Alberta Environment, 1986). The NWT portion of the Slave River basin is located downstream of all three jurisdictions. Bilateral discussions

between the NWT and Alberta identified potential impacts on downstream water resources as the most important issue in transboundary negotiations (Letourneau *et al.*, 1988).

The Slave River is important to the northern subsistence lifestyle. It is a direct source of drinking water, provides habitat for fish and wildlife species, is a major source of country foods and is both culturally and spiritually significant. Over 5,000 people live along the NWT portion of the river, mainly in Fort Resolution and Fort Smith.

In the late 1980s, industrial activity increased in the upstream portion of the basin (Figure 1-1). Two of the existing five pulp and paper operations had doubled their capacity and approvals were in place for four new mills. Three oil sands plants were to expand with a new one to be established. The agricultural sector in Alberta was also expanding. Evidence of impacts far downstream from such developments had been demonstrated by closures of fisheries in British Columbia due to pulp mill contaminants and in Lake Athabasca due to an Alberta tar sands spill. Since all contaminants discharged by upstream developments could be deposited in the NWT, serious concerns were raised about the potential for similar problems on the Slave River in the Northwest Territories, as well as Great Slave Lake and the Mackenzie River which it feeds. The Alberta Pacific (ALPAC) Pulp Mill environmental assessment hearings of 1989 intensified interest. People wanted to know “Can we drink the water?” and “Can we eat the fish?”

Not enough information was known about the NWT portion of the Slave River to assess the impacts of increasing development on the aquatic ecosystem. In order to provide accurate baseline data and monitor changes due to upstream development, it became apparent that a comprehensive monitoring program was required for the Slave River.

In January 1990, the Slave River Technical Advisory Committee was formed with membership from DIAND Water Resources, GNWT Renewable Resources, DFO and DOE. Its main roles were to plan, design, and implement a multi-media monitoring program on the Slave River, and to achieve and maintain consistency and a high level of quality in the data produced. A basin assessment report was prepared to examine the existing and potential contaminant sources within the upper basin, outline the users of the NWT portion of the Slave River and summarize all of the information known to date on the environmental quality of the basin (MacDonald, 1990). In March 1990, the committee held a workshop to develop a practical environmental monitoring program for the Slave River with aquatic environmental quality experts from government agencies and the public sector (MacDonald and Smith, 1990). Using these reports, the Committee designed and implemented the SREQMP.

Figure 1-1 Mackenzie River Basin - Upstream Industrial Activity (Source, NRBS Report to the Ministers, 1996)





## WHAT WAS STUDIED: THE ECOSYSTEM APPROACH

The Slave program was designed to search for the most likely contaminants in the most appropriate media (Table 2.1). By studying different components of the aquatic environment, the SREQMP incorporated an ecosystem approach to monitoring.

<b>Table 2.1. Summary of Analytical Parameters and Sampling Media.</b>						
<b>Parameter</b>	<b>Grab Water</b>	<b>Centrifugate Water</b>	<b>Suspended Sediments</b>	<b>Fish muscle/bile/liver</b>		
<b>Metals</b>	X	X	X	X	-	X
<b>EOCl</b>	-	X	X	X	X	X
<b>Chlorophenols</b>	-	X	X	X	X	X
<b>Organochlorine Pesticides</b>	-	X	X	X	-	X
<b>PCBs</b>	-	-	X	X	-	X
<b>PAHs</b>	-	X	X	GCMS	HPLC	GCMS
<b>Dioxins/Furans</b>	-	-	X	X	-	X
<b>MFOS</b>	-	-	-	-	-	X
<b>Basic Parameters</b>	Physicals, BOD, Major Ions	-	particle size, TOC, toxicity tests	age, sex, weight, length, % lipids		

## WHAT WAS LOOKED FOR: ANALYTICAL PARAMETERS

The parameters were selected based on the current knowledge of the chemical composition, fate and effects of the effluents from developments upstream in the basin, including pulp and paper mills, oil and gas development and agricultural activities (MacDonald, 1990).

Metals have both natural and anthropogenic sources, including mining and oil and gas developments. Most are required in small quantities by all living things, but in large quantities they can be harmful to biota.

Halogenated hydrocarbons (hydrocarbons containing chlorine, bromine, fluorine or iodine) are

released into the environment through a variety of anthropogenic sources including agriculture, chemical manufacturing, and the production of bleached pulp and paper. The Extractable Organic Chlorine (EOCl) method provides an index of the amount of contamination by chlorinated organic compounds and is capable of detecting all solvent extractable halogenated compounds (Birkholz, 1993).

Chlorinated phenolics have a variety of uses including disinfectants, pesticides, dyes and wood preservatives and are released into the aquatic environment from pulp and paper operations, bleached kraft mills, wood processing and treatment plants, and sewage treatment plants (Pastershank and Muir, 1996). These compounds are toxic, persistent and are known to bioaccumulate (Kovacs *et al.*, 1984) and include chlorinated guaiacols, catechols, vanillins, syringaldehydes and veratroles.

Polycyclic aromatic hydrocarbons (PAHs) are associated with the effluents from hydrocarbon developments, including tar sands and mining operations. Several are highly toxic to aquatic organisms (Eisler, 1987) and may be carcinogenic.

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are large families of chlorinated hydrocarbons consisting of 75 PCDD and 135 PCDF congeners (each congener having a different chlorine substitution pattern). The most toxic congeners are those which are substituted at the 2,3,7, and 8 position (Safe and Phil, 1990). PCDDs are by-products of various processes from chemical, pulp and paper, metallurgical and dry-cleaning industries and have been detected in the effluent of bleached kraft pulp and paper mills (Swanson *et al.*, 1993). PCDDs tend to be rapidly sorbed to most soils and sediments (Isensee and Jones, 1975), but can also be transported through the atmosphere over long distances (Fiedler *et al.* 1990). These substances have been associated with a wide range of toxic effects in animals. 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic isomer, is readily bioaccumulated by a number of aquatic organisms (Fletcher and McKay, 1993).

Organochlorine pesticides, including DDT, toxaphene, dieldrin, mirex, chlordane and lindane, were analyzed. These compounds are characterized by their persistence, toxicity, widespread occurrence and tendency to bioaccumulate (CCREM, 1987).

Toxaphene (camphechlor) is a complex mixture of chlorinated camphene and bornane derivatives which have different physical and chemical properties (CCREM, 1987) and a broad spectrum of pesticidal activity. In Canada, toxaphene was experimentally utilized as a pesticide but was

banned in 1982.

Polychlorinated biphenyls (PCBs) are chlorinated aromatic hydrocarbons which are highly lipophilic, persistent in the environment and have been found to bioconcentrate (CCREM, 1987). Sources of PCBs entering the environment include incomplete combustion of PCB wastes, sewage and leaching from dumps and landfills (Hammond, 1972). Exposure to PCBs may result in a wide variety of effects on aquatic organisms including acute and chronic toxicity, reproductive toxicity, developmental abnormalities, and growth retardation (Moore and Walker, 1991). In 1980, the use and importation of PCBs was totally prohibited in Canada (Environment Canada, 1980).

## **WHERE WERE THEY LOOKED FOR: SAMPLING MEDIA**

One of the main goals of the sampling program was to compare baseline quality with known guidelines, most of which relate to water. However, since many organic contaminants which can impact the aquatic environment are not detectable in the water column, monitoring water alone was insufficient. Contaminants were monitored in the environmental media (i.e. water, sediment, biota) where they were likely to be present, accumulate and cause impacts.

### **Water**

Grab and centrifugate water samples were analysed due to drinking water concerns, for comparison to water quality guidelines and to set water quality objectives for transboundary negotiations. Grab samples are raw river water samples which contain suspended sediment and can be compared to historic values. Centrifugate water samples are collected from the outflow of the centrifuge, so the suspended sediment has been removed (Figure 2-7), allowing each component to be studied separately. Collection of large volumes of centrifugate allowed for better recovery rates, an important consideration since organic contaminant levels were expected to be near detection limits.

### **Suspended Sediment**

Suspended sediment samples were collected because metals and organic contaminants tend to adsorb to the sediment and particles which are suspended in the water column. In fast flowing waters such as the Slave River, these particles remain suspended in the water column for a long period and can be transported great distances downstream (MacDonald and Smith, 1990; Swanson *et al.*, 1993). Many toxic chemicals have been closely associated with suspended particulates, even when levels were below detection in the water samples (Ongley *et al.*, 1988). As a result,

it was felt that monitoring suspended sediment would serve as an early warning of environmental degradation. As no historic sediment quality data were available for the Slave River, this monitoring would also help meet the program's goal of establishing baseline environmental conditions.

## **Fish**

Fish were sampled because they serve as a good early warning system for contamination in an aquatic environment, due to their ability to bioaccumulate environmental pollutants. Fish can be a large part of people's diet in the NWT, so there is an immediate public health concern. Results could be compared to existing Health Canada guidelines and would establish baseline conditions.

Fish species were chosen based on their presence and residency time, their importance in human consumption patterns, potential for the fish to accumulate contaminants, their trophic level in the aquatic food chain, and degree of sediment exposure (MacDonald and Smith, 1990). Burbot (*Lota lota*), lake whitefish (*Coregonus clupeaformis*), walleye (*Stizostedion vitreum*) and northern pike (*Esox lucius*) were selected as the best candidate species for the monitoring program.

Muscle, bile, liver and/or whole fish samples were collected from each species. Whole fish contaminant analysis provided an indication of the ecosystem level availability of contaminants (Whittle, 1989), while fish muscle samples were analysed as they are consumed by people and dogs.

Burbot livers were analysed as they are also eaten as part of a subsistence diet (Lutra Associates Ltd., 1989). As a detoxifying organ and filter, the liver is a major site for the deposition of any toxic compounds in the fish. In addition, burbot liver has a high lipid (fat) content which makes it attractive to lipophilic chlorinated organic contaminants (Voss and Yunker, 1983). Liver MFO enzyme activity can also indicate exposure to specific contaminants.

Bile is produced by the liver and plays a major role in the excretion of foreign substances (Figure 3-30). Concentrations of those compounds which are rapidly metabolized by fish can therefore be much higher in bile than in other fish tissues (Swanson *et al.*, 1993).

Figure 2-7 The water collected after centrifuging (centrifugate) did not contain any appreciable amount of sediment.

Figure 3-30 Bile was collected with a sterile syringe taking care not to break the gall bladder, in order to avoid contamination of the liver.



## WHERE AND HOW THE SAMPLES WERE COLLECTED: SAMPLING METHODS

### General

Samples were collected from the Slave River at Fort Smith, Northwest Territories below the Rapids of the Drowned (Figures 2-3 and 2-5). As this site was downstream of the Alberta-NWT border and upstream of any major tributaries in the NWT, it was representative of waters flowing into the NWT. Collection of grab and centrifugate water, suspended sediment, and fish samples from approximately the same location on the Slave River allowed for the integration of the study components and comparison of the biological and chemical data.

### Water and Sediment

In order to choose a representative water quality site, water from a cross-sectional transect of the river was sampled. The results from the site evaluation showed no detectable difference between sites or depths indicating that the river was well mixed. Grab water samples were collected monthly from just below the water surface. Centrifugate water and suspended sediment samples were collected by pumping river water from a one meter depth through a Sedi-Samp II Continuous Flow Centrifuge (Figure 2-7; Puznicki, 1993). The centrifuge removes and stores the suspended sediment (Figure 3-15) and the remaining water sample is referred to as centrifugate. Sampling took place four times a year, to coincide with stages of the hydrological cycle - spring freshet, summer low flow, post-freeze up and pre-breakup (Figure 2-2), in order to determine seasonal variability (Table 3.1).

<b>Year</b>	1990-91	1991-92	1992-93	1993-94	1994-95
<b>Dates</b>	- Oct 17 Dec 17 Feb 18	Aug 8 Sept 18 Dec 17 Feb 20	June 11 Sept 17 Jan 13 -	June 11 Aug 23 Jan 13 Mar 8	June 15 Sept 22 Jan 10 Mar 7

## **Fish**

Fish sampling sites were determined through consultation with local fishermen. The four sets of rapids upstream of the site acted as a natural barrier to fish movement, ensuring that fish samples were resident in the NWT (Figure 2-3). The life history of the species selected and the timing of the Slave River domestic fishing dictated two sampling sessions per year. Walleye, northern pike and lake whitefish were gill netted from the Slave River just below the Rapids of the Drowned and from Leland Lake during the open water season in September. Net sizes used in the SREQMP were similar to those used by local fishermen (mesh sizes of 89 and 114 mm and lengths of 23 or 46 m), in order to provide a good indication of the contaminant levels in those fish which are likely to be consumed (Figure 3-20). Burbot were caught with baited hooks under the ice in December from Bell Rock on the Slave River as per the advice of local fishermen and from Alexie Lake in March. Biological data (weight, fork length, sex, gonad maturity and gonad weight) were recorded and ageing structures removed (Figure 3-21 and 3-31). Fish tissues were sampled according to the requirements specified by each analytical lab.

## **Control Sites**

Control sites for the fish sampling program (Leland and Chitty/Alexie Lakes: Figure 1-1) were chosen to account for natural variability, and to differentiate between changes due to upstream sources and natural processes (including long range atmospheric transport and other regional non-point sources). No river comparable to the Slave River in terms of flow and sediment regime exists in the western NWT, so two lakes were chosen which were outside of the influence of existing development, and provided the necessary fish species, size and numbers. Although these sites were valid for fish, the geographical variability was too great to allow for direct comparison of water and sediment data. As a result, there were no control sites for water and sediment samples. Instead, water quality data were compared to historic values collected from the Slave River at Fitzgerald between 1960 and 1992 (WER Agra Ltd., 1993). Blanks, spiked samples and Standard Reference Materials also provided Quality Assurance and Quality Control (QA/QC) for these samples.



Figure 2-3 SREQMP - Fort Smith, NWT Sampling Sites



Figure 2-5 Slave River, Rapids of the Drowned at Fort Smith - Winter: The river does not freeze completely due to the turbulence caused by the rapids.

Figure 3-15 The sediment was scraped from the sides and bottom of the centrifuge bowl with clean Teflon-covered stainless steel spatulas and mixed thoroughly.



Figure 2-2 SREQMP - Pre- and Post-Dam Mean Annual Hydrographs - Slave River at Fitzgerald



Figure 3-20 During open water season, fish were captureed using 89mm and 114 mm stretched mesh gillnets.

Figure 3-21 Fish samples collected from the Slave River were taken to the DIAND Fort Smith District warehouse, where a temporoary lab was set up for processing.





Figure 3-31 Otoliths were collected from the cranial cavity.



## WHAT WAS FOUND: RESULTS AND DISCUSSION

A large portion of the results were below the detection limit, which limited the extent of statistical analysis that was possible. Also the detection limits for individual parameters varied over the course of the program, as a result of improved analytical methods and differences in laboratory techniques. Due to these factors, for most parameters the means were not calculated, as they would not accurately reflect the data. Instead, maximum and minimum values were included in the summary tables, as well as the total number of samples and the number below detection. The range of values presented are conservative, in that the highest concentrations were used. For example, in the case of replicate samples, the highest value was retained. If the result was less than detection, the full detection limit was recorded.

All sediment data were presented on a dry weight basis, while fish results were recorded on a wet weight basis. Sediment results were not corrected for surrogate recoveries, with the exception of the dioxin and furan analysis. For fish samples, results from the organochlorine pesticide, PCB, and dioxin and furan analyses were corrected for surrogate recoveries.

### WATER SUMMARY

The two types of water samples (grab water and centrifugate) were analyzed separately. The grab samples were analyzed for 37 physical, biological and chemical (major ions, nutrients and metals) parameters, while centrifugate samples were tested for 29 physical and chemical parameters, as well as organic compounds (EOCl, 44 chlorinated phenolics, 13 pesticides, total PCBs and 17 PAHs).

#### Water: Physicals and Metals

The Slave River water at Fort Smith is soft to moderately soft, with a median pH of 7.9. BOD readings are characteristic of an unpolluted site (McNeely *et al.*, 1979) and the fecal coliform count is low (<3 to 12 colonies/100ml). The presence of the rapids causes the water to be well oxygenated and may be responsible for the resuspension of particulate matter during the winter.

SREQMP water sample data were compared to the range of historical results collected between 1960 and 1992, from the Slave River at Fitzgerald, Alberta (WER Agra Ltd., 1993). Regression analyses on turbidity and TSS data from Fort Smith showed no flow dependency (McCarthy *et al.*, 1997a). Therefore the data were summarized with descriptive statistics (means and standard deviation) by seasons; spring (May and June), summer (July and August), fall (September and October) and winter (November to April) (Figure 5-1). This allowed seasonal patterns to be

identified and visually compared. Statistical comparisons of means were not attempted due to the low number of samples and the high standard deviations. For Fitzgerald water quality data, WER Agra (1993) assessed the dependence of the parameters on flow using regression analyses, while seasonal trends were tested statistically with the Kruskal-Wallis test.

Trends observed for physical and chemical parameters in grab water at the Fort Smith site are generally similar to those detected at Fitzgerald. One exception was total suspended sediment (TSS), which was higher in winter at Fort Smith. This was likely a result of under ice frazil slush at the former site, produced by the supercooled water from the upstream rapids (Ashton, 1986), scouring the river bed and resuspending sediments, especially sand (Figure 5-2). This local effect could explain why the metal concentrations in the winter were between the high spring and low fall values and also why TSS did not show flow dependency at Fort Smith. At Fitzgerald, both metals and TSS levels were highest in the spring, decreased through summer and fall, and were lowest in the winter. Some parameters, such as turbidity, color, sulphate and phosphorus, exhibited this trend at both Fort Smith and Fitzgerald (Table 5.1, 5.2, 5.4).

<b>Table 5.1, 5.2, 5.4 Grab Water Samples - Mean Seasonal Concentrations</b>				
<b>Parameter</b>	<b>Spring</b>	<b>Summer</b>	<b>Fall</b>	<b>Winter</b>
<b>TSS (mg/L)</b> (SD; n)	215.1 (148.5; 10)	72.8 (48.1; 5)	74.6 (54.8; 7)	132.3 (155.7; 22)
<b>Colour (units)</b> (SD; n)	190.4 (348.7; 12)	74.2 (39.9; 5)	38.9 (15.4; 9)	18.0 (12.5; 24)
<b>Chloride</b> (SD; n)	4.5 (1.5; 12)	4.7 (1.2; 5)	6.3 (1.1; 9)	6.0 (2.7; 24)
<b>Copper</b> (SD; n)	9.1 (6.2; 8)	5.3 (2.1; 3)	2.6 (2.1; 5)	3.7 (3.8; 12)
<b>Iron</b> (SD; n)	7001.3 (4368.8; 8)	4583.3 (2270.5; 3)	1385.6 (621.7; 5)	3372.8 (3709.2; 12)
<b>Nickel</b> (SD; n)	10.9 (8.5; 7)	6.3 (2.1; 3)	2.2 (1.1; 5)	5.6 (4.5; 13)
<b>Zinc</b> (SD; n)	31.8 (24.9; 8)	17.0 (7.6; 3)	6.6 (3.2; 5)	22.6 (25.1; 12)

Figure 5-1 SREQMP - Grab and Centrifugate Water Sampling Dates (Fort Smith) vs Mean Daily Discharge (Fitzgerald)



Figure 5-2 Average Percentage of Particle Size Distribution by Season





Other parameters, such as chloride, were lowest in spring and summer and highest during fall and winter at both sites (Table 5.1, 5.2, 5.4). This may be a result of the higher flows in spring and summer diluting the concentrations of these compounds contributed by groundwater (WER Agra Ltd., 1993).

A number of parameters showed only slight changes throughout the year. A comparison of data from the Slave and Hay Rivers (WER Agra Ltd., 1993) showed a much lower flow dependency for water quality parameters from the Slave River. This may be a result of the mixing effects of Lake Athabasca and the influence of flow regulation by the Bennett Dam on water quality in the Peace River (Shaw *et al.*, 1990; Figure 2-2).

Findings suggest that the metals detected in the Slave River are associated with suspended sediments. A comparison between grab and centrifugate results showed that levels of dissolved parameters, such as conductivity and major ions, were similar in both types of samples (Table 5.5). However, characteristics such as turbidity, colour and metals were lower after centrifugation, indicating that they are associated with suspended sediments.

<b>Table 5.5 Comparison of Concentrations (µg/L) in Grab vs Centrifugate Samples</b>				
	<b>Sept 22, 1994</b>		<b>March 7, 1995</b>	
<b>Parameter</b>	<b>Grab</b>	<b>Centrifugate</b>	<b>Grab</b>	<b>Centrifugate</b>
<b>Conductivity</b>	218	218	246	243
<b>Calcium</b>	31.5	25.5	27.1	25.1
<b>Magnesium</b>	6.1	6.1	6.48	6.02
<b>Sodium</b>	6.53	6.47	7.22	6.93
<b>Chloride</b>	6.95	6.93	7.37	7.21
<b>Turbidity</b>	24	3	19	6.2
<b>TSS</b>	39	<3	108	4
<b>Arsenic</b>	0.7	0.4	0.8	<0.3
<b>Cobalt</b>	0.3	<0.1	0.5	<0.1
<b>Copper</b>	1.8	1.2	5.8	0.7
<b>Iron</b>	1200	167	1720	163
<b>Lead</b>	1.3	0.3	4.3	0.4
<b>Manganese</b>	32.5	5.2	27.8	7
<b>Nickel</b>	2.6	1.2	3.7	1.2
<b>Zinc</b>	<5	<5	13.4	<0.5

### **Water: Organic Parameters**

Only a limited number of organic parameters were detected in Slave River centrifugate water samples, and at very low levels. Still, their presence indicates the possibility of downstream transport. The chlorinated phenolic compounds detected at Fort Smith have been detected downstream of the bleached kraft pulp mill at Grande Prairie, and shown to be transported over long distances (Swanson *et al.*, 1993). Low molecular weight PAHs (naphthalene and methylnaphthalene) were present in a few centrifugate samples. EOC1 and pesticides were not detected, but this could be a result of the high detection limits.

### **Water: Overall**

SREQMP data were compared to the Guidelines for Canadian Drinking Water Quality (CDWQ) and the Canadian Guidelines for the Protection of Freshwater Aquatic Life (CPFAL). The concentrations of all organic and inorganic parameters measured in water during the SREQMP were below existing guidelines, with the exception of chromium, copper, iron, lead, manganese, and zinc in grab water samples. However these levels were within the range of historical values, which WER Agra Ltd. (1993) considered to be the result of natural weathering of rocks. While it is unlikely then that these concentrations would cause any adverse impacts to aquatic life, further research may be warranted, since toxicity of metals tends to increase in softer waters such as those observed at the Fort Smith site.

A review of sampling dates and daily discharge rates (Figure 5-1) reveals that samples were collected at representative times and flows. This fact, along with the comparability to historical data, indicate that the SREQMP water data can be considered representative of the current conditions. It can be expected therefore that the sediment and fish data are also representative of the aquatic system. The data set can also serve as a baseline against which future changes can be measured.

## **SUSPENDED SEDIMENT SUMMARY**

During the SREQMP, suspended sediment samples were tested for total organic carbon (TOC), metals, EOC1, chlorinated phenolics, dioxins and furans, pesticides and PAHs. No historic data were available for quality of suspended sediment from the Slave River. Therefore the information provided by this study constitutes the first database for suspended sediment, and can be used as a baseline against which future monitoring can be compared.

Suspended sediment results were compared to the Draft Interim Freshwater Bottom Sediment Quality (FSQ) Guidelines (Environment Canada, 1995). Two assessment values were generated

for each element, the threshold effect level (TEL) and the probable effect level (PEL). The TEL represents the concentration below which the adverse effects are expected to occur rarely. The PEL defines the level above which adverse effects are predicted to occur frequently. Values which fall in the range between the two levels are occasionally expected to be associated with adverse biological effects.

Results were also compared to the Ontario Sediment Quality (OSQ) Guidelines for bottom sediments (OSQG, 1992), if national guidelines were unavailable. Sediment with concentrations above the Lowest Effect Level (LEL) Guidelines have the potential to adversely affect the aquatic biota. Sediment samples with concentrations above the Severe Effect Level (SEL) Guidelines must be assessed for biological impact and remediation must be implemented.

It should be noted, however, that the above guidelines have been developed for bottom sediments, not suspended sediments. Therefore they are included only as a reference for comparative purposes.

#### **Suspended Sediment: Particle Size Distribution**

The suspended sediment samples collected from the Slave River below the Rapids of the Drowned are composed of sand, silt and clay particles, the proportions of which vary with the seasons (Figure 5-2). Sand content was found to be highest in the winter, most likely a result of under ice frazil slush, scouring the river bed and resuspending sediments.

Suspended sediments have been recognized as important carriers of contaminants. As contaminants sorb strongly to the finer particulates, their concentrations should be highest when silt and clay levels are at a maximum (CCREM, 1987). This trend was observed during the SREQMP, as correlations were noted between metal levels and clay with  $r^2$  values ranging from 0.26 to 0.71. However, the strongest correlations were observed between metal levels and organic content, as  $r^2$  values ranged between 0.5 and 0.9 (McCarthy *et al.*, 1997a). These results are supported by studies which show that arsenic, lead, nickel, and zinc can be removed from solution by the presence of suspended solids, organic matter and clays (CCREM, 1987).

#### **Suspended Sediment: Metals**

Suspended sediment samples were analyzed for 29 inorganic elements, of which aluminum, barium, boron, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, phosphorous, strontium, titanium, vanadium and zinc were detected in all samples. This suggests that metals are associated with suspended sediment, an observation which was supported

by the comparison of centrifugate and grab water sample results (Table 5.5). Those metals found in high concentrations in the grab water samples were also detected at elevated levels in the suspended sediment samples.

A few samples had concentrations of arsenic, cadmium, chromium, copper, manganese, nickel and zinc above the Threshold Effect Levels (TEL) or Lowest Effect Levels (LEL) . However, arsenic and nickel were the only metals detected above the Probable Effect Levels (PEL), in one and four samples (n=18), respectively. All metal concentrations but one manganese result, were substantially below the Severe Effect Level (SEL). As the source of metals in the grab samples is likely to be natural, this would hold true for the suspended sediments also. Therefore it is unlikely that the metal levels would have an adverse impact on the aquatic biota of Fort Smith. However the toxicity of mixtures of metals has been shown to be more than additive (Reeder *et al.*, 1979), and may be modified by the presence of organic matter (US EPA, 1979). Therefore, follow up studies on the toxicity and natural variability of the metals in the suspended sediments in the Slave River at Fort Smith could be warranted.

<b>Metal</b>	<b># of samples above detection limit</b>	<b>TEL *</b>	<b># of samples above TEL</b>	<b>PEL **</b>	<b># of samples above PEL</b>
<b>Arsenic</b>	12	5.9	9	17.0	1
<b>Cadmium</b>	15	0.596	7	3.53	0
<b>Chromium</b>	18	37.3	3	90.0	0
<b>Copper</b>	18	35.7	2	197	0
<b>Lead</b>	18	35.0	0	91.3	0
<b>Mercury</b>	18	0.174	0	0.486	0
<b>Nickel</b>	18	18.0	16	35.9	4
<b>Zinc</b>	18	123	1	315	0

\* TEL = Threshold Effect Levels (Environment Canada, 1995)

\*\* PEL = Probable Effect Levels (Environment Canada, 1995)

### **Suspended Sediment: Organic Parameters**

Levels of organic contaminants measured in the suspended sediment samples were generally low. EOCs, organochlorine pesticides and PCBs were below the detection limits in all sediment samples tested during the SREQMP, and therefore below guidelines. Results of the *Daphnia magna* and Microtox bioassays indicated that the suspended sediment samples collected during the SREQMP were not acutely toxic.

### **Suspended Sediment: Chlorophenols**

Of the 44 chlorinated phenolic compounds analyzed in suspended sediment samples, only 21 were detected; five types of chlorophenols, seven chlorocatechols, four chloroguaiacols, three chloroveratroles and one chlorovanillin. Although no guidelines are available for comparison, the low levels and frequency of detection suggest that adverse impacts on the environment are unlikely. However, further monitoring may be warranted, as suspended sediments in the Wapiti/Smoky system were found to be important carriers of chlorinated phenolics, and were shown to be transported over long distances (Swanson *et al.*, 1993). Similar compounds to those which were detected downstream of the Grande Prairie mill were also detected at Fort Smith, which could indicate downstream transport of these contaminants.

### **Suspended Sediment: Dioxins and Furans**

Five of the 17 dioxin and furan isomers tested (2,3,4,7,8 P<sub>5</sub>CDF; OCDF; 2,3,7,8 TCDF; 1,2,3,4,6,7,8 H<sub>7</sub>CDD and OCDD) were detected in the suspended sediment samples. In addition, six of the eight homologues were present in the samples analyzed. Although the most toxic isomer, 2,3,7,8 TCDD, was below detection in all samples, the 2,3,7,8-substituted dioxin and furan isomers have the potential to degrade to this compound (McCubbin *et al.*, 1992). Suspended sediments were found to be important carriers of dioxins and furans in the Wapiti/Smoky River system and transported over long distances (Swanson *et al.*, 1993). The presence of similar compounds in the suspended sediment of the Slave River (although at lower levels and frequency of detection), may also indicate downstream transport of these contaminants and thus warrant further study. No guidelines presently exist for dioxins and furans in suspended or bottom sediments, but their detection in only a few samples and at low levels suggest that they are unlikely to have adverse impacts on the environment.

### **Suspended Sediment: PAHs**

All of the 17 PAHs tested for, with the exception of acenaphthylene, were present in at least one suspended sediment sample. This would be expected as concentrations of PAHs in aquatic ecosystems are generally highest in sediments (NRCC, 1983). The frequency of detection of high

molecular weight compounds is supported by those studies which found that sorption is the primary removal mechanism for PAHs (Knap and Williams, 1982) and that these compounds are sorbed rapidly by organic and inorganic materials (Meyers and Quinn, 1973). Most hydrophobic compounds are associated with the finer silt and clay particles of the suspended sediment (Forstner, 1991). This was observed in the SREQMP, as PAH concentrations appear to be highest during the summer sampling season, when the silt and clay contents were at a maximum (Figure 5-2).

Although PAHs with fewer than three rings are not usually sorbed as extensively as high molecular weight PAHs (Karickhoff *et al.*, 1979), low molecular weight PAHs were detected in many of the suspended sediment samples collected from the Slave River, often with higher maximum concentrations. This finding could indicate the need for further studies on the source and transport mechanism of low molecular weight PAHs in this system.

Although some PAH concentrations were above the TEL and/or LEL, all results were well below the PEL and the SEL. Chronic bioassays conducted on Lake Erie sediments with similar PAH concentrations concluded that these levels were not sufficient to cause adverse effects. It is unlikely therefore, that the PAH levels detected in the Slave River sediments would adversely impact the aquatic biota (McCarthy *et al.*, 1997a). However, since the concentrations and frequency of detection of PAHs in suspended sediment are high, further monitoring of these compounds may be warranted.

### **Suspended Sediment: Overall**

The above results indicate that suspended sediment is a good medium for the monitoring of organic and inorganic contaminants. Although the overall concentrations of contaminants were low, interesting results were noted that could warrant further study, such as identifying the source of metals and PAH compounds. Future results could be compared to this database to verify the occurrence of downstream transport or detect an increase in contaminant levels. A comparison of the SREQMP data to the bottom sediment data collected in the depositional areas of the Slave River Delta and results from sediment cores from Great Slave Lake, would be useful in studying the fate and transport of contaminants.

## **FISH SUMMARY**

### **Fish: Biological**

Comparison of K factors (plumpness) to other NWT fish indicate that walleye, northern pike, lake whitefish and burbot collected from the Slave River, Leland Lake and Alexie Lake can be considered robust.

### **Fish: Metals**

Analyses for 29 inorganic parameters were conducted on the muscle of lake whitefish, northern pike, and walleye, and the muscle and liver of burbot. Many of the elements (calcium, copper, iron, magnesium, manganese, mercury, potassium, phosphorous, sodium, strontium and zinc) were detected in most muscle and liver samples (86 to 100%) from both the Slave River and control lakes. Of the other metals, aluminum, barium, boron, chromium, lead and nickel were present in a greater percentage of fish muscle samples, while tin and cadmium were found in a greater percentage of liver samples. This implies that certain metals tend to be preferentially accumulated. Some metals (beryllium, cobalt, and vanadium) were detected in fewer than 6 percent of the samples, while others were all below detection limit (antimony, bismuth, molybdenum and silver).

The percentages of detection and the range of values were generally comparable between the Slave River and the control lakes. This suggests similar sources of metals, either geological or airborne. However, Slave River fish samples usually had higher maximum metal concentrations than those from the control sites, especially arsenic, where the range of values was always higher in Slave River fish samples. The main exception to these findings was northern pike from Leland Lake, which had the highest maximum concentrations of iron, mercury and zinc. These variations may reflect differences in the biological characteristics of the fish samples, such as age, or in the environmental conditions (lake vs river) between the sampling sites.

Comparison of metal concentrations in SREQMP fish muscle to data from other sites in the NWT, revealed higher maximum concentrations of arsenic, chromium, mercury, nickel and zinc in fish from this study. However, further investigations such as age comparisons, would be required to determine if these differences were significant. The source of nickel, iron and zinc is probably natural, since values detected in grab water samples were historically high. Although arsenic was higher in the Slave River, the values are still low. Chromium was high in water and sediment but no historical data are available to determine if sources are natural.

### Fish: Mercury

Mercury was detected in all of the 492 muscle samples analyzed during the SREQMP with values ranging from 0.02 to 1.09 µg/g, and in 56 of the 58 liver tissues tested, with levels between 0.01 and 0.09 µg/g (Table 5.18). These results are comparable to data collected in 1988 and 1989 from the Slave River, where concentrations ranged from 0.13 to 0.80 µg/g in muscle of walleye, and from 0.17 to 0.54 µg/g in northern pike muscle (Grey *et al.*, 1995).

Species	Muscle			Liver	
	Slave	Leland	Alexie	Slave	Alexie
<b>Walleye</b>	0.28 0.05-0.97 (72)	0.34 0.11-0.80 (38)	-	-	-
<b>Northern pike</b>	0.25 0.06-0.52 (66)	0.30 0.11-1.09 (32)	-	-	-
<b>Lake whitefish</b>	0.04 0.02-0.12 (76)	0.09 0.03-0.30 (40)	-	-	-
<b>Burbot</b>	0.12 0.02-0.21 (36)	-	0.13 0.07-0.24 (22)	0.02 <0.0025-0.07 (36)	0.03 0.01-0.09 (22)

Fish absorb the methylated form of mercury from the environment and store it in their body (Sorensen, 1991). As a consequence, mercury biomagnifies through the food chain, the result being that piscivorous species show the highest concentrations of the metal (Lafontaine, 1994). This is seen in the muscle samples from the Slave River where walleye, northern pike and burbot had higher mercury levels than lake whitefish (Table 5.18).

Within the southern NWT, there are several geological zones with relatively high mercury content, including the area around Great Slave Lake. The occurrence of comparable levels of mercury in the Slave River, control lakes and other NWT sites, may reflect geological sources or atmospheric deposition rather than anthropogenic point sources (Grey *et al.*, 1995).

In Canada, the maximum allowable level of mercury in the edible portion of commercial fish is



0.5 µg/g, while a tolerance concentration of 0.2 µg/g has been set for frequent consumption (Health and Welfare Canada, 1969 and 1984). Although some muscle samples from the SREQMP had mercury concentrations higher than these limits, the average values were below the guideline of 0.5 µg/g for commercial fish (Table 5.18). Average values for pike and walleye were above the guideline of 0.2 µg/g for subsistence consumption. These results are undergoing a human health assessment by Health Canada. Further monitoring of mercury in fish may be warranted, especially since fish from the Slave River are an important part of the subsistence diet.

The presence of elevated levels of some metals may justify further study to ascertain the source of metals in the Slave River and the impact of these metal on the aquatic system. Since accumulation of metals is influenced by biological factors such as species and age, further analysis of the data may also be warranted to highlight species specific trends.

### **Fish: Organic Parameters**

During the SREQMP, muscle of lake whitefish, northern pike, walleye and burbot, and liver of burbot were analyzed for chlorinated phenolics, organochlorine pesticides, PCBs, PCDDs and PCDFs, and PAHs. In addition, bile samples were tested for general contamination of the fish by EOC1 and PAHs.

Concentrations of chlorinated phenolics, organochlorine pesticides, PCBs, toxaphene and PCCD/Fs were generally highest in burbot livers. Their high lipid (fat) content (12 to 48%) makes them attractive to lipophilic chlorinated organic contaminants (Voss and Yunker, 1983). As a detoxifying organ and filter, the liver is a major site for the deposition of many toxic compounds in the fish. The usefulness of burbot liver as a bioindicator has been proven in this study both because of its importance in a subsistence diet and as a sink for contaminants. Future monitoring should focus on this medium as it fulfills both public health and scientific criteria.

In the wholefish samples, walleye had higher values and a wider range of contaminants than lake whitefish and northern pike and therefore could also serve as a good indicator of environmental pollution. Compared to the composite muscle samples, individual whole fish and liver analysis revealed the presence of a larger variety of isomers, as well as a wider range of concentrations. The presence of EOC1, chlorinated phenolics, organochlorine pesticides, PCBs, toxaphene and PCCD/Fs in both the Slave River and the control sites suggests that the contaminants are being transported via the atmosphere. This is not unusual given the volatility of these compounds and their persistence in the environment. Atmospheric transport has been found to be important in the global movement of chlorinated compounds (Hoff *et al*, 1992). In addition, several studies have

documented the atmospheric transport and deposition of these contaminants to remote locations in the north (Muir *et al.*, 1996).

The contribution of atmospheric deposition to the total concentration seemed to vary with the type of organochlorine compound. For example there was no significant difference in concentrations of HCH isomers between the Slave River and the control lakes (McCarthy *et al.*, 1997b), whereas for many compounds, levels are higher in the Slave River than the control sites. This suggests that these fish are exposed to an additional source of organochlorines, most likely associated with upstream development. Another possible explanation could be differences in the length of the food chain between the Slave River and the control sites. These explanations are discussed further using chlorinated phenolics, dioxins and furans and toxaphene, respectively, as examples.

#### **Fish: Chlorinated Phenolics**

Higher levels of chlorinated phenolics and PCDD/Fs in the Slave River than the control lakes could reasonably be linked to the downstream transport of the bleached kraft pulp mill effluent. For example, chlorophenols and chloroguaiacols, found in bile samples from Slave River fish, were also detected in bile samples from fish captured downstream of the Grande Prairie Pulp Mill (Swanson *et al.*, 1993). 3,4,5-trichloroguaiacol, the most common chlorophenolic found near bleached kraft pulp mills (Kirkegaard and Renberg, 1988), was only detected in walleye and lake whitefish bile samples from the Slave River. Further monitoring of these chlorinated phenolics may therefore be warranted.

#### **Fish: Dioxins and Furans- General**

PCDDs were present in burbot liver and wholefish samples of all species from the Slave River and the control lakes, with hexa-, hepta-, and octa- isomers being detected the most often. The highest concentrations measured were usually of the octa- congeners. 2,3,7,8-TCDD was found in all species except northern pike. The higher chlorinated congeners were also detected by Muir and Pastershank (1997) in fish from the Athabasca, Peace and Slave River basins, especially in burbot livers. However, their study found that in muscle of fish caught downstream of Hinton, and burbot livers throughout the basins, the major PCDD/F congeners were 2,3,7,8-TCDD and -TCDF.

For PCDFs, 2,3,7,8-TCDF and OCDF were found in burbot liver and wholefish samples of all species from the Slave River and the control lakes, except lake whitefish from Leland Lake. PCDFs with 6 and 7 chlorine atoms were also detected in a few specimens of every species investigated. The presence of the high molecular weight isomers could suggest a source of tetra- and pentachlorophenol fungicide (Hagenmaier and Brunner, 1987). 2,3,7,8-TCDF was the most

frequently detected congener in fish muscle from the Fort Chipewyan domestic fishery, longnose sucker and northern pike livers from the Wapiti/Smoky and Peace Rivers, muscle of fish from downstream of Hinton, as well as burbot livers from northern Alberta (Muir and Pastershank, 1997).

### **Fish: Dioxins and Furans - Detailed**

The walleye wholefish and burbot liver results are discussed in further detail, since higher concentrations and a wider variety of PCDD/F congeners were detected in these samples. This was also observed in northern Alberta burbot liver (Muir and Pastershank, 1997).

Results for 2,3,7,8-TCDD, 2,3,7,8-TCDF and total TCDD/Fs in walleye wholefish and burbot liver from the Slave River and the control sites are presented in Figures 5-3 to 5-6. The data consist mainly of a large number of non-detection values. This, together with multiple detection limits (the result of improved analytical methods and differences in laboratory techniques) limited statistical analysis. As a result, time-based scattergrams were used to analyze the data.

In walleye, 2,3,7,8-TCDD and 2,3,7,8-TCDF made up 100 percent of the total TCDD and TCDF detected, in all cases but one (Figure 5-3 and 5-4). This was generally true for TCDF in burbot livers from both sites (Figure 5-6), but not for TCDD (Figure 5-5). Non 2,3,7,8-TCDD congeners contributed to the total TCDD value in burbot livers, especially in the early years of the study. This decline in non 2,3,7,8-TCDD congeners parallels the changes in the pulp mill bleaching process (Swanson *et al.*, 1993; Pastershank and Muir, 1995)

In walleye from the Slave River, 2,3,7,8-TCDD was found above detection in 8 samples from 1991-92, two in 1993-94 and one in 1994-95 (Figure 5-3). Only one of the samples from Leland Lake revealed the presence of this congener. Figure 5-4 shows that 2,3,7,8-TCDF was above detection in the first two years from both sites. In 1993 and 1994, only a few samples from the Slave River were above the detection limit.

2,3,7,8-TCDD was detected in most burbot liver samples collected from the Slave River, but only in those samples collected in 1990-91 from Alexie Lake (Figure 5-5). 2,3,7,8-TCDF was detected in almost all burbot liver samples from both sites (Figure 5-6). This compound was found in 86% of all burbot liver samples reviewed by Muir and Pastershank (1997) from the Athabasca, Peace and Slave River basins. Values in the Slave River samples appeared to decrease after 1991, a trend which was also observed by Swanson *et al.* (1993) and Muir and Pastershank (1997).

However, it should be noted that in 1991 the analytical methods for the SREQMP improved. Analysis and quantification performed by GC-low resolution mass spectrometry was replaced by GC-high resolution mass spectrometry, which has greater selectivity and sensitivity (ie. lower detection limits). This caused detection limits to decrease for the samples and potentially resulted in more peaks identified as PCDDs and PCDFs. However due to the greater selectivity of this method, there was also the potential that peaks which would be rejected by the high resolution method may have been included in the previous low resolution results. This could result in higher values before 1991, which appear to decrease in later years. Also in early years, the laboratory did not monitor for chlorinated diphenyl ethers. These compounds have been found to cause interferences in the determination of PCDD/Fs (ie. false positives; Huestis and Sergeant, 1992). It is therefore possible that the decrease in values over the years may be partially explained by changes in analytical methods.

Total TCDD levels were higher in burbot liver (maximum 17 pg/g) than walleye wholefish (maximum 2.56 pg/g) samples. This was the same for total TCDF values (burbot maximum 45 pg/g, walleye maximum 2.34 pg/g). This is likely due to the greater lipid content in burbot liver compared to walleye whole fish.

For walleye, TCDD and TCDF values were only slightly higher in the Slave River than the control site, suggesting atmospheric sources. In burbot liver, the levels were higher in the Slave River than the control lake, especially for TCDFs. This indicates riverine sources, most likely the pulp mills upstream. The presence of PCDDs and PCDFs in fish and sediment downstream of pulp mills using chlorine bleaching, such as those found in northern Alberta, has been well documented and is summarized in Muir and Pastershank (1997). The predominant TCDD/Fs identified in the effluents of bleached kraft pulp mills were 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,7,8-TCDF (Muller and Halliburton, 1990).

Total TCDF values were two to five times higher than total TCDD levels in burbot liver samples from the Slave River. Routinely, tetra furan isomer concentrations were two to ten times higher than those of tetra dioxin at sites where the major source of contamination is suspected to originate from bleached kraft mill discharges (Whittle, 1989; Pastershank and Muir, 1995; Muir and Pastershank, 1997).

**Figure 5-3** SREQMP TCDD Levels in Walleye Wholefish - Slave River and Control Site



**Figure 5-4 SREQMP TCDF Levels in Walleye Wholefish - Slave River and Control Site**





**Figure 5-5** SREQMP TCDD Levels in Burbot Liver - Slave River and Control Site



**Figure 5-6** SREQMP TCDF Levels in Burbot Liver - Slave River and Control Site



The detection of TCDDs and TCDFs in Slave River samples, although at lower levels than those detected in northern Alberta sites, indicates that these compounds are present in the environment even thousands of kilometres downstream of the closest pulp mill. There appeared to be a decrease in total TCDD/F levels in burbot livers after 1990, which agrees with the findings of Muir and Pastershank (1997) and Swanson *et al.*, 1993 and may be an indication of process changes in the pulp mills due to substitution of molecular chlorine with chlorine dioxide. However, the decline could also be due to analytical method changes.

A regulatory limit of 20 pg/g 2,3,7,8-TCDD in the edible portion of fish was set by Health Canada for commercial fish sale and export (Department of Health, 1996). All of the concentrations of 2,3,7,8 TCDD measured during the SREQMP were substantially below this level. Dioxin and furan results in fish samples from 1988 to 1991-1992 were assessed by Health Canada for human consumption and no concerns were noted. Results from fish collected after 1992 are still undergoing assessment.

For compounds such as DDT and related pesticides, higher concentrations in Slave River burbot liver than those from Alexie Lake may have been a result of past use in the Athabasca River system for biting fly control (Somers *et al.*, 1987).

Another factor contributing to the higher levels found in the Slave River fish might be related to the length of the food chain. Burbot from the Slave River may have been feeding at a higher trophic level than those from Alexie Lake (Pastershank and Muir, 1996). This was confirmed by stable isotope information and stomach content analysis collected for fish from Great Slave Lake and the Slave River, which had similar levels of PCB and toxaphene to those samples collected from the SREQMP (Evans, 1994; Pastershank and Muir, 1996; Tallman *et al.*, 1996).

### **Fish: Toxaphene**

The ranges of concentrations of toxaphene measured in fish are given in Table 5.30. Whole fish samples of walleye, northern pike and lake whitefish from the Slave River showed concentrations ranging from <0.002 to 0.137 µg/g, with the highest levels detected in walleye. In Leland Lake samples, only walleye had detectable levels. Toxaphene was detected in burbot livers from both sites, in all of the samples but one, with a maximum of 1.97 µg/g. For all species, concentrations in the control lakes were consistently lower than those in the Slave River.

<b>Species</b>	<b>Site</b>	<b>Toxaphene</b>
<b>Walleye (Whole)</b>	Slave	<0.002-0.137 (44)
	Leland	<0.002-0.090 (27)
<b>Northern pike (Whole)</b>	Slave	<0.03-0.035 (30)
<b>Lake whitefish (Whole)</b>	Slave	<0.03-0.063 (20)
<b>Burbot (Liver)</b>	Slave	0.061-1.97 (100)
	Alexie	0.015-0.112 (96)

The levels of toxaphene measured in fish collected in 1990-91 were not considered to pose a health hazard by Health Canada (Kirkpatrick, 1992). However, in the ten burbot samples collected from the Slave River in 1991-92, the levels of toxaphene were higher than in the previous year.

In order to set regulatory limits for contaminants that may be found in foods, Health Canada uses Tolerable Daily Intakes (TDIs). The TDI refers to an amount of a substance or chemical contaminant that can be safely consumed every day of your life and is based on body weight. For toxaphene, the TDI has been established at 0.2 µg/kg of body weight per day (Huston, 1992). Based on the mean level of toxaphene detected in the Slave River burbot livers collected in 1991-92 (0.897 µg/g), Health Canada stated that a 60 kg person could safely eat 13.4 grams per day or 93.8 grams per week (Huston, 1992). This is approximately one burbot liver per week. Since

Health Canada assumed that people in the NWT ate 20 grams of burbot liver per day (Huston, 1992), a consumption limit was issued. This limit states that those people who eat burbot liver should not eat more than one per week (GNWT, 1992).

The results collected since 1992 are currently undergoing an assessment for human health risks. It should be noted however, that in subsequent years, the mean and maximum values of toxaphene in burbot livers appear to decrease and are similar to or less than those detected in 1990 (Table 5.31), for which Health Canada did not advise limits on consumption. This decrease in levels may be reflected in the final assessment by Health Canada which has not been received to date.

<b>Table 5.31 Toxaphene Concentrations (µg/g) in Burbot Liver Samples</b>					
<b>Year</b>	<b>1990-91</b>	<b>1991-92</b>	<b>1992-93</b>	<b>1993-94</b>	<b>1994-95</b>
<b>Mean</b>	0.362	0.897	0.226	0.451	0.405
<b>Range</b>	0.090-1.057	0.137-1.887	0.061-0.374	0.283-0.783	0.153-0.961
<b>n</b>	11	10	10	10	10

Advances in the analysis for toxaphene, which occurred in 1992, may have contributed to this apparent decrease in values. Before this, toxaphene was quantitated based on 12 peaks on the chromatograph, some of which might have had interferences from organochlorines, thereby giving higher values (Sergeant, pers.comm., 1997). After 1992, quantitation was based on a different set of 20 peaks. Although the detection limit increased from 2 to 30 ng/g, the new methodology allowed for more accurate results (Huestis *et al.*, 1995). This detection limit was still considered an acceptable limit for health risk assessments (Andrews, 1993).

There is no record of specific use of toxaphene in the NWT (GNWT, 1992) but it has been detected in other northern fish studies (Kidd *et al.*, 1995; Muir *et al.*, 1996) at levels similar to or higher than those detected in the SREQMP. Concentrations of toxaphene in burbot liver samples collected from Great Slave Lake and Slave River Delta are comparable to levels observed at Fort Smith (Evans, 1994; Pastershank and Muir, 1996).

The results of this study (Table 5.30 and 5.31) indicate that toxaphene is present and bioavailable in the environment of the Slave River and the control lakes, which indicates an atmospheric source. It has accumulated in fish muscle, but higher levels were found in burbot livers which is probably due to the lipophilic nature of the contaminant. Further monitoring of toxaphene in the Slave River may be warranted.

### **Fish: PAHs**

Several factors point to a natural source of PAHs in the Slave River. The results of the HPLC/Fluorescence screening at the benzo(a)pyrene and phenanthrene wavelengths showed that both types of fluorescent aromatic compounds (FACs) were detected in the majority of the bile samples tested, indicating a general exposure to polycyclic aromatic materials. The control sites had lower values and different profiles than those from the Slave River, which suggests that there were sources of PAHs in the Slave River which were not present in the control lakes. Although the levels of both groups of FACs present in the bile samples from the Slave River were consistent with those observed for contaminated sites (Birkholz, 1994), the chromatograms were not similar to those reported for the bile of fish associated with oil spill events or petroleum products (Krahn *et al.*, 1987; 1992). Only low molecular weight PAH parent compounds were detected in Slave River muscle and liver samples, suggesting natural or atmospheric sources.

### **HEALTH ASSESSMENT**

All data collected from this study have been sent to Health Canada, but a human health assessment has not yet been completed. Therefore, existing Health Canada guidelines for the consumption of fish were included for comparative purposes only. All levels of organic contaminants were below existing Health Canada guidelines.



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