Water and Suspended Sediment Quality of the Transboundary Reach of the Slave River, Northwest Territories

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EXECUTIVE SUMMARY

Introduction

This report describes the water and suspended sediment quality conditions in the Slave River at Fort Smith. The status and long-term trends in water quality from the Slave River at Fitzgerald are also examined. Additionally, seasonal flow patterns and long-term temporal hydrological trends for the Slave River at Fitzgerald are assessed. A summary of the geology and upstream activities in the Slave River Catchment is also provided. Current monitoring efforts are assessed and recommendations are made for future monitoring.

The Slave River is the largest transboundary river in the Northwest Territories and it is an integral component of the Mackenzie River Basin, contributing approximately 75% of the inflow to Great Slave Lake. Its vast catchment area includes the Peace River, the Athabasca River and Lake Athabasca sub-basins, which extend across the provinces of Alberta, British Columbia and Saskatchewan. The Slave River originates in the northeastern region of Alberta at the confluence of the Peace River and the Rivière des Rochers, the primary outlet channel of Lake Athabasca and the Peace-Athabasca Delta.

The Slave River Catchment has experienced increased resource development over the last several decades. Predominant industrial activities include oil and gas developments, oil sands operations, pulp and paper mills, coal and uranium mining, agriculture, and forestry. Further, the W.A.C Bennett Dam, a hydroelectric development on the Peace River in northern British Columbia, exists upstream in the Slave River watershed. As these upstream developments have the potential to affect water resources, Northerners have raised concerns about impacts on the Slave River, and further downstream in the Mackenzie River basin. In addition, climate change may have the potential to influence the Slave River. Concerns and questions about the quality of the water, and ultimately the health of wildlife and people who drink the water, are especially relevant in the North, given the subsistence lifestyle and the close connection to the land still prevalent today among the predominantly Aboriginal population along the Slave River. In conjunction with other monitoring initiatives, this report strives to characterize the water and suspended sediment quality conditions of the Slave River and inform future research.

The main objectives of this report were to:

- Provide a general overview of the current state of water quality, suspended sediment quality and flows in the transboundary reach of the Slave River;
- Determine if water quality and flows have changed over time;
- Help to address community concerns about metals and organic compounds in the river;
- Support the development of water quality objectives for transboundary agreements; and;
- Outline potential areas where the existing Aboriginal Affairs and Northern Development Canada (AANDC) Slave River monitoring program could be improved.

It is hoped that the information contained in this report can be used to help make sound decisions and build policies that will ensure the ecological health of this important transboundary river. Combining the results from this study with information generated from other Slave River and Slave River Delta monitoring programs and research will help Northerners gain a better understanding of the health of the Slave River system.

Sampling Sites, Media and Parameters

Water and suspended sediment quality data for this report were obtained from three long-term sampling sites located on the transboundary reach of the Slave River. Flow data were obtained from the hydrometric (flow) monitoring station operated within this portion of the Slave River. These include:

1. The Slave River at Fort Smith surface water, centrifugate water and suspended sediment quality sampling mid-river site (1990 to present) led by AANDC Water Resources Division. This program is comprised of two parts:
    a) Slave River Environmental Quality Monitoring Program (SREQMP; 1990-1995), and
    b) Follow-Up Study (2000-2010).
2. The Slave River at Fort Smith surface water quality sampling shore site (1982 to present) led by the AANDC Fort Smith District office.

3. The Slave River at Fitzgerald surface water quality sampling site (1960 to present) led by Environment Canada.
4. The Slave River at Fitzgerald hydrometric station (1960 to present) led by Environment Canada (Water Survey of Canada).

Centrifugate water samples, as well as surface water, were included in the monitoring program to address water quality concerns, to allow comparison with existing guidelines and to help establish water quality objectives for the Slave River. By separating the suspended sediment from the water using the centrifuge, it is possible to study each media type separately. Due to the size and organic content of the suspended sediment in the Slave River, metals and organic compounds tend to attach to these particles and can be carried long distances from their source.

To understand the basic chemistry of the water and suspended sediment quality of the Slave River, samples were regularly analyzed for routine parameters, nutrients and major ions.

To help address concerns regarding upstream activities, water and suspended sediment samples were also tested for metals and organic compounds such as chlorophenols, organochlorine pesticides, PCBs, dioxins, furans and hydrocarbons. Some of these substances can be natural, but some are known to be associated with upstream development.

Evaluation Methods

To evaluate the Slave River water and suspended sediment quality data, comparisons to existing guidelines were made and long-term trends in water quality were examined. The water quality data from both Fort Smith and Fitzgerald were compared to the CCME Canadian Water Quality Guidelines for the Protection of Freshwater Aquatic Life (CPFAL). In the absence of CCME CPFAL guidelines for suspended sediment, suspended sediment quality data were compared to the CCME Draft Interim Freshwater Bottom Sediment Quality Guidelines (SQG; CCME, 1999). For those parameters that did not have a national guideline, water quality guidelines developed by the province of British Columbia or bottom sediment guidelines developed by the Ministry of Ontario were used. These guidelines are meant to protect all forms of aquatic life, including the most sensitive life stage of the most sensitive species over the long-term. It should be noted that these are national guidelines and, therefore, may not reflect specific local conditions, especially sediment-laden northern rivers and ecosystems.

The Slave River at Fitzgerald water quality data were assessed for long-term trends to determine whether water quality conditions have changed over the period of record (annual trends). Trends were also examined separately for each season (spring, summer, fall and winter). As river flow can influence the outcome of water quality trend analyses, the water quality data for each parameter were tested for a relationship with flow. If a relationship with flow was found, trend analyses were conducted on both the non flow-adjusted (raw) and flow-adjusted data. If a relationship with flow was not found, then long-term temporal trends were only assessed for the raw data.

In this report, long-term trends were declared statistically significant if the p-value for that test is less than 0.05; this represents a 95% level of confidence. Trends with a 90% level of confidence are also highlighted throughout the report, as this allows for the identification of parameters that should also be watched carefully.

Key Findings

Hydrology

Flow in the Slave River is greatly influenced by the Peace River, which contributes about 60% of the Slave River flow volume. The regulation of the Peace River for BC Hydro operations has, therefore, affected the Slave River flow regime. Flows in the Slave River still decrease in the fall, reach a minimum in the winter under ice and then peak in the spring during and just after breakup. However, since regulation, the hydrograph has been dampened, in that mean winter low flows have increased by 75% and mean spring peak flows have been reduced by 20%. It is important to note that the total amount of water flowing into the Northwest Territories has not changed, rather changes to the timing of when the water arrives have been observed.

Other changes in the flow of the Slave River may be due to regulation, or an increase in climatic variability in the catchment. For example, high freshet peaks were generally experienced in June before dam construction, but are now often in May. A trend toward more annual peaks or blips on the annual hydrographs has also been identified and secondary peaks now appear in some years during winter.

In 2010, record low water levels were experienced on the Slave River, on Great Slave Lake and in the upper Mackenzie River. Many of the tributaries to the Williston Lake Reservoir behind the W.A.C. Bennett Dam also experienced record lows that year. This suggests that the low water levels in the NWT that year were likely due to low snowpack and low rainfall in the upper portion of the Slave River watershed.

Long-term trend analysis of Fitzgerald flow data revealed significant decreasing trends in the summer and fall flows and a significant increasing trend in winter flows. No trends were found in the spring or annual flows. Additional work is required to understand the ecological significance of these trends and determine if these trends are the result of upstream regulation or climate change or both.

Surface Water Quality

Physicals and Major Ions

The transboundary reach of the Slave River has moderately hard water (58-152 mg/L $CaCO_3$), with a median pH of 7.9. Total dissolved solids concentrations range from 46-387 mg/L, which are typical of freshwater systems. Dissolved solids are dominated by bicarbonate, calcium, sulphate, and to a lesser extent, magnesium, sodium and chloride; these contributions are universal among fresh inland waters. Dissolved oxygen levels in the river are generally high, particularly at Fort Smith where the presence of the rapids causes the water to be well mixed and oxygenated.

None of the physical parameters or major ions exceeded their respective CCME CPFAL guidelines.

At Fitzgerald, with the non flow-adjusted data, dissolved sulphate and dissolved sodium demonstrated increasing annual trends, while total dissolved solids and dissolved calcium showed decreasing annual trends. Dissolved potassium also revealed a decreasing trend during the spring. When the data was adjusted for flow, dissolved sulphate and dissolved sodium continued to exhibit increasing trends and total dissolved solids continued to show decreasing trends. Dissolved calcium and dissolved potassium no longer revealed any trends. Further work is required to determine the significance, if any, of these trends.

Nutrients

Detectable levels of ammonia in the Slave River ranged from 0.001 to 0.33 mg/L at Fitzgerald and 0.002 to 0.52 mg/L at Fort Smith. None of these values exceeded CCME CPFAL guidelines.

At Fitzgerald, dissolved organic carbon ranged from 1.5 to 40.4 mg/L, whereas particulate organic carbon ranged from 0.13 to 84.0 mg/L. There are no CCME CPFAL guidelines for organic carbon.

Total and dissolved phosphorus at Fitzgerald ranged from 0.006 to 4.67 mg/L and 0.002 to 0.0343 mg/L, respectively. At Fort Smith, total and dissolved phosphorus ranged from 0.014 to 4.4 mg/L and 0.008 to 0.02 mg/L, respectively. There are no CCME CPFAL guidelines for phosphorus.

At Fitzgerald, only the flow-adjusted total phosphorus data revealed a significant increasing annual trend. For dissolved phosphorus, a significant increasing trend was found in the spring and winter in both the non flow-adjusted and flow-adjusted data. Continued sampling and observations are important to assess phosphorus levels given that land users have observed more algae on the rocks and in fishing nets, and denser willows and other plants are growing along the shore.

The Slave River has high levels of suspended sediment with values ranging from < 3 to 5600 mg/L. This is mainly due to the fact that its two major tributaries, the Athabasca and Peace Rivers, flow through the Interior Plains, an area that is underlain with easily eroded sedimentary rocks and soils.

Metals

Sediment load affects metal levels. Rivers that carry large amounts of sediment tend to have higher levels of metals. This is because metals can adsorb to sediment particles. Metal levels in water are often the result of the natural weathering of rocks and the underlying geology through which a river flows, but human activities can also release metals to the environment.

Metals in water exist in a number of soluble (i.e., dissolved) and insoluble (i.e., attached to clays or organic matter) forms, with the dissolved form generally more biologically available for uptake by aquatic organisms. For most metals in the Slave River, the dissolved levels are considerably lower than the total levels, suggesting that they are less available to aquatic life.

Total metal levels in the Slave River were compared to the CCME guidelines for the protection of aquatic life (CPFAL). As these guidelines are national in scope, they do not reflect the unique conditions of the Slave River, but they are useful for comparative purposes.

Total metals such as cadmium, chromium, copper, iron, lead and mercury were higher than their respective CCME CPFAL guideline more than 25% of the time. A greater proportion of these metals was in the particulate form and therefore likely less biologically available. However, for cadmium and copper the dissolved fraction accounted for a large percentage of the total, suggesting that a greater proportion of cadmium and copper is potentially more biologically available. In addition, dissolved concentrations of cadmium, chromium, copper and iron exceeded the total metal guideline on occasion. It is important to keep monitoring and assessing these metals since it is the dissolved form which is generally more available to fish.

Total metals that exceeded the CCME CPFAL guideline less than 25% of the time were arsenic, barium, manganese, nickel, selenium, silver, vanadium and zinc. There were no guideline exceedances for total antimony, total beryllium, total cobalt, total molybdenum, total thallium and total uranium.

Many times, when generic guidelines are used to assess water quality, the guidelines are exceeded due to natural conditions such as underlying geology and high sediment loads. In addition, for some parameters, the generic guideline may be significantly higher than the natural conditions and, therefore, may not be protective. Guidelines, based on the concentrations of substances in the river, are known as site-specific water quality objectives. These objectives would allow for a more accurate assessment of the metal levels in the Slave River and provide a relevant set of benchmarks against which future data can be compared. Also where generic guidelines do not currently exist for certain parameters of concern (e.g., phosphorus), the development of site-specific water quality objectives would help to fill these gaps.

All metals at Fitzgerald were considered for long-term trend assessment but only ten (10) met the data quality criteria requirements. Of these, total aluminum, total chromium and total molybdenum exhibited trends.

Total aluminum and total chromium exhibited decreasing trends during the summer season. Following flow-adjustment, these summer trends were no longer evident, which may be a reflection of the decreasing trend in summer flows that was identified. However, the flow-adjusted total chromium data did exhibit an increasing trend during the winter season.

The non flow-adjusted total molybdenum data revealed a decreasing trend in the spring and summer seasons. Since total molybdenum did not reveal a relationship with flow, the flow-adjusted molybdenum data was not assessed for trends.

It is recommended that further work be undertaken to determine the effects of these trends on the aquatic environment of the Slave River. In addition, trend analysis should be conducted on dissolved metal data once enough data becomes available.

Changes in Seasonal Water Quality

Water quality and quantity are very closely linked. In natural unregulated rivers, dissolved substances are typically higher during the winter because a larger percentage of water comes from groundwater inflows. In the Slave River, however, this pattern is not observed. Many of the dissolved substances (total dissolved solids, potassium, sulphate, fluoride, dissolved organic carbon, phosphorus) have higher concentrations in the spring and summer, than in the winter. For other dissolved substances (specific conductance, alkalinity, calcium, magnesium, sodium, hardness, ammonia), concentrations in the Slave River were similar among seasons. Based on the analyses, these changes appear to be the result of the altered flow regime of the Slave River due to upstream flow regulation of the Peace River; higher observed winter flows and the mixing effects of Lake Athabasca and Williston Lake. These changes may also be linked to climate change.

For total dissolved solids, alkalinity and hardness, these seasonal patterns appear to be occurring as far downstream as the Slave River at the Mouth (just upstream of Great Slave Lake), although a higher frequency of sampling would be required to confirm this.

Further study would be required to determine if these seasonal changes in water quality, which can be linked to changes in quantity, are having any ecological effects on the Slave River aquatic ecosystem.

Organic Compounds in Water

Centrifugate and/or surface water samples collected from the Slave River were analyzed for chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyls (PCBs) and chlorinated benzenes. Data from the Follow-Up Study (2000-2010) were compared to the results from the SREQMP (1990-1995) and to relevant guidelines. It should be noted that for some organic parameters, detection limits were higher in the Follow-Up Study than the SREQMP. According to the laboratory used to analyze the samples for organics, the rules that govern laboratory reporting have changed such that the laboratory must report values with a much higher level of certainty than what was needed in the past. As such, the very low detection limits achieved during the SREQMP are not available today. In some cases, this makes comparison of results difficult, however, further monitoring will allow for trend analyses to be conducted which will help determine if changes are occurring.

No polychlorinated biphenyls (PCBs), organochlorine pesticides or chlorinated benzene compounds were detected in centrifugate water samples collected from Fort Smith during the SREQMP (1990-1995) or the Follow-Up Study (2000-2010). At Fitzgerald, where lower detection limits were achieved, some organochlorine pesticides were detected in the surface water before 1986, but all were below water quality guidelines.

During the SREQMP (1990-1995), seven chlorophenol compounds were detected in centrifugate samples; all values were below CCME CPFAL guidelines. During the Follow-Up Study (2000-2010), these compounds were not detected. This apparent decrease in chlorophenols could be due to the stricter limits for the pulp and paper industry, which were imposed by the Canadian Government in the 1990s. However, in some cases the very low detection limits obtained during the earlier study are not available today, so further monitoring is required to confirm these findings.

Parent PAH compounds, including naphthalene, methylnaphthalenes and pyrene, were present in a few centrifugate water samples collected from Fort Smith and surface water samples from Fitzgerald. All concentrations were below CCME CPFAL guidelines. Small sample sizes make statistical analyses difficult; however, concentrations of these compounds were lower in the Follow-Up Study (2000-2010) than during the SREQMP (1990-1995).

In May 2007, centrifugate water samples from Fort Smith were analyzed for alkylated PAHs for the first time and in September 2010, naphthenic acids were also added. These compounds have been associated with upstream activities in the Slave River. While two C2 and one C3 substituted alkylated PAHs were detected, naphthenic acids were not. There are currently no CCME CPFAL guidelines for alkylated PAHs or naphthenic acids.

A limited number of organic compounds were detected in the centrifugate and surface water samples, but only at very low concentrations. Still, their presence indicates the possibility of transport from upstream and/or atmospheric deposition; hence, continued monitoring is warranted. For certain compounds, detection limits were above the CCME CPFAL guidelines, thus, it was not possible to draw any substantial conclusions with respect to potential impacts on aquatic life. Therefore, it is imperative to ensure that appropriate detection limits are achieved during future monitoring.

Suspended Sediment

Particle Size and Total Organic Carbon

The suspended sediment samples collected from the Slave River at Fort Smith were comprised of sand, silt and clay particles, the proportions of which varied seasonally.

Sand content was highest in the winter. The quantity of clay particles was highest during the open water season, particularly in the fall, while the amount of silt particles remained relatively constant over the year. The total organic carbon (TOC) content of the Slave River suspended sediments averaged only 1.23%, which is at the lower end of the natural range for rivers of the boreal forest region.

As metals and organic compounds adsorb strongly to finer suspended particulates, their concentrations are expected to be highest when silt and clay are at a maximum. This was observed on the Slave River. Statistically significant correlations were noted between metal concentrations and clay content; however, the strongest significant correlations were observed between metal levels and total organic carbon concentrations.

Metals in Suspended Sediment

Concentrations of most metals in suspended sediment were greater in the summer and fall than in the winter, which followed the same pattern that was displayed for organic carbon and clay content. This supports the theory that metals adsorb to the finer particulates.

Metal concentrations in the suspended sediment samples collected during the SREQMP were compared to samples collected during the Follow-Up Study. As significant differences were not observed, the data from the two time frames were combined.

As there are no guidelines available for suspended sediment, results were compared to the Draft Interim Freshwater Sediment Quality Guidelines threshold effect level (TEL) and probable effect level (PEL) or the Ontario Sediment Quality Guidelines lowest effect level (LEL) and severe effect level (SEL) for bottom sediment dwelling organisms.

Concentrations of lead and mercury in Slave River suspended sediment samples were always lower than the TEL. On occasion, concentrations of arsenic, cadmium, chromium, copper and zinc exceeded the TEL, but were always below the PEL. As there are no national guidelines for nickel and manganese, concentrations of these metals were compared to the Ontario Sediment Quality Guidelines. Nickel concentrations in Slave River suspended sediment samples were greater than the LEL guideline in almost every sample, however, the SEL was not exceeded. Manganese concentrations in sediment were greater than the LEL on nine of 25 occasions and exceeded the SEL twice.

The lack of guidelines for suspended sediment makes it difficult to draw any definitive conclusions with respect to potential effects on biota. Given the conservative nature of the guidelines and the infrequent exceedances of the upper effect levels, it is unlikely that the metal concentrations in the Slave River would have adverse impacts on aquatic life. However, it is very important to continue monitoring metals in suspended sediment. Further, the frequency of suspended sediment sampling should be increased to be able to generate enough data to examine trends over time. The collection of bottom sediments in depositional areas of the Slave River should also be considered.

Organic Compounds in Suspended Sediment

Suspended sediment samples collected from the Slave River at Fort Smith have been tested for chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated benzenes and dioxins and furans. Data from the Follow-Up Study (2000-2010) were compared to the results from the SREQMP (1990-1995). As noted previously, the very low detection limits achieved during the SREQMP are not available today.

During the SREQMP, 20 chlorophenol compounds were detected in suspended sediment samples at very low levels. During the Follow-Up Study, none of these compounds were detected. This apparent decrease in chlorophenols could be due to the stricter limits for the pulp and paper industry, which were imposed by the Canadian Government in the 1990s. However, in some cases the very low detection limits obtained during the earlier study are not available today, so further monitoring is required to confirm these findings. The only chlorophenol compounds detected in the Follow-Up Study were two compounds that were not part of the SREQMP Study: p-cresol and phenol. These compounds will continue to be a part of the monitoring program. There are currently no CCME CPFAL guidelines for chlorinated phenolics in sediment.

Organochlorine pesticides were below the detection limits in all suspended sediment samples tested during the SREQMP and the Follow-Up Study. As the detection limits were sometimes higher than the sediment quality guidelines and concentrations detected in upstream studies, conclusions relative to the potential effects on aquatic organisms cannot always be made. Therefore, it is important to ensure that appropriate detection limits are achieved during future monitoring.

During the Follow-Up Study (2000-2010), concentrations of PAH parent compounds in suspended sediment from the Slave River were lower than those measured in the SREQMP (1990-1995). Of the compounds that are comparable, fewer values exceeded the TEL and LEL guidelines in 2000 - 2010 and all were lower than the PEL and SEL guidelines.

Starting in 2001, suspended sediment samples were analysed for an expanded list of PAH compounds, which allowed for comparison to total PAH guidelines[1] for bottom sediment. Total PAH levels in Slave River suspended sediments were found to be at least ten times lower than this guideline, which was established for the protection of bottom-dwelling aquatic animals

In 2007, alkylated PAHs were added to the suspended sediment monitoring program and detected at low levels in the two samples collected. Although there are currently no Canadian guidelines for alkylated PAHs, the results were well below the United States Environmental Protection Agency (USEPA) benchmark established for the protection of bottom dwelling aquatic animals.

As PAHs have both natural and anthropogenic sources, it is important to continue to monitor for these compounds.

Total PCBs and Aroclors were not detected in the suspended sediment samples. In May, 2007, for the first time, the suspended sediment sample was analyzed for a wide list of individual PCB congeners with very low detection limits; few were detected and all values were well below low the TEL guideline for the protection of freshwater aquatic life.

Over the period of record, 20 suspended sediment samples were analyzed for a suite of 17 dioxins and furans. The most toxic isomer, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), was not detected in any of the suspended sediment samples collected from the Slave River. Of the seven congeners that were detected, only three were above detection more than two times. 2,3,7,8-TCDF which has been linked to pulp mill effluent, was detected in nine out of 11 samples in the SREQMP, but in only one out of nine samples in the Follow-Up Study. This apparent decrease could also be linked to regulation changes for pulp mills. For the other two compounds, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (H_7CDD), and octachlorodibenzo-p-dioxin (OCDD), the range of concentrations were the same over the entire period of record. The presence of these compounds could indicate atmospheric or point sources. All Toxic Equivalent (TEQ) values for suspended sediment samples from this study were below the CCME TEL of 0.85 pg TEQ/g and the PEL of 21.5 pg TEQ/g.

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[1] In the absence of a national guideline for total PAHs in bottom sediments, the Ontario guideline was used.

Conclusions

Overall, this study has enhanced the knowledge of water quality, suspended sediment quality and hydrology of the Slave River.

Long-term trend analysis of Fitzgerald flow data revealed significant decreasing trends in flow during the summer and fall seasons and a significant increasing trend in winter flows. Further study needs to be undertaken to determine if these trends are an effect of regulation or an increase in climatic variability in the catchment.

Some long-term trends in non flow-adjusted surface water quality in the Slave River at Fitzgerald were also identified. These included increasing trends in dissolved sulphate, dissolved sodium and dissolved phosphorus and decreasing trends in total dissolved solids, calcium, potassium, total aluminum, total chromium and total molybdenum.

Following flow-adjustment, dissolved sulphate, dissolved sodium, total phosphorus, dissolved phosphorus and total chromium exhibited increasing trends, while total dissolved solids and total molybdenum exhibited decreasing trends. Additional work is required to examine the relationship between water quantity and quality on the Slave River, including these long term trends results.

Certain metals were found to exceed the CCME guidelines for the protection of aquatic life. The development of site-specific water quality objectives, based on the historical water quality data, will allow for a more accurate assessment of the metal levels in the Slave River. Also as CCME CPFAL guidelines do not exist for certain parameters of concern (ie phosphorus), site-specific objectives would help to fill this gap.

In the Slave River at Fitzgerald, it appears that the higher winter flows and the mixing effects of Lake Athabasca and Williston Lake have changed the natural seasonal pattern of the concentrations of dissolved parameters. Many of the dissolved parameters revealed higher concentrations in the spring and summer, rather than in the winter. For other dissolved parameters, concentrations were similar among seasons. Further work is recommended to understand the effects of these changes on the aquatic environment of the Slave River.

In general, fewer organic compounds, and at lower levels, were found in both centrifugate water and suspended sediment samples during the Follow-Up Study (2000-2010) than during the SREQMP (1990-1995). Still, their detection highlights the need for continued monitoring in both water and suspended sediment. Hydrocarbons, which have both human and natural sources, have been found at levels which are lower than the aquatic life guidelines in water. Some hydrocarbons in suspended sediment have exceeded the bottom sediment guidelines, however all values were below the total PAH guideline. Further study on the presence and sources of PAHs is required, including the continued analysis of emerging parameters of concern such as alkylated PAHs and naphthenic acids.

In conjunction with the Environment Canada monitoring programs at Fitzgerald, the AANDC monitoring program at Fort Smith provides a large amount of data from the Slave River. These programs are critical to better understand changes in aquatic environment and form the basis of many different research and monitoring initiatives.

Overall, the Slave River report provides an overview of the data collected in past years. Monitoring will continue and, where possible, improvements to the monitoring program will be made. Incorporating additional data and information will help assess any environmental change in the Slave River over time. It is important that all monitoring programs attempt to collect data in a consistent manner. Consistent data collection and sharing, including across jurisdictions, can be extremely useful as it will allow for more thorough water quality assessments and provide a better understanding of change in the watershed.

Next Steps

AANDC is continuing to carry out the Slave River monitoring program through the collection of water and suspended sediment samples. AANDC will work with Environment Canada to assess Slave River water quality and quantity data when new data become available.

The Department will also continue to be active within other regional monitoring initiatives, such as the Slave River and Delta Partnership. This partnership, consisting of members from aboriginal, federal and territorial government, Aurora College and communities along the Slave River, has resulted in several initiatives including community workshops, Slave River Delta sediment sampling, the deployment of passive samplers in the Slave River and the Slave River fish sampling program. In addition to these efforts, Environment Canada has implemented an expanded oil sands monitoring program that includes the Slave River and Slave River Delta. Collaboratively, these research and monitoring initiatives will continue to expand the knowledge and understanding of the Slave River aquatic ecosystem.

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LIST OF ACRONYMS

pg/g: picogram/gram
µg/g: microgram/gram
µg/L: microgram/litre
ug/kg: microgram/kilogram
AANDC: Aboriginal Affairs and Northern Development
ALS: Analytical Laboratory Services
BC MOE: British Columbia Ministry of the Environment
BKM: Bleached Kraft Mill
CCME: Canadian Council of Ministers of the Environment
CCREM: Canadian Council of Resource and Environment Ministers
COPC: Compound of Potential Concern
CPFAL: Canadian Guidelines for the Protection of Freshwater Aquatic life
DO: Dissolved Oxygen
DOC: Dissolved Organic Carbon
EMPC: estimated maximum possible concentration
ENR: Department of Environment and Natural Resources
ETL: Envirotest Laboratories Limited
GNWT: Government of the Northwest Territories
GSL: Great Slave Lake
INAC: Indian and Northern Affairs Canada
I-TEF: International Toxicity Equivalent Factor
JTU: Jackson Turbidity Units
LEL: Lowest effect level
MESL: MacDonald Environmental Sciences Limited
mg/L: milligram/litre
MRBB: Mackenzie River Basin Board
MRBC: Mackenzie River Basin Committee
NATO: North American Treaty Organization
NDR: non-detect ratio
NEL: No Effect Level
ng/g: nanogram/gram
NLET: National Laboratory of Environmental Testing
NRBS: Northern Rivers Basin Study
NREI: Northern Rivers Ecosystem Initiative
NTU: Nephelometric Turbidity Units
OCDD: octachlorodibenzo-p-dioxin
OCDF: octachlorodibenzofuran
PAD: Peace-Athabasca Delta
PAH: Polycyclic Aromatic Hydrocarbon
PCB: Polychlorinated Biphenyl
PCDD: Polychlorinated Dibenzodioxin
PCDF: Polychlorinated Dibenzofuran
PEL: Probable Effect Level
POC: Particulate Organic Carbon
SEL: Severe Effect Level
SQG: Sediment Quality Guidelines
SREQMP: Slave River Environmental Quality Monitoring Program
TCDD: tetrachlorodibenzo-*p*-dioxin
TCDF tetrachlorodibenzofuran
TDS: Total Dissolved Solids
TEL: Threshold Effect Level
TEQ: Toxicity Equivalency Quotient
TSS: Total Suspended Solids
USEPA: United States Environmental Protection Agency
USGS: United States Geological Survey
WHO: World Health Organization

1.0 INTRODUCTION

1.1 Background

The Slave River is the largest transboundary river in the Northwest Territories. Its vast catchment area includes the Peace River, the Athabasca River and Lake Athabasca sub-basins, which extend across the provinces of Alberta, British Columbia and Saskatchewan (Figure 1.1). The Slave River originates in the northeastern region of Alberta at the confluence of the Peace River and the Rivière des Rochers, the primary outlet channel of Lake Athabasca and the Peace-Athabasca Delta. The Slave River is an integral component of the Mackenzie River Basin, contributing approximately 77% of the inflow to Great Slave Lake.

Industrial activity in the upstream portion of the Slave River Catchment is extensive and has continued to increase over the last decade (Holroyd and Simieritsch, 2009). Predominant industrial activities include oil and gas developments, oil sands operations, pulp and paper mills, coal and uranium mining, agriculture, and forestry. Further, the W.A.C Bennett Dam, a hydroelectric development on the Peace River in northern British Columbia, exists upstream in the Slave River watershed. As these upstream developments have the potential to affect water resources, Northerners have raised concerns about the potential for adverse effects on the aquatic resources of the Slave River, as well as those further downstream in the Mackenzie River basin. In addition, climate change may have the potential to influence the Slave River. Concerns and questions have been raised regarding the quality of the water and, ultimately, the health of wildlife and people who drink the water and eat the fish. These questions are especially relevant in the North, given the subsistence lifestyle and the close connection to the land still prevalent today amongst the predominantly Aboriginal population along the Slave River. In response to these concerns, several aquatic monitoring programs have been, and continue to be, carried out on the Slave River, including the AANDC water and suspended quality monitoring program.

1.2 Purpose of Report

The primary objectives of this report are to:

- Provide a general overview of the current state of water quality, suspended sediment quality and flows in the transboundary reach of the Slave River;

- Determine if water quality and flows have changed over time;

- Help to address community concerns about metals and organic compounds in the river;

- Support the development of water quality objectives for transboundary agreements; and;

- Outline potential areas where the existing Aboriginal Affairs and Northern Development Canada (AANDC) Slave River monitoring program could be improved.

It is hoped that the information contained in this report can be used to help make sound decisions and build policies that will ensure the ecological health of this important transboundary river. Combining the results from this study with information generated from other Slave River and Slave River Delta monitoring programs and research will help Northerners gain a better understanding of the health of the Slave River system.

Updated information on the status and trends of water and suspended sediment quality, as well as hydrology, in the transboundary reach of the Slave River is presented in this report. In addition to informing Northerners about the state of the river, the report will support upcoming Alberta-NWT transboundary negotiations. This report serves as a follow up to the Slave River Environmental Quality Monitoring Program (SREQMP) report, which characterized the conditions of water, suspended sediment and fish quality in the Slave River at Fort Smith from 1990 to 1995 (Sanderson *et al*., 1997).

1.3 Data and Information Analyzed in the Report

Presently, there are three long-term water quality sampling programs and one hydrometric station along the transboundary reach of the Slave River. The data from these programs were used to evaluate and assess the state of water and suspended sediment quality and hydrology, as well as to identify any trends and/or changes in conditions over time. These programs, which will be described in further detail throughout the report, include:

1. The Slave River at Fort Smith (mid-river) Water and Suspended Sediment Monitoring Program (1990 to present) led by AANDC Water Resources Division.

   This program is comprised of two parts:

   a) Slave River Environmental Quality Monitoring Program (SREQMP) (1990-1995), and
   b) Follow-up Study (2000-2010).

2. The Slave River at Fort Smith (shore) Water Quality Monitoring Program (1982 to present) led by the AANDC Fort Smith District office.

3. The Slave River at Fitzgerald Water Quality Monitoring Program (1960 to present) led by Environment Canada.

4. The Slave River at Fitzgerald Hydrometric Program (1960 to present) led by Environment Canada (Water Survey of Canada).

1.4 Organization of the Report

This report is divided into ten chapters presenting relevant background information, details of the monitoring programs, the analyses undertaken to assess the state of the Slave River, as well as results and conclusions. In Chapter 2, the importance of the Slave River to NWT residents is discussed, along with current water management initiatives, to underscore the significance of monitoring the Slave River. Chapter 3 describes the environmental setting of the three sub-basins of the Slave River Catchment, outlining the climate, physiography, geology, communities and developments in the region.

Compounds of potential concern (COPCs), such as metals, organic compounds and nutrients, which may be associated with upstream developments are identified and discussed in Chapter 4, along with a brief overview of the potential fate and pathways of these compounds. An overview of the sampling program, including sampling locations, period of record, media sampled, field methodology and analytical laboratory methods is provided in Chapter 5, along with descriptions of the methods utilized to compile, audit and assess the data.

Chapter 6 presents a brief hydrological overview of the Slave River Catchment, and includes both current status and trends in the flow of the river. Surface water quality results and trends are discussed in Chapter 7. Chapter 8 outlines centrifugate water quality results, while the suspended sediment quality results are discussed in Chapter 9. Recommendations for future monitoring are provided in Chapter 10. References and a series of Appendices with detailed or supplementary information are also included at the end of the report.

Figure 1.1: Slave River Catchment in relation to the Mackenzie River Basin.

Base map sources: see References.

2.0 THE IMPORTANCE OF THE SLAVE RIVER

2.1 Introduction

This chapter provides a brief discussion of the importance and significance of the Slave River to Northerners and sets the context for this report. A summary of the upcoming transboundary negotiations between the NWT and Alberta and the recently released NWT Water Stewardship Strategy is also provided. Ensuring that all waters in and entering the NWT are clean, abundant and productive for all time is a priority for the NWT (GNWT and AANDC, 2010). Information from this report will inform the transboundary negotiations and help to support the goals and objectives of the Strategy.

2.2 The Importance of the Slave River to Northerners

"*Aboriginal people, who make up about 48 percent of the total population of the NWT and 90 percent of the population in smaller communities, draw their spiritual and cultural integrity and their strength from the land and water, and expect their traditional ways of life and cultures to be preserved and maintained*" (GNWT and AANDC, 2010).

The Slave River serves as a direct source of drinking water for the people and wildlife residing along its shores. It also provides habitat for many wildlife species that are hunted, fished and trapped by Northerners. Traditional foods, including fish, waterfowl and mammals, are vital to the subsistence way of life and for some, make up a significant part of the diet.

Over the last decade, industrial activity in the upstream portion of the Slave River Catchment has continued to increase (Holroyd and Simieritsh, 2009). Residents have raised concerns about contamination in the Slave River due to upstream activities along the Peace and Athabasca rivers, which could negatively impact the aquatic ecosystem and the health of the people of the NWT. Upstream activities include oil sands operations, oil and gas developments, coal and uranium mining, hydroelectric developments, pulp and paper mills, forestry, agricultural activities, fuel burning electricity plants, municipal wastewater discharges, and transportation corridors.

Aboriginal and First Nations peoples, and Northerners in general, have clearly stated their view on the importance of water. Since 2006 several Aboriginal water gatherings have taken place to discuss and emphasize the significance of water (Keepers of the Water, 2012). These gatherings have brought together Aboriginal leaders, elders, youth, concerned citizens, environmental experts, territorial and federal representatives and non-government organizations. The gatherings have given people an opportunity to raise issues and voice their concerns with respect to water. In addition, following each gathering, resolutions and/or declarations have been made to support the work required to protect the waters of the Mackenzie River Basin that ultimately drain into the Arctic Ocean.

In Fort Smith, the *Tu Beta Ts'ena – Water is Life* gathering was held in August 2007 and concerns were raised regarding the unprecedented rate and expansion of oil sands development in Northern Alberta (Akaitcho Territory Government, 2008; Keepers of the Water, 2012). People called for proper consultation before any future development occurs in order to protect the environment. It was recognized at this gathering that the environment and its biological diversity are of central importance to the livelihood and socio-cultural integrity of the peoples of the Slave River Catchment who use the area for hunting, trapping, fishing, gathering, transportation, teaching youth and spiritual purposes.

2.3 Mackenzie River Basin Transboundary Bilateral Negotiations Background and Current Status

In 1981, the Mackenzie River Basin Committee (MRBC), with members from provincial, territorial, and federal water resources agencies, completed the Mackenzie River Basin Study Report (MRBC, 1981). The report's first recommendation was that water management agreements be drawn up for the transboundary waters of the Mackenzie River Basin. The report was endorsed by Ministers from all jurisdictions within the Mackenzie River Basin, including British Columbia, Alberta, Saskatchewan, Yukon and the NWT, as well as the Government of Canada.

In 1983, Indian and Northern Affairs Canada (INAC), now known as Aboriginal Affairs and Northern Development Canada (AANDC) (on behalf of the Government of Canada) and the Government of the Northwest Territories (GNWT) began discussions with the Government of Alberta. As part of these discussions, AANDC and the GNWT produced a paper titled *NWT Interests and Needs,* which identified the potential impacts of upstream developments on downstream water resources, as related to subsistence lifestyles, as the single most important issue in transboundary negotiations (Letourneau *et al*. 1988). The authors stressed the importance of collecting information to document current conditions and levels of contamination in transboundary rivers. In the late 1980's, several studies were initiated to collect and analyze information on the Slave River, eventually leading to the Slave River Environmental Quality Monitoring Program (SREQMP), which took place between 1990 and 1995.

In 1997, the *Mackenzie River Basin Transboundary Waters Master Agreement* was signed by Canada, British Columbia, Alberta, Saskatchewan, Yukon and the NWT (MRBB, 1997). This agreement committed all six governments to work together to manage the water resources of the Mackenzie River Basin and to develop bilateral or multilateral sub-agreements. The purpose of the sub-agreements is to provide an effective basis for sound management of the transboundary waters that flow between the different jurisdictions of the Mackenzie River Basin.

The Alberta-NWT Bilateral Water Management Agreement Negotiations Memorandum of Understanding (AB-NWT MOU; Alberta Environment *et al*., 2007) was signed in 2007 between the governments of Alberta (Alberta Environment), the NWT (Environment and Natural Resources) and Canada (AANDC). The AB-NWT MOU provides a framework and outlines the process, schedule, principles and information required to move forward with transboundary water negotiations between Alberta and the NWT. It recognizes that a healthy and sustainable water supply is vital to the long-term prosperity of Alberta and the NWT, and that the residents of these jurisdictions depend on clean water resources to support Aboriginal cultures, growing communities and economic development. The AB-NWT MOU further recognizes existing developments and interests that are critical to the economic well-being of both jurisdictions.

As directed in the AB-NT MOU, work is underway by each jurisdiction to compile existing data and information on the state of key transboundary rivers, such as the Slave River. The results of the present report will help to satisfy specific information needs outlined in the AB-NWT MOU, namely providing current water and sediment quality conditions for the Slave River. Negotiations between Alberta and the NWT are underway.

2.4 Northern Voices, Northern Waters: The NWT Water Stewardship Strategy

Recognizing the importance of protecting the waters of the NWT, the GNWT and AANDC began talks with First Nations and Aboriginal people and governments regarding the development of an NWT Water Stewardship Strategy; a strategy that would be developed by Northerners for Northerners.

Northern Voices, Northern Waters: The NWT Water Stewardship Strategy, (the Strategy), was released in 2010 by the GNWT and AANDC, on behalf of an Aboriginal Steering Committee. The Vision statement, “The waters of the NWT will remain clean, abundant and productive for all time” is at the core of the Strategy’s framework (GNWT and AANDC, 2010). The Strategy states that, as residents of the NWT, we have an obligation to protect and steward our water resources for ourselves, for future generations and for all living things that rely on water. One of the key goals of the Strategy is to ensure that waters that flow into, within or through the NWT, are substantially unaltered in quality, quantity and rates of flow.

The Strategy is intended to inform the development of the various sub-agreements outlined in the Mackenzie River Basin Transboundary Waters Master Agreement. It is designed to improve decision-making processes, information sharing, and communication among all parties or water partners involved in water stewardship in the NWT. In May 2011, the final action plan entitled *NWT Water Stewardship: A Plan for Action 2011-2015* was released (GNWT and AANDC, 2011). It outlines the Strategy's Keys to Success along with defining action items for successful implementation. The results of the present report will help fulfill some of the Keys to Success outlined in the Strategy and, in turn, support transboundary negotiations.

3.0 STUDY AREA

3.1 Introduction

The Slave River Catchment, including the Lower Slave River, Peace River and Athabasca Sub-basins are illustrated in Figure 3.1. Although the specific monitoring locations which are the focus of this report, are located on the transboundary reach of the Slave River itself, information on upstream waters and potential impacts to these rivers is necessary to understand and describe the downstream aquatic environment. A summary of each sub-basin, including location of communities, land uses, contaminant sources, as well as basic physiography, is provided. A brief description of the climate for the Slave River Catchment is also included.

3.2 Basin Characteristics

3.2.1 Lower Slave River Sub-basin

3.2.1.1 Land Use Patterns

The Lower Slave River Sub-basin includes the Slave River and the Slave River Delta. Although the Lower Slave River Sub-basin covers an area of only 15,096 km^2, it draws its flow from a catchment area of 613,000 km^2, which is a land mass of approximately half the size of the NWT. The catchment area includes the Peace River, Athabasca and Lower Slave River Sub-basins (MacLock *et al*., 1997; Figure 3.1). Approximately 66% of the total Slave River Catchment area is located within Alberta, 24% is located within British Columbia, 10% is located in Saskatchewan (part of the Athabasca Sub-basin), and less than 1% (the Lower Slave River Sub-basin) is located within the NWT (Hatfield, 2009). It is important to note that the NWT portion of the Slave River is located downstream of all the other jurisdictions. Thus, the quality of Slave River water and sediment within the NWT is influenced almost entirely by environmental conditions and industrial activities which take place upstream of the NWT. Land uses in the Lower Slave River Sub-basin are predominantly subsistence-based and include traditional hunting and fishing, as well as recreational uses.

With a mean annual discharge of 3400 m^3/s, the Slave River is the largest tributary to Great Slave Lake. It is 434 km long and originates at the confluence of the Peace River (which accounts for 60% of the Slave River's flow) and Rivière des Rochers, which is the primary outlet channel of Lake Athabasca (Figure 3.2 and 3.3; MacLock *et al*., 1997). From the Peace-Athabasca Delta (PAD), the Slave River flows north, serving as the eastern border of Wood Buffalo National Park.

Just south of the NWT border, the Slave River flows past the small Chipewyan community of Fitzgerald (Table 3.1; Figure 3.2). Over the next 24 km, the river drops 35m as it flows through a series of four major rapids: Cassette Rapids, Pelican Rapids, Mountain Rapids, and the Rapids of the Drowned (MRBC 1981; Figure 3.4). The rapids impede river travel and form a natural barrier to the upstream movement of fish (MacLock *et al*., 1997). The rapids are culturally and historically significant, in addition to being a world class white-water paddling and bird-watching destination (Town of Fort Smith, 2012).

Table 3.1: Populations of cities and towns in the Slave River Catchment.

SUB-BASIN	**COMMUNITY (Population Greater than 1000)[1]**	**POPULATION[2]**	**RECEIVING WATER FOR MUNICIPAL WASTEWATER[3]**
Peace	Beaverlodge, AB	2264	Beaverlodge River
Peace	Chetwynd, BC	2633	
Peace	Dawson Creek, BC	10994	
Peace	Fairview, AB	3297	Boucher Creek
Peace	Fort St. John, BC	17402	
Peace	Fox Creek, AB	2278	Iosegun Lake
Peace	Fox Lake, AB	1753	
Peace	Grande Cache, AB	3783	Smoky River
Peace	Grande Prairie, AB	47076	Wapiti River
Peace	Grimshaw, AB	2537	Peace River
Peace	High Level, AB	3887	Bushe River
Peace	Hudson's Hope, BC	1012	
Peace	John D'Or Prairie, AB	1025	
Peace	Mackenzie, BC	4539	
Peace	Manning, AB	1493	Notikewin River
Peace	Peace River, AB	6315	Peace River
Peace	Sexsmith, AB	1959	Kleskum Creek
Peace	Spirit River, AB	1148	Rat Creek
Peace	Sturgeon Lake, AB	1051	
Peace	Taylor, BC	1384	
Peace	Tumbler Ridge, BC	2454	
Peace	Valleyview, AB	1725	Little Smoky River
Peace	Wabasca/Desmarais, AB	2056	North Wabasca Lake

SUB-BASIN	COMMUNITY (Population Greater than 1000)[1]	POPULATION[2]	RECEIVING WATER FOR MUNICIPAL WASTEWATER[3]
Peace	Wembley, AB	1443	Wapiti River
Athabasca	Athabasca, AB	2990	Athabasca River
Athabasca	Barrhead, AB	4432	Pad dle River
Athabasca	Edson, AB	8475	McLeod River
Athabasca	Fort Chipewyan, AB	*1261	Rivière des Rochers
Athabasca	Fort McMurray, AB	*76797	Athabasca River
Athabasca	High Prairie, AB	2600	
Athabasca	Hinton, AB	9640	Athabasca River
Athabasca	Jasper, AB	4265	Athabasca River
Athabasca	Lac La Biche, AB	2758	Field Lake
Athabasca	Mayerthorpe, AB	1474	Paddle River
Athabasca	Slave Lake, AB	6703	Lesser Slave River
Athabasca	Swan Hills, AB	1645	Athabasca River
Athabasca	Westlock, AB	5008	Pembina River
Athabasca	Whitecourt, AB	8971	Athabasca River
Slave	Fitzgerald, AB[1]	*8	Slave River
Slave	Fort Resolution, NT	474	Slave River
Slave	Fort Smith, NT	2093	Slave River
Slave	Salt River	292[4]	

[1] All communities in the Lower Slave River Sub-basin have been included, even though some are less than 1000.

[2] Population figures from Statistics Canada's 2011 census (Statistics Canada, 2012), unless otherwise noted.

[3] Receiving water information from Hatfield (2009) report, unless otherwise noted.

[4] Population figures are from the Government of Canada, Aboriginal Canada Portal (Govt of Canada, 2004)

*Population figures are from the Regional Municipality of Wood Buffalo (RMWB) 2010 census (RMWB, 2010).

The Slave River crosses into the NWT upstream of the Rapids of the Drowned near Fort Smith (Figure 3.4). Although there is no industrial development in the Lower Slave River Sub-basin, the town of Fort Smith does continually discharge treated municipal wastewater into the Slave River (MVLWB Public Registry, 2012). From Fort Smith, the river flows approximately 320 km north to Great Slave Lake and is joined by the Salt River about 30 km downstream of the NWT-Alberta border (Figure 3.2). This lower reach of the Slave River has a gentle gradient, dropping about 10.7 m over 250 km (MRBC, 1981). This reach was a former estuary of Great Slave Lake, which was filled in by the river sediment that is actively building up the Slave River Delta (MRBC, 1981). The delta lies on the southeast portion of Great Slave Lake immediately northeast of Fort Resolution and covers an area of 640 km^2 (Figure 3.2). The wedge-shaped active portion of the delta covers an area of approximately 75 km^2 and consists of four major channels. It extends for 20 km along the south shore of Great Slave Lake and it is 10 km to the head of the delta in the south. Like all delta ecosystems, it depends on the continued deposition of fresh sediment and periodic flooding to maintain its biological productivity (MRBC, 1981). The delta provides essential habitat for numerous species of mammals, fish and waterfowl. It is situated on three major flyways and is an important staging and breeding area for many species of birds (MacLock *et al*., 1997).

3.2.1.2 Physiography/Geology

The Slave River straddles two physiographic regions: the erosion-resistant Precambrian Shield to the east and the Interior Plains to the west (MRBB, 2004). Although the west bank is comprised primarily of Interior Plain sediments, there are numerous outcrops of Precambrian Shield rocks. The rapids in the middle reach of the river are caused by spurs of the shield crossing the river in an east-west direction (MRBC, 1981). Exposed bedrock can be found along the river in addition to alluvial islands, abandoned channels and oxbow lakes (Culp *et al*., 2005). The shield portion of the basin exhibits rolling terrain and is characterized by open, stunted taiga forest, lakes, black spruce and peatland (MRBB, 2004; Prowse and Conly, 1996). The bedrock is predominantly Precambrian granites, gneisses, and metasedimentary rocks (Alberta Environment, 1987).

The Interior Plains portion of the basin is mainly forested with aspen and white spruce. Sedge-grass meadow and shrubs are found along the river channels and in the Slave River Delta, while grasslands are found in the drier areas (Prowse and Conly, 1996). In the south-west portion of the plains, which includes the Salt River catchment, gypsum deposits are overlain by resistant Devonian carbonate rocks. The existence of Karst topography in this area contributes to increased concentrations of sodium and chloride in the Slave River (MacLock *et al*., 1997; Alberta Environment, 1987).

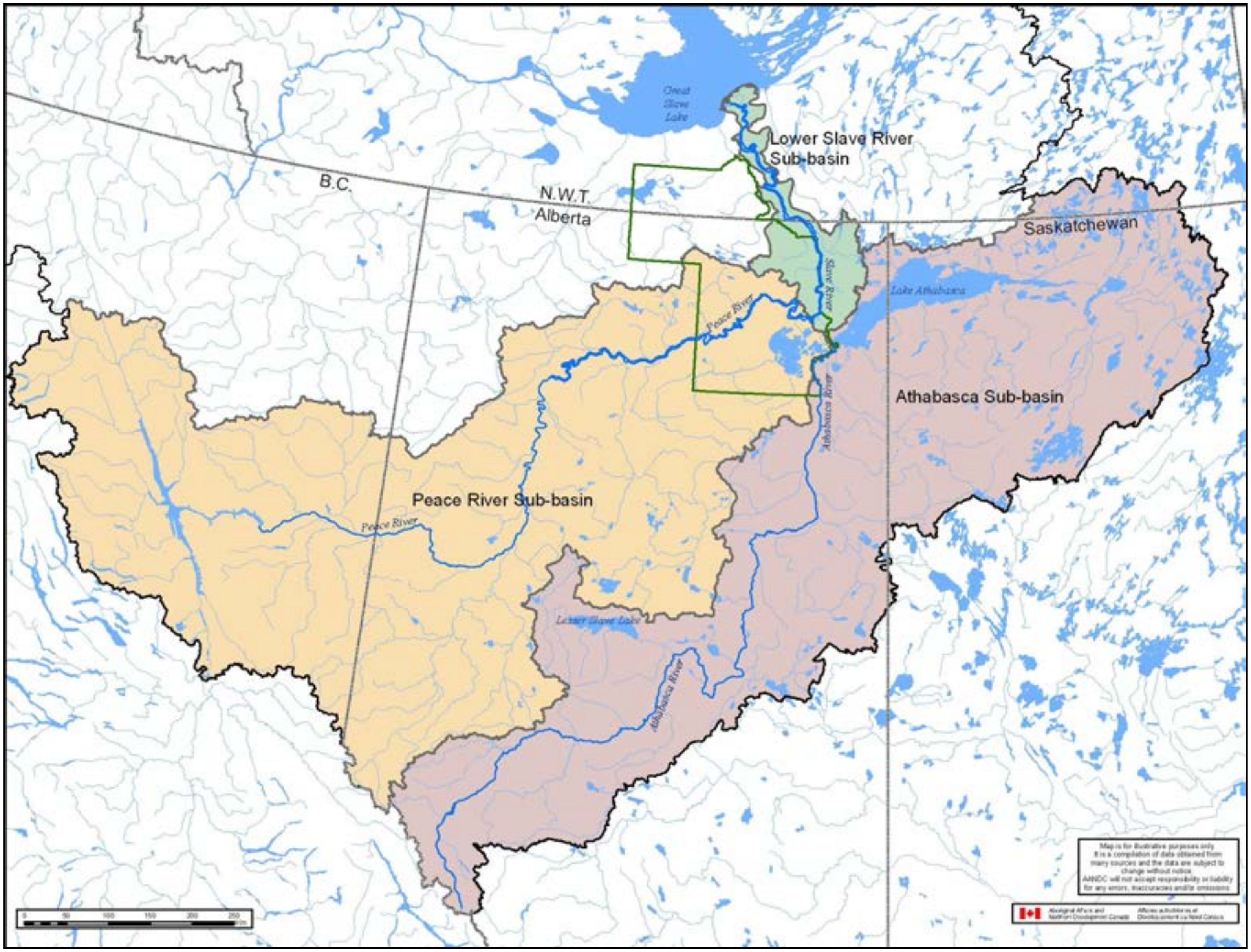


Figure 3.1: The Slave River Catchment including the Lower Slave River, Peace River and Athabasca Sub-basins.

Base map sources: see References.

Map is for illustrative purposes only.
It is a compilation of data obtained from
many sources and the data are subject to
change without notice.
AANDC will not accept responsibility or liability
for any errors, inaccuracies and/or omissions.

Figure 3.2: The Lower Slave River Sub-basin.

Base map sources: see References.

Figure 3.3: The Peace-Athabasca Delta (PAD). The Slave River is formed by the confluence of the Peace River and the Rivière des Rochers, the primary outlet of the Peace-Athabasca Delta. Adapted from MRBC, 1981.
Base map sources: see References.

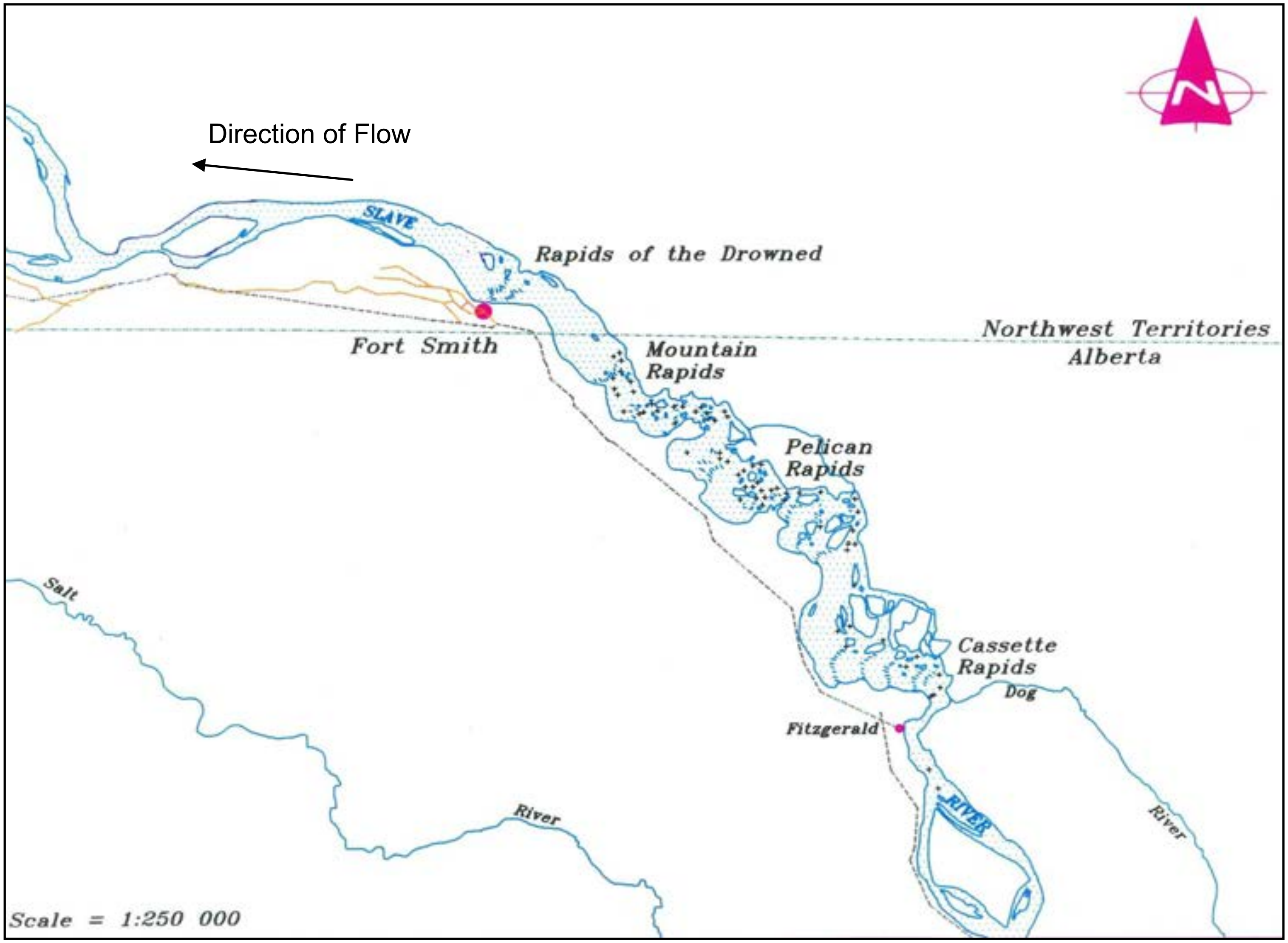


Figure 3.4: The Slave River from Fitzgerald, Alberta to Fort Smith, Northwest Territories.
Adapted from Sanderson *et al.*, 1997.

3.2.2 Peace River Sub-basin

3.2.2.1 Land Use Patterns

The Peace River Sub-basin drains much of northeastern British Columbia and northern Alberta, covering an area of 326,000 km^2 and representing over 50 percent of the Slave River Catchment (Figures 3.1 and 3.5). The Peace River originates in the Rocky Mountains and flows over 2000 km to its confluence with Rivière des Rochers in Alberta's Peace-Athabasca Delta. Development in the Peace River Sub-basin is varied, with a combination of hydroelectric facilities, pulp and paper mills, coal mines, coal-fired power plants, oil and gas activities and oil sands operations (MacLock *et al*., 1997; Tables 3.2 and 3.3; Figures 3.5 and 3.6).

The tributaries which make up the river's headwaters flow from the mountains into Williston Lake reservoir, which was formed by the construction of the W.A.C. Bennett Dam, near the town of Hudson's Hope, British Columbia. The completion of the dam in 1968 resulted in the flooding of the Finley and Parsnip River valleys, forming the Williston Lake reservoir in four years (MacLock *et al*., 1997). There are three pulp mills located in the general area of the reservoir: the Paper Excellence and Conifex Timber Incorporated Mills are located in the town of Mackenzie and have licences to discharge effluent into Williston Lake (Paper Excellence, 2011; Conifex, 2012; Glozier *et al*., 2009) (Table 3.3; Figure 3.5). The Tembec Chetwynd Pulp Mill, which is located east of Chetwynd, does not release effluent into Williston Lake (Glozier *et al*., 2009; MacLock *et al*., 1997).

The Peace River flows eastward from the Bennett Dam through rapids and gorges, and passes through the Peace Canyon Dam, which was completed in 1980 (MRBC, 1981). The river then flows through the proposed location of the Site C dam upstream of Fort St. John (BC Hydro, 2012; Table 3.2; Figure 3.5). The city of Fort St. John, like other communities along the river, releases treated municipal wastewater into the Peace River (Table 3.1). Flowing east, the river is joined by the Pine River near the town of Taylor, the location of the Canfor Forest Products Limited pulp mill, which is licensed to release effluent into the Peace River (Glozier *et al*., 2009; MacLock *et al*., 1997; Tables 3.1 and 3.3).

Table 3.2: Current and Proposed Hydroelectric Operations in the Peace River Sub-basin.

NAME	**LOCATION**	**RESERVOIR FOOTPRINT (hectares)**	**CAPACITY (MW)**	**AVERAGE GWh PER YEAR**	**STATUS**
Bennett Dam[1]	Hudson's Hope, BC	177000	2730	14179	built 1968
Peace Canyon Dam[1]	Hudson's Hope, BC	890	694	3263	built 1980
Proposed Site C Dam[1]	Fort St John, BC	9310	900	4600	EIA stage
Proposed Dunvegan Dam[2]	Fairview, AB	2000	100	600	EIA completed, geotechnical development phase

Sources: [1]BC Hydro, 2012; [2]Transalta, 2011.

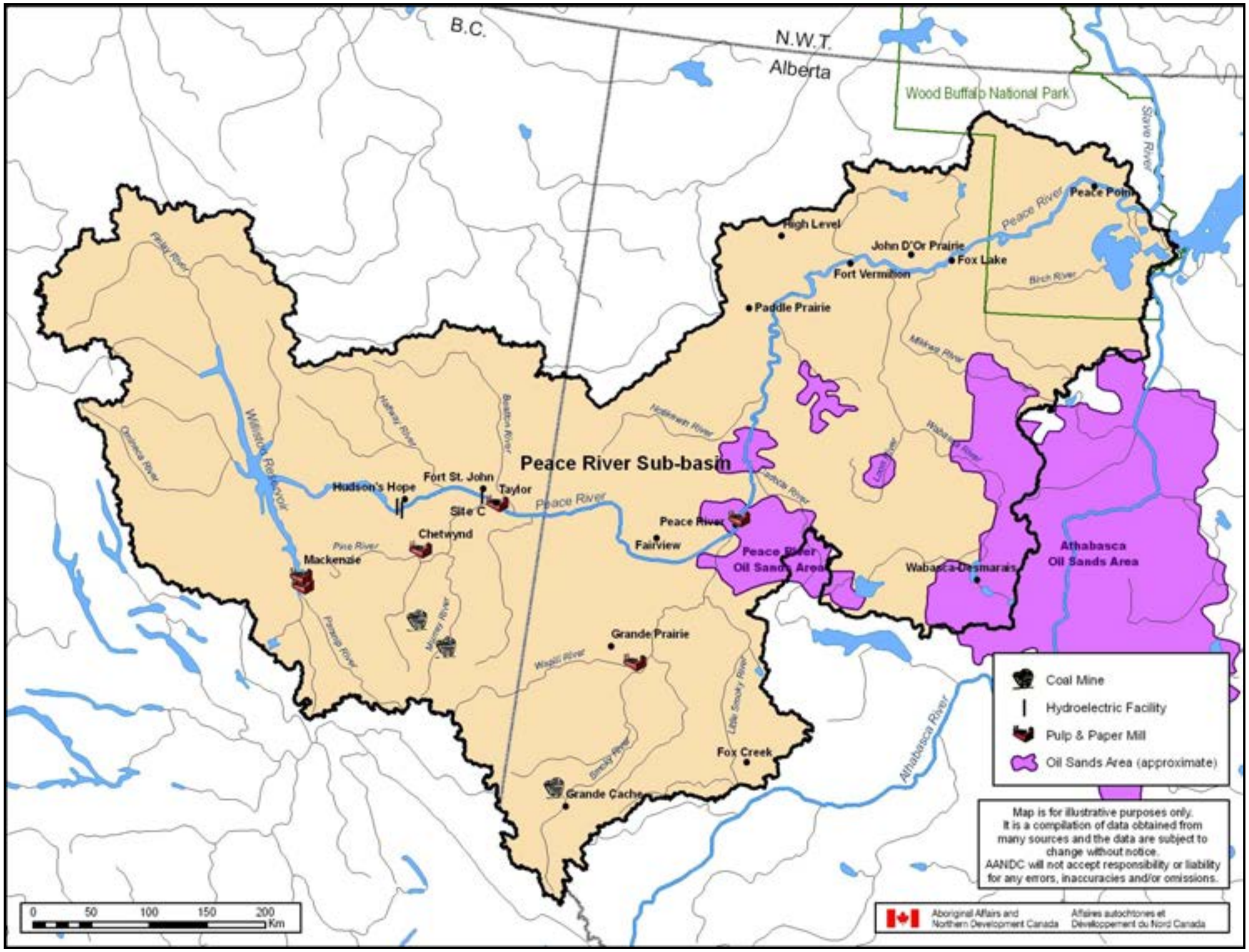


Figure 3.5: Current activities in the Peace River Sub-basin (Note: specific oil sands operations in the Peace River area are illustrated in Figure 3.6). Base map sources: see References.

Table 3.3: List of Pulp and Paper Operations, Power Plants and Coal Mines within the Slave River Catchment.

SUB-BASIN	COMPANY NAME	RECEIVING WATER	LOCATION (TOWN)	START UP (YEAR)	PRODUCT
Peace	Paper Excellence at Mackenzie [1]	Williston Lake	Mackenzie, BC	1972	Bleached Kraft Pulp
Peace	Conifex Timber Inc / Mackenzie Sawmill[1]	Williston Lake	Mackenzie, BC	1969	Saw mill
Peace	Tembec / Chetwynd Pulp[1]	N/A	Chetwynd, BC	1991	Bleached chemi-thermomechanical pulp
Peace	Canfor Corporation / Taylor Pulp[1]	Peace River	Taylor, BC	1988	Bleached chemi-thermomechanical pulp
Peace	Maxim Power Corp / H.R. Milner Station[1]	Smoky River	Grande Cache, AB	1972	Coal-fired power plant
Peace	Maxim Power Corp / H.R. Milner Expansion Project	Smoky River	Grande Cache, AB	completion 2015	Coal-fired power plant
Peace	Grande Cache Coal Corporation / Smoky River Mine	Smoky River	Grande Cache, AB	Pit No.7 (2004) Pit No.8 (2010*)	Coal mine
Peace	Weyerhaeuser Canada / Grande Prairie Operations	Wapiti River	Grande Prairie, AB	1973	Bleached Kraft Pulp
Peace	Daishowa-Marubeni / Peace River Pulp Mill	Peace River	Peace River, AB	1990	Bleached Kraft Pulp
Athabasca	Sherritt / Obed Mountain Mine	Athabasca River	Hinton, AB	1984-2003; reopened 2009	Coal mine
Athabasca	Teck / Cardinal River Mine	McLeod River	Hinton, AB	opened 1970; new pit 2005	Coal mine
Athabasca	Sherritt / Gregg River Mine	McLeod River	Hinton, AB	1983-2000; inactive	Coal mine
Athabasca	West Fraser Timber Co. Ltd / Hinton Pulp[1]	Athabasca River	Hinton, AB	1957	Bleached Kraft Pulp
Athabasca	Sherritt / Coal Valley Mine	Pembina River	Edson, AB (near)	1978 plus some expansions	Coal mine
Athabasca	Alberta Newsprint Co. Ltd.	Athabasca River	Whitecourt, AB	1990	Thermomechanical pulp, de-inked paper

SUB-BASIN	COMPANY NAME	RECEIVING WATER	LOCATION (TOWN)	START UP (YEAR)	PRODUCT
Athabasca	Millar Western Forest Products Ltd.	Athabasca River	Whitecourt, AB	1988	Bleached chemi-thermomechanical pulp
Athabasca	Whitecourt Power / Thermal Electric Power Plant	Athabasca River	Whitecourt, AB	1994	Power co-generation
Athabasca	West Fraser Timber Co. Ltd / Slave Lake Pulp	Lesser Slave River	Slave Lake, AB	1991	Bleached chemi-thermomechanical pulp
Athabasca	Alberta Pacific (Al-Pac) Forest Industries Inc.	Athabasca River	Boyle, AB	1993	Bleached Kraft Pulpmill

Sources: Hatfield (2009); Glozier (2009); Company websites (see Reference List)

[1] Previous names of some companies are as follows: Paper Excellence was Pope and Talbot Mackenzie or Fletcher Challenge; Conifex Timber Inc Mackenzie was Abitibi Bowater or Finlay Forest; Tembec Chetwynd was Louisiana-Pacific; Canfor Corporation Taylor was Fibreco; Maxim Power Corp Grande Cache was Atco Power; West Fraser Timber Co. Ltd Hinton was Weldwood of Canada.

[2] BC mills effluent release type is from the Reach For Unbleached Foundation (rfu.org).

[*] Smoky River Coal Fields have been mined since the 1960s. There are currently 2 open mines (Grand Cache Coal, 2012)

Note: most coal mines have more than one pit, both open pit and underground.

As the river flows towards Alberta, the topography changes from montane forest to prairie parkland (Glozier *et al.*, 2009). The Peace River agricultural region contains half the cultivated crop land of British Columbia, as well as commercial cattle, bison, elk and sheep farms and produces 30% of Canada’s honey (MacLock *et al.*, 1997). At kilometre 160, the Peace River crosses the British Columbia/Alberta border into Alberta’s northern Peace River agricultural region, which stretches from Grande Prairie in the south to Fort Vermilion in the north (MacLock *et al.*, 1997; Figure 3.5). Gently rolling plains are made up of fields (cereal grains, oilseeds and forage crops) and forests (aspen and balsam poplar interspersed with white spruce and jack pine). The fine soils and agricultural development in this area make it particularly prone to erosion (MacLock *et al.*, 1997).

The Peace River flows south of the agricultural town of Fairview, past the canyon-like reach which is the proposed site of the Dunvegan run-of-the-river hydroelectric project (Transalta, 2011; Table 3.2). It is then joined by the Smoky River, which drains a catchment area of 50,000 km^2, and is developed extensively with forestry, agricultural, pulp and paper, coal, and oil and gas activities (MacLock *et al.*, 1997; Figure 3.5). The Smoky River flows past Grand Cache, home of both a surface and underground coal mine (Grand Cache Coal, 2012). One of the largest producing conventional oil and gas fields in Canada is located at Fox Creek on the Little Smoky River, a tributary of the Smoky River (MacLock *et al.*, 1997). The Smoky River is fed by the Wapiti River, which flows past Grande Prairie and receives effluent from the Weyerhaeuser Canada pulp mill and the Elmworth oil and gas field (Hatfield, 2009; MacLock *et al.*, 1997).

Downstream of the confluence of the Smoky River, the Peace River flows northward, passing the town of Peace River and the Daishowa-Marubeni pulp mill, both of which release effluent to the river (Glozier *et al*., 2009). Here, the river is joined by the Cadotte River, which drains an area underlain by the Peace River oil sands deposit (Figures 3.5 and 3.6). The Peace River oil sands area constitutes the most significant petroleum deposit in the region (Shaw *et al*., 1990). As the river passes the community of Paddle Prairie, it turns east again and flows past Fort Vermilion where it is joined by the Wabasca River. As the river flows through the Vermilion Chutes rapids, it drops 3.5 m, posing a major obstacle for transportation and fish movements. The river passes the Jean D'Or Prairie and Fox Lake reserves before entering a UNESCO World Heritage Site and Canada's largest national park, Wood Buffalo National Park. It then takes on a meandering pattern at Peace Point before joining with the Rivière des Rochers, the primary outlet channel of Lake Athabasca, to form the Slave River (MacLock *et al*., 1997; Figure 3.3).

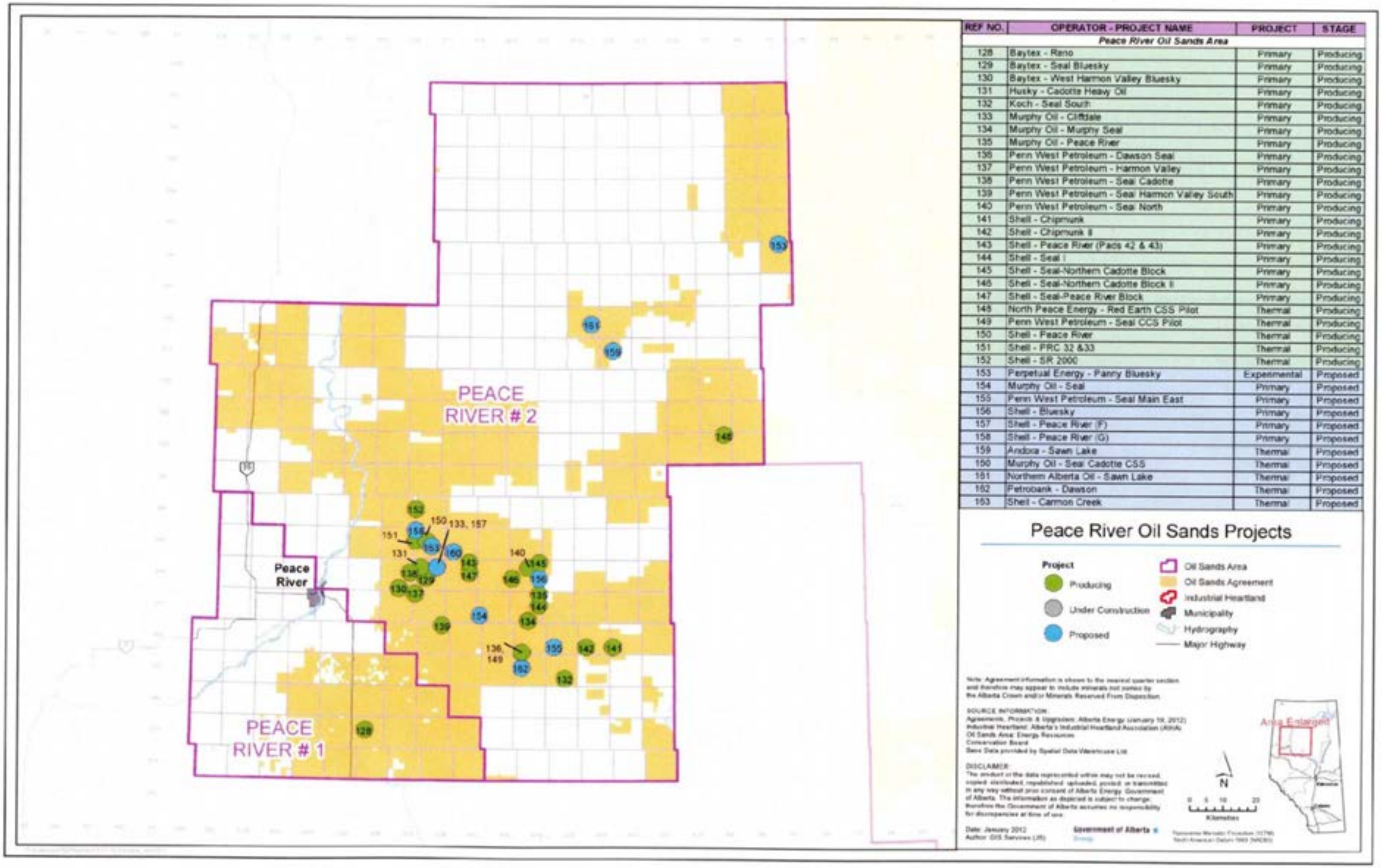
3.2.2.2 Physiography/Geology

The Peace River flows primarily through two main physiographic regions, the Western Cordillera and the Interior Plains (MacLock *et al.*, 1997). The Western Cordillera covers much of the southwestern portion of the basin, including the Rocky Mountains, and is composed of sedimentary rocks with deep valleys and high plateaus covered by glacial tills (Prowse and Conly, 1996). The Peace River's headwaters in British Columbia are within the Western Cordilleran region.

The Peace River also flows through the Interior Plains, which are relatively flat and vast expanses of sedimentary bedrock, limestone and shale overlain with till. The reach from the Peace Canyon Dam to the Town of Peace River has few tributaries, relatively clear water, high dissolved oxygen and low nutrients, organic matter, metals and salts. The river cuts more than 200 m into the Alberta Plateau, often creating unstable walls which are prone to slumping and mass movements. The river bed and bank are composed primarily of gravel over bedrock (MacLock *et al*., 1997).

From the town of Peace River to Fort Vermilion, the river's incision into the plain decreases from 200 m to 30 m, thus creating more stability along the valley walls. The river bed materials are mainly sand and fine gravel, with silt and bedrock along the banks (Kellerhals *et al.*, 1972). In this stretch of the river, the concentrations of most water quality parameters increase due to the contributions from tributaries (Shaw *et al*., 1990).

The river changes past Fort Vermilion, cutting into the bedrock, and resulting in the Vermilion chutes, waterfalls and rapids. Downstream of these features, the river is 1500 m wide with split channels and island complexes but eventually narrows to 700 m at Peace Point and takes on a meandering pattern (Kellerhals *et al.*, 1972; Prowse and Conly, 1996). River bed and bank change from gravel to sand and silt in this reach of the river, resulting in higher concentrations of suspended particles and those compounds associated with clay particles such as metals (Prowse and Conly, 1996).



REF NO.	OPERATOR - PROJECT NAME	PROJECT	STAGE
	Peace River Oil Sands Area		
128	Baytex - Reno	Primary	Producing
129	Baytex - Seal Bluesky	Primary	Producing
130	Baytex - West Harmon Valley Bluesky	Primary	Producing
131	Husky - Cadotte Heavy Oil	Primary	Producing
132	Koch - Seal South	Primary	Producing
133	Murphy Oil - Cliffdale	Primary	Producing
134	Murphy Oil - Murphy Seal	Primary	Producing
135	Murphy Oil - Peace River	Primary	Producing
136	Penn West Petroleum - Dawson Seal	Primary	Producing
137	Penn West Petroleum - Harmon Valley	Primary	Producing
138	Penn West Petroleum - Seal Cadotte	Primary	Producing
139	Penn West Petroleum - Seal Harmon Valley South	Primary	Producing
140	Penn West Petroleum - Seal North	Primary	Producing
141	Shell - Chipmunk	Primary	Producing
142	Shell - Chipmunk II	Primary	Producing
143	Shell - Peace River (Pads 42 & 43)	Primary	Producing
144	Shell - Seal I	Primary	Producing
145	Shell - Seal-Northern Cadotte Block	Primary	Producing
146	Shell - Seal-Northern Cadotte Block II	Primary	Producing
147	Shell - Seal-Peace River Block	Primary	Producing
148	North Peace Energy - Red Earth CSS Pilot	Thermal	Producing
149	Penn West Petroleum - Seal CCS Pilot	Thermal	Producing
150	Shell - Peace River	Thermal	Producing
151	Shell - PRC 32 &33	Thermal	Producing
152	Shell - SR 2000	Thermal	Producing
153	Perpetual Energy - Panny Bluesky	Experimental	Proposed
154	Murphy Oil - Seal	Primary	Proposed
155	Penn West Petroleum - Seal Main East	Primary	Proposed
156	Shell - Bluesky	Primary	Proposed
157	Shell - Peace River (F)	Primary	Proposed
158	Shell - Peace River (G)	Primary	Proposed
159	Andora - Sawn Lake	Thermal	Proposed
160	Murphy Oil - Seal Cadotte CSS	Thermal	Proposed
161	Northern Alberta Oil - Sawn Lake	Thermal	Proposed
162	Petrobank - Dawson	Thermal	Proposed
163	Shell - Carmon Creek	Thermal	Proposed

Figure 3.6: Peace River Oil Sands Projects (used with permission from the Government of Alberta).
Source: Government of Alberta, 2012d.

3.2.3 Athabasca Sub-basin

3.2.3.1 Land Use Patterns

The Athabasca Sub-basin drains a large portion of central Alberta and northwestern Saskatchewan, covering an area of 269,000 km^2 and includes drainage for both the Athabasca River and Lake Athabasca (MRBB, 2004). The Athabasca River is one of the longest unregulated rivers in the prairies, originating in the Rocky Mountains' Columbia Icefield in Jasper National Park, and flowing 1,538 km to Lake Athabasca in northern Alberta (Figure 3.7; Glozier *et al.*, 2009). The 168 km long reach of the river which lies within Jasper National Park has been designated as a Canadian Heritage River. Here, the silt-laden river flows swiftly through the mountains, sometimes through narrow, confined channels, with gorges, rapids and waterfalls. At other times, wide, open, braided river channels with alluvial flats more than 1 km wide are common (Canadian Heritage Rivers System, 2011; Swainson, 2009). The water at this point is hard and alkaline with a silty grey color due to the finely ground particles of rock in the water formed by glacial action (Noton and Saffran, 1995).

As the Athabasca River leaves Jasper National Park, it travels through the foothills region, home to some of western Canada's largest active open-pit coal mines (Figure 3.7). The Athabasca River flows through Hinton, where the West Fraser pulp mill is located, and Whitecourt, home to the Alberta Newsprint and Millar Western pulp mills (MacLock *et al.,* 1997; Glozier *et al.*, 2009). These communities and pulp mills have licences to discharge effluent to the river (Tables 3.1 and 3.3). The Whitecourt Thermal Electric Power Plant also discharges process water to the river (Hatfield, 2009). The Athabasca River is then joined by the McLeod River, which drains areas with open-pit coal mines and limestone quarries to the south. Oil and natural gas deposits are found in the Swan Hills to Fox Creek regions, north of the Athabasca River (Figure 3.7). The nearby Swan Hills Hazardous Waste Treatment Centre, the only facility of its kind in Canada, handles and processes a variety of hazardous wastes (Swan Hills Treatment Centre, 2011).

From Swan Hills, the Athabasca River flows north and is joined by the Pembina River, draining agricultural lands to the south (MacLock *et al.*, 1997). Agricultural development in the Athabasca Sub-basin is concentrated around the communities of Mayerthorpe, Barrhead, Westlock, Athabasca and Lac La Biche, with both crop (canola, wheat, oats and peas) and livestock production important in this region (MacLock *et al.*, 1997; Table 3.1). Downstream, the Athabasca is joined by the Lesser Slave River, the site of the Slave Lake pulp mill. The river flows south past the town of Athabasca, and then north past the Alberta Pacific Forest Industries pulp mill. Both of these mills and the town are licensed to release effluents to the river (Glozier *et al.*, 2009; Tables 3.1 & 3.3). Continuing north, the river is joined by the La Biche River, which drains regions known for agricultural, forestry, and oil and natural gas developments. The river continues northward through a series of rapids, which serve as a barrier to river travel and a major spawning area for fish. The river's dissolved oxygen levels are also replenished in this area (MacLock *et al*., 1997).

Beyond the rapids, the river flows past the city of Fort McMurray and is joined by its largest tributary, the Clearwater River, flowing from Saskatchewan (Figure 3.7). The Christina River, the major tributary to the Clearwater, drains an area with extensive oil and gas development (MacLock *et al*., 1997). The boreal forest region north of Fort McMurray is the location of a number of producing and proposed Athabasca oil sands developments (Figure 3.8). As of 2012, there were 19 producing oil sands projects within the Athabasca River basin (Government of Alberta, 2012b). In addition there were 63 potential projects listed, with 27 of these having start dates ranging from 2010-2017 (Government of Alberta, 2012c). Crude bitumen production in the area is expected to increase from 1.6 million barrels per day in 2010 to 3.5 million barrels per day in 2020 (Government of Alberta, 2012a). Current technology requires between two and four barrels of water for each barrel of oil produced, and most of this water is withdrawn from the Athabasca River (Swainson, 2009).

As the Athabasca River flows north, it next passes by the community of Fort MacKay before it becomes the eastern border of Wood Buffalo National Park and is joined by the Richardson River (MacLock *et al*., 1997). The Athabasca River then flows through the Peace-Athabasca Delta via several distributary channels, including the Embarras River, (Figure 3.3) and into Lake Athabasca just south of the community of Fort Chipewyan. The delta is a patchwork of marshes, lakes, mudflats, sedge meadows, willow and shrub thickets and forests and supports a diverse mixture of animal and birds species. All of the four major North American flyways converge on the Peace-Athabasca Delta.

The catchment area for Lake Athabasca is primarily located in Saskatchewan, which is also home to several uranium mines (Glozier *et al*., 2009; Figures 3.7 and 4.1). Lake Athabasca has two major tributaries in Saskatchewan, the Cree and Fond du Lac rivers, plus numerous smaller tributaries, including William and McFarlane rivers flowing in from the south, and the Grease River and Charlot River (with the Tazin diversion) flowing in from the north. Lake Athabasca discharges through three channels, Chenal des Quatre Fourches, Rivière des Rochers and Revillon Coupe, in the Peace-Athabasca Delta (MRBC, 1981; Figure 3.3).

It is important to note that the water, wildlife and fisheries resources produced in the Athabasca Sub-basin are used to support the traditional culture and subsistence lifestyle (hunting, trapping and fishing) of the residents of Fort MacKay and Fort Chipewyan, along with the other downstream communities in the Mackenzie River Basin. Commercial and recreational fisheries are supported in Lake Athabasca.

3.2.3.2 Physiography/Geology

Three main physiographic regions make up the Athabasca Sub-basin. The Athabasca River headwaters are in the Western Cordillera, which includes glaciers, alpine meadows and mountain forests (MRBB, 2004). Here, the river is shallow, steep and fast-flowing with a gravel/cobble substrate and the landscape changes from alpine to subalpine to montane. The water in this section of the river is high in calcium bicarbonate and suspended solids and low in organic carbon due to the sedimentary bedrock in the region (MacLock *et al.,* 1997).

The largest portion of the basin lies on the Interior Plains, which is characterized primarily by boreal forest and muskeg. The boreal forest is dominated by spruce, aspen and poplar (MacLock *et al*., 1997). Tributaries draining areas of boreal forest contribute both organic carbon and colour to the river as it flows northeast (Noton and Saffran, 1995). In this reach of the river, the slope and velocity decrease and the substrate is dominated by sands and silts (Glozier *et al.*, 2009). The water is coloured brown, due to soils and other materials it has picked up along its course (MacLock *et al.*, 1997).

To the northeast, near the confluence with the Peace River, and in the Saskatchewan region, the Athabasca Sub-basin lies within the Precambrian Shield region (MacLock *et al.*, 1997).

3.3 Climate of the Slave River Catchment

Given the vast area of the Slave River Catchment, temperature and precipitation amounts vary widely based on latitude and elevation. The climate of the Slave River Catchment is characterized as having warm continental temperate summers and cold to extreme cold continental temperate winters. January mean air temperatures vary from -10 to -29°C, whereas July temperatures throughout the catchment average between 10 and 23°C (Environment Canada, 2012).

The area spans several permafrost zones, which have conditions ranging from no permafrost to discontinuous permafrost. Precipitation in the region is generally low and decreases toward the northern portion of the catchment (Alberta Environment, 1987).

Since potential annual evaporation and transpiration exceed precipitation, the area is considered semi-arid. Snowfall is particularly important in the area, as peak flows in the rivers are associated with spring snowmelt (MacLock *et al.*, 1997). While the length of the frost-free period can be a limiting factor to agricultural activity in the basin, it also has a high number of daylight hours during the growing season. Spring break-up in the Slave River Catchment starts in the south and progresses slowly north (MacLock *et al.*, 1997). It is important to note that in recent years, residents within the catchment have reported warmer temperatures, thinner ice, freezing occurring later than usual and melting that is occurring earlier than usual (MRBB, 2003; AANDC and GNWT ENR, 2012).

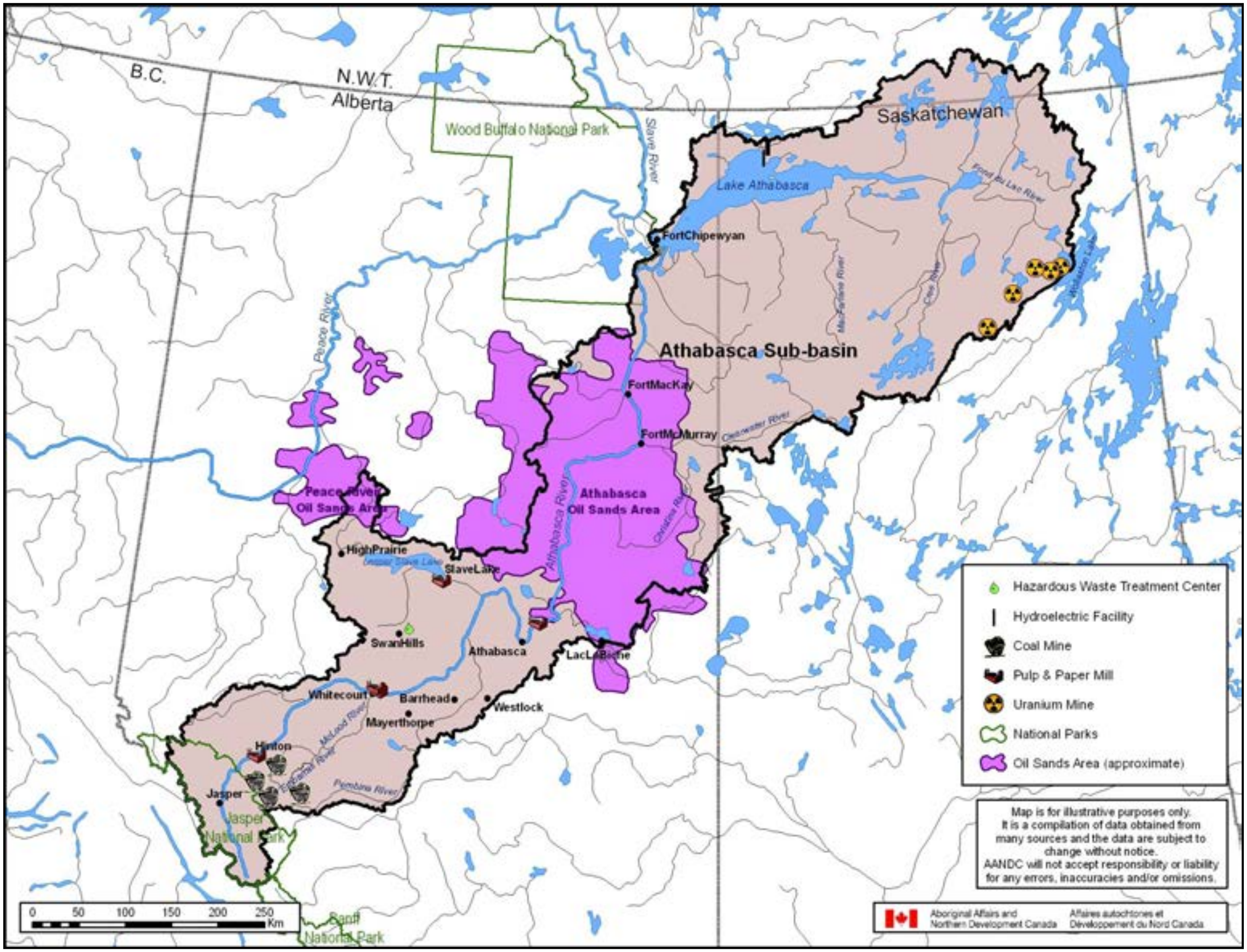


Figure 3.7: Current activities in the Athabasca River Sub-basin (Note: specific oil sands operations in the Athabasca region are shown in Figure 3.8). Base map sources: see References.

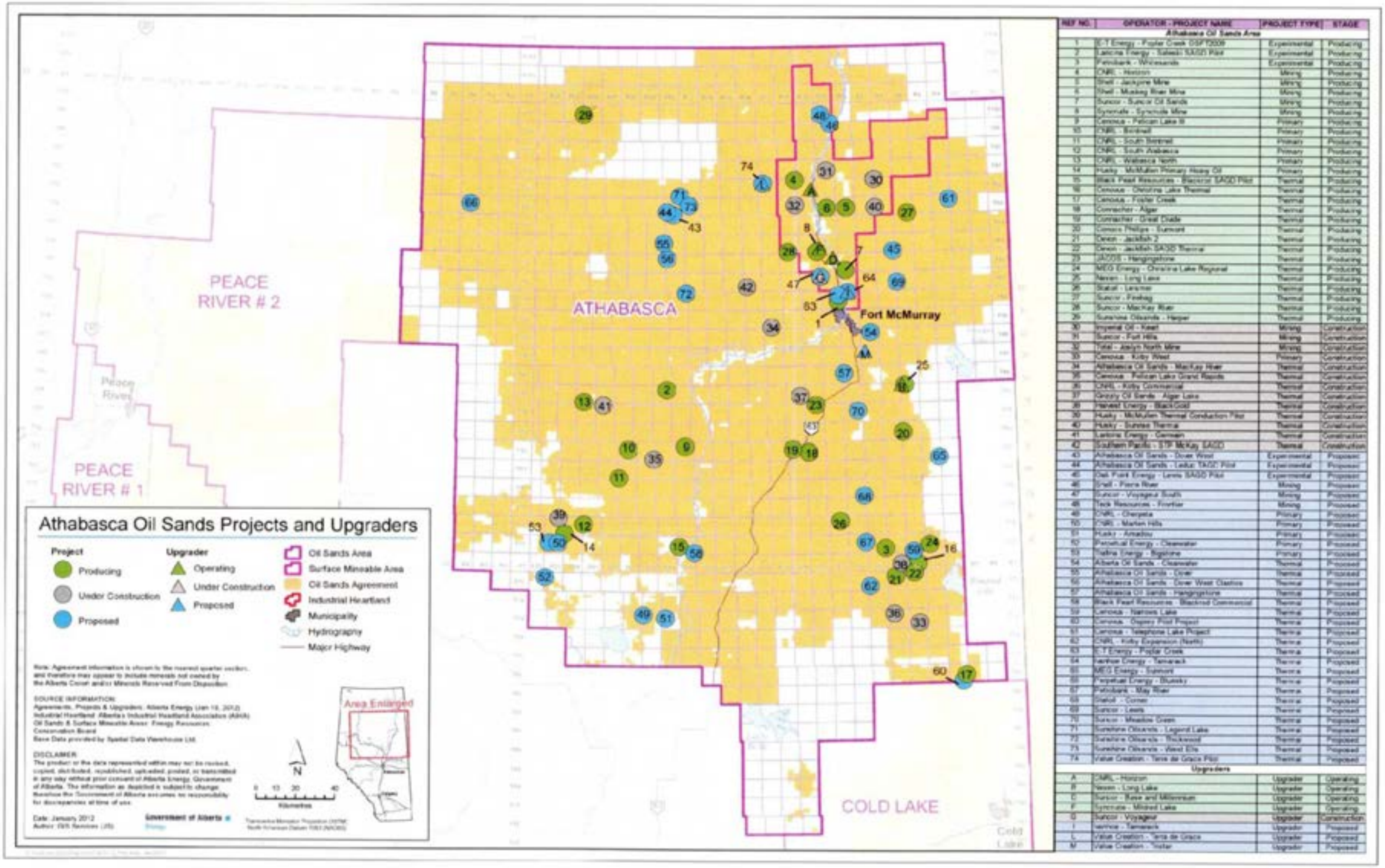


Figure 3.8: Athabasca River Oil Sands Projects (used with permission from the Government of Alberta).
Source: Government of Alberta, 2012d.

4.0 COMPOUNDS OF POTENTIAL CONCERN

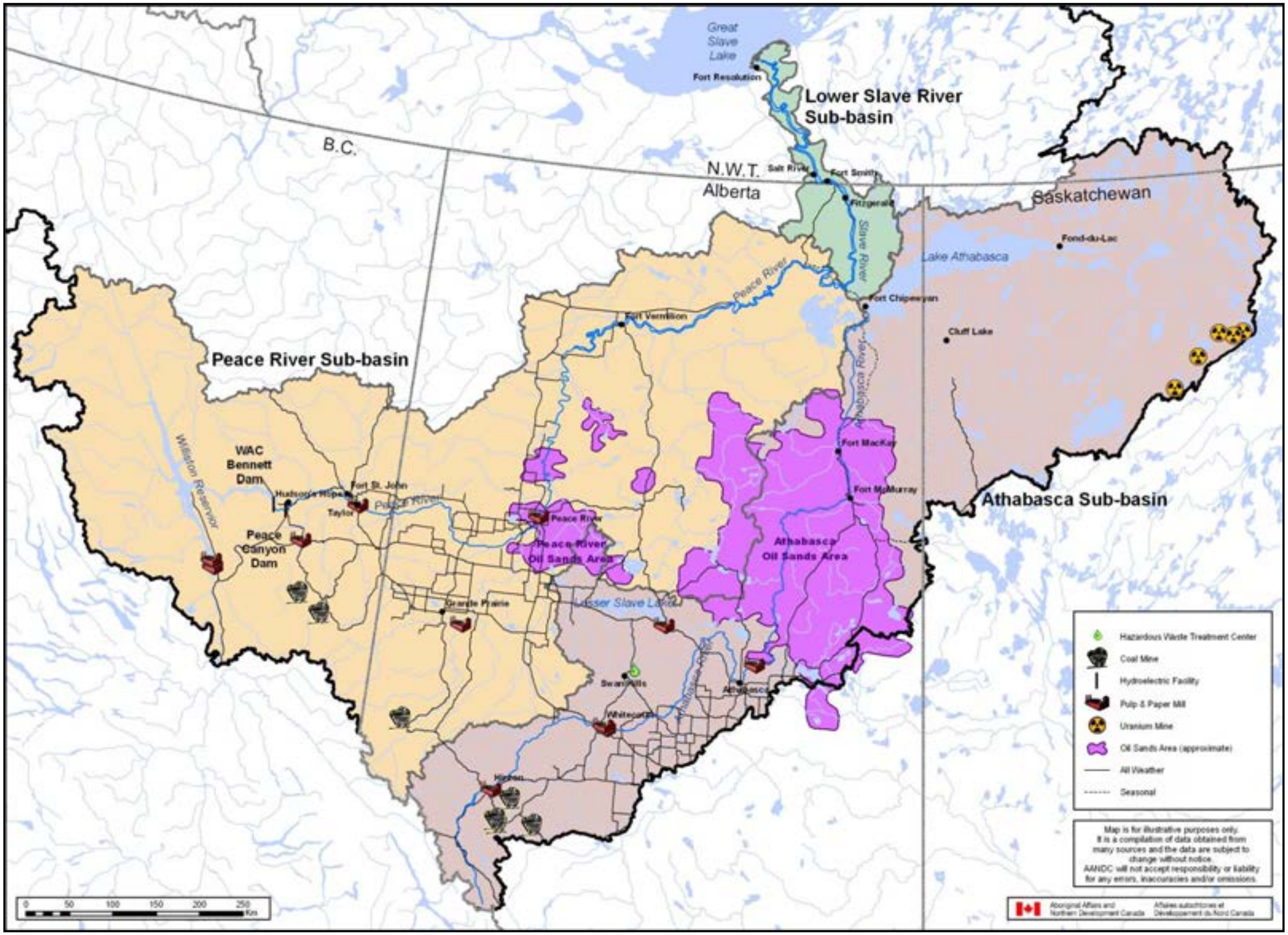
4.1 Introduction

There are various developments and activities located within the Slave River Catchment, including oil sands developments, pulp and paper mills, mining operations, municipal activities, as well as conventional oil and gas development, forestry, agriculture, power generation and transportation corridors (Figure 4.1). Such developments are all potential sources of compounds of potential concern (COPCs) to the Slave River, which may result in physical changes to the water. COPCs are divided into groups based on their chemical class (i.e., nutrients, metals, organics, etc.) and their fate once they enter the environment. Examples of physical change include changes in the water level or temperature and/or changes in pH.

Riverine systems, such as the Peace, Athabasca and Slave rivers, play a very important role in both transporting and modifying the nature of COPCs (MacLock *et al*., 1997). The land surrounding these rivers can often contain diffuse, non-point-sources of COPCs, originating from agricultural and/or municipal activities (NRBS, 1999; NREI, 2004). During the spring melt, these COPCs may be transported from the land to the river environment. Other COPCs can be directly discharged to the aquatic environment from discharges of municipal or industrial wastewater. There are also COPCs, such as certain metals, which enter the aquatic environment naturally as a result of erosion and weathering of geologic formations with significant mineralization (Environment Canada, 2010c). However, some anthropogenic processes, such as land clearing for agriculture or removal of overburden for industrial development, can release these naturally occurring metals, but at elevated levels. In addition, COPCs can enter the river systems via atmospheric deposition, either locally from developments within the Slave River Catchment (Hazewinkel *et al*., 2008; Kelly *et al*., 2009) or through long-range transport from regions elsewhere in Canada and the world (Barrie *et al*., 1992; MacDonald *et. al*., 2000; MacLock *et al*., 1997).

The ultimate fate of COPCs released to the environment is determined by a variety of physical, chemical and biological processes (Environment Canada, 2010d). COPCs may be transported great distances from their source or may be localized. They can be transformed both in concentration and chemical structure within the aquatic environment.

This chapter provides a short description of bioaccumulative COPCs (those that accumulate in the tissue of organisms) and COPCs that partition into sediment, soil and water. Further, a summary of the potential physical changes and COPCs associated with each type of development existing within the Slave River Catchment is discussed. Locations of current activities are described by sub-basin in Chapter 3.



Map is for illustrative purposes only.
It is a compilation of data obtained from many sources and the data are subject to change without notice.
AANDC will not accept responsibility or liability for any errors, inaccuracies and/or omissions.

Figure 4.1: Current activities in the Slave River Catchment (Note: specific oil and gas and oil sands operations are shown in Figures 4.2 and 4.3). Base map sources: see References.

4.2 Fate of Compounds in the Aquatic Environment

4.2.1 COPCs in Water

Several of the COPCs which may be found in the Slave River Catchment partition into water. These include metals, major ions (calcium, potassium, sodium and sulphate), nutrients (ammonia, ammonium, nitrite, nitrate and phosphorus), chloride, total suspended solids, certain pesticides (eg. lindane), and microbial constituents (i.e., fecal coliforms, *E. Coli*, Enterococci) (Timoney and Lee, 2009).

For organisms that live in the water (wildlife, fish and invertebrates), direct contact is the major pathway of exposure (MacDonald *et al*., 2002; Farag *et al.,* 2004). Uptake is most often through the skin (or exoskeleton) and/or the gills. Terrestrial wildlife and humans are most often exposed to these COPCs through drinking contaminated water (USEPA, 1993; Strenge and Smith 2006) or eating wild foods (Alaska Dept. of Environmental Conservation, 2005).

4.2.2 COPCs in Sediments and Soils

Several of the COPCs that may be found in the Slave River Catchment tend to partition into sediments and soils. These substances include: metals, PAHs, PCBs, resin acids, fatty acids, other non-polar organic compounds, chlorinated organic compounds, certain pesticides, PCDDs/PCDFs and phosphorus (Timoney and Lee, 2009; MacDonald *et al*., 2003).

For organisms such as aquatic and terrestrial invertebrates, aquatic plants, benthic fish and amphibians, that live in the sediments and soil, direct contact is the major pathway of exposure. Some invertebrates (e.g., earthworms) ingest soil and process it for food, which is an additional route of exposure. Birds and wildlife that probe the sediment looking for food are also likely to ingest sediment during the feeding process (Beyer *et al*., 1997).

4.2.3 Bioaccumulative COPCs

Bioaccumulative COPCs are compounds that tend to accumulate in the tissues of organisms. The principal bioaccumulative COPCs that may occur in the Slave River Catchment include certain metals, polycyclic aromatic hydrocarbons (PAHs; e.g., benzo(a)pyrene), polychlorinated bipenyls (PCBs), organochlorine pesticides, chlorinated organic compounds, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs; MacDonald *et al.,* 2003). Aquatic organisms and wildlife can be exposed to these COPCs via several pathways. For humans and wildlife, exposure is often through ingestion of contaminated plant or animal tissues (Alaska Dept. of Environmental Conservation, 2005). For other organisms (e.g., insects and fish) the predominant exposure pathway is direct contact with contaminated water, sediments and/or soil (MacDonald *et al*., 2002; Farag *et al.,* 2004).

4.3 Developments in the Slave River Catchment

4.3.1 Oil Sands Development

Mining of oil sands involves the recovery of bitumen and the subsequent extraction of oil. Oil sands developments cover a vast area of the Slave River Catchment (Government of Alberta, 2009). Large deposits of bitumen are present within the Athabasca Sub-basin and to a lesser extent within the Peace River Sub-basin (Figures 4.1 and 4.2). Commercial production of oil from the Athabasca oil sands began in 1967 and has expanded substantially in the last decade. An estimated 1.6 million barrels per day were produced in 2010 (Government of Alberta, 2012a), with production estimated to exceed 6 million barrels/day by 2030 (Kinnear, 2009). The industrial footprint increased from 40 km^2 in 1974 to 650 km^2 in 2008 (Timoney and Lee, 2009).

Bitumen is a thick, heavy type of petroleum consisting of a mixture of hydrocarbons containing carbon, hydrogen, sulphur, oxygen, nitrogen and trace quantities of methane, hydrogen sulphide and metals (The Canadian Encyclopedia, 2012; Timoney and Lee, 2009). Oil sands developments utilize either surface mining or *in situ* techniques to recover the bitumen (Government of Alberta, 2012a). Surface mining involves removal of vegetation and overburden in order to access the deposit; open pit techniques are then used to recover the bitumen. Complex oil-water-sand separation technologies are used to extract the heavy oil. Wastewaters from this process are discharged to large tailings ponds, which are in some cases located in close proximity to the bank of the Athabasca River (MacLock *et al.,* 1997). *In situ* extraction involves drilling into the oil sands, and then injecting either steam or solvents into the deposit to make the bitumen fluid enough to be pumped to the surface (Government of Alberta, 2012a).

Potential sources of aquatic stressors or COPCs attributed to oil sands development include:

- Leaks and seepage from tailings ponds (containing salts, trace metals, polycyclic aromatic hydrocarbons (PAHs) and naphthenic acids; Timoney and Lee, 2009);
- Major spills of bitumen, oil and wastewater (Timoney, 2007);
- Refinery effluent (secondary treatment; NREI, 2004);

- Sewage effluent from camps servicing the oil sands (secondary treatment; NREI, 2004);
- Removal of muskeg and overburden drainage during site preparation (NREI, 2004);
- Mine runoff via sedimentation ponds (NREI, 2004);
- Airborne particulates from upgrading facilities and refineries (Kelly *et al.,* 2009, 2010);
- Stack emissions and emissions from heavy equipment (Timoney and Lee, 2009);
- Coke dust and windblown dry tailings dust (Timoney and Lee, 2009);
- Land disturbances and subsequent releases of naturally occurring metals and PAHs (Kelly *et al*., 2009); and,
- Use of large quantities of water for bitumen extraction and processing (Swainson, 2009).

The main COPCs associated with the oil sands are various forms of PAHs, naphthenic acids and metals. There are documented cases of PAHs in water (Timoney, 2007; Timoney and Lee 2009) and in snow as a result of airborne deposition of particulates associated with PAHs and metals (Kelly *et al.,* 2009; 2010). Additionally, there are concerns with increased metal concentrations (e.g. antimony, arsenic, iron, mercury, vanadium and zinc) in water and sediment downstream of the oil sands (Timoney and Lee, 2009; Kelly *et al*., 2010; Environment Canada, 2010b).

The Athabasca oil sand deposit is rich in vanadium, which concentrates during oil sands processing (Government of Alberta, 2012a). However, vanadium was last produced in Canada in 1990/91 by Carbovan Inc., who recovered the material from the Suncor Inc. oil refinery during the processing of bituminous sands (MBendi, 2011).

Although oil sands process waters are stored on site and are isolated from the surrounding environment, potential leaks from tailings ponds, emissions from the refineries and the close proximity of the massive tailings ponds to the Athabasca River are ongoing reasons for concern (Glozier *et al*., 2009). Furthermore, it has been acknowledged that there is a poor understanding of the long-term impacts on aquatic ecosystems associated with development in and around the oil sands region (Environment Canada, 2010b).

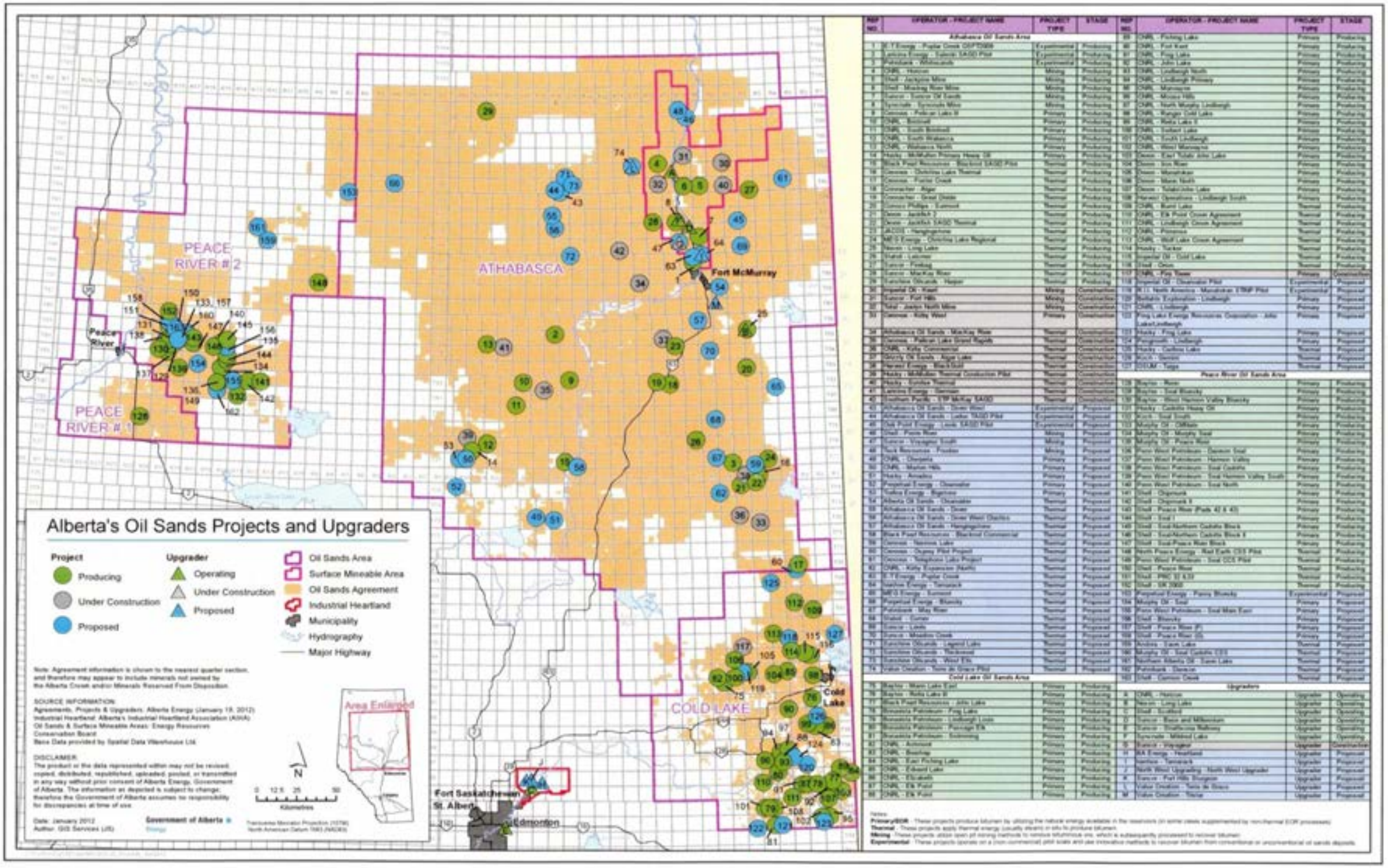


Figure 4.2: Alberta's Oil Sands Projects and Upgraders (used with permission from Government of Alberta).

Source: Government of Alberta, 2012d.

4.3.2 Oil and Gas Development

Conventional oil and gas developments are present throughout the Slave River Catchment (Figure 4.3; Government of Alberta, 2012d). These developments include crude oil and natural gas wells, along with associated exploration and production activities.

Conventional oil extraction is performed using drilled wells. Unlike the bitumen in the oil sands, conventional crude oil will flow at ambient temperatures (Government of Alberta, 2012a). Natural gas wells are often associated with both oil and gas deposits, as raw natural gas is often mixed with the crude oil (Cuddihy *et al.*, 2005).

Potential sources of aquatic stressors or COPCs attributed to conventional oil and gas developments include:

- Drilling mud and fluids discharged into the environment (Reis, 1996);
- Major spills;
- Emissions from flares, venting and consumption of fuels (Cuddihy *et al.*, 2005);
- Contaminated process water releases (Cuddihy *et al.*, 2005);
- Erosion of lands and soils associated with infrastructure development; and,
- Contamination of ground water aquifers due to injection of brine solution (MacLock *et al.,* 1997).

The main COPCs associated with conventional oil and gas development are PAHs and other hydrocarbons. Compounds contained in the drilling mud and fluids (e.g., paraffin oils, diesel, barite, zinc), and those contained in the process water (including hydrocarbons and metals that leach from the deposit and surrounding rock) may also be of concern (Cuddihy *et al.*, 2005).

Emissions from flares and venting during exploration and production activities are known to include volatile organic compounds and greenhouse gases, such as methane, carbon monoxide and nitrous oxides (Cuddihy *et al.*, 2005).

Hydraulic fracturing, commonly referred to as fracking, is a technique used to recover oil and natural gas from deep shale, coal bed and tight sand formations. Hydraulic fracturing is a process that results in the creation of fractures in the rocks. The fracturing is done from a wellbore drilled into reservoir rock formations to increase the rate and ultimate recovery of oil and natural gas (USEPA, 2012g). The fracture width is typically maintained after the injection by introducing a proppant into the injected fluid. Proppant is a material, such as grains of sand, ceramic, or other particulates that prevent the fractures from closing when the injection is stopped and the pressure is released (USEPA, 2011).

Environmental and human health concerns associated with hydraulic fracturing include the chemicals used in fracking operations, accidental spills, contamination of ground water, risks to air quality and the migration of gases and hydraulic fracturing chemicals to the surface (Parfitt, 2010).

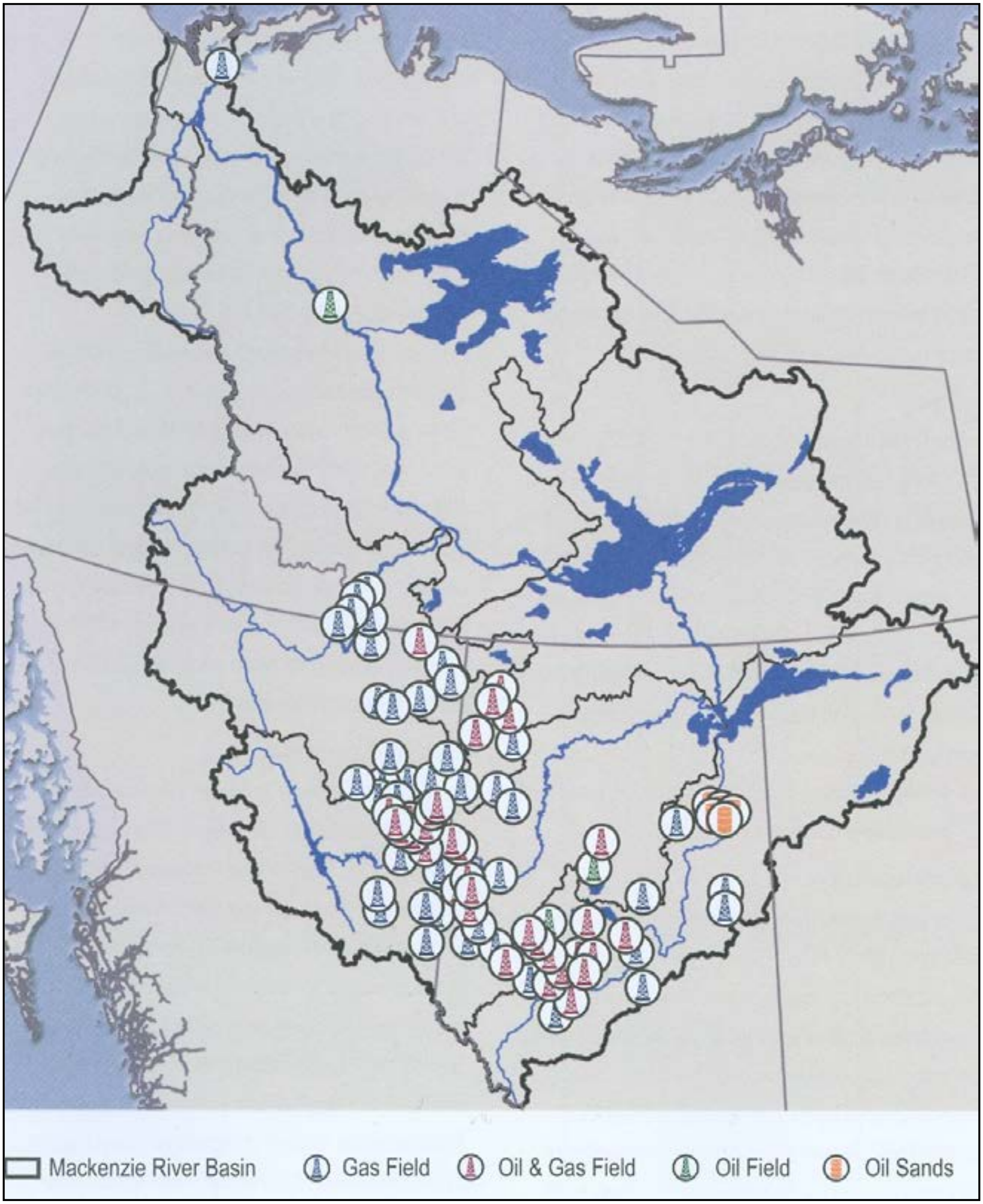


Figure 4.3: Oil and gas fields and oil sands developments in the Mackenzie River Basin (from the State of the Aquatic Ecosystem Report 2003, MRBB, 2004).

4.3.3 Mining

Coal is the most actively mined fossil fuel in the Alberta portion of the Slave River Catchment (NRBS, 1999). Uranium mining continues in the far eastern portion of the Athabasca Sub-basin (Saskatchewan Mining Association, 2010). Other mining activities in the area include sand and gravel, sulphur and peat moss. There is also mining potential for salt, limestone, granite, gypsum and silica (MacLock *et al.,* 1997).

4.3.3.1 Coal Mining

Coal mines are located in the southern portion of the Slave River Catchment (Figure 4.1, Table 3.3) in both Alberta and B.C. Coal is generally extracted using surface mining methods (Government of Alberta, 2012e) with associated stripping of vegetation and topsoil. Abandoned coal mines can also contribute COPCs to the environment; the weathering of exposed rock faces can allow metals to be transferred from drainage water to adjacent water bodies (DeNicola and Stapleton, 2002).

Potential sources of stressors or COPCs attributed to coal mining include:

- Leaching of metals, including iron and selenium (weathering of waste rock; DeNicola and Stapleton, 2002);
- Acid rock drainage (depending on pH of drainage water; DeNicola and Stapleton, 2002);
- Coal dust and other mining waste (e.g. waste water, landfill runoff, etc.; NRBS, 1999);
- Land disturbance (MacLock *et al.,* 1997); and,
- Emissions from heavy equipment (Environment Canada, 2010d).

4.3.3.2 Uranium Mining

Active uranium mines are located in the Athabasca Sub-basin in northwestern Saskatchewan (Figure 4.1). Uranium mined in Saskatchewan accounts for 30% of the world's production (Government of Saskatchewan, 2012). Some uranium is still mined from open pits, while the techniques used for deeper ore deposits are primarily underground mines. Ore is recovered and processed underground then pumped as slurry to storage tanks on the surface (Canadian Nuclear Association, 2010). Some open pit mines which have had their resources exhausted are now serving as tailings ponds for ore-refining facilities.

Weathering of exposed rock faces in the open pits can affect nearby water bodies through leaching and transport of metals and radioactive materials (DeNicola and Stapleton, 2002).

Potential sources of stressors or COPCs attributed to uranium mining and processing include:

- Acid rock drainage (depending on pH of drainage water; DeNicola and Stapleton, 2002);
- Release of radioactive elements such as uranium, thorium, radium and polonium (Timoney, 2007);
- Leaching of metals, including arsenic, copper, lead, nickel and zinc (DeNicola and Stapleton, 2002); and,
- Discharges and/or leakage from tailings ponds.

4.3.4 Pulp and Paper Industry

There are a total of eleven pulp and paper mills in the Slave River Catchment (Figure 4.1, Table 3.3). The pulping processes used by these mills can be separated into three categories: bleached kraft, bleached chemi-thermomechanical (BCTM), and thermo-mechanical. Bleached kraft mills use both chemicals and heat to break down wood chips into soft pulp. The pulp is then chemically bleached to produce very bright white pulp. Historically, molecular chlorine was the primary bleaching agent; however, newer technologies include the use of chlorine dioxide or peroxide, along with oxygen delignification (NREI, 2004), to reduce the formation of chlorinated organic compounds in the effluent (Carey *et al*., 1997; MacLock *et al.,* 1997).

BCTM pulp mills use a combination of chemicals, heat and mechanical grinding to produce the pulp. These mills use fewer chemicals, but the product is not as bright as the pulp produced by bleached kraft pulp mills. Thermo-mechanical pulp mills use heat and mechanical action to break wood chips into pulp, and produce the darkest pulp (MacLock *et al.,* 1997).

Potential sources of COPCs attributed to the pulp and paper industry include:

- Effluent discharge (including chlorinated compounds; Swanson *et al.,* 1993); and,
- Airborne emissions.

Depending on the bleaching method, effluent discharge streams can contain a variety of chlorinated and/or non-chlorinated organic compounds, including dioxins, furans, organic acids, chlorinated terpenes and PAHs (Environment Canada, 2008; Wrona *et al.,* 2000). Discharge of organic compounds can result in increased biological oxygen demand in the receiving waters. Other water quality concerns associated with pulp mill effluents include increases in chemical oxygen demand (COD), total suspended solids (TSS) and nutrients (MacLock *et al.,* 1997). Plant terpenes and aromatic compounds can also cause taste and odour issues in drinking water (NREI, 2004). The odour associated with air emissions from pulp and paper mills is a result of the sulphuric acid used during processing.

Federal legislation implemented in 1992 requires pulp mills to conduct environmental effects monitoring to assess the impacts of these operations (NREI, 2004). In Alberta, improvements to effluent treatment methods have resulted in significant reductions in contaminant loading, such that daily contaminant loads have declined or remained steady in spite of increased pulp production (NREI, 2004).

4.3.5 Forestry

The environmental impacts associated with forestry are largely related to the timber harvesting activities. As land is cleared by harvesting, there is a resultant loss of, or change in, wildlife habitat. Cleared land is also vulnerable to erosion by wind and water, thus leading to the potential release into rivers and lakes of larger quantities of compounds naturally found in the environment, as well as an increase in suspended solids to receiving water bodies (Trombulak and Frissell, 2000; McIvor and Starr, 2000).

Potential sources of COPCs attributed to forestry include:

- Erosion and runoff from cleared land and associated roads (Trombulak and Frissell, 2000).

4.3.6 Municipal Development

Relative to southern Canada, the Slave River Catchment is sparsely populated, with population density ranging from 0.0 (Northwest Territories) to 5.1 (Alberta) individuals per square kilometre, as compared to Ontario with a density of 13.4. The largest community in the Slave River Catchment is Fort McMurray, Alberta, with a population of more than 70,000 people, based on the 2010 municipal census (RMWB, 2010; Table 3.1). Most communities within the Catchment discharge treated effluent to rivers.

Potential sources of COPCs attributed to municipal development include:

- Sewage effluent discharge (nutrients, metals, domestic disinfectants, organic compounds, microbiota ; NREI, 2004) ;
- Stormwater runoff (oils, chemicals, lawn fertilizers, pesticides, animal waste; NRBS, 1999);
- Landfill leachate (NRBS, 1999); and,
- Runoff from airports and roads (metals, PAHs, salts and glycols; NRBS, 1999).

Compounds typically associated with municipal effluent include: metals, PAHs, polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), pharmaceuticals and personal care products, and road salts (Pham and Proulx, 1997; Song *et al*., 2006; Heberer, 2002). Municipal effluent can also be a major source of nutrients to receiving waters, which can significantly impact aquatic ecosystems by promoting increased growth of aquatic vegetation, and ammonia, which can be toxic to aquatic organisms (Chambers and Prepas, 1994). Substances found in runoff from airports include de-icing and anti-icing agents that may consist of glycols or be urea-based, potentially contributing significant amounts of nitrogen to receiving waters (Corsi *et al*., 2009).

4.3.7 Linear Development

Linear development includes activities such as road, rail and pipeline construction, as well as seismic lines used in oil and gas exploration. Much of the road network in the study area can be attributed to oil sands development, oil and gas exploration, mining and other industrial developments. Forestry-related activities also necessitate road building.

Potential sources of COPCs attributed to linear development include (Trombulak and Frissell, 2000):

- Alteration or disturbance to land, vegetation and surrounding waters during construction;
- Soil erosion as a result of land disturbance; and,
- Runoff from roads (NRBS, 1999).

Erosion of soil into surrounding water bodies can result in high turbidity, which lowers light penetration, and, in turn, can reduce the growth of aquatic vegetation. Suspended solids can also be abrasive to fish gills. Subsequent sedimentation can have minimal to severe effects depending on the quantity of material and location within the water body. For example, erosion of soil into an area of fish spawning habitat can have detrimental effects. Road maintenance activities in winter can result in releases of sand, as well as chlorides and/or glycols.

4.3.8 Power Generation

In the Slave River Catchment, energy is produced by coal-fired, gas-fired and biomass-fired power plants, as well as hydroelectric operations (Figure 4.1; Table 3.2; Canadian Centre for Energy Information, 2012). The largest of these is the W.A.C Bennett Dam on the Peace River.

Potential sources of stressors and COPCs attributed to power generation include:

- Emissions as a result of burning fuels;
- Flooding of surrounding land as a result of hydroelectric development; and,
- Changes in water levels and flow as a result of hydroelectric development.

While the coal and gas-fired plants involve the combustion of fossil fuels, biomass-fired plants utilize organic material such as wood and wood wastes, cardboard, paper and agricultural wastes. Emissions from burning fossil and bio-fuels include greenhouse gases and other air contaminants, such as particulate matter. In 2008, power generation was responsible for approximately one quarter of Alberta's greenhouse gas emissions (Alberta Environment, 2008).

Hydroelectric energy uses the power of flowing water to generate energy. Effects on the aquatic environment include activities related to dam construction and subsequent flooding upstream of the dam. The creation of reservoirs changes the aquatic habitat from riverine to lacustrine, and compounds present in the terrestrial environment, such as mercury, may transfer to the aquatic environment. Mercury in water can be converted to methylmercury by bacteria and other processes which can pose a potential health threat to fish-eating animals and people (Environment Canada, 2010a). The downstream seasonal flow regime can also be significantly altered by flow regulation due to the changes in the timing and volume of the water released (MacLock *et al.,* 1997).

4.3.9 Agriculture

Agriculture is one of the main economic activities in the Slave River Catchment, with cultivated land primarily found in two locations, the Peace River Lowlands and the Pembina River area south of the Athabasca River (MacLock *et al.*, 1997). The agriculture industry includes both livestock (e.g. cattle, bison, elk and sheep) and crop production (e.g. canola, wheat, grains and forage crops) (NRBS, 1999). There are no major agricultural activities in the Lower Slave River Sub-basin (NREI, 2004).

Potential sources of stressors or COPCs attributed to agriculture include:

- Application of pesticides or fertilizers to crops;
- Management of manure produced by livestock and the use of manure as fertilizer (Government of Alberta, 2012f);
- Erosion and runoff from agricultural areas (NRBS, 1999);
- Use of large quantities of water for irrigation (Environment Canada, 2010c); and,
- Evaporation of pesticides into the atmosphere.

Runoff from agricultural areas can carry COPCs into local water bodies (NRBS, 1999). In the Peace River Sub-basin, Anderson (2005) reported that over a seven year period, four herbicides (dicamba, MCPA, triallate and bromacil) and one insecticide (lindane) exceeded water quality guidelines in the Peace River. Pesticides can also be transported into the atmosphere through evaporation and later deposited via precipitation (MacLock *et al.,* 1997).

Fertilizers, including manure, are a source of nitrogen and phosphorus (nutrients) and can contribute to soil acidification (MacLock *et al.,* 1997). These compounds can significantly impact aquatic ecosystems by promoting increased growth of aquatic vegetation, such as algae and phytoplankton. Additionally, manure is a source of fecal coliform bacteria, including *E. coli.* and enterococci.

Land clearing, land drainage and summer fallowing are agricultural practices that can lead to increases in soil erosion. Erosion can result in soils with poor water-holding capacity and low nutrient and organic content. It can also increase the levels of total suspended solids in receiving water bodies (MacLock *et al.,* 1997).

A further environmental concern related to agriculture is the use of substantial amounts of water for irrigation and livestock watering, of which only 30 percent is generally returned to the source (Environment Canada, 2010c).

4.3.10 Hazardous Waste Treatment

The Swan Hills hazardous waste treatment centre (Figure 4.1), located in the southern portion of the Athabasca Sub-basin, is the only one of its kind in Canada. Hazardous wastes, such as PCBs, dioxins and other hazardous substances are treated and disposed of at this location (Swan Hills Treatment Centre, 2011).

Potential sources of COPCs attributed to hazardous waste treatment activities include:

- Leaks from onsite landfills, leading to potential groundwater contamination;
- Releases of hazardous wastes; and,
- Air emissions from the incineration of hazardous and non-hazardous wastes.

4.3.11 Long-Range Transport of Atmospheric Pollutants

The deposition of persistent organic pollutants, heavy metals (especially cadmium, mercury and lead), acids, radionuclides, pesticides, PCBs and PAHs in northern Canada is well documented (Macdonald *et al*., 2000; Canadian Arctic Contaminants Assessment Report (CACAR), 2003). In warm climates, these compounds can evaporate into the air and be carried by air currents for great distances from where they originated. When they reach colder climates, they condense and fall to the earth. Many of these compounds tend to be long-lived in nature and resistant to breakdown; therefore, they can become widely dispersed through the food web due to bioaccumulation. While some of the compounds may come from natural sources (such as cadmium and mercury), others such as organic compounds and radionuclides originate completely from anthropogenic sources. These contaminants originate from industrial developments located largely in other parts of the world and elsewhere in Canada (CACAR, 2003).

Potential sources of COPCs attributed to long-range transport of atmospheric pollutants include:

- Direct application: evaporation of pesticides applied to crops in Canada and other countries worldwide; and,
- Air/stack emissions from industrial operations, combustion, refineries and other sources (including landfills and waste sites) in Canada and other countries worldwide.

5.0 DESCRIPTION OF THE SLAVE RIVER SAMPLING PROGRAMS

5.1 Introduction

Along the transboundary reach of the Slave River, there are three long-term sampling locations operated through three distinct water quality monitoring programs. A hydrometric program is also operated within this portion of the Slave River. These programs include:

1. The Slave River at Fort Smith (mid-river) Water and Suspended Sediment Monitoring Program (1990 to present) led by AANDC Water Resources Division. This program is comprised of the:
    a) Slave River Environmental Quality Monitoring Program (SREQMP) (1990-1995); and,
    b) Follow-Up Study (2000-2010).
2. The Slave River at Fort Smith (shore) Water Quality Monitoring Program (1982 to present) led by the AANDC Fort Smith District office.
3. The Slave River at Fitzgerald Water Quality Monitoring Program (1960 to present) led by Environment Canada.
4. The Slave River at Fitzgerald Hydrometric Program (1960 to present) led by Environment Canada (Water Survey of Canada).

Descriptions of each sampling program, including the rationale for establishment, period of record, operating agency, frequency of sampling and media sampled, are outlined in the first section of this chapter. Detailed information on the media sampled (surface water, centrifugate water, suspended sediment) is also presented, followed by a description of the field methods carried out at each location.

A summary of the types of samples sent to each analytical laboratory is provided, as well as a brief overview of the analytical methods and the QAQC programs employed. The analytical laboratories involved in the sampling programs and a summary of the compounds analyzed are included in Appendices 5-1and 5-2, respectively, along with a discussion of the issue of comparable results (Appendix 5-3). Lastly, data compilation, handling and auditing methods are summarized, with further information included in Appendix 5-4.

5.2 Monitoring Programs

5.2.1 Slave River at Fort Smith (mid-river) Water and Suspended Sediment Monitoring Program

The Slave River at Fort Smith (mid-river) Monitoring Program is operated jointly by AANDC's Water Resources Division in Yellowknife and the South Mackenzie Sub-District Office in Fort Smith. The sampling location for this program is located below the Rapids of the Drowned at the Town of Fort Smith (Figure 5.1). This site was originally selected for the Slave River Environmental Quality Monitoring Program (SREQMP) (1990-1995), since it was located downstream of the Alberta/NWT border, upstream of any major tributaries in the NWT, and best represented waters flowing into the NWT (Sanderson *et al*., 1997).

The four sets of rapids located between the border and the sampling site act as natural barriers to upstream movement of fish, ensuring that any fish collected during the SREQMP (1990-1995) were resident of the NWT (Chapter 3: Figure 3.4). Transect (river cross-section) samples collected during the original study indicated that the river was well mixed at this site location (Sanderson *et al*., 1997). These factors were important in site selection, since the main objective of the SREQMP was to determine environmental conditions for the NWT transboundary reach of the Slave River. It also meant that samples collected mid-stream were representative of the water quality of the river.

The SREQMP's integrated monitoring program was designed to look for contaminants where they were expected to be found, accumulate and potentially cause impacts, namely in water (surface and centrifugate water[2]), suspended sediment, and fish (MacDonald and Smith, 1990). During the SREQMP (1990-1995), surface water, centrifugate water and suspended sediment samples were collected approximately four times a year. For the Follow-Up Study (2000-2010), surface water, centrifugate water and suspended sediment from the Slave River were sampled on nine occasions (Table 5.1). The list of parameters analyzed over the period of record is presented in Appendix 5-2.

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[2] Centrifugate water samples are collected from the outflow of the centrifuge and, therefore, do not contain suspended sediment. Surface water samples are raw river water samples collected just below the surface of the water and may contain suspended sediment.

Table 5.1: Follow-Up Study (2000 to 2010) sampling schedule.

Sampling Events during the Follow-Up Study (2000-2010)	Surface Water	Centrifugate Water	Suspended Sediment
September 2000	✓	✓	✓
February 2001	✓	✓	✓
June 2001	✓		✓
June 2003	✓	✓	✓
June 2006	✓		✓
August 2006	✓	✓	✓
March 2007	✓	✓	✓
May 2007	✓	✓	✓
September 2010	✓	✓	✓

5.2.2 Slave River at Fort Smith (shore) Water Quality Monitoring Program

The Slave River at Fort Smith (shore) Monitoring Program is operated by AANDC staff from the South Mackenzie Sub-District Office in Fort Smith. The water quality sampling was initiated to document water quality conditions in the Slave River. The water quality sampling location is located next to the town of Fort Smith boat launch (Figure 5.1). Since 1982, surface water samples have routinely been collected two times per year in the spring and fall (typically May and October). During the SREQMP (1990-1995), sampling at the shore site increased to monthly sampling. During the open water season, samples were collected from the shore just below the waters' surface. During the winter, samples were collected under ice, far enough from shore to ensure that the sample collected was representative of the river mainstem. For this report, the surface water quality data from both the shore and mid-river sites (see 5.2.1) were combined, as they were found to be statistically similar (p=0.170 to 0.972; Zajdlik, 2010a). This provided a larger database for trend analyses. The list of parameters analyzed over the period of record is found in Appendix 5-2.

5.2.3 Slave River at Fitzgerald Water Quality Monitoring Program

Environment Canada has operated the Slave River at Fitzgerald Monitoring Program since 1960. The water quality sampling location is located near the community of Fitzgerald in Alberta, approximately 20 km upstream of Fort Smith (Figure 5.1). During the open water season, surface water samples are collected just below the water surface from a boat at mid-channel. In winter months, a hole is drilled through the ice several metres offshore to collect the water samples. Water quality sampling at Fitzgerald was initiated to document transboundary water quality conditions. During the period of record for this site, samples have been collected from two to thirteen times a year. Presently, samples are collected eight times per year. During the open water season, samples are collected in May, July, September and October, and during the winter, under ice samples are collected in December, February, March and April (K. Pippy. Environment Canada. Yellowknife, NWT. Pers. comm.). The list of parameters analyzed over the period of record is found in Appendix 5-2.

5.2.4 Slave River Hydrometric Program

The Water Survey of Canada (WSC) hydrometric gauging station is co-located with the Fitzgerald water quality sampling location and is also operated by Environment Canada. Hydrometric (water level and discharge) data have been collected since May 1959. The Slave River gauge operated for brief periods in the early 1920s and 1930s, seasonally from 1953-1958 and continuously since, to produce mean daily water level and streamflow data. Daily data for sediment concentrations (mg/L) and sediment loads (tonnes/day) are also available seasonally from 1971-1994.

The water level at Slave River at Fitzgerald (Station No. 07NB001) is measured every five minutes by a pressure transducer attached to a gas purge system. The data are transmitted and posted on the Water Survey website in real-time. The water level sensors are calibrated by WSC technicians when they visit the site and manually survey the water level. The mean daily water level is then used to produce daily mean discharge values using a stage-discharge curve. The stage-discharge curve is the relationship between the water level (stage) and flow (discharge). The curve is created by measuring discharges at numerous water levels.

Summer discharge measurements of the Slave River at Fitzgerald are made using an Acoustic Doppler Current Profiler (ADCP) from a boat. The ADCP sends out pulses through the water and measures the depth and velocity of the river and uses that information to compute the total discharge value. The winter stage-discharge curve is used when there is ice cover. Water Survey of Canada technicians visit the site about eight times a year to survey the water level, calibrate the pressure transducer, conduct discharge measurements and verify the stage-discharge curve (L. McGregor. WSC, Environment Canada. Yellowknife, NWT. Pers. comm).

Hydrometric gauges are also operated by WSC on many rivers within the Slave River catchment, including the Peace River at Peace Point (07KC001), the Athabasca River below Fort McMurray (07DA001) and at numerous upstream locations and tributaries along these rivers. A list of these sites can be retrieved from the Water Survey of Canada public website (Environment Canada, 2011).

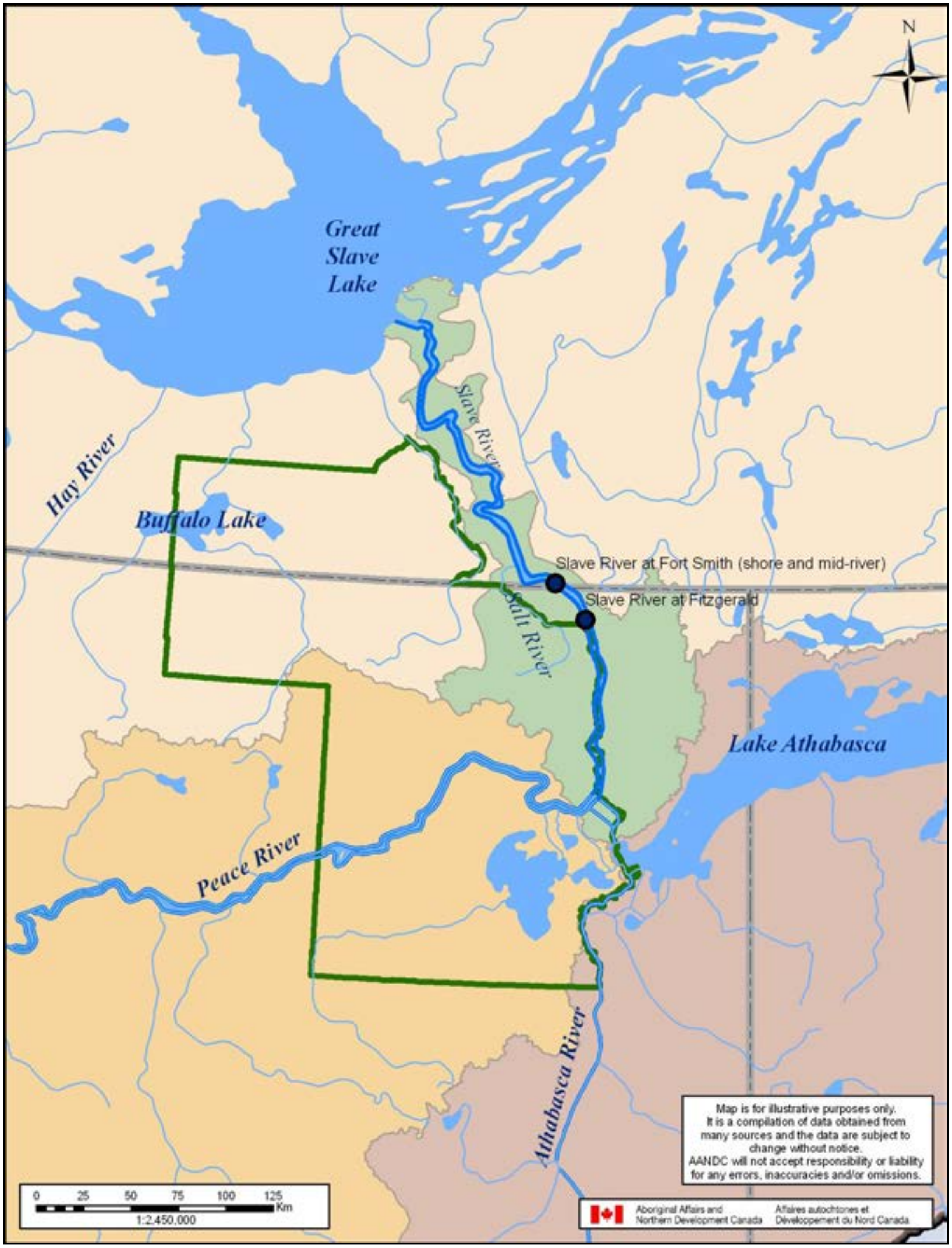


Figure 5.1: Monitoring site locations on the transboundary reach of the Slave River.

5.3 Media Sampled

One of the main goals of the Slave River at Fort Smith (mid river) Monitoring Program was to support the development of water quality objectives for use in transboundary negotiations. Typically, water quality objectives are set by specifying concentrations of compounds not to be exceeded in water, to ensure sufficient protection of the aquatic ecosystem.

However, many organic compounds which can impact the aquatic environment are not detectable by conventional water quality sampling and analytical methods. In fact, some organic compounds can cause harm to aquatic life well before their measured concentration in water indicates that there is a problem (MacDonald and Smith, 1990). Therefore, monitoring surface water alone was considered insufficient for the protection of aquatic ecosystems along the Slave River. Contaminants had to be monitored in the different environmental media (water, suspended sediment and fish) where they would be expected to be present, accumulate and cause impacts (MacDonald and Smith, 1990). To address this need, the SREQMP (1990-1995) was designed as a multi-media monitoring program, to study the different components of the aquatic environment by taking an ecosystem approach to monitoring (Sanderson *et al*., 1997). The Follow-Up Study (2000-2010) focused on water and suspended sediment monitoring. A description of the media sampled during the Follow-Up Study is provided below.

5.3.1 Surface Water

Surface water samples are raw river water samples that contain suspended sediment. Surface water samples are collected from all three sampling locations: Slave River at Fort Smith (mid-river) by AANDC, Slave River at Fort Smith (shore) by AANDC and Slave River at Fitzgerald by Environment Canada. The analysis of surface water samples provides information on water quality and general aquatic ecosystem health, and is required for the interpretation of other results. For example, the pH, hardness and dissolved oxygen levels in water can affect the toxicity of certain metals to aquatic life (CCREM), 1987). The general condition and status of surface water quality can be assessed by comparing results to the Canadian Council of Ministers of the Environment (CCME, 2007) National water quality guidelines, which are intended to provide protection of freshwater aquatic life. Long-term datasets can also be used to evaluate seasonal and/or long-term temporal trends over time.

5.3.2 Centrifugate Water

Centrifugate water is water collected from the outflow of the centrifuge. The centrifuge is a device that separates the suspended sediments from the raw surface water. By including centrifugate water in the sampling program, compounds associated with suspended sediments can be differentiated from those found in the water. Centrifugate water samples were collected from the Slave River at Fort Smith (mid-river) sampling location only.

5.3.3 Suspended Sediment

Suspended sediments are comprised of small plants and animals, silt and clay materials, bits of decaying matter and large gelatinous organic molecules that are suspended in the water column (Swanson *et al.,* 1993). Some metals and compounds of potential concern (COPCs) that go undetected in water, have been found to be very closely associated (and, therefore, detectable) with suspended sediment. The higher organic content and finer clay/silt content of suspended sediment provide a greater surface area for the compounds to adhere to (Swanson *et al*., 1993).

The concentration of compounds in suspended sediment have been found to be several orders of magnitude higher in suspended sediments than in water, and also higher than in bed sediments (Crosley, 1996a; Swanson *et al.,* 1993). As a result, suspended sediment can serve as an early warning of environmental degradation. In fast flowing waters, such as the Slave River, these particles remain suspended in the water column for a long period and, therefore, COPCs associated with them can be transported great distances downstream from their source (MacDonald and Smith, 1990; Swanson *et al*., 1993). Suspended sediment samples were collected by centrifuge from the Slave River at Fort Smith (mid-river) sampling location.

5.4 Field Methods

This section describes the methods that were used to collect, process, handle and transport samples for the three sampling programs discussed in this report. A description of the field sampling methods for surface water, centrifugate water and suspended sediment, is included, along with the associated quality assurance and quality control (QA/QC) procedures.

5.4.1 Surface Water Sampling

5.4.1.1 Field Sampling Methods

Surface water samples were collected from all three locations as per published field methods (Soniassy, 1980; Environment Canada, 1983; EMAN-North, 2005). All samples were collected in pre-cleaned bottles of appropriate size and composition for the target analyte group. Following collection, water samples were preserved by chilling and/or acidification, as required by the AANDC Taiga Environmental Laboratory in Yellowknife (Taiga) or Environment Canada's National Laboratory of Environmental Testing (NLET) in Saskatoon, Saskatchewan and Burlington, Ontario. The samples were shipped to the appropriate laboratory by air on the same day (if possible) for analyses. Field sheets/notes were completed for each set of samples and included information such as date and time of sampling, location, depth of collection, name of sampler and weather conditions. At the Fitzgerald site, field measurements (pH, specific conductance and temperature) were typically taken with hand-held YSI^{TM} field instruments. When available, a water quality multi-probe (Hydrolab^{TM}) was used at Fort Smith sites (mid-river and shore), to document pH, specific conductance, turbidity, temperature, depth, dissolved oxygen and total dissolved solids at the time of sampling. Field sampling equipment was regularly calibrated and properly maintained.

5.4.1.2 Quality Assurance and Quality Control (QA/QC)

QA/QC procedures were followed for all three surface water monitoring programs.

Unless otherwise requested by the lab, sample bottles were rinsed three times with river water before the sample was collected. Care was taken throughout the sampling procedure to ensure that the bottles were kept clean and free from contamination, and gloves were always worn by samplers.

Blank samples were included as part of the field QA/QC programs to ensure that no contamination was introduced through the sampling procedures and to test the accuracy of the analytical procedures. For blank water samples, a set of bottles was filled with Type I water in the field, instead of river water. Type I water is prepared by the lab by passing distilled water through the Millipore filtration system to remove bacteria, dissolved ions and organics. All other aspects of the sampling, labelling, preservation and analysis were kept the same, which ensured that the blank samples were treated like a regular sample. During the Follow-Up Study, six blank samples were collected.

Replicate samples were also included as part of the field QA/QC program. Replicate samples are usually two (referred to as duplicates) or three bottles (referred to as triplicates) consecutively filled from the same site and depth, preserved and shipped to the lab for analysis. In reality, this type of replicate sample is a co-located sample since a true replicate would be produced by splitting one larger sample using a sample splitter. Replicate water samples were collected to determine the precision of measurements, taking into account any imprecision due to field sampling conditions. This aspect of the QA/QC program served as a check on the consistency of the sampling procedures as well as the analytical laboratory techniques. During the Follow-Up Study, eight sets of triplicate surface water samples were collected.

5.4.2 Centrifugate Water Sampling

5.4.2.1 Field Sampling Methods

A portable field centrifuge (the Sedisamp II Continuous Flow Centrifuge; Photo 5.1) was used to remove suspended sediment from surface river water at the Fort Smith (mid-river) sampling location, providing both centrifugate water samples and suspended sediment samples.

Detailed field sampling procedures for the centrifuge are included in Puznicki (1993). This sampler was shown to collect all particle sizes, including the very fine particles most prone to adsorb chlorinated organic compounds (Swanson *et al*., 1993).

During the open water months, centrifugate samples were collected from a boat anchored in the river (Photo 5.2). During the winter sampling events, a shelter equipped with an electric heater was set up on the ice to house the centrifuge, and ensure that the equipment did not freeze (Photos 5.3 and 5.4). Samples were collected as close to the regular sampling site as possible, at a depth of one meter below the water surface. In winter, variations in sampling location did occur, due to the presence of under-ice frazil slush, produced by the super cooled water from the upstream rapids (Ashton, 1986). This ice had to be avoided as it would quickly plug the intake to the centrifuge pump. On other occasions, slight alterations to the sampling location were required due to back eddies caused by low flow conditions. Based on the results of the earlier station evaluation, small changes in site location were not considered to affect the representativeness of the samples. Detailed field methods for collecting centrifugate water and suspended sediment samples can be found in Sanderson *et al*. (1997).

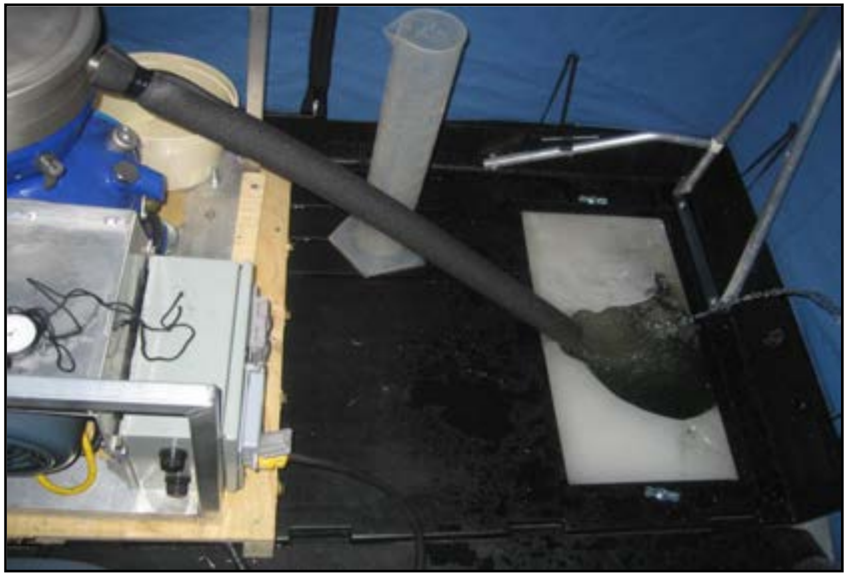
All sample bottles were specially cleaned by the laboratory for each parameter group. Analytical Lab Services (ALS; previously Envirotest Laboratories), prepared the bottles for organic compound analysis by soaking them overnight in a detergent solution, rinsing with distilled and de-ionized water, pesticide grade acetone and dichloromethane, and drying at 250°C for four hours.

Centrifugate water samples were typically collected during the first three hours of centrifuge operation. This involved filling an appropriate number of sample bottles (for routine and metals analyses) and 4 L glass bottles (for organic compound analysis). Wearing gloves, the sampler would rinse each bottle three times with centrifugate water before it was filled and capped. All samples were collected in appropriate bottles and preserved in accordance with analytical method requirements. The samples were stored in coolers and were shipped by air the same day or next, depending on the analyses, to the Taiga Lab in Yellowknife or ALS in Edmonton.

5.4.2.2 Quality Assurance and Quality Control (QA/QC)

In the field, before starting the collection of centrifugate water and suspended sediment, the pump and hose were run for several minutes in order to rinse out the equipment. Once the rinse was completed, the pump and hose were attached to the centrifuge. Gloves were worn at all times during sampling. While the centrifuge was operating, care was taken to ensure that all sources of fuel and exhaust, including generators, outboard motors, and gas cans, were located downwind as far as possible from the centrifuge (either outside the tent or at the back of the boat).

For centrifugate water samples, blanks and replicate samples were used to evaluate data quality. Blank centrifugate water samples were prepared by filling 4 L glass bottles with Fisher Scientific HPLC Water (supplied by ALS), instead of centrifugate water. All other aspects of the sampling, preservation and analysis were kept the same. Blanks and replicate samples were collected to ensure that no contamination was introduced through the sampling procedures and to test the accuracy and precision of the analytical procedures. During the Follow-Up Study, six replicate centrifugate samples and eight blank samples were collected and analyzed for organic parameters. Field spikes were part of the sampling program from 1990 until 2001, but were discontinued due to inconsistent supply from the laboratory.



From left to right. Photo 5.1: Open centrifuge, showing the bowl where the suspended sediments collect. Photo 5.2: Summer centrifuge sampling. River water is pumped through the stainless steel hose to the top of the centrifuge. The clear water flowing from the outflow tube is centrifugate water. Photo 5.3: Winter centrifuge sampling shelter. Photo 5.4: Winter centrifuge sampling – equipment set-up inside the shelter. The outflow tube directs water back into a hole through the ice.

5.4.3 Suspended Sediment Sampling

5.4.3.1 Field Sampling Methods

To fulfil laboratory analytical requirements, at least 450 grams of suspended sediment had to be collected during each sampling event. The time required to collect this amount of sample (between 7 and 24 hours) was estimated based on the turbidity of the river water and an optimum centrifuge flow rate of 4 to 6 L/min. Once this time had elapsed, the centrifuge was stopped, and all equipment was transported back to AANDC's Fort Smith Sub-District office. At the office, the centrifuge bowl (where the suspended sediment collects) was carefully removed and disassembled, including removal of the distributor and disc set. Any water trapped in the bowl was decanted. The suspended sediment was collected from the sides and bottom of the bowl with clean Teflon-covered stainless steel spatulas (Photo 5.5), and divided according to the amount required by each laboratory. Sediment was placed in pre-cleaned glass jars with Teflon lined lids, and then shipped by air to the appropriate laboratory for analysis.

5.4.3.2 Quality Assurance and Quality Control (QA/QC)

All of the equipment used in the operation of the centrifuge, including trays, beakers, hoses and spatulas, were cleaned with Contrad 70 soap and rinsed consecutively three times with each of Type I water, acetone and dichloromethane (DCM). Polyethylene gloves were worn throughout the cleaning process and used to cover any openings of the centrifuge to prevent contamination during equipment transport.

Photo 5.5: Slave River suspended sediment sample – September 2010.

5.5 Analytical Laboratory Methods

In order to ensure comparability of results, every effort was made to document the analytical methods used for each of the samples summarized in this report. However, as some of the data were analyzed several decades ago, it was sometimes difficult to obtain details on the laboratories' historical analytical or QA/QC methods. A brief overview of the analytical methodologies used by Taiga and ALS laboratories involved in the analyses of the Slave River samples discussed in this report are included in Appendix 5-5.

The following section provides a summary of the types of samples sent to each lab by year. It should be noted, that all three of the laboratories that analyzed samples for this study are accredited by the Canadian Association for Laboratory Accreditation (CALA). As part of the accreditation, each lab must participate in CALA's Inter-Laboratory Proficiency Testing Program, which monitors their performance and compares results against those of similar laboratories (Appendix 5-6). Accreditation indicates that a laboratory performs the tests and reports results within the accepted criteria limits. Therefore, accredited laboratories are considered to generate comparable data for the parameters that they are accredited for.

The laboratories that participate in this certification program also carry out ongoing internal QA/QC programs that often meet or exceed national and international standards. These programs measure the precision, accuracy, and sensitivity of the analytical methods, and include reagent blanks, method blanks, surrogate spikes, matrix spikes, laboratory control samples, and certified reference materials. A complete list of the quality control protocols incorporated into the analytical methods is presented in Appendix 5-7 (Taiga) and Appendix 5-8 (ALS). Further details on the procedures are available from the respective laboratories.

5.5.1 Taiga Environmental Laboratory (Taiga)

Surface water samples from the Slave River at Fort Smith (both shore and mid-river sites) were sent to Taiga Environmental Laboratory (Taiga) throughout the period of record and analyzed for physical parameters, major ions, nutrients and metals. Some centrifugate samples were also sent to Taiga for routine analyses. In addition, during the Follow-Up Study (2000-2010), Taiga determined the particle size, % moisture, total organic carbon, and total inorganic carbon in suspended sediment samples. During the SREQMP (1990-1995), these analyses were performed by different laboratories.

For samples collected prior to 1990, Taiga followed the analytical methodologies outlined in American Public Health Association Standard Methods 18th edition (Greenburg *et al.,* 1992), and Environment Canada's (1979) Analytical Methods Manual. Since 1993, Taiga has been accredited by the Canadian Association for Laboratory Accreditation (CALA, 2012) for the various types of tests listed in the scope of accreditation (Appendix 5-6). Current analytical methods are based on Standard US Environmental Protection Agency (EPA) Methods and the Standard Methods for the Examination of Water and Wastewater (21st edition) (AANDC, 2010).

5.5.2 Analytical Laboratory Services (ALS; previously Envirotest Laboratories)

Throughout the period of record, ALS analyzed centrifugate water and suspended sediment samples from the Slave River at Fort Smith (mid-river) for all organic parameters including chlorinated phenolics, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxin and furans. Metal analysis on suspended sediment samples were also conducted at ALS during the Follow-Up Study. The analytical methodologies for centrifugate water and suspended sediment samples collected during the SREQMP are presented in Sanderson *et al*. (1997). Methods used during the Follow-Up Study are documented in Appendix 5-5. Efforts were made to document the changes in methodology and ascertain the comparability of the Follow-Up Study results to the results obtained during the SREQMP (Appendix 5-3).

It should be noted that for some parameters, detection limits were higher in the Follow-Up Study than in the SREQMP. The following explanation was offered by the lab manager from ALS:

"The lab's policies regarding acceptable changes to methodology have changed over the years. The extremely low detection limits reported in the past were based on one-time, custom changes to approved methods, and while theoretically capable of seeing the reported detection limits, they were not based on rugged, validated methodology. Since regulations have changed in the 2000s to place greater emphasis on method uncertainty, laboratory practices have responded by being much more conservative in modifications to established methods, to ensure the best and most consistent data quality possible. As a result, we can report only our validated, default detection limits for the tests we offer."(S. Johnston, (ALS). Edmonton, Alberta, Pers. Comm.)

ALS Laboratory Group (ALS) in Edmonton, formerly Envirotest (ETL), became a member of CALA in June 1990 and has participated in CALA proficiency testing since 1990, when it was first offered. The lab received accreditation in 1993. Previous to

1990, ETL participated in proficiency testing programs for EPA and AIHA (S. Luchka, (ALS). Edmonton, Alberta, Pers. Comm.)

5.5.3 Environment Canada Laboratory

Starting in 1960, surface water samples from the Slave River at Fitzgerald were collected by Environment Canada staff and analyzed at National Laboratories for Environmental Testing (NLET) in Saskatoon, Saskatchewan for nutrients and in Burlington, Ontario for metals and major ions (Glozier *et al*., 2009). Beginning in April 1993, some of these analyses (specific conductance, pH, turbidity, dissolved phosphorus, total phosphorus, fecal coliforms, total coliforms, filterable residues, and non-filterable residues) were conducted at the Taiga Environmental Laboratory in Yellowknife. In 1996, dissolved nitrogen, ammonia, and nitrate + nitrite were added to the Taiga parameters list. In April 2000, total alkalinity and dissolved organic carbon were also added to the suite of parameters analyzed by Taiga. Published analytical protocols were used for all chemical analyses (Glozier *et al.,* 2009).

Organic compounds, including PAHs, organochlorine herbicides, pesticides and organophosphate pesticides, were measured in surface water samples between 1979 and 2006. For the later years, it is assumed that the methods used to evaluate organic parameters are defined in the NLET Schedule of Services for the corresponding years of sample collection.

Environment Canada's National Laboratories for Environmental Testing (NLET) has been accredited by CALA (the Canadian Association for Laboratory Accreditation) to the standard ISO/IEC 17025, since March 1995. NLET is an active participant in major national and international inter-laboratory performance-testing programs.

Reasonable efforts were made to document the methodologies used by Environment Canada since 1969; however, as is common when dealing with historic date, detailed accounts of historical methods were not always found. Glozier *et al*. (2009) highlighted this difficulty with historic records (pre 1990) and recommended that "Environment Canada ensure that clear and accessible records are kept regarding any future changes in analytical techniques." This recommendation is the current standard for Environment Canada data holdings.

5.6 Data Handling

5.6.1 Data Compilation

A substantial quantity of data and information has been generated on environmental quality conditions within the Slave River Catchment. Water and suspended sediment quality data were compiled for this report from the three long-term monitoring programs and hydrological data from a fourth program (see section 5.1).

These programs provided information with which to evaluate environmental conditions in the Slave River, including surface water quality data, centrifugate water quality data, suspended sediment quality data, and hydrometric flow data. These data were initially compiled in spreadsheets in MS Excel format by AANDC staff. Subsequently, these data were translated into a relational database in MS Access format by MacDonald Environmental Sciences Limited (MESL). Further details on the compilation and handling of the data can be found in Appendix 5-4.

The Slave River at Fort Smith has been sampled at two sites (shore and mid-river) by AANDC since 1982 and 1990, respectively. In order to increase the sample size and power of the dataset, the surface water quality data from the two sampling locations were combined. Testing was conducted to determine if the water quality data collected from the shore was statistically different from the data collected from midstream. Using the two-sample comparison and/or Kruskal-Wallis tests, no statistically significant differences due to sampling location could be detected (at the 95% level of significance; p=0.170 to 0.972; Zajdlik, 2010a). The only exception was sodium, which showed no statistically significant differences at the 90% level of significance (p=0.063; Zajdlik, 2010a). The test used depended on whether or not the data met model assumptions (homogeneity of variance and normality).

5.6.2 Data Auditing

Database auditing of the MS Access database was conducted to ensure the accuracy and completeness of the data used in the status and trends assessment. The auditing process initially targeted outliers identified during preliminary investigation of the data. Anomalous data points that appeared to fall out of the range of the majority of the data were identified based on reviews of summary tables (i.e., maximum and minimum values for each parameter), detection limits and their ranges, seasonal relationships, parameter versus flow relationships, and parameter versus total suspended solid relationships. Such anomalous values were first checked against the translated MS Excel sheets and, if further verification was needed, they were then checked against the original laboratory reports and data sheets, if available. If the identified issue was not resolved at this stage of the process, communications were made with those who collected the data, and/or laboratory personnel to resolve any data quality issues. This ongoing iterative process throughout the data analysis phase allowed for corrections to be made to the database, confirmation of the validity of outliers or support for their exclusion, and overall completeness and accuracy of the database.

The data in the MS Access database were then further evaluated to assure the quality of the data used in the assessment. This process involved:

- Further analyses of outliers (i.e., to identify inconsistencies with units);
- Analyses of data completeness (i.e., to identify missing samples or missing data);
- Examination of data qualifier fields (i.e., to assure internal consistency in database);
- Distinguishing the measured concentrations of parameters in water as either the dissolved or total fraction (particularly metals);
- Verification of sample identification numbers (i.e., to ensure that data were not duplicated);
- Verification of date formats (i.e., to ensure consistency);
- Reviewing all chemical names in the database (i.e., to ensure that the same parameter was not reported under multiple synonyms or nomenclatures, e.g., nitrate & nitrite filtered and nitrogen dissolved NO_3 &NO_2).

The hydrometric flow data used in this analysis were retrieved from the Water Survey of Canada public website (Environment Canada, 2011). A quality-assurance check was included when incorporating flow data into the MS Access database to ensure the dates of the flow measurements matched the dates that the water quality samples were collected. For sample dates where there was no corresponding flow data, no flow value was entered into the database. As there are no significant inflows to the Slave River between Fitzgerald and Fort Smith, the hydrometric data from the gauge "Slave River at Fitzgerald" are considered representative of the streamflow at Fort Smith (Stevens and DeBoer, 1986).

Additional quality assurance of the water quality data was conducted with the assistance of Zajdlik and Associates (2010b), who produced graphical summaries of all the routine (physical parameters, major ions, nutrients and metals) data from Slave River at Fort Smith (mid-river and shore) and Slave River at Fitzgerald. The purpose of this was to highlight any further issues and/or discrepancies with the data and to assess the suitability of each routine parameter for statistical long-term trend analyses. For example, an analytical method change was apparent on the dissolved selenium time series graph. It indicated that the laboratory changed its reporting methods from one significant digit (which resulted in low variability in the observed values) to two significant digits. Due to the low variability and apparent step changes in the dissolved selenium data, it was considered unsuitable for long-term trend analyses.

In addition, changes in analytical methods often resulted in changes in detection limits. Several steps were taken to ensure that changing detection limits did not affect the statistical interpretation. The following is summarized from Zajdlik (2011b). The process began by graphing the data and observing the distribution of censored[3] data over the period of record to see if:

1. The censored observations could induce a trend;
2. The censored observations were few in number and could be deleted or ignored; and,
3. The censored observations were randomly scattered over the period of record or occurred during a single time period (which would likely indicate a change in analytical method).

A few options were taken depending upon the pattern of censoring:

1. Run the analysis with and without the censored observations to see if a difference was noted (this was always reported);
2. Delete the observations, if censored values were few in number;
3. Delete all observations prior to a certain date to avoid biasing the analysis by using only non-censored (i.e., higher concentrations) observations;
4. Analyze the data using survival analysis (methods discussed in section “Survival Analysis”) if the assumption of normality could be met (known as Tobit regression);
5. Not run the analysis if censoring was greater than 30%[4].

In all cases where censoring was observed:

1. Any modifications to the raw data were noted and discussed;

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[3] Censored data are values that are reported as less than the detection limit.

[4] The parameters (mostly metals) demonstrating a high (>30%) number of censored values were not assessed for long-term trends in this report.

2. The implications of any potentially injudicious modelling methods were pointed out as caveats; and,
3. Recommendations for more sophisticated modelling are provided.

Overall, the results of the water quality and hydrometric data compilation and auditing indicate that the information used in the assessment generally met the project data quality objectives. However, as expected for data collected over an extended period of time from multiple sources, it was not possible to confirm the accuracy of every data record. Although every reasonable effort was made to ensure the accuracy of the data, some anomalies may still exist in the underlying data.

6.0 SLAVE RIVER FLOWS

Summary
Flow in the Slave River is greatly influenced by the Peace River, which contributes about 60% of the Slave River flow volume. Given this, the regulation of the Peace River for BC Hydro operations has affected the Slave River flow regime, including a 75% increase in mean winter low flows and a 20% reduction in the mean spring peak flows.

Other changes in the flow of the Slave River may be due to regulation, or an increase in climatic variability in the catchment. For example, high freshet peaks were generally experienced in June before dam construction, but are now often in May. A trend toward more annual peaks or blips on the annual hydrographs has also been identified and secondary peaks now appear in some years during winter.

In 2010, record low water levels were experienced on the Slave River, on Great Slave Lake and in the upper Mackenzie River. Several gauged tributaries to Williston Lake, behind the W.A.C. Bennett Dam, also experienced record lows during 2010. This implies that the record lows experienced downstream of the dam can be attributed primarily to the effects of low snowpack and low rainfall in the headwaters and the catchment area.

Long-term trend analysis of Fitzgerald flow data revealed significant decreasing trends in the summer and fall flows and a significant increasing trend in winter flow; no significant trends were revealed in the spring or annual flows. Additional work is required to understand the ecological significance of these trends and determine if they are the result of upstream regulation or climate change or both.

6.1 Introduction

The Slave River has a massive basin area of approximately 613,000 km² (Figure 3.1) and a mean annual flow volume of almost 108 km³ (Seneka and Faria, 2011). The river flows approximately 435 km from the outflow of the Peace-Athabasca Delta (PAD) until it empties into Great Slave Lake. There it deposits its sediments to form the active portion of the Slave River Delta, covering approximately 640 km^2 (NRBS, 1996) (Section 3.2.1.1).

There are three major tributaries to the Slave River: the Peace River, with its headwaters in BC; the Athabasca River, with its headwaters in Alberta; and Lake Athabasca, with its headwaters in Saskatchewan (Figure 3.1). Two other areas contribute significantly less: the Lake Claire catchment nestled between the lower Peace River and Athabasca River catchments flows into the PAD; and the Slave River valley catchment downstream of the PAD to Great Slave Lake (Figure 3.2). Flow in the Slave River is greatly influenced by the Peace River, which contributes about 60% of the Slave River flow volume (Figures 6.1 and 6.2).

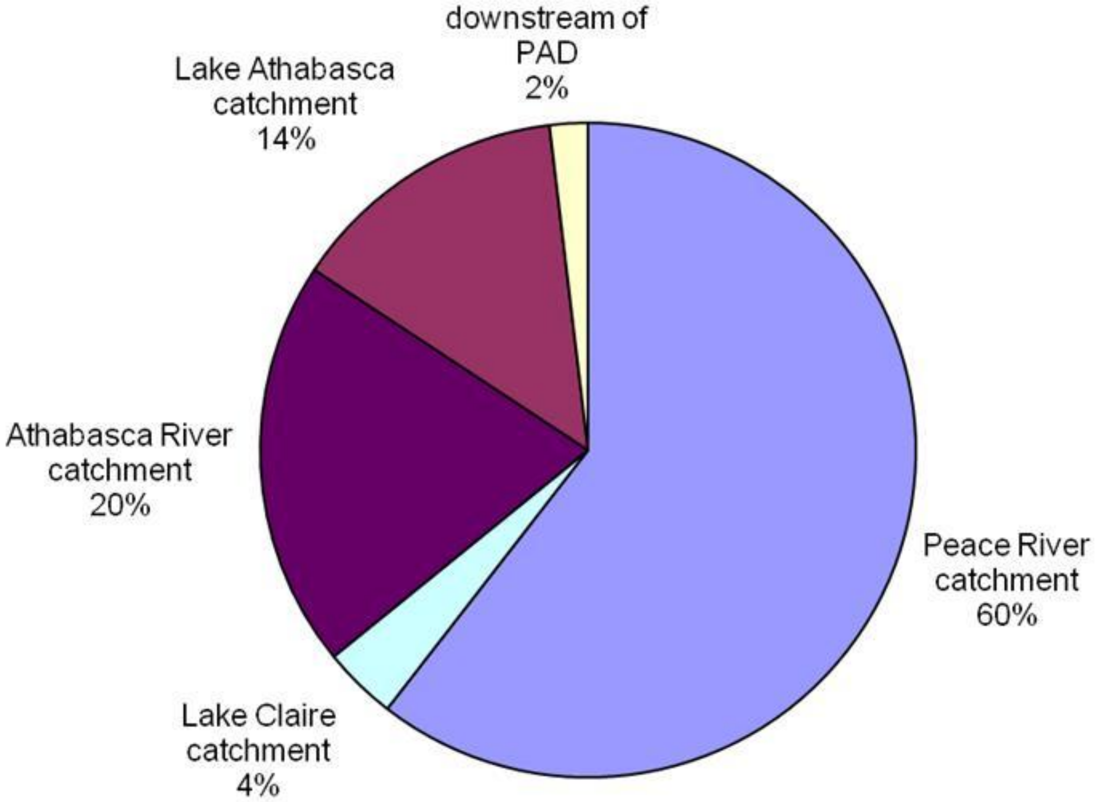

Figure 6.1: Relative flow contribution of each Slave River tributary catchment.

The tributary headwaters of the Peace and Athabasca rivers lie in the Rocky Mountains, while those of Lake Athabasca lie in the Canadian Shield and Interior Plains. Lower portions of the Peace and Athabasca sub-basins are also fed by streams and lakes of the Interior Plains. As a result of the contrasting landscapes and climatic influences, the flow regimes of the Slave River tributaries vary.

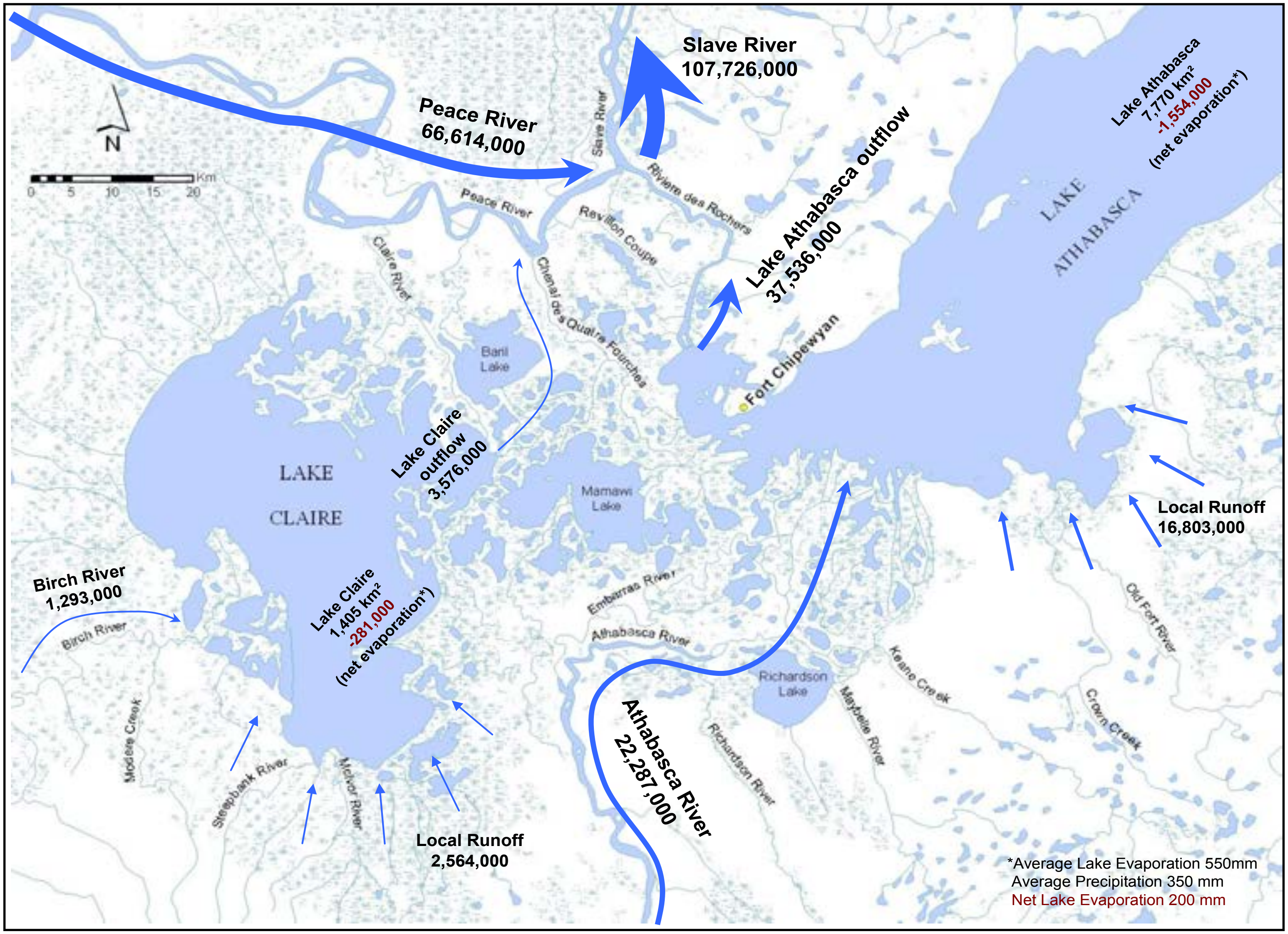

Figure 6.2: Approximate average annual water balance of the Peace-Athabasca Delta complex up to 2007, inflows and outflows in cubic decametres (dam³). One dam³ = one thousand m³. Water balance quantities are by Water Policy Branch, Alberta Environment (Seneka and Faria, 2011).

In the lower portion of the Athabasca, the influence of snowmelt runoff in the plains during spring is evident in the data; high elevation snowmelt and glacial runoff effects are also apparent throughout the summer (Woo and Thorne, 2003). Although the downstream Peace River regime is primarily regulated by the W.A.C. Bennett Dam, the influence of snowmelt and rainfall in tributaries downstream of the Dam is still evident at the Peace Point hydrometric monitoring station (Peters and Prowse, 2001; Woo and Thorne, 2003).

At the heart of the Slave River Catchment is the Peace-Athabasca Delta (PAD), an extensive area of delta lakes and delta channels where the major tributaries converge to form the Slave River (Figure 6.2). Hydrology of the Peace-Athabasca Delta is complex with its low relief, numerous lakes, and many channels. Inflows to the delta are generally from the Athabasca River, Lake Athabasca and Lake Claire. However, connectivity between the delta lakes and channels changes during high flows on the Peace River, particularly during spring ice-jams and extreme summer rainfall flood events (Prowse and Lalonde, 1996). High water levels on the Peace River can act as a dam to block flow from the PAD system (Peters and Prowse, 2001). In addition, if the water level on the Peace is sufficiently high, it can occasionally result in reversal of flow direction through the PAD, with water from the Peace River moving into the delta lakes and Lake Athabasca (Peters and Buttle, 2010; Prowse and Lalonde, 1996). The lakes and wetlands of the PAD and Lake Athabasca provide a large surface area that attenuates flows into the Slave River.

The Slave River contributes approximately 75% of the inflow to Great Slave Lake and therefore has a strong influence on the lake's water levels (Gibson *et al.,* 2006a; Kerr, 1997; MRBB, 2003). Great Slave Lake is the fourth largest lake in Canada and the second largest lake in the Mackenzie River Basin. Because of its size, Great Slave Lake moderates the flow of the upper Mackenzie River by delaying high flow and extending recession flows downstream (Woo and Thorne, 2003).

Flows in the Mackenzie River are significantly influenced by flow contributions from the Slave River, as its catchment area is about 36% of the total Mackenzie River Basin area at Tsiigehtchic (Figure 1.1) where the flow contribution of the Slave River can vary between 34 and 40% (Woo & Thorne, 2003).

6.2 Impacts of Regulation and Climate Change on the Slave River Flow Regime

Changes to flow

Given the large percentage of flow derived from the Peace River, its regulation by the W.A.C. Bennett Dam for BC Hydro operations has also affected the flow regime of the Slave River. The Bennett Dam was completed in 1967, and filling of the reservoir from late 1967 to early 1971 resulted in a decrease in the Slave River's total annual flow for those years (Figure 6.3). Subsequent to the reservoir filling period, operation of the dam has not significantly changed the total annual volume of water in the Slave River (Seneka and Faria, 2011). In addition, lowest flows on the Slave River still occur in winter and the highest flows during spring freshet.

However, since regulation, the hydrograph has been dampened, in that mean winter low flows have increased by 75% and mean spring peak flows have been reduced by 20% (Figure 6.4; MRBB, 2003).

Examination of the hydrometric data also reveals that the annual timing of peaks and low flows has been somewhat altered (Figure 6.5). High freshet peaks were generally experienced in June prior to dam construction, but are now often in May. A 2011 study indicated that there are now more blips[5] (ups and downs) on the annual hydrographs (1970-2005) than there have been in the past (Monk *et al*., 2011), which suggests either an increase in climatic variability in the catchment or possibly another effect of regulation. Secondary peaks also now appear in some years during winter (Figure 6.5).

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[5] Those occasions where the hydrograph experiences minor flow increases are referred to, in this report, as 'blips'.

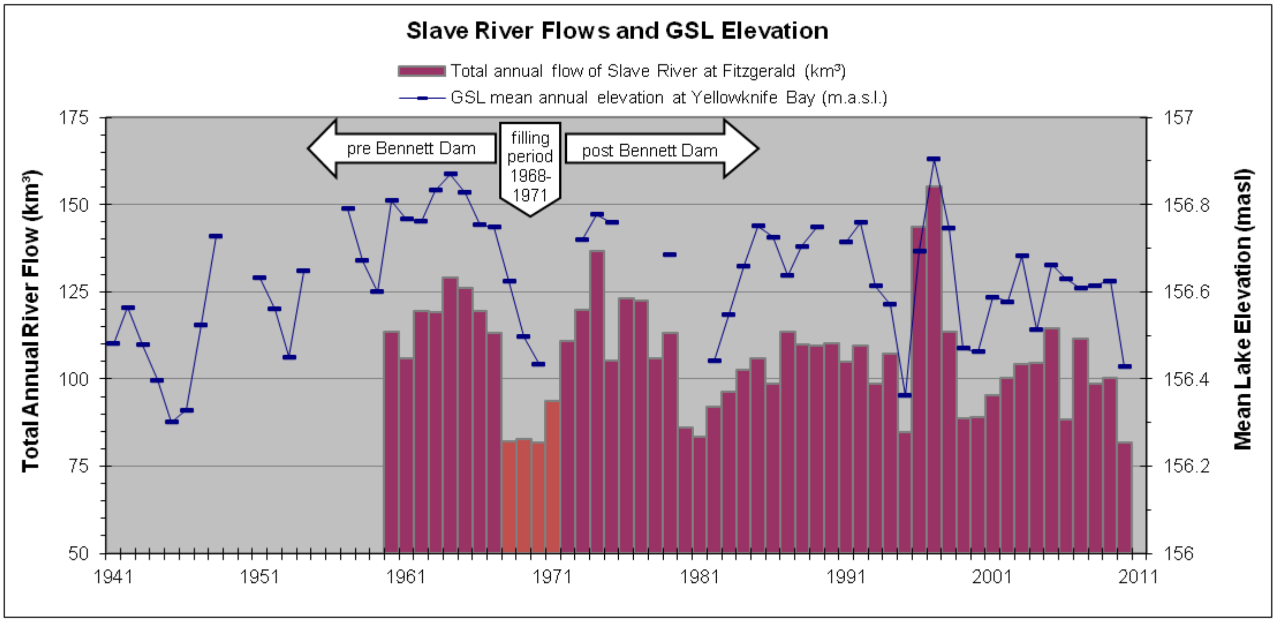

Figure 6.3: Total annual flow of the Slave River at Fitzgerald and mean annual elevation of Great Slave Lake at Yellowknife Bay (Water Survey of Canada – 07NB001, 1960-2010; 07SB001, 1941-2010).

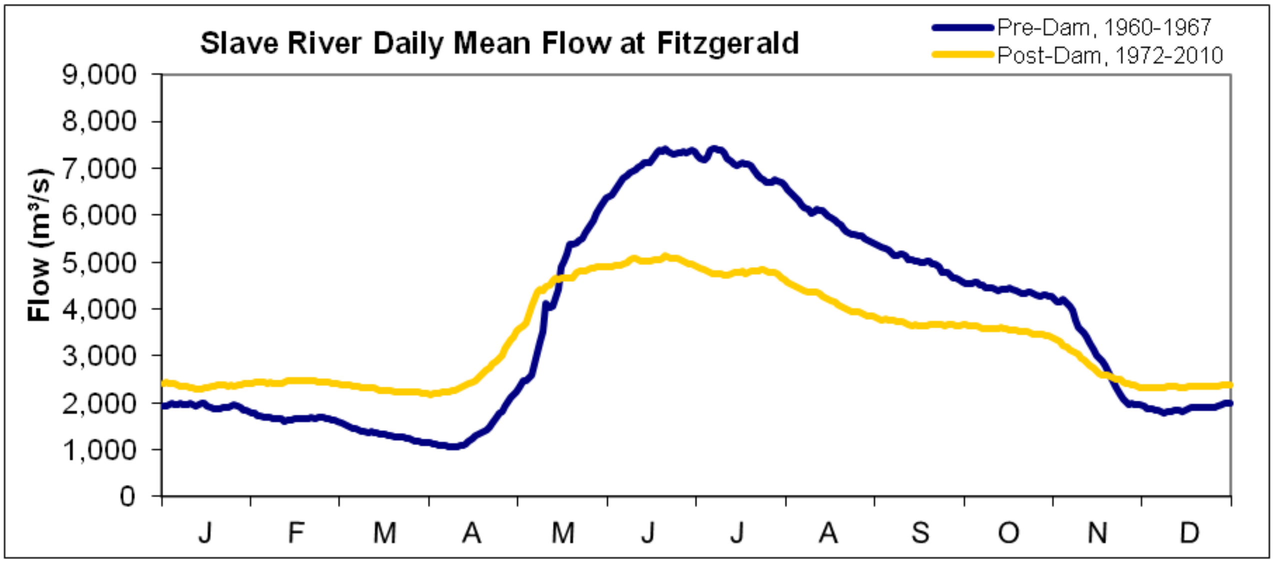

Figure 6.4: Mean annual hydrographs of the Slave River at Fitzgerald for pre-dam (1960-1967) and post-dam (1972-2010) years (Water Survey of Canada – 07NB001). Adapted from MRBB, 2003.

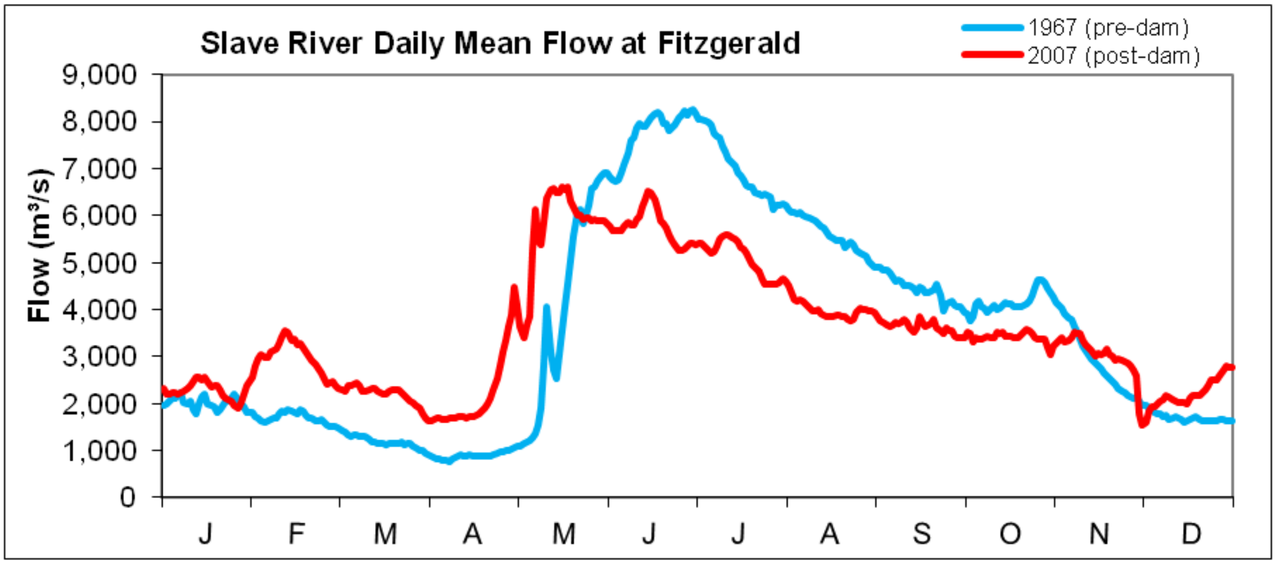

Figure 6.5: Examples of annual hydrographs of the Slave River at Fitzgerald for a pre-dam (1967) and a post-dam (2007) year (Water Survey of Canada – 07NB001).

Changes to Sediment Regime

The observed changes in the seasonal hydrological regime (Figure 6.5) have altered the annual sediment regime of the river and the Slave River Delta, by decreasing the annual sediment load (English *et al*., 1996). The relationship between sediment bearing capacity and river flow is non-linear, with load capacity increasing exponentially in response to flow increases; therefore the 21% reduction in the June high flows has resulted in a proportionally greater 33% reduction in the annual sediment load of the river (English *et al*., 1996). The advance of the Slave Delta into Great Slave Lake since 1930 was estimated to be on average 3.0 km per century with growth spurts and lags (MRBC, 1981). While reduced peak flows on the Slave River as a result of upstream regulation have decreased sediment yields (English *et al*., 1996), with expansion of the delta over the centuries it has protruded into deeper water of Great Slave Lake, which further reduces expansion rates (Prowse *et al*., 2006).

Climate Change

Climate change effects on Slave River flow are difficult to discern using the 1960-2010 data record from the hydrometric gauge at Fitzgerald, for a number of reasons:

- the periodicity of climatic cycles varies (from decadal to multi millennial)
- in a long-term historical context, the data record is relatively short (50 years)
- Slave River flows are a product of several complex systems (including the Peace-Athabasca Delta and the Bennett Dam)

- the influence of upstream land-use change, water use and flow regulation on observed flows is difficult to quantify and to distinguish from climatic fluctuations and change

However, longer water-level records exist for Great Slave Lake (GSL) which is dominated by Slave River inflows. GSL also acts to integrate cumulative climatic effects in its watershed (Schindler, 2009). Before and after the 1968-1971 onset of regulation, Seneka and Faria (2011) observed a change in GSL water level trends, from a positive trend during 1934-1967 to a negative trend during 1972-2007. Climate change was cited as a possible driver of this observed change in trends (Baines and Folland, 2007). In addition, Seneka and Faria (2011) found that variability in water levels on GSL had decreased since 1971 as an expected consequence of regulation. Similarly, when comparing simulated naturalized levels to recorded levels on GSL, Gibson *et al.* (2006b) identified that reductions observed in the annual peak and amplitude of water levels were both due to regulation. However, these reductions were found to have been counter-balanced by climatic impacts, and the primary driving force behind water level fluctuations in GSL, including the post-regulation period, was found to be climate-driven precipitation on the upstream Peace-Athabasca basins (Prowse *et al.,* 2006).

Trends toward earlier spring freshets and annual peak flows are also exhibited as a likely effect of climate warming in the Mackenzie River Basin (MRBB, 2003). The Northern Rivers Ecosystem Initiative Synthesis Report (NREI, 2004) reported that water levels had decreased in lakes, rivers, and delta regions within the Slave River Catchment over the preceding 20 years (NREI, 2004).

Longer term records

Recent multidisciplinary studies suggest there is a much longer trend toward drier conditions. Wolfe *et al*. (2008) indicate that water levels on Lake Athabasca have declined over the last 200 years and that the frequency and magnitude of Peace River floods in the northern portion of the PAD have also declined over the last 500 years. Limnological studies of Slave River Delta lakes suggest that the lowest water levels over the last 80 years may predate regulation at Bennett Dam (Brock *et al*., 2010). Multidisciplinary studies by Johnston *et al*. (2010) estimate that water levels on Lake Athabasca were, on average, 2.3 metres higher during the Little Ice Age (~1600-1900 A.D.) than they have been since the WSC hydrometric record began circa 1930. Sediment core data from a Slave River Delta lake indicate that Great Slave Lake was also higher by at least 3.5 metres during that same period (~1600-1900 A.D.) (B. Wolfe, Wilfrid Laurier University, Personal communication; Ennis, 2010).

Recent high flow and low flow years
The high total annual flow for the Slave River in 1996 (Figure 6.3) resulted from wetter than normal conditions in the basin coupled with emergency releases of water from Bennett Dam. While high flow volumes were being experienced on the Peace River in 1996, Athabasca River volume was raising the level on Lake Athabasca, resulting in storage release to the Slave River (Woo and Thorne, 2003). High volumes were sustained on the Slave River through 1997 (Figure 6.3), as high snowmelt volumes were received in the Peace (downstream of the dam) and Athabasca basins (Woo and Thorne, 2003).

Record low water levels were experienced during 2010 in the Slave River (Figure 6.3), on Great Slave Lake and in the upper Mackenzie River. Several gauged tributaries to Williston Lake, the reservoir behind W.A.C. Bennett Dam in the upper Peace River Sub-basin, also experienced record lows during 2010 (WSC, 2010), which implies that the record lows experienced downstream of the dam can be attributed primarily to the effects of low snowpack and low rainfall in the region. This view is supported by lower than average flows observed during the spring and summer of 2010 in two major unregulated tributaries downstream of Bennett Dam (Smoky River and Wabasca River) and in the Athabasca River below Fort McMurray.

6.3 Trends of Flows in the Slave, Peace and Athabasca Rivers

Flow data for the Slave River date back as far as 1921; however, there are only very small amounts of data prior to 1953, collected over four years (1921-22; 1930-31). Between 1953 and 1959, the amount of data for each year varies between 140 and 353 days. It is only since 1960 that the data record became continuous. Given that there are only eight full years of data prior to regulation of the Peace River, a trend analysis on pre-dam flow data is not possible. The 1968–1971 filling of the Williston Reservoir was a unique event of the regulated-flow period, therefore trend analysis on the Slave River was limited to the post-1971 flow data.

An analysis of the 1972-2010 dataset of daily flows was undertaken for this study. As seasonal differences in flow give rise to seasonal differences in water quality, post dam trends in flow were also investigated for each season[6], and a visual inspection of annual hydrographs was used to determine a unique division of seasons in each year. The non-parametric Mann-Kendall (M-K) test showed no significant trends in spring or annual flows ($p>0.05$; Figure 6.6, Appendix 6.1). However, significant decreasing

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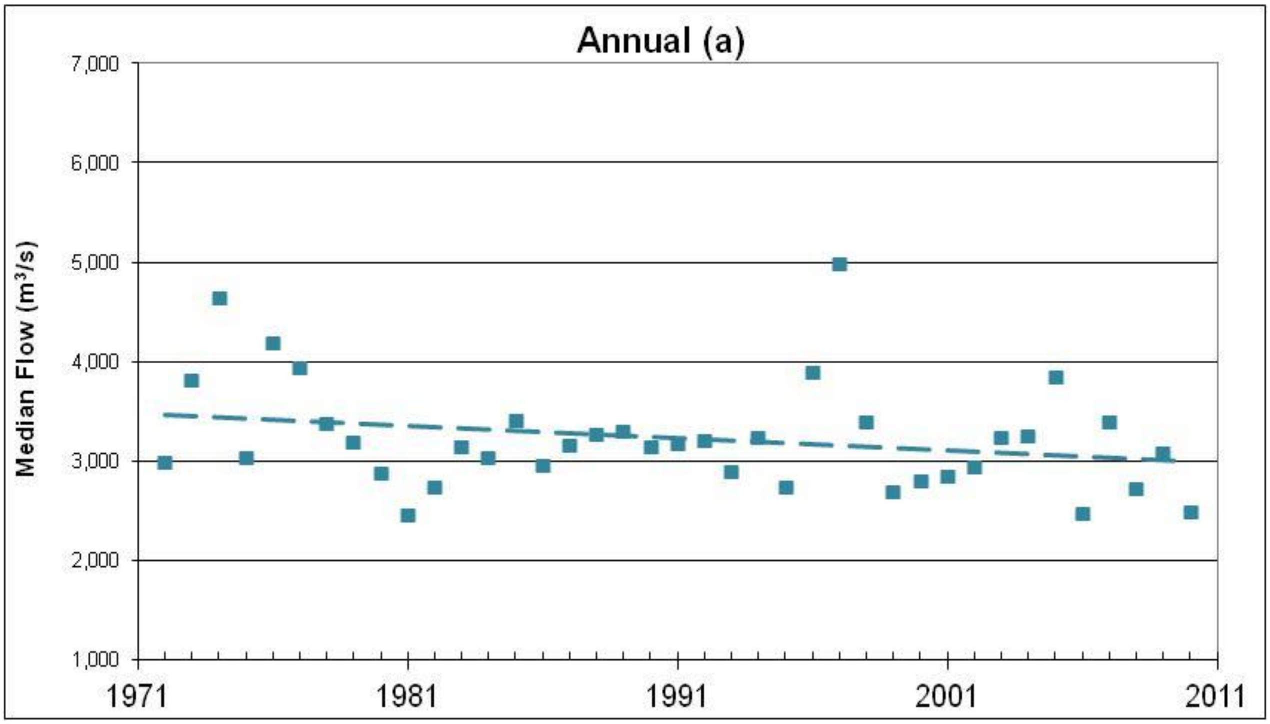
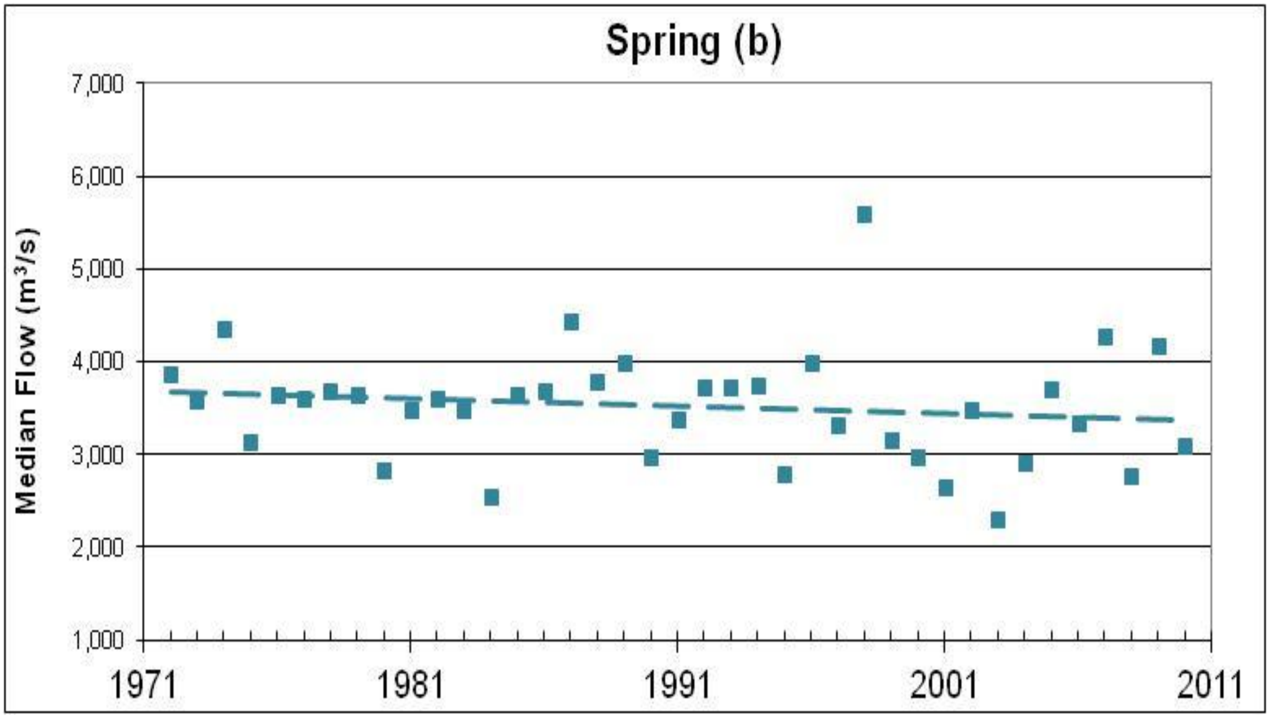
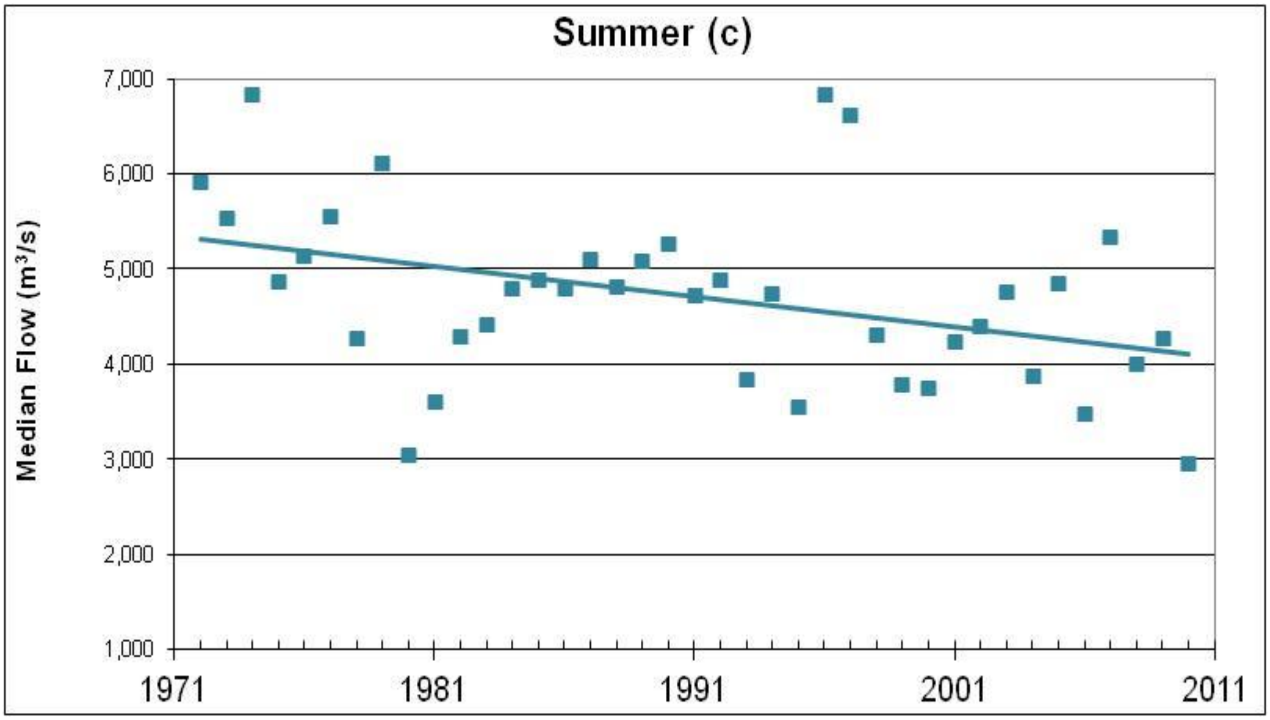
[6] Daily flows for each year were categorized seasonally as winter, spring, summer or fall based on each annual hydrograph. The seasonal designation process is described fully in Chapter 7, Section 7.2.3.

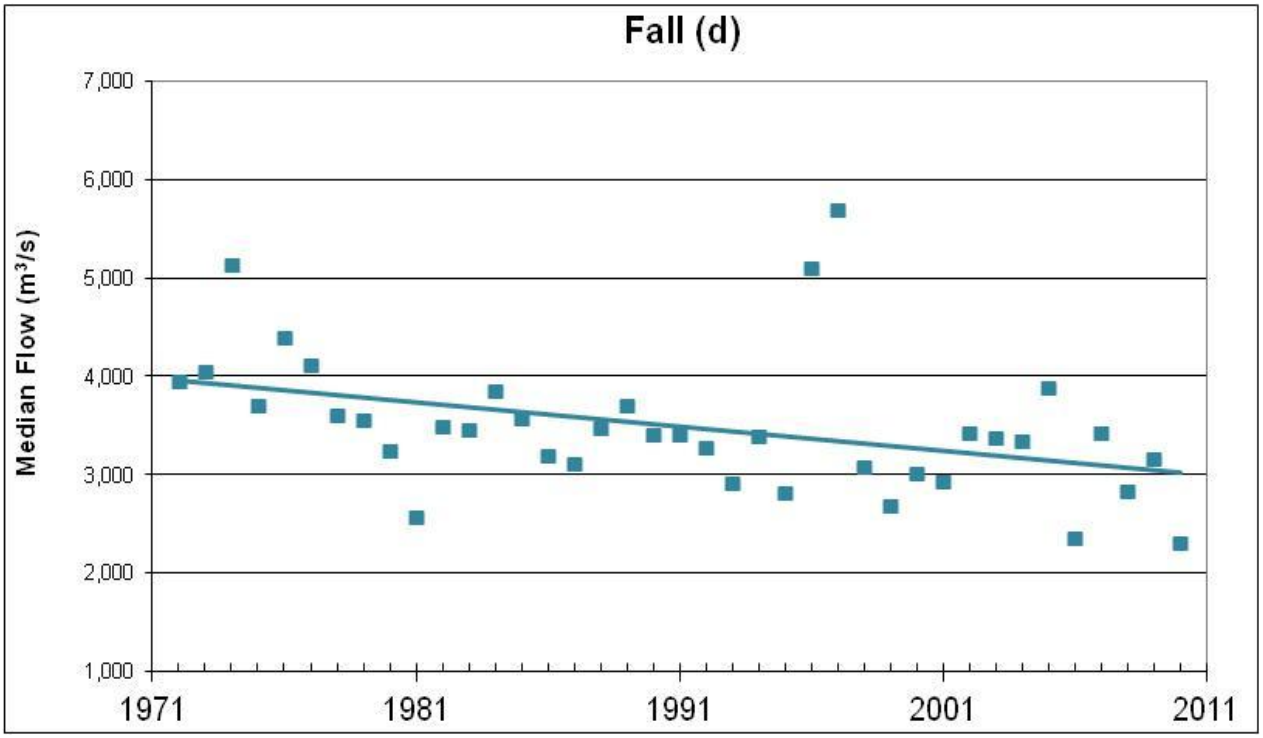
trends ($p<0.05$) in flow during the summer and fall and a significant increasing trend ($p<0.05$) in flow during the winter were revealed.

Conversely, a review of winter flow trends between 1972-2010 on the Slave River by Woo and Thorne (2012) did not reveal any significant trend. Woo and Thorne (2012) defined the winter season with fixed dates from November 1 to March 31, whereas in this study the annual hydrographs were examined to determine the winter season for each individual year. The winter season was deemed to begin from the point on the annual hydrograph where the hydrograph began to flatten out, due to storage effects and the formation of ice; the winter season was deemed to end in the following year when the hydrograph began to rise due to the spring freshet. In addition, this study examined the effect of seasonal flow characteristics on water quality in the Slave River specifically, while Woo and Thorne (2012) were comparing winter low flows amongst key hydrometric stations throughout the Mackenzie River Basin. It is likely, therefore, that the differing winter trend results are due to the different methods of defining the seasons.




Spring (b)
Median Flow (m³/s)
7,000
6,000
5,000
4,000
3,000
2,000
1,000
1971
1981
1991
2001
2011


Summer (c)
Median Flow (m³/s)
7,000
6,000
5,000
4,000
3,000
2,000
1,000
1971
1981
1991
2001
2011



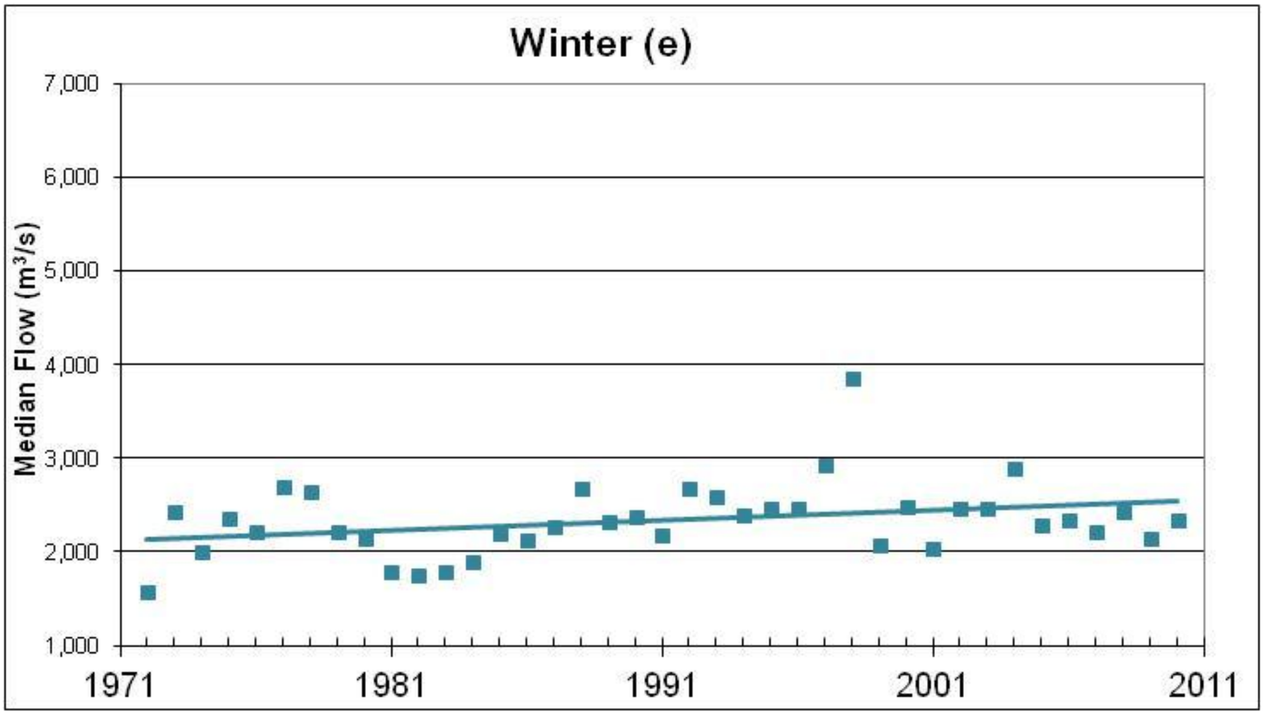


Figure 6.6: Medians of 1972-2010 annual (a) and seasonal (b, c, d & e) Slave River daily flows at Fitzgerald (WSC Hydat, 2010). Solid lines indicate 95% confidence in the trend; dashed lines indicate trends with less than 95% confidence.

Trend analyses were performed by Seneka and Faria (2011) on the Peace and Athabasca rivers. While no statistical trend in annual flow was evident in the Athabasca River using 87 years of data (1913-2007), a statistically significant positive trend was observed in the Peace River at Peace River (95% confidence, +0.19%/year) using 66 years of data (1916-2007).

Using annual flow volume can mask potential seasonal changes in a river's flow regime. For seasonal data, Schindler and Donahue (2006) reported a 33% reduction in summer (May-August) flows on the Athabasca River below Fort McMurray during 1970-2003, following the reported global shift in climate indicators and a 20% reduction during the overall 1958-2003 period of record ($p<0.05$). They also reported a 42% reduction in 1915-2003 summer flows on the Peace River at Peace River ($p<0.0001$) (Schindler and Donahue, 2006), while Seneka and Faria (2011) have indicated that Dec-Mar winter flows have more than tripled at that hydrometric station as a consequence of regulation.

Trend Summary

As is evident from the various pieces of information presented, trend analysis has its limitations. Climatic cycles, climate change impacts, flow regulation, and water and land use changes within the upstream catchment of the Slave River result in a complex flow regime. It is critical that appropriate monitoring of stream flows is conducted such that, combined with local knowledge, accurate interpretations and assessments can be made concerning the state of water quantity on the Slave River. Over the period 1972-2010 we have identified decreasing trends in summer and fall and an increasing winter trend (Figure 6.6), but additional work is recommended to identify the individual effects of upstream regulation and climate change on the identified trends.

7.0 SURFACE WATER RESULTS AND DISCUSSION

7.1 Introduction

Surface water quality samples are water samples that have been collected just below the water's surface from shore, a boat or through the ice. The analysis of surface water provides information on water chemistry and general aquatic ecosystem health. Long-term datasets can also be used to evaluate the seasonality of water quality and to discern any long-term temporal trends. The information from these evaluations can be used to:

- Understand more about the water quality of the Slave River;
- Determine if water quality has changed over time;
- Help to address community concerns; and,
- Support the development of water quality objectives for transboundary agreements.

This section of the report reviews the surface water quality data collected from two long-term monitoring locations, namely: the Slave River at Fitzgerald and the Slave River at Fort Smith.

Slave River at Fitzgerald

Since 1960, the Slave River at Fitzgerald sampling location has been operated by Environment Canada. Surface water samples have been collected 4-12 times per year and analyzed for physical parameters, major ions, nutrients and metals. Although water quality samples have been collected from Fitzgerald since 1960, for the purposes of this report, only the post-dam (1972 -2010) data were examined. The pre-regulation data (1960-1967) for the Slave River at Fitzgerald is not a continuous record (missing years: 1964 and 1965) and includes observations for only a limited number of parameters, mainly major ions.

The post-dam water quality data were evaluated to determine current conditions and compared to water quality guidelines. The correlation and strength of the relationships between certain parameters were examined to better understand the water chemistry in the Slave River. Long-term temporal trends of surface water at Fitzgerald were also examined to determine if the water quality of the Slave River has changed over time. Due to the longer period of record and the higher frequency of sampling throughout the year, only the data from the Fitzgerald sampling location was used to assess long-term trends of the surface water quality of the Slave River.

Slave River at Fort Smith

The Slave River at Fort Smith sampling location has been operated by AANDC since 1982. Surface water samples from the Slave River at Fort Smith have been collected 2-12 times per year and analyzed for physical parameters, major ions, nutrients and metals. The data collected from 1982 to 2010 were used to assess the current status of the river at Fort Smith. Calculations of basic statistics, such as averages, maximum values and minimum values were prepared. Correlations and the strengths of relationships between certain parameters were also examined.

7.2 Evaluation Methods

This section provides an overview of the various methods used to describe the current status, correlation between parameters, seasonality and long-term trends of surface water quality of the Slave River.

7.2.1 Current Status of Water Quality Conditions

To provide an overview of the current status of the water quality in the transboundary reach of the Slave River, surface water quality data from the Slave River at Fort Smith (1982-2010) were first compared to the data collected from the Slave River at Fitzgerald (post dam: 1972-2010). Comparisons were also made to the surface water quality data from the Peel River above Fort McPherson (1980-2005) and the Liard River at the Mouth (1980-2005); both of these sites are operated by Environment Canada. Although the Liard and Peel rivers are underlain by different geology and geography than the Slave River, both are heavily sediment laden rivers like the Slave and, thus, comparisons were made to provide additional context.

To assess the current status of the Slave River surface water quality, results were also compared to the CCME Canadian Water Quality Guidelines for the Protection of Freshwater Aquatic Life (CPFAL; CCME, 1999). These guidelines are intended to protect freshwater aquatic life from anthropogenic stressors, such as chemical inputs or changes to the physical components of water (i.e., pH, temperature and debris). The guidelines are meant to protect all forms of aquatic life, including the most sensitive life stage of the most sensitive species over the long-term (CCME, 1999). It is important to note however, that these are national guidelines and, therefore, may not reflect specific local conditions, especially sediment-laden northern rivers and ecosystems. For those parameters that did not have a national guideline, surface water quality guidelines for the protection of freshwater aquatic life developed by the province of British Columbia were used (BC MOE, 2006a and b).

For each parameter group (physical parameters, major ions, nutrients and metals), data were summarized in tables at the beginning of each section. Median values were reported instead of mean values, as the latter can be strongly influenced by high or low isolated values (i.e., outliers). These outliers are sometimes greatly different from the rest of the dataset, especially for those parameters associated with particulate matter. In addition, median values are useful to describe data that are not normally distributed, such as the water quality data of the Slave River.

Water quality datasets often contain values below the limit of detection. These values, referred to as censored data, only mean that the concentration of a particular parameter is less than what can be detected by the laboratory's analytical techniques. In this report, censored data was replaced with their respective detection limit. For instance, if a particular value was reported as "<5", a value of 5 was used to compute detailed summary statistics such as the mean, standard deviation, median, minimum, maximum and 90th percentile. Although using the reported detection limit in calculations (instead of zero or half the detection limit, which is also sometimes used) may bias the results towards being higher than they actually are, it is a more conservative and protective approach for the Slave River. These basic statistics, as well as the number of values reported as less than the detection limit (censored data), are included at the end of each surface water section.

Descriptive statistics were calculated using Excel 2003 and/or Statgraphics Centurion XV, Version 15.1.03 (Microsoft, 2003; Statgraphics, 2011). Scatterplots, histograms and box and whisker plots were used to illustrate characteristics and distributions of the data.

7.2.2 Correlation between Water Quality Parameters

As parameters such as turbidity, phosphorus and metals are associated with particulate matter, the relationships between these parameters and total suspended solids (TSS) were investigated using the Spearman rank-order correlation test. In contrast to the more common Pearson correlation, the Spearman coefficients are computed from the ranks of the data values rather than from the values themselves (Sokal and Rohlf, 1995). Consequently, the Spearman coefficients are less sensitive to outliers than the Pearson coefficients. The Spearman rank-order statistic produces a coefficient called the Spearman 'rho' (r_s), which ranges between -1 and +1 and measures the strength of the association between the parameters (Dytham, 2007). The test also provides a P-value which tests the statistical significance of the estimated correlations. P-values below 0.05 indicated statistically significant correlations at the 95.0% confidence level.

In this report, the relationship between water quality parameters was considered statistically significant if the probability was less than 0.05 ($p<0.05$) and strong if the Spearman's rho (r_s) was greater than 0.7. Only paired observations (same sample and date) were used in the correlation assessment. The correlations between parameters were estimated using Statgraphics Centurion XV, Version 15.1.03 (Statgraphics, 2011).

7.2.3 Long-term Temporal Trends in Surface Water Quality

Long-term trend assessments at Fitzgerald were conducted to determine if the concentrations of selected water quality parameters in the Slave River have changed over time. Long-term trends can reflect climate change or impacts due to human activities. Long-term temporal trend analyses can contribute to the understanding of aquatic ecosystems and allow water managers to make more informed decisions.

The parameters selected for long-term trend assessment were based on the following criteria:

1) public interest;
2) potential toxicity to aquatic life;
3) an adequate record (at least 10[7] years); and,
4) less than 30%[8] censored data.

Water quality parameters meeting the above criteria are included in Table 7.1.

Table 7.1: List of parameters which were considered for long-term trend analysis.

Physical Parameters	**Major ions**	**Nutrients**	**Metals***
pH	Dissolved calcium	Dissolved ammonia	Total aluminum
Alkalinity	Dissolved magnesium	Dissolved organic carbon	Total chromium
Total suspended solids	Dissolved sodium	Particulate organic carbon	Total cobalt
Total dissolved solids	Dissolved potassium	Total phosphorus	Total copper
Turbidity	Dissolved sulphate	Dissolved phosphorus	Total iron
Specific conductance	Water hardness		Total lead
			Total manganese
			Total molybdenum

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[7] It is generally recommended that a minimum of 10 years is required to ensure the robustness of specific long term trend analysis (Aroner, 1994; as referenced in Hebben, 2009).

[8] Censored data can have an influence on long-term trend assessment, particularly if the detection limit varies over time (Hebben, 2009). The parameters (mostly metals) demonstrating a high (>30%) degree of censoring (high number of values reported as less than the detection limit) were not assessed for long-term trends in this report.

Physical Parameters	Major ions	Nutrients	Metals*
			Total nickel
			Total vanadium
			Total zinc
			Dissolved arsenic

* Dissolved metals (other than arsenic) data were not assessed for long-term trends because they did not meet the 10 year minimum data criteria (specific details regarding trend assessment are included in the section on individual parameters).

The purpose of the long-term trend assessment was to examine whether water quality conditions have changed over the period of record (annual trends). Trends were also examined separately for each season. Recent studies have reported that loadings to the snowpack from stack emissions in the oil sands development area were high (Kelly *et al.,* 2009, 2010). These studies have shown that oil sands developments, through airborne or water pathways, release compounds such as polycyclic aromatic hydrocarbons (PAHs) and metals to the Athabasca River and its watershed. In order to capture the spring melt from the snowpack in the Athabasca River region and its potential influence on the water quality of the Slave River, it was important to investigate trends over time by individual season, particularly in the spring (Kelly *et al.,* 2009, 2010; Timoney and Lee, 2009). In addition, seasonal trends were examined separately to ensure that a trend in one season did not mask a trend in another season. For instance, an increasing trend in the spring and a decreasing trend in the fall may have resulted in a non-significant annual trend, when there may actually be changes occurring in the water quality of the river.

Key questions upon which the trend analyses were conducted include:

1. Do the spring data demonstrate a change over time?
2. Do the summer data demonstrate a change over time?
3. Do the fall data demonstrate a change over time?
4. Do the winter data demonstrate a change over time?
5. Does the entire dataset demonstrate a change over time?

For the purpose of defining seasons, annual hydrographs for the Slave River at Fitzgerald were generated for each year between 1972 and 2010. Each hydrograph was examined to define the seasons (spring, summer, fall and winter) based on flow. Annual hydrographs for the Peace and Athabasca rivers were also reviewed for each corresponding year. For the purposes of this report, the seasons were defined as follows:

Spring – constituted the rising limb and first or second peak of the hydrograph. Spring may include some under ice conditions, but should be mainly representative of the spring melt runoff from the south, as well as local runoff inputs.

Summer – constituted the subsequent summer hydrograph peaks and part of the falling limb of the hydrograph. Summer conditions reflect local, as well upstream, summer rain events. Summer should also be representative of the spring runoff from the mountains in the upper sub-basins.

Fall – constituted the remainder of the falling limb of the hydrograph and included fall rain events from both local and upstream sub-basins.

Winter – constituted the point at which the hydrograph begins to flatten out because of storage effects and the formation of ice. Winter ends at the beginning of spring in the following calendar year.

If a trend was found, the change in concentration was estimated by reporting the difference in the predicted concentration of the parameter at the beginning and end of the period of record (Zajdlik, 2011b). In simple terms, the difference represented the ‘rise’ or ‘fall’ over the period of record for each parameter.

7.2.3.1 Methods to Assess Long-Term Temporal Trends

Statistical models were used to describe long-term trends. Models were fit with the goal of best describing the variability of each parameter. The potential explanatory variables considered were flow, time, season and an interaction[9] between season and year. If a variable was found to be statistically significant, it was included in the final model. If a variable did not describe the parameter, it was removed from the model. Model adequacy meant that the model chosen for each parameter described the predominant pattern(s) in the data (Zajdlik, 2011b). All long-term temporal statistical analyses and graphics were performed within the statistical package “R” (R Development Core Team, 2010). Specific “R” packages used and associated rationales are provided in Zajdlik (2011b).

Modelling for long-term trend assessment proceeded as follows:

1. The first step was to test for an interaction between season and year. If an interaction existed it meant that the trend was different in at least two seasons.

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[9] An interaction occurs if trends are different among seasons. For instance, if there is an increasing trend in the fall and a decreasing trend in winter, an interaction is said to exist.

When this occurred, trend assessments were carried out for each individual season and for the whole dataset (annual data). In this case p-values are available for each season and the annual data.

2. If there was no interaction between season and year (i.e., the trends were the same regardless of season), the data was only assessed for the presence of an annual trend and therefore only the annual trend p-value is available. When no interaction occurred, any trend found in the annual data was implied for the seasonal data (seasonal trends were not tested and therefore no seasonal p-values are presented).

3. If there was no interaction between season and year and no annual trend, it was implied that there is no trend in the seasonal data. In these cases, the p-value for the annual data is expressed as $p > 0.1$, showing that there is no trend at the 90% confidence level (p-values are not available for the individual seasons). The In these cases, although seasonal trends were not detected, the seasonal graphics show the annual trend line result (no trend) and highlight the different median concentrations found in each season.

A summary of the long-term trend results are presented in Appendix 7-1.

To assess long-term trends in the Slave River, two parametric models were used: the MM robust analysis method (Rousseeuw and Yohai, 1984) and the Tobit regression survival analysis method (Lawless, 1982; Harrell, 2001).

Parametric methods assume a specific distribution for the model residuals and make other assumptions. Parametric models are used in this report due to increase in statistical power relative to nonparametric models, greater flexibility in modelling and ability to explicitly model potential interactions between trend and seasons.

Model assumptions for both the robust MM and the survival analysis models were that the data were independent, that the variability was similar among seasons (homoskedasticity) and that the data were normally distributed. Given that most of the Slave River data is not normally distributed, unless otherwise noted, all data were log-transformed prior to either method being used.

Robust Method

Water quality data is typically “heavy-tailed” relative to a standard normal distribution. Model building procedures that rely on this assumption when the assumption is not satisfied may produce models that are unduly influenced by observations in the tails.

This results in a model that does not describe the majority of the data as well as possible. The heavy-tailed distribution also adversely affects confidence intervals which may not achieve the stated coverage and may be incorrectly wide. Therefore robust linear models are used when the assumption of normality is not tenable for these water quality data with expected heavy tails. Many parameters in the Slave River dataset exhibited statistical distributions that were slightly asymmetric or symmetric but heavy-tailed. The robust method used in this report is the MM robust analysis method, developed by Rousseeuw and Yohai (1984).

Survival Analysis

The Slave River dataset contains observations that fall below the detection limit (censored data). If more than one detection limit is present in a dataset, for example due to changes in analytical methods, then observations are “multiply censored”. Some of the parameters in the Slave River dataset are multiply censored. Parametric survival regression models allow for multiply censored observations; the survival analysis used in this report is the Tobit regression method. Survival analyses are described in Lawless (1982) and Harrell (2001).

7.2.3.2 Level of Significance

In this report, trends are declared statistically significant if the p-value for that test is less than 0.05; this represents a 95% level of confidence. Because water quality is variable, a more conservative p-value ($0.05 \leq p \leq 0.1$; 90% level of confidence) allows for the identification of trends that are weakly detectable and therefore represent parameters that should also be watched carefully in the future. These trends are also reported throughout the report.

When presenting long-term trend results, only statistically significant trends (at the 95% confidence level) are graphically displayed as a solid line.

All p-values are noted in this report; estimated model coefficients and standard errors are presented in Zajdlik (2011b).

7.2.3.3 Flow Adjustment

River flow can influence the outcome of water quality trend analyses. For instance, during high-flow years, increased erosion and runoff can result in higher levels of particulate-associated parameters, such as iron, even if there are no changes in releases from point source inputs. On the other hand, during low-flow years when there is less dilution, certain parameters such as dissolved calcium, may seem higher, even though mass inputs of the compound have remained the same. As it is important to differentiate increases due to flow from those associated with point source inputs, the water quality data for each parameter were tested for a relationship with flow using the MM robust regression or Tobit regression survival analyses (Zajdlik, 2011b). If a relationship with flow was not found, then statistical tests were only conducted on the non flow-adjusted (raw) data. If a relationship with flow was found (at the 95% significance level), long-term temporal trends were assessed on both the raw and flow-adjusted data. Because the sequential sums of squares analysis was used, flow – adjusted data were not plotted and graphics are not available. Further explanation on the flow-weighting methodology can be found in Zajdlik (2011b). For the purposes of this report, flows from the Slave River at Fitzgerald hydrometric station (WSC Station ID 07NB001) were used for the flow-adjusted trend analyses. Daily means reported by the WSC on the date for which the water quality sample was collected were used.

7.2.3.4 Trend Result Comparisons

In 2009, Glozier *et al.* prepared the report: "Wood Buffalo National Park Water Quality: Status and Trends from 1989-2006 in Three Major Rivers; Athabasca, Peace and Slave". Annual trends were examined using Mann-Kendall on non flow-adjusted (raw) data and flow-adjusted data from 1989-2006 as well as the last decade (1997-2006; Glozier *et al.,* 2009). For the Slave River, Glozier found little to no change in the trend results between the non flow-adjusted and the flow-adjusted data, only the non flow-adjusted results were presented in that report.

In this report, temporal trend assessments were conducted on the water quality data from the entire period of record (1972-2010). When these trend results differed from those found in Glozier *et al.* (2009), additional annual temporal trend assessments were conducted on data from the 1989–2006 time period (the time period which was used by Glozier, 2009). This allowed for comparisons to be made between the two studies.

7.2.4 Dissolved versus Total Concentrations

Although the availability of metals associated with the solid phase varies, it is generally the dissolved form that is more toxic and biologically available for uptake by aquatic organisms (Glozier *et al*., 2009; MRBC, 1981). To explore this relationship further, the ratio of the dissolved metal concentration to the total concentration was calculated for each metal, for those samples where both forms were measured. The ratios for each metal were then averaged and presented in Section 7.3.5. As dissolved metals are not measured at Fort Smith, the ratios could only be calculated using data collected from the Fitzgerald site.

7.2.5 Seasonal Differences

The amount and timing of water flowing through a river can affect its water quality (USEPA, 2012i). As stream flow changes during the year, water quality conditions of the Slave River at Fitzgerald during high flows were compared to the water quality during low flows. All of the spring and summer values were combined to constitute high-flow conditions; winter values constituted low-flow conditions. The Mann-Whitney (Wilcoxon) non-parametric test was used to compare the high-flow median values to the low-flow (winter) median values for each parameter[10]. Differences were declared significant when the p-value was less than 0.05. The tests were carried out using Statgraphics Centurion XV (Version 15.1.03; Statgraphics, 2011). Due to the longer period of record and the higher frequency of sampling throughout the year, only the data from the Fitzgerald sampling location were used to assess seasonal differences of the surface water quality of the Slave River. In general, all parameters analyzed for seasonal differences had at least 10 years worth of continuous data and no more than 30% censored data. Further discussion on seasonal differences is included in Section 7.4.

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[10] The fall data was not used in this investigation as the fall samples were collected at a time of year when flows are typically somewhere in between high and low flows.

7.3 Results and Discussion

The discussion of results is grouped by the following surface water parameters: physical parameters, major ions, nutrients and metals. A brief introduction is provided for each parameter, followed by descriptive statistics for each sampling location: Slave River at Fitzgerald and Slave River at Fort Smith. Where applicable, values are compared to the relevant water quality guidelines for the protection of freshwater aquatic life (National guidelines or Provincial guidelines) and the relationship(s) between selected parameters are explored. For the Fitzgerald data, any long-term water quality trends are also discussed.

7.3.1 Physical Parameters

Summary
None of the physical parameters exceeded their respective CCME CPFAL guidelines.

pH - An increasing annual trend was found (at the 95% confidence level) in the 1989-2006 pH data, but not in the 1972-2010 dataset.

TDS - A decreasing annual trend was found in TDS (1993-2010) in non-flow-adjusted and flow-adjusted data (at the 95% confidence level).

TSS - TSS levels at both sites are higher than expected in winter; this could be due to sampling location and/or increased winter flows on the river. This should be investigated further.

Recommendation
Continued monitoring for physical parameters is recommended as they provide basic information on the water quality of rivers and can affect the behaviour and fate of metals. In addition, further investigation into the trends in pH and TDS and the potential impacts on the aquatic environment is recommended. The higher TSS levels in the winter should be researched, including an assessment of the winter sampling locations.

Physical parameters provide basic information on the water quality of rivers and can affect the behaviour and fate of metals. Accordingly, these parameters are very important for the interpretation of other results. The physical parameters discussed in this section include pH, specific conductance, total dissolved solids, total suspended solids, turbidity, dissolved oxygen and alkalinity. Table 7.2 summarizes the median values for each of the physical parameters from both sampling sites along the Slave River. A detailed summary table is included at the end of this section (Table 7.5).

Table 7.2: Median concentrations of physical parameters in Slave River surface water.

Parameter	**Units**	**Slave River at Fitzgerald**		**Slave River at Fort Smith**	
		n	**median**	**n**	**median**
pH	pH units	241	7.91	105	7.99
Specific Conductance	uS/cm	241	217	107	210
Total Dissolved Solids	mg/L	100	134	71	140
Total Suspended Solids	mg/L	229	76	99	108
Turbidity	NTU	241	54	104	61
Dissolved Oxygen	mg/L	126	11.8	10	14.4
Alkalinity	mg/L	237	84.3	84	82.2

At Fitzgerald, pH and specific conductance were measured in the field at the time of sampling. However, as only laboratory data for these parameters are available for Fort Smith, field measurements from Fitzgerald are not presented in this report.

7.3.1.1 pH

Background

The acidity or basic nature of a solution is expressed as pH. It is measured on a scale of 0-14 pH units, where a pH of 7 indicates a neutral condition (typically drinking water). A solution with a pH value less than 7 is considered to be acidic, whereas a solution with a pH value greater than 7 is considered basic (CCME, 1999). Each change in pH unit represents a tenfold change in acidity (CCME, 1999). For example, a solution at pH 3 is ten times more acidic than a solution at pH 4. The pH of water is determined by the geology of the watershed and is influenced by the seasonal and daily variations in photosynthesis, respiration and decomposition. Municipal and industrial effluents which result in increased photosynthesis in a river may cause long-term increases in pH (Michaud, 1991). Additional anthropogenic activities which may affect pH include mining, agriculture, and acidic precipitation (BC MOE, 1998).

The pH of water determines the solubility and biological availability of chemical constituents such as nutrients and heavy metals. For example, in addition to affecting how much and what form of phosphorus is most abundant in the water, pH also determines whether aquatic life can use it. Heavy metals tend to be more toxic at lower pH because they are more soluble (Michaud, 1991).

The CCME CPFAL guideline for pH ranges from 6.5 to 9.0.

Results

In the Slave River at Fort Smith, measurements of pH ranged from 7.30 to 8.40 (n=105; 1982-2010), which was within the range measured at Fitzgerald (6.80 to 8.68; n=241; 1972-2010). The pH values from both sites were within the CPFAL guideline range (6.5-9.0). As a comparison, pH levels in the Peel River ranged from 6.73 to 8.55 (n=151) and from 7.52 to 8.33 in the Liard River (n=166).

Long-term temporal trend assessment of the 1972-2010 pH data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.1).

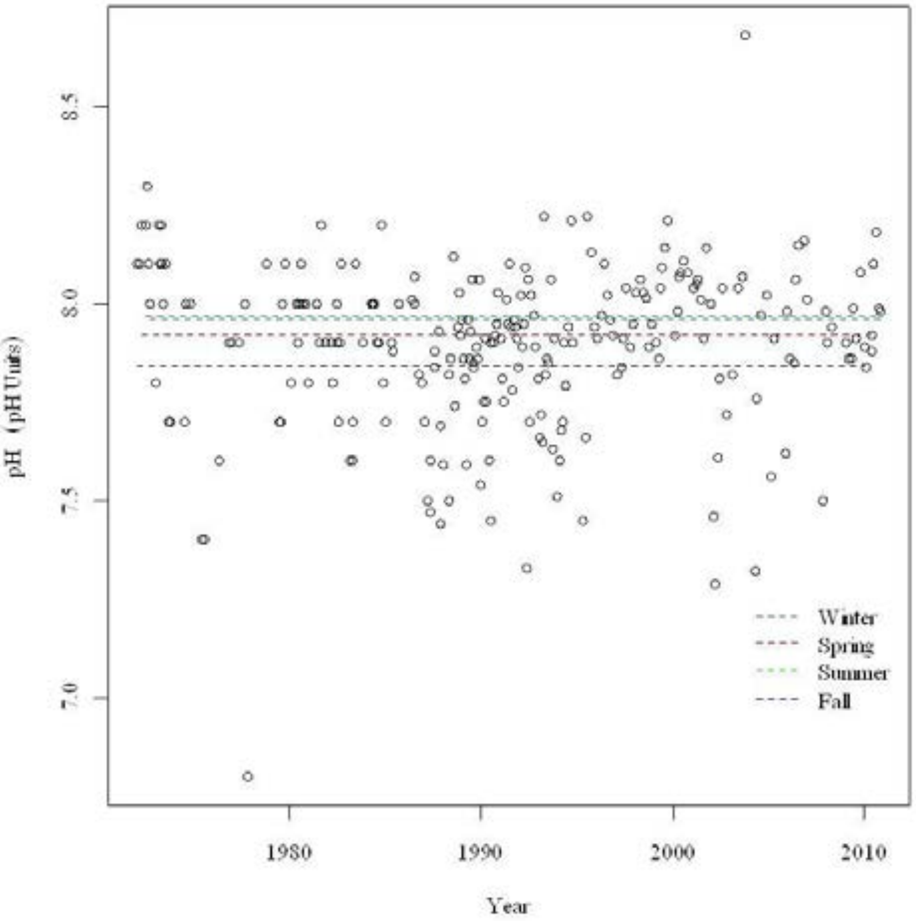

Figure 7.1: Trend Results - Non flow-adjusted pH concentrations from Fitzgerald (1972-2010). No significant trends were found at the 90% or 95% confidence level (from Zajdlik, 2011b). pH data were not log transformed.

However, Glozier *et al.* (2009) reported a significant increasing annual trend in the 1989-2006 pH data. When the database was truncated to match the1989-2006 time period used by Environment Canada, the results of the two analyses agreed; a significant increasing annual trend was found (p=0.004; Appendix 7-1; Zajdlik, 2011a). Long-term increasing trends in pH in the Slave River were also identified by WER Agra (1993) during two time periods: 1960-1992 and 1980-1992. It was suggested that the increase in pH was due to increased biological activity in the river (WER Agra, 1993). These comparisons highlight the influence of time period on the trend results and emphasize the importance of developing standard protocols for long-term statistical trend analysis.

As pH did not reveal a relationship with flow, trends with the flow-adjusted data were not examined.

Recommendation

All pH values met the CCME CPFAL guidelines of 6.5 to 9.0. However, in light of increasing trends identified by Glozier *et al.* and WER Agra and replicated in this report for the 1989-2006 time period, research into the cause and impacts of a potential increasing trend should be considered. Comparisons to other rivers throughout this region and Canada should also be made, to determine if increases are occurring on a regional and/or national scale.

7.3.1.2 Specific Conductance

Background

Specific conductance is a measure of the ability of an aqueous solution to conduct an electrical current and is a useful indicator of the amount of salts in a sample (such as Ca, Mg, Na, K, and certain dissolved metals). Specific conductance of most natural surface waters range from 50 to 1500 µS/cm (McNeely *et al.*, 1979). The conductivity of a river is determined by the geology of the watershed, with rivers which run through granite bedrock having lower conductivity levels than those which run through limestone and clay soils. Conductivity is also influenced by anthropogenic sources such as road salt, urban runoff and industrial inputs (LCRA, 2011). Significant changes in conductivity can be an indicator that a discharge or some other source of pollution has entered a stream.

There is currently no CCME CPFAL guideline for specific conductivity.

Results

The laboratory measurements of specific conductance in water samples collected from Fort Smith ranged from 169 to 340 µS/cm (n=107; 1982-2010) and fell within the range recorded at Fitzgerald (138 to 364 µS/cm; n=241; 1972-2010). As a comparison, specific conductance levels in the Peel River ranged from 130-520 µS/cm (n=152) and from 180-474 µS/cm in the Liard River (n=166).

Long-term temporal trend assessment of the 1972-2010 specific conductance data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). No significant trends were found annually or in the individual seasons at the 90% or 95% confidence level (p-values range from 0.1779 to 0.8331; Figure 7.2).

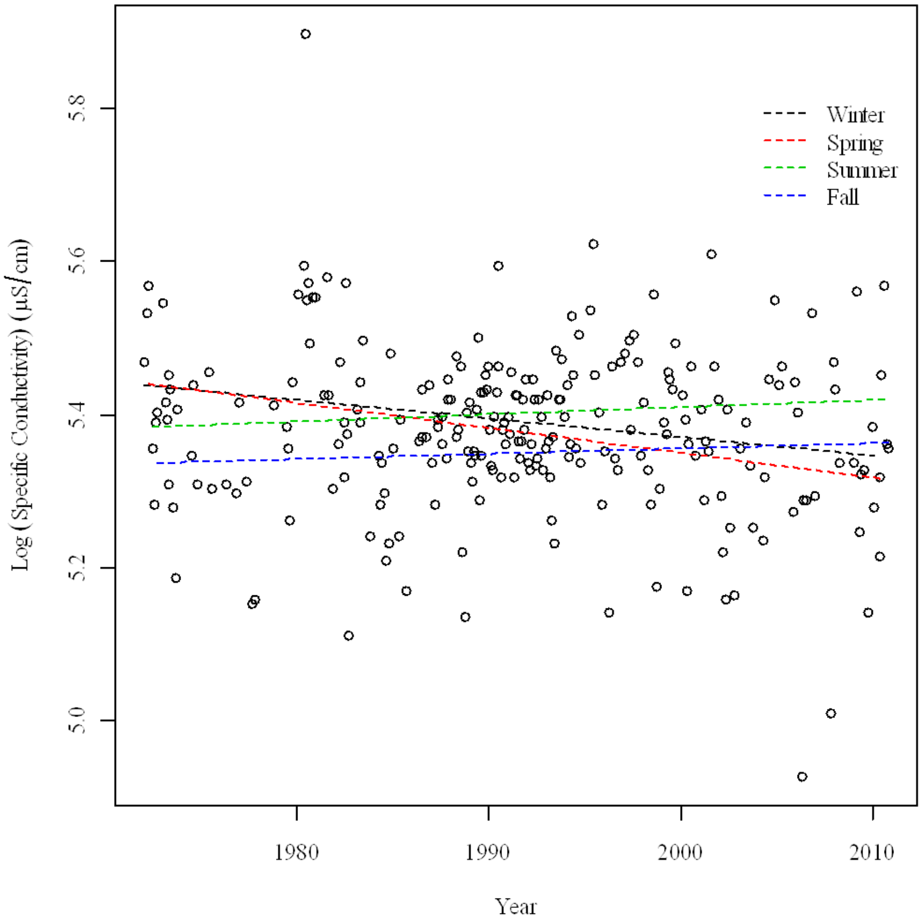

Figure 7.2: Trend Results - Non flow-adjusted specific conductance concentrations from Fitzgerald (1972-2010). Although trend lines have been displayed for all seasons, none are significant at the 90% or 95% confidence level (from Zajdlik, 2011b).

Environment Canada also reported no significant annual trends in specific conductance during the 1989-2006 period of record, or during the last decade (1997-2006; Glozier *et al.*, 2009).

As specific conductance did not reveal a relationship with flow, trends with the flow-adjusted data were not examined.

Recommendation

Conductivity is useful as a general measure of stream water quality and can be used to monitor changes in the aquatic environment (USEPA, 2012h). For these reasons, it is recommended to continue as a part of the monitoring program on the Slave River.

7.3.1.3 Total Dissolved Solids

Background

Total dissolved solids (TDS), like specific conductance, is also a measure of the concentration of dissolved substances in water (bicarbonate, chloride, sulphate, calcium, magnesium, sodium and potassium) (CCREM, 1987). TDS is separated from total suspended solids (TSS) by filtration and is a measure of the dissolved inorganic ions and organic matter that will pass through a 1.2 µm pore sized filter (Taiga, 2011a). Total dissolved solids in water supplies originate from natural sources, sewage, urban and agricultural runoff and industrial wastewater. Concentrations of TDS are highly variable in Canadian surface waters owing mainly to different mineral solubilities in different geological regions (Health Canada, 1991). Throughout the North, average TDS levels ranged from 7 to 265 mg/L in 20 different rivers monitored in the NWT (Environment Canada, 1990).

There is currently no CCME CPFAL guideline for total dissolved solids.

Results

Fitzgerald and Fort Smith had very similar average TDS values of 145 mg/L (65-387 mg/L; n=100; 1993-2010) and 142 mg/L (46-240 mg/L; n=71; 1982-2010), respectively. For comparison, the average TDS value in the Peel River was 234 mg/L and range from 110 to 320 mg/L (n=64; 1993-2005). In the Liard River, the average TDS value was 186 mg/L and range from 78 to 289 mg/L (n=61; 1993-2005).

Long-term trend assessment of the 1993-2010[11] TDS data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends. A significant decreasing trend was found in the annual data at the 95% confidence level (p=0.0340), which is implied for each of the individual seasons (Figure 7.3). The average decrease in concentration over the period of record (1993-2010) was estimated to be 19.5 mg/L (see Section 7.2.3 of this report).

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[11] Note: Prior to 1993, TDS was calculated from other data. From 1993-2007, TDS was measured directly. In this report, only the 1993-2007 data was used.

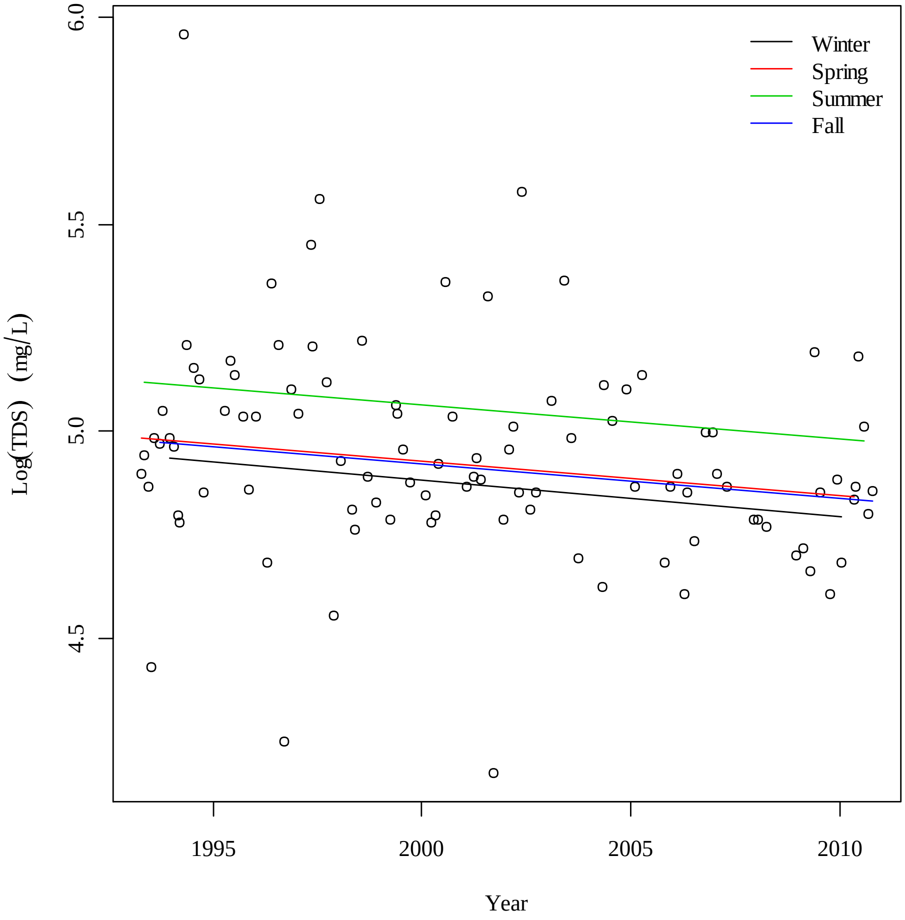


Figure 7.3: Trend Results - Non flow-adjusted TDS concentrations from Fitzgerald (1993-2010). The significant decreasing annual trend (p=0.0340) is implied for all 4 seasons (from Zajdlik, 2011b).

Because TDS revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year (Appendix 7-1). The data continued to reveal a significant decreasing annual trend in TDS (p=0.0264), which is implied for each of the seasons.

Although Glozier *et al.* (2009), reported no significant annual trend with the 1989-2006 data, they did report a significant decreasing trend over the last decade (1997-2006), which aligns with the results found in this report.

<u>Recommendation</u>
It is recommended that the reason and potential impacts of the decreasing trend of total dissolved solids in the river be investigated.

7.3.1.4 Total Suspended Solids

<u>Background</u>
Total suspended solids (TSS) is a particularly important physical parameter because it can influence the concentrations of many water quality parameters in the river, such as metals (Michaud, 1991). TSS is a measure of all the material (silt, clay and sand particles) suspended in the water column that will not pass through a 1.2 µm porosity filter (CCME, 1999; Taiga, 2011b). Organic material, such as plankton, bacteria and detritus, which are washed into the river from the surrounding land, can also contribute to the TSS level of water. Natural erosion of underlying geological formations is the most common source of suspended sediments to a water body (CCME, 1999).

As watersheds develop, there is an increase in disturbed areas (e.g., cropland or clearing of overburden at construction and/or mining sites), a decrease in vegetation, and increases in the rate of runoff. These all cause increases in erosion, particulate matter, and nutrients (Michaud, 1991). Human activities that can contribute sediment to water bodies include forestry, road construction, navigation dredging, agriculture, wastewater discharges, mining activities and other land disturbances (CCME, 1999).

There is currently no CCME CPFAL guideline for total suspended solids.

<u>Results</u>
TSS levels tend to be variable in highly sediment laden rivers and the Slave River is no exception. TSS levels ranged from <3 to 5600 mg/L (n=229; 1972-2010) at Fitzgerald and from <3 to 2800 mg/L (n=99; 1982-2010) at Fort Smith. High median TSS concentrations were recorded with 76 mg/L at Fitzgerald and 108 mg/L at Fort Smith. As a comparison, Environment Canada recorded TSS levels between 1 and 3627 mg/L in the Liard River (n=172; median=31 mg/L, and 1 to 1853 mg/L in the Peel River (n=153; median=17 mg/L).

Fitzgerald Sampling Site
Typically, TSS concentrations are related to river flow, with highest concentrations of TSS occurring during the open-water season, when water levels are high. The lowest TSS concentrations are usually observed during the winter, when the river is ice covered. At Fitzgerald, TSS concentrations generally followed this pattern (Figure 7.4).

In the summer, values ranged from 6 - 5600 mg/L, with a median value of 176 mg/L. In the spring, values ranged from 8 to 2630 mg/L (median = 133 mg/L). Lower levels were observed in the fall (12 - 523 mg/L; median = 64 mg/L). While the winter median value of 14 mg/L was low, the range of TSS values in the winter was higher and more variable than expected (<3 - 1110 mg/L; Figure 7.5).

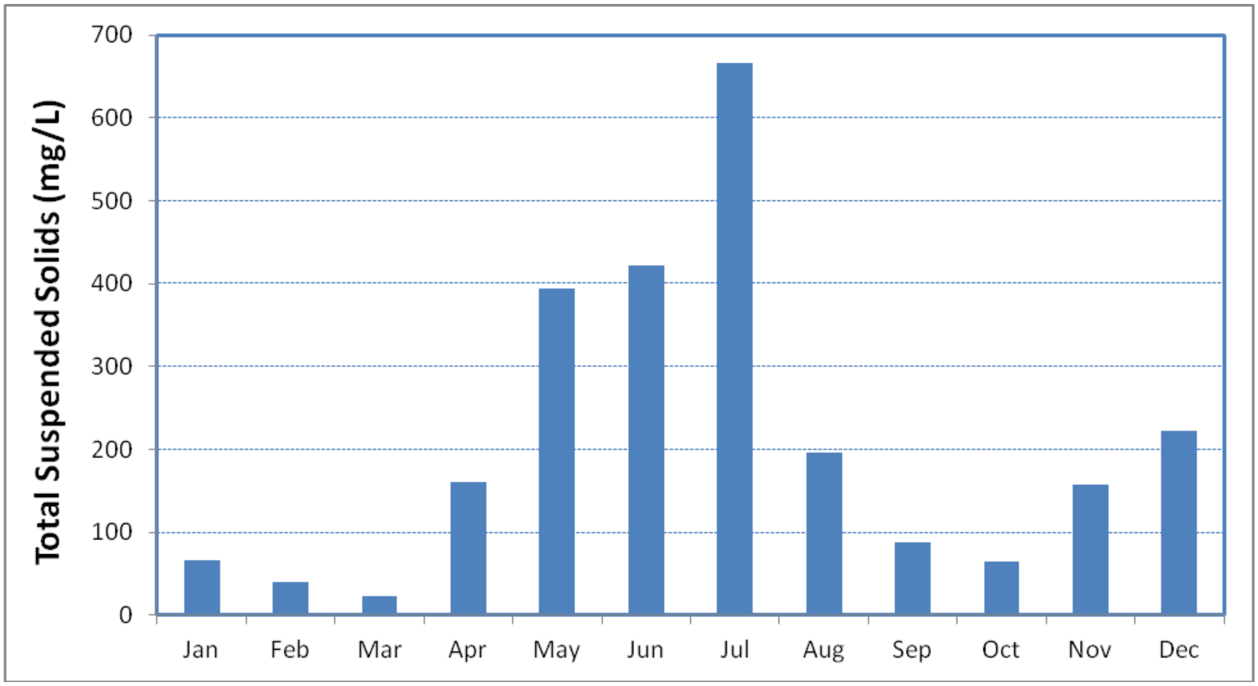
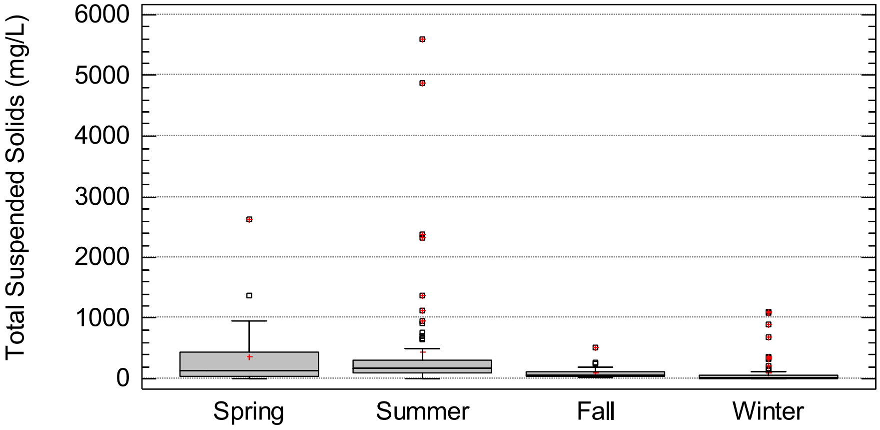


Figure 7.4: Mean monthly TSS concentrations (mg/L) at Fitzgerald (1972-2010)



In November at Fitzgerald, the higher TSS levels could be the result of freeze up processes as winter settles in on the river. During December and January however, when the river is already ice-covered, TSS levels are higher than expected. One possible explanation of this could due to sampling location. Field technicians have reported that due to the occurrence of a back eddy at the sampling location, it is sometimes difficult to effectively flush the ice hole prior to collecting the water sample (C. McCann. WSC, Environment Canada. Yellowknife, NWT. Pers. comm.). This could result in higher levels of TSS than would be expected in winter surface water samples. It is recommended that the winter sampling location be assessed to ensure that the site is representative of winter water quality in the Slave River at Fitzgerald.

Fort Smith Sampling Site

At Fort Smith, TSS concentrations also generally followed the pattern of higher levels during the open-water season and lower levels during the winter (Figure 7.6). In the summer, values ranged from 3 - 2800 mg/L (median: 216 mg/L) and in the spring, values ranged from 22 - 363 mg/L (median = 193 mg/L). Lower levels were observed in the fall (16 - 195 mg/L; median = 64 mg/L) (Figure 7.7). Similar to Fitzgerald, higher than expected winter TSS values were observed at the Fort Smith location (18 - 719 mg/L; median (73 mg/L)). The higher winter TSS values at Fort Smith are likely due to the upstream rapids, which remain open throughout the winter, causing frazil ice to form. The ice scours the river bottom and resuspends sand particles, resulting in higher levels of TSS than would be expected in a winter water sample (Sanderson *et al*., 1998).

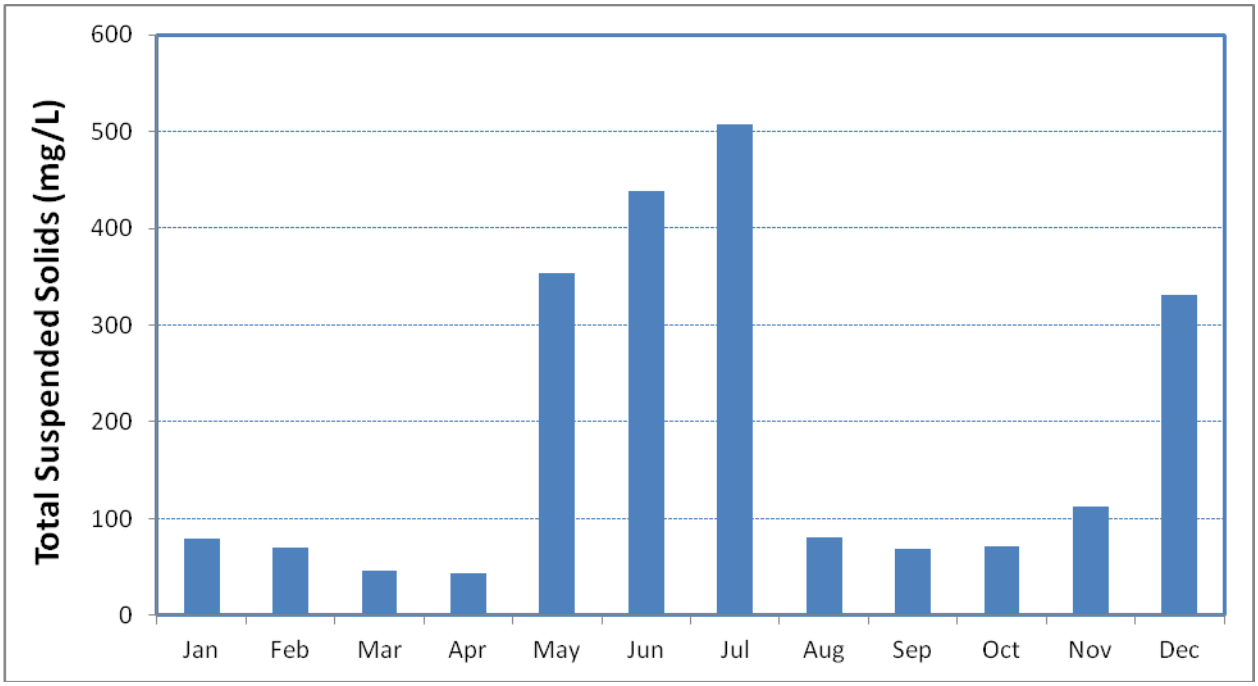


Figure 7.6: Mean monthly TSS concentrations (mg/L) at Fort Smith (1982-2010).

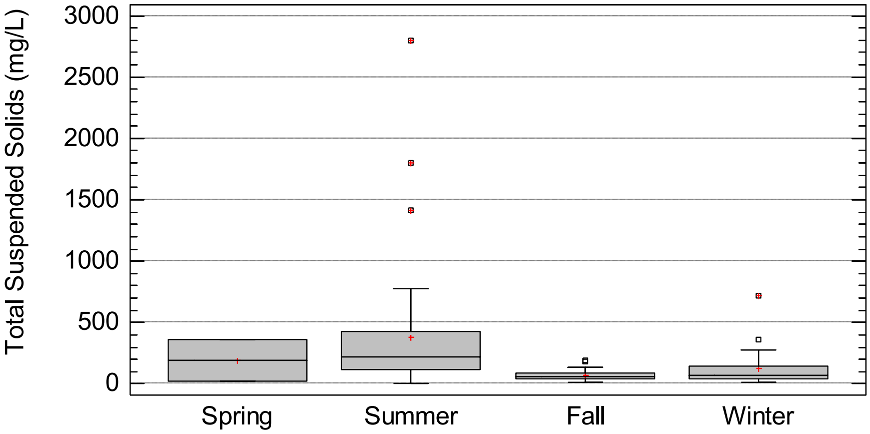


Figure 7.7: Seasonal pattern of TSS levels (mg/L) at Fort Smith (1982-2010).

It is important to point out however, that the higher winter TSS levels identified at both sampling locations on the Slave River may also be the result of increasing flows in the winter (see Chapter 6). It is recommended that further work be completed to determine if the significant increasing trend in winter flows are having an impact on winter water quality.

TSS and Flow

The relationship between TSS and flow in the Slave River was examined using the Spearman rank correlation test which measures the strength of the association between the two parameters. In order to evaluate paired samples, the mean daily flow was calculated for those days on which water quality samples were collected.

There is a moderate relationship between TSS and flow over the entire year at both sampling locations (Fitzgerald: r_s=0.64 and Fort Smith: r_s=0.62). When examined by season, the strongest correlations occur during the spring (r_s=0.88) and summer (r_s rs= 0.60) at Fitzgerald and during the summer at Fort Smith (r_s=0.58) (Table 7.3). As mentioned previously, the issues with sampling location and the significant increasing trends in winter flows may account for the lack of correlation in the winter, which would in turn affect the annual correlation results.

Table 7.3: Spearman rank correlation coefficients (r_s) and probabilities (p) between flow and TSS (overall and by season) at Fitzgerald and Fort Smith.

	Full Data Set		**Spring**		**Summer**		**Fall**		**Winter**	
	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)
Fitzgerald	0.64	<<0.05	0.88	<<0.05	0.60	<<0.05	0.28	NSS	0.02	NSS
Fort Smith	0.62	<<0.05	not enough data		0.58	0.0002	0.52	0.0046	0.23	NSS

NSS: not statistically significant

Long-term temporal trend assessment of the 1972-2010 TSS data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.8).

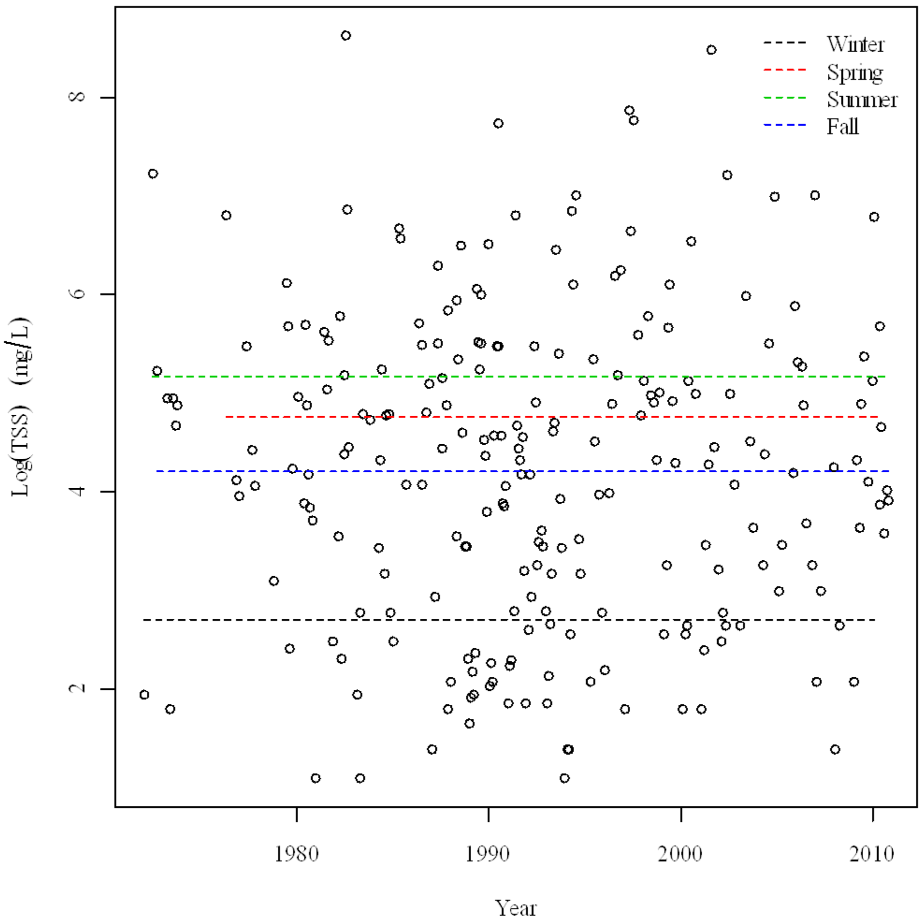


Figure 7.8: Trend Results - Non flow-adjusted TSS concentrations from Fitzgerald (1972-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Because TSS revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

The study conducted by Environment Canada (2009) did not assess temporal trends in TSS.

Recommendation

TSS is a very useful measure of stream water quality and can be used to monitor change in the aquatic environment. Given that metals and organic compounds tend to attach to suspended sediments, and can be transported downstream long distances from their source, TSS should continue to be a part of the Slave River monitoring program. It is recommended that further work be completed to determine if the significant increasing trend in winter flows is having an impact on water quality.

It is also recommended that the winter sampling location be assessed to ensure that the site is representative of winter water quality in the Slave River at Fitzgerald.

7.3.1.5 Turbidity

Background

Total suspended solids (TSS) and turbidity are both indicators of the amount of solids suspended in the water, whether mineral (e.g., soil particles) or organic (e.g., algae). While the TSS test measures an actual weight of material per volume of water, turbidity measures the amount of light scattered from a sample; more suspended particles cause greater scattering (Michaud, 1991). Turbidity is, therefore, is an indirect measure of the amount of suspended particles in water (silt, clay, organic matter and microscopic organism) which are held in suspension by turbulent flow (McNeely *et al*., 1979). These particles originate from surface runoff, instream bank and bed erosion, algal growth and anthropogenic sources, such as land disturbances, forest harvesting, agriculture and sewage, mining and industrial effluents (MRBC, 1985; BC MOE, 1998). Turbidity can also increase as a result of rainfall events or land disturbances.

Turbidity values, measured in Nephelometric Turbidity Units (NTU), reflect both the amount of suspended material in the water and its nature. Fine clay particles, for example, create higher turbidity levels than an equal mass of sand particles (Taylor *et al*., 1998). Higher turbidity reduces the amount of light penetrating the water, which reduces photosynthesis and the production of DO (USEPA, 2012k).

There is currently no CCME CPFAL guideline for turbidity.

Results

Turbidity[12] varied greatly in the Slave River. Values ranged from 4 to 1870 NTU (n=104; 1982-2010) at Fort Smith, while at Fitzgerald, levels were between 3 to 6400 NTU (n= 241; 1972-2010). As a comparison, Environment Canada recorded turbidity levels between 1 and 2872 NTU in the Liard River (n=173) and 1 to 1340 NTU (n=159) in the Peel River.

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[12] Note that the Fitzgerald turbidity values (formerly measured in Jackson Turbidity Units (JTU) and more recently in Nephelometric Turbidity Units (NTU)) were merged as no significant difference was found between the two time periods (1972-1984 and 1985-2010) at the 95% confidence level (Mann-Whitney test; p=0.7902).

Mean monthly turbidity concentrations at Fitzgerald and Fort Smith are provided in Figures 7.9 and 7.10. Generally, at Fitzgerald, turbidity levels were highest during the open-water season and lower during the winter. Similar to that observed in TSS measurements, high levels of turbidity occurred in November and December. As discussed in the TSS section this may be a result of the winter sampling location and/or increases in winter flows. At Fort Smith, turbidity levels were highest from May to July and generally decreased from August to April (Figure 7.10).

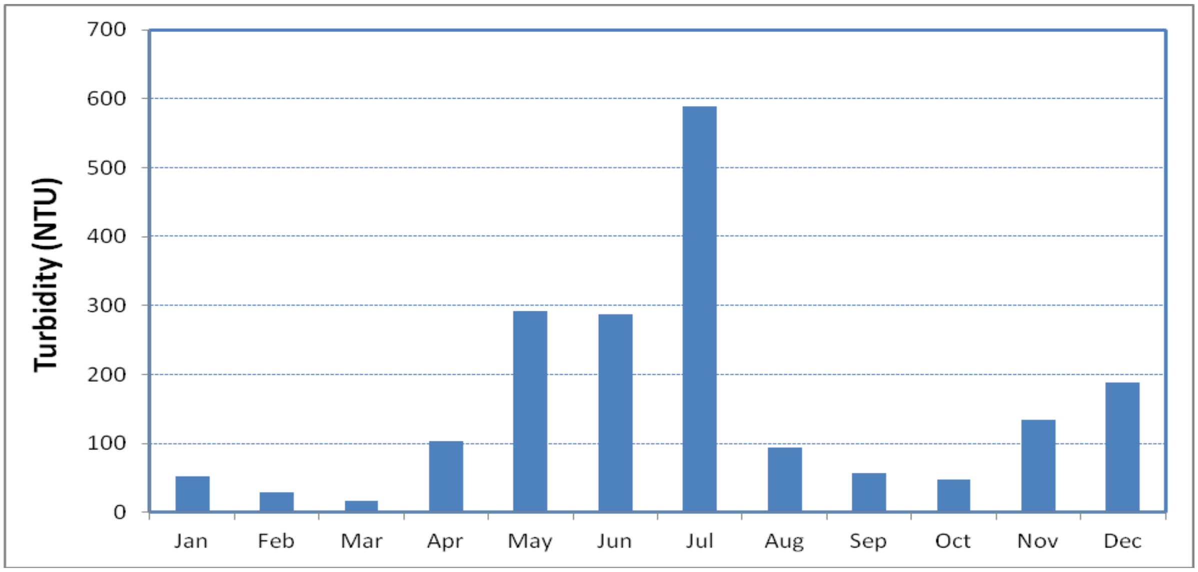

Figure 7.9: Mean monthly turbidity levels (NTU) from Fitzgerald (1972-2010).

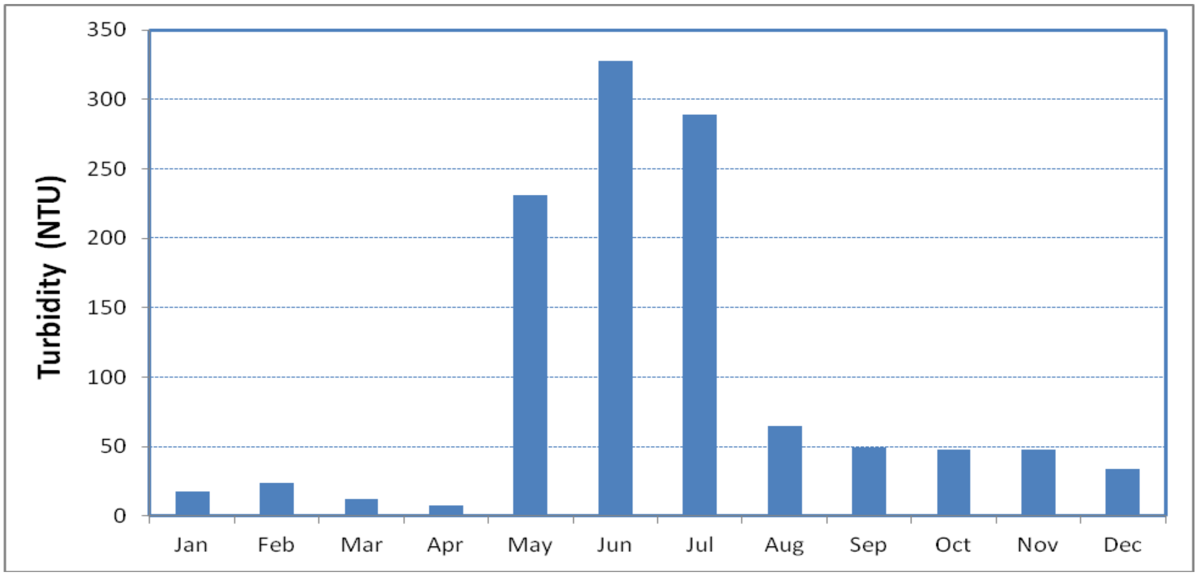

Figure 7.10: Mean monthly turbidity levels (NTU) from Fort Smith (1982-2010).

To understand the relationship between TSS and turbidity, the Spearman-rank correlation test was used (Table 7.4). As expected, at both locations, correlations were statistically significant and strong for the entire year and for most of the seasons. The slightly weaker correlation in the winter at Fort Smith is likely due to the presence of sand particles in the samples, which would increase the TSS results, but have less influence on the turbidity values.

Table 7.4: Spearman rank correlation coefficients (r_s) and probabilities (p) between TSS and turbidity (overall and by season) at Fitzgerald and Fort Smith.

	Full Data Set		**Spring**		**Summer**		**Fall**		**Winter**	
	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)	r_s	prob (p)
Fitzgerald	0.90	<<0.05	0.96	<<0.05	0.83	<<0.05	0.80	<<0.05	0.87	<<0.05
Fort Smith	0.75	<<0.05	not enough data		0.84	<<0.05	0.94	<<0.05	0.64	0.0026

Long-term temporal trend assessment of the 1972-2010 turbidity data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). No significant trends were found annually or in the individual seasons at the 90% or 95% confidence level (p-values range from 0.5924 to 0.8041; Figure 7.11).

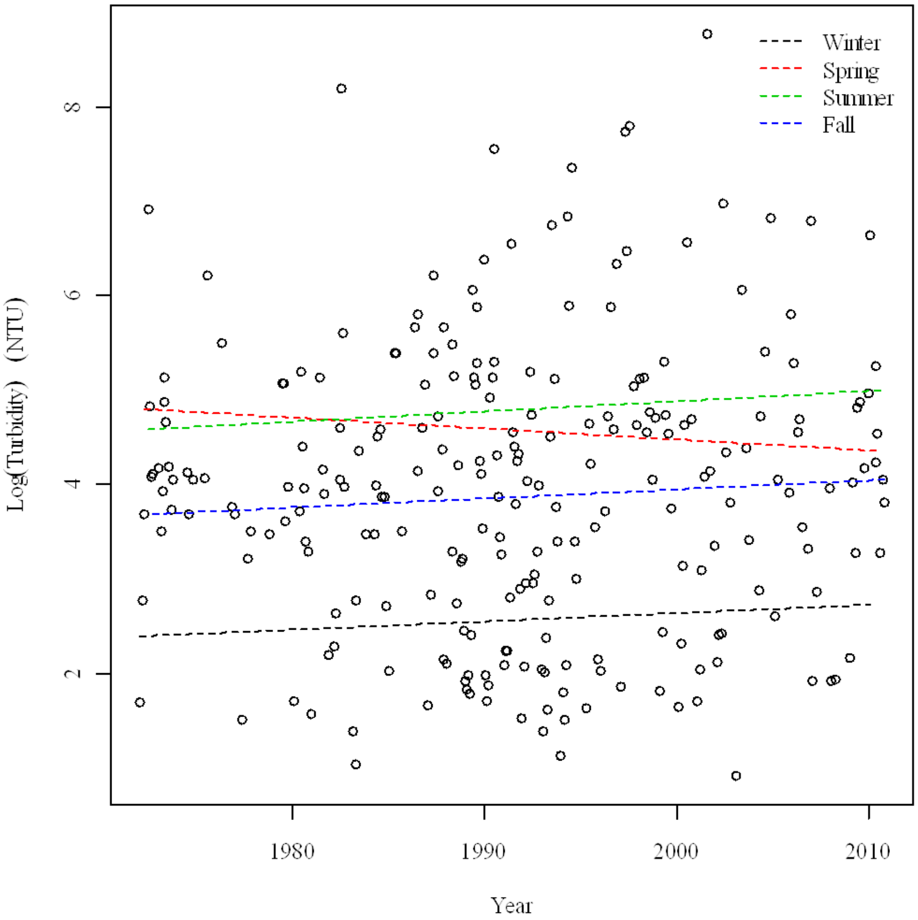

Figure 7.11: Trend Results - Non flow-adjusted turbidity concentrations from Fitzgerald (1972-2010). Although trend lines have been displayed for all seasons, none are statistically significant (at the 95% confidence interval; Zajdlik, 2011b).

Because turbidity revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be an interaction between season and year, but no significant temporal trends were found annually or in the individual seasons at the 90% or 95% confidence level (p-values range from 0.1522 to 0.9832; Appendix 7-1).

Environment Canada also reported no significant annual trends in turbidity with the 1989-2006 data or during the last decade (1997-2006; Glozier *et al.*, 2009).

Recommendation

Given that turbidity is a useful measure of stream water quality and can be used to monitor change in the aquatic environment and help to assess sampling locations, it is recommended that this parameter continue to be monitored in the Slave River.

7.3.1.6 Dissolved Oxygen

Background
Dissolved oxygen is a measurement of the amount of gaseous oxygen (O_2) dissolved in water. Oxygen gets into the water by diffusion from the surrounding air, by aeration (wind, waves, or rapids), and as a by-product of photosynthesis (CCME, 1999). Anthropogenic activities that can change the DO content of water include municipal wastewater, industrial effluent, pulp mills, forest harvesting, agriculture and stormwater runoff (Michaud, 1991; BC MOE, 1998). These activities often release chemical or biological constituents which consume large amounts of oxygen to during decomposition. Consequently, DO concentrations often decrease in waters located in developed watersheds (Michaud, 1991). Adequate dissolved oxygen levels are fundamental to maintain a healthy aquatic ecosystem (CCME, 1999). The amount of dissolved oxygen affects the solubility and availability of nutrients, and therefore the productivity of aquatic ecosystems (BC MOE, 1998).

Because the level of DO in freshwater is partly dependent on temperature (DO increases as temperature decreases), there are two CCME CPFAL guidelines for DO: 6 mg/L in warm water and 9.5 mg/L for cold water (CCME, 1999).

Results
Dissolved oxygen concentrations in the Slave River at Fitzgerald ranged between 6.0 and 16.6 mg/L over the period of record (n=126; 1989-2010). The median concentration of 11.8 mg/L met the CPFAL guideline established to protect aquatic organisms (6.0-9.5 mg/L) (CCREM, 1987). Dissolved oxygen was not measured at Fort Smith in recent years, but a review of the historical data for this location revealed that the water was typically well oxygenated (10.1-15.2 mg/L; n=10; 1990-1991), likely due to the four sets of rapids upstream. Dissolved oxygen levels are not measured in the Peel and Liard rivers.

In this report, long-term temporal trends in dissolved oxygen levels were not examined. However, Environment Canada did assess the Fitzgerald data for trends and found a significant increasing annual trend in dissolved oxygen from 1989-2006, as well as in the last decade (1997-2006; Glozier *et al*., 2009).

Recommendation
Additional studies on the causes and impacts of these increases should be implemented as per Environment Canada’s recommendation.

7.3.1.7 Alkalinity

Background

Alkalinity is a measure of the water's ability to neutralize an acid and is expressed as an equivalent of calcium carbonate. Calcium and magnesium carbonate contribute carbonate ions to water, increasing the alkalinity and buffering capacity of the water. In natural waters, alkalinity does not usually exceed 500 mg/L (CCREM, 1987). Alkalinity in streams is influenced by rocks, soils, salts and plant activities, as well as mining, industrial effluents and acidic precipitation (USEPA, 2012j; BC MOE, 1998).

Although there are currently no national CCME CPFAL guidelines for alkalinity, the USEPA has established a guideline of greater than 20 mg/L for the protection of aquatic life (USEPA, 1976).

Results

Concentrations recorded from the Slave River ranged from 60 to 130 (n=84; 1982-2010) at Fort Smith and 50 to 121 mg/L (n=237; 1972-2010) at Fitzgerald. The values recorded for the Slave River indicate that the river has a good buffering capacity to acidic inputs. As a comparison, Environment Canada recorded alkalinity concentrations ranging from 74 to 187 mg/L in the Liard River (n=177), and 52 to 174 mg/L in the Peel River (n=147).

For the period of record assessed in this report (1972-2010), none of the variables described a significant proportion of the variability in the alkalinity data (Zajdlik, 2011b). Consequently, no model could be fit, so a long-term trend analysis was not conducted for alkalinity. Further, as alkalinity did not reveal a relationship with flow, trends with the flow-adjusted data were not examined.

Glozier *et al.* (2009) reported no significant annual trends in alkalinity during the 1989-2006 period of record or during the last decade (1997-2006).

Recommendation

As alkalinity provides a general measure of stream water quality and can be used to monitor changes in the aquatic environment, it is recommended that alkalinity continue to be included in the monitoring program on the Slave River.

Table 7.5: Detailed statistical summaries for physical parameters - Slave River at Fitzgerald; Slave River at Fort Smith.

Slave River at Fitzgerald										
Physicals	**Period of Record**	**Units**	**n**	**# of NDs**	**Mean**	**St Dev**	**Median**	**Min**	**Max**	**90th %ile**
Alkalinity (as total $CaCO_3$)	1972-2010	mg/L	237	0	84.1	9.01	84.3	49.6	121	94.2
Oxygen Dissolved	1989-2010	mg/L	126	0	11.3	2.1	11.8	6	16.6	13.6
pH (Lab)	1972-2010	pH units	241	0	7.89	0.21	7.91	6.80	8.68	8.10
Specific Conductance (Lab)	1972-2010	us/cm	241	0	218	24	217	138	364	245
Total Dissolved Solids	1993-2010	mg/L	100	0	145	42	134	65	387	183
Total Suspended Solids	1972-2010	mg/L	229	1	241	593	76	<3	5600	528
Turbidity	1972-2010	NTU	241	0	187	555	54	3	6400	358

Slave River at Fort Smith										
Physicals	**Period of Record**	**Units**	**n**	**# of NDs**	**Mean**	**St Dev**	**Median**	**Min**	**Max**	**90th %ile**
Alkalinity (as total $CaCO_3$)	1982-2010	mg/L	84	0	84.2	12.2	82.2	59.4	130	95.8
Oxygen Dissolved	1990-1991	mg/L	10	0	13.5	2.1	14.4	10.1	15.2	15.1
pH (Lab)	1982-2010	pH units	105	0	7.93	0.21	7.99	7.30	8.40	8.15
Specific Conductance (Lab)	1982-2010	us/cm	107	0	213	24	210	169	340	238
Total Dissolved Solids	1982-2010	mg/L	71	0	142.2	32.6	140	46	240	179
Total Suspended Solids	1982-2010	mg/L	99	1	222	375	108	<3	2800	446
Turbidity	1982-2010	NTU	104	0	139	257	60.5	4	1870	337

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*NDs: number of values reported below the detection limit (censored observations).

Major Ions

Summary

Chloride was the only major ion for which CCME CPFAL guidelines exist. The guideline was not exceeded.

Sodium - Increasing spring and summer trends were found (at the 95% confidence level); increasing annual and fall trends were found (at the 90% confidence level). Following flow-adjustment, an increasing annual trend was found (at the 95% confidence level) which was implied for each of the individual seasons.

Sulphate –An increasing annual trend was found (at the 95% confidence level) which was implied for each of the individual seasons. Following flow-adjustment, summer and winter increasing trends were found (at the 95% confidence level); annual and fall increasing trends were found (at the 90% confidence level).

Potassium – A decreasing spring trend was found (at the 95% confidence level); following flow-adjustment, the data no longer exhibited a trend

Calcium – A decreasing annual trend was found (at the 90% confidence level) which was implied for each of the individual seasons. After flow-adjustment the data no longer exhibited a trend.

Recommendation

Continued monitoring for major ions is recommended to further investigate these trends and the potential impacts on the aquatic environment.

The major ions discussed in this section include the cations calcium, magnesium, potassium, and sodium; the anions discussed include sulphate, chloride, and fluoride. Slave River water hardness is also discussed. A detailed summary table can be found at the end of this section (Table 7.7).

Median concentrations of major ions for Slave River at Fitzgerald and Fort Smith are shown in Table 7.6. The laboratory reports major ions as either total or dissolved concentrations, but only total concentrations are available for Fort Smith. While both total and dissolved values are available for the Fitzgerald sampling location, due to the longer dataset, only dissolved concentrations[13] from Fitzgerald are discussed in detail in this report.

Table 7.6: Median concentrations of major ions.

Parameter	**Units**	**Slave River at Fitzgerald**		**Slave River at Fort Smith**	
		n	**median**	**n**	**median**
Calcium Dissolved	mg/L	242	28.3	--	--
Calcium Total	mg/L	59	29.5	95	27.8
Magnesium Dissolved	mg/L	216	6.6	--	--
Magnesium Total	mg/L	59	6.97	96	6.63
Sodium Dissolved	mg/L	242	6.3	--	--
Sodium Total	mg/L	59	5.3	74	6.27
Potassium Dissolved	mg/L	243	0.9	--	--
Potassium Total	mg/L	59	1.2	72	0.98
Sulphate Dissolved	mg/L	242	18.0	--	--
Sulphate Total	mg/L	--	--	106	18
Chloride Dissolved	mg/L	242	5.1	--	--
Chloride Total	mg/L	--	--	107	5.02
Fluoride Dissolved	mg/L	228	0.08	2	0.09
Bicarbonate (calcd)	mg/L	121	102	--	--
Hardness Total (calcd) $CaCO_3$	mg/L	204	98	101	96

As the weathering of rocks is the main source of ions in natural waters, concentrations in surface water vary according to regional geology. In the Slave River, calcium is the predominate cation, followed by magnesium and sodium; potassium makes only up a small portion of total cation concentrations. Major anions, in order of predominance (by equivalent weight) include bicarbonate, sulphate and chloride, with fluoride making up a very tiny contribution (Figure 7.12; Glozier *et al.*, 2009). This succession of major ions is almost universal among fresh inland waters of North America (Wetzel, 2001), thus the Slave River is typical in its ion composition.

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[13] At Fitzgerald, total concentrations of major ions were part of the Environment Canada monitoring program between 1993 and 2002, whereas dissolved concentrations of major ions have been analyzed from 1972 – present.

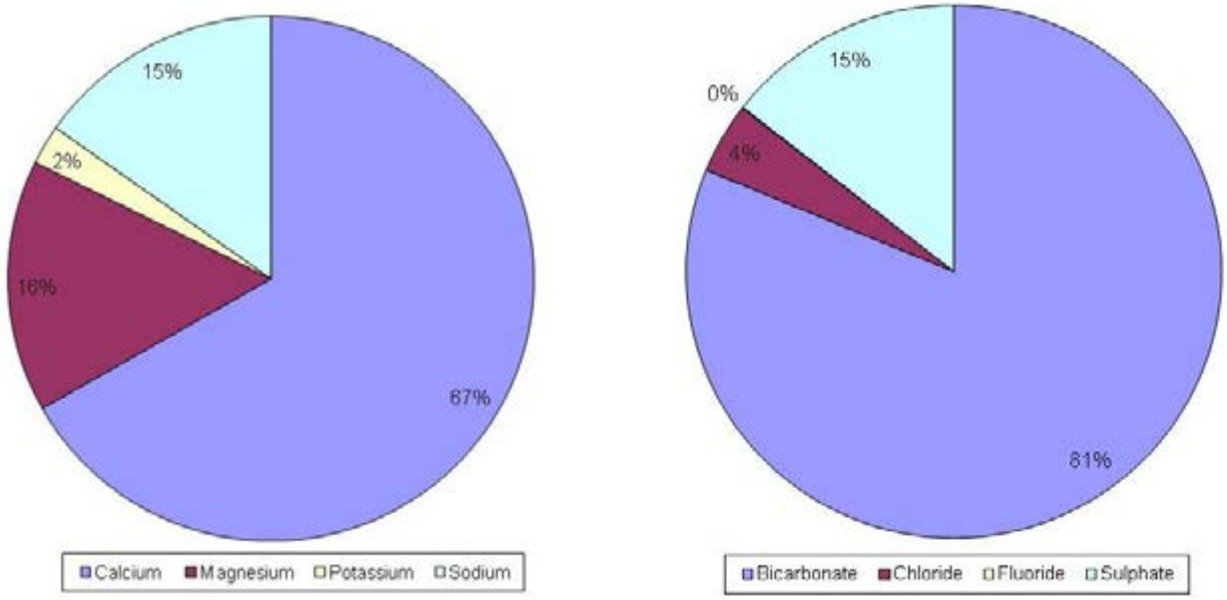

Figure 7.12: Average cation and anion percent contributions to Slave River water quality. Note: fluoride's contribution to water chemistry in the Slave River is 0.0006%.

7.3.2.1 Calcium

Background

Calcium is considered to be an essential element for all living organisms (Taylor, 2009). Calcium ions are among the most common ions occurring in nature (McNeely *et al.*, 1979) and enter the aquatic environment through the weathering of rocks, especially limestone, and from the soil, through seepage and runoff (CCREM, 1987). Lime (calcium oxide) is used in a variety of industries and as a wastewater treatment chemical (Health Canada, 1987). Levels of calcium in freshwaters range from 15 mg/L to 100 mg/L (CCREM, 1987). Calcium is an important parameter in regards to surface water quality, largely due to its influence on water hardness. Water hardness also plays a key role since the toxicity of several metals such as cadmium, copper, lead and nickel (CCREM, 1987) and zinc (BC MOE, 1999) decreases as water hardness increases.

There is currently no CCME CPFAL guideline for calcium.

Results

Concentrations of total calcium at Fort Smith ranged between 18 and 45 mg/L (n=95; 1982-2010), while dissolved calcium levels ranged from 16 to 42 mg/L at Fitzgerald (n=242; 1972-2010). As a comparison, Environment Canada recorded dissolved calcium levels between 12 and 68 mg/L in the Liard River (n=181) and from 22 to 63 mg/L (n=152) in the Peel River.

Long-term trend assessment of the 1972-2010 dissolved calcium data from Fitzgerald revealed no interaction between season and year (Appendix 7-1) and therefore, only the annual data was assessed for trends. Although the annual data did not show a significant trend at the 95% confidence level, a decreasing trend was found at the 90% confidence level (p=0.0947). This trend is implied for each of the individual seasons (Figure 7.13).

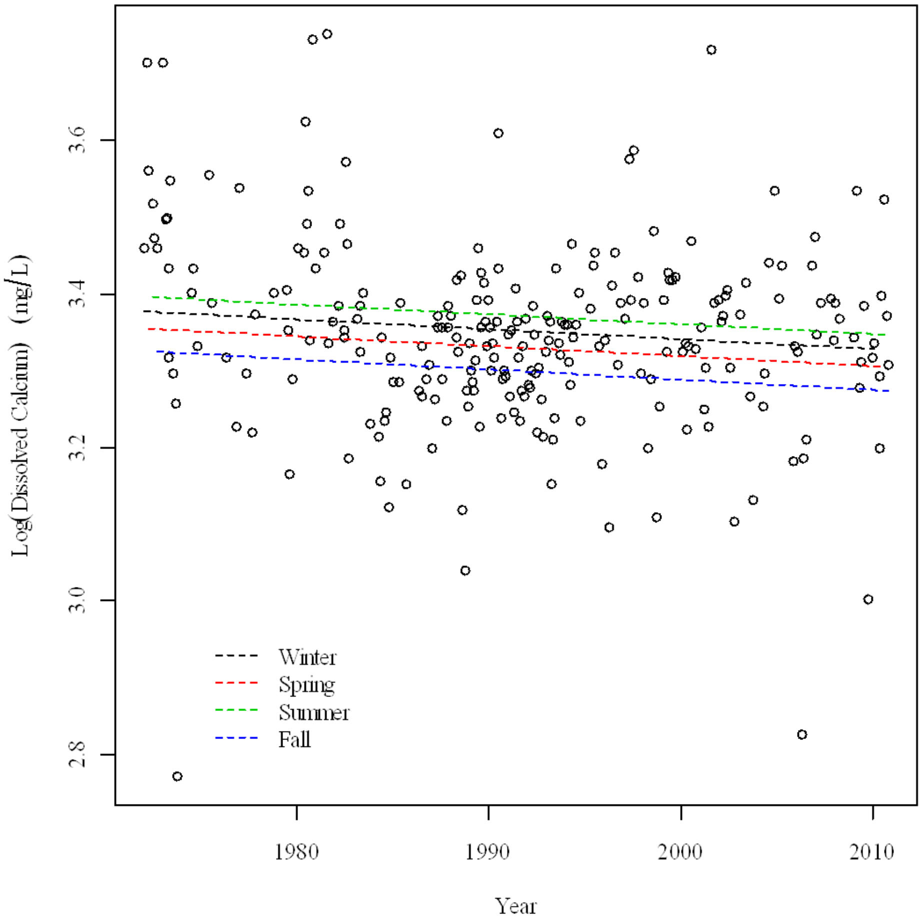

Figure 7.13: Trend Results - Non flow-adjusted dissolved calcium concentrations from Fitzgerald (1972-2010). Although trend lines have been displayed for all seasons, none are statistically significant at the 95% confidence interval (from Zajdlik, 2011b).

Because dissolved calcium revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year. The annual flow-adjusted data revealed no significant trend at the 90 or 95% confidence levels (Appendix 7-1).

Environment Canada also reported no significant trends during the 1989-2006 period of record or during the last decade for dissolved calcium data (1997-2006; Glozier *et al*., 2009).

Recommendation

Calcium is an important component of water hardness, which influences the toxicity of several metals. Therefore, it is recommended that calcium continue to be a part of the Slave River monitoring program.

7.3.2.2 Magnesium

Background

Magnesium is a common constituent of natural water and similar to calcium plays an important role in regards to water hardness (CCREM, 1987). Magnesium is considered to be an essential element for all living organisms (Taylor, 2009). Natural sources of magnesium are from the weathering of minerals, mainly dolomite (CCREM, 1987). Anthropogenic sources include discharges of cation-rich waters from operating and abandoned rock quarries (EPA, 1986). Water in watersheds with magnesium-containing rock may have magnesium in the concentration range of 1 to 100 mg/l (Taylor, 2009).

There is currently no CCME CPFAL guideline for magnesium.

Results

Concentrations of total magnesium at Fort Smith ranged between 2.5 and 10.6 mg/L (n=96; 1982-2010), while dissolved magnesium concentrations ranged from 4.1 to 8.8 mg/L at Fitzgerald (n=216; 1978-2010). As a comparison, Environment Canada recorded dissolved magnesium levels between 9 and 38 mg/L in the Liard River (n=43), and between 6 and 20 mg/L in the Peel River (n=152).

Long-term temporal trend assessment of the 1978-2010 dissolved magnesium data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.14).

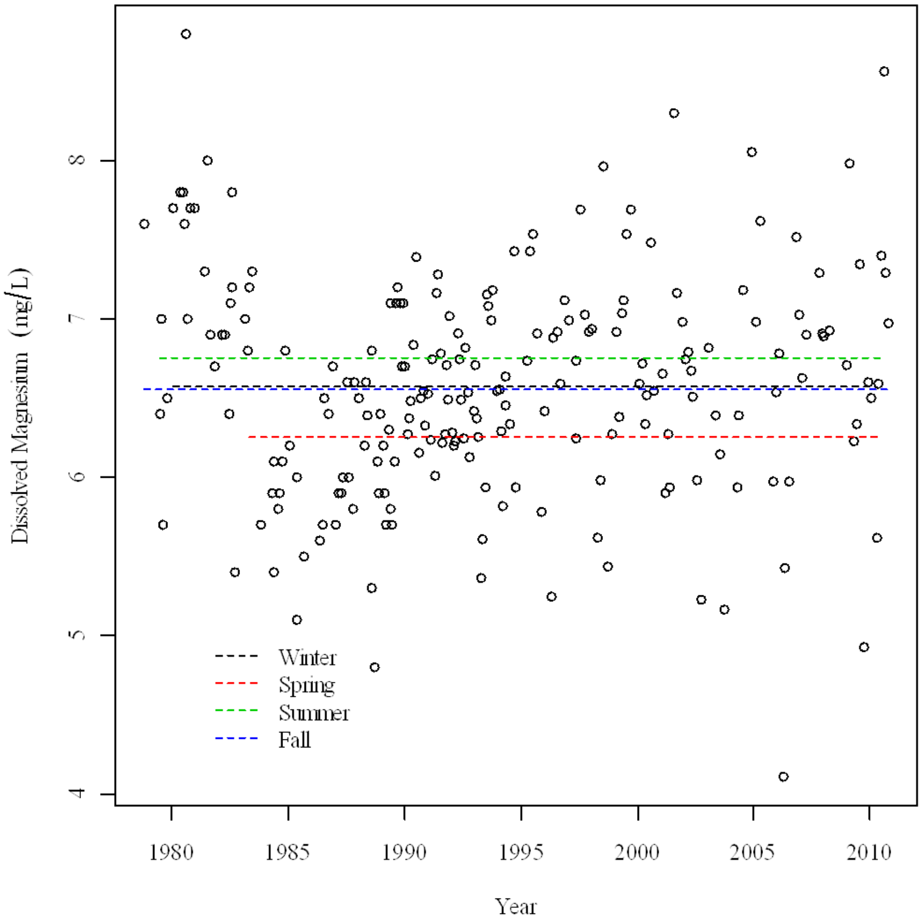

Figure 7.14:Trend Results - Non flow-adjusted dissolved magnesium concentrations from Fitzgerald (1972-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b). Dissolved magnesium data were not log-transformed.

As dissolved magnesium did not reveal a relationship with flow, trends with the flow-adjusted data were not examined.

Environment Canada also reported no significant trends during the 1989-2006 period of record or during the last decade (1997-2006; Glozier *et al.*, 2009).

Recommendation

Magnesium is an important component of water hardness, which influences the toxicity of several metals. Therefore, it is recommended that magnesium continue to be a part of the Slave River monitoring program.

7.3.2.3 Hardness

Background

Water hardness is calculated as the sum of calcium carbonate and magnesium carbonate concentrations. It is expressed as an equivalent of calcium carbonate using the following formula (Eaton *et al*., 2005).

$[CaCO_3] = 2.497 \times [Ca^{2+}] + 4.117 \times [Mg^{2+}]$

Water hardness is a measure of the capacity of water to react with soap to form suds (McNeely *et al*., 1979). As the calcium and magnesium ions in water combine with soap molecules, hard water requires a considerable amount of soap to produce lather. Hard water also leads to scaling of hot water pipes, boilers and other household appliances (Health Canada, 1979).

Information on water hardness is necessary for the interpretation of other water quality results, as it affects the toxicity of several metals (Alabaster and Lloyd, 1982) such as cadmium, copper, lead and nickel (CCREM, 1987) and zinc (BC MOE, 1999).

There is currently no CCME CPFAL guideline for hardness.

The United States Geological Survey (USGS; 2011) uses the following general guidelines to characterize the hardness of bodies of freshwater.

Hardness as Calcium Carbonate (mg/L)	Category (Degree of Hardness)
0-60 mg/L	Soft water
61-120 mg/L	Moderately hard water
121-180 mg/L	Hard water
>180 mg/L	Very hard water

The hardness of water is determined by the geology of the watershed. Typically, waters originating from carbonate bedrock are hard, whereas waters draining igneous rock are soft. Water hardness may also be influenced by mining and industrial effluents (BC MOE, 1998).

Results

Water hardness at Fort Smith ranged from 58 to 152 mg/L (n=101; median=96 mg/L; 1982-2010), and from 59 to 138 mg/L at Fitzgerald (n=204; median=98 mg/L; 1972-2010). Under the above USGS classification system, the Slave River would be characterized as having moderately hard waters.

As the Slave River flows along the boundary between the Interior Plains (carbonate-type bedrock) and the Precambrian Shield (igneous-type geology), it is not surprising that its water falls within the middle range category (Figure 7.15; MacLock *et al*., 1997).

Figure 7.15: The main physiographic regions of the Mackenzie River Basin.

As a comparison, Environment Canada recorded hardness concentrations between 58 and 249 mg/L in the Liard River (n=154), and, between 78 and 239 mg/L in the Peel River (n=128).

Long-term temporal trend assessment of the 1972-2010 water hardness data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.16).

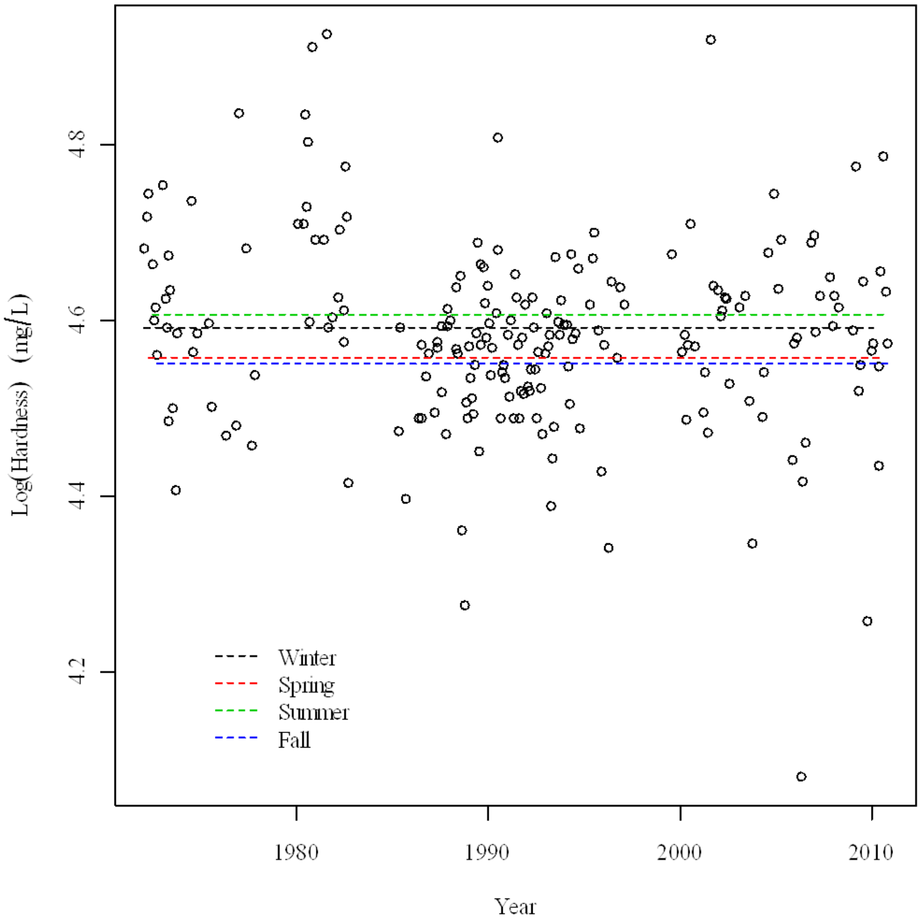

Figure 7.16: Trend Results - Non flow-adjusted water hardness concentrations from Fitzgerald (1972-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

As water hardness did not reveal a relationship with flow, trends with the flow-adjusted data were not examined. Environment Canada did not examine temporal trends in water hardness.

Recommendation

As water hardness is useful as a general measure of stream water quality and affects the toxicity of several metals, it should continue to be included in future monitoring on the Slave River.

7.3.2.4 Sodium

Background

Sodium is a non-toxic metal which is abundant, widely distributed in nature, and present to some extent in all natural waters (Taylor, 2009; McNeely *et al*., 1979). The principal natural sources of sodium are from the weathering of igneous rock and salt deposits, as well as the leaching of soils. Anthropogenic sources include road de-icing salt, manufacture of detergents and pulp and paper industries (CCREM, 1987; Taylor, 2009). Sodium minerals are highly soluble and once dissolved, tend to remain in solution.

In Canadian surface waters, sodium ranges from less than 1 mg/L to more than 300 mg/L, depending on the geography and underlying geology of the area, as well as rainfall and evaporation (Ontario MOE, 1981; Taylor, 2009).

Currently, there is no CCME freshwater aquatic life guideline for sodium. However, the Canadian Drinking Water Quality (CDWQ) aesthetic guideline for sodium is <200 mg/L (Health Canada, 1992). Aesthetic guidelines ensure that water quality is of good aesthetic quality (appearance, smell and taste).

Results

Total sodium concentrations at Fort Smith ranged from 1.1 to 15.7 mg/L (n=74; 1988-2010). At Fitzgerald, dissolved sodium concentrations ranged from 1.2 to 10.0 mg/L (n=242; 1972-2010). As a comparison, Environment Canada recorded dissolved sodium levels between 0.7 and 8.3 mg/L in the Liard River (n=181), and between 1.8 and 9.9 mg/L in the Peel River (n=157).

Long-term temporal trend assessment of the 1972-2010 dissolved sodium data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). Significant increasing trends, at the 95% confidence level, were found during the spring and summer seasons (1972-2010; p_{spring}=0.0352 and p_{summer}=0.0097; Figure 7.17). The average increase in concentration over the period of record (1972-2010) during the spring and summer was estimated to be 1.5 mg/L (see Section 7.2.3 of this report). Note that annual and fall increasing trends were significant at the 90% level of confidence (p=0.0572 for both) and no significant trend was found in the winter data (p= 0.7595; Appendix 7-1).

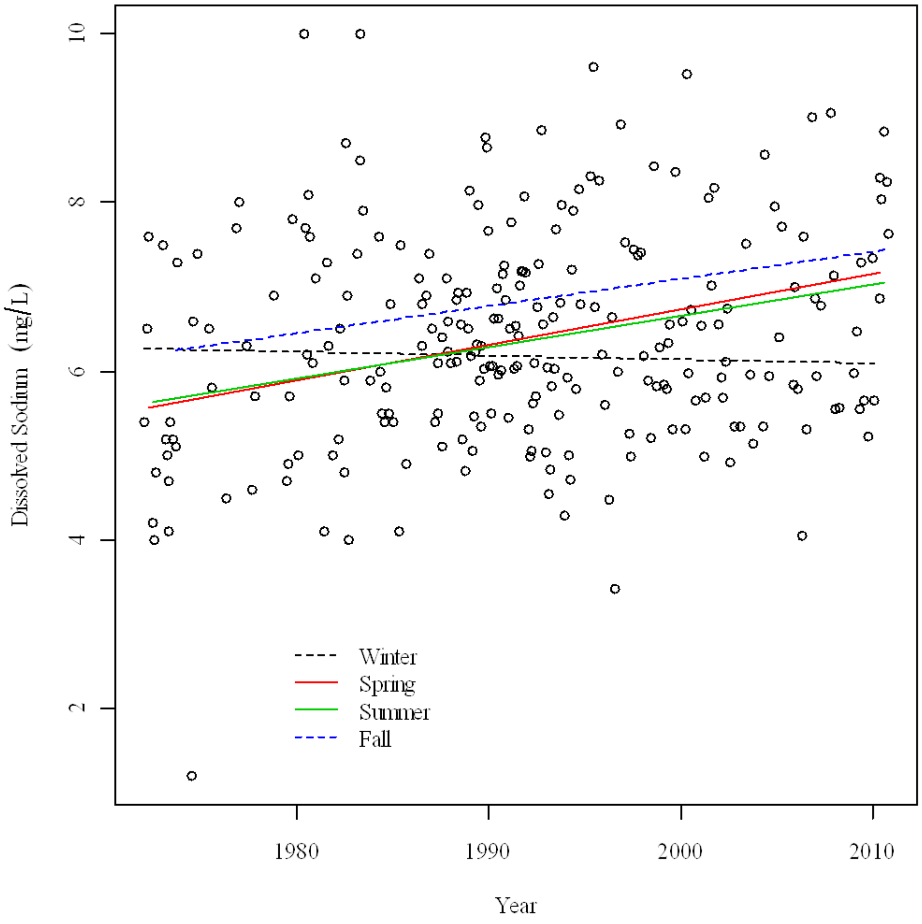

Figure 7.17: Trend Results - Non flow-adjusted dissolved sodium concentrations from Fitzgerald (1972-2010). Although trend lines have been displayed for all seasons, only the increasing trends for spring and summer are statistically significant at the 95% confidence level (from Zajdlik, 2011b). Dissolved sodium data were not log-transformed.

Because dissolved sodium revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there was no longer an interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends. A significant increasing annual trend (at the 95% confidence level; p=0.0228) was found and this trend is implied for each of the individual seasons.

Environment Canada reported no significant annual trends in the dissolved sodium data during the 1989-2006 period of record or during the last decade (1997-2006; Glozier *et al.*, 2009). However, when the database was truncated to match the1989-2006 time period used by Glozier *et al.* (2009), the results of the two analyses agreed; no significant trends were found (p>0.05; Appendix 7-1; Zajdlik, 2011a). This comparison highlights the influence of time period on the trend results and emphasizes the importance of developing standard protocols for long-term statistical trend analysis.

Recommendation

Continued monitoring for sodium is recommended to further investigate the increasing trend and the potential impacts on the aquatic environment.

7.3.2.5 Potassium

Background

Potassium is a widely distributed non-toxic element which is an essential nutrient for plant and animal growth (Taylor, 2009). Unlike sodium, potassium is more resistant to weathering and is usually readily associated with stable minerals, such as clay (McNeely *et al*., 1979; CCREM, 1987). Potassium compounds are used primarily in the production of fertilizers (KCl; CCREM, 1987). Concentrations of potassium in surface water are usually less than 10 mg/L (McNeely *et al*., 1979).

There is currently no CCME CPFAL guideline for potassium (CCME, 1999).

Results

At Fort Smith, total potassium concentrations were between 0.6 to 3.2 mg/L (n=72; 1988-2010). At Fitzgerald, dissolved concentrations ranged from 0.4 to 3.6 mg/L (n=243; 1972-2010). As a comparison, Environment Canada recorded dissolved potassium levels between 0.2 and 2.2 mg/L in the Liard River (n=181); and between 0.3 and 1.1 mg/L in the Peel River (n=157).

Long-term temporal trend assessment of the 1972-2010 dissolved potassium data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). A significant decreasing trend, at the 95% confidence level, was revealed during the spring (p=0.0002; Figure 7.18). The average decrease in concentration over the period of record (1972-2010) during the spring was estimated to be 0.7 mg/L (see Section 7.2.3 of this report). No trends were revealed in the other seasons or with the annual data (p-values range from 0.1401 to 0.7317; Appendix 7-1).

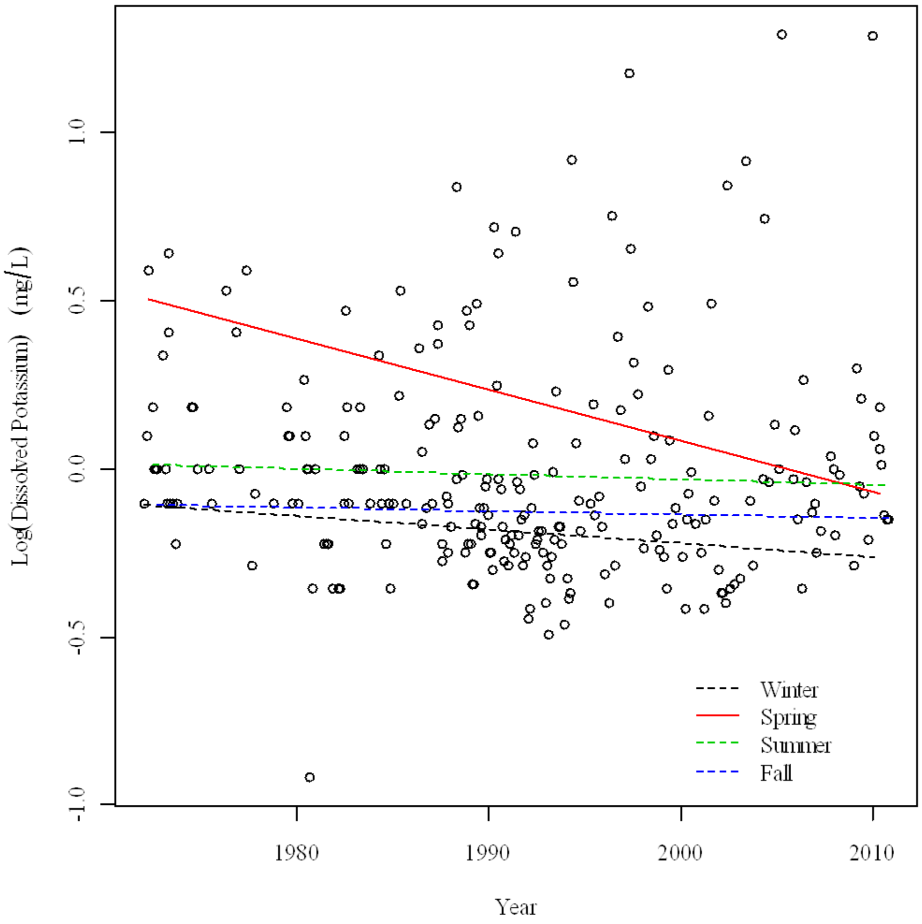

Figure 7.18: Trend Results - Non flow-adjusted dissolved potassium concentrations from Fitzgerald (1972-2010). Although trend lines have been displayed for all seasons, only the decreasing trend for spring is statistically significant at the 95% confidence interval (from Zajdlik, 2011b).

Because dissolved potassium revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there was no longer an interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. After flow-adjustment, a significant trend was no longer evident at either the 90 or 95 % confidence levels (Appendix 7.1).

Environment Canada also reported no significant annual trend in the dissolved potassium data during the 1989-2006 period of record or during the last decade (1997-2006; Glozier *et al*., 2009), which agrees with the flow-adjusted results of this report.

Recommendation

Continued monitoring for potassium is recommended as it is an essential nutrient for plant and animal growth.

7.3.2.6 Sulphate

Background

Sulphur is an essential plant nutrient that is required by aquatic organisms. The most common form of sulphur in well-oxygenated waters is sulphate. Concentrations of sulphate normally vary from 10 to 80 mg/l in naturally occurring surface waters (CCREM, 1987). When sulphate is less than 0.5 mg/L, algal growth will not occur.

Sulphate may be leached from most sedimentary rocks, including shales, gypsum and anhydrite (Taylor, 2009). Other natural sources of sulphate include volcanoes and decomposition and combustion of organic matter (BC MOE, 2000). Sulphates and sulphuric acid products are used to make chemicals, pesticides, dyes, soaps, glass and paper. Anthropogenic sources of sulphates include discharge water from mines, smelters, kraft pulp and paper mills, textile mills and tanneries (BC MOE, 2000). The burning of fossil fuels is also a large source of sulphur to the atmosphere and may contribute sulphate to surface waters (BC MOE, 2000). Sulphate fertilizers are also an important source of sulphate to source waters (BC MOE, 2000).

There is currently no national CCME CPFAL guideline for sulphate. However, BC MOE has a freshwater aquatic life guideline for sulphate of 100 mg/L (BC MOE, 2000).

Results

At Fort Smith, total sulphate concentrations ranged from 3.0 to 61.0 mg/L (n=106; 1982-2010), while at Fitzgerald, dissolved sulphate levels were between 3.9 and 37.2 mg/L (n=242; 1972-2010). All sulphate values detected in the Slave River were below the BC MOE freshwater aquatic life guideline for sulphate (BC MOE, 2000). As a comparison, Environment Canada recorded dissolved sulphate levels between 2.6 and 70.6 mg/L in the Liard River (n=181), and in the Peel River, concentrations ranged from 17.5 to 89.1 mg/L (n=157).

Long-term trend assessment of the 1972-2010 dissolved sulphate data from Fitzgerald revealed no interaction between season and year (Appendix 7-1) and therefore, only the annual data was assessed for trends. A significant increasing trend was found, at the 95% confidence level (p=0.0011), which is implied for each of the individual seasons (Figure 7.19). The change in concentration over the period of record (1972-2010) was estimated to be 3.0 mg/L (see Section 7.2.3 of this report).

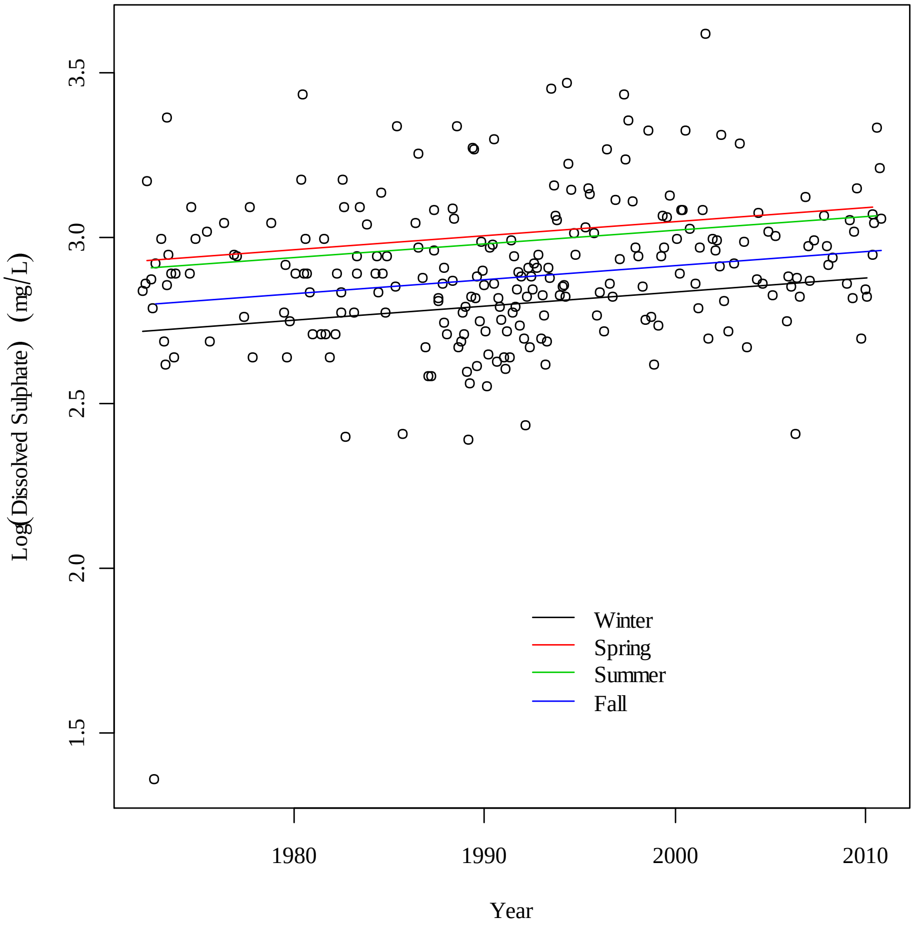

Figure 7.19: Trend Results - Non flow-adjusted dissolved sulphate concentrations at Fitzgerald (1972-2010). Statistically significant increasing trends were found in all four seasons at the 95% confidence interval (from Zajdlik, 2011b).

Because dissolved sulphate revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, the data demonstrated an interaction between season and year (Appendix 7-1). Only the summer and winter data continued to reveal significant increasing trends at the 95% confidence level (p_{summer}=0.0010; p_{winter}=0.0165). The fall and annual data revealed significant trends, but only at the 90% confidence level (p=0.0788 for both) whereas the spring data showed no significant trends (p=0.5022).

Environment Canada also reported a significant increasing trend (1989-2006) in dissolved sulphate in the Slave River, which agreed with the findings of this report. However, the trend was not significant for the most recent decade (1997-2006), (Glozier *et al*., 2009). In their report, the authors note that although recent concentrations remain elevated above earlier concentrations, levels were no longer increasing. As higher sulphate concentrations were noted in several other rivers, including mountain headwater streams, the authors concluded that the increase was a signal of global changes in water chemistry as opposed to inputs from point sources.

Recommendation

Continued monitoring for sulphate is recommended to further investigate this trend, its sources and the potential impacts on the aquatic environment.

7.3.2.7 Chloride

Background

Chloride is widely distributed in the environment, mostly in the form of sodium (NaCl) and potassium (KCl) salts. Chloride is an essential element for aquatic and terrestrial biota, including humans. Higher chloride concentrations can reduce the toxicity of nitrite to aquatic life (BC MOE, 1998).

The weathering and leaching of sedimentary rocks and soils and the dissolution of salt deposits release chlorides to water (Mc Neely *et al*. 1979). Natural concentrations of chloride in fresh surface waters range between 1 to 100 mg/L; by far, the greatest contributions of chloride found in nature are in the oceans (BC MOE, 2003). The use of road salts is the primary anthropogenic source of chloride to the environment (BC MOE, 2003). Other anthropogenic sources include municipal water supply disinfection, sewage treatment plant effluents, urban developments, industrial effluents and mining (BC MOE, 1998).

The CCME CPFAL guideline for chloride is set at 130 mg/L (CCME, 2011).

Results

At Fort Smith, total chloride concentrations ranged from 2 to 18 mg/L (n=107; 1982-2010), while at Fitzgerald, dissolved chloride levels were between 1 to 11 mg/L (n=242; 1972-2010). As a comparison, chloride levels in the Liard River ranged from 0.1-9 mg/L; in the Peel River, levels ranged from 1 to 11 mg/L.

In this report, long-term temporal trends for dissolved chloride were not examined. However, Environment Canada found significant decreasing trends in dissolved chloride over time (1989-2006) and in the last decade (1997-2006) (Glozier *et al*., 2009).

Recommendation

Continued monitoring for chloride is recommended to further investigate the trend identified by Environment Canada and the potential impacts on the aquatic environment.

7.3.2.8 Fluoride

Background

Fluoride is present in trace amounts in soils and rocks and is released naturally to the aquatic environment through geochemical weathering (CCREM, 1987). Anthropogenic sources include the addition of fluoride to domestic water supplies and resulting sewage discharge, as well as mining and smelting activities (McNeely *et al*., 1979; BC MOE, 1998). While fluoride can prevent tooth decay, excessive amounts can result in mottled tooth enamel (BC MOE, 1998).

Although there is currently no CCME CPFAL guideline for fluoride, the maximum acceptable concentration in drinking water is 1.5 mg/L (Health Canada, 2010).

Results

Fluoride levels make the smallest contribution to the total major anions load in the Slave River (Figure 7.10), with dissolved concentrations ranging from <0.01 to 0.2 mg/L at Fitzgerald (n=228; 1972-2010) and total concentrations of 0.07 and 0.1 mg/L at Fort Smith (n=2; 2003, 2007). As a comparison, Environment Canada recorded dissolved fluoride levels between 0.02 and 0.30 mg/L in the Liard River (n=180) and between 0.01 to 0.15 mg/L in the Peel River (n=152).

In this report, long-term temporal trends of dissolved fluoride were not examined. However, Environment Canada reported no significant temporal trends in dissolved fluoride during the 1989-2006 period of record or during the last decade (1997-2006; Glozier *et al*., 2009).

Recommendation

Continued monitoring for fluoride is recommended to maintain the long-term record.

Table 7.7: Detailed statistical summaries for major ions - Slave River at Fitzgerald; Slave River at Fort Smith.

Slave River at Fitzgerald										
Major Ions	**Period of Record**	**units**	**n**	**# of NDs**	**Mean**	**St Dev**	**Median**	**Min**	**Max**	**90th %ile**
Bicarbonate Calcd	1980-1996	mg/L	121	0	102	9.4	102	77.5	131.7	112.3
Calcium Dissolved	1972-2010	mg/L	242	0	28.6	3.6	28.3	16	42	32.28
Calcium Total	1993-2002	mg/L	59	0	31.7	8.4	29.5	21.8	70.3	39.9
Chloride Dissolved	1972-2010	mg/L	242	0	5.2	1.69	5.09	0.5	11	7.19
Fluoride Dissolved	1972-2010	mg/L	228	5	0.08	0.02	0.08	<0.01	0.2	0.1
Hardness Total Calcd $CaCO_3$	1972-2010	mg/L	204	0	98.4	10.7	98	59	138	110.2
Magnesium Dissolved	1978-2010	mg/L	216	0	6.58	0.7	6.59	4.11	8.80	7.46
Magnesium Total	1993-2002	mg/L	59	0	7.83	3	6.97	4.90	23.1	9.91
Potassium Dissolved	1972-2010	mg/L	243	0	1.05	0.44	0.9	0.4	3.63	1.53
Potassium Total	1993-2002	mg/L	59	9	1.5	0.93	1.22	0.59	5.37	2.02
Sodium Dissolved	1972-2010	mg/L	242	0	6.39	1.3	6.29	1.2	10	8.07
Sodium Total	1993-2002	mg/L	59	0	5.47	1.46	5.27	2	8.8	7.41
Sulphate Dissolved	1972-2010	mg/L	242	0	18.7	4.22	18	3.9	37.2	23.77

Slave River at Fort Smith										
Major Ions	**Period of Record**	**units**	**n**	**# of NDs**	**Mean**	**St Dev**	**Median**	**Min**	**Max**	**90th %ile**
Calcium Total	1982-2010	mg/L	95	0	28.04	4.54	27.8	17.9	44.9	32.52
Chloride Total	1982-2010	mg/L	107	0	5.5	2.15	5.02	1.6	18.02	7.54
Fluoride Total	2003, 2007	mg/L	2	1	0.09	0.02	0.09	0.07	0.1	0.1
Hardness Total Calcd $CaCO_3$	1982-2010	mg/L	101	0	97.3	14.8	96	58.3	152	111
Magnesium Total	1982-2010	mg/L	96	0	6.7	0.96	6.6	2.5	10.6	7.8
Potassium Total	1988-2010	mg/L	72	0	1.12	0.48	0.98	0.55	3.17	1.7
Sodium Total	1988-2010	mg/L	74	0	6.38	1.66	6.27	1.07	15.7	8
Sulphate Total	1982-2010	mg/L	106	0	19.2	6.31	18	3	61	24
Sulphide	1990-93, 2000-07	mg/L	27	26	0.07	0.07	0.05	<0.005	<0.3	0.14

*ND: number of values reported below the detection limit (censored observations).

7.3.3 Nutrients

Summary

Total Phosphorus – Although no trend was found in the non flow-adjusted data, following flow-adjustment, an increasing annual trend was found (at the 95% confidence level) which was implied for each of the individual seasons.

Dissolved Phosphorus - An increasing spring and winter trend was found in both the non flow-adjusted and flow-adjusted data (at the 95% confidence level).

Recommendation

Given the increased agricultural and resource extraction activities in the upstream portion of the catchment, continued monitoring for nutrients is recommended to further investigate these trends and their potential impacts on the aquatic environment.

Nutrients, such as phosphorus, nitrogen and carbon, are essential for plants to grow and are found naturally in the environment (Chambers *et al*., 2001). Nutrients may exist in a number of different chemical forms as they are cycled through the aquatic, terrestrial and atmospheric systems. Their sources may be both inorganic and organic, and they may be present in a dissolved or particulate form (MRBC, 1981).

Phosphorus and nitrogen are particularly important water quality parameters, as these nutrients, along with factors such as light and temperature, are essential elements that control the growth rate and abundance of aquatic plants. At high concentrations and under favorable conditions, these nutrients can cause excessive plant growth in water bodies (MRBC, 1981). This can ultimately result in low oxygen levels, due to aerobic respiration of the microorganisms that feed on the dead or decaying plants. The biological effects due to the addition of excessive nutrients to a water body is known as

The nutrients discussed in this section include total and dissolved phosphorus, ammonia and both particulate and dissolved organic carbon. A table showing the median values for both sampling locations is shown below (Table 7.8). A detailed summary table is included at the end of this section (Table 7.9).

Table 7.8: Median concentrations of nutrients.

Parameter	**Units**	**Slave River at Fitzgerald**		**Slave River at Fort Smith**	
		n	**Median**	**n**	**Median**
Ammonia Dissolved	mg/L	99	0.016	--	--
Ammonia Total	mg/L	--	--	83	0.02
Phosphorus Dissolved	mg/L	215	0.010	6	0.010
Phosphorus Total	mg/L	223	0.082	82	0.105
Carbon, Dissolved Organic (DOC)	mg/L	213	5.4	6	8.86
Carbon, Particulate Organic (POC)	mg/L	193	1.8	--	--

7.3.3.1 Phosphorus

Background

Phosphorus is a key element necessary for the growth of aquatic plants and is often the most limiting nutrient to plant growth in fresh water. It is not commonly toxic to humans, animals or fish (McNeely *et al*., 1979). The major natural source of phosphorus to the aquatic environment is through the weathering of phosphorus-bearing rock (Glozier *et al*., 2010), which can be chemically and biologically transformed to the bioavailable form of phosphorus: phosphate.

Effluent from municipal (i.e., human waste and detergents) and industrial wastewater, as well as runoff from agricultural activities (i.e., fertilizers), are the largest non-natural sources of phosphorus to the environment (BC MOE, 1998). Approximately 80 to 85% of all phosphate produced in the world is used in fertilizers (Public Works and Government Services Canada, 2001). Since phosphorus is usually the most limiting nutrient, increased input of this parameter to freshwater systems can cause excessive algal growth (BC MOE, 1998).

Phosphorus in freshwater systems exists in inorganic and organic compounds and in both particulate and dissolved forms; the latter two forms make up the total phosphorus (TP) content of the water (BC MOE, 1998). Dissolved phosphorus (DP) is a measure of the amount of phosphorus that will pass through a 0.45 µm porosity filter and is the fraction that is most readily bioavailable for plant growth.

There are currently no CCME CPFAL guidelines for phosphorus.

Results

Total phosphorus

At Fort Smith, total phosphorus (TP) ranged from 0.014 to 4.4 mg/L (n=82; 1982-2010), while at Fitzgerald TP ranged from 0.006 to 4.67 mg/L (n=223; 1974-2010). As a comparison, Environment Canada recorded total phosphorus levels in the Liard River between 0.001 and 2.48 mg/L (n=168) and between 0.002 and 1.88 mg/L (n=156) in the Peel River.

On average, 81% of the phosphorus in the Slave River at Fitzgerald was particulate ($n_{\text{paired TP\&DP values}}=213$) and concentrations of TP were highly correlated to TSS ($r_s=0.93$; $p<0.05$; n=218). TP was also correlated with TSS at Fort Smith ($r_s=0.70$; $p<0.05$; n=76), suggesting that a large portion of the TP at both sites was of the particulate form. Long-term trend assessment of the 1974-2010 total phosphorus data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.20).

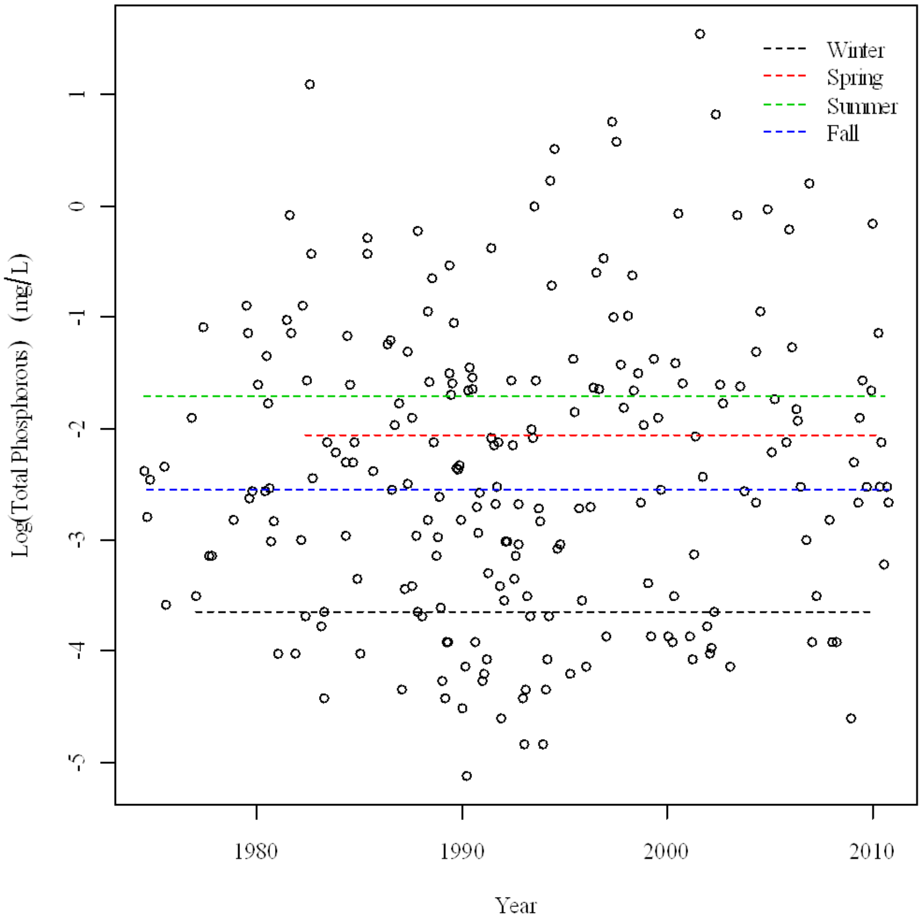

Figure 7.20: Trend Results - Non flow-adjusted total phosphorus concentrations from Fitzgerald (1974-2010). No statistically significant trends were found (at the 95% confidence level; Zajdlik, 2011b).

Because the total phosphorus data revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year. The annual flow-adjusted data revealed a significant increasing trend at the 95% confidence level and this trend is implied for the individual seasons (p=0.0255; Appendix 7-1).

Glozier *et al*. (2009) also found a significant increasing trend in total phosphorus data collected during the 1989-2006 time period. Note that when Glozier *et al*. (2009) evaluated the last decade of data (1997-2006), however, no trends were found.

Dissolved Phosphorus

At Fort Smith, dissolved phosphorus levels ranged from 0.008 to 0.02 mg/L (n=6; 2000, 2003, 2006-2007), while at Fitzgerald dissolved concentrations ranged from <0.002 to 0.343 mg/L (n=215; 1978-2010). As a comparison, Environment Canada recorded dissolved phosphorus levels in the Liard River between 0.001 and 0.5 mg/L (n=168) and between 0.002 and 0.37 mg/L (n=157) in the Peel River.

Long-term temporal trend assessment of the 1978-2004[14] dissolved phosphorus data at Fitzgerald revealed an interaction between season and year (Appendix 7-1). Significant increasing trends, at the 95% confidence level, were found during the spring and winter seasons (p_{spring}=0.005; p_{winter}=0.018; Figure 7.21). The average increase in dissolved phosphorus concentration was estimated to be 0.18 mg/L (Zajdlik, 2011b; see Section 7.2.3 of this report). Note that no significant trends were found in the summer, fall or annual data (p-values range from 0.3113 to 0.3408; Appendix 7-1).

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[14] Although the period of record for dissolved phosphorus extends from 1978-2010, due to a large majority of censored data after November 2004, trends were only examined for 1978-2004.

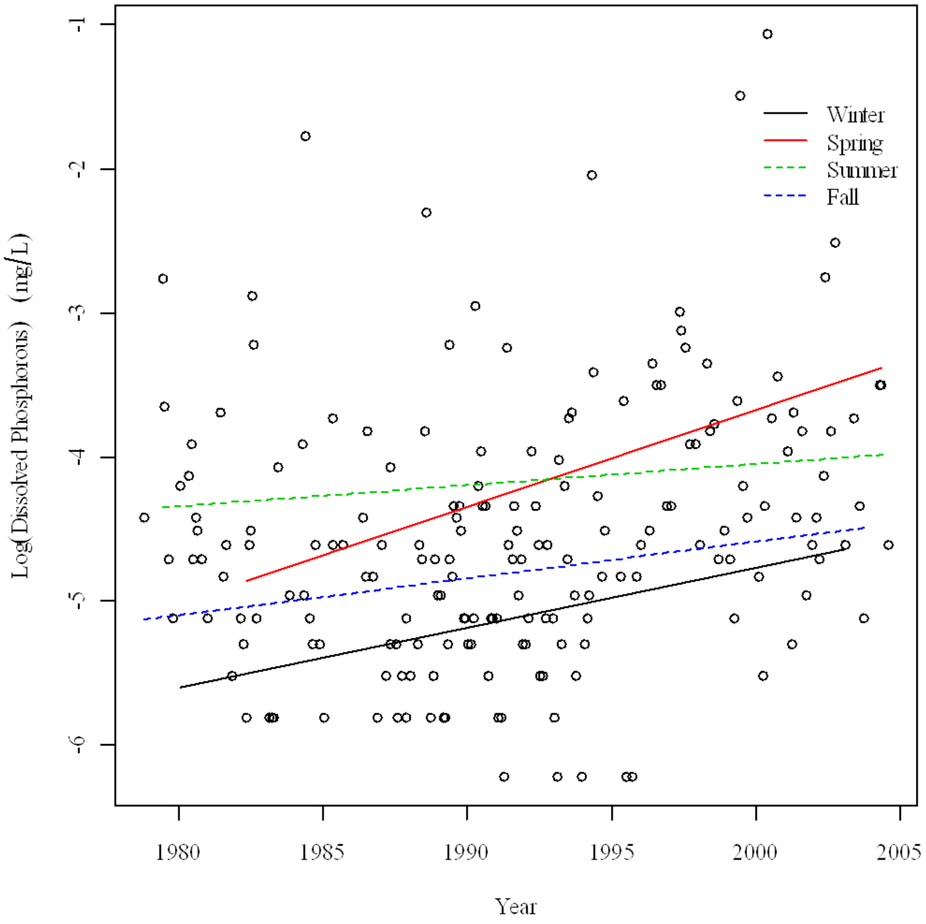

Figure 7.21: Trend Results - Non flow-adjusted dissolved phosphorus levels from Fitzgerald (1978-2004). Although trend lines have been displayed for all seasons, only the increasing trends for spring and winter are statistically significant at the 95% confidence interval (Zajdlik, 2011b).

Because dissolved phosphorus revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be an interaction between season and year (Appendix 7-1) and the spring and winter data continued to exhibit significant increasing trends at the 95% confidence level ($p_{spring}<0.0001$; $p_{winter}=0.0027$). Note that there were no significant trends found in the flow-adjusted summer, fall or annual data (p-values range from 0.3986 to 0.9322; Appendix 7-1).

Glozier *et al.* (2009) also reported significant increasing trends in dissolved phosphorus over the 1989-2006 time period. Although no trends were found in phosphorus concentrations from the last decade (1997-2006), levels were found to be higher than previous years (Glozier *et al.*, 2009).

The increasing trends found in the longer dataset may be associated with the fact that during the past 30 years, agricultural activities have become more intensive within the Peace and Athabasca Sub-basins. As reported in the 2003 State of the Aquatic Ecosystem Report, the number of cattle in this area has doubled to nearly 1 million; fertilizer applications have increased by more than 500% and the amount of money spent on chemicals has increased by more than 1400% (after accounting for inflation; MRBB, 2003). Erosion and runoff into surface waters, associated with land clearing from agricultural practices and removal of overburden associated with resource extraction activities, may also be contributing to these increasing trends.

In March 2011, a community-based workshop to discuss monitoring and aquatic ecological health indicators for the Slave River was held in Fort Smith (AANDC and GNWT, 2012). At this workshop, participants acknowledged that there have been more algae on the rocks and in fishing nets in the Slave River and denser growth of willows and other river plants along the river banks. These important observations, shared by traditional land users, may be the result of increasing phosphorus in the Slave River. In 2012, community personnel along the Slave River deployed a YSI™ automatic water quality meter with 'chlorophyll' sensors. These sensors will provide a measure of the amount of primary biomass and biological production in the river (YSI, 2012), useful information for gaining a better understanding of the seasonal nutrient fluctuations in the river.

Recommendation

Continued monitoring for phosphorus is recommended to further investigate these trends and the potential impacts on the aquatic environment, especially in light of the increased agricultural and resource extraction activities in the upstream portion of the catchment. Given the oligotrophic status of many lakes in Canada's North and considering the amount of water carried by the Slave River to Great Slave Lake, phosphorus levels need to be monitored closely.

7.3.3.2 Nitrogen

Background

Nitrogen is another essential plant nutrient that can influence the growth of aquatic algae and plants. Forms of nitrogen in freshwater include dissolved molecular nitrogen (N_2), ammonia nitrogen (NH_3), ammonium (NH_4^+), nitrite (NO_2) and nitrate (NO_3) (Wetzel, 2001). In this report, ammonia (NH_3) is summarized and discussed.

Natural sources of nitrogen to the environment include precipitation, particulate matter and nitrogen fixation. Major anthropogenic sources of nitrogen to the environment include: coal combustion, petroleum products and natural gas products, all of which add NO to the atmosphere; fertilizer production, which fixes nitrogen gas (N_2) as ammonia; and cultivation of crops, which enhances biological production beyond natural levels (Chambers *et al*., 2001). Less prominent sources of ammonia include sewage treatment plant effluents, industrial effluents, blasting residuals from mining and runoff from urban areas (BC MOE, 1998).

Ammonia

Background

Ammonia is a non-persistent, non-bioaccumulative substance that results naturally from either the decomposition of organic matter or the microbial reduction of nitrate or nitrite under anaerobic conditions. Anthropogenic sources include treated sewage and commercial fertilizers. High levels of ammonia in waterbodies is a concern as it contributes to eutrophication and has been shown to reduce the oxygen carrying capacity in the blood of fish (BC MOE, 1998; McNeely *et al*., 1979).

The toxicity of ammonia varies with both pH and temperature. Ammonia levels are more toxic with increasing temperature and pH (CCME, 1999).

Taking into account the temperature and pH of the water at the time of sampling, the CCME CPFAL ammonia guideline was calculated[15] for each water sample. The range of temperatures (0-22ºC) and pH (6.80-8.68) from both sites resulted in a range of ammonia guidelines of 0.3 to 11.6 mg/L.

Results

Total ammonia values for the Slave River at Fort Smith (0.002-0.52 mg/L; n=83; 1982-2010) and dissolved ammonia values from Fitzgerald (<0.001-0.33 mg/L; n=99; 1993-2010) complied with the guideline. As a comparison, Environment Canada recorded dissolved ammonia levels between 0.001 and 0.11 mg/L in the Liard River (n=71); in the Peel River, concentrations ranged from 0.001 to 0.17 mg/L (n=62).

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[15] pKa=0.09018 + (2729.92/273.2+temperature); FDA= $1/[1 + (10^{pKa-pH})]$
pKa: acid dissociation constant; FDA: fraction of deionized ammonia.
$WQG_{ammonia}$ = temperature/FDA (S. Roe. National Standards Office, Environment Canada. Gatineau, Quebec, Pers. comm.).

Long-term trend assessments (1972-2010) were not conducted for ammonia because none of the variables described a significant proportion of the variability. Consequently, no model was fit (Zajdlik, 2011b). Glozier *et al*. (2009) reported no significant trends in the ammonia data during the 1989-2006 period of record or during the last decade (1997-2006). This highlights the need for standard protocols for long-term statistical trend analysis, including statistical methods.

Recommendation

Continued monitoring for ammonia is recommended in light of the increased agricultural and resource extraction activities in the upstream portion of the catchment.

7.3.3.3 Carbon

Background

Organic carbon compounds are created by photosynthesis in the aquatic environment, and can also be contributed from the biodegradation of plant and animal materials (BC MOE, 1998). Although carbon is a required nutrient for biological systems, the breakdown of organic carbon can deplete dissolved oxygen levels (McNeely *et al.*, 1979). Organic carbon is typically highest in the spring, when the input of organic material to the river from runoff is highest. Anthropogenic sources of carbon include discharges from municipalities and pulp mills, as well as runoff from agricultural lands (BC MOE, 1998).

Organic carbon is found in natural waters as dissolved organic carbon (DOC) or particulate organic carbon (POC), together constituting total organic carbon (TOC). The DOC is separated from POC by filtration (through a 0.45μm membrane filter). Studies have shown strong correlations between POC and particulate mercury as well as between DOC and dissolved mercury levels (Dittman *et al*., 2010). In addition, high concentrations of DOC may complex with methyl mercury, diminishing its bioavailability (Driscoll *et al.,* 1995). Neither DOC nor POC were analyzed at Fort Smith.

There are currently no CCME CPFAL guidelines for dissolved organic carbon (DOC), particulate organic carbon (POC), or total organic carbon (TOC).

Dissolved Organic Carbon

Results

At Fitzgerald, dissolved organic carbon ranged from 1.5-40.4 mg/L (n=213; 1978-2010), while at Fort Smith, values were between 2.8 and 14.6 mg/L (n=6; 2000-2007). As a comparison, Environment Canada recorded dissolved organic carbon levels between

0.1 and 33 mg/L in the Liard River (n=175); in the Peel River, concentrations ranged from 0.3 to 24.6 mg/L (n=141).

Long-term temporal trend assessment of the 1978-2010 dissolved organic carbon data from Fitzgerald revealed no interaction between season and year (Appendix 7.1). Therefore only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95 % confidence levels (Figure 7.22).

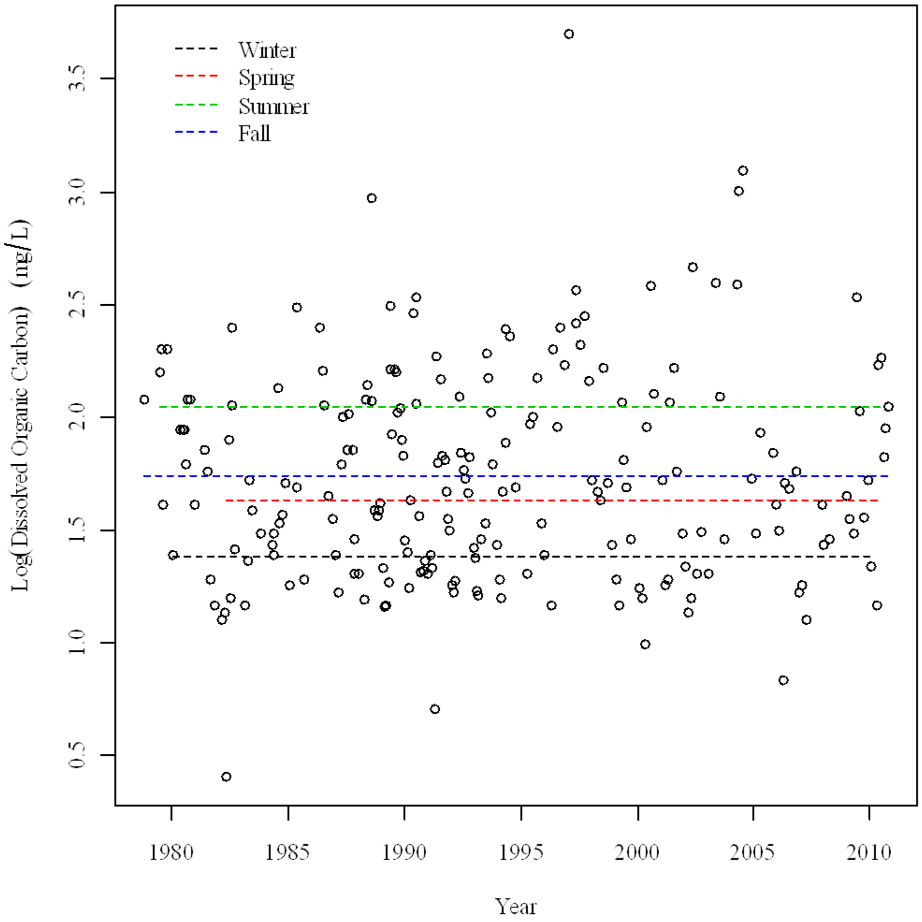

Figure 7.22: Trend Results - Non flow-adjusted dissolved organic carbon levels from Fitzgerald (1978-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Because DOC revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year. No significant trend was found at the 90 or 95% confidence levels (Appendix 7.1).

Environment Canada also reported no significant trends during the 1989-2006 period of record or during the last decade (1997-2006; Glozier *et al*., 2009).

Particulate Organic Carbon (POC)

<u>Results</u>

At Fitzgerald, POC concentrations ranged from 0.13 to 84.0 mg/L (n=211; 1978-2010). POC was not analyzed at Fort Smith. As a comparison, Environment Canada recorded POC levels between 0.005 and 40 mg/L in the Liard River (n=183), and in the Peel River, POC concentrations ranged from 0.036 to 39 mg/L (n=147).

Long-term trend assessment of the 1978-2010 particulate organic carbon data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.23).

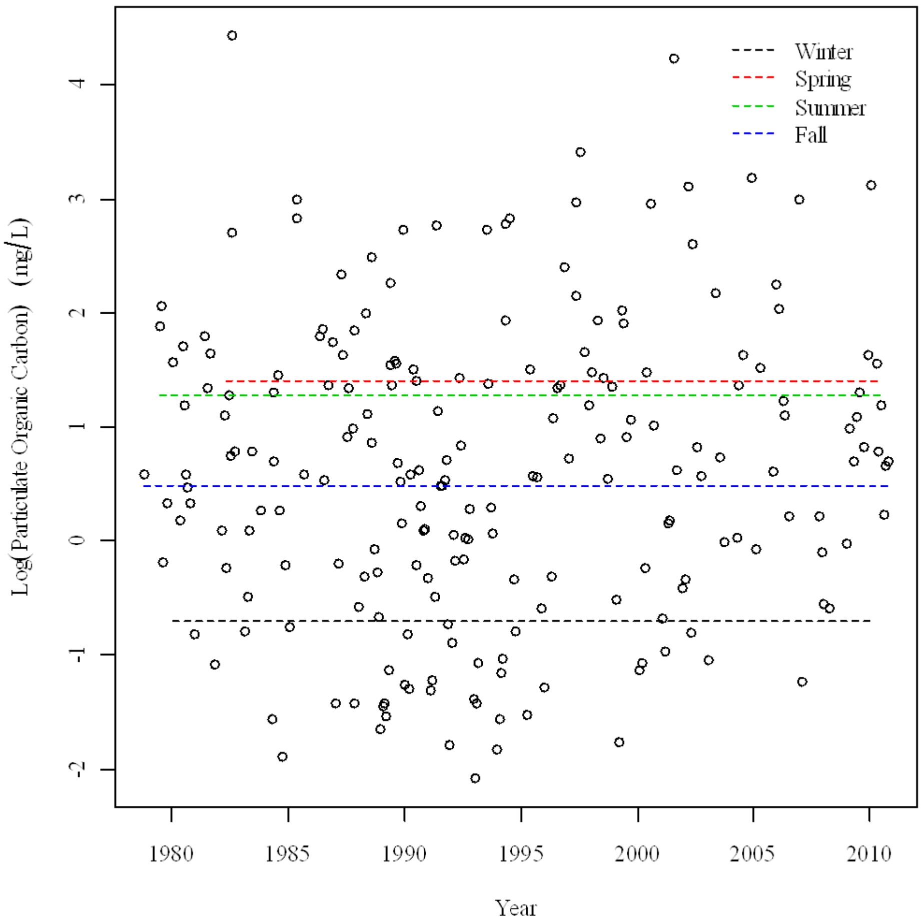

Figure 7.23: Trend Results - Non flow-adjusted particulate organic carbon levels from Fitzgerald (1978-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Because the POC data revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year. The annual flow-adjusted data revealed no significant trend at the 90 or 95% confidence levels (Appendix 7-1).

Glozier *et al*. (2009) however did report a significant increasing annual trend in particulate organic carbon data collected from 1989-2006, as well as in the last decade. When the database was truncated to match the time period used by Environment Canada, still no trend was found, which appears to contradict the Glozier *et al*. (2009) report (p>0.1; Appendix 7-1; Zajdlik, 2011a). This apparent contradiction is likely due to the different methods used and emphasizes the importance of developing standard protocols for long-term statistical trend analysis.

Recommendation

Continued monitoring for organic carbon is recommended as this parameter is required for biological processes and its concentration can affect the toxicity of certain metals. It is also recommended that long-term trend analysis should be re-examined after more data have been collected.

Table 7.9: Detailed statistical summaries for nutrients - Slave River at Fitzgerald; Slave River at Fort Smith.

Slave River at Fitzgerald

Nutrients	Period of Record	units	n	# of NDs	Mean	St Dev	Median	Min	Max	90th %ile	Detection Limits	
											from Environment Canada database	from Glozier *et al*, 2009 (1989-2006)
Ammonia Dissolved	1993-2010	mg/L	99	8	0.03	0.047	0.016	<0.001	0.33	0.068	0.005-0.01	0.005
Nitrogen Dissolved	1978-2010	mg/L	206	0	0.261	0.192	0.211	0.039	2.0	0.433	--	0.01
Nitrogen Particulate	1978-2010	mg/L	211	3	0.573	2.118	0.192	0.002	28.7	1.06	0.01	0.01
Dissolved Organic Carbon	1978-2010	mg/L	213	0	6.41	3.916	5.4	1.5	40.4	10.16	--	0.1
Phosphorus Dissolved	1978-2010	mg/L	215	24	0.018	0.033	0.01	<0.002	0.343	0.033	0.002-0.05	0.002
Phosphorus Total	1974-2010	mg/L	223	0	0.235	0.483	0.082	0.006	4.67	0.547	--	0.002
Particulate Organic Carbon	1978-2010	mg/L	211	0	4.4	8.72	1.83	0.125	84	9.62	--	0.1

Slave River at Fort Smith

Nutrients	Period of Record	units	n	# of NDs	Mean	St Dev	Median	Min	Max	90th %ile	Detection Limits
Ammonia Total	1982-2010	mg/L	83	14	0.038	0.074	0.02	0.002	0.52	0.06	0.002-1.0
Nitrate & Nitrite Filtered	1982-2010	mg/L	82	16	0.047	0.04	0.039	0.008	0.2	0.116	0.008-0.2
Nitrate as Nitrogen	1994, 2001-2006	mg/L	6	1	0.038	0.02	0.036	0.008	0.07	0.058	0.008-0.01
Nitrite as Nitrogen	2001-2006	mg/L	5	5	0.01	0.001	0.01	0.009	0.01	0.01	0.009-0.01
Nitrogen Total Kjeldahl	1982-1987	mg/L	7	0	0.459	0.542	0.3	0.003	1.6	1	--
Dissolved Organic Carbon	2000-2007	mg/L	6	0	8.77	3.8	8.86	2.8	14.6	12.2	--
Ortho-Phosphate as P	1993-2007	mg/L	15	3	0.0073	0.0064	0.005	0.002	0.024	0.0152	0.002-0.004
Phosphorus Dissolved	2000, 2003, 2006-2007	mg/L	6	2	0.0118	0.0042	0.01	<0.008	0.0198	0.016	0.008-0.01
Phosphorus Total	1982-2010	mg/L	82	3	0.2505	0.534	0.1045	0.014	4.4	0.531	0.002-0.05

ND: number of observations reported below the detection limit (censored observations). n: number of values; --: not provided;
Detection Limits (from Environment Canada database): The dataset provided by Environment Canada only included the detection limits for the values that were reported below the detection limit. When values were reported below the detection limit, the detection limit was recorded. Detection Limits (from Glozier *et al*, 2009): These detection limits were reported in the Glozier report (Appendix 2) and cover the 1989-2006 time period.

7.3.4 Metals

Metal Guideline Exceedances

Summary

Total metals in the Slave River that frequently (>25%) exceeded the total metal guideline for the protection of freshwater aquatic life included cadmium, chromium, copper, iron, lead and mercury. For these parameters, most of the metal was in the particulate form and therefore potentially less biologically available. However for cadmium and copper, the dissolved fraction accounted for a large percentage of the total metal concentration, suggesting that these metals are potentially more biologically available. In addition, dissolved concentrations of cadmium, chromium, copper and iron exceeded the total metal guideline, on occasion.

Total metals that exceeded the guideline less frequently (<25%) were arsenic, barium, manganese, nickel, selenium, silver, vanadium and zinc. There were no guideline exceedances for total antimony, total beryllium, total cobalt, total molybdenum, total thallium and total uranium.

Recommendation

It is recommended that analyses of dissolved metals continue at Fitzgerald and be initiated at Fort Smith. In addition, it is strongly recommended that site-specific water quality objectives be developed for total and dissolved metals to better assess the metal concentrations observed in the Slave River.

Long-term Trends

Summary

All metals were considered for long-term trend assessment but only ten met data quality criteria requirements. Of these, only aluminum, chromium and molybdenum exhibited trends.

- *Aluminum - A decreasing summer trend was found (at the 90% confidence level); following flow-adjustment, the data no longer exhibited a trend.*
- *Chromium - A decreasing summer trend was found (at the 95% confidence level); following flow-adjustment, the summer data no longer exhibited a trend, however, the winter data exhibited an increasing trend (at the 90% confidence level).*
- *Molybdenum - A decreasing spring trend was found (at the 95% confidence level) and a decreasing summer trend was found (at the 90% confidence level); as molybdenum did not reveal a relationship with flow, flow-adjusted trends analyses were not conducted.*

Recommendation

Continued monitoring for metals is recommended to further investigate these trends and the potential impacts on the aquatic environment. It is also recommended that long-term trend analysis should be conducted for arsenic, cadmium, cobalt, mercury, selenium and mercury once an adequate dataset is available. Further trend analysis should be conducted regularly for all metals.

Background

Metals in surface water can originate from natural sources and from a variety of human activities, including atmospheric emissions, industrial and municipal effluents, agricultural runoff and accidental spills (MRBC, 1981). It is normal to find metals in surface waters, as small amounts are contributed naturally due to weathering of bedrocks and soils. However, some anthropogenic processes, such as land clearing for agriculture or removal of overburden for industrial development, can release these naturally occurring metals, but at elevated levels.

Certain metals, such as cobalt, copper, manganese, molybdenum, nickel, selenium and zinc are required for the growth of plants and animals. However, some metals, such as mercury, can be toxic at elevated levels and bioaccumulate in the food chain resulting in human health concerns (CCME, 2003).

Metals in water exist in a number of soluble (i.e., free metal ions, associated with colloids) and insoluble (i.e., attached to clays or organic matter) forms. The effect of a metal on the aquatic environment depends on its availability to aquatic life, which is dependent on the physical and chemical properties of the water, such as pH, hardness, temperature and dissolved organic carbon and whether the metals are dissolved or attached to suspended sediment (CCME, 1999; MRBC, 1981). At high pH, metals form hydroxides or carbonates, which are typically insoluble because they precipitate and fall out of solution. At lower pH, the solubility of most metals tends to increase (Shaw, 1990). Although the availability of metals associated with the solid phase varies, typically, it is the dissolved form that is more toxic and biologically available for uptake by aquatic organisms (Glozier *et al*., 2009; MRBC, 1981).

Laboratories typically report metals as either dissolved or total concentrations. Total concentrations reflect both the dissolved and particulate forms. To determine the concentration of a total metal, the laboratory analysis is completed on the unfiltered water sample. To determine the dissolved concentration, the laboratory filters the water sample prior to analysis. Although, total metals[16] have been consistently reported for both sampling locations, dissolved metals were only added to the Slave River at Fitzgerald sampling program in 2006, and have not been analyzed at Fort Smith. A detailed summary table is included at the end of this section (Tables 7.13-7.15).

Median metal concentrations from both sampling locations are presented in Table 7.10.

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[16] The exceptions are arsenic and selenium at Fitzgerald. Dissolved arsenic and dissolved selenium have been routinely analyzed for at Fitzgerald since 1978; total arsenic and total selenium were added to the Fitzgerald program in 2003.

Although the ranges of total metals concentrations from the two sampling locations overlapped, maximum values of most total metals were typically higher at Fitzgerald, while the minimum values were lower. This is likely due to the greater variability in the dataset because of the longer period of record.

Table 7.10: Median concentrations of total and dissolved metals.

Parameter		**Slave River at Fitzgerald**		**Slave River at Fort Smith**	
	units	**n**	**Median**	**n**	**Median**
Aluminum (dissolved)	µg/L	24	30		
Aluminum (total)	µg/L	102	990	5	4360
Antimony (dissolved)	µg/L	24	0.17		
Antimony (total)	µg/L	43	0.14	5	0.53
Arsenic (dissolved)	µg/L	202	0.4		
Arsenic (total)	µg/L	37	1.1	54	1.7
Beryllium (dissolved)	µg/L	24	0.001		
Beryllium (total)	µg/L	101	0.005	5	0.333
Barium (dissolved)	µg/L	24	47		
Barium (total)	µg/L	207	80	5	158
Cadmium (dissolved)	µg/L	24	0.03		
Cadmium (total)	µg/L	210	0.28	85	0.20
Chromium (dissolved)	µg/L	24	0.18		
Chromium (total)	µg/L	102	1.76	83	4.20
Cobalt (dissolved)	µg/L	24	0.07		
Cobalt (total)	µg/L	211	1.2	65	1.4
Copper (dissolved)	µg/L	28	2.4		
Copper (total)	µg/L	211	4.0	84	5.2
Iron (dissolved)	µg/L	29	90		
Iron (total)	µg/L	101	2020	84	3526
Lead (dissolved)	µg/L	28	0.24		
Lead (total)	µg/L	211	2.1	83	2.3
Manganese (dissolved)	µg/L	29	4		
Manganese (total)	µg/L	102	58	65	67
Mercury (total)	µg/L	12	0.02	21	0.04
Molybdenum (dissolved)	µg/L	24	0.75		
Molybdenum (total)	µg/L	102	0.66	5	1.90
Nickel (dissolved)	µg/L	24	1.4		
Nickel (total)	µg/L	210	3.4	84	6.0
Selenium (dissolved)	µg/L	203	0.22		

Parameter		**Slave River at Fitzgerald**		**Slave River at Fort Smith**	
	units	**n**	**Median**	**n**	**Median**
Selenium (total)	µg/L	37	0.24	9	5.33
Silver (dissolved)	µg/L	24	0.003		
Silver (total)	µg/L	79	0.100	5	0.20
Strontium (dissolved)	µg/L	24	139		
Strontium (total)	µg/L	101	140	5	147
Thallium (dissolved)	µg/L	24	0.01		
Thallium (total)	µg/L	43	0.03	5	0.10
Tin (dissolved)	µg/L	24	0.013		
Tin (total)	µg/L	43	0.006		
Vanadium (dissolved)	µg/L	24	0.33		
Vanadium (total)	µg/L	209	2.50	5	13.9
Zinc (dissolved)	µg/L	28	2.8		
Zinc (total)	µg/L	209	12.0	84	17

Parameters highlighted in yellow are included in the US Environmental Protection Agency (US EPA) list of priority pollutants and/or the Canadian Environmental Protection Act's priority substances list.

Several of these metals are included on the US Environmental Protection Agency (EPA) list of priority pollutants and/or the Canadian Environmental Protection Act's priority substances list and are highlighted in grey in Table 7.10. Priority pollutants do not readily break down in the environment and can bioaccumulate in food chains to levels that can be harmful to human and/or ecological health (USEPA, 2012f).

Metal concentrations in samples from Fort Smith and Fitzgerald were compared to the Canadian Guidelines for the Protection of Freshwater Aquatic Life (CPFAL). In the absence of a national guideline, British Columbia Ministry of the Environment's surface water guidelines for the protection of aquatic life were used for comparative purposes.

National records of analytical laboratory methods for metals have been kept since 1980 (VMV codes dictionary). It should be noted that laboratory methods for some metals have changed up to five times over the period of record, resulting in changing detection limits and recovery rates. The influences of these changes, including the pattern and distribution of censored data were considered while assessing the suitability of each metal for long-term trend analyses (Section 5.6.2; Zajdlik, 2011b). For instance, long-term trends were not conducted on total cobalt because a large number of the observations were below detection limits (i.e., censored data) and there was a progressive improvement in detection limits. In addition, more than 30% of the cadmium, total silver and total tin values were censored, so long-term trend assessments were not conducted on these metals. Considerations with regard to changing laboratory methods are discussed within the pertinent metal section write-ups.

Note that although Environment Canada did assess long-term trends for select metal concentrations in the Peace and Athabasca Rivers, long-term trends for metal concentrations in the Slave River were not examined (Glozier *et al*., 2009).

It is important to re-iterate that within the analyses conducted under this report, if a value was reported as less than the detection limit, the full detection limit was used in the calculation of basic statistics such as mean, median and standard deviation. Although this may bias the results towards being higher than they actually are, it is a more conservative assessment approach.

7.3.4.1 Aluminum

Background

Aluminum is the third most abundant element in the earth's crust. It is rapidly sorbed to sediments and precipitated from solution (BC MOE, 1998). The dissolved form of aluminum is more toxic than the particulate form, with the greatest toxicity occurring in waters having a pH of less than 6 (CCREM, 1987). Natural sources of aluminum include the weathering of igneous and sedimentary rocks, especially clay. Anthropogenic sources of aluminum include air emissions, waste water effluents, metal leaching associated with acid mine drainage and solid waste related to aluminum production (McNeely *et al.*, 1979; BC MOE, 1998). As aluminum is found naturally in soils, some anthropogenic processes, such as land clearing for development, can release these naturally occurring metals, but at elevated levels.

The CCME CPFAL guideline for aluminum applies to the dissolved form of the metal; for pH values greater than 6.5 (as found in the Slave River), it is recommended that dissolved aluminum concentrations not exceed 100 µg/L (CCME, 1999).

Results

Levels of aluminum were among the highest of any of the metals measured in the Slave River, consistent with erosional inputs and the sediment-laden character of the river. Concentrations of total aluminum at Fort Smith ranged from 338 to 26,700 µg/L (n=5; 2001-2010). At Fitzgerald, levels were higher and more variable, ranging from 9 to 48,700 µg/L (n=102; 1993-2010). The broader range of values at Fitzgerald is probably indicative of the longer period of record. As a comparison, total aluminum levels ranged from 11 to 19,900 µg/L in the Peel River (n=58, 1993-2005) and 7 to 65,100 µg/L in the Liard River (n=77; 1993-2005).

Dissolved aluminum levels at Fitzgerald were much lower than total levels, ranging between 11 and 548 µg/L (n=24; 2006-2010); four of the values exceeded the dissolved aluminum guideline. Dissolved aluminum levels are not measured at Fort Smith.

For those sample dates on which both total and dissolved aluminum concentrations are available (n=24; 2006-2010), dissolved aluminum accounted for only 15% (average value) of the total concentration. It was also found that total aluminum at Fitzgerald was highly correlated with TSS (r_s=0.92; p<0.05; n=101). These facts, along with the low dissolved values, suggest that the aluminum in the Slave River is mostly associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

Long-term trend assessments of the total aluminum data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). A decreasing summer trend, at the 90% confidence level, was found (p=0.0839; Figure 7.24). Note that no significant trends, at the 90% or 95% confidence level, were found annually or in the other individual seasons (p-values range from 0.4347 to 0.5983; Appendix 7.1).

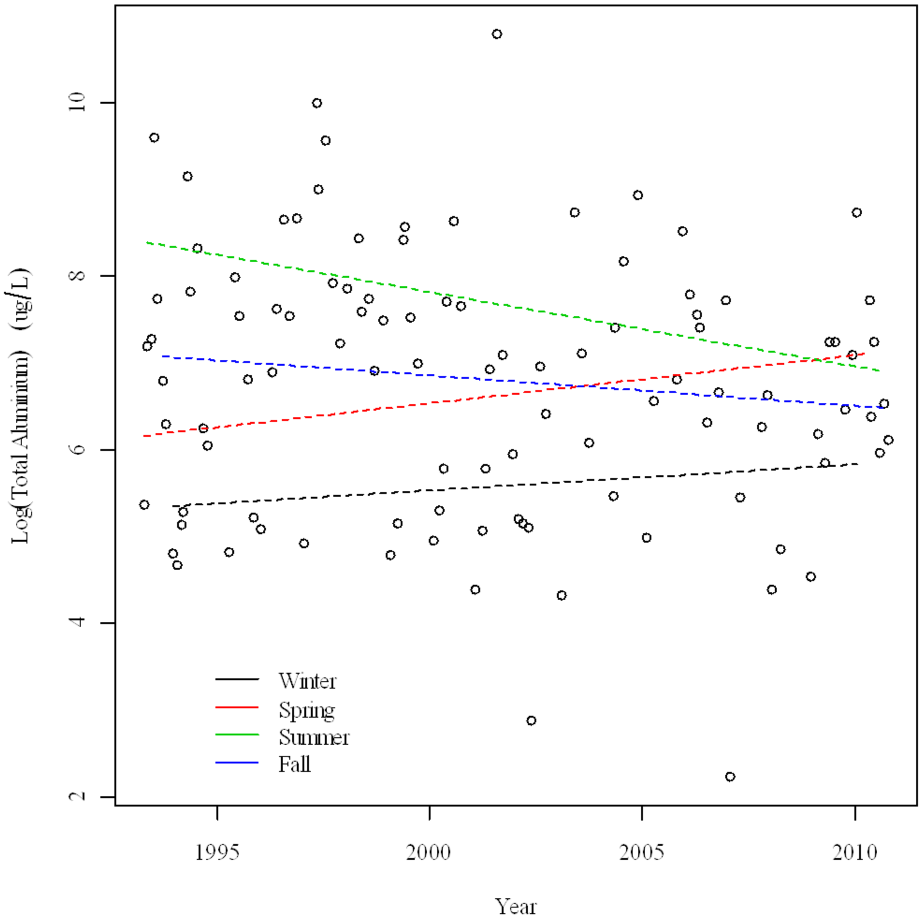

Figure 7.24: Trend Results - Non flow-adjusted total aluminum concentrations from Fitzgerald (1993-2010). Although trend lines have been displayed for each season, none are statistically significant at the 95% confidence level (from Zajdlik, 2011b).

Because total aluminum revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there was no longer an interaction between season and year. Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Appendix 7.1). The lack of a trend in the flow-adjusted aluminum data may be a reflection of the decreasing trend in summer flows that was identified.

Recommendation
It is recommended that total and dissolved aluminum continue to be monitored at Fitzgerald and that dissolved aluminum should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that long-term trend analysis should be conducted for dissolved aluminum once a longer dataset is available. Given the high sediment load of the Slave River, it is also recommended that site-specific objectives be developed to allow for a better assessment of the aluminum levels in the river.

7.3.4.2 Antimony

Background
Antimony is considered a non-essential element and is toxic to most organisms at elevated concentrations. Its bioavailability and toxicological effects depend on its chemical form and oxidation state. Antimony is naturally found in trace amounts in surface water, as a result of geochemical weathering of rocks and runoff from surrounding soils (CCREM, 1987). Anthropogenic sources of antimony include inputs from industrial land clearing, municipal and mining discharges and atmospheric inputs from coal power plants and copper smelters (CCREM, 1987). In addition, certain gasolines can have high levels of antimony. Antimony has been identified as one of the priority toxic elements related to process-affected water (tailings water) from oil sands activities (Environment Canada, 2010b).

There is currently no national CCME CPFAL guideline for antimony. However, BC MOE has a draft total antimony guideline of 20 µg/L[17] for the protection of freshwater aquatic life (BC MOE, 2006a).

Results
At Fort Smith, total concentrations of antimony were between <0.1 and 4.4 µg/L (n=5; 2001-2010). At Fitzgerald, total antimony ranged from 0.02 to 1.36 µg/L (n=43; 2002-2010), while dissolved concentrations ranged from 0.001 to 0.695 µg/L (n=24; 2006-2010). Values of antimony detected in the Slave River were always below the BC guideline. As a comparison, from 2002-2005, total antimony concentrations in the Peel and Liard rivers were the same, ranging from 0.1 to 0.4 µg/L (n_{Peel}=14; n_{Liard}=19).

For those sample dates on which both total and dissolved antimony concentrations are available (n=24; 2006-2010), all of the antimony (100%) was in the dissolved form. The

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[17] Adopted from the Province of Ontario

correlation between total antimony and TSS was significant but not very strong (r_s=0.50; p<0.05; n=42). This information suggests that antimony in the Slave River occurs mainly in the dissolved form and is potentially more biologically available to aquatic life.

At Fitzgerald, total antimony has only been analyzed since 2002, resulting in a small sample size (n=43). Therefore, long-term temporal trends were not examined.

Recommendation

Since antimony is associated with oil sands process waters and has been identified as a priority toxic element by Environment Canada, it is recommended that total and dissolved antimony continue to be monitored at Fitzgerald and that dissolved antimony should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that long-term trend analysis should be conducted for antimony once a longer dataset is available.

7.3.4.3 Arsenic

Background

Arsenic occurs naturally as a result of weathering of rocks and soils, and from anthropogenic sources such as emissions from gold, iron and steel industries, as well as inputs from industrial land clearing (CCREM, 1987). Arsenic is also used in herbicide, pharmaceutical, glass and wood preservative manufacturing (CCME, 2001). Levels of arsenic in natural source waters ranges between 2 and 50 µg/L (CCME, 2001). Similar to antimony, arsenic has also been identified as one of the priority toxic elements related to process-affected water from the oil sands (Environment Canada, 2010b).

The current CCME CPFAL guideline for total arsenic is 5 µg/L.

Results

In the Slave River at Fort Smith, total arsenic values ranged from 0.3 to 15.7 µg/L (1982-2010), and the CCME CPFAL guideline was exceeded in five of 54 samples. Four of these exceedances occurred in June (5.5 – 15.7 µg/L) when flows and sediment load are high, and once in October (6.8 µg/L). At Fitzgerald, total arsenic values ranged from 0.25 to 4.67 µg/L (n=37; 2003-2010) and dissolved concentrations ranged from <0.1 to 3.8 µg/L (n=202; 1978-2010); all arsenic concentrations from Fitzgerald were below the total arsenic guideline (Figure 7.25).

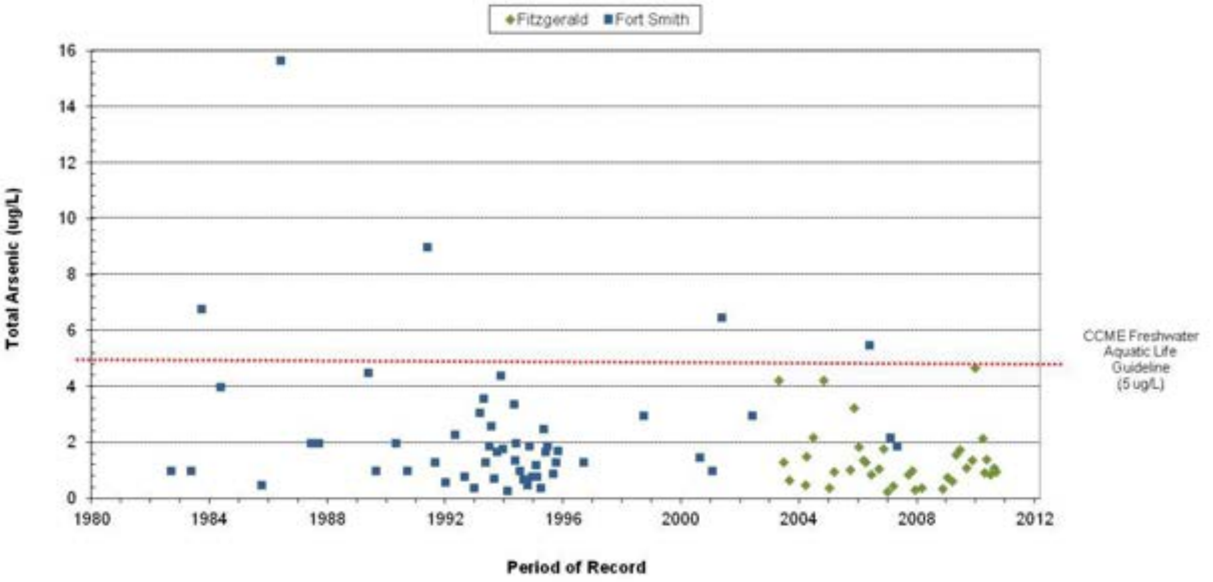

Figure 7.25: Comparison to Guidelines - Non flow-adjusted total arsenic concentrations from Fitzgerald (2003-2010) and Fort Smith (1982-2010). Total arsenic data were not log transformed.

As a comparison, total arsenic levels ranged from 0.2 to 6.3 µg/L in the Liard River (n=14; 1 guideline exceedance). In the Peel River, total arsenic concentrations ranged from 0.1 to 12.2 µg/L (n=9; 1 guideline exceedance).

For those sample dates on which both total and dissolved arsenic concentrations are available, 48% (average value) of the arsenic in the Slave River at Fitzgerald was in the dissolved fraction (n=24; 2006-2010). Total arsenic and suspended solids were strongly correlated at Fitzgerald (r_s=0.95; p<0.05; n=36) whereas at Fort Smith, the correlation between these variables was significant, but not as strong (r_s=0.66; p<0.05; n=49). This information suggests that a considerable portion of the arsenic in the Slave River is in the particulate form and would therefore be less biologically available to aquatic life. However, it is recommended that further monitoring of both forms of the metal should continue in order to confirm the current assessment.

At Fitzgerald, due to the small sample size and limited years of record (n=37, 2002-2010), total arsenic data did not meet the data quality criteria for conducting long-term trend assessments.

Although the period of record was adequate (1978-2010), the assessment of the long-term temporal trends of dissolved arsenic was challenged by the high degree of censoring at the beginning of the record and the low variability in the observations, particularly between 1983 and 2002. Therefore, the Fitzgerald dissolved arsenic was not examined for long-term trends. The low variability in the observations, was most likely due to the laboratory reporting of observations at the detection limit as being non-censored (Zajdlik, 2011b; Figure 7.26[18]) or the values being reported by the laboratory at only one significant figure.

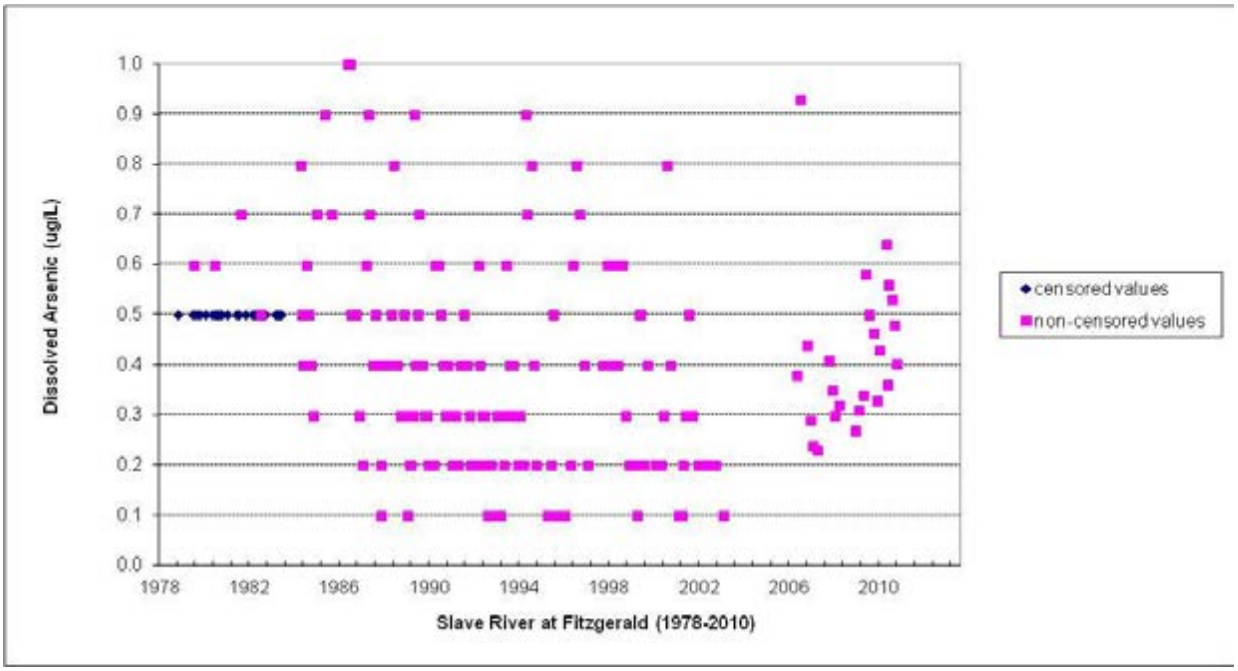

Figure 7.26: Time Series - Non flow-adjusted dissolved arsenic concentrations from Fitzgerald (1978-2010) showing the censoring (mostly before 1983) and the considerable lack of variability in the data (between 1983 and 2005). Dissolved arsenic data is not log-transformed.

Recommendation

Arsenic is an important metal from a public interest perspective and because of its association with oil sands process-water. Therefore, it is recommended that total and dissolved arsenic continue to be analyzed at Fitzgerald and dissolved arsenic become part of the routine analyses conducted at Fort Smith. It is also recommended that long-term trend analysis be conducted after 10 years of data with a minimum of two significant figures have been generated. Site-specific objectives should be developed for arsenic to allow for a more accurate assessment of the arsenic levels in the Slave River.

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[18] Note: All values greater than 1.0 μg/L (n=8) were removed for illustration purposes.

7.3.4.4 Barium

Background
Barium can be released into the environment by the weathering of naturally occurring barite bearing materials, which are often associated with metallic ore deposits. Barium occurs naturally in almost all surface waters, in concentrations ranging from 2 to 340 µg/L (USEPA, 2010). Barium is used in the petroleum industry as a weighting agent in oil and gas well drilling (USEPA, 2010). Barium is released to water and soil through the discharge and disposal of drilling wastes, from the smelting of copper, and from the manufacture of motor vehicle parts and accessories (USEPA, 2010). It is also is used in the manufacturing of metal alloys, paints, soap, linoleum, cement and many other products (CCREM, 1987).

There is currently no national CCME CPFAL guideline for barium. However, BC MOE has established a draft total barium guideline of 1000 µg/L for the protection of freshwater aquatic life (BC MOE, 2006a).

Results
Concentrations of total barium at Fort Smith ranged from 63 to 453 µg/L (n=5; 2001-2010), with no samples exceeding the BC guideline. At Fitzgerald, total concentrations ranged from 40 to 2200 µg/L (n=207; 1980-2010), with two values exceeding the BC guideline. As a comparison, in the Liard River, total barium levels ranged from 40-161 µg/L (1990-2005; n=153) and from 73-726 µg/L (1990-2005; n=130) in the Peel River. Dissolved concentrations of barium in the Slave River at Fitzgerald were lower than the observed total concentrations and ranged from 38 to 59 µg/L (n=24; 2006-2010).

For the sample dates for which both dissolved and total barium concentrations are available (n=24; 2006-2010), the dissolved fraction comprised a considerable portion [68% (average value)] of the total. This suggests that a large proportion of barium in the Slave River is potentially biologically available.

However a strong correlation between total barium and TSS (r_s=0.80; $p<0.05$; n=205) suggests that barium in the Slave River is mostly associated with particulate matter and, therefore, less biologically available for uptake by aquatic organisms.

This apparent contradiction is likely due to the limited number of dissolved barium values. In order to further understand the bioavailability of barium, it is important to continue monitoring, at regular frequencies, both total and dissolved barium.

Long-term temporal trends for total barium were not examined at Fitzgerald in this report.

Recommendation

It is recommended that total and dissolved barium continue to be analyzed at Fitzgerald and that dissolved barium become part of the routine analyses conducted at Fort Smith. Using this longer dataset, long-term trend analysis should be conducted for both total and dissolved barium.

7.3.4.5 Beryllium

Background

In most surface waters, the average levels of beryllium have been estimated to be less than 1 µg/L (CCREM, 1987). The major source of beryllium in the environment is from the combustion of fossil fuels (CCREM, 1987); however, beryllium can also enter waterways from the atmosphere, through the weathering of rocks and soils, and with discharges from industrial and municipal operations (USEPA, 2012e). Pure beryllium and its metal alloys are used in electrical components, structural components for aircraft and satellites and other metal-fabricating uses. Beryllium also has applications in the manufacturing of televisions, calculators and personal computers (USEPA, 2012e).

There is currently no national CCME CPFAL guideline for beryllium. However, BC MOE has established a draft total beryllium guideline of 5.3 µg/L for the protection of freshwater aquatic life (BC MOE, 2006a).

Results

Concentrations of total beryllium at Fort Smith ranged from <0.1 to <2.0 µg/L (n=5. 2001-2010). At Fitzgerald, total concentrations ranged from <0.00 to 2.19 µg/L (n=101; 1993-2010) and dissolved concentrations ranged from 0.002 to 0.04 µg/L (n=24; 2006-2010). Beryllium values measured in the Slave River have always been below the draft BC guideline.

In the Slave River at Fitzgerald, most of the beryllium was in the particulate fraction; dissolved beryllium accounted for only 22% (average value) of the total. Total beryllium was highly correlated with suspended solids (r_s=0.92; p<0.05; n=100). This suggests that the beryllium in the Slave River is mostly associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

As beryllium had not been raised as a parameter of public concern and the dataset had a moderately high degree of censoring, long-term temporal trends for total beryllium were not examined at Fitzgerald.

Recommendation
It is recommended that total and dissolved beryllium continue to be analyzed at Fitzgerald and that dissolved beryllium become part of the routine analyses conducted at Fort Smith. It is also recommended that long-term trend analysis should be conducted for beryllium in future reports, when a longer dataset of non-censored data is available.

7.3.4.6 Cadmium

Background
Cadmium and cadmium compounds are usually present at low levels in natural waters, in the range of 0.1 to 10 µg/L (CCREM, 1987). Cadmium is closely associated with zinc and lead in the natural environment. Natural sources of cadmium include forest fires, volcanic emissions and weathering of soil, till, and bedrock (Health Canada, 2007a). Some anthropogenic sources of cadmium include nickel- cadmium batteries, pigments, coatings and stabilizers in plastics and synthetic products (CCME, 2001). Cadmium may also be emitted into the air from zinc, lead, or copper refining, coal combustion, and mine wastewater discharges (USEPA, 2012c).

Aquatic biota exhibit acute and chronic toxicity to cadmium at relatively low levels (CCME 1999). The toxicity of cadmium is dependent on water hardness and pH (McNeely *et al.*, 1979). Heavy metals such as zinc and copper are known to increase cadmium's toxicity (BC MOE, 1998). Cadmium can be difficult to assess because many laboratories have difficulty providing detection limits that are lower than the guideline.

Like other metals, the toxicity of cadmium is highly influenced by water hardness; the toxicity increases with decreased water hardness (CCME, 1999). The CCME CPFAL guideline for total cadmium is based on the following equation:

$$WQG_{Cd} = 10\{^{0.86[\log(hardness)] - 3.2}\}\ \mu g/L$$

Using this formula, the hardness-corrected water quality guideline for total cadmium was calculated for each sample. Given the range of hardness values measured at both sampling locations, the CCME CPFAL total cadmium guideline for the Slave River ranged between 0.02 and 0.04 µg/L.

Results

Total cadmium at Fitzgerald ranged from 0.02 to 11.3 µg/L (n=210; 1980-2010). Of the 140 non-censored values, 99% of these values exceeded the guideline. For the 70 censored values, the detection limits are greater than the guideline and therefore, comparisons cannot be made (Figure 7.27). Dissolved cadmium concentrations at Fitzgerald were all above detection and ranged from 0.01 to 0.36 µg/L (n=24; 2006-2010).

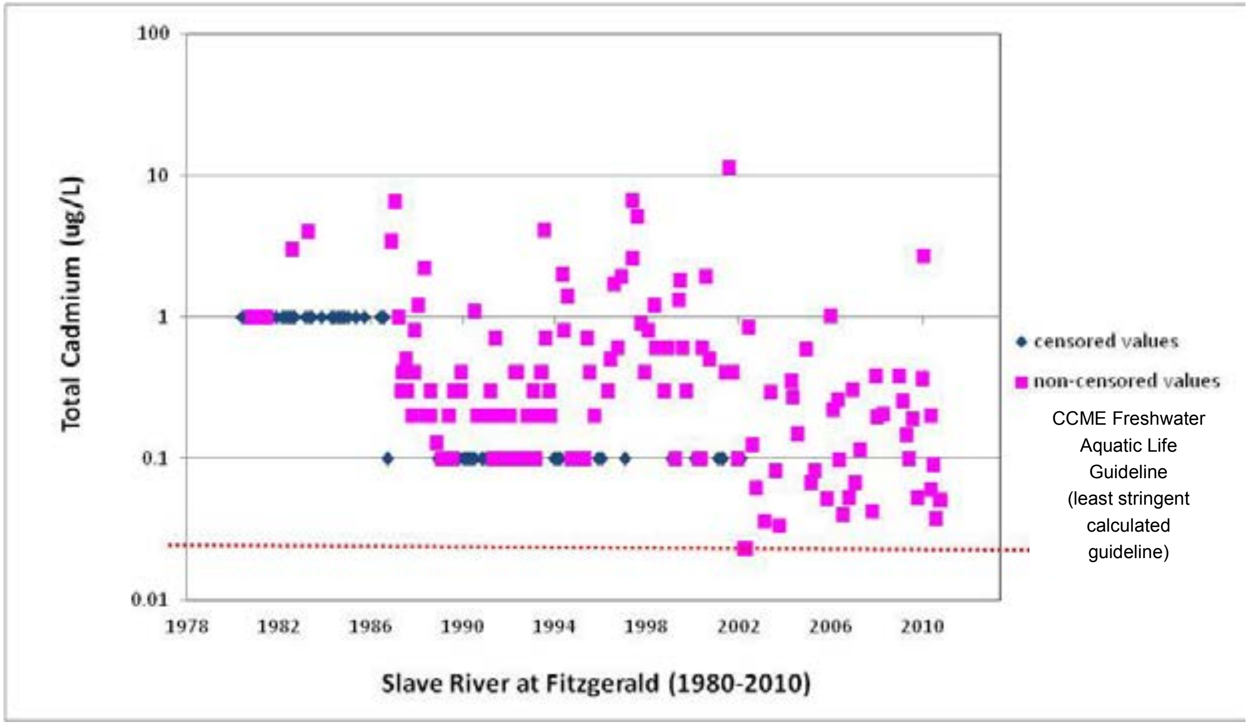

Figure 7.27: Comparison to Guidelines - Non flow-adjusted total cadmium concentrations from Fitzgerald (1980-2010). Total cadmium data were not log transformed.

At Fort Smith, 36 of 85 total cadmium values (1982-2010) were non-censored (i.e., above detection), all of which exceeded the total cadmium guideline for freshwater aquatic life. Similar to Fitzgerald, of the 49 censored values that had detection limits above the guideline, comparisons could not be made (Figure 7.28).

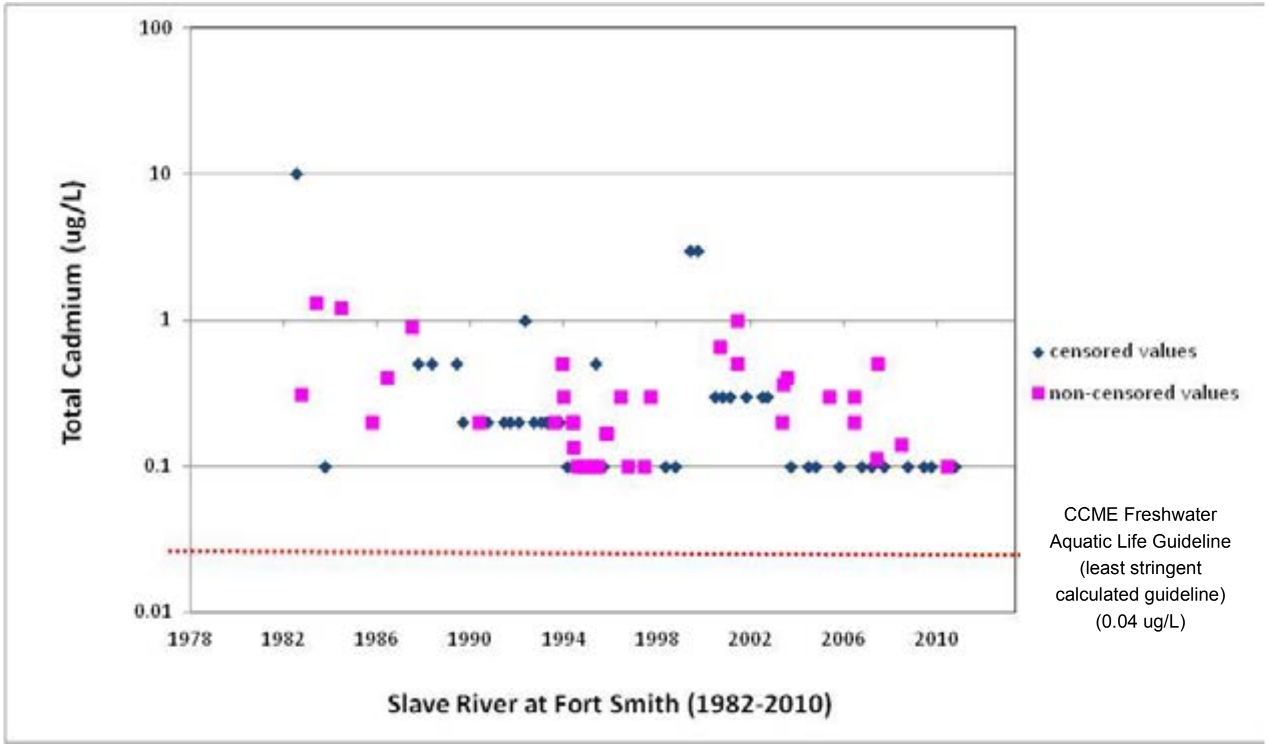

Figure 7.28: Comparison to Guidelines - Non flow-adjusted total cadmium concentrations from Fort Smith (1982-2010). Total cadmium data were not log transformed.

As a comparison, Environment Canada recorded total cadmium levels in the Liard River that ranged from 0.03 to 10.9 µg/L (n=157) and from 0.03 to 5.69 µg/L (n=131) in the Peel River. These datasets also had detection limits that were reported above the guideline.

These results highlight the need to review the appropriateness of the national guideline for use on the Slave River and other northern rivers. A water quality guideline for dissolved cadmium would provide a useful measure for turbid rivers that carry a lot of sediment.

For those sample dates at Fitzgerald for which both dissolved and total cadmium values are available (n=24; 2006-2010), dissolved cadmium made up of 47% (average value) of the total.

Although this assessment identifies that a large portion of the cadmium in the Slave River is in the particulate form and is, therefore, less biologically available, further monitoring of both forms of the metal should continue in order to confirm this conclusion.

Due to the heavy amount of censored data for total cadmium at Fitzgerald (>30%), correlation with TSS and temporal trend analyses were not completed (Table 7.11). Given the recent improvement in detection limits, further monitoring data will allow for these relationships to be examined.

Table 7.11: Degree of censoring for total cadmium at Fitzgerald.

Degree of Censoring at Fitzgerald				
Complete dataset	**Spring**	**Summer**	**Fall**	**Winter**
33%	27%	32%	32%	39%

<u>Recommendation</u>

It is recommended that both total and dissolved cadmium continue to be monitored on the Slave River to determine the bioavailability of this metal. It is also recommended that long-term trend analysis should be conducted for cadmium once a longer dataset with non-censored data has been established. Site-specific water quality objectives for cadmium should be developed, to allow a more accurate assessment of the cadmium levels in the Slave River.

7.3.4.7 Chromium

<u>Background</u>

Chromium occurs naturally in small amounts in all rocks and soils, and is released into the aquatic environment in limited quantities by weathering and erosion of these materials (McNeely *et al*., 1979). Chromium enters the atmosphere in Canada from such non-anthropogenic sources as windblown dusts, volcanic emissions, seasalt aerosols, dusts from wild fires, and vegetative debris (Health Canada, 2007b). Concentrations of chromium in some of Canada's pristine lakes and rivers have been reported as high as 5 µg/L (CCME, 1999).

Anthropogenic sources of chromium include fossil fuel combustion, iron and steel production, chemical processing and transportation-related activities such as motor vehicle operation (Health Canada, 2007b). Chromium compounds are used in metal plating and finishing, pigments and paints, leather tanning and wood preservatives, as well as in corrosion inhibition, cosmetic production, rubber products, soaps and cleaning products (CCME, 1999).

Although chromium can exist in nine different oxidation states, from (-II) to (VI), only chromium (III) and (VI) are common in natural environments. Trivalent chromium tends to be associated with relatively inert solid phases. Chromium(III) can therefore accumulate and persist in sediments and soils, but its availability for uptake by biota may be limited. Most forms of Cr(VI) compounds are quite soluble and are not readily adsorbed onto particulate matter. Chromium(VI) can thus persist in bioavailable form in aerobic surface waters and soil pore waters, but it is reduced to the less mobile forms of Cr(III) in anaerobic conditions (Health Canada, 2007b). Chromium's toxicity to aquatic life is dependent on water temperature and pH (McNeely *et al.*, 1979).

The current CCME CPFAL guideline for trivalent chromium is 8.9 µg/L and the hexavalent guideline is 1.0 µg/L. Laboratory results from the Slave programs did not identify the state of the chromium, so to be conservative, results were compared to the more stringent CPFAL guideline for hexavalent chromium (1.0 µg/L). It is recommended that in future monitoring, concentrations for individual chromium species (CrIII or CrVI) be requested.

Results

Total chromium concentrations at Fort Smith ranged from 0.3 to 86.0 µg/L (n=83; 1983-2010). Of the 83 samples, one value could not be compared to the guideline as the detection limit was too high. Of the remaining 82 samples, 65 (79%) exceeded the guideline (Figure 7.29). At Fitzgerald, total chromium concentrations ranged from <0.2 to 50.4 µg/L (n=102; 1993-2010); 67 samples (66%) exceeded the guideline (Figure 7.29). Dissolved chromium concentrations at Fitzgerald were much lower, ranging from 0.1 to 2.1 µg/L (n=24; 2006-2010).

As a comparison, total chromium levels in the Liard River ranged from 0.1 to 32.1 µg/L (n=78, 1993-2005); the guideline was exceeded 45% of the time. In the Peel River, over the same period of record, concentrations ranged from 0.1 to 29.8 µg/L (n=62) exceeding the guideline 44% of the time.

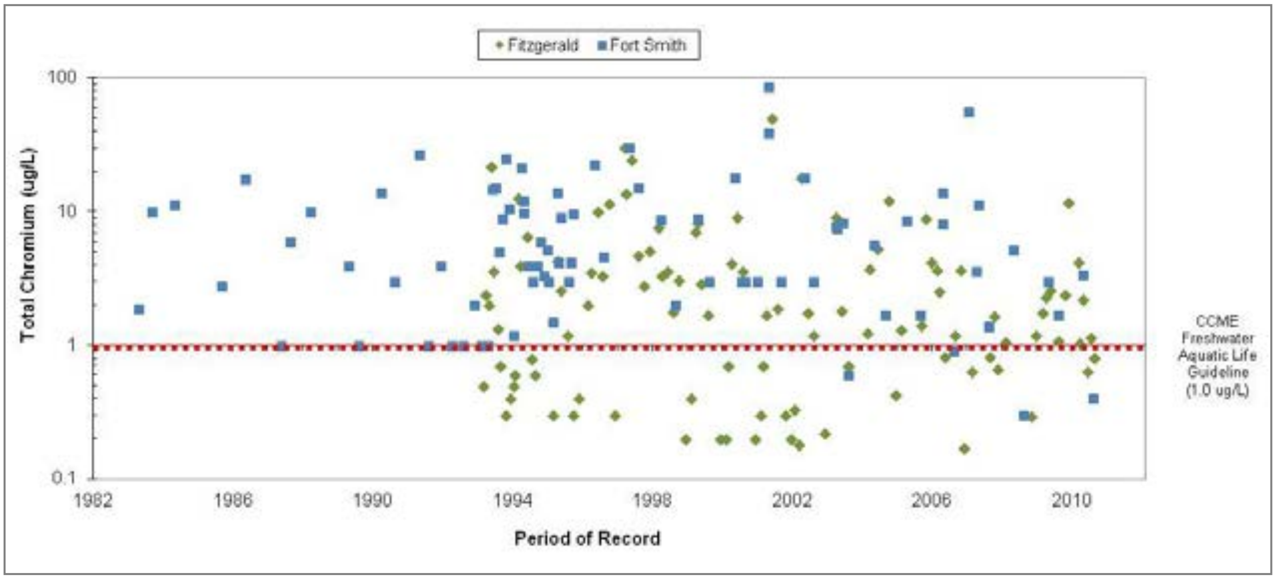

Figure 7.29: Comparison to Guidelines - Non flow-adjusted total chromium concentrations from Fitzgerald (1993-2010) and Fort Smith (1982-2010). Total chromium data were not log transformed.

For those sample dates at Fitzgerald for which both dissolved and total chromium values are available (n=24; 2006-2010), dissolved chromium accounted for only 34% average value) of the total. The correlation between total chromium and TSS was significant and strong (r_s=0.96; p<0.05; n=101). This suggests that a majority of the chromium in the Slave River is associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

Long-term temporal trend assessment of the 1993-2010 total chromium data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). A significant decreasing trend, at the 95% confidence level, was found during the summer (p=0.0362; Figure 7.30). The average decrease in concentration over the summer period of record was estimated to be 5.3 µg/L (see Section 7.2.3 of this report). No significant trends, at the 90% or 95% confidence level, were found annually or in the other individual seasons (p-values range from 0.2609 to 0.7019).

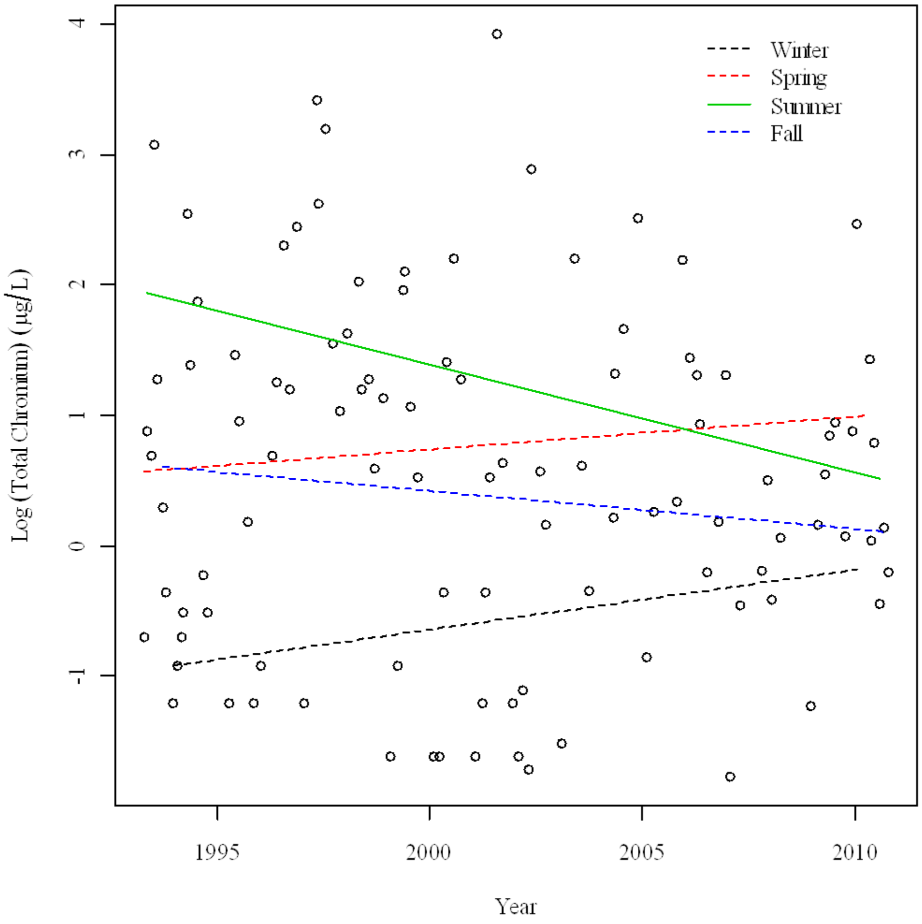

Figure 7.30: Trend Results - Non flow-adjusted total chromium concentrations from Fitzgerald (1993-2010). Although trend lines have been displayed for all seasons, only the decreasing trend for summer is statistically significant at the 95% confidence interval (from Zajdlik, 2011b). Total chromium data were log-transformed.

Because total chromium revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be an interaction between season and year (Appendix 7-1). An increasing winter trend was found at the 90% confidence level (p=0.0529). However, there was no longer a trend, at the 90% or 95% confidence level, for the summer data (p=0.3242) and no other significant long-term trends were revealed (p-values range from 0.8329 to 0.9860; Appendix 7-1). The lack of a trend in the flow-adjusted summer data may be a reflection of the decreasing trend in summer flows that was identified.

Recommendation

It is recommended that total and dissolved chromium continue to be monitored at Fitzgerald and that dissolved chromium be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that in future monitoring, concentrations for individual chromium species (CrIII or CrVI) be requested from the laboratory. Long-term trend analysis should be conducted for both total and dissolved chromium once a longer dataset is available, to confirm any existing trends. Site-specific water quality objectives for chromium should be developed, to allow a more accurate assessment of the chromium levels in the Slave River.

7.3.4.8 Cobalt

Background

Cobalt is found in a number of different rock types, including granite, basalt, shale, limestone and sandstone and trace amounts are essential for human life (CCREM, 1987; Ontario MOE, 2001). Natural concentrations of cobalt in Canadian surface waters, due primarily to weathering, volcanic eruptions and forest fires, range from less than 0.1 to 47 µg/L (CCREM, 1987; Nagpal, 2004). Human sources of cobalt to the atmosphere include coal-fired power plants and incinerators, and exhaust from vehicles. Cobalt mining and processing activities, the production of alloys and chemicals containing cobalt, sewage effluents, urban run-off, and agricultural run-off are other major anthropogenic contributors of cobalt to the aquatic environment (Nagpal, 2004).

There is currently no national CCME CPFAL guideline for cobalt. However, BC MOE has established a total cobalt guideline of 110 µg/L for the protection of freshwater aquatic life (Nagpal, 2004).

Results

The Fort Smith total cobalt concentrations ranged from <0.1 to 16 µg/L (n=65; 1993-2010). At Fitzgerald, total cobalt levels ranged from 0.05 to 47 µg/L (n=211; 1980-2010), whereas dissolved values ranged from 0.03 to 0.53 µg/L (n=24; 2006-2010). Based on the available data, the provincial guideline for cobalt has not been exceeded in the Slave River. As a comparison, total cobalt levels in the Liard River ranged from 0.02 to 21.7 µg/L (n=157). In the Peel River, concentrations ranged from 0.03 to 14.4 µg/L (n=131).

For those sample dates at Fitzgerald for which both dissolved and total cobalt values are available, most of the cobalt was in the particulate fraction (n=24; 2006-2010);, dissolved cobalt accounted for only 21% (average value) of the total. The relationship between total cobalt and TSS was statistically significant and strong at both Fitzgerald

(r_s=0.83; p<0.05; n=209) and Fort Smith (r_s=0.86; p<0.05; n=64). This information suggests that cobalt in the Slave River is mostly associated with particulate matter and therefore less bioavailable to aquatic life.

Long-term trend assessments for total cobalt at Fitzgerald (1980-2010) were challenged by the large number of censored observations and a progressive improvement in detection limits during the early portion of the period of record (Zajdlik, 2011b; Figure 7.31). In addition, a number of non-censored observations, which were reported at the detection limit, contributed to the difficulty in assessing trends (Figure 7.31). Therefore, the Fitzgerald total cobalt data were not examined for long-term trends.

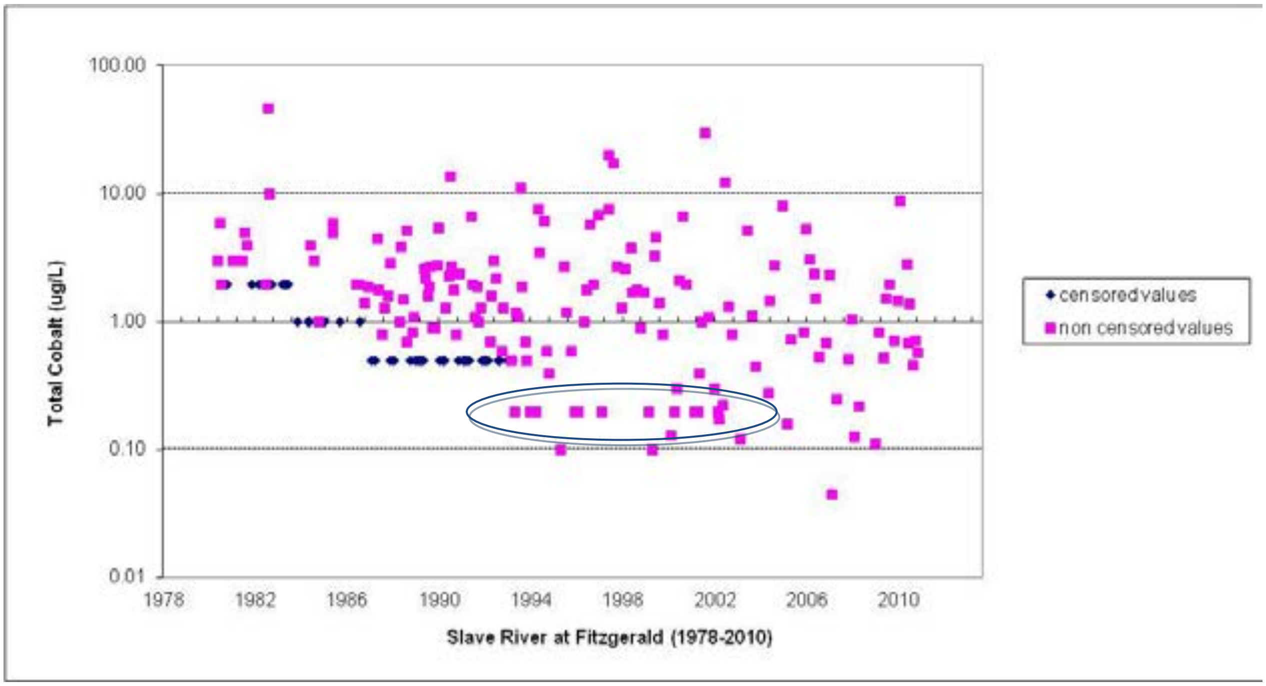

Figure 7.31: Time Series - Non flow-adjusted total cobalt concentrations from Fitzgerald (1980-2010) illustrating the large degree of censoring prior to 1994. Circled data represent non-censored data that were reported at the detection limit. Total cobalt data were not log-transformed.

Recommendation

It is recommended that total and dissolved cobalt continue to be monitored at Fitzgerald and that dissolved cobalt should be included as part of the routine analyses at the Fort Smith. It is also recommended that long-term trend analysis should be conducted for both total and dissolved cobalt once longer datasets are available.

7.3.4.9 Copper

Background

Although copper is an essential nutrient for all living organisms, it is acutely toxic to most forms of life at relatively low concentrations (BC MOE, 1998; McNeely *et al*., 1979). A predominant natural source of copper in water is the weathering of copper minerals. Natural concentrations of copper in water range from trace amounts up to 50 µg/L (McNeely *et al*., 1979; CCREM, 1987). Anthropogenic sources of copper include corrosion of copper and brass pipes, discharge from sewage treatment plant effluents, industrial effluents, mining effluents and runoff from agricultural lands (CCREM, 1987; BC MOE, 1998).

Like other metals, the toxicity of copper is highly influenced by water hardness; the toxicity increases with decreased water hardness (Alabaster and Lloyd, 1982). The CCME CPFAL guideline for total copper is based on the following equation:

$$\mathrm{WQG}_{\mathrm{Cu}} = e^{0.8545[\ln(\underline{\mathrm{hardness}})]-1.465} * 0.2 \ \mu\mathrm{g/L}$$

Using this formula, the hardness-corrected water quality guideline for total copper was calculated for each sample. Given the range of hardness values measured at both sampling locations, the CCME CPFAL total copper guideline for the Slave River ranged between 1.5 and 3.4 µg/L.

Results

At Fort Smith, total copper ranged from 0.5 to 43 µg/L (n=84; 1982-2010). Two of the 84 samples could not be compared to guidelines as the detection limits were too high. Of the remaining 82 values, 47 (57%) exceeded guidelines. At Fitzgerald, total copper values, all of which were non-censored, ranged from 0.4 to 200 µg/L (1980-2010). At this site, samples exceeded the guideline 73% of the time (154 of 211). The exceptionally high total copper value of 200 µg/L occurred in July 1982, on the same day that the highest TSS level during the entire period of record was recorded (5600 mg/L). As a comparison, total copper levels ranged from 0.2 to 57 µg/L (n=131) in the Peel River and from 0.1 to 132 µg/L in the Liard River (n=157). At Fitzgerald, dissolved copper concentrations were between 1 and 10.6 µg/L (n=28; 2006-2010).

Total copper values from both Slave River sampling locations were found to be correlated with TSS (Fitz: r_s=0.78; $p<0.05$; n=209 and Fort Smith: r_s=0.89; $p<0.05$; n=78). This suggests that copper in the Slave River is mostly associated with particulate matter and therefore, is less biologically available for uptake by aquatic organisms.

However, on the sample dates for which both dissolved and total copper concentrations are available (n=24; 2006-2010), the dissolved fraction comprised a considerable portion [67% (average value)] of the total. This suggests that a large proportion of the copper is potentially biologically available.

This apparent contradiction may be due to the limited number of dissolved copper values (short period of record). In order to further understand the bioavailability of copper, it is important to continue monitoring, at regular frequencies, both total and dissolved copper.

Long-term temporal trend assessment of the 1980-2010 total copper data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.32).

Because total copper revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

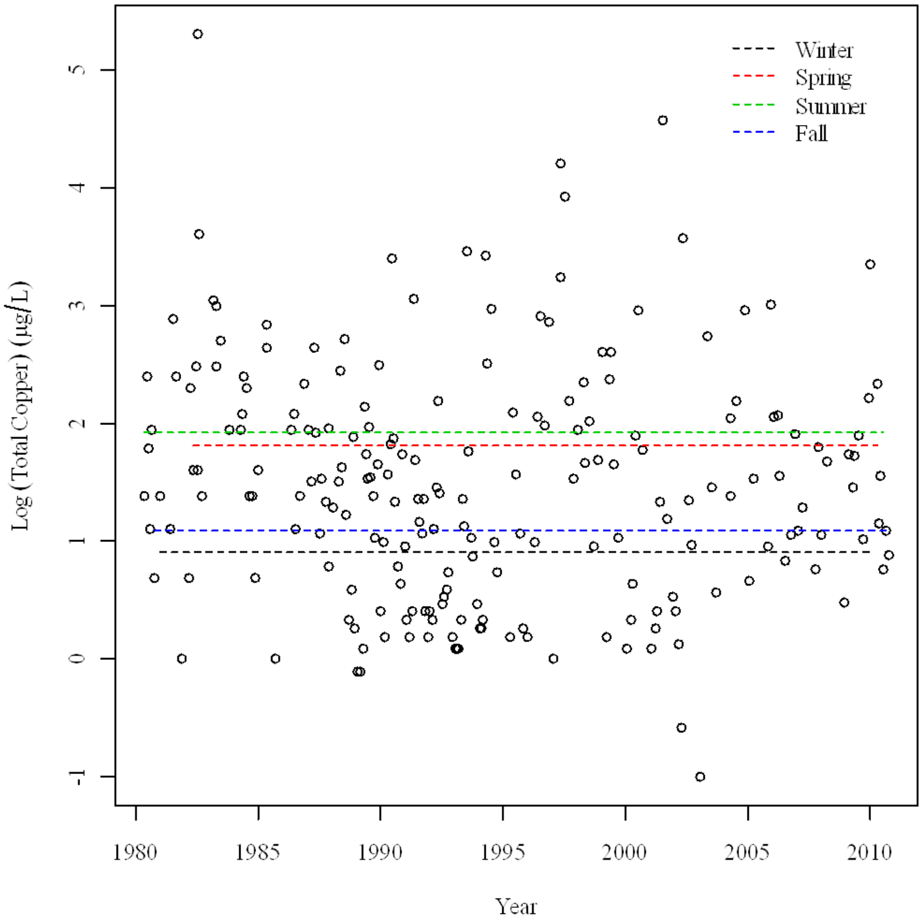

Figure 7.32: Trend Results - Non flow-adjusted total copper concentrations from Fitzgerald (1980-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Recommendation

It is recommended that total and dissolved copper continue to be monitored at Fitzgerald and that dissolved copper should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that long-term trend analysis should be conducted for dissolved copper once a longer dataset is available. Site-specific water quality objectives for copper should be developed to allow for a more accurate assessment of the copper levels in the river.

7.3.4.10 Iron

Background

Iron is the fourth most common element in the earth's crust (CCREM, 1987). It is naturally released into the environment from the weathering of sulphide ores and leaching from sandstones (CCREM, 1987). Iron can also be released to the environment by human activities, such as land clearing associated with industrial development, burning of coke and coal, metal leaching associated with acid mine drainage, mineral processing and corrosion of steel and iron products (McNeely *et al*., 1979).

The national CCME CPFAL guideline for total iron is 300 µg/L (CCREM, 1987). In addition, BC MOE has adopted freshwater aquatic life guidelines of 1000 µg/L for total iron and 350 µg/L for dissolved iron (BC MOE, 2008).

Results

The Slave River is rich in iron. Total iron concentrations at Fort Smith ranged from 180 to 24,700 µg/L (n=84; 1982-2010), with 99% of the values exceeding the CCME CPFAL guideline (300 µg/L) and 84% exceeding the BC MOE guideline (1000 µg/L). At Fitzgerald, total iron concentrations ranged from 59 to 128,000 µg/L (n=101; 1993-2010), with 89% of the measurements exceeding the CCME CPFAL guideline and 68% exceeding the BC MOE guideline (Figure 7.33). The maximum iron value of 128,000 µg/L measured at Fitzgerald was recorded on July 29, 2001, on the same day that the second highest TSS result on record (4880 mg/L) was recorded. Dissolved iron levels at Fitzgerald were much lower, ranging from 20 to 1210 µg/L (n=29; 2006-2010); three of which exceeded the BC MOE dissolved iron guideline.

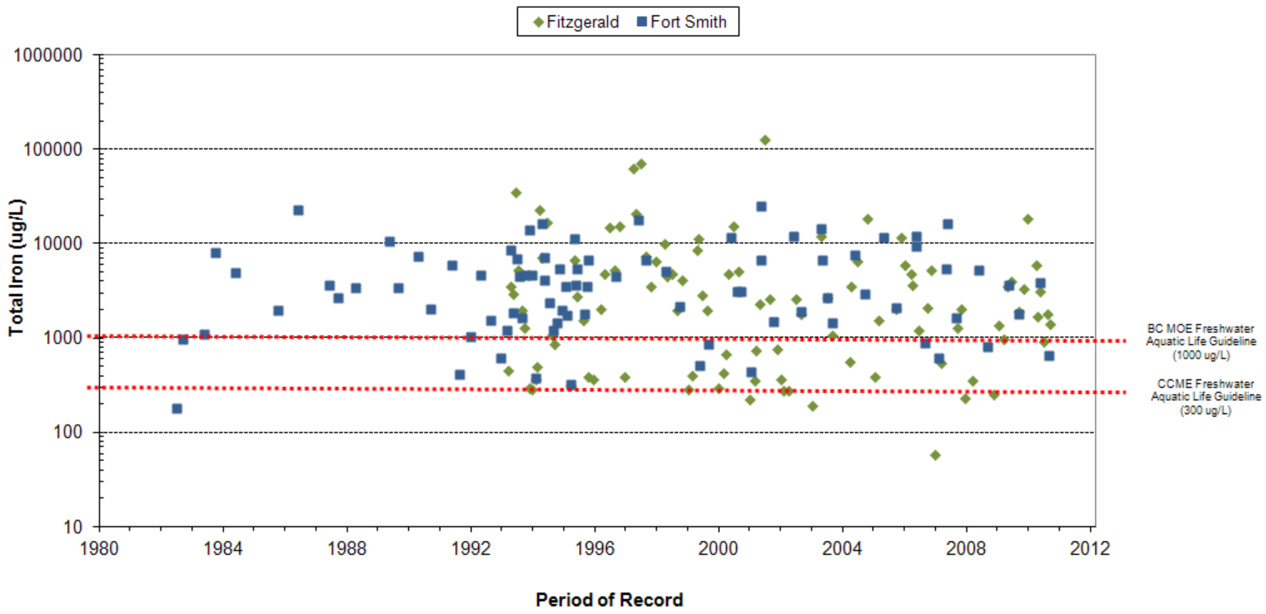

Figure 7.33: Comparison to Guidelines - Non flow-adjusted total iron concentrations from Fitzgerald (1993-2010) and Fort Smith (1982-2010). Total iron data were not log transformed.

As a comparison, in the Peel River, total iron levels ranged from 44 to 61,600 µg/L (n=61, 1993-2005). Over the same time period, in the Liard River, levels ranged from 1 to 93,500 µg/L (n=78). The CCME CPFAL guideline for total iron was exceeded in 49% and 65% of the data for each river, respectively.

In the Slave River at Fitzgerald, most of the iron was in the particulate fraction. Of the sample dates for which both dissolved and total copper concentrations were available (n=24; 2006-2010), dissolved iron accounted for only 17% (average value) of the total. The correlations between TSS and total iron were significant and strong at both locations (Fitz: r_s=0.97; p<0.05; n=100 and at Fort Smith (r_s=0.74; p<0.05; n=78). As particulate iron is not considered biologically active (Wetzel, 2001), the high total iron levels are likely not a concern for water quality in the Slave River.

Further, McCarthy *et al*., (1997), suggested that most of the iron of the Slave River was likely complexed with organic matter, which tends to reduce the impact on aquatic life. The strong and statistically significant correlation between total iron and total organic carbon content (r_s=0.86, p<0.05, n=21; Table 9.2) in the suspended sediments supports this suggestion that much of the iron in the Slave River is associated with the organic carbon.

Long-term temporal trend assessment of the 1972-2010 total iron data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend is implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.34).

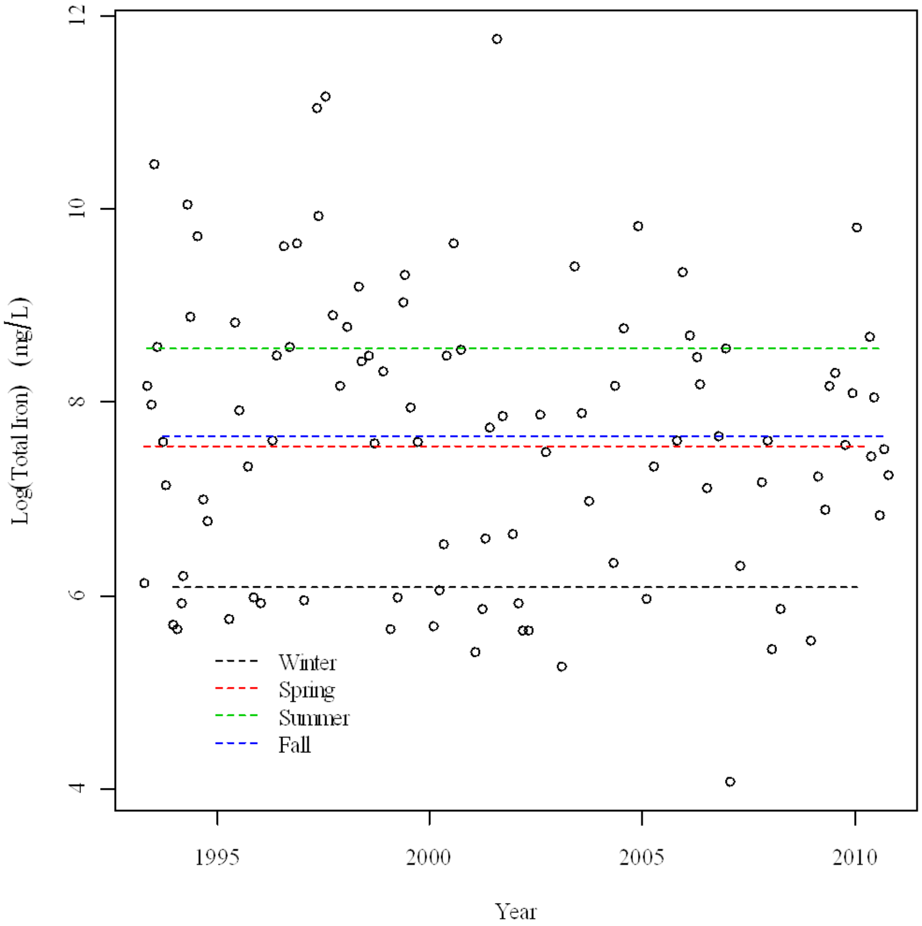

Figure 7.34: Trend Results - Non flow-adjusted total iron concentrations from Fitzgerald (1972-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Because total iron revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

Recommendation

It is recommended that total and dissolved iron continue to be monitored at Fitzgerald and that dissolved iron should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that site-specific water objectives be developed for iron to allow for a more accurate assessment of the iron levels in the Slave River.

7.3.4.11 Lead

Background

Although lead occurs naturally in the environment, it is a toxic element that can accumulate in bones (Health Canada, 2011). Small amounts of lead are naturally found in surface waters through the weathering of sulphide ores, especially galena (CCREM, 1987). Lead has been observed in natural waters ranging from trace levels up to 40 µg/L, in both the soluble and particulate forms (McNeely *et al.*, 1979).

Anthropogenic sources include emissions from automobiles, and mining and industry, which can impact waters through atmospheric transport and deposition (McNeely *et al.*, 1979). Lead and its compounds are also used in the production of batteries, manufacturing of chemical compounds, veterinary medicines, ammunition, corrosive liquid containers, solder and piping (CCREM, 1987).

The toxicity of lead is dependent on the hardness, pH, alkalinity, and dissolved oxygen content of the water (CCREM, 1987). The toxicity of lead increases with decreasing hardness. The CCME CPFAL guideline for total lead is based on the following equation:

$$WQG_{Pb} = e^{1.273[\ln(\underline{hardness})]-4.705}\ \mu g/L$$

Using this formula, the hardness-corrected water quality guideline for total lead was calculated for each sample. Given the range of hardness values measured at both sampling locations, the CCME CPFAL total lead guideline for the Slave River ranged between 1.6 and 5.4 µg/L.

Results

At Fort Smith, total lead values ranged from <0.1 to 22 µg/L (n=83; 1983-2010) and the guideline was exceeded 39% of the time (32/83). At Fitzgerald, total lead concentrations ranged from 0.16 to 77 µg/L (n=211; 1980-2010). Of the 211 samples, 15 could not be compared to guidelines as the detection limits were too high. Of the remaining 196 samples, 60 (31%) exceeded the guideline When the two highest ever recorded lead values (51 and 77 µg/L) are removed from the dataset, total lead values at Fitzgerald ranged between 0.16 and 31 µg/L. Note that these high lead values corresponded to the two highest TSS values on record. Dissolved lead values at Fitzgerald were lower and ranged from 0.04 to 1.0 µg/L (n=28; 2006-2010).

By comparison, Environment Canada recorded a maximum total lead concentration of 33.4 µg/L and a minimum of 0.02 µg/L in the Liard River (n=157). In the Peel River, total lead levels ranged from <0.2 to 22.8 µg/L (n=131).

In the Slave River at Fitzgerald, most of the lead was in the particulate fraction. On the days for which both total and dissolved lead values are available (n=24; 2006-2010), dissolved lead accounted for only 24% (average value) of the total. Strong correlations between total lead levels and TSS were observed at Fitzgerald (r_s=0.77; p<0.05; n=209) and at Fort Smith (r_s=0.81; p<0.05; n=77). These relationships, as well as the record high lead concentrations corresponding to record high TSS values, suggest that most of the lead in the Slave River is associated with particulate matter and is therefore less biologically available for uptake by aquatic organisms.

Long-term trend assessment of the 1980-2010 total lead data from Fitzgerald revealed an interaction between season and year (Appendix 7-1). No significant temporal trends, at the 90% or 95% confidence level, were found annually or in the spring, summer or fall (p-values range from 0.2408 to 0.4828; Figure 7.35). Note that, due to the heavy amount of censoring (>30%; Table 7.12), the winter total lead data did not meet data quality standards for long-term trend assessment.

Table 7.12: Degree of censoring for total lead at Fitzgerald.

Degree of Censoring at Fitzgerald				
Complete dataset	**Spring**	**Summer**	**Fall**	**Winter**
21%	17%	12%	17%	33%

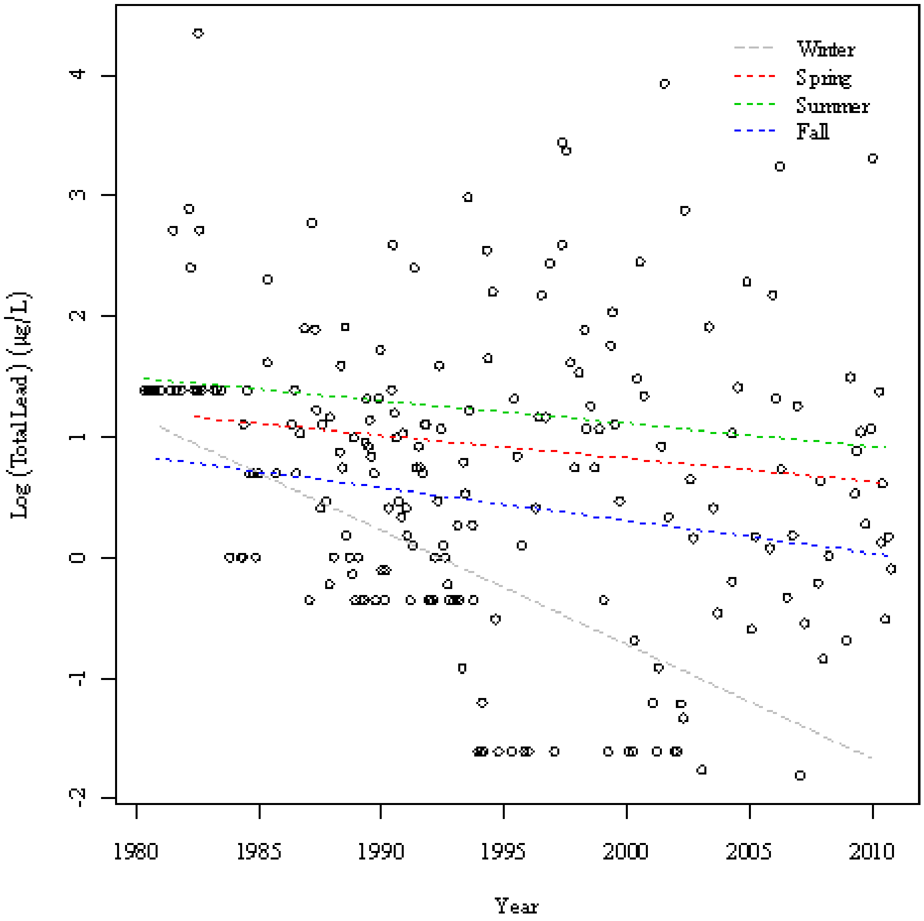

Figure 7.35: Trend Results - Non flow-adjusted total lead concentrations from Fitzgerald (1980-2010). Although trend lines have been displayed for spring, summer and fall, none are statistically significant at the 95% confidence level (from Zajdlik, 2011b). Although a winter trend line has been included, the winter data DID NOT meet data quality standards for trend assessment.

Because total lead revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow adjustment, there was no longer an interaction between season and year (Appendix 7-1) which meant that only the annual data would be assessed for trends. However, due to the highly censored winter data, and its potential to artificially affect the annual trend, it was decided not to assess long-term trends in the flow-adjusted annual data.

Recommendation
It is recommended that total and dissolved lead continue to be monitored at Fitzgerald and that dissolved lead should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that lower detection limits be achieved to address the winter censoring issue, in order to complete the long-term trend analysis. Site-specific water quality objectives for lead should be developed to allow for a more accurate assessment of the lead levels in the Slave River.

7.3.4.12 Manganese

Background
Manganese is an essential element in humans and animals and is regarded as one of the least toxic elements (Health Canada, 2009). Manganese is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans (Health Canada, 2009). It is an important element for soil fertility and plant and animal nutrition. Manganese seldom reaches concentrations of 1000 µg/L in natural waters and is usually present in quantities of 200 µg/L or less (CCREM, 1987). Soils, sediments and metamorphic and sedimentary rocks are significant natural sources of manganese (CCREM, 1987). Main anthropogenic sources include the steel industry, the manufacture of batteries and the chemical industry (Health Canada, 2009).

Manganese is found to preferentially bind to particulate matter. However, soluble species of the metal are considered to be the most toxic as they are readily available for biological reactions (BC MOE, 2001).

There is currently no national CCME CPFAL guideline for manganese. However, BC MOE has established a chronic total manganese guideline which is dependent on the hardness of the water. Based on the average hardness of the Slave River (98 mg/L), the BC MOE guideline is 1000 µg/L for the protection of freshwater aquatic life (BC MOE, 2001).

Results
Values of total and dissolved manganese at Fitzgerald ranged from 3 to 1980 µg/L (n=102; 1993-2010) and 1 to 40 µg/L (n=29; 2006-2010), respectively. Two of the 102

total manganese values exceeded the BC MOE guideline. At Fort Smith, total manganese values ranged between 6 and 482 µg/L (n=65; 1993-2010) and there were no guideline exceedances.

As a comparison, total manganese levels ranged from 7 to 865 µg/L (n=62, 1993-2005) in the Peel River and from 1 to 1300 µg/L in the Liard River (n=78, 1993-2005).

In the Slave River at Fitzgerald, most of the manganese was in the particulate fraction. On the days on which both total and dissolved values were available (n=24; 2006-2010), dissolved manganese accounted for only 20% (average value) of the total. Total manganese was highly correlated with TSS at both sampling locations (Fitz: r_s=0.98; p<0.05; n=101 and Fort Smith: r_s=0.91; p<0.05; n=64). These relationships suggest that manganese in the Slave River is mostly associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

Long-term trend assessments of the 1993-2010 total manganese data from Fitzgerald revealed an interaction between season and year (Appendix 7.1). No significant temporal trends, at the 90% or 95% confidence level were found annually or in the individual seasons (p-values range from 0.2762 to 0.9805; Figure 7.36).

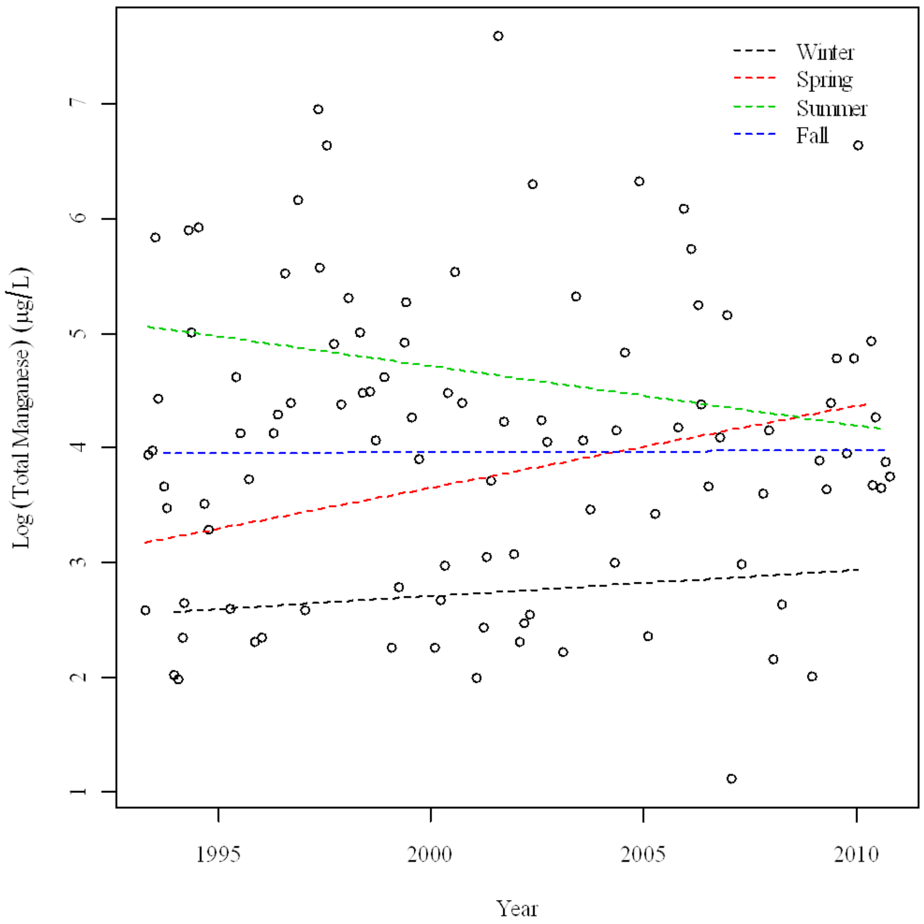

Figure 7.36: Trend Results - Non flow-adjusted total manganese concentrations from Fitzgerald (1993-2010). Although trend lines have been displayed for all seasons, none are statistically significant at the 95% confidence level (from Zajdlik, 2011b).

Since total manganese revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow adjustment, there was no longer an interaction between season and year. Therefore, only the annual data was assessed for trends and this trend was implied for each of the individual seasons. No significant trend was found at the 90 or 95 % confidence levels (Appendix 7.1).

Recommendation

It is recommended that total and dissolved manganese continue to be monitored at Fitzgerald and that dissolved manganese should be included as part of the routine analyses at the Fort Smith sampling location. Site-specific water quality objective for manganese be developed to allow for a more accurate assessment of the manganese levels in the Slave River.

7.3.4.13 Mercury

Background
Mercury is a naturally occurring element found in air, water and soil. It exists in three forms; elemental, inorganic and organic (methyl mercury; USEPA, 2012a). Mercury is found in the environment naturally from the weathering of rocks. Due to the fact that mercury is volatile, atmospheric deposition is a major pathway to aquatic systems (BC MOE, 1998). It can also enter the ecosystem through anthropogenic emissions and discharges, including municipal waste incinerations and sewage, metal smelting, and combustion of coal and other fossil fuels (CCME, 2003).

Inorganic mercury, under the right conditions, can be changed by microorganisms into methyl mercury (USEPA, 2012a). Methyl mercury is a concern in natural surface waters because it is acutely and chronically toxic and is known to biomagnify in aquatic food webs (CCME, 2003). Mercury concentrations tend to increase at higher trophic levels in the food chain, with high concentrations found in predacious pelagic fish (CCME, 2003). High mercury levels may pose a health hazard in the long-term to people who regularly consume fish and to predators, such as fish-eating birds (CCREM, 1987).

The current CCME CPFAL guideline for total mercury is 0.02 µg/L.

Results
Mercury was not routinely monitored at Fitzgerald, but the historical mercury data (1979-1981) ranged from <0.02 to 0.1 µg/L (n=12). Five of the results exceeded the CPFAL guideline. It should be noted that Environment Canada considers the pre-2002 data to be suspect due to inadequate field techniques so the data should be interpreted with care (Glozier *et al*., 2009). Since 2011, Environment Canada began analyzing the Fitzgerald surface water samples for total and methyl mercury (D. Lindeman, Aquatic Scientist, Environment Canada, Saskatoon, Saskatchewan, Pers. comm.). Mercury is not analyzed as part of the Peel or Liard River water quality monitoring programs.

At Fort Smith, the analyses of total mercury in surface water have been sporadic (1982-1990; 1993; 1995; 2000-2010), with values ranging from <0.01 to 0.22 µg/L (n=21). Within the dataset, 13 samples exceeded the guideline.

Grey *et al*., (1995) reported that there are several geological zones with relatively high mercury content in the southern Northwest Territories. The levels in the Slave River, which are comparable to other NWT sampling locations, likely reflect geological sources of mercury, rather than an anthropogenic source (Grey *et al*., 1995).

Long-term temporal trends in total mercury were not examined at Fitzgerald due to the small sample size and discontinuous record.

Recommendation

It is recommended that total, dissolved and methyl mercury continue to be monitored at Fitzgerald and that these parameters are included in the routine analyses at Fort Smith. It is also recommended that long-term trend analysis be conducted for both total and dissolved mercury once a longer dataset is available. Site-specific water quality objectives should be developed for mercury to allow for a more accurate assessment of mercury levels in the Slave River.

7.3.4.14 Molybdenum

Background

Molybdenum is a metal found in trace amounts in Canadian waters, ranging from less than 0.01 µg/L to 500 µg/L (CCME, 1999). This element can enter the aquatic ecosystem through natural sources, such as the weathering of rocks, especially shale. Anthropogenic sources include atmospheric deposition from fossil fuel burning, steel alloy and electronics manufacturing, fertilizers and mining (CCME, 1999; BC MOE, 1998). Molybdenum aids nitrogen fixation and is essential, in trace amounts, for the metabolism of aquatic plants. However, at high levels, it can be toxic to freshwater fish (CCME, 1999). While molybdenum does not bioaccumulate in animal tissue, it can accumulate in plant tissue (BC MOE, 1988).

The current CCME CPFAL guideline for total molybdenum is 73 µg/L.

Results

At Fort Smith, total molybdenum concentrations ranged from <0.1 to 6.5 µg/L (n=5; 2001-2010); at Fitzgerald, total levels ranged from <0.1 to 3.0 (n=102; 1993-2010). Dissolved molybdenum levels at Fitzgerald were lower, ranging from 0.5 to 1.1 µg/L (n=24; 2006-2010). Molybdenum concentrations never exceeded the guideline in Slave River samples.

As a comparison, total molybdenum levels ranged from 0.1 to 3.6 µg/L (n=62, 1993-2005) in the Peel River and from 1.4 to 5.6 µg/L in the Liard River (n=78, 1993-2005).

For the days on which both total and dissolved molybdenum values are available (n=24; 2006-2010), 98 to 100% was in the dissolved form. The correlation between total molybdenum and TSS was not significant (r_s=0.03; p>0.05; n=101). These relationships suggest that the molybdenum in the Slave River is potentially more biologically available to aquatic life than some of the other metals.

Long-term trend assessment of the 1993-2010 total molybdenum data from Fitzgerald revealed an interaction between season and year (Appendix 7.1). A significant decreasing trend, at the 95% confidence level, was found during the spring season (p=0.0314; Figure 7.37). The average decrease in concentration over the spring period of record was estimated to be 0.32 µg/L (see Section 7.2.3 of this report). In addition, a decreasing trend, at the 90% confidence level, was found during the summer (p=0.0866; Figure 7.37). No other significant long-term temporal trends were revealed annually or during the fall and winter (p-values range from 0.1313 to 0.7343; Appendix 7.1).

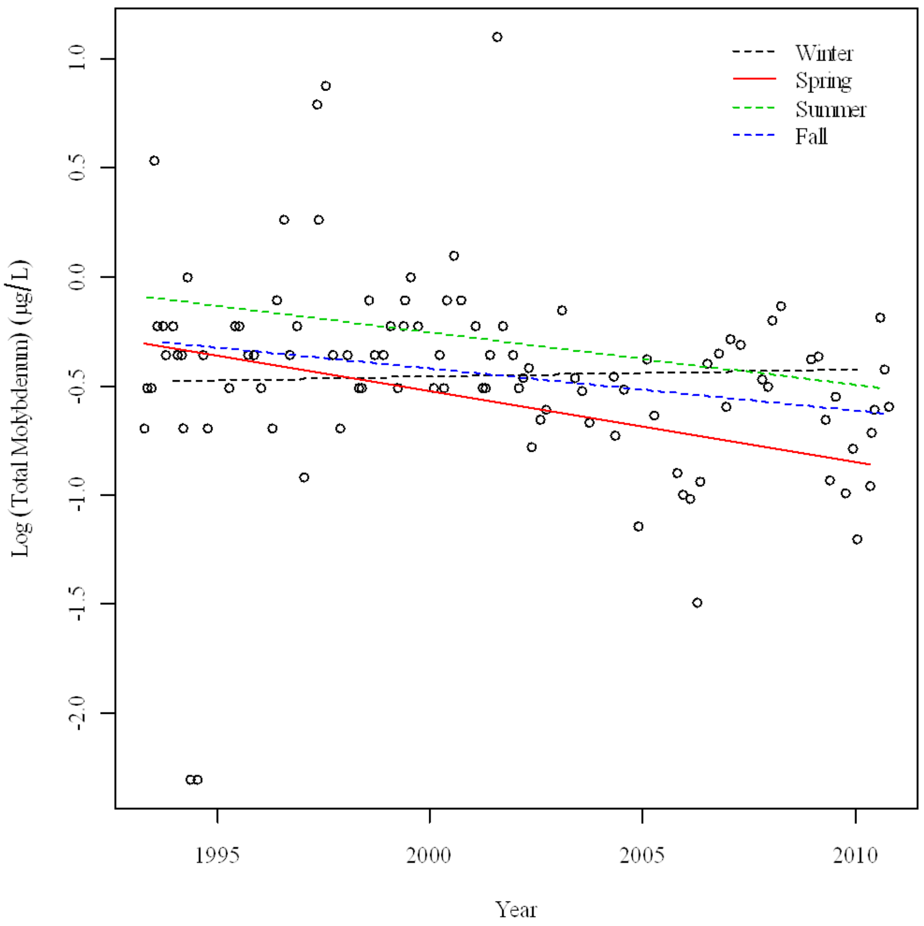

Figure 7.37: Trend Results - Non flow-adjusted total molybdenum concentrations from Fitzgerald (1993-2010). Although trend lines have been displayed for all seasons, only the decreasing trend for spring is statistically significant at the 95% confidence interval (from Zajdlik, 2011b).

Total molybdenum did not reveal a relationship with flow and, therefore, trends with the flow-adjusted data were not examined.

Recommendation

It is recommended that total and dissolved molybdenum continue to be monitored at Fitzgerald and that dissolved molybdenum should be included as part of the routine analyses at the Fort Smith sampling location. It is also recommended that further work be undertaken to determine if the decreasing trend is having an impact on water quality. Long-term trend analysis should be conducted for dissolved molybdenum once a longer dataset is available. Site-specific water quality objectives should be developed for molybdenum to allow for a more accurate assessment of molybdenum levels in the Slave River especially considering that the CCME guideline might not be protective given that the levels in the Slave River are so much lower that the guideline.

7.3.4.15 Nickel

<u>Background</u>

Nickel enters surface waters as a result of weathering processes and is usually insoluble; however some nickel salts (such as nickel chloride) are soluble in water (McNeely *et al.,* 1979). Anthropogenic sources of nickel include oil and coal combustion, nickel metal refining, sewage sludge incineration and manufacturing facilities (USEPA, 2000b). Nickel is required in trace quantities by organisms, but it is toxic to most organisms at relatively low concentrations (CCREM, 1987).

The CCME CPFAL guideline for total nickel is dependent on water hardness, with the toxicity of nickel increasing with decreasing hardness (CCREM, 1987). The CPFAL guideline for total nickel was calculated using the following equation:

$$WQG_{Ni} = e^{0.76[\ln(\text{hardness})]+1.06}\ \mu g/L$$

Using this formula, the hardness-corrected water quality guideline for total nickel was calculated for each sample. Given the range of hardness values measured at both sampling locations, the CCME CPFAL total nickel guideline for the Slave River ranged between 64 and 131µg/L.

<u>Results</u>

At Fort Smith, total nickel concentrations ranged from <1 to 57 µg/L (n=84; 1982-2010); all values were below the guideline. At Fitzgerald, total nickel concentrations were between <0.5 and 280 µg/L (n=210; 1980-2010), while dissolved concentrations ranged between 0.8 and 2.3 µg/L (n=24; 2006-2010). At Fitzgerald, the guideline was exceeded in only one sample, collected on July 26, 1982, the same day that the highest TSS value in the dataset was recorded. The next highest value of total nickel measured at Fitzgerald was 92 µg/L.

As a comparison, levels of total nickel in the Peel River ranged from 0.5 to 49.1 µg/L (n=131), and concentrations in the Liard River were between 0.5 and 64.9 µg/L (n=156).

For those sample dates on which both total and dissolved nickel concentrations are available (n=24; 2006-2010), dissolved nickel accounted for 50% (average value) of the total. Total nickel and TSS were strongly correlated at Fitzgerald (r_s=0.89; p<0.05;

n=208) and at Fort Smith (r_s=0.89; p<0.05; n=78). The data suggests that a large portion of the nickel in the Slave River is in particulate form and therefore less biologically available. However, additional monitoring of both forms of the metal should continue in order to confirm this assessment.

Long-term temporal trend assessment of the 1972-2010 total nickel data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend was implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.38).

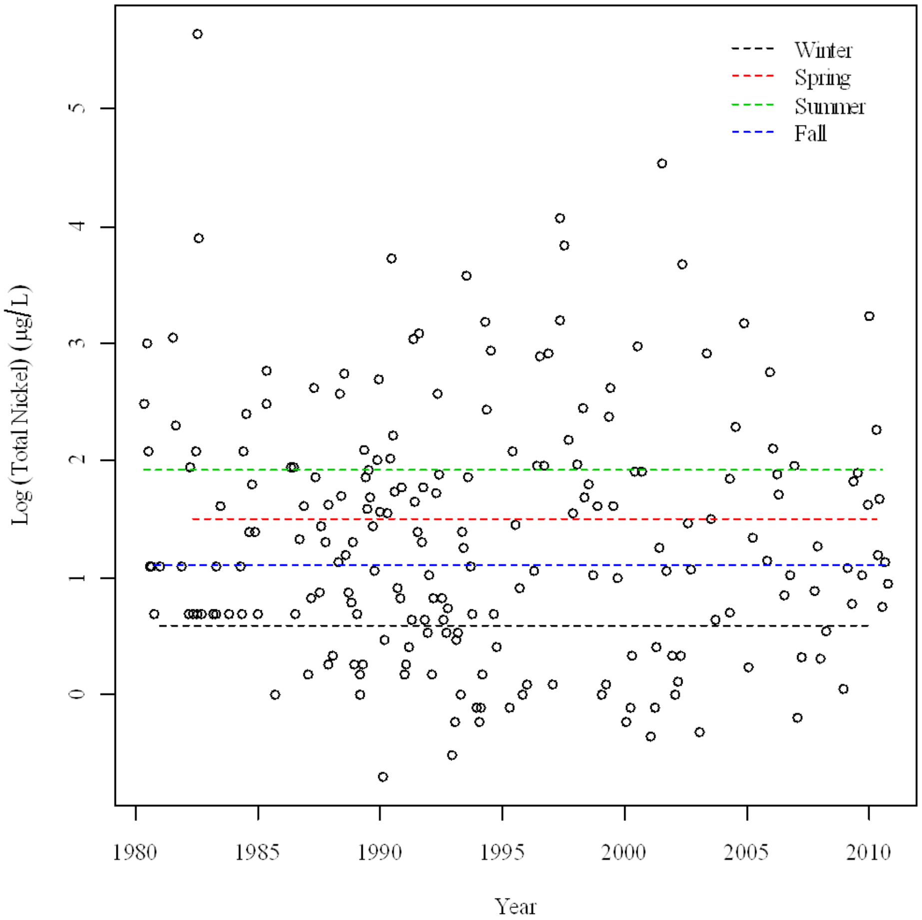

Figure 7.38: Trend Results - Non flow-adjusted total nickel concentrations from Fitzgerald (1980-2010). No statistically significant trends were found (from Zajdlik, 2011b).

Because total nickel revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

Recommendation
It is recommended that total and dissolved nickel continue to be monitored at Fitzgerald and that dissolved nickel be included as part of the routine analyses at Fort Smith. Site-specific water quality objectives should be developed for nickel to allow for a more accurate assessment of nickel levels in the Slave River especially considering that the CCME guideline might not be protective given that the levels in the Slave River rarely exceed the guideline.

7.3.4.16 Selenium

Background
Although selenium occurs naturally and is nutritionally essential, it is a bioaccumulative substance that can be toxic to both aquatic life and wildlife at elevated concentrations (USEPA, 2012d). In nature, volcanic events, and the weathering of shale, coals, and sulphide ores can introduce selenium into the aquatic environment (CCREM, 1987). Anthropogenic sources include mining, coal-fired power plants, burning of fossil fuels, petroleum refinery effluents and various manufacturing processes (McNeely *et al*., 1979; USEPA, 2012d). Selenium generally forms oxidized inorganic compounds in aqueous solution. Insoluble elemental selenium can be adsorbed by particulate matter and transported downstream.

The current CCME CPFAL guideline for total selenium is 1 µg/L.

Results
At Fort Smith, total values ranged from <1 to <10 µg/L (n=9; 1994, 2000-2010). Only two of nine total selenium values (4 and 5 µg/L) were non-censored, both of which exceeded the CPFAL guideline. Total concentrations at Fitzgerald ranged from 0.1 to 0.5 µg/L (n=37; 2003-2010), all of which were non-censored and below the CPFAL guideline. Of the 203 dissolved selenium values available from Fitzgerald, 171 values were non-censored with concentrations ranging from 0.1 to 0.7 µg/L (1978-2010).

As a comparison, in the Peel River, dissolved selenium values ranged from 0.3 to 1.2 µg/L (n=150; 1980-2005) and total concentrations ranged from 0.6 to 1.9 µg/L (n=13; 2003-2005). Selenium data for the Liard River were unavailable.

For the days on which both total and dissolved selenium values[19] are available (n=24; 2006-2010), 89% (average value) of the selenium in the Slave River at Fitzgerald was in the dissolved form. The correlation between total selenium and TSS was significant but not very strong (r_s=0.55; $p<0.05$; n=36). These relationships suggest that a greater proportion of selenium in the Slave River is potentially more biologically available to aquatic life than some of the other metals.

At Fitzgerald, assessment of the long-term temporal trends in dissolved selenium was challenged by a moderate degree of censoring (16%) and low variability in the observations, particularly between 1983 and 2002, most likely due to the laboratory reporting of observations at the detection limit as being non-censored (Zajdlik, 2011b; Figure 7.39) or the values being reported by the laboratory at only one significant figure. Therefore, the Fitzgerald dissolved selenium data were not examined for long-term trends.

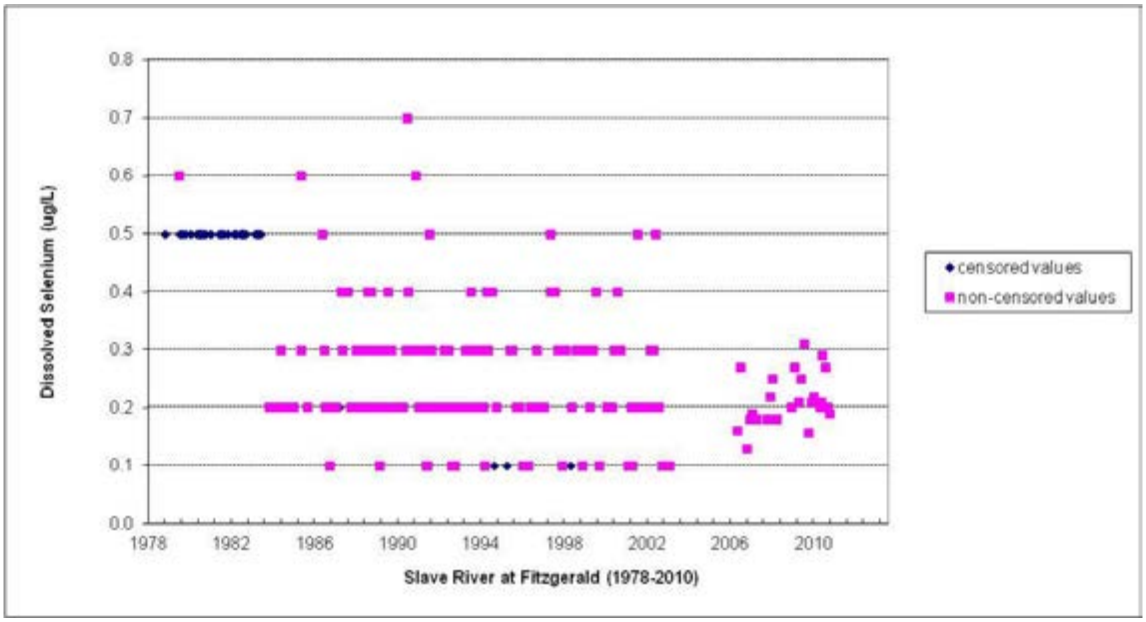

Figure 7.39: Time Series - Non flow-adjusted dissolved selenium concentrations from Fitzgerald (1978-2010) illustrating the censoring (mostly before 1985) and the considerable lack of variability in the data (between 1983 and 2005). Dissolved selenium data was not log-transformed.

Recommendation

It is recommended that total and dissolved selenium continue to be monitored at Fitzgerald and that dissolved selenium be included as part of the routine analyses at

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[19] All of which (2006-2010) are non-censored.

Fort Smith. It is also recommended that long-term trend analysis be conducted for both total and dissolved selenium after 10 years of data with a minimum of two significant figures have been generated.

7.3.4.17 Silver

Background

Silver is one of the least common but most widely distributed elements in the earth's crust (CCREM, 1987). As silver compounds are not very soluble, only trace amounts are found in water, with most silver being adsorbed to soils. Naturally, silver is weathered from ores containing silver sulphide and lead-zinc-silver, as well as from coals, shale, and soils. Volcanic activity also contributes silver to the environment. Anthropogenic sources of silver include coin and jewelry production, photography, manufacture of chemicals and ink, mining, emissions from the steel industry, cement industry and coal combustion (CCREM, 1987; BC MOE, 1998). At elevated concentrations, silver can be toxic to aquatic organisms (McNeely *et al.*, 1979; BC MOE, 1998).

The current CCME CPFAL guideline for total silver is 0.1 µg/L.

Results

At Fort Smith, only five surface water quality samples were analyzed for total silver; concentrations ranged between <0.1 and 0.7 µg/L (2001-2010). Two of the five samples had levels that exceeded the CPFAL guideline, while the other three values were less than the detection limit of 0.1 µg/L. At Fitzgerald, total silver concentrations ranged between <0.002 to 1.3 µg/L (n=79; 1996-2010), with ten samples exceeding the CPFAL guideline (ranging from 0.1 to 1.3 µg/L; Figure 7.40). Dissolved silver concentrations at Fitzgerald ranged from <0.001 to 0.073 µg/L (n=24; 2006-2010).

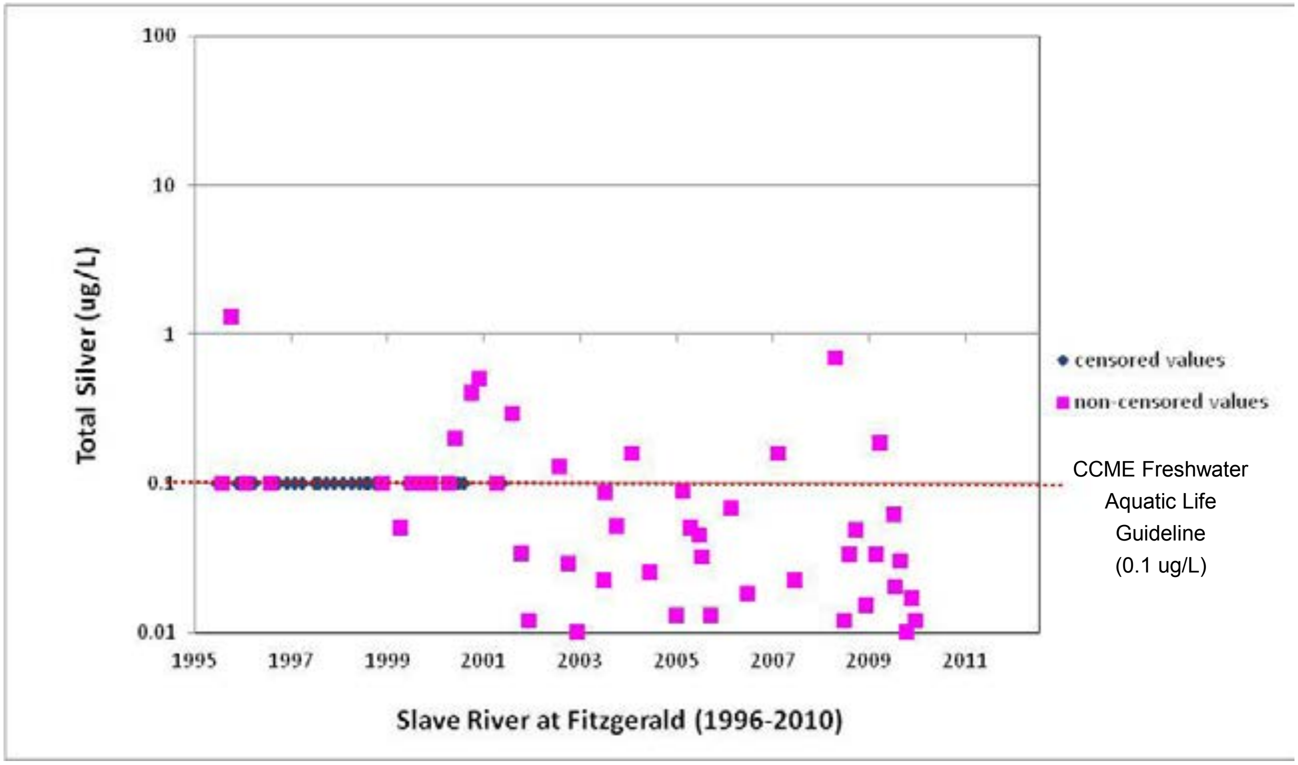

Figure 7.40: Comparison to Guidelines - Non flow-adjusted total silver concentrations from Fitzgerald (1996-2010) showing the censoring (mostly before 2003). Data was not log-transformed.

As a comparison, in the Peel River, total silver ranged from 0.002 to 0.297 µg/L (n=30), with two values exceeding the CPFAL guideline. In the Liard River, values ranged from 0.001 to 0.1 µg/L (n=25), and seven values within the dataset exceeded the guideline.

For those sample dates at Fitzgerald for which both dissolved and total silver values are available (n=24; 2006-2010), dissolved silver accounted for 34% (average value) of the total. Given the considerable amount of censoring of the total silver data between 1996 and 2002, the correlation between total silver and TSS was examined with the 2003-2010 data only, which produced a significant and strong correlation (r_s=0.84; $p<0.05$; n=37). This suggests that a majority of the silver in the Slave River is associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

Over the entire period of record (1996-2010), 30% of the data for total silver was censored, almost all of which occurred between 1996 and 2002 (29%). The latter half of the dataset (2003-2010) was not examined for long-term trends because of the short period of record (<10 years).

Recommendation

It is recommended that total and dissolved silver continue to be monitored at Fitzgerald and that dissolved silver be included as part of the routine analyses at Fort Smith. Long-term trend analysis should be conducted for both total and dissolved silver after 10 years of data have been generated.

7.3.4.18 Thallium

Background

Thallium is a rare but widespread element found throughout the world (Peter and Viraraghavan, 2004). Weathering is the main natural source of thallium to the environment and concentrations of total thallium in Canadian freshwaters naturally range from 1 to 100 µg/L (CCME, 1999). Anthropogenic sources include the production of metals, roasting of pyrite for sulphuric acid production, and mining and smelting operations of copper, gold, zinc, lead and cadmium (McNeely *et al*., 1979). Thallium is released to the environment through the combustion of fossil fuels, refinement of oil fractions, the smelting of ores, cement production and brick works (USEPA, 2008). There is currently no national CCME CPFAL guideline for thallium. However, BC MOE has a draft total thallium guideline of 0.3 µg/L[20] for the protection of freshwater aquatic life (BC MOE, 2006a).

Results

Total thallium concentrations in the Slave River at Fort Smith ranged from <0.1 to 0.5 µg/L (n=5; 2001-2010). At Fitzgerald, the levels ranged between 0.004 and 0.313 µg/L (n=43; 2002-2010). Only 1 value from Fitzgerald exceeded the BC MOE guideline (Figure 7.41). Dissolved concentrations at Fitzgerald ranged from 0.001 to 0.079 µg/L (n=24; 2006-2010). As a comparison, total thallium concentrations in the Peel and Liard rivers (2002 to 2005) ranged from 0.008 to 0.018 µg/L (n=4) and 0.004 to 0.212 µg/L (n=19), respectively. Dissolved thallium concentrations were not available for either of these rivers.

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[20] Adopted from the Province of Ontario.

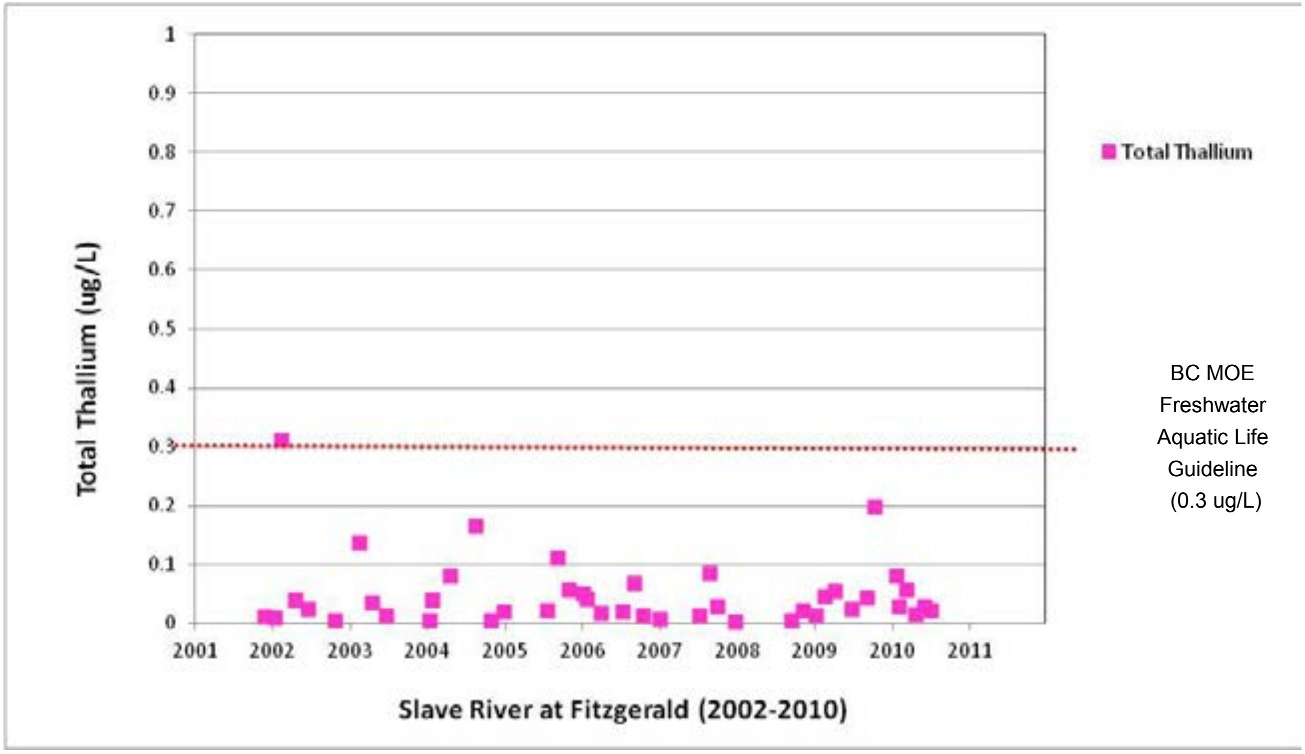

Figure 7.41: Comparison to Guidelines - Non flow-adjusted total thallium concentrations from Fitzgerald (2002-2010). Data were not log-transformed.

At Fitzgerald, the correlation between total thallium and TSS was significant and strong (r_s=0.91; p<0.05; n=41), which suggests that much of the thallium in the Slave River is associated with particulate matter. Correlation analysis was not performed on the Fort Smith data due to the small sample size.

For those sample dates on which both total and dissolved thallium concentrations are available (n=24; 2006-2010), 41% (average value) of the thallium in the Slave River at Fitzgerald was in the dissolved fraction. Total thallium and TSS were strongly correlated at Fitzgerald (r_s=0.91; p<0.05; n=41). It would appear that a large portion of the thallium in the Slave River is in the particulate form and therefore is less biologically available. However, it is recommended that further monitoring of both forms of the metal should continue in order to confirm this.

At Fitzgerald, total thallium has only been part of the metals analyses since 2002, resulting in a small sample size (n=43). Therefore, long-term temporal trends were not examined.

Recommendation

It is recommended that total and dissolved thallium continue to be monitored at Fitzgerald and that dissolved thallium be included as part of the routine analyses at Fort Smith. Long-term trend analysis should be conducted for both total and dissolved thallium after 10 years of data have been generated.

7.3.4.19 Tin

Background

Tin is a minor constituent of the earth's crust and, therefore, is found naturally in minute quantities in surface waters (McNeely *et al*., 1979). Freshwater concentrations typically do not exceed 0.8 μg/L (McNeely *et al*., 1979). Tin is released naturally to the environment by the weathering of igneous rocks that contain tin minerals. Major anthropogenic sources include industrial discharges from mining operations, refineries, food processing and packaging plants, steel manufacturing factories and construction activities (CCREM, 1987).

There are currently no CCME CPFAL or BC MOE guidelines for total tin.

Results

At Fitzgerald, levels ranged from <0.005 to 0.1 μg/L (n=43; 2002-2010), whereas dissolved tin concentrations ranged from 0.005 to 0.161 μg/L (n=24; 2006-2010). Tin is not analyzed at Fort Smith.

In the Liard River, total tin was only detectable in seven of 19 samples and of those, levels ranged from 0.022 to 0.07 μg/L. In the Peel River, of the detectable tin values (7/17), values ranged between 0.015 and 0.053 μg/L.

At Fitzgerald, total tin has only been part of the metals analyses since 2002, resulting in a small sample size (n=43). Because of this and a high percentage of censoring, correlation analyses and long-term temporal trends were not examined.

Recommendation

It is recommended that total and dissolved tin continue to be monitored at Fitzgerald and that total and dissolved tin be added to the routine analyses at Fort Smith. Long-term trend analysis should be conducted for tin after 10 years of data have been generated. In the absence of a National guideline for tin, it is recommended that site-specific objectives be developed.

7.3.4.20 Uranium

Background

Uranium is a naturally-occurring element found at low levels in virtually all rock, soil, and water (USEPA, 2012b). Uranium has many uses including specialized bulb filaments in photography and movie projectors, colouring of glasses and glazes, staining and dying agents (leather, wood and silk industries), and the production of high energy x-rays (CCME, 2011). The main use of mined uranium is fuel for nuclear-powered electrical generating stations (CCREM, 1987). Anthropogenic uranium can reach the aquatic environment through uranium mill tailings, mining effluents and stack emissions (CCME, 2011).

The CCME CPFAL guideline for total uranium is 15 µg/L, as a long-term exposure guideline and 33 µg/L, as a short-term exposure guideline (CCME, 2011).

Results

Total uranium ranged from 0.5 to 1.4 µg/L (n=5; 2001-2010) at Fort Smith and 0.33 to 2.37 µg/L (n=43; 2002-2010) at Fitzgerald. All values measured in the Slave River were below the CPFAL guidelines. As a comparison, in the Peel River (2003-2005), total uranium values ranged from 1.16 to 1.89 µg/L (n=13); whereas in the Liard River values ranged from 1.26 to 1.82 µg/L (n=14).

At Fitzgerald, total uranium and TSS were found to be correlated (r_s=0.74; p<0.05; n=42) which suggests that the uranium in the Slave River is mostly associated with particulate matter and therefore less biologically available for uptake by aquatic organisms.

Although the dissolved concentrations of uranium at Fitzgerald are lower (0.27 to 0.72 µg/L; n=24; 2006-2010), for the sample dates for which both dissolved and total uranium concentrations are available (n=24; 2006-2010), the dissolved fraction comprised a considerable portion [83% (average value)] of the total. This suggests that a large proportion of the uranium is potentially biologically available.

This apparent contradiction may be due to the limited number of dissolved uranium values (short period of record). In order to further understand the bioavailability of uranium, it is important to continue monitoring both forms of the metal.

At Fitzgerald, total uranium has only been part of the metals analyses since 2002, resulting in a small sample size (n=43). Therefore, long-term temporal trends were not examined.

Recommendation

It is recommended that total and dissolved uranium continue to be monitored at Fitzgerald and that dissolved uranium is added to the routine analyses at Fort Smith. Long-term trend analysis should be conducted for both total and dissolved uranium after 10 years of data have been generated. Site-specific objectives should be developed for uranium to allow for a better assessment of the uranium levels in the Slave River.

7.3.4.21 Vanadium

Background

Vanadium is a ubiquitous element found to occur in all Canadian provinces and territories (van Zinderen Bakker and Jaworski, 1980). In surface waters, vanadium concentrations can be as high as 300 µg/L, but are usually less than 50 µg/L (McNeely *et al.*, 1979). One natural source of vanadium is the seepage from carbonaceous deposits (van Zinderen Bakker and Jaworski, 1980). Vanadium compounds are used widely in the production of steel, alloys and iron castings, glass manufacturing, photography and textile dyeing and printing (McNeely *et al.*, 1979). Power and heat-producing plants burning fossil fuels (petroleum, coal and oil) are also anthropogenic sources of vanadium to the environment (CCME, 2011). Vanadium has been identified as one of the priority toxic elements related to process-affected water (tailings water) from oil sands activities (Environment Canada, 2010b).

There is currently no national CCME CPFAL guideline for vanadium. However, BC MOE (2006) has a draft total vanadium guideline of 6 µg/L[21] for the protection of freshwater aquatic life.

Results

At Fort Smith, only five surface water quality samples were analyzed for total vanadium, with concentrations ranging between 3.4 and 88.7 µg/L (2001-2010). Four of the values exceeded the CPFAL guideline for total vanadium. At Fitzgerald, total vanadium concentrations ranged from 0.2 to 84.8 µg/L (n=209; 1980-2010); the CPFAL guideline for total vanadium was exceeded 48 times (Figure 7.42). Dissolved vanadium concentrations at Fitzgerald were lower and ranged from 0.2 to 1.8 µg/L (n=24; 2006-2010).

As a comparison, Environment Canada reported total vanadium values that ranged from 0.1 to 70.7 µg/L (n=136) in the Peel River; exceeding the guideline 31% of the time. In

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[21] Adopted from the Province of Ontario.

the Liard River, levels ranged from 0.1 to 68.1 µg/L (n=157); exceeding the guideline 24% of the time.

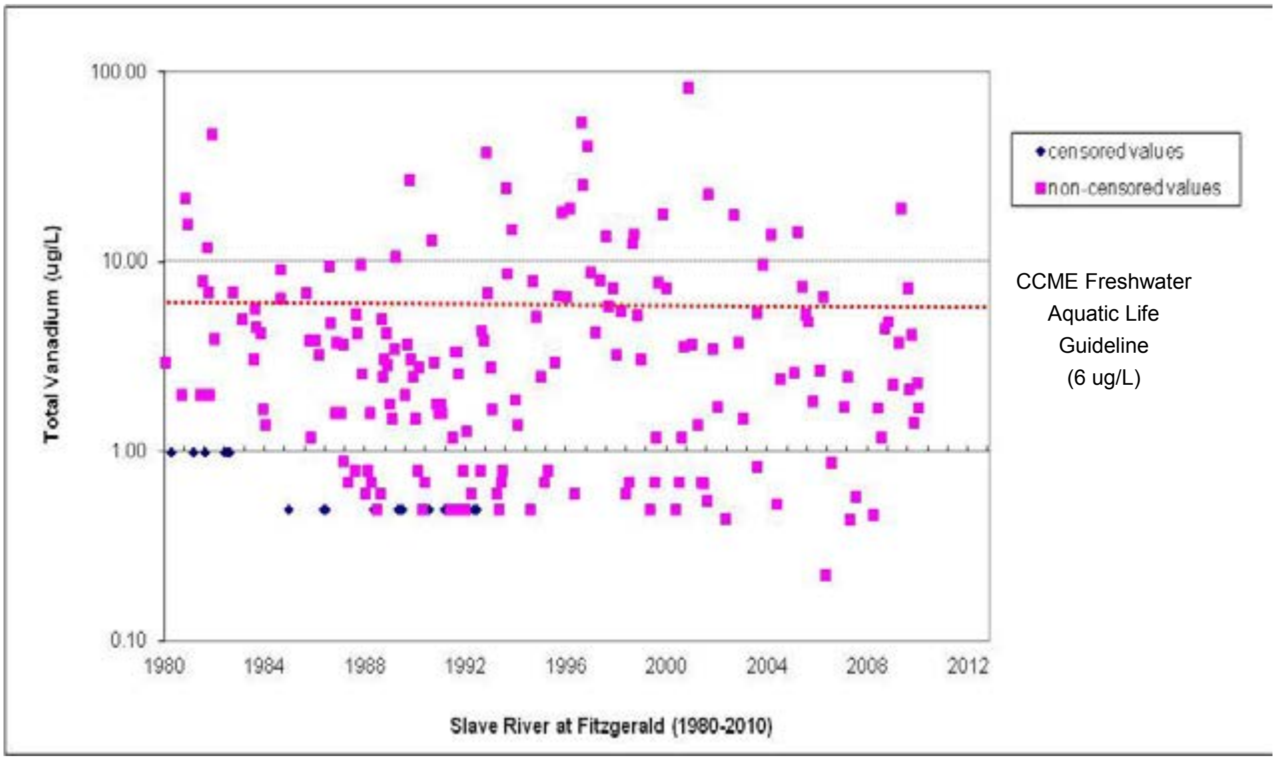

Figure 7.42: Comparison to Guidelines - Non flow-adjusted total vanadium concentrations from Fitzgerald (1980-2010). Data were not log-transformed.

In the Slave River at Fitzgerald, most of the vanadium was in the particulate fraction. On the days for which both total and dissolved values are available, dissolved vanadium accounted for 25% (average value) of the total. In addition, the correlation between total vanadium and TSS was significant and strong (r_s=0.88, $p<0.05$, n=207). This information suggests that most of the vanadium in the Slave River is associated with particulate matter and is therefore less biologically available for uptake by aquatic organisms.

Long-term temporal trend assessment of the 1980-2010 total vanadium data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend was implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.43).

Because total vanadium revealed a significant relationship with flow, the flow-adjusted were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

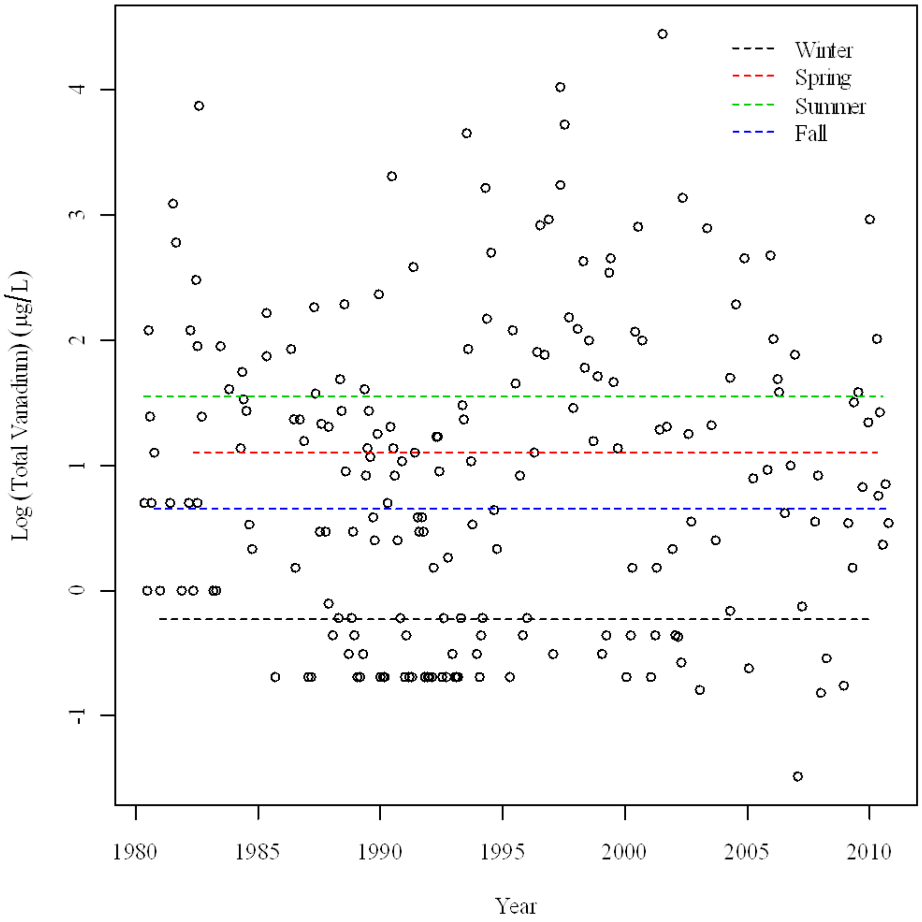

Figure 7.43: Trend Results - Non flow-adjusted total vanadium concentrations from Fitzgerald (1980-2010). No statistically significant trends were found (from Zajdlik, 2011b).

It should be noted that winter data collected at Fitzgerald, prior to 1993 exhibited a moderate degree of censoring (24%).[22] There was also an apparent improvement in detection limits over time (Figure 7.41). Since only the annual data was assessed for trends, and this includes the highly censored winter data, total vanadium trend results should be interpreted with care (Zajdlik, 2011b).

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[22] The degree of censoring in the other seasons was less: spring (7%), summer (3%) and fall (7%).

Recommendation

Vanadium has been identified as one of the priority toxic elements related to process-affected water from the oil sands (Environment Canada, 2010b). As a result, it is recommended that total and dissolved vanadium continue to be measured at Fitzgerald and that dissolved vanadium is added to the routine analyses at Fort Smith. It is also recommended that long-term trends be re-examined once an adequate winter dataset has been established. Site-specific water quality objectives should be developed for vanadium to be able to better assess the vanadium levels in the Slave River.

7.3.4.22 Zinc

Background

In natural waters the concentrations of zinc are usually below 50 µg/L (McNeely *et al*., 1979). Zinc enters the environment naturally through the weathering of rocks and soils, while anthropogenic sources include automobiles and industrial processes, mining activities, industries (paints, rubber, textiles, printing), agriculture (fertilizers, pesticides) and urban runoff (CCREM, 1987; BC MOE, 1998,1999). Zinc is an essential element for plants and animals as it is necessary for the functioning of certain enzymes. It is relatively non-toxic to terrestrial organisms, but can be acutely and chronically toxic to aquatic organisms, especially fish (BC MOE,1998). The toxicity of zinc increases with decreasing dissolved oxygen and water hardness. Zinc also becomes more toxic with increasing temperature and greater concentrations of copper and cadmium (McNeely *et al*., 1979).

The current CCME CPFAL guideline for zinc is 30 µg/L.

Results

At Fort Smith, total zinc levels ranged from <3 to 162 µg/L (n=84; 1982-2010). Twenty-one samples (25%) had levels that exceeded the CPFAL guideline. At Fitzgerald, total zinc concentrations ranged from 0.7 to 561 µg/L, and 18% (38 of 209; 1980-2010) of the values exceeded the CPFAL guideline (Figure 7.44). Dissolved zinc concentrations at Fitzgerald were lower and ranged from 0.3 to 28 µg/L (n=28; 2006-2010).

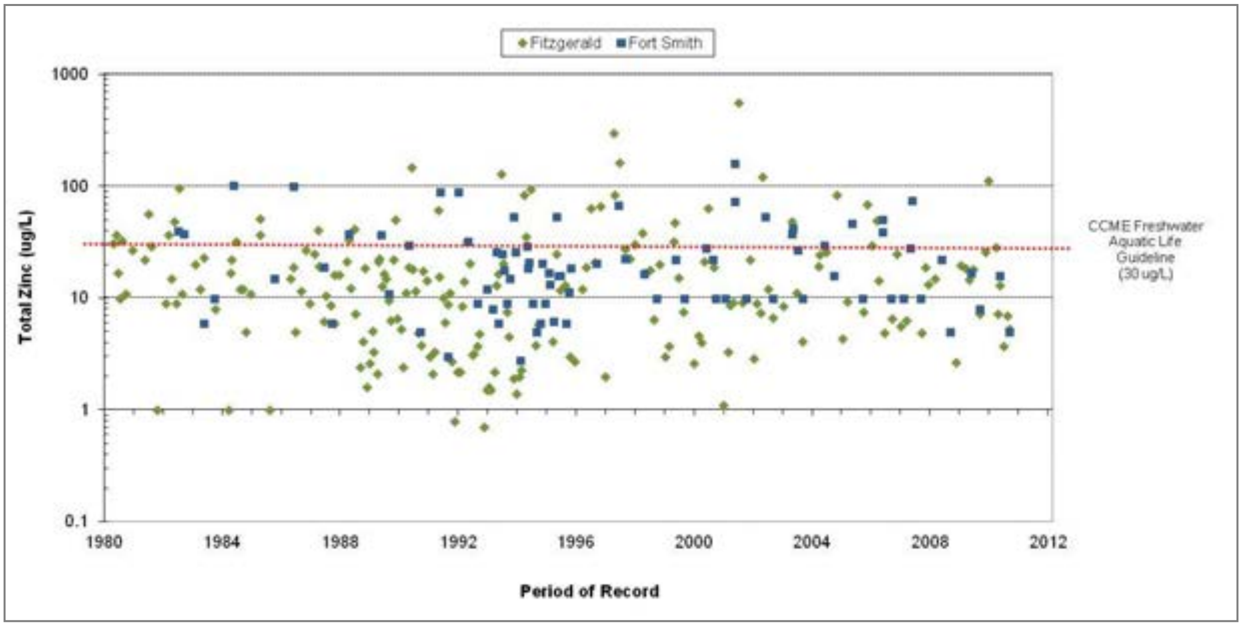


Figure 7.44: Comparison to Guidelines - Non flow-adjusted total zinc concentrations from Fitzgerald (1980-2010) and Fort Smith (1982-2010). Total zinc data were not log transformed.

As a comparison, in 157 samples from the Liard River, total zinc concentrations ranged from 0.8 to 388 µg/L. The CPFAL guideline was exceeded by 17% of these samples. In the Peel River, concentrations ranged from 0.5 to 212 µg/L (n=132); values exceeded the guideline 30% of the time.

For those sample days at Fitzgerald for which both total and dissolved zinc values are available, most of the zinc was in the particulate fraction; dissolved zinc accounted for 34% (average value) of the total. The correlation between TSS and total zinc was strong at Fitzgerald (r_s=0.79, p<0.05, n=207) and at Fort Smith (r_s=0.80, p<0.05, n=78). Given these relationships and the lower concentrations of dissolved zinc, it is likely that most zinc in the Slave River is associated with particulate matter and, therefore, less biologically available for uptake by aquatic life.

Long-term temporal trend assessment of the 1980-2010 total zinc data from Fitzgerald revealed no interaction between season and year (Appendix 7-1). Therefore, only the annual data was assessed for trends and this trend was implied for each of the individual seasons. No significant trend was found at the 90 or 95% confidence levels (Figure 7.45).

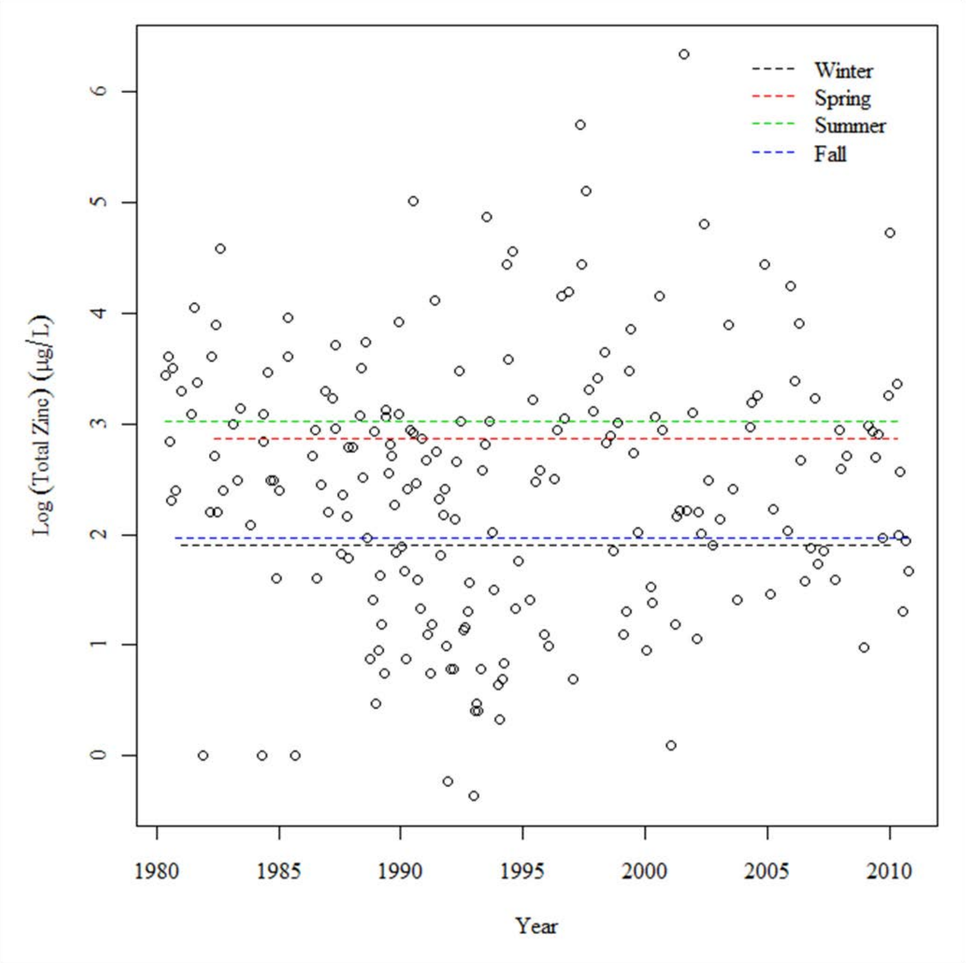


Figure 7.45: Trend Results - Non flow-adjusted total zinc concentrations from Fitzgerald (1980-2010). No statistically significant trends (at the 95% confidence level) were found (from Zajdlik, 2011b).

Since total zinc revealed a significant relationship with flow, the flow-adjusted data were also assessed for long-term trends. Following flow-adjustment, there continued to be no interaction between season and year and no significant annual trend at the 90 or 95% confidence levels (Appendix 7-1).

Recommendation

It is recommended that total and dissolved zinc continue to be analyzed at Fitzgerald and that dissolved zinc be added to the routine analyses at Fort Smith. Site-specific water quality objectives should be developed for zinc to be able to better assess the zinc levels in the Slave River.

Table 7.13: Slave River at Fitzgerald total metals (μg/L) statistical summaries.

Parameter	Period of Record	n	# of NDs	Mean	Std Dev	Median	Minimum	Maximum	90th perc.	Water Quality Guideline for the Protection of Aquatic Life	Detection Limits		% <DL
											from Environment Canada database	from Glozier *et al*, 2009 (1989-2006)	
Aluminum	1993-2010	102	0	2547	5687	990	9	48700	5698	n/a	--	0.2	0
Antimony	2002-2010	43	0	0.20	0.22	0.14	0.02	1.36	0.28	**20	--	--	0
Arsenic	2003-2010	37	0	1.4	1.1	1.1	0.3	4.7	2.6	*5	--	--	0
Barium	1980-2010	207	0	130	208	80	39	2200	209	*1000	--	0.05-80	0
Beryllium	1993-2010	101	21	0.187	0.317	0.070	<0.001	2.190	0.510	**5.3	0.05	0.001-50	21
Bismuth	2002-2010	37	3	0.024	0.021	0.018	<0.001	0.100	0.050	n/a	0.01	--	8
Boron	2001-2010	43	0	13	4	13	3	20	19	n/a	--	--	0
Cadmium	1980-2010	210	70	0.66	1.19	0.28	0.02	11.30	1.00	*calculation	0.1-1	0.001-0.1	33
Cerium	2002-2010	43	0	4.47	6.14	2.19	0.04	28.30	11.80	n/a	--	--	0
Cesium	2002-2010	43	1	0.305	0.344	0.188	<0.005	1.530	0.710	n/a	0.005	--	2
Chromium	1993-2010	102	4	4.08	6.97	1.76	0.17	50.4	9.90	*1	0.2	0.2	4
Cobalt	1980-2010	211	48	2.41	4.56	1.20	0.05	47	5.20	**110	0.5-2	0.002-0.5	23
Copper	1980-2010	211	0	8.1	16.9	4.0	0.4	200	17.0	*calculation	--	0.02	0
Gallium	2002-2010	43	0	0.53	0.74	0.24	0.00	3.53	1.40	n/a	--	--	0
Iron	1993-2010	101	0	6754	16130	2020	59	128000	15500	*300	--	0.5	1
Lanthanum	2002-2010	43	0	1.96	2.67	0.99	0.02	12.10	5.30	n/a	--	--	0
Lead	1980-2010	211	44	4.2	7.8	2.1	0.2	77.0	9.0	*calculation	0.2-4	0.2-0.7	21
Lithium	1993-2010	102	0	9.2	9.9	6.2	2.2	56.9	16.7	n/a	--	0.2	0
Manganese	1993-2010	102	0	135	255	58	3	1980	339	**1000	--	0.05	0
Mercury	1979-1980	12	4	0.03	0.02	0.02	0.02	0.10	0.06	*0.02	0.02	5-10	33
Molybdenum	1993-2010	102	2	0.71	0.39	0.66	0.10	3.00	0.90	*73	0.1	0.005-0.1	2
Nickel	1980-2010	210	8	8.2	21.5	3.4	<0.5	280.0	16.2	*calculation	0.5-2	0.02-2	4
Niobium	2002-2010	43	0	0.037	0.035	0.029	0.001	0.196	0.070	n/a	--	--	0
Platinum	2002-2010	43	36	0.002	0.002	0.001	<0.001	0.014	0.002	n/a	0.001-0.002	--	84
Rubidium	2002-2010	43	0	4.0	4.4	2.4	0.6	20.4	9.5	n/a	--	--	0
Selenium	2003-2010	37	0	0.25	0.08	0.24	0.09	0.50	0.33	*1	--	--	0
Silver	1996-2010	79	24	0.103	0.172	0.100	0.002	1.300	0.160	*0.1	0.001-0.1	0.001-0.1	30
Strontium	1993-2010	101	0	145	28	140	86	290	172	n/a	--	0.05	0
Thallium	2002-2010	43	0	0.05	0.06	0.03	0.00	0.31	0.11	**0.3	--	--	0
Tin	2002-2010	43	15	0.022	0.027	0.006	<0.005	0.100	0.070	n/a	0.005	--	35
Tungsten	2002-2010	43	6	0.008	0.013	0.004	<0.001	0.072	0.010	n/a	0.001-0.002	--	14
Uranium	2002-2010	43	0	0.610	0.350	0.510	0.333	2.370	0.830	*15	--	--	0
Vanadium	1980-2010	209	24	5.4	9.5	2.5	0.2	84.8	13.4	**6	0.5-1	0.5	11
Yttrium	2002-2010	43	0	2.3	3.3	1.1	0.0	16.8	5.4	n/a	--	--	0
Zinc	1980-2010	209	0	24	49	12	1	561	49	*30	--	0.05	0

n: number of values;
NDs: number of values reported below the detection limit (censored observations);
--: not provided; n/a: not available
* CCME National Water Quality Guideline for the Protection of Aquatic Life;
** BC MOE Provincial Water Quality Guideline for the Protection of Aquatic Life;
% <DL: percentage of observations reported at the detection limit.

Detection Limits (from Environment Canada database): The dataset provided by Environment Canada only included the detection limits for the values that were reported below the detection limit. When values were reported below the detection limit, the detection limit was recorded in the above table. Detection Limits (from Glozier *et al*, 2009): These detection limits were reported in the Glozier report (Appendix 2) and cover the 1989-2006 time period.

Table 7.14: Slave River at Fitzgerald dissolved metals (µg/L) statistical summaries.

Parameter	Period of Record	n	# of NDs	Mean	Std Dev	Median	Minimum	Maximum	90th perc.	Water Quality Guideline for the Protection of Aquatic Life	Detection Limits		% <DL
											from Environment Canada database	from Glozier *et al*, 2009 (1989-2006)	
Aluminum	2006-2010	24	0	67	113	30	11	548	128	*100	--	0.2-20	0
Antimony	2006-2010	24	1	0.20	0.14	0.16	<0.001	0.70	0.35	n/a	0.001	--	4
Arsenic	1978-2010	202	24	0.5	0.4	0.4	<0.1	3.8	0.7	n/a	0.5	0.01	12
Barium	2006-2010	24	0	47	5	47	38	59	52	n/a	--	0.05	0
Beryllium	2006-2010	24	0	0.007	0.008	0.005	0.002	0.040	0.011	n/a	--	1-500	0
Bismuth	2006-2010	24	2	0.003	0.004	0.002	<0.001	0.016	0.008	n/a	0.001	--	8
Boron	1980-1988; 2006-2010	76	0	50	29	60	9	110	80	n/a	--	2-10	0
Cadmium	2006-2010	24	0	0.07	0.09	0.03	0.01	0.36	0.18	n/a	--	1	0
Cerium	2006-2010	24	0	0.23	0.31	0.15	0.04	1.53	0.38	n/a	--	--	0
Cesium	2006-2010	24	2	0.018	0.029	0.008	<0.005	0.128	0.041	n/a	0.005	--	8
Chromium	2006-2010	24	0	0.36	0.45	0.18	0.09	2.09	0.74	n/a	--	1	0
Cobalt	2006-2010	24	0	0.11	0.11	0.07	0.03	0.53	0.18	n/a	--	0.002-1	0
Copper	2006-2010	28	0	2.8	2.0	2.4	1.0	10.6	4.1	n/a	--	0.02-1	0
Gallium	2006-2010	24	0	0.02	0.03	0.01	0.00	0.16	0.05	n/a	--	--	0
Iron	2006-2010	29	0	162	229	90	20	1210	329	**350	--	0.5	0
Lanthanum	2006-2010	24	0	0.11	0.13	0.07	0.02	0.67	0.18	n/a	--	--	0
Lead	2006-2010	28	0	0.4	0.3	0.2	0.0	1.0	1.0	n/a	--	0.005-2	0
Lithium	2006-2010	24	0	4.1	0.9	3.9	2.7	5.4	5.3	n/a	--	0.2	0
Manganese	2006-2010	29	0	8	10	4	1	40	14	n/a	--	0.05-1	0
Molybdenum	2006-2010	24	0	0.75	0.13	0.75	0.53	1.07	0.89	n/a	--	0.005-0.1	0
Nickel	2006-2010	24	0	1.4	0.4	1.4	0.8	2.3	2.1	n/a	--	2	0
Niobium	2006-2010	24	0	0.005	0.005	0.003	0.001	0.020	0.010	n/a	--	--	0
Platinum	2006-2010	24	24	0.001	0	0.001	0.001	0.001	0.001	n/a	0.001	--	100
Rubidium	2006-2010	24	0	0.8	0.3	0.7	0.5	1.9	1.4	n/a	--	--	0
Selenium	1978-2010	203	32	0.28	0.13	0.22	0.10	0.70	0.50	n/a	0.1-0.5	0.05-0.1	16
Silver	2006-2010	24	3	0.009	0.016	0.003	0.001	0.073	0.021	n/a	0.001	--	13
Strontium	2006-2010	24	0	139	19	139	104	186	155	n/a	--	0.05	0
Thallium	2006-2010	24	0	0.01	0.02	0.01	0.001	0.08	0.02	n/a	--	--	0
Tin	2006-2010	24	4	0.033	0.041	0.013	0.005	0.161	0.063	n/a	0.005	--	17
Tungsten	2006-2010	24	2	0.009	0.019	0.004	<0.001	0.095	0.016	n/a	0.001	--	8
Uranium	2006-2010	24	0	0.427	0.082	0.412	0.268	0.718	0.479	n/a	--	--	0
Vanadium	2006-2010	24	0	0.4	0.3	0.3	0.2	1.8	0.6	n/a	--	1	0
Yttrium	2006-2010	24	0	0.14	0.14	0.11	0.05	0.70	0.21	n/a	--	--	0
Zinc	2006-2010	28	0	4.0	5.5	2.8	0.3	27.5	7.4	n/a	--	0.05-2	0

n: number of values;
NDs: number of values reported below the detection limit (censored observations);
--: not provided; n/a: not available
* CCME National Water Quality Guideline for the Protection of Aquatic Life;
** BC MOE Provincial Water Quality Guideline for the Protection of Aquatic Life;
% <DL: percentage of observations reported at the detection limit.

Detection Limits (from Environment Canada database): The dataset provided by Environment Canada only included the detection limits for the values that were reported below the detection limit. When values were reported below the detection limit, the detection limit was recorded in the above table. Detection Limits (from Glozier *et al*, 2009): These detection limits were reported in the Glozier report (Appendix 2) and cover the 1989-2006 time period.

Table 7.15: Slave River at Fort Smith total metals (µg/L) statistical summaries.

Parameter	Period of Record	n	# of NDs	Mean	Std Dev	Median	Minimum	Maximum	90th perc.	Water Quality Guideline for the Protection of Aquatic Life	Detection Limits	% <DL
Aluminum	2001-2010	5	0	7834	10748	4360	338	26700	18304	n/a	0.2-30	0
Antimony	2001-2010	5	1	1.35	1.76	0.53	0.10	4.40	3.17	**20	0.008-0.5	20
Arsenic	1982-2010	54	7	2.4	2.5	1.7	0.3	15.7	4.5	*5	0.2-2	13
Barium	2001-2010	5	0	217	148	158	63	453	373	*1000	0.02-1	0
Beryllium	2001-2010	5	2	0.61	0.79	0.33	0.10	2.00	1.37	**5.3	0.02-2	40
Bismuth	2001-2010	2	2	2.6	--	2.6	<0.2	<5	--	n/a	0.1-10	100
Boron	2007-2010	1	0	8.3	--	8.3	8.3	8.3	--	n/a	0.5-50	0
Cadmium	1982-2010	85	49	0.4	1.2	0.2	<0.1	<10	0.6	*calculation	0.02-10	58
Cesium	2001-2010	5	1	1.37	1.52	0.97	0.10	3.90	2.95	n/a	0.08-0.4	20
Chromium	1983-2010	83	13	8.96	12.59	4.20	0.30	86	18	*1	0.1-10	16
Cobalt	1993-2010	65	7	2.11	2.34	1.40	0.10	16.00	4.34	**110	0.08-4	11
Copper	1982-2010	84	4	7.39	7.19	5.15	0.50	43.00	15.27	*calculation	0.08-10	5
Iron	1982-2010	84	0	5097	5099	3526	180	24700	11840	*300	5-50	0
Lead	1983-2010	83	9	3.6	3.4	2.3	<0.1	22.0	8.0	*calculation	0.02-10	11
Lithium	2001-2010	5	0	12.7	9.7	10.7	3.0	28.7	22.5	n/a	0.1-3	0
Manganese	1993-2010	65	0	92	79	67	6	482	195	**1000	0.02-1	0
Mercury	1982-1990; 1993, 1995; 2000-2010	21	4	0.06	0.06	0.04	<0.01	0.22	0.12	*0.02	0.005-0.1	19
Molybdenum	2001-2010	5	1	2.32	2.46	1.90	0.10	6.50	4.70	*73	0.02-1	20
Nickel	1982-2010	84	5	8.4	8.9	6.0	<1	57.0	15.8	*calculation	0.1-10	6
Rubidium	2001-2010	5	0	17	9	9	2	52	37.38	n/a	0.01-0.5	0
Selenium	1994; 2000-2010	9	6	5.81	4.23	5.33	<1	<10	10.00	*1	0.1-10	67
Silver	2001-2010	5	3	0.24	0.26	0.10	<0.1	0.70	0.50	*0.1	0.006-0.3	60
Strontium	2001-2010	5	0	150	23	147	123	180	174	n/a	0.02-1	0
Thallium	2001-2010	5	2	0.19	0.16	0.10	<0.1	0.47	0.36	**0.3	0.1-0.4	40
Titanium	2001-2010	5	0	59	77	36	6	194	135	n/a	0.02-3	0
Uranium	2001-2010	5	0	0.93	0.40	0.80	0.50	1.40	1.36	*15	0.008-0.3	0
Vanadium	2001-2010	5	0	26.7	35.3	13.9	3.4	88.7	61.5	**6	0.003-1	0
Zinc	1982-2010	84	13	26	27	17	3	162	54	*30	0.4-15	15

n: number of values

NDs: number of values reported at the detection limit (censored observations);

n/a: not available

* CCME National Water Quality Guideline for the Protection of Aquatic Life;

** BC MOE Provincial Water Quality Guideline for the Protection of Aquatic Life;

% <DL: percentage of observations reported at the detection limit.

7.3.5 Metal Guideline Exceedances

Metals in the Slave River that frequently (between 25-100% of the time) exceeded the total metal guideline for the protection of freshwater aquatic life included total cadmium, total chromium, total copper, total iron, total lead and total mercury. Metals that exceeded the guideline less frequently (between 1-25% of the time) were total arsenic, total barium, total manganese, total nickel, total selenium, total silver, total vanadium and total zinc (Table 7.16). There were no guideline exceedances for total antimony, total beryllium, total cobalt, total molybdenum, total thallium and total uranium. Freshwater aquatic life guidelines were not available for total aluminum and total tin.

Table 7.16: Percentage of total metal values exceeding the total metal guideline for the protection of aquatic life in the Slave River at Fitzgerald and Fort Smith.

	Slave River at Fitzgerald		**Slave River at Fort Smith**	
Metal	**n**	**%**	**n**	**%**
Total arsenic*	37	0 (0/37)	54	9 (5/54)
Total barium**	207	1 (2/207)	5	0 (0/5)
Total cadmium*	210	99 (139/140***)	85	100 (36/36)
Total chromium*	102	66 (67/102)	83	36 (65/82***)
Total copper*	211	73 (154/211)	84	57 (47/82*)
Total iron*	101	89 (90/101)	84	99 (83/84)
Total lead*	211	31 (60/196***)	83	39 (32/83)
Total manganese**	102	2 (2/102)	65	0 (0/65)
Total mercury*	12	42 (5/12)	21	62 (13/21)
Total nickel*	210	0.5 (1/210)	84	0 (0/84)
Total selenium*	37	0 (0/37)	9	22 (2/9)
Total silver*	79	13 (10/79)	5	40 (2/5)
Total vanadium*	209	23 (48/209)	5	80 (4/5)
Total zinc*	209	18 (38/209)	84	25 (21/84)

* Comparisons were made to the CCME CPFAL National Guidelines for the protection of aquatic life.

** Comparisons were made to the BC MOE Provincial Guidelines for the protection of aquatic life.

*** On occasion, for certain metals, the detection limit used/reported by the laboratory has been higher than the respective guideline. When this occurred, those samples were not included in the calculation of percent exceedance.

As mentioned previously within the parameter specific sections, metals in water exist in a number of soluble (free metal ions, associated with colloids) and insoluble forms (attached to clays, or organic matter). Although the availability of metals associated with the solid phase varies, typically, it is the dissolved form (un-complexed metal ion) that is more toxic and biologically available for uptake by aquatic organisms (Glozier *et al*., 2009; MRBC, 1981). Increased sorption of a metal to sediment reduces its level in the water column and, therefore, decreases exposure of aquatic organisms and transport to other parts of the ecosystem, such as fish and other aquatic life (USGS, 2000). This concept was further explored within the Slave River at Fitzgerald dataset by calculating the ratio of the dissolved metal concentration to the total (Table 7.17).

For many of the metals which frequently exceeded guidelines, a small proportion is in the dissolved form, suggesting that most of the metal is in the particulate form and not biologically available (Table 7.17). This holds true for chromium, iron and lead.

Table 7.17: Average percentage of the dissolved metal fraction in a total metal water sample from the Slave River at Fitzgerald.

Slave River at Fitzgerald						
Metal	**% Dissolved**	**n**		**Metal**	**% Dissolved**	**n**
aluminum	15	24		manganese	20	24
antimony	100	24		molybdenum	100	24
arsenic	48	24		nickel	50	24
barium	68	24		selenium	89	24
beryllium	22	24		silver	34	24
boron	95	23		strontium	95	24
cadmium	47	24		thallium	41	24
chromium	34	24		uranium	83	24
cobalt	21	24		vanadium	25	24
copper	67	24		zinc	34	24
iron	17	24				
lead	24	24				

* Note: 1. Ratios were only calculated for the metals for the days on which both total and dissolved metal values were available. 2. Dissolved metals not currently part of sampling program at Fort Smith.

However, for some metals which frequently exceed guidelines, the dissolved fraction makes up a greater percentage of the total metal value (eg. cadmium and copper; Table 7.17). This suggests that these metals are potentially more biologically available. In addition, some dissolved metals, such as cadmium (12 samples out of 24 samples), chromium (2 of 24), copper (13 of 28) and iron (4 of 29), have, on occasion, exceeded the total metal guideline.

As a result it is recommended that dissolved metals continue to be monitored at Fitzgerald and these analyses should be initiated at Fort Smith. In addition, it is strongly recommended that site-specific water quality objectives be developed for both total and dissolved metals, to be able to better determine the potential impacts of metal concentrations in the Slave River.

The site-specific objectives would be based on the historical data from the Slave River and would provide a more accurate context for the review and assessment of the water quality results.

Many of the metals that exceeded the guidelines in the Slave River also exceeded the guidelines in the Peel and Liard rivers. This would suggest that the National guidelines for total metals may not be appropriate for heavily sediment laden rivers and site-specific objectives should be developed.

7.4 Changes in Seasonal Water Quality

As described in Chapter 6 (Hydrology), flows in the Slave River are largely influenced by the Peace River, which contributes about 60% of the Slave River flow volume. As such, regulation of the Peace River by B.C Hydro's W.A.C. Bennett Dam has affected seasonal flows of the Slave River by increasing winter flows by about 75% and reducing the spring freshet flows by about 20% from pre-dam flows. Although upstream regulation has not caused considerable changes in total annual flow of the Slave River, the timing of water releases from the dam has dampened the high spring and summer peak flows and increased winter low flows (Figure 7.46). As noted in Chapter 6, the changes in the Slave River flow regime may also be a result of changes in the climatic regime.

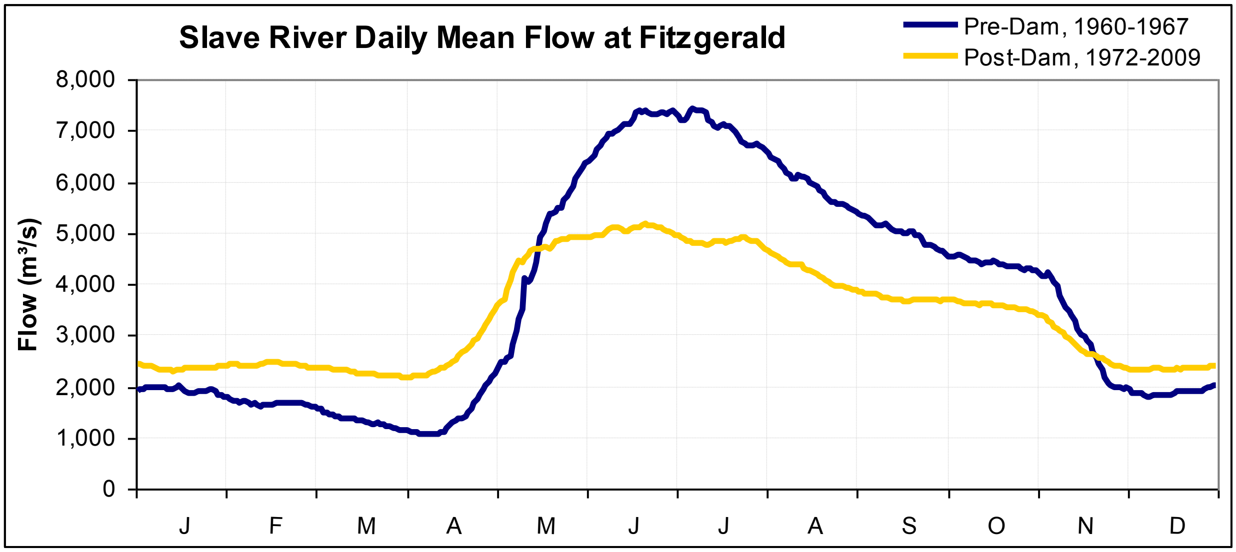


Figure 7.46: Mean annual hydrographs of the Slave River at Fitzgerald, pre-dam (1960-1967) and post-dam (1972-2009) (Water Survey of Canada – 07NB001).

Natural changes in water chemistry over the year (seasonality) are largely related to changes in river flow. Typically, concentrations of total suspended solids and associated parameters (total metals and nutrients) increase with increasing discharge, as a result of more surface inputs from the surrounding land and more scouring of the river beds and shorelines. Conversely, concentrations of dissolved compounds such as total dissolved solids, dissolved metals and major ions tend to decrease with increasing discharge due to a dilution-effect. In natural, unregulated rivers, most of the dissolved compounds are highest during the winter low flows, when the water quality of the river is primarily influenced by groundwater.

The seasonal differences in surface water quality of the Slave River at Fitzgerald (1972-2010) were examined. Spring and summer values were combined to constitute high-flow conditions and then compared to low-flow conditions.

For the most part, results of the Mann-Whitney tests conducted on the Slave River dataset showed that parameters associated with particulate matter (TSS, turbidity, total metals) had higher concentrations in the spring and summer, and lower concentrations during the winter, which was expected. However, similar to Glozier *et al.* (2009), most of the dissolved parameters also had higher concentrations during the spring and summer than in the winter (high-flow levels > low-flow levels) or a less discrete pattern (i.e., similar or equal concentrations in both seasons: high-flow levels = low-flows levels), which is not typical. These parameters are highlighted in yellow in Table 7.18.

Table 7.18: Mann-Whitney (Wilcoxon) test results for significant seasonality for physical parameters, major ions, nutrients and metals.

Parameters	**Seasonality Water Quality at Fitzgerald**
Physical Parameters	
pH	High-flow levels = Low-flow levels
Specific conductance	High-flow levels = Low-flow levels
Total dissolved solids	High-flow levels > Low-flow levels ✓
Total suspended solids	High-flow levels > Low-flow levels ✓
Turbidity	High-flow levels > Low-flow levels ✓
Alkalinity	High-flow levels = Low-flow levels
Major Ions	
Dissolved calcium	High-flow levels = Low-flow levels
Dissolved magnesium	High-flow levels = Low-flow levels
Dissolved sodium	High-flow levels = Low-flow levels
Dissolved potassium	High-flow levels > Low-flow levels ✓
Dissolved sulphate	High-flow levels > Low-flow levels ✓
Dissolved fluoride	High-flow levels > Low-flow levels ✓
Dissolved chloride	High-flow levels < Low-flow levels ✓
Total hardness	High-flow levels = Low-flow levels
Nutrients	
Dissolved Ammonia	High-flow levels = Low-flow levels
Dissolved organic carbon	High-flow levels > Low-flow levels ✓

Parameters	**Seasonality Water Quality at Fitzgerald**
Particulate organic carbon	High-flow levels > Low-flow levels ✓
Total phosphorus	High-flow levels > Low-flow levels ✓
Dissolved phosphorus	High-flow levels > Low-flow levels ✓
Metals	
Aluminum, total	High-flow levels > Low-flow levels ✓
Arsenic, dissolved	High-flow levels > Low-flow levels ✓
Chromium, total	High-flow levels > Low-flow levels ✓
Cobalt, total	High-flow levels > Low-flow levels ✓
Copper, total	High-flow levels > Low-flow levels ✓
Iron, total	High-flow levels > Low-flow levels ✓
Manganese, total	High-flow levels > Low-flow levels ✓
Molybdenum, total	High-flow levels = Low-flow levels
Nickel, total	High-flow levels > Low-flow levels ✓
Lead, total	High-flow levels > Low-flow levels ✓
Vanadium, total	High-flow levels > Low-flow levels ✓
Zinc, total	High-flow levels > Low-flow levels ✓

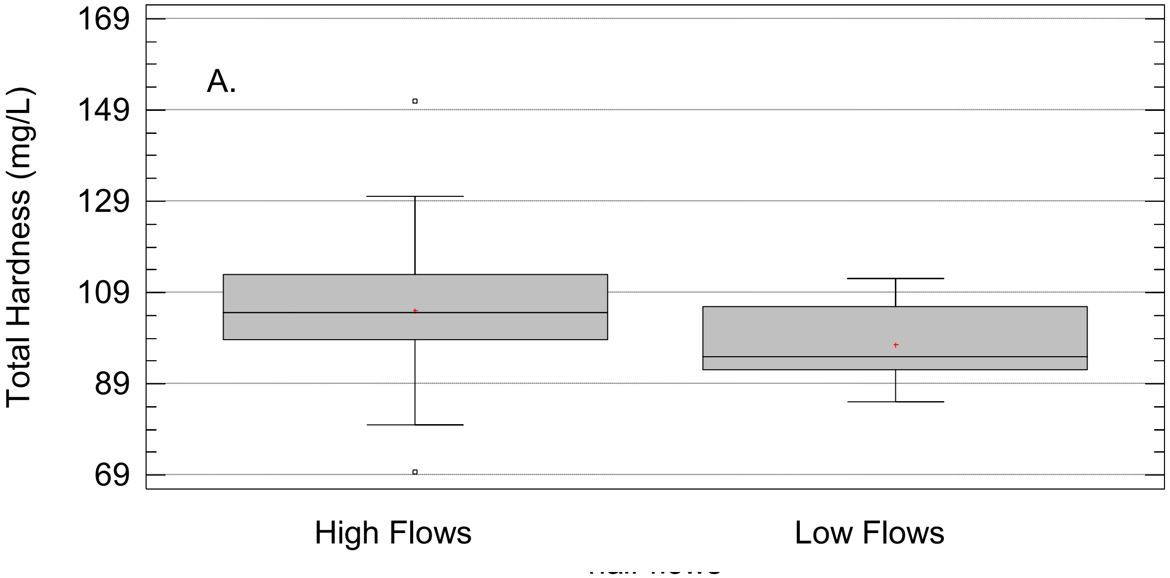
Parameters highlighted in yellow exhibited a reversal in seasonality or parameters that had similarly equal concentrations in each season. Statistically significant differences at the 95% confidence interval ($p<0.05$) are identified with an "✓".

Similar analyses of the relationship between water quality concentrations and flow have been conducted by Shaw (1990) on the Peace River and by Glozier *et al.* (2009) for the Peace, Athabasca and Slave Rivers.

Shaw (1990) found that dissolved constituents, which were typically inversely related to flow (such as TDS and many major ions), did not show any flow dependency. It was suggested that, due to the effect of pooling, water which is released from the reservoir behind the Bennett Dam, is of a more constant quality than would occur naturally in the river.

Glozier *et al.* (2009) found that for the Peace River (which is regulated) and the Slave River (which is strongly influenced by the regulation of the Peace), most dissolved parameters exhibited a complete reversal in seasonality (highest during the spring-summer season rather than during the winter season) or a less distinct pattern of similarly high concentrations in the two seasons. These current patterns were attributed to changes in flow related to the Bennett dam, which retains water in the reservoir during the spring and summer high flow period for release during the winter to produce electricity (Glozier *et al*., 2009).

To understand the spatial extent of the effects of upstream regulation on Slave River surface water quality, (i.e., due to the change in the timing of peak flows), a few parameters from the Slave River at the Mouth (1982-2010) were examined within the context of this report. The Slave River at the Mouth sampling location is located further downstream just above the Slave River Delta and Great Slave Lake. Three related dissolved parameters were examined, including total hardness, alkalinity and total dissolved solids (TDS). Although the data is limited, all three showed slightly higher concentrations during the high-flow period of spring and summer (n=25) and lower concentrations during the low-flow period of winter (n=5) (Figure 7.47 A, B, and C). At the 95% confidence level, only TDS concentrations were significantly higher during high-flow than low-flows (Mann-Whitney (Wilcoxon) test; p=0.0225).



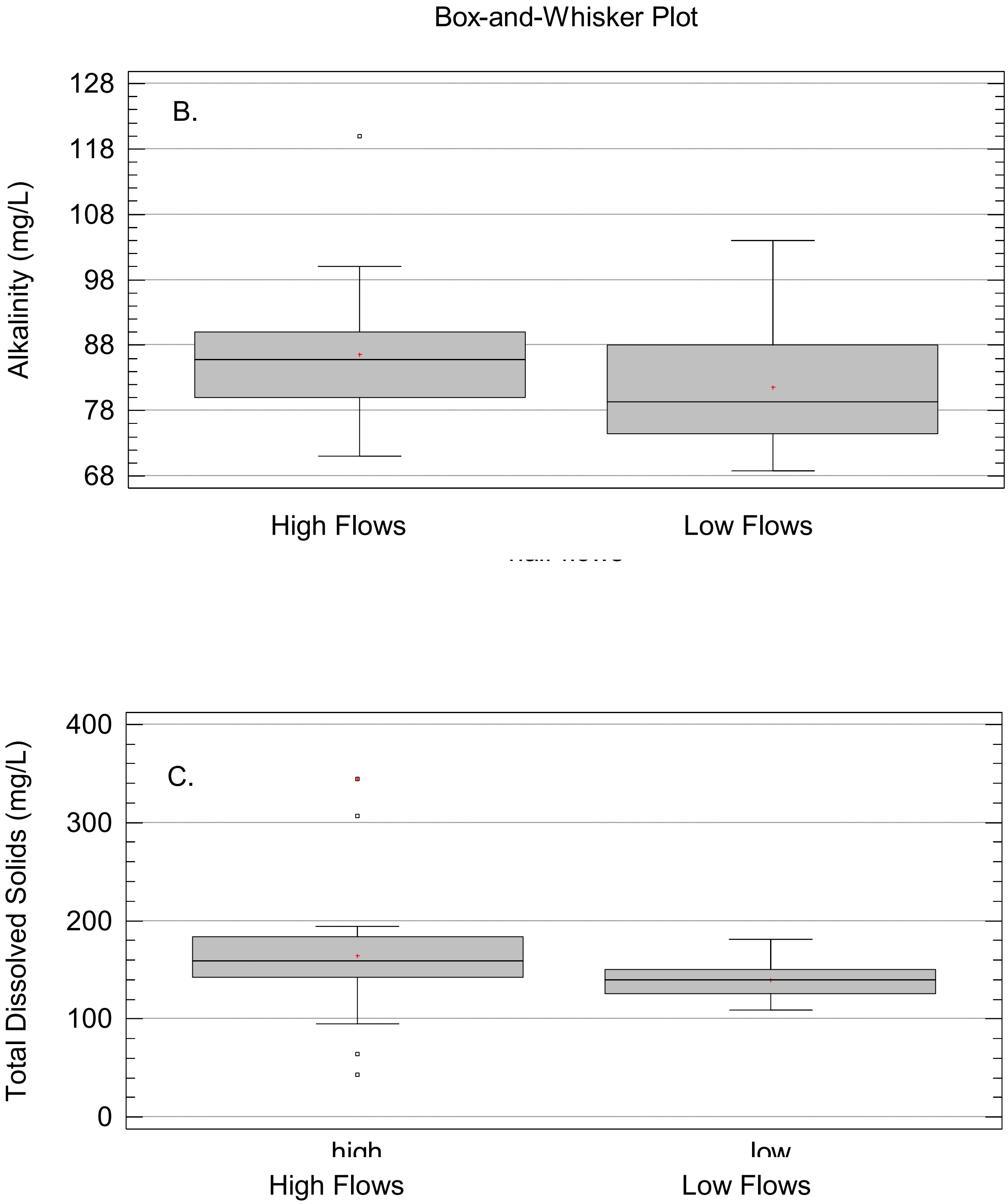


Figure 7.47: Comparison of the concentrations of total hardness (A), alkalinity (B) and total dissolved solids (C) during high flows (spring and summer) and low flows (winter) from Slave River at the Mouth (1982-2010).

This suggests that the effects of the regulation of the Peace River on water quality seem evident even as far downstream as the Slave River at the Mouth. Accordingly, it is recommended the frequency of sampling be increased at the Slave River at the Mouth and that the samples are collected throughout the year to achieve good seasonal coverage.

Further, as pointed out by Glozier *et al.*, 2009, the associated influences on the downstream Slave River aquatic environment are not fully understood. A March 2011 community-based workshop held in Fort Smith discussed monitoring and appropriate aquatic ecological health indicators for the Slave River (AANDC and GNWT ENR, 2012). At that workshop, numerous participants shared concerns that higher flows during the winter may be linked to changes in ice characteristics, resulting in declining muskrat and beaver populations. Therefore, it is also recommended that the effects on the aquatic ecosystem of the Slave River due to flow regulation on the Peace River be evaluated.

8.0 CENTRIFUGATE WATER RESULTS AND DISCUSSION

8.1 Introduction

Water samples collected from the outflow of the centrifuge are referred to as centrifugate water samples. Since the centrifuge removes suspended sediments from the water, the two media components: sediment free water and suspended sediments, can be analyzed separately. By including centrifugate water in the sampling program, compounds associated with suspended sediments could be differentiated from those found in the water. Centrifugate water samples were collected from the Slave River at the Fort Smith mid-river sampling location only. Details on centrifuge equipment and sampling methodology are included in Chapter 5.

Centrifugate water samples have been collected at the Slave River at Fort Smith mid-river site since 1990. Samples were collected during 18 sampling events from 1990-1995 (SREQMP) and during nine sampling events from 2000-2010 (Follow-Up Study). Samples were analyzed for nutrients (phosphorus), metals, and organic compounds including chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated benzenes.

Results of the centrifugate water samples (1990-2010) are summarized in Appendix 8-1. Data from two centrifuge samples in June 2001 and June 2006 were excluded from the summary table and write-up. On both of these occasions, high levels of suspended sediments in the river filled the centrifuge bowl with suspended sediment before the centrifuge water samples could be collected. As the centrifuge can no longer remove suspended sediment from the river water effectively once the bowl is filled, water that flows from the centrifuge outflow tube cannot be analyzed as centrifugate water.

8.2 Comparison of Centrifugate Water Samples to Surface Water Samples

Since 1990, centrifugate and surface water samples have been collected simultaneously on six occasions. To illustrate the effect of centrifugation on raw river water quality, the results from both centrifugate and surface water samples were compared for each sample date.

Table 8.1 presents the range of observed values for both centrifugate and surface water samples. Means from triplicate samples were used in the comparison and any values reported as “less than the detection limit” were treated as equal to the detection limit.

The parameters that were largely affected by centrifugation have been highlighted in yellow in Table 8.1. These were the parameters for which the concentration in centrifugate water was less than 25%[23] of the concentration in the surface water sample (on more than one sample date).

For example, if the concentration of lead was 1 ug/L in the surface water sample and 0.25 ug/L in the centrifugate water sample, this parameter would be considered largely affected by centrifugation.

As would be expected, parameters such as pH, specific conductance, and major ions were largely unaffected by centrifugation, as these parameters are typically associated with the dissolved fraction of water (found in solution). In contrast, parameters associated with suspended sediment, including total suspended solids, turbidity, total phosphorus and total metals, were reduced by centrifugation. For instance, total lead values ranged from 1 to 6.13 µg/L in surface water samples and 0.3 to 1.4 µg/L in centrifugate water samples. These comparisons support the earlier suggestion that, in the Slave River, most metals are largely associated with suspended sediments.

Table 8.1: Comparison of water quality in surface and centrifugate water samples from the Slave River at Fort Smith (mid-river; 1990-2010)

		Surface Water	Centrifugate Water
Parameter	**n**	**Range**	**Range**
pH (pH units)	6	7.74 - 8.1	5.99 - 8.14
Specific Conductance (µS/cm)	6	208 - 246	156 - 243
Turbidity (NTU)	6	11 – 515	2 - 32
TSS (mg/L)	6	18 – 748	3 - 4.33
TDS (mg/L)	5	113 - 152	100 - 254
Calcium Total (mg/L)	6	24.9 – 31.5	18.9 - 32.1
Magnesium Total (mg/L)	6	5.8 - 7.7	4.1 - 7.5
Potassium Total (mg/L)	6	0.7 - 2.71	0.69 - 1.63
Sodium Total (mg/L)	6	5.3 - 7.2	5.1 - 6.9
Chloride Total (mg/L)	6	2.1 - 7.37	2.1 - 7.21
Sulphate Total (mg/L)	6	17 – 23	17 - 22
Hardness Total (Calcd.)	6	88 – 110	64 - 111

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[23] Twenty-five (25%) percent is arbitrary and was chosen to simply quantify the 'large' effect due to centrifugation.

		Surface Water	Centrifugate Water
Parameter	**n**	**Range**	**Range**
Alkalinity Total (mg/L)	6	73.9 - 130	58.5 - 123
Nitrate & Nitrite Filtered (mg/L)	5	0.03 - 0.109	0.008 - 0.104
Ammonia Total (mg/L)	6	0.005 - 0.036	0.003 - 0.026
Phosphorus Total (mg/L)	6	0.020 - 0.802	0.006 - 0.055
Aluminum Total (µg/L)	3	338 - 4360	46 - 957
Arsenic Total ((µg/L)	5	0.7 - 2.2	0.3 - 2.1
Cadmium Total (µg/L)	6	0.1 - 0.4	0.1 - 0.3
Chromium Total (µg/L)	6	3 - 56.7	0.2 - 56.1
Cobalt Total (µg/L)	6	0.3 - 4.13	0.1 - 1
Copper Total (µg/L)	6	1.2 - 12.2	0.7 - 4.07
Iron Total (µg/L)	6	443 - 6747	0.1 - 1660
Lead Total (µg/L)	5	1 - 6.13	0.3 - 1.4
Manganese Total (µg/L)	5	16.3 - 186	5.2 - 15.7
Nickel Total (µg/L)	6	1.5 - 13.9	0.9 - 3.9
Zinc Total (µg/L)	6	5 - 42	0.5 – 10

Note: Parameters highlighted in yellow were largely affected by centrifugation.

To provide a detailed example of the affect of centrifugation, Table 8.2 includes the values for turbidity, total iron and specific conductance on the sample dates for which centrifugate and surface water samples were collected simultaneously. On each sample date, the concentrations of turbidity and total iron in surface water were much higher than the concentrations in the centrifugate water. There was virtually no difference in specific conductance concentration between the two types of water samples. As expected, centrifugation of the Slave River water removes those parameters associated with sediment but has little effect on the dissolved parameters.

Table 8.2: Comparison of turbidity, iron concentrations and specific conductance in surface and centrifugate water from the Slave River at Fort Smith (mid-river; 1990-2010)

	Turbidity (NTU)		**Total Iron (µg/L)**		**Specific Conductance (µS/cm)**	
Sample Date	**Surface Water**	**Centrifugate Water**	**Surface Water**	**Centrifugate Water**	**Surface Water**	**Centrifugate Water**
9/22/1994	24	3	1200	167	218	218
3/7/1995	19	6	1720	163	246	243
2/20/2001	13	2	443	0.1	210	209
6/9/2003	305	31	6747	1660	208	157
3/6/2007	10.9	2	618	114	234	232
5/29/2007	515	32	5470	766	215	215

8.3 Organic Compounds in Water Samples

AANDC has been collecting centrifugate water samples from the Slave River at Fort Smith (mid-river) since 1990. The samples have been analyzed to determine the levels of chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated benzenes. A complete list of parameters analyzed can be found in Appendices 8-2 to 8-4.

The following section provides a summary of the organic compounds found in the centrifugate water samples collected as part of the Slave River at Fort Smith Monitoring Program during the Follow-Up Study (2000-2010). To determine if conditions have changed, centrifugate data from the Follow-Up Study (2000-2010) were compared[24] to centrifugate data from the original SREQMP (1990-1995). A complete discussion of the results from 1990-1995 is included in Sanderson *et al*. (1997).

It should be noted that for some organic parameters, detection limits were higher in the Follow-Up Study than the SREQMP. According to the laboratory used to analyze the samples for organics, the rules that govern laboratory reporting have changed such that the laboratory must report values with a much higher level of certainty than what was needed in the past. As such, the very low detection limits achieved during the SREQMP are not available today. In some cases, this makes comparison of results difficult, however, further monitoring will allow for trend analyses to be conducted which will help determine if changes are occurring.

The organic compounds detected in the surface water samples collected as part of Environment Canada's Slave River at Fitzgerald Monitoring Program were also presented. As the organic compound analyses conducted by Environment Canada is specifically on surface water, not centrifugate water, the results between the two monitoring programs are not directly comparable. However, the data are included for completeness and interest.

Centrifugate water results from the Slave River at Fort Smith Monitoring Program were also compared to various results generated under the Northern River Basins Study, which took place from 1991 to 1995. The Northern River Basins Study was designed to characterize the cumulative effects of development on the water and aquatic environment of the Peace-Athabasca-Slave Basin (i.e., the Slave River Catchment) (NRBS, 1996). Where possible, the Slave River at Fort Smith centrifugate results were compared to the results from centrifugate samples collected from a 200 km reach of the

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[24] Due to the amount of data censoring, statistical comparisons between the SREQMP (1990-1995) and the Follow-Up Study (2000-2010) were not made.

Athabasca River between Hinton and Whitecourt (Crosley, 1996a). Comparisons made to results from this reach of the river provided some information on the effects of municipal and pulp mill effluents, as this stretch of the river receives municipal effluent from the Town of Hinton and bleached kraft mill effluent from the Weldwood pulp mill. Fort Smith centrifugate water sample results were also compared to results from a study of the Wapiti/Smoky River ecosystem, which receives effluent from the Weyerhaeuser bleached kraft pulp mill (Swanson *et al*., 1993).

To assess the current water quality conditions of the transboundary reach of the Slave River, centrifugate water results were compared to the CCME Canadian Water Quality Guidelines for the Protection of Freshwater Aquatic Life (CPFAL), where possible. These guidelines are intended to provide protection for freshwater aquatic life from anthropogenic stressors, such as chemical inputs or changes to physical components (pH, temperature, etc). The guidelines are meant to protect all forms of aquatic life, including the most sensitive life stage of the most sensitive species (CCME, 1999). It should be noted, however, that these are national guidelines and may not reflect specific local conditions, especially northern rivers and ecosystems.

8.3.1 Chlorinated Phenolics

Summary
During the SREQMP (1990-95), seven chlorophenol compounds were detected in centrifugate samples, and all values were below CCME CPFAL guidelines. During the Follow-Up Study (2000-2010), chlorinated phenolic compounds were not found; however the detection limits were not always as low.

Recommendation
To confirm these recent results, monitoring of chlorophenols, with lower detection limits, is required.

Background
Chlorinated phenolics is a general term that refers to a family of commercially produced compounds which have a variety of uses, including disinfectants, pesticides, dyes and wood preservatives (CCREM, 1987; USEPA, 1980a). They can be released into the aquatic environment from pulp and paper operations, bleached kraft mills, wood processing and treatment plants, and sewage treatment plants (Health Canada, 1980; Pastershank and Muir, 1995). Chlorinated phenolic compounds are toxic, persistent and known to bioaccumulate (Kovacs *et al*., 1984). Further background information on chlorinated phenolics can be found in Appendix 8-5.

Based on acute toxicity to aquatic life, the CCME CPFAL guidelines for pentachlorophenols, tetrachlorophenols and trichlorophenols are 0.5, 1.0 and 18 µg/L, respectively. The guidelines for monochlorophenols (7 µg/L) and dichlorophenols (0.2 µg/L) are based on flavour impairment (CCREM, 1987).

Results
A broad suite of chlorinated phenolics were measured in the centrifugate water at Fort Smith (Appendix 8.2). During the SREQMP (1990-1995), seven of these chlorophenolic compounds were detected in one or more samples (Table 8.3). Several of these compounds, such as 2,4,6-trichlorophenol, 3,4,5-trichlorocatechol, tetrachlorocatechol, 3,4,5-trichloroguaiacol and tetrachloroguaiacol, had also been observed in pulp mill effluents and in centrifugate water samples downstream of pulp mills, although at much higher levels (Crosley, 1996a and Swanson *et al*., 1993).

Table 8.3: Concentrations of chlorinated phenolics in centrifugate water samples collected from the Slave River at Fort Smith (mid-river) during the SREQMP (1990-1995).

Compound	**#of values above the detection limits**	**n**	**Concentration (µg/L)**
2,4,6- trichlorophenol	6	24	0.00044 (NDR*), 0.00058 (NDR*), 0.002, 0.002, 0.002, 0.0028
3,4,5-trichlorocatechol	5	26	0.003, 0.01, 0.015, 0.021, 0.0016
tetrachlorocatechol	6	26	0.0033 (NDR*), 0.006, 0.008, 0.023, 0.03, 0.05
3,4,5-trichloroguaiacol	3	26	0.002, 0.002, 0.002
tetrachloroguaiacol	3	15	0.001, 0.005, 0.025
3,4,5-trichloroveratrole	1	26	0.002
2-chlorosyringaldehyde	1	26	0.001

From: Sanderson *et al*., 1997. *NDR=non detectable ratios; conservative estimates of the total.

During the Follow-Up Study (2000-2010), chlorinated phenolic compounds were not detected in any centrifugate water samples. Although the detection limits for the chlorophenol compounds analyzed during the Follow-Up Study were low (0.0004-0.02 µg/L), the very low detection limits obtained during the earlier study are not available today due to changes in laboratory reporting requirements. Accordingly, it cannot be stated with certainty that the more recently measured chlorophenol concentrations are lower than they were in the early 1990’s. However, studies conducted during the Northern River Basins Study, as well as studies conducted by Swanson *et al*. (1993) did find dramatic decreases in chlorophenol concentrations downstream of pulp mills, following changes to the bleaching process (Carey *et al*., 1997).

Surface water samples from the Fitzgerald sampling location were not analyzed for chlorinated phenolic compounds.

All of the chlorophenol values detected in the Slave River centrifugate water samples were below CCME CPFAL guidelines.

<u>Recommendation</u>

It is recommended that centrifugate samples from the Slave River continue to be analyzed for chlorinated phenolics, with the lowest detection limits available, to confirm the recent results.

8.3.2 Organochlorine Pesticides

Summary
Organochlorine pesticides have not been detected in any centrifugate samples collected from the Slave River at Fort Smith. A few pesticides have been detected in surface water samples collected from the Slave River at Fort Fitzgerald, but these were always below the CPFAL guidelines.

Recommendation
Given the agricultural activity in the upstream portion of the catchment, monitoring for organochlorine pesticides should continue. Low detection limits are required.

Background
The term 'organochlorine pesticides' refers to all chlorinated chemicals that are used to control pests (AXYS, 2010b). For the purposes of this report, organochlorine (OC) pesticides include herbicides (which are used to control weeds and invasive, non-native plants) and insecticides (which are used to control nuisance or non-native insects).

Organochlorine (OC) pesticides are human-made hydrocarbon compounds containing multiple chlorine substitutions. OC pesticides are hydrophobic, lipophilic and very stable, which makes them highly persistent and bioaccumulative in aquatic organisms (AXYS, 2010b; USEPA, 1976). OC pesticides can enter the aquatic environment through the direct application of commercial and domestic sprays for insect control and crop protection, runoff from agricultural lands, as well as through the long range transport of atmospheric pollutants to northern regions (USEPA, 1979).

The CCME CPFAL guidelines for organochlorine pesticides are included in Table 8.4.

Results
During the SREQMP (1990-1995), 14 centrifugate water samples from the Slave River at Fort Smith were analyzed for up to 13 different organochlorine pesticides. During the Follow-Up Study (2000-2010), six samples were analyzed for 34 different OC compounds (Appendix 8-3). Samples from September 2010 were not analyzed for OC pesticides. Over the entire period of record (1990-2007), concentrations of OC pesticides were always below detection limits (0.002-1 µg/L).

At the Fitzgerald sampling location, surface water samples have been analyzed for up to 60 different pesticides from 1979-1986, in 1998 and from 2004-2006 (Hatfield, 2009). During these periods, 11 pesticides were detected; nine of which were detected only once (n=9 to 43, depending on the compound) and 2,4-D, which was detected on two occasions (n=43). 2,4-D is an active ingredient in a wide variety of brand names such as Killex®, a herbicidal product for lawn weeds that is available from regular hardware stores.

Alpha-BHC (benzenehexachloride) was the only pesticide found more than twice in the water at the Fitzgerald sampling location, being detected in 31 of 43 samples, with a mean and median concentration of 0.003 µg/L. However, since 1986, this compound has not been detected at this site, even with lower detection limits in recent years. Alpha-BHC is a by-product of the production of the insecticide, lindane (gamma-BHC). Although use of lindane as a pesticide has been banned, it is found in some shampoos which are used to treat head and body lice (Stockholm Convention, 2009; U.S Dept. of Health and Human Services, 2009).

All of the OC pesticide results from both sampling locations, over the entire period of record, were well below CCME CPFAL guidelines. For all but two compounds, the detection limits were lower than the guidelines, allowing for appropriate comparisons (Table 8.4).

It should be noted that the detection of OC pesticides at Fitzgerald and not at Fort Smith is likely due to three factors: at Fitzgerald, lower detection limits were achieved, the period of record is longer and surface water samples contain suspended sediment whereas centrifugate water does not.

Table 8.4: CPFAL guidelines for OC pesticides compared to the range of detection limits achieved with the Fitzgerald (surface water) and Fort Smith (mid-river; centrifugate water) OC pesticide data.

Compound	**CPFAL Guideline (µg/L)**	**Fitzgerald Detection Limits (µg/L)**	**n**	**Fort Smith Detection Limits (µg/L)**	**n**
2,4-D	4.0	<0.004 to <0.03	43	<0.002 to <0.9	22
atrazine	1.8	<0.005	2		0
bromoxynil	5.0	<0.005	2	<0.005 to <0.01	4
chlorpyrifos	0.0035	<0.005	2		0
dicamba	10	<0.02 to <0.03	9	<0.005 to <0.1	4
diclofop-methyl	6.1	<0.02	2	<0.005 to <0.1	4
endosulfan I	0.02	<0.00022 to <0.005	43	<0.02 to <0.1	6
Lindane	0.01	<0.00015 to	43	<0.02 to <0.1	6

Compound	CPFAL Guideline (µg/L)	Fitzgerald Detection Limits (µg/L)	n	Fort Smith Detection Limits (µg/L)	n
(gamma BHC)		<0.005			
MCPA	2.6	<0.005 to <0.2	42	<0.002 to <0.9	22
picloram	29	<0.005 to <0.2	37	<0.02 to <0.1	4
triallate	0.24	<0.005	2	<0.002 to <0.1	5
trifluralin	0.2	<0.005	2	<0.002 to <0.1	5

As a comparison, centrifugate river water samples were collected from the reach of the Athabasca River between Hinton and Whitecourt, in 1992, as part of the Northern River Basins Study. Samples were analyzed for a suite of 19 OC pesticides and none were detected (detection limit: 0.01 µg/L; Crosley, 1996a).

Recommendation

Given the agricultural activity in the upstream portion of the catchment, it is recommended that monitoring for organochlorine pesticides should continue, if low detection limits can be obtained to allow for meaningful comparisons to guidelines. It is also recommended that the list of pesticides include those which are in use in the catchment area, but not currently being monitored.

8.3.3 Polycyclic Aromatic Hydrocarbons

Summary
At Fort Smith, from 1990-95, pyrene, methylnaphthalene and naphthalene were detected in centrifugate water samples (one, two and five times, respectively). During the Follow-Up Study (2000-2010), these compounds were detected in two samples but at lower levels. In 2007, the parameter list was expanded and detection limits lowered, resulting in more compounds being detected, but still at low levels.

At Fitzgerald, eight surface water samples were analyzed for 23 different parent PAH compounds from 2004 to 2006, with ten compounds being detected.

All of the parent PAH compounds detected in centrifugate water samples from Fort Smith and surface water from Fitzgerald were below CCME CPFAL guidelines.

Recommendation
Given the increased oil sands developments occurring upstream, it is recommended that parent and alkylated PAHs, as well as naphthenic acids remain on the parameter list with lowest detection limits available.

Background

Parent PAH Compounds
Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous compounds that have been detected in numerous aquatic and terrestrial ecosystems (AXYS, 2010a). PAHs are stable, organic molecules composed of two to seven fused benzene rings. The lower molecular weight, unsubstituted parent PAH compounds containing two or three rings include naphthalene, methylnaphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene. These PAHs are generally more water soluble, more bioavailable to aquatic life and may be acutely toxic to aquatic organisms (AXYS, 2010a; Eisler, 1987).

High molecular weight PAHs containing four to seven rings include benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene, with the most toxic being benzo(a)pyrene (AXYS, 2010a). Some of these heavier compounds have carcinogenic properties and may bioaccumulate in organisms (Eisler, 1987). Being less volatile and less soluble, high molecular weight PAHs favour adherence to solid particles and are generally found in soil and sediment as complex mixtures (AXYS, 2010a). PAHs attached to sediment particles may be desorbed into the gut of aquatic animals, where they accumulate in tissues (de Voogt *et al*., 1991; Clements *et al*., 1994).

PAHs in the environment primarily originate from two types of sources: petrogenic (of geologic origin; i.e., oil sands) and pyrogenic (created during combustion processes; Bobak, 2010). Biosynthesis PAHs also make up a small contribution (Neff, 1979). Most human-made pyrogenic sources fall into two categories: the combustion of materials for energy supply (e.g., burning of coal, oil, gas, wood) and waste incineration (Maliszewska-Kordybach, 1999). Pyrogenic PAH compounds also arise naturally from forest fires and volcanic eruptions (Nagpal, 1993; Neff, 1979). PAHs are also found in tobacco smoke, creosote-treated wood and grilled meat where charcoal has been used (National Research Council, 1983).

For petrogenic PAHs, anthropogenic sources include effluents from oil sands and mining operations, refining and transport of product, as well as spills and leaks from tailings ponds and waste sites (NRCC, 1983; Neff, 1979; Burgess, 2009). PAHs occur naturally in bituminous fossil fuels, such as coal and crude oil deposits (BC MOE, 1993). Further background information on PAHs can be found in Appendix 8-5.

CCME CPFAL guidelines for PAHs are included in Table 8.5. There are currently no guidelines for alkylated PAHs or naphthenic acids.

Alkylated PAH Compounds

Alkylated PAHs are another class of PAH compounds that were recently added to the monitoring program at Fort Smith. PAH compounds containing a straight carbon side chain are referred to as alkylated PAHs (AXYS, 2010a). Alkylated PAHs are more abundant, persist for a longer time, and are sometimes more toxic than the parent PAH compounds (Irwin *et al*., 1997). They also tend to bioaccumulate to a greater degree. As the compound becomes more alkylated, its acute toxicity, lipophilicity and biological activity increases and its solubility decreases (Irwin *et al*., 1997).

Alkylated PAHs are often more abundant in fresh petroleum products than their parent compounds, and the proportion of alkylated PAHs to parent compound PAHs increases as the oil ages (Irwin *et al*., 1997). Therefore, parent and the alkylated PAHs are important target analytes when assessing impacts to the environment from oil spills and tailings leaks (Irwin *et al*., 1997).

Samples from oil sands operational process effluent collected from 1989 to 1994 were found to contain a mixture of alkylated PAHs (Carey *et al*., 1997).

Naphthenic Acids

Naphthenic acids (NAs) are natural constituents in many petroleum sources, including bitumen in the oil sands of Northern Alberta (Scott *et al*., 2005). NAs have a relatively high solubility in water, low affinity for sediment/soil particles and are concentrated in tailings (McMartin, 2003). Samples from the oil sands operational process effluent collected from 1989 to 1994 were found to contain naphthenic acids (Carey *et al*., 1997) Naphthenic acids released during bitumen extraction are the primary source of toxicity in oil sands tailings pond water (Allen, 2008).

Results

During the SREQMP (1990-1995), fourteen centrifugate water samples were analyzed for a suite of 17 different PAH compounds. At that time, the compounds naphthalene, methylnaphthalene and pyrene were detected (Table 8.5). During the Follow-Up Study (2000-2010; n=7), these compounds were detected in two samples; May 2007 and Sept 2010, at lower levels than those detected during the SREQMP (1990-1995; Appendix 8-4). During the May 2007 and September 2010 sampling events, the centrifugate water samples were also analyzed for a larger suite of parent PAH compounds, and for the first time, alkylated PAHs. In September 2010, naphthenic acids were included in the monitoring and they were not detected.

Table 8.5 presents the results for the parent and alkylated PAH compounds that were detected in the SREQMP or Follow-Up Study centrifugate water samples.

Table 8.5: Parent and alkylated PAHs detected in centrifugate water samples collected from the Slave River at Fort Smith (mid-river).

Compound	**1990-95 (n=14) (µg/L)**	**May 2007 (µg/L)**	**Sept 2010 (µg/L)**	**CPFAL Guideline (µg/L)**
benzo(a)anthracene	<0.003 - <0.1	0.001	0.001	0.018
biphenyl	Not analyzed	0.001	0.001	--
C2 substituted naphthalene	Not analyzed	0.006	<0.004	--
C2 substituted phenanthrene/anthracene	Not analyzed	0.007	<0.004	--
C3 sub'd naphthalene	Not analyzed	0.007	0.004	--
fluoranthene	<0.003 - <0.1	0.001	0.001	0.04
fluorene	<0.003 - <0.1	0.001	0.001	3

Compound	1990-95 (n=14) (µg/L)	May 2007 (µg/L)	Sept 2010 (µg/L)	CPFAL Guideline (µg/L)
methyl phenanthrene/anthracene	<0.003 - <0.05	0.009	Not analyzed	--
methylnaphthalene	0.003 and 0.007	0.003	0.001	--
2-methylnapthalene	<0.014 – <0.05	Not analyzed	0.001	--
naphthalene	0.013, 0.015, 0.022, 0.1, 0.47	0.002	0.005	1.1
phenanthrene	<0.003 - <0.1	0.003	0.001	0.4
perylene	<0.003 - <0.05	Not analyzed	0.001	--
pyrene	0.006	0.001	0.001	0.025
retene	Not analyzed	Not analyzed	0.001	--
Naphthenic acids	Not analyzed	Not analyzed	<1.0 mg/L	--

At Fitzgerald, eight surface water samples were analyzed for 23 different parent PAH compounds from 2004 to 2006. Those PAH compounds with values above analytical detection limits are shown in Table 8.6.

Table 8.6: PAHs detected in surface water samples collected from the Slave River at Fitzgerald (2004-2006).

Date	PAH Compound	Concentration (µg/L)	CPFAL Guideline (µg/L)
12/15/2005	1-methylnaphthalene	0.12	--
7/26/2004	2-methylnaphthalene	0.0279	--
12/15/2005	2-methylnaphthalene	0.119	--
10/26/2005	acenaphthene	0.028	5.8
7/26/2004	naphthalene	0.03075	1.1
10/26/2005	naphthalene	0.0495	1.1
12/15/2005	naphthalene	0.134	1.1
2/8/2006	perylene	0.08264	--
12/15/2005	pyrene	0.00926	0.025
2/8/2006	pyrene	0.00827	0.025

All of the parent PAH compounds that were detected in centrifugate water from Fort Smith or surface water from Fitzgerald were below the available CPFAL guidelines (Tables 8.5 and 8.6).

Although there are currently no guidelines for the alkylated PAHs, most alkylated PAHs appear to be at least as toxic or hazardous as the parent compound (Irwin *et al*., 1997). Thus, for now, United States (US) risk assessment experts suggest adding all alkyl homolog concentrations to their constituent parent concentration, and interpreting that grouped value (Irwin *et al*., 1997). For example, the US experts suggest adding the reported concentrations for C1-, C2-, C3-, and C4-naphthalenes to the reported naphthalene concentration, and comparing that total value against the guideline for naphthalene (Irwin *et al*., 1997). Using this methodology, for the May 2007 and September 2010 results, the concentrations of both parent and alkyl PAHs were still below CPFAL guidelines.

In general, the concentrations of PAHs in surface water at Fitzgerald and in centrifugate water at Fort Smith were relatively low. Among the parent PAHs measured, naphthalene occurred at the highest concentration, with a maximum of 0.134 µg/L at Fitzgerald and 0.47 µg/L at Fort Smith. The naphthalenes have less than three aromatic rings, so are considered a low molecular weight PAH. These PAHs are the most soluble (CCREM, 1987), which could explain their detection in both centrifugate and surface water samples.

Recommendation

Given the increased oil sands developments occurring upstream, it is recommended that parent PAH compounds continue to be monitored in the Slave River centrifugate samples.

Although there are currently no guidelines for alkylated PAHs, these compounds are more abundant, persist for a longer time, bioaccumulate to a greater degree and are sometimes more toxic than the parent PAHs (Irwin *et al*., 1997). They have been found in oil sands operation process effluent and are common in petroleum and crude oil. For these reasons, it is recommended that any future monitoring program include the analyses of alkylated PAHs.

Given the toxic nature of naphthenic acids to aquatic life (Scott *et al*., 2005; Allen, 2008) and the fact that they have also been detected in oil sands operation process effluent, it is recommended that these compounds be included in any future monitoring.

8.3.4 Polychlorinated Biphenyls (PCBs)

Summary
PCBs were not detected in any of the water samples collected from the Slave River at Fort Smith or Fitzgerald.

Recommendation
Analysis of PCBs in water should continue, if detection limits below guidelines can be obtained.

Background

PCBs are a group of synthetic aromatic hydrocarbons which contain a varying number of chlorine atoms, substituted on a biphenyl molecule (i.e. two benzene rings bonded at one carbon). There are 209 possible PCB congeners which are identified by the number and position of the chlorine atoms around the biphenyl rings (Cook, 1972; Hutzinger *et al*., 1974; Columbia Analytical Services, 2010). PCBs were typically synthesized by chlorinating biphenyl with chlorine gas, substituting chlorine atoms for hydrogen atoms on the biphenyl molecule. Varying the conditions of the chlorination process produced different mixtures of congeners with different physical properties. These mixtures were sold as products called Aroclors (Columbia Analytical Services, 2010).

Individual PCBs vary widely in their physical and chemical properties according to the degree and position of chlorination (USEPA, 1979). PCBs that lack chlorines next to the phenyl-phenyl bond are referred to as coplanar. Coplanar congeners have stronger adsorption and bioaccumulation capacities, and are considered the most toxic (Ahlborg *et al*., 1994). As chlorine content increases, lipophilicity and resistance to biodegradation and biotransformation increase, while solubility and volatility decrease (USEPA, 1979; Roberts *et al*., 1978). Therefore, those PCBs with five or more chlorine atoms per molecule are relatively more persistent in the environment than those which have four or fewer chlorine atoms (Roberts *et al*., 1978; USEPA, 1979).

PCBs, as a class, are nonpolar and, therefore, only slightly soluble in water. Solubility declines with increasing chlorine substitution, but all PCBs have a strong affinity to sediment, especially fine grained particles. Sorption to sediments is the predominant mechanism removing PCBs from the water column (Nagpal, 1992; USEPA, 1979; Jaagumagi, 1990). PCBs are also soluble in the lipids of biological organisms and tend to accumulate in fatty tissues. Therefore, very low levels of PCB contamination in aquatic ecosystems can result in the accumulation of relatively high PCBs levels in biota (Roberts *et al*., 1978; USEPA, 1980b).

PCBs were widely used in industrial applications because of their thermal stability, inertness, solubility in organic solvents, and resistance to oxidation and reduction (Safe *et al*., 1982). They are among the most persistent pollutants in the global ecosystem (Nagpal, 1992). Exposure to PCBs may result in a wide variety of effects on aquatic organisms, including acute and chronic toxicity and reproductive impairment (Moore and Walker, 1991). Due to their toxicity and persistence in the environment, the use and importation of PCBs was prohibited in 1980 in Canada (Environment Canada, 1980).

PCBs enter the environment through accidents and improper use or disposal, including incomplete combustion of PCB-containing wastes, spills, and leaching from dumps and landfills (Hammond, 1972). Volatilization and transport as an aerosol, followed by atmospheric deposition are probably responsible for the global dispersion of PCBs (CCREM, 1987). Further background information on PCBs can be found in Appendix 8-5.

There are currently no CCME CPFAL guidelines for PCBs, but the US EPA has established a chronic guideline of 0.014 µg/L and an acute guideline of 2.0 µg/L for protection of freshwater aquatic life.

Results

At Fort Smith, centrifugate water samples collected in 1993 and 2001 were analyzed for total PCBs (detection limit: <1.0 µg/L). In 2006 and 2007, centrifugate water samples were analyzed for a suite of nine Aroclors (detection limits: < 0.01µg/L). At Fitzgerald, surface water samples were analyzed for three Aroclors from 1979 until 1986 (n=26; detection limits: 0.002-0.02 µg/L). PCBs were not detected in any of the water samples collected from the Slave River at Fort Smith or Fitzgerald.

Although guidelines were never exceeded in any of the samples, the higher detection limits do not always allow for a complete comparison.

As a comparison, the centrifugate river water samples which were collected in the reach of the Athabasca River between Hinton and Whitecourt, in 1992 as part of the NRBS, were also analyzed for PCBs, but none were detected (detection limit: 0.01 µg/L; Crosley, 1996a).

Recommendation

It is recommended that analysis of PCBs in water should continue, if detection limits below guidelines can be obtained.

8.3.5 Chlorinated Benzenes

Summary
Concentrations of chlorinated benzenes were below detection limits in both surface grab and centrifugate water samples collected from the Slave River at Fort Smith and at Fitzgerald over the entire period of record. Detection limits were well below the CPFAL guidelines.

Recommendation
Continued monitoring of chlorinated benzenes should be reviewed.

Background
Chlorinated benzenes are a group of cyclic aromatic compounds in which the hydrogen atoms of a benzene ring have been replaced by up to six chlorine substituents. These compounds are used as solvents, electrical equipment insulators, pesticides and flame retardants (Peirano, 1985). Chlorinated benzenes can enter the environment in discharge of chlorinated waste water, as well as from side reactions in the production of chlorinated compounds. Their lipophilic nature and slow degradation in the environment, results in the potential for these substances to can accumulate through the food chain (Jan and Malnersic, 1980).

The CCME CPFAL guidelines for hexachlorobutadiene and pentachlorobenzene are 1.3 µg/L and 6 µg/L, respectively. There are currently no CCME CPFAL guidelines for hexachlorobenzene.

Results
At Fort Smith, centrifugate water samples collected in 1993, 2001 and 2003 were analyzed for hexachlorobenzene (HCB) and pentachlorobenzene (n = 3, detection limits: 0.1 - 1 µg/L). These two compounds, as well as hexachlorobutadiene (HCBD), were measured in surface water from Fitzgerald from 1979 to 1986 and 2004 to 2006 (n = 3 to 41; detection limits: 0.00017 - 0.001 µg/L). Concentrations were below detection limits in all water samples collected from both sites on the Slave River. As the detection limits are well below the guidelines, no exceedances of the guidelines occurred.

Recommendation
Given the lack of detection of chlorinated benzenes, it is recommended that the further analysis of these compounds in centrifugate water samples be reviewed.

8.4 Summary – Organic Compounds in Water

Centrifugate and surface water samples collected from the Slave River were analyzed for chlorinated phenolics, organochlorine pesticides, PAHs, PCBs and chlorinated benzenes. A limited number of organic compounds were detected in the samples, but only at very low levels. Still, their presence indicates the potential for downstream transport and/or atmospheric deposition and continued monitoring is warranted. For certain compounds, where detection limits were above the CCME CPFAL guidelines, it was not possible to draw any conclusions with respect to possible impacts on aquatic life. Therefore, it is imperative to ensure that the lowest detection limits possible are achieved in future monitoring and to continue monitoring organic compounds in centrifugate water to enable comparisons to past results.

The chlorinated phenolic compounds detected at Fort Smith during the SREQMP (1990-1995) were all below CCME CPFAL guidelines. However these compounds were also detected downstream of the Grande Prairie pulp mill, suggesting that upstream activities likely represented sources in the Slave River. No chlorinated phenolic compounds were detected during the Follow-Up Study (2000-2010). These findings could be due to improvements in process changes by the mills (replacement of elemental chlorine with chlorine dioxide; Environment Canada, 2008) or because of higher detection limits for some of the analytes. Therefore, further monitoring of chlorophenols with lower detection limits is recommended to confirm these results.

At Fort Smith, the concentrations of organochlorine pesticides were below detection limits (0.002-1 µg/L) in all centrifugate water samples (1990-2007). Although no sample results exceeded guidelines, only those which had detection limits below the guidelines can be compared to guidelines. The detection of some organochlorine compounds in the surface water at Fitzgerald may suggest downstream transport and/or atmospheric deposition. It is recommended to continue monitoring for organochlorine pesticides, due to the agricultural activities in the upstream portion of the catchment. Low detection limits would be required. In addition, it would be prudent to commence monitoring of pesticides that have the highest use in upstream areas.

Parent PAH compounds, including naphthalene, methylnaphthalenes and pyrene, were present in a few centrifugate water samples. Although not statistically tested, levels of these compounds were lower in the Follow-Up Study (2000-2010) than during the SREQMP (1990-1995). All of the parent PAH compounds which were detected in both centrifugate water samples from Fort Smith and surface water from Fitzgerald met the CCME CPFAL guidelines. In May 2007 and September 2010, alkylated PAHs were analyzed for the first time and certain compounds were detected. Naphthenic acids were analyzed for the first time in September 2010, but were not detected. Given the increased oil sands developments occurring upstream, it is recommended that parent PAH compounds, alkylated PAHs and naphthenic acids continue to be monitored in the Slave River.

Polychlorinated biphenyls (PCBs) or chlorinated benzenes were not detected in any water sample collected from the Slave River at Fort Smith or Fitzgerald.

9.0 SUSPENDED SEDIMENT RESULTS AND DISCUSSION

9.1 Introduction

Sediments are ecologically important to aquatic ecosystems because they contain minerals and nutrients that are vital to the health of aquatic habitats (USEPA, 2003a). For the purposes of water monitoring, sediment can be classified as deposited or suspended. Deposited (bed or bottom) sediments are found on the bed of a river or lake. Suspended sediments, which are part of the AANDC monitoring program, are found in the water column, where they are transported by moving water. Suspended sediments are also commonly referred to as particulate matter, suspended matter and suspended solids.

The amount of sediments entering the Slave River from the Athabasca River Sub-basin is limited due to the deposition of sediments in the Athabasca delta and Lake Athabasca (Culp *et al*., 2005). Therefore, the majority of particulate matter entering the Slave River from upstream sources likely originates from the Peace River (Hatfield, 2009).

Suspended sediments are composed of clay, silt and sand particles, bits of decaying matter, tiny plants and animals, and large gelatinous organic molecules that are suspended in the water column (Swanson *et al.,* 1993). Contaminant concentrations in suspended sediments have been found to be several orders of magnitude higher than in water, and also higher than in deposited (bed) sediments (Crosley, 1996a; Swanson *et al.,* 1993; Carey *et al*., 1997). This is due to the higher organic content and finer clay/silt content of suspended sediment, which provides a greater surface area for the compounds to adhere to (Swanson *et al*., 1993). In fast flowing waters, suspended sediments can remain in the water column for a long period of time and, therefore, any metals and organic compounds associated with them can be transported long distances downstream from their source (MacDonald and Smith, 1990; Swanson *et al*., 1993). As a result, suspended sediments can be an important medium for the transport of heavy metals and organic compounds that may become sources of contaminants to plants and animals in downstream aquatic environments (USEPA, 2003a).

In the absence of CCME CPFAL guidelines for suspended sediment, monitoring results were compared to the Draft Interim Freshwater Bottom Sediment Quality Guidelines (SQG) which were developed by CCME (1999) for bottom sediments. As sediments can act as long-term reservoirs of chemicals to the aquatic environment and to the organisms living in or having direct contact with these sediments, exposure to certain substances at certain concentrations in sediment represent a potentially significant hazard to the health of these organisms (CCME, 1999). However, given the different nature of bottom and suspended sediments, the guidelines can be used for comparative purposes only; it is difficult to draw any definitive conclusions with respect to effects on biota.

Within the guidelines, two assessment values are presented for each chemical. The lower value, referred to as the threshold effect level (TEL), represents the concentration below which adverse biological effects are rarely expected to occur. The upper value, the probable effects level (PEL), gives the limit above which adverse effects are expected to occur frequently. Values between the TEL and PEL fall within the possible effect range, which represents the range within which adverse effects occur occasionally (CCME, 1999).

The province of Ontario has developed a similar set of numerical guidelines for the protection of bottom sediment-dwelling organisms (Ontario MOE, 2008). The guidelines establish three levels of effect: No Effect Level (NEL), Lowest Effect Level (LEL) and Severe Effect Level (SEL). The Lowest Effect Level and Severe Effect Level are based on the long-term effect which the contaminants may have on the sediment-dwelling organisms. The No Effect Level is based on levels of chemicals which are so low that significant amounts of the contaminant are not expected to be passed through the food chain (Ontario MOE, 2008). In this report, the Ontario Bottom Sediment Quality Guidelines were used for parameters for which no national guidelines were available.

It should be noted, however, that similar to the National and Provincial Guidelines for surface water, the CCME and Ontario MOE bottom sediment guidelines may not reflect specific local conditions, especially northern rivers and ecosystems.

Suspended sediments have been collected from the Slave River at Fort Smith since 1990. Samples were collected approximately four times per year from 1990-1995 (n=18) and approximately three times per year every five years since (2000-01, 2006-07 and 2010; n=9). A complete discussion of the results from 1990-1995 is included in Sanderson *et al*., 1998. Suspended sediment samples have not been collected from Fitzgerald.

Suspended sediment samples were analyzed for physical characteristics (particle size), metals, and organic compounds, including chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated benzenes and polychlorinated dibenzodioxins/furans. Results of the suspended sediment samples are presented in the following sections: Physical Characteristics (Section 9.2), Metals (Section 9.3) and Organic Compounds (Section 9.4).

9.2 Particle Size Distribution and Total Organic Carbon

Background

The role of sediment in chemical pollution is tied both to the particle size of sediment, and to the amount of particulate organic carbon associated with the sediment (Ongley, 1995). Understanding the fractions of the different particle sizes is important because many metals and organic compounds have a strong affinity for adsorption to finer sized particles (such as silt and clay) due to the large surface area of these small particles (Forstner, 1991). Organic carbon has also been known to influence the sorption (process by which one substance attaches to another) of metals to suspended sediment (Swanson *et al*., 1993). Many of the persistent, bioaccumulating and toxic organic contaminants, especially chlorinated compounds, are strongly associated with sediment and especially with the organic carbon that is transported as part of the sediment load in rivers (Ongley, 1995).

Results

Particle Size

Over the entire study period, 23 suspended sediment samples collected from the Slave River at Fort Smith were sent for particle size analysis. Suspended sediments were classified according to particle size as sand, silt or clay. The particle size results and the proportions of each by season[25] are shown in Figure 9.1.

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[25] For the definition of season, please refer to Chapter 7, Section 7.2.3. Centrifuging was not conducted in the spring due to dangerous river conditions.

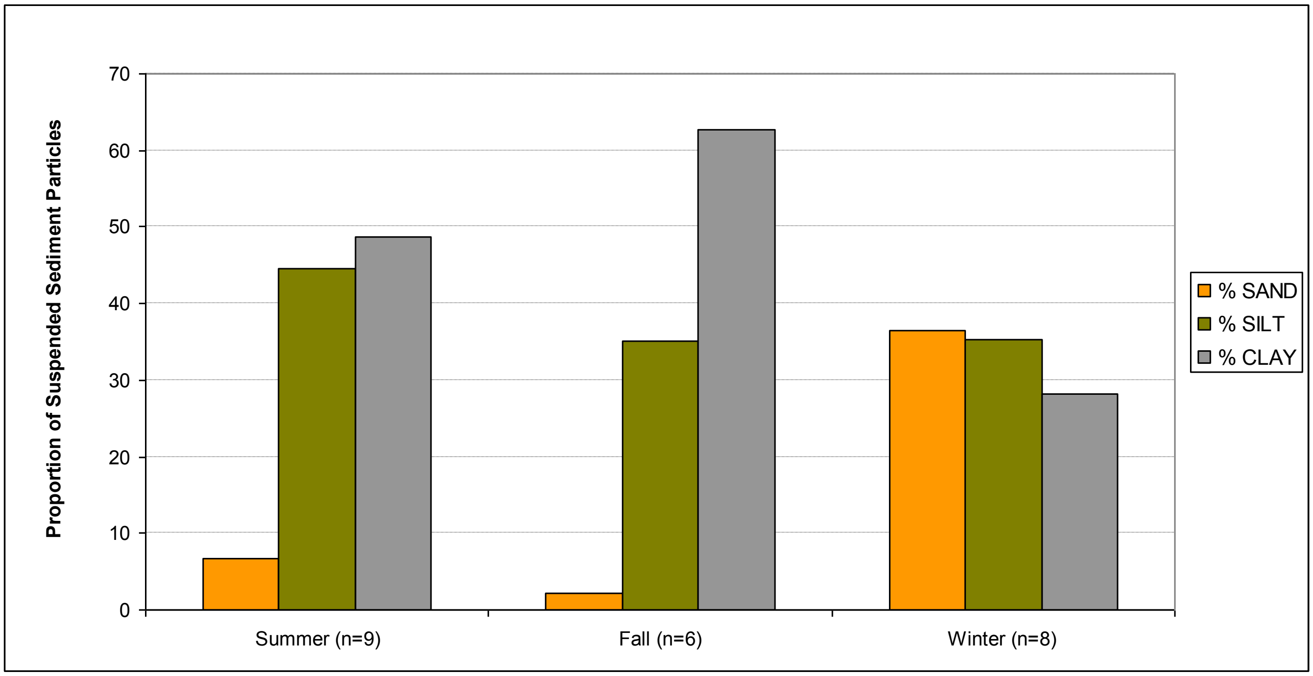

Figure 9.1: Average percentage of particle size distribution by season in suspended sediment samples from the Slave River at Fort Smith (1990-2010).

In many rivers, the proportion of larger-sized particles (eg. sand) tends to be lowest during winter due to the lower flows and associated lower carrying capacity of the river. During low flows the heavier particles are more likely to drop out of the water column. Below the rapids at Fort Smith, however, this is not the case. The percentage of sand is actually highest during the winter months, which is caused by under-ice frazil slush ice associated with the nearby rapids (Ashton, 1986). The frazil slush ice scours the river bed and re-suspends bottom sediments (Sanderson *et al*., 1997; Figure 9.1).

During the open water season, the sand fraction is minimal and the majority of the suspended sediment is of the clay/silt size. Figure 9.1 also shows that clay particles are highest during the open water season, particularly in the fall, and that silt particles remain relatively constant over the year. No spring samples were collected.

Organic Carbon

The total organic carbon (TOC) content of the Slave River at Fort Smith suspended sediments averaged 1.23% (range: 0.21 to 2.4 percent, n=22). For comparison, the percentage of TOC measured in the suspended sediments throughout the Wapiti/Smoky rivers ranged from 0.2 to 8.4% (n=16) which was considered low compared to other values in the literature (Swanson *et al.*, 1993). Based on this, the organic carbon content in the Slave River is considered to be at the lower end of the natural range for rivers of the boreal forest region.

Recommendation
Given the role that organic carbon and particle size plays in the adsorption of compounds to the suspended sediment particles, it is recommended that both continue to be monitored in suspended sediment samples collected from the Slave River.

9.3 Metals in Suspended Sediment

Background
The following section provides a summary of the data on metal concentrations in the suspended sediment from the Slave River at Fort Smith. Over the entire study period (1990-2010), 27 suspended sediment samples have been collected and analyzed for up to 30 different metals. To provide context, metal results were compared to the available bottom sediment quality guidelines, as well as the suspended sediment metal data collected from the Peel River. This river, similar to the Slave River is a transboundary river with a relatively high suspended sediment load.

Concentrations of metals from the SREQMP (1990-1995) were compared to those from the Follow-Up Study (2000-2010) (Table 9.1). A review of the analytical methods from each study period, conducted by ALS Laboratories, found the methodologies to be comparable (Appendix 5-3).

Background information on the individual metals can be found in Section 7.3.4 of this report.

Table 9.1: Statistical summaries of metal concentrations in suspended sediment (ug/g) from the Slave River at Fort Smith - SREQMP (1990-1995) and Follow-Up Study (2000-2010).

	SREQMP (1990-1995)					**Follow-Up (2000-2010)**				
Total Metal	**n**	**Ndets**	**Median**	**Range (ug/g)**	**DLs**	**n**	**ndets**	**Median**	**Range (ug/g)**	**DLs**
Aluminum	18	0	12,300	4,960-39,100	--	7	0	12,500	4,950-22,400	50
Antimony	18	18	8	<8-15	8-15	5	4	0.1	<0.1-0.46	0.1
Arsenic	18	5	8.7	<0.05-<20	0.05-20	5	0	10.4	6.8-12.4	0.1
Barium	18	0	235	105-607	--	9	0	290	121-419	0.5
Beryllium	18	18	0.8	<0.15-<1.50	0.15-1.5	9	4	1	0.5-1.1	0.2-1
Bismuth	11	11	25	<25-<25	25	5	4	0.5	<0.2-<0.5	0.2-0.5
Boron	18	0	22	8-72	--	5	0	11	6-19	--

	SREQMP (1990-1995)					Follow-Up (2000-2010)				
Total Metal	**n**	**Ndets**	**Median**	**Range (ug/g)**	**DLs**	**n**	**ndets**	**Median**	**Range (ug/g)**	**DLs**
Cadmium	18	3	0.5	<0.25-1.02	0.25	9	2	0.5	<0.5-1	0.1-0.5
Chromium	18	0	19.5	11.5-58	--	9	0	28.4	19-77.2	0.2-0.5
Cobalt	18	0	8.34	3.6-19.6	--	9	0	10	8-16.4	0.1-1
Copper	18	0	16.3	6.3-95	--	9	0	25.9	15.3-34.2	0.5-1
Iron	18	0	21,300	11,600-62,600	--	7	0	27,600	16,600-34,700	200
Lead	18	0	7.7	3.6-21.1	--	9	0	13	7-19.9	0.5-5
Manganese	18	0	336	162-1117	--	7	0	380	250-1340	1
Mercury	18	0	0.046	0.017-0.150	--	6	3	0.05	<0.05-0.07	0.05
Molybdenum	18	18	4	<4-<10	4-10	9	2	1	0.9-1.8	0.1
Nickel	18	0	27	11-66	--	9	0	32	25-55	0.5
Selenium	15	15	0.5	<0.5-<3	0.5-3	5	0	0.8	0.6-1.9	0.2
Silver	18	18	1.5	<1.5-<2	1.2-2	8	7	0.65	0.2-1	0.2-1
Strontium	18	0	57	30-147	--	9	0	66	46-89	1
Thallium	0					9	5	0.39	0.05-<1	1
Tin	18	17	1.5	<0.5-<10	0.5-10	9	9	2	2-5	0.05-5
Titanium	18	0	21	4.3-148	--	7	0	40	16-80	1
Uranium	0					5	0	1.35	0.87-1.64	0.05
Vanadium	18	0	36.2	17.7-97	--	9	0	35	25.8-45.6	0.2-1
Zinc	18	0	82	46-200	--	9	0	100	65-150	0.5-5

Notes: ndets: number of censored data reported as less than the detection limit; DLs: detection limits

Results

As indicated in Table 9.1, antimony, beryllium, bismuth, molybdenum, selenium, silver and tin were all below the detection limit in most cases, whereas arsenic, cadmium, mercury and thallium were below detection in only a few cases. All other metals were detected in every suspended sediment sample.

Metal concentrations in the suspended sediment samples collected during the SREQMP were compared to samples collected during the Follow-Up Study. Due to the high degree of censoring (almost 100% in some cases) for total antimony, beryllium, bismuth, molybdenum, silver, selenium, tin and thallium, these metals were not tested for significant differences between the two study periods. Further, given that total uranium was not analyzed during the SREQMP, the test could not be performed for this parameter. For boron, a significant difference was detected between the two sample periods (Figure 9.2; Mann-Whitney test; p=0.017), with concentrations being lower during the Follow-Up Study.

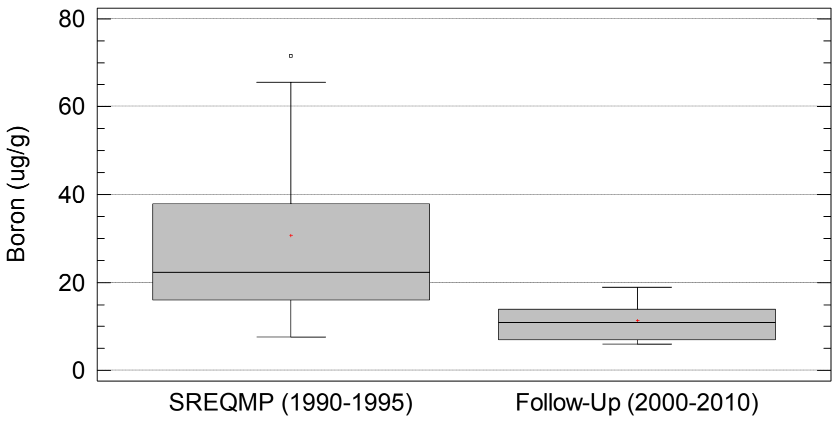

Figure 9.2. Comparison of boron concentrations (µg/g) in the Slave River suspended sediments at Fort Smith (1990-2010); n_{SREQMP}=18, $n_{Follow-Up}$=5

Significant differences were not observed for the remainder of the metal concentrations in the suspended sediment samples collected during the SREQMP and the Follow-Up Study. As a result it was considered acceptable to combine the data from the two time frames. A review of this analysis is provided in the following sections.

9.3.1 Relationship of Metals with Flow, Particle Size and Total Organic Carbon

It is generally accepted that smaller particles with higher levels of organic carbon content increase the carrying capacity of the suspended sediment for metals and organic compounds, due to the large surface area of these particles (Forstner, 1991). To examine this relationship, correlation analyses were conducted to measure the strength of the relationship (Spearman 'rho' coefficient: r_s) between select metals and flow, total organic carbon and the different particle sizes (clay, silt and sand) (Table 9.2).

Table 9.2: Relationship of suspended sediment metal concentrations with flow, particle size and total organic carbon for the Slave River at Fort Smith (1990-2010).

Statistically significant relationships are shaded yellow (where $p<0.05$); statistically significant and strong relationships are shaded pink (where $rs>0.7$)[26].

Metal	Flow (prob, n)	Clay (prob, n)	Sand (prob, n)	Silt (prob, n)	Total Organic Carbon (prob, n)
Aluminum	0.6542	0.7416	-0.6275	0.0026	0.7727
	(0.0017, 24)	(0.0009, 21)	(0.005, 21)	(0.9907, 21)	(0.0005, 21)
Arsenic	0.4101	0.6023	-0.4805	0.2011	0.3265
	(0.0602, 22)	(0.0106, 19)	(0.0415, 19)	(0.3937, 19)	(0.166, 19)
Cadmium	0.2572	0.2077	-0.0785	0.1973	0.4729
	(0.1985, 26)	(0.3299, 23)	(0.7126, 23)	(0.3548, 23)	(0.0302, 22)
Chromium	0.359	0.5555	-0.431	0.0707	0.4620
	(0.0726, 26)	(0.0092, 23)	(0.0432, 23)	(0.7403, 23)	(0.0342, 22)
Cobalt	0.4127	0.4797	-0.3621	0.2265	0.7211
	(0.0391, 26)	(0.0244, 23)	(0.0894, 23)	(0.288, 23)	(0.001, 22)
Copper	0.4806	0.5767	-0.4093	0.1804	0.7512
	(0.0163, 26)	(0.0068, 23)	(0.0549, 23)	(0.3975, 23)	(0.0006, 22)
Iron	0.4588	0.5943	-0.384	0.0669	0.8581
	(0.0278, 24)	(0.0079, 21)	(0.0859, 21)	(0.7648, 21)	(0.0001, 21)
Lead	0.5451	0.5161	-0.3857	0.1997	0.7047
	(0.0064, 26)	(0.0155, 23)	(0.0705, 23)	(0.3489, 23)	(0.0012, 22)
Manganese	0.5229	0.5807	-0.4516	0.1539	0.8438
	(0.0121, 24)	(0.0094, 21)	(0.0434, 21)	(0.4912, 21)	(0.0002, 21)
Mercury	0.5153	0.4538	-0.3707	0.2292	0.8149
	(0.0157, 23)	(0.0479, 20)	(0.1062, 20)	(0.3178, 20)	(0.0005, 19)
Nickel	0.3597	0.4397	-0.3143	0.2787	0.5313
	(0.0721, 26)	(0.0392, 23)	(0.1404, 23)	(0.1912, 23)	(0.0149, 22)
Strontium	0.5161	0.5158	-0.339	0.1759	0.7945
	(0.0099, 26)	(0.0155, 23)	(0.1118, 23)	(0.4094, 23)	(0.0003, 22)
Vanadium	0.2865	0.6751	-0.4825	-0.0198	0.6529
	(0.1520, 26)	(0.0015, 23)	(0.0236, 23)	(0.9261, 23)	(0.0028, 22)
Zinc	0.5072	0.4713	-0.2906	0.2213	0.7086
	(0.0112, 26)	(0.027, 23)	(0.1729, 23)	(0.2992, 23)	(0.0012, 22)

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[26] This table shows the Spearman rank correlations between each pair of variables. These correlation coefficients (r_s) range between -1 and +1 and measure the strength of the association between the variables (1st number). The second number in each location of the table is the P-value which tests the statistical significance of the estimated correlations. P-values below 0.05 indicate statistically significant non-zero correlations at the 95.0% confidence level. The third number shown is the number of pairs of data values used to compute each coefficient.

Statistically significant relationships were revealed between certain metals and flow, clay and sand. Of the different particle sizes, clay showed the most positive correlations with metals, which supports the hypothesis that there are strong correlations between increasing metal concentration and decreasing particle size (Milburn and Prowse, 1998). However although the relationships between clay and most metals were statistically significant, the relationships were not particularly strong (r_s: 0.44 to 0.68; Table 9.2). Milburn and Prowse (1998) suggested that the lack of strong correlations between metal concentrations and particle size in sediment from the Slave River could be explained more by the geochemical (composition) of the suspended sediments and recommended that future work should focus on further defining this relationship.

The relationships between metal concentrations and TOC of the Slave River suspended sediments were also examined. Strong statistically significant relationships were revealed between TOC and aluminum, cobalt, copper, iron, lead, manganese, mercury, strontium and zinc (r_s: 0.70-0.86; Table 9.2). These results suggest that organic carbon has a considerable influence on the sorption potential of the suspended sediments of the Slave River.

Recommendation

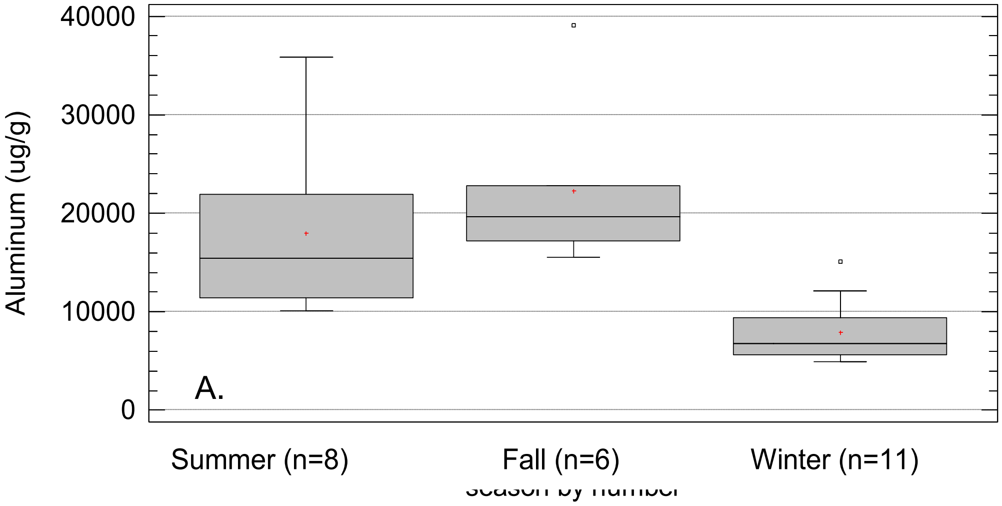
It would be beneficial to examine the seasonal changes in suspended sediment chemistry and the role of organic carbon as it affects the adsorption and transport of certain metals.

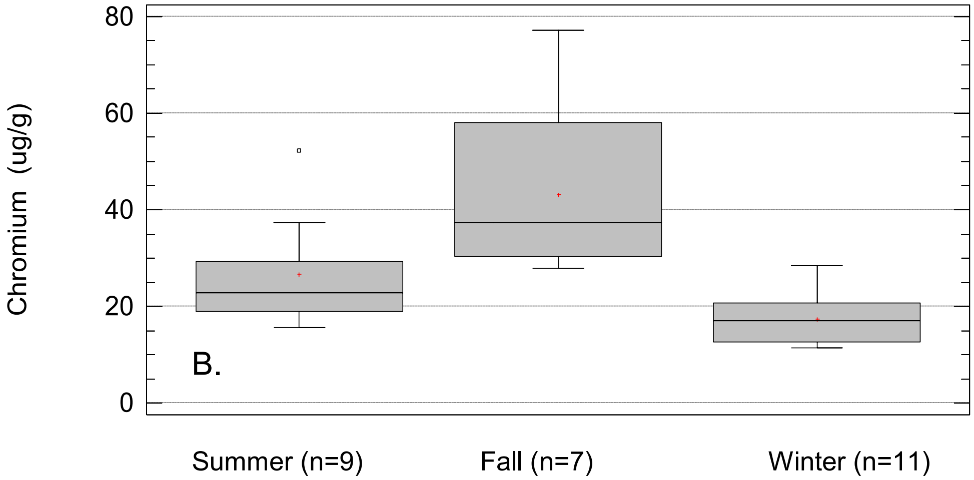
9.3.2 Seasonal Patterns of the Metal Concentrations in the Suspended Sediments of the Slave River

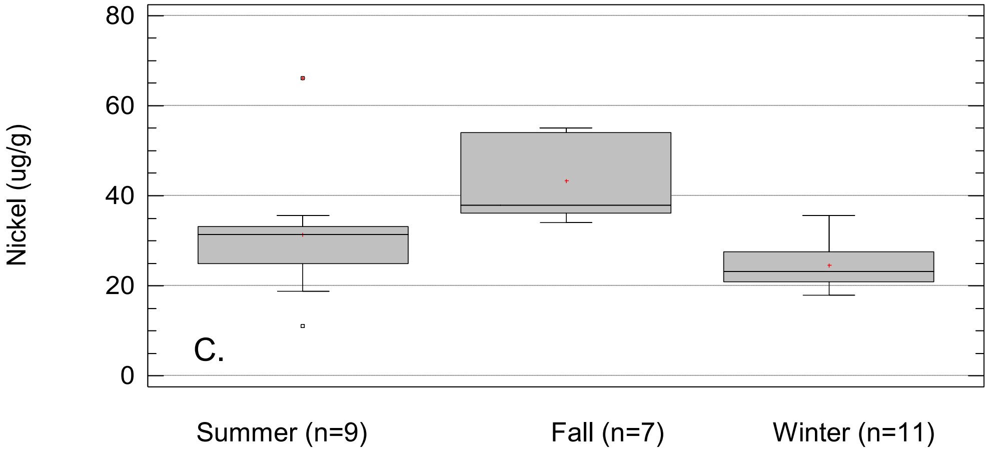
To determine if the sediment chemistry changed over the year, the data were sorted by season and comparisons were made. The presence of significant seasonal patterns in suspended sediment chemistry was examined using the non-parametric Kruskal-Wallis test. This statistical method tests for significant differences (at the 95% confidence level) among the medians of three or more groups of data (in this case, season).

Testing revealed three different statistically significant seasonal patterns. Most metals, including aluminum, barium, lead, mercury, strontium, vanadium and zinc, had higher concentrations during summer and fall than in the winter, with no statistically significant differences found between the summer and fall medians. Figure 9.3A illustrates this pattern for aluminum. Another common pattern that emerged with chromium, cobalt, copper, iron and manganese, was that highest concentrations were observed in the fall, with lower levels occurring in the summer and the lowest levels occurring in the winter. This seasonal pattern for chromium can be seen in Figure 9.3B.

Nickel showed higher concentrations during the fall than in the summer and winter with no statistically significant differences in the concentrations of nickel between summer and winter seasons (Figure 9.3 C). There were not enough samples and/or too many censored values to investigate seasonal patterns for antimony, beryllium, bismuth, molybdenum, selenium, silver, thallium, tin, and uranium.

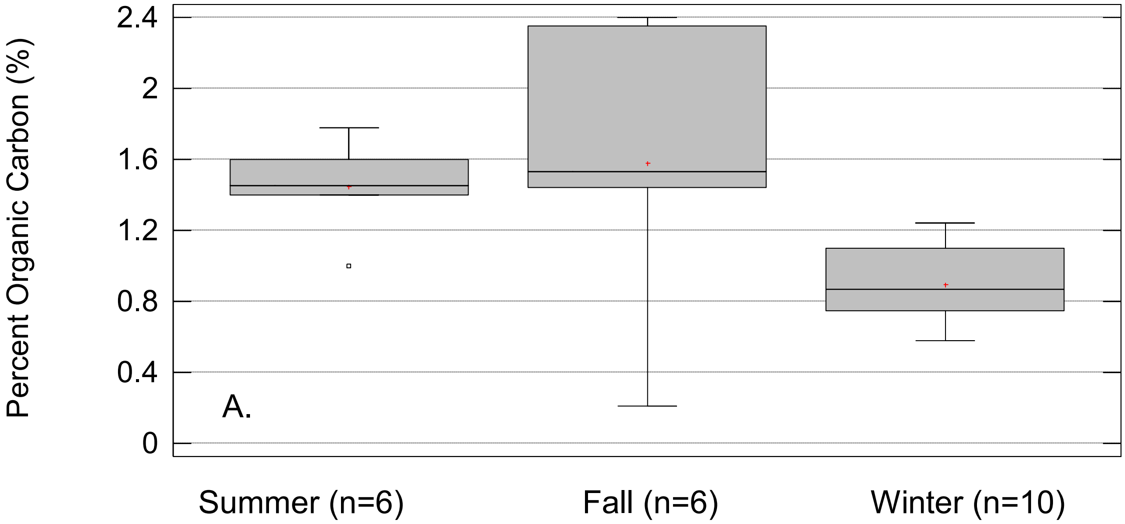


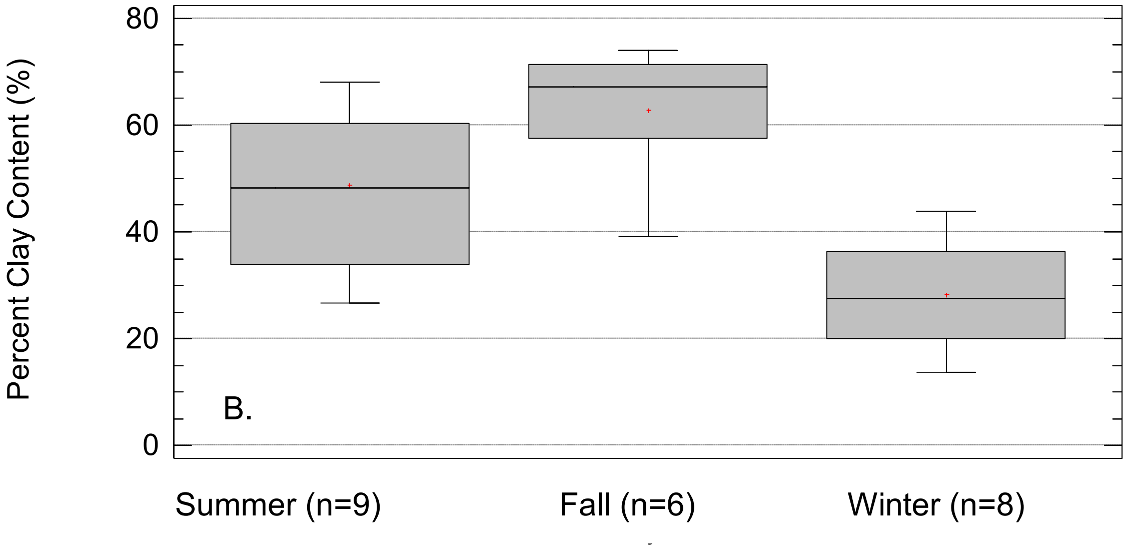




sediment collected from the Slave River at Fort Smith (1990-2010).

Not surprisingly, the seasonal pattern described above for most of the metals (aluminum, barium, lead, mercury, strontium, vanadium and zinc; Figure 9.3A) was similar to that of organic carbon and % clay content in the Slave River, specifically





sediment collected from the Slave River at Fort Smith (1990-2010).

These results support the suggestion that transport of substances (such as aluminum, barium, lead, mercury, strontium, vanadium and zinc) is influenced by the size of the sediment particle and organic carbon content of the suspended sediment samples.

Recommendation
Again, it would be beneficial to examine the seasonal changes in suspended sediment chemistry and the role of organic carbon as it affects the adsorption and transport of certain metals. This could be accomplished with a more regular and higher frequency sampling program.

9.3.3 Comparisons of Metal Concentrations to Guidelines

In Table 9.3, suspended sediment metal results were compared to the Canadian Draft Interim Freshwater Bottom Sediment Quality Guidelines (SQGs) and the Province of Ontario's Bottom SQGs (CCME, 1999; Ontario MOE, 2008). Of the 26 metals analyzed in the Slave River suspended sediment, national SQGs exist for only seven (arsenic, cadmium, chromium, copper, lead, mercury and zinc). In the absence of a national guideline, the Ontario SQGs were used for manganese and nickel.

Table 9.3: Comparison of metal concentrations (ug/g) in suspended sediment to bottom sediment guidelines for the protection of freshwater aquatic life.

Total Metal	**# of samples above detection limit/n**	**range of values above detection limit (µg /g)**	**TEL or LEL Guideline (µg/g)**	**# of samples above TEL or LEL**	**PEL or SEL Guideline (µg/g)**	**# of samples above PEL or SEL**
Arsenic	18/23	4.2-16.6	5.9[1]	15	17.0[2]	0
Cadmium	22/27	0.27-1.015	0.6[1]	7	3.5[2]	0
Chromium	27/27	11.5-77.2	37.3[1]	6	90.0[2]	0
Copper	27/27	6.3-95	35.7[1]	2	197.0[2]	0
Lead	27/27	3.6-21.1	35[1]	0	91.3[2]	0
Manganese	25/25	162-1340	460[3]	9	1100[4]	2
Mercury	21/24	0.02-0.15	0.17[1]	0	0.486[2]	0
Nickel	27/27	11.1-66.1	16[3]	26	75[4]	0
Zinc	27/27	46-200	123[1]	5	315[2]	0

[1] CCME National Guideline (TEL: Threshold Effect Level; concentrations below which adverse biological effects are expected rarely)

[2] CCME National Guideline (PEL: Probable Effect Level; concentrations above which adverse effects are expected to occur more frequently)

[3] Ontario Provincial Guideline (LEL: Lowest Effect Level; concentrations below which adverse biological effects are expected rarely in freshwater bottom dwelling organisms)

[4] Ontario Provincial Guideline (SEL: Severe Effect Level; concentrations at which pronounced disturbance of the sediment-dwelling community can be expected in freshwater bottom dwelling organisms)

Table 9.3 shows that concentrations of lead and mercury were always below the TEL. Arsenic, cadmium, chromium, copper and zinc exceeded the lower level TEL from two to 15 times, but none of these metals ever exceeded the probable effect level (PEL). Nickel and manganese were found in higher concentrations relative to the guidelines. Nickel exceeded the LEL (16 µg/g) in almost every sample however the SEL (75 µg/g) was not exceeded. Manganese exceeded the LEL on nine of 25 occasions and the SEL of 1100 µg/g on two occasions (June 1994 - 1117 µg/g and August 2006 - 1340 µg/g).

As a comparison, in the Peel River, levels of arsenic, manganese and nickel in the suspended sediments range from 10.8 to 14.7 µg/g (n=6), 162 to 498 µg/g (n=6) and 38.4 to 52.8 µg/g (n=8), respectively. While the Peel River has comparatively fewer upstream developments and activities that could potentially impact aquatic resources, these values do not differ substantially from the Slave River. Values of arsenic, manganese and nickel in the suspended sediments of the Liard River range from 7.7 to 11.4 µg/g (n=5), 86 to 741 µg/g (n=5) and 5 to 42 µg/g (n=5), respectively.

As the suspended sediment data can only be compared to SQGs for bottom sediments (due to a lack of guidelines specifically for suspended sediments), it was difficult to draw any definitive conclusions with respect to effects on biota despite the fact that the data only exhibited infrequent exceedances of the upper effects levels.

Recommendation
It is recommended that monitoring metals in suspended sediment be continued to be able to compare to past results, and provide a consistent record for historic analysis should suspended sediment guidelines be developed.

Table 9.4 summarizes the metal and physical data for suspended sediment samples collected from the Slave River at Fort Smith (1990-2010). As suspended sediments are important sources of major ions and nutrients to the Slave River, these data are also included.

Table 9.4: Moisture (%), Particle Size (%), Total Organic Carbon (%), Total Inorganic Carbon (%), Major Ions (µg/g), Phosphorus (µg/g) and Metals (µg/g) in suspended sediment samples collected from the Slave River at Fort Smith (1990-2010).

Minimum and maximum values for metals from the Peel River above Fort McPherson (2002-2007) are also included.

	Slave River at Fort Smith (1990-2010)										Peel River above Fort McPherson		
	n	# of NDs	mean	std dev	median	min	max	90th percentile	det limits	SQG	n	min	max
% Clay	23	0	45.3	18.8	42.2	13.7	74.0	69.5	0.01				
% Moisture	24	0	35.3	11.0	34.2	5.0	58.7	47.7	0.01				
% Sand	23	0	15.9	21.7	6.1	0.0	75.7	49.8	0.01				
% Silt	23	0	38.9	15.9	34.9	10.6	66.2	59.8	0.01				
Total Organic Carbon	22	0	1.23	0.54	1.19	0.21	2.40	1.76	0.01				
Total Inorganic Carbon	7	0	0.95	0.80	0.65	0.14	2.39	1.86	0.01				
Aluminum	25	0	14563	8971	12500	4950	39100	22640	50		6	9100	16900
Antimony	23	22	7.0	4.0	8.0	<0.1	<15.0	10	0.1-15				
Arsenic	23	5	10	5.00	9.5	<0.05	<20.00	16	0.05-20	5.9	6	10.8	14.7
Barium	27	0	267	109	258	105	607	387	0.5		8	525	1010
Beryllium	27	22	0.86	0.35	0.90	<0.15	<1.50	1.26	0.15-1.5		8	0.5	<1.0
Bismuth	16	15	17.3	11.7	25.0	<0.5	<25.0	25.0	0.5-25		6	<0.5	<0.5
Boron	23	0	26.6	20.0	19.0	6.0	71.5	60.2	2		6	6	18
Cadmium	27	5	0.53	0.19	0.51	<0.25	1.02	0.68	0.1-0.5	0.6	8	0.5	1
Calcium	25	0	17800	5999	17700	5610	36200	22640	100		6	6200	37000
Chromium	27	0	27	15	22	12	77	45	0.2-0.5	37.3	8	25.8	41.4
Cobalt	27	0	10.1	3.5	10.0	3.6	19.6	14.2	0.1-1		8	10.1	14.5
Copper	27	0	24.5	17.9	22.0	6.3	95.0	38.9	0.5-1	35.7	8	31.0	39.3

	Slave River at Fort Smith (1990-2010)										Peel River above Fort McPherson		
	n	# of NDs	mean	std dev	median	min	max	90th percentile	det limits	SQG	n	min	max
Iron	25	0	26232	11381	21700	11600	62600	35120	200	21200	6	27300	36700
Lead	27	0	10.7	5.0	11.0	3.6	21.1	16.4	0.5-5	35	8	13.6	17.7
Magnesium	25	0	7407	2689	7170	2900	17400	9434	20		6	4830	17200
Manganese	25	0	513	337	380	162	1340	944	1	460	6	162	498
Mercury	24	3	0.058	0.031	0.050	0.017	0.15	0.081	0.05	0.17		1.4	3.1
Molybdenum	27	20	3.5	2.3	4.0	0.9	<10.0	4.0	0.1-10		8		
Nickel	275	0	31.7	12.6	30.0	11.1	66.1	51.2	0.5	16	8	38.4	52.8
Phosphorus	24	0	1991	1108	2030	520	5345	3052	--				
Potassium	20	1	1919	1117	1945	<10	4035	3253	10-100		6	1440	3400
Selenium	20	15	0.90	0.81	0.50	<0.50	<3.00	2.01	0.2-3	5	6	0.9	1.7
Silver	26	25	1.28	0.59	1.50	<0.20	<2.00	2.00	0.2-2	0.5	8	<0.2	<1.0
Sodium	25	1	263	494	160	<5	2600	311	5-100		6	190	400
Strontium	27	0	65	25	63	30	147	85	1		8	54	81
Thallium	9	5	0.60	0.39	0.39	<0.05	<1.00	1.00	0.05-1		8	0.29	<1.00
Tin	27	26	3.4	2.6	2.0	<0.5	<10.0	5.8	0.05-10		8	<0.1	<5.0
Titanium	25	0	38.2	35.4	24.0	4.3	148.0	85.4	1		6	6.4	19
Uranium	5	0	1.28	0.29	1.35	0.87	1.64	1.55	0.05		6	1.1	1.6
Vanadium	27	0	37.9	16.7	35.0	17.7	97.0	50.7	0.2-1		8	39.2	67.1
Zinc	27	0	95	37	89	46	200	143	0.5-5	123	8	138	208

- SQG: sediment quality guideline; NDs: non-detects (censored data); std dev: standard deviation about the mean
- Source for Peel River data (AANDC, Water Resources Division, unpublished data)

9.4 Organic Compounds in Suspended Sediment

As described in Chapter 4, industrial activities in upstream jurisdictions have the potential to release a variety of compounds of potential concern (COPCs) into waters that drain into the Slave River. For example, oil sands operations and conventional oil and gas developments may release a wide range of hydrocarbon-based compounds into the environment. Pulp mills have, historically, discharged different types of chlorinated organic compounds, including chlorophenols, dioxins and furans. Agricultural and forest management activities can result in the release of various herbicides, insecticides and other pesticides. Additionally, long-range transport of persistent organic pollutants from more southerly locations and other parts of the world can also contribute COPCs to surface waters of the North.

Sediment survey results collected during the Northern River Basin Studies (1991-1995) indicated that sediments were an important transporting medium for many contaminants analyzed within the study. Concentrations in the suspended sediments were generally several orders higher than in the water and moderately higher than in depositional sediments (Carey *et al*., 1997). Also, Swanson *et al.* (1993) found that suspended sediments were important carriers for organic compounds released by the Weyerhaeuser bleached kraft pulp mill.

Accordingly, AANDC has been collecting suspended sediments from the Slave River at Fort Smith since 1990. The samples have been analyzed to determine the levels of chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile and semi-volatile organic compounds (VOCs and SVOCs), and polychlorinated dibenzodioxins/furans.

The following sections provide a summary of the concentrations of organic compounds in suspended sediment samples from the Slave River at Fort Smith. During the SREQMP (1990-1995), suspended sediment samples were collected three to four times per year (n=18). During the Follow-Up Study (2000-2010), suspended sediment samples were collected on nine occasions. Summary tables are provided in Appendix 9-1.

To determine if conditions have changed over time, suspended sediment data from the Follow-Up Study (2000-2010) were compared[27] to suspended sediment data from the original SREQMP (1990-1995)[28]. It should be noted that for some organic parameters,

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[27] Due to the small number of values, the historical and more recent data were not compared statistically.

[28] A complete discussion of the SREQMP results is included in Sanderson *et al*. (1997).

detection limits were higher in the Follow-Up Study than the SREQMP. According to the laboratory used to analyze the samples for organics, the rules that govern laboratory reporting have changed such that the laboratory must report values with a much higher level of certainty than what was needed in the past. As such, the very low detection limits achieved during the SREQMP are not available today.

Organic compounds in suspended sediment were not assessed for long-term trends because very few values were reported above the detection limit, however, further monitoring may allow for trend analyses to be conducted.

To provide further context to the Slave River data, results were compared, where appropriate, to the following:

- Bottom sediment data collected from the Slave River Delta (Milburn, 1998);
- Bottom sediment data collected from Great Slave Lake near the mouth of the Slave River (Evans *et al*., 1996 and Mudroch *et al*., 1992);
- Sediment core data collected from the West Basin of Great Slave Lake (Evans *et al*., 1996);
- Water, suspended sediment, bottom sediment and effluent sample data that were collected from a 200 km reach of the Athabasca River between Hinton and Whitecourt[29] (Crosley, 1996a & c; Pastershank and Muir, 1995);
- Bottom sediment data collected from 26 different sites throughout the Peace and Athabasca River Basins in 1988, 1990 and 1992 (Brownlee *et al*., 1997);
- Bottom sediment data from 5 depositional zones in the Wapiti, Smoky, Peace and Athabasca rivers (Crosley 1996b); and,
- Depositional sediment data from Lake Athabasca (Bourbonniere *et al*., 1996).

Finally results were compared to the Draft Interim Freshwater Bottom Sediment Quality Guidelines (SQG) which were developed by CCME (1999) for bottom sediments. The Ontario Bottom Sediment Quality Guidelines were used for parameters for which no national guidelines were available (Ontario MOE, 2008), as these guidelines were used for comparison in the original SREQMP. As mentioned in Section 9.1 suspended sediment guidelines do not exist.

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[29] Note: this section of the river receives municipal effluent from the town of Hinton and bleached kraft mill effluent from the Weldwood pulp mill.

9.4.1 Chlorinated Phenolics

Summary

During the SREQMP (1990-1995), 20 chlorinated phenolic compounds were detected in suspended sediment samples at very low levels. During the Follow-Up Study (2000-2010), none of these compounds were detected; however, the detection limits were not always as low as in the earlier investigation. The only compounds detected in the Follow-Up Study were two compounds that were not part of the SREQMP Study: p-cresol and phenol.

Recommendation

As more chlorinated phenolic compounds were detected in the suspended sediments than in the centrifugate water samples, monitoring of chlorophenols in suspended sediment samples should continue. Analyses should be conducted using the lowest detection limits available.

Background

Chlorinated phenolics are a general term that refers to a family of compounds (including chlorinated guaiacols, catechols, vanillins, syringealdehydes and veratroles) that have been associated with effluent discharges from kraft bleaching mills (Remberger *et al*., 1986). Suspended sediments downstream of mills have been found to be important carriers of these chlorinated compounds, which are toxic, persistent and known to bioaccumulate (Swanson *et al*., 1993; Kovacs *et al*., 1984; CCREM, 1987). Additional background information on chlorophenols can be found in Chapter 8, Section 8.3.1 and Appendix 8-5 of this report.

Phenol is released to the Canadian environment from municipal wastewater treatment plants, pulp and paper mills, chemical and steel production and the petroleum refining industry (Environment Canada, 2000). Phenol may occur naturally in water and soil from the decomposition of plants, vegetation and animal waste and from forest fires (Environment Canada, 2000).

Sources of cresols include car exhaust, electrical power plants, municipal solid waste incinerators, oil refineries, and cigarettes. People in residential areas where homes are heated with coal, oil, or wood may also be exposed to mixed cresols in the air (USEPA, 2000a).

There are currently no CCME CPFAL guidelines for chlorinated phenolics in sediment.

Results

From 1990-1995, 18 suspended sediment samples from the Slave River at Fort Smith were analyzed for 34 to 44 different chlorinated phenolic compounds. Of these compounds, 20 were detected (Table 9.5). These compounds were above the detection limit in 39 instances, with concentrations ranging from 0.5 to 60 ng/g. Some of these compounds, including 4,5-dichlorocatechol, 3,4,5 and 3,4,6-trichlorocatechol, had been detected in suspended sediment downstream of the Weyerhaeuser pulp mill (Swanson *et al*., 1993). In 1992, 3,4,5- trichloroguaiaicol was detected (700 to 3600 ng/g) in the effluent samples of what is now known as the West Fraser Mill at Hinton, Alberta.

The predominant chlorophenol compounds detected in bottom sediments in the Peace and Athabasca River (1994 and 1995) were 6-chlorovanillin, 3,4-dichlorocatechol, 2,4-dichlorophenol, 3,4,5-trichloroguiaicol and 3,4,5-trichlorocatechol (Crosley, 1996b). Elevated levels of 4,5-dichlorocatechol, 6-chlorovanillin and 3,4,5-trichlorocatechol were also found in the bottom sediment downstream of the two bleached kraft mills at Hinton and Grande Prairie (2.3 - 248.4 ng/g; Brownlee *et al*., 1997).

Table 9.5: Concentrations of chlorinated phenolics in suspended sediment samples from the Slave River at Fort Smith - SREQMP (1990-1995).

SREQMP (1990-1995)		
Compound	# of detects/ total n	Range of detected values (ng/g)
4-chlorophenol	3/15	0.2 - 3
2,4-dichlorophenol	6/18	0.42 - 60
2,4,6-trichlorophenol	3/18	1-2
2,3,4,6-tetrachlorophenol	1/16	0.1
Pentachlorophenol	1/18	1.9
4-chlorocatechol	2/14	2
3,4-dichlorocatechol	3/18	2 - 7
3,5-dichlorocatechol	1/18	1
4,5-dichlorocatechol	1/18	3
3,4,5-trichlorocatechol	3/18	1.1 - 34
3,4,6-trichlorocatechol	1/18	17

SREQMP (1990-1995)		
Compound	# of detects/ total n	Range of detected values (ng/g)
Tetrachlorocatechol	4/18	1 – 20
4-chloroguaiacol	1/14	2
4,5-dichloroguaiacol	1/18	1.4
3,4,5-trichloroguiaicol	2/18	0.5
Tetrachloroguiaicol	2/18	1 – 16
4,5-dichloroveratrole	1/18	0.5
3,4,5-trichloroveratrole	1/18	1.5
Tetrachloroveratrole	1/18	3.5
6-chlorovanillin	1/18	1

During the Follow-Up Study (2000-2010), nine suspended sediment samples were analyzed for up to 59 chlorinated phenolic compounds (44 original and 15 new compounds). None of the compounds from the original list were detected (Appendix 9-1). Although the detection limits for the chlorophenol compounds analyzed during the Follow-Up Study were low (0.4 to 2000 ng/g), the very low detection limits obtained during the earlier study are not available today due to changes in laboratory reporting requirements. Accordingly, it cannot be stated with certainty that the more recently measured chlorophenol concentrations are lower than they were in the early 1990's. However, studies conducted during the Northern River Basins Study, as well as studies conducted by Swanson *et al*. (1993) did find dramatic decreases in chlorophenol concentrations downstream of pulp mills, following changes to the bleaching process (Carey *et al*., 1997).

Of the 15 additional chlorinated phenolic compounds analyzed during the Follow-Up Study, only two were detected: phenol and p-cresol. P-cresol was detected three times (n= 4) with values ranging from 90-465 ng/g and phenol was detected twice (n=4) with a range of 10-27 ng/g. No other chlorinated phenolic compounds were detected in the Follow-Up Study (2000-2010).

Recommendation

Suspended sediment samples from the Slave River should continue to be monitored for chlorinated phenolics to confirm that levels have decreased. Phenol and p-cresol should continue to be a part of the compound list. Analyses should be conducted using the lowest detection limits available.

Further, considering that more chlorinated phenolic compounds were detected in the suspended sediments than in the centrifugate water samples, the former may be a better medium for future monitoring of these compounds.

9.4.2 Organochlorine Pesticides

Summary
Organochlorine pesticides were not detected in suspended sediment samples from the Slave River.

Recommendation
Given the agricultural activity in the upstream portion of the catchment and the potential for long-range transport from other areas, monitoring for organochlorine pesticides should continue. Lower detection limits are required for future monitoring, to allow for a more complete comparison to guidelines and upstream studies.

Background
Organochlorine (OC) pesticides are chlorinated chemicals that include insecticides, herbicides and fungicides (AXYS, 2010b). For the purposes of this report, OC pesticides include herbicides (which are used to control weeds and invasive, non-native plants) and insecticides (which are used to control nuisance or non-native insects).

OC pesticides are hydrophobic, lipophilic and very stable, which makes them highly persistent and bioaccumulative in aquatic organisms (AXYS, 2010b; USEPA, 1976). These compounds can enter the aquatic environment through the direct application of commercial and domestic sprays for insect control and crop protection, runoff from agricultural lands, as well as through the long-range transport of atmospheric pollutants to northern regions (USEPA, 1979). Further background information on these compounds can be found in Chapter 8, Section 8.3.2 and Appendix 8-5.

Results
During the SREQMP (1990-1995), 13 suspended sediment samples were analyzed for up to 29 organochlorine pesticides and herbicides. All values were found to be below detection limits (1.0 to 80 ng/g). During the Follow-Up Study (2000-2007), eight samples were analyzed for up to 39 organochlorine pesticides and herbicides (Appendix 9-1). Similarly, all values were found to be below detection limits (1.0 to 10 ng/g). Suspended sediment samples from 2010 were not analyzed for OC pesticides.

As a comparison, Mudroch *et al.* (1992) measured pesticides in the bottom sediments of Great Slave Lake and found them to be in the range of <0.01 to 1 ng/g. Likewise, Evans *et al.* (1996) found concentrations of these compounds in surficial sediments of Great Slave Lake ranging from 0.2 to 1 ng/g.

As the detection limits in both the SREQMP and the Follow-Up Study were sometimes higher than the sediment quality guidelines and upstream studies, comparisons cannot be made. Accordingly, lower detection limits are required for future monitoring, to facilitate such comparisons.

Recommendation

Given the agricultural activity in the upstream portion of the catchment and the potential for long-range transport from other areas, it is recommended that monitoring for organochlorine pesticides should continue. Lower detection limits are required for future monitoring, to allow for a more complete comparison to guidelines and upstream studies. It is also recommended that other in-use pesticides be identified and analyzed in the future, to ensure that the monitoring program is capable of detecting the presence of these compounds in the Slave River.

9.4.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Summary

During the Follow-Up Study (2000-2010), the PAH values in the suspended sediment were lower than in the SREQMP (1990-1995), and fewer values exceeded the lower effect levels guidelines. All results were well below the levels at which adverse effects are predicted to occur frequently.

Concentrations of total PAHs, estimated by summing the concentrations of 16 individual parent PAHs, were lower than the total PAHs sediment quality guideline for the protection of freshwater aquatic life (Ontario MOE/LEL).

Recommendation

Given the increased oil sands developments occurring upstream, continued monitoring for parent and alkylated PAHs, as well as naphthenic acids, is recommended, with the lowest detection limits available.

Background

PAHs in the environment originate primarily from two sources: petrogenic and pyrogenic (Burgess, 2009). Biosynthesis PAHs also make up a small contribution (Neff, 1979). Petrogenic PAHs originate from petroleum sources including different types of oils, coals and organic shale. Anthropogenic sources of these substances include industrial production, refining and transport, and they may also enter waters through potential spills and leaks from tailings ponds and waste sites. Natural seeps and bituminous outcrops, rocks and soils are natural sources of petrogenic PAHs (Burgess, 2009). Pyrogenic (burning) PAH sources include a large number of industrial applications involving the combustion of organic materials (Burgess, 2009). Natural pyrogenic sources include volcanic eruptions and forest fires (Nagpal, 1993).

Two basic types of PAHs exist: parent and alkylated. Parent PAHs are stable organic molecules composed of two to seven fused benzene rings. As the number of rings increase, there are rapid declines in natural abundance, solubility in water, volatility, and rate of microbial degradation. The tendency of these compounds to partition into the solid phase, and to bioaccumulate in organisms, is also greatest for the larger, multi-ring compounds (Southworth, 1979; MacKay *et al*., 1980; Herbes, 1981). PAH compounds attached to sediment particles may be desorbed into the gut of aquatic animals, where they accumulate in tissues (de Voogt *et al*., 1991, Clements *et al*., 1994).

PAH compounds containing a straight carbon side chain are referred to as alkylated PAHs (AXYS, 2010a). These compounds are more abundant, persist for a longer time, and are sometimes more toxic than the parent PAH compounds (Irwin *et al*., 1997). Alkylated PAHs are often more abundant in fresh petroleum products than their parent compounds and were found in the process effluent from an oil sand operation collected from 1989 to 1994 (Carey *et al*., 1997).

Naphthenic acids (NAs) are natural constituents in many petroleum sources, including bitumen in the oil sands of Northern Alberta (Scott *et al*., 2005) and have also been detected in the oil sands operations process effluent (Carey *et al*., 1997). NAs have a relatively high solubility in water, low affinity for sediment/soil particles, and are concentrated in tailings (McMartin, 2003).

Results for parent and alkylated PAHs, as well as naphthenic acids are presented here. Further information on PAHs can be found in Section 8.3.3 and Appendix 8-5.

The CCME CPFAL and Ontario MOE sediment quality guidelines for bottom sediments are included in Table 9.6.

PAH Parent compounds

Results

During the SREQMP (1990-1995), 13 suspended sediment samples were analyzed for up to 17 PAH parent compounds (Table 9.6). All of the substances tested for, with the exception of acenaphthylene, were present in at least one sample; concentrations varied between 4 to 580 ng/g. During the Follow-Up Study (2000-2010), nine suspended sediment samples were analyzed for up to 28 PAH parent compounds; 26 of the compounds were detected with concentrations ranging between 2 and 180 ng/g (Appendix 9-1).

For those compounds which are comparable, the ranges of values above detection tended to be lower in the Follow-Up Study than in the earlier study (Table 9.6). A good example of this is naphthalene, with concentrations ranging from 10-580 ng/g during the SREQMP and from 10-50 ng/g during the Follow-Up Study (Figure 9.5; Table 9.6).

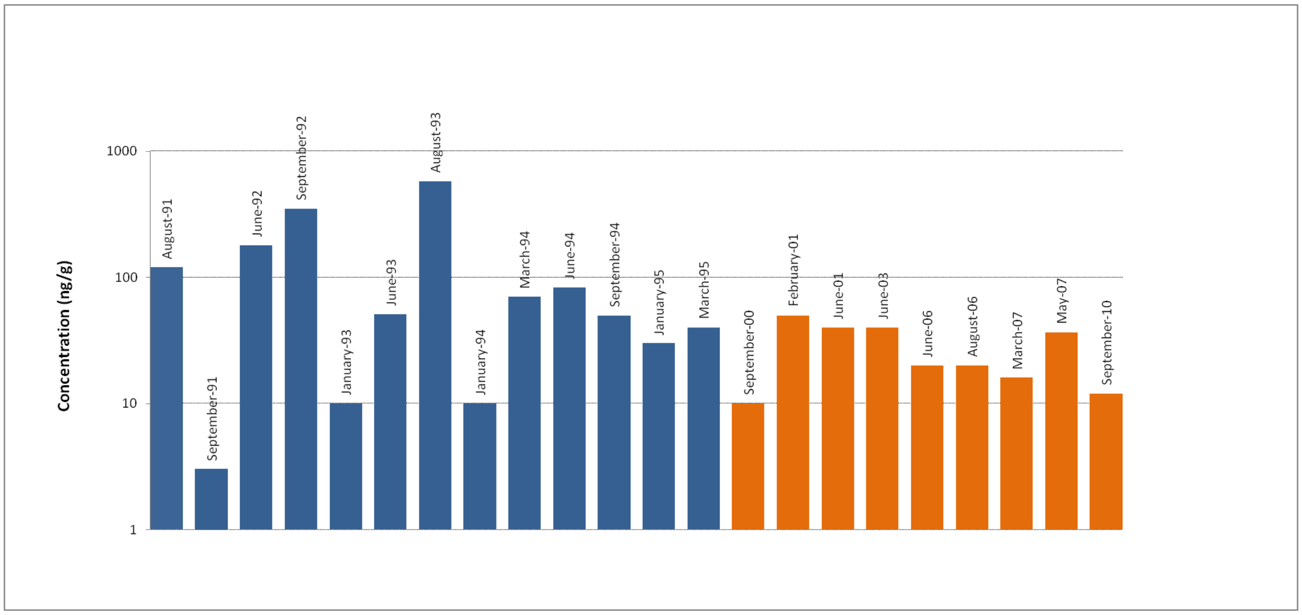

Figure 9.5: Comparing the Concentrations of Naphthalene in the Suspended Sediments of the Slave River between the SREQMP (1990-1995) and the Follow-Up Study (2000-2010).

Table 9.6: Comparison of PAH parent concentrations in suspended sediment samples to guidelines for the protection of freshwater aquatic life for bottom sediments (ng/g).

	SREQMP (1990-1995)			**Follow-Up Study (2000-2010)**			
PAH Compound	**# of samples above detection limit/n**	**range of values above detection limit (ng/g)**	**# of samples above CCME - TEL**	**# of samples above detection limit/n**	**range of values above detection limit (ng/g)**	**# of samples above CCME - TEL**	**Guideline (CCME - TEL/PEL) *unless otherwise noted**
Acenaphthene	4/13	8-17	4	3/9	2-10	1	6.71 / 88.9
Acenaphthylene	0/13	----	0	0/9	----	0	5.87 / 128
Anthracene	N/A	----	----	1/8	10	0	46.9 / 245
Benzo(a)anthracene	N/A	----	----	5/8	5-20	0	31.7 / 385
Chrysene	N/A	----	----	8/8	7-50	0	57.1 / 862
Benzo(a)anthracene/ Chrysene	12/13	10-66	----	1/1	30	0	----
Benzo(a)pyrene	7/13	10-42	1	4/9	7-10.5	0	31.9 / 7982
Benzo(k)fluoranthene	N/A	----	----	4/8	3-10	0	240[1]
Benzo(b or k)fluoranthene	11/13	7-53	0	2/2	20-32	0	----

	SREQMP (1990-1995)			Follow-Up Study (2000-2010)			
PAH Compound	**# of samples above detection limit/n**	**range of values above detection limit (ng/g)**	**# of samples above CCME - TEL**	**# of samples above detection limit/n**	**range of values above detection limit (ng/g)**	**# of samples above CCME - TEL**	**Guideline (CCME - TEL/PEL) *unless otherwise noted**
Benzo(b)fluoranthene	N/A	----	----	5/7	10-33	----	----
Benzo(b&j)fluoranthene	N/A	----	----	1/1	20	----	----
Benzo(e)pyrene	N/A	----	----	1/1	19	----	----
Benzo(g,h,i) perylene	10/13	5-44	----	8/9	8-40	----	----
Dibenzo(a,h)anthracene	1/13	26	1	3/9	4-10	1	6.22 / 135
Fluorene	6/13	14-31	2	5/9	7-20	0	21.2 / 144
Fluoranthene	8/13	10-25.3	0	7/9	8-20	0	111 / 2355
Indeno(1,2,3-*c,d*)pyrene	1/13	17	0	4/9	7-10	0	200[1]
1-methylnaphthalene	N/A	----	----	1/1	25	----	----
2-Methylnaphthalene	2/2	75-107.6	2	2/2	31-33	2	20.2 / 201
Methylnaphthalenes	13/13	18-350	----	8/8	50-180	----	----
Naphthalene	11/13	10-580	9	9/9	10-50	4	34.6 / 391
Perylene	11/13	28-330	----	2/3	133-160	----	----
Phenanthrene	2/3	14-49	1	8/8	28-100	5	41.9 / 515
Phenanthrene/Anthracene	10/10	30-137	----	1/1	30	0	----
Pyrene	11/13	4-40	0	8/9	10-40	0	53 / 875
Retene	N/A	----	----	1/1	60	----	----
Acridine	N/A	----	----	0/1	----	----	----
Quinoline	N/A	----	----	0/1	----	----	----
Total PAH	N/A	----	----	8/8	148-320	0	4000

N/A – Not Analyzed;

[1] Ontario MOE Bottom Sediment Quality Guideline (LEL)

Levels of PAHs in suspended sediment from the entire period of record at Fort Smith were compared to the CCME and Ontario Provincial guidelines for bottom sediments, as there are currently no suspended sediment quality guidelines available (Table 9.6; CCME, 2001; Ontario MOE, 2008). Although some PAH values exceeded the threshold effect level (TEL), all results were lower than the probable effect level (PEL), at which adverse effects are predicted to occur frequently (CCME, 2001).

A review of Table 9.6 reveals that many of the same PAH compounds exceeded guidelines during both the SREQMP and the Follow-Up Study, and for those compounds which are comparable, fewer samples were above guidelines in the Follow-Up Study (Figure 9.5).

These findings are similar to those found by Evans *et al*. (1996). All of the parent PAH compounds which were detected in the Slave River at Fort Smith study were also detected in 1993 and 1994 in surficial sediments from the mouth of the Slave River, as well as in core samples collected in the West Basin of Great Slave Lake. The most abundant PAHs in the surficial sediments were benzo(g,h,i)perylene, benzo(e)pyrene, phenanthrene and benzo(b)fluoranthene, with naphthalene, indeno(1,2,3-cd-)pyrene and chrysene found at lower concentrations. In the core samples, naphthalene, 1-methylnaphthalene and 2- methylnaphthalene were found to be major components and could be indicative of increased industrial activity in the basin (Evans *et al*., 1996).

Further, Crosley (1996b) and Brownlee *et al.* (1997) found phenanthrene to be a major component of the bottom sediments collected from the Peace and Athabasca rivers from 1988 to 1992 and 1994 to 1995, respectively. Concentrations were found to be higher in the Peace than in the Athabasca Rivers. In addition, naphthalene, phenanthrene and pyrene were found to be major constituents of the wastewater discharge from the Suncor Incorporated oil sands plant in Fort McMurray, Alberta. These substances have also been found in natural discharges from oil sands mines and rivers which drain watersheds in the oil sands regions (Bourbonniere *et al*., 1996).

In 1992 and 1993, bottom sediment cores and surficial sediment samples were collected from Lake Athabasca (Bourbonniere *et al*., 1996). Bottom sediment samples collected from Lake Athabasca contained many of the same PAH compounds detected in the Slave River at Fort Smith suspended sediments. For the higher molecular weight PAHs, which are often associated with combustion sources, the Bourbonniere study did not reveal any spatial trends in PAH concentrations in Lake Athabasca, which suggested atmospheric sources were the main control (Bourbonniere *et al*., 1996; Carey *et al.,* 1997). However, for 1-methylnaphthalene, 2-methylnaphthalene and phenanthrene, a slight trend from west to east in Lake Athabasca was found. These PAHs are commonly observed in water samples in areas receiving hydrocarbon pollution. Their presence at higher concentrations in the western-most samples is suggestive of a riverine source (Bourbonniere *et al*., 1996; Carey *et al.,* 1997).

These findings suggest that the PAH compounds detected in the Slave River suspended sediment samples appear to have both atmospheric and riverine sources and may be a result of both natural discharges and increased industrial activity in the basin.

Recommendation

Given the increased oil sands developments occurring upstream, it is recommended that parent PAH compounds continue to be monitored in the Slave River suspended sediment samples.

Total PAHs

Background

The term "Total PAHs" can be misleading as there are tens of thousands of possible parent PAH structures which exist (Burgess, 2009). The Slave River monitoring program included routine analysis for 17 to 28 PAH compounds, 16 of which have been identified by the US Environmental Protection Agency as priority PAH pollutants. For this report, concentrations of total PAHs were calculated for each sample by summing the concentrations of these 16 individual parent PAHs: acenaphthene, acenaphthylene, anthracene, benzo(k)fluoranthene, benzo(b)fluorene, benzo(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, pyrene(Ontario MOE, 2008). When results were reported as less than the detection limit, the value of the detection limit was used in the total PAH calculation.

Results

Following the above criteria, total PAH concentrations could be estimated for eight of the suspended sediment samples which were collected from 2001 to 2010 (Figure 9.6). Concentrations ranged from 145 to 410 ng/g with a mean concentration of 274 ng/g (SD=88 ng/g). All total PAH levels were lower than the Ontario MOE total PAH sediment quality guideline of 4000 ng/g for the protection of freshwater aquatic life (BC MOE, 2008).

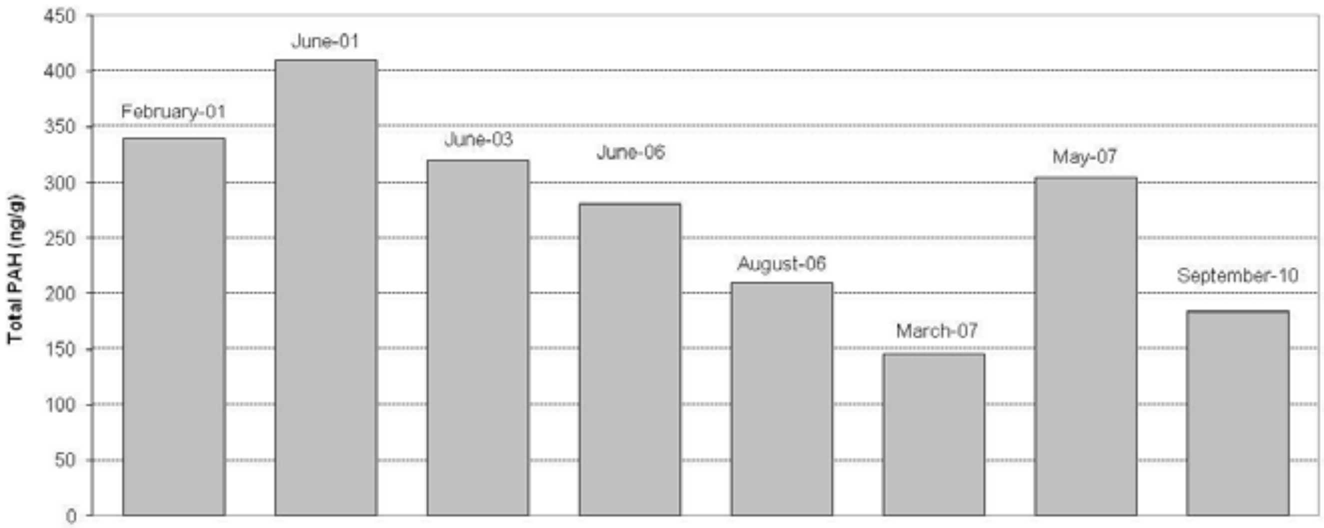

Figure 9.6: Total polycyclic aromatic hydrocarbon (PAH) concentrations by sample date during the Follow-Up Study (2000-2010).

Alkylated PAHs

Results

In May 2007 and September 2010, suspended sediment samples were analyzed for an expanded suite of PAH parent compounds, as well as alkylated PAHs, biphenyl and dibenzothiophene (Table 9.7; Appendix 9-1).

Although there are currently no Canadian guidelines for alkylated PAHs, the United States Environmental Protection Agency (USEPA, 2003b) uses data from parent and alkylated PAHs samples in a tool for evaluating the hazards posed to aquatic organisms by exposure to PAHs in sediments. Using the EPA approach, equilibrium partitioning-based sediment benchmark toxic units (ESB-TUs) are calculated from data for 34 parent and alkylated PAHs (18 parent and 16 alkylated). When ESB-TUs exceed 1.0, toxicity to benthic invertebrates is predicted. The USEPA approach was calculated using hydrocarbon results from the September 2010[30] suspended sediment sample. The ESB-TU from this sample measured 0.079 which was well below the ESB (ΣESBTU > 1.0) for PAH mixtures that are considered unacceptable for the protection of benthic organisms.

For this approach to be used as intended, it is imperative that future monitoring include the analyses of the 34 parent and alkylated PAHs (as well as percent TOC) needed to calculate the ESB-TUs. Without the complete PAH list (including alkylated PAHs), the

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[30] The September 2010 sample is the only sample to date where the required 34 alkylated PAHs and %TOC were available to perform the ESB-TU calculation.

total toxicological contributions of the PAH mixtures are likely greatly underestimated (D. Birkholz. ALS Laboratories. Edmonton, Alberta. Pers comm.).

Table 9.7: Concentrations of alkylated PAHs measured in the May 2007 and September 2010 suspended sediment samples.

Compound	**May 2007 (ng/g)**	**Sept 2010 (ng/g)**
methyl acenaphthene	20	<4
methyl B(a)A/chrysene	70	61
methyl acenaphthene	20	<4
methyl B(a)A/chrysene	70	61
methyl B(b&k)F/B(a)P	100	43
methyl biphenyl	40	23
methyl dibenzothiophene	30	17
methyl fluoranthene/pyrene	70	44
methyl fluorine	30	15
methyl phenanthrene/anthracene	200	108
C2 sub'd B(a)A/chrysene	60	68
C2 sub'd B(b&k)F/B(a)P	50	29
C2 sub'd biphenyl	30	16
C2 sub'd dibenzothiophene	40	27
C2 Fluoranthenes/Pyrenes	N/A	59
C2 sub'd fluorene	60	27
C2 sub'd naphthalene	250	121
C2 sub'd phenanthrene/anth.	160	113
C3 Benzoanthracenes/Chrysenes	N/A	32
C3 sub'd dibenzothiophene	40	34
C3 Fluoranthenes/Pyrenes	N/A	56
C3 sub'd fluorene	N/A	35
C3 sub'd naphthalene	170	97
C3 sub'd phenanthrene/anth.	120	84
C4 Benzoanthracenes/Chrysenes	N/A	11
C4 sub'd dibenzothiophene	10	41
C4 Fluoranthenes/Pyrenes	N/A	48
C4 sub'd naphthalene	120	64
C4 sub'd phenanthrene/anth.	120	164

Compound	May 2007 (ng/g)	Sept 2010 (ng/g)
Dibenzothiophene	11	6
biphenyl	20	10
Naphthenic acids	N/A	<5000

Sub'd - substituted

Recommendation

For the above reasons, and due to the expansion and intensity of oil sands developments in upstream regions, it is recommended that future monitoring on the Slave River should include the analyses of alkylated PAHs, along with the parent PAH compounds.

Naphthenic Acids

Results

In 2010, naphthenic acids (NAs) were included in the monitoring in the transboundary reach of the Slave River, but they were not detected.

Recommendation

Given the toxic nature of NAs to aquatic life (Scott *et al*., 2005), and their known presence in oil sand operational process effluent ((Carey *et al*., 1997), it is recommended that any future monitoring include the analyses of naphthenic acids.

9.4.4 Polychlorinated Biphenyls

Summary
PCB concentrations in suspended sediment samples collected from the Slave River were always below the SQGs.

Recommendation
Although the detection limits for the total and Aroclor PCBs analyses are higher than those for the individual PCB congener analysis, the values are still lower than available guidelines. It is recommended that suspended sediment samples continue to be analyzed for total and Arochlor PCBs.

Background
As mentioned previously, PCBs are a group of 209 synthetic aromatic hydrocarbons, which are among the most persistent pollutants in the global ecosystem (Nagpal, 1992). PCBs were typically synthesized by chlorinating biphenyl with chlorine gas. Varying the conditions of the chlorination process produced different mixtures of congeners with different physical properties. These mixtures were sold as products called Aroclors (Columbia Analytical Services, 2010).

Solubility of PCBs declines with increasing chlorine substitution, but all PCBs have a strong affinity to sediment, especially fine grained particles. Sorption to sediments is the predominant mechanism removing PCBs from the water column (Nagpal, 1992; USEPA, 1979; Jaagumagi, 1990). Further background information on PCBs is available in Section 8.3.4 and Appendix 8-5 of this report.

CCME has developed SQGs (TEL) for the protection of aquatic life for Aroclor 1254 (60 ng/g) and total PCBs (34.1 ng/g; CCME 1999, 2002).

Results
During the SREQMP (1990-1995), 14 suspended sediment samples were analyzed for total PCBs and all values were found to be below the detection limit (2-300 ng/g).

During the Follow-Up Study (2000-2010), PCB analysis was expanded after 2003 (Appendix 9-1). The four samples collected from 2000 to 2003 were analyzed for total PCBs and all samples had values below the detection limit (2-50 ng/g). The four samples collected after 2003 (June 14, 2006; August 29, 2006, March 6, 2007 and

September 2010) were analyzed for a suite of nine Aroclors. Again all samples had concentrations below the detection limit (2-10 ng/g).

In May 2007, the suspended sediment sample was analyzed for 177 PCB congeners (PCB 2 to 209) with much lower detection limits. Table 9.8 highlights PCB congeners having concentrations above the detection limit.

Table 9.8: Detected PCB congeners in May 2007 suspended sediment sample collected from the Slave River at Fort Smith.

PCB Congener	**Concentration (ng/g)**
PCB 147/149	0.011
PCB 43/52	0.024
PCB 81	0.012
PCB 95	0.012
Total HexaCB	0.011
Total Mono-TriCB	0.03
Total PentaCB	0.012
Total TetraCB	0.055
Total PCBs	0.039

Although detection limits for total and Aroclor PCB are higher than those for the individual congeners, the detection limits are still low enough to allow for comparison to guidelines. All suspended sediment samples collected from the Slave River at Fort Smith had levels of these PCBs below the guidelines. The concentration of total PCBs in the May 2007 suspended sediment sample was 800 X below the bottom sediment guideline for the protection of freshwater aquatic life.

For comparison, surficial sediment samples collected in the Slave River delta in 1993 had total PCB concentrations that ranged from 4.8-15.2 ng/g (Evans *et al.*, 1996). The volatile, lower chlorinated congeners (mono- and di- chlorobiphenyls) made up an average of 40% of the total PCB value, which suggested that the atmosphere was the primary source of these PCBs (Evans *et al.*, 1996; Mudroch *et al.*, 1992). Total PCB concentrations in core samples collected in Great Slave Lake were lower (ranging from 0.7-9.0 ng/g) and were dominated by the tri- to hexa- chlorobiphenyls.

Recommendation

Although PCB Congener results are only available for one sample, the detection of tri- to hexa- chlorobiphenyls could suggest that the suspended sediment from the Slave River are being deposited into Great Slave Lake. It is recommended that suspended sediment samples continue to be monitored for PCBs.

9.4.5 Chlorinated Benzenes

Summary
Concentrations of chlorinated benzenes were below detection limits in suspended sediment samples collected from the Slave River at Fort Smith.

Recommendation
Continued monitoring of chlorinated benzenes should be reviewed.

Background
As mentioned previously, chlorinated benzenes are a group of cyclic aromatic compounds that are used as solvents, electrical equipment insulators, pesticides and flame retardants (Peirano, 1985). Due to their low water solubility, most chlorinated benzenes will evaporate or be removed though adsorbtion to sediment particles (Peirano, 1985). Their lipophilic nature and slow degradation in the environment, results in the potential for these substances to can accumulate through the food chain (Jan and Malnersic, 1980). Further background information on chlorinated benzenes can be found in Section 8.3.5 of this report.

Results
During the SREQMP (1990-1995), and in February 2001, suspended sediment samples were analyzed for pentachlorobenzene (n=9) and hexachlorobenzene (n=11). Levels for all samples were below detection limits (1-10 ng/g). There are currently no sediment quality guidelines for chlorinated benzenes..

Given that chlorinated benzene compounds have not been detected, it is recommended that the further analysis of these compounds in suspended sediment samples be reviewed.

9.4.6 Polychlorinated Dibenzodioxins and Dibenzofurans

Summary

The most toxic isomer, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), was not detected in any of the suspended sediment samples collected from the Slave River. All TEQ values for suspended sediment samples from this study were below the Interim Sediment Quality Guideline of 0.85 pg TEQ/g and the PEL of 21.5 pg TEQ/g.

Of the seven congeners that were detected, three were above detection more than two times; 2,3,7,8-TCDF (detected in 10 of 20 samples), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (H_7CDD; 14/20), and OCDD (18/20)).

Several of the NRBS studies concluded that 2,3,7,8-TCDF was a good sediment marker for effluent discharged from bleached kraft pulp mills. This congener was detected in nine of 11 samples in the SREQMP and one of nine samples in the Follow-Up Study. This apparent decrease may be attributed to changes made by pulp mills to the bleaching process, but further sampling is required to confirm.

Of the six higher chlorinated congeners that were detected in this study, only H_7CDD and OCDD were detected more than twice. Although these compounds have been detected in pulp mill and wastewater effluent, their presence is often indicative of combustion sources.

Although mono, di and tri -substituted PCDD/Fs are not as toxic as other congeners, they are considered good markers of pulp mill effluent.

Recommendations

It is recommended that suspended sediment samples continue to be monitored for dioxin and furans, including 2,3,7,8-TCDF and the higher chlorinated congeners. Consideration should also be given to including mono, di and tri -substituted PCDD/Fs in future monitoring.

Background

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are large families of chlorinated hydrocarbons with one (furan) or two (dioxin) oxygen atoms connecting two benzene rings. Dioxins and furans share similar molecular, physical and chemical properties (McKay *et al*., 1992). There are 75 PCDD and 135 PCDF congeners, each congener having a different number and arrangement of chlorine atoms substituted on the carbons of the benzene rings (NRCC, 1981).

Increased chemical and environmental stability, hydrophobocity (i.e. insolubility in water), lipophilicity (i.e. strong affinity for lipids) and persistence, occur with increased chlorine substitution (NRCC, 1981; Pastershank and Muir, 1995). The most toxic congeners are those for which the chlorine molecule is substituted on carbons 2, 3, 7, and 8 (Safe and Phil, 1990).

The main sources of dioxins and furans to the environment are chemical production and combustion (Fletcher and McKay, 1993). Chemical processes include the bleaching of wood pulp with chlorine to produce paper products, manufacturing of chlorinated organic compounds such as herbicides, and metal smelting (Evans *et al*., 1996). Chlorinated dioxins and furans that have been detected in pulp mill effluents include 2,3,7,8-tetrachlorodibenzofuran (TCDF), 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and octachlorodibenzo-*p*-dioxin (OCDD) (Clement *et al*., 1989). The presence of dioxins and furans downstream from bleached kraft pulp mills has been documented; however, improvements in pulp bleaching processes and effluent treatment have greatly decreased effluent concentrations (Muir and Pastershank, 1997; Swanson *et al*., 1993; Crosley, 1996c).

PCDDs and PCDFs are also produced during the combustion of organic matter in the presence of chlorine. Examples of this include exhaust from motor vehicles, and incineration of municipal, chemical and hospital wastes (Fiedler *et al*., 1990, NRCC, 1981). Natural sources of dioxins and furans include forest fires (Crosley, 1996b).

Dioxins and furans tend to rapidly adsorb to most soils and sediments, but can also be transported through the atmosphere over long distances (McKay *et al*., 1992; Fiedler *et al*., 1990). In aquatic ecosystems, the smallest particle sizes (<10 um) generally contain the highest organic carbon and are potentially good carriers of bound PCDD/Fs (Pastershank and Muir, 1995; Isensee and Jones, 1975; Ward and Matsumura, 1977; Firestone, 1977). Suspended sediments have been recognized as an important transport mechanism for dioxins and furans and have been found to be important carriers of these contaminants in the Wapiti/Smoky system (Rosa *et al*., 1991; Swanson *et al*., 1993). Crosley (1996a&c) found that downstream of Hinton and the Weldwood pulp mill, as well as along the Athabasca River mainstem, contaminant concentrations in suspended sediment samples were generally many times higher than in water and moderately higher than in depositional sediments.

Based on stable isotope assessment, it appears that the most important food chain pathway for the uptake of dioxins and furans in the Athabasca River is the transfer from effluent to fine suspended particulates in the water, which are subsequently trapped by filter-feeding organisms like caddisfly larvae, which are in turn fed upon by fish

(Pastershank and Muir, 1995). Dioxins and furans are readily bioaccumulated by a number of aquatic organisms and are toxic at extremely low concentrations compared with other groups of organic compounds (Fletcher and McKay, 1993; NRCC, 1981).

Results

During the SREQMP (1990-1995), 11 suspended sediment samples were analyzed for a series of dioxin and furan congeners. Of the 17 congeners analyzed, five were detected, four of which were the higher chlorinated dioxins and furans. In the Follow-Up Study (2000-2010), nine suspended sediment samples were collected and analyzed for the same suite of dioxin and furan congeners (Appendix 9-1). Similar results were found, in that six of the 17 congeners were detected, five of which were the higher chlorinated dioxins and furans. The only difference between the two study periods was that 1,2,3,7,8-pentachlorodibenzofuran (P_5CDF) and 1,2,3,4,7,8-hexachlorodibenzofuran (H_6CDF) were detected only during the Follow-Up Study and 2,3,4,7,8- P_5CDF was detected only during the SREQMP (Table 9.9).

Table 9.9: Dioxin and furan concentrations in suspended sediment samples (SREQMP and Follow-Up Study).

	SREQMP (1990-1995)		**Follow-Up Study (2000-2010)**	
Parameter	**Number of values above detection limit/n**	**Range of values detected (pg/g)[1]**	**Number of values above detection limit/n**	**Range[1] of values detected (pg/g)**
Congeners				
1,2,3,4,6,7,8 H_7CDD	6/11	0.4 -1.4	8/9 (1 NDR)	0.39 – 1.44
OCDD	9/11 (4 NDR)	5.1 -13	9/9 (2 NDR)	3.1 – 11
2,3,7,8-TCDF	9/11	0.1 -1.4	1/9	0.1 (EMPC[2])
1,2,3,7,8-P_5CDF	0/11	-	1/9	0.12
2,3,4,7,8-P_5CDF	1/11	(0.5) NDR	0/9	-
1,2,3,4,7,8-H_6CDF	0/11	-	1/9	0.23
OCDF	1/11	0.3	2/9	0.27-0.47

[1] does not include Non Detectable Ratios (NDR) values, as these are approximate estimates of the total concentration

[2] EMPC = estimated maximum possible concentration

Higher Chlorinated Congeners (5-8 chlorine atoms)

Results

Of the congeners detected, six were higher chlorinated dioxins and furans (Table 9.9). In addition to the two P_5CDFs, octachlorodibenzofuran (OCDF) was detected once in the SREQMP and twice in the Follow-Up Study. 1,2,3,4,7,8- hexachlorodibenzofuran (H_6CDF) was only detected during the Follow-Up study. 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (H_7CDD) was detected six times in the SREQMP (1990 – 1995) and eight times during the Follow-Up Study (2000 – 2007); while OCDD was detected nine times in each study.

The presence of higher chlorinated dioxins and furans has been documented in several studies that have taken place in the Slave River Catchment, both upstream and downstream of the Slave River sampling locations. In Great Slave Lake, H_7CDD, OCDD, H_7CDF and OCDF were detected in core samples and OCDD was the predominant higher dioxin compound found in the surficial sediment samples collected around the mouth of the Slave River (Evans *et al.,* 1996).

During the NRBS (1991-1995), liquid effluent and sediment sludge from Weldwood, Alberta Newsprint, Millar Western and Slave Lake pulp mills, as well as sewage effluent from Whitecourt, Athabasca and Fort McMurray, were analyzed for dioxins and furans. OCDD was detected in all of the effluents, while the remaining higher chlorinated compounds were each detected in at least five of the seven effluents (Crosley, 1996c).

H_7CDD (7.1 to 9.7 pg/g) and OCDD (41 to 62 pg/g) were detected in suspended sediment samples collected downstream of the Weyerhaeuser pulp mill and in lower concentrations in samples upstream of the mill (Swanson *et al*., 1993). Similar results were found in suspended sediment samples collected upstream and downstream of the bleached kraft mill at Hinton. OCDD, H_7CDD, OCDF and H7CDF were detected in suspended sediment downstream of the Hinton/Weldwood combined effluent and at much lower concentrations in the upstream samples (Crosley, 1996a; Pastershank and Muir, 1995). Crosley (1996c) also found OCDD in suspended sediment samples collected all along the mainstem Athabasca River and its tributaries. OCDD, $H_7CDD$and OCDF were the most frequently detected congeners in bottom sediments samples collected from sites in the Peace, Athabasca, Wapiti and Smoky rivers (Crosley, 1996b; Brownlee *et al.,* 1997). OCDD in the bottom sediments showed a broad distribution pattern which suggested diffuse sources (Brownlee *et al*., 1997). H_7CDD, OCDD, H_7CDF and OCDF were found in surficial sediments from Lake Athabasca and OCDD and OCDF were the prominent higher chlorinated congeners found in cores from the lake (Bourbonniere *et al*., 1996).

The detection of higher chlorinated PCDDs and PCDFs in effluents from both pulp mills and sewage treatment plants, and in suspended sediments downstream of these sources, indicates that these are likely point sources of these compounds. However, these compounds have also been detected in samples collected from upstream sites, (although at lower levels), as well as both mainstem and tributary samples. These findings may indicate background atmospheric deposition of combustion related PCDD/F sources such as vehicle exhaust and other types of incineration (Swanson *et al*., 1993; Pastershank and Muir, 1995; Crosley, 1996b) or forest fires, which produce the higher chlorinated PCDD/Fs (Fielder, *et al.,* 1990; Kjeller *et al*., 1991; Hites, 1990). The detection of the higher chlorinated dioxins and furans may also be related to the increased chemical and environmental stability that occurs with increasing chlorine substitution (NRCC, 1981).

Recommendation

The detection of higher chlorinated PCDDs and PCDFs in suspended sediment samples collected from the Slave River could indicate atmospheric or point sources along the river, or both. It is recommended that Slave River suspended sediment samples continue to be analyzed for higher chlorinated PCDDs and PCDFs.

Tetra-Chlorinated Congeners

Results

2,3,7,8-tetrachlorodibenzofuran (TCDF) was the only tetra-chlorinated congener detected in suspended sediment samples collected from the Slave River throughout the entire period of record. During the SREQMP (1990-1995), 2,3,7,8-TCDF was measurable in nine out of 11 samples, at a range of 0.1 to 1.4 pg/g. During the Follow-Up Study (2000 – 2007), this compound was only detected once out of nine samples collected, at a concentration of 0.1 pg/g. The most toxic isomer, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), was not detected in Slave River suspended sediment over the entire period of record.

Evans *et al.* (1996) found similar results in the surficial sediment samples collected in Great Slave Lake around the mouth of the Slave River and in the core samples collected further offshore; specifically, that low levels of 2,3,7,8-TCDF were detected, and 2,3,7,8-TCDD was never detected.

Swanson *et al*. (1993) found that the primary PCDD/F congeners formed in softwood bleached kraft mills (BKM) using chlorine gas included 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,7,8-TCDD. In addition, from 1990-92, 2,3,7,8-TCDD and 2,3,7,8-TCDF were detected in the discharge effluent from the three Alberta kraft mills at concentrations ranging from 1.8 to 7.3 pg/L and 4.5 to 28.4 pg/L respectively (McCubbin and Folke, 1993). In 1992, 2,3,7,8-TCDD and 2,3,7,8-TCDF were also detected in the combined Hinton/Weldwood effluent, with concentrations of 11 pg/g and 40 pg/g respectively (Pastershank and Muir, 1995; Crosley, 1996a). The detection of tetrachloro-dioxin and -furan compounds in pulp mill and wastewater effluent indicates that point sources for these compounds exist in the study area (Carey *et al*., 1997).

Accordingly, tetra dioxins and furans were detected in suspended and depositional sediments downstream of the bleached kraft mills. In 1992, 2,3,7,8-TCDD remained measurable in the suspended (1.0 pg/g) and depositional sediment (0.3-2.6 pg/g) samples collected throughout the 200 km reach of the Athabasca River to Whitecourt, while the concentration of 2,3,7,8-TCDF in suspended sediments ranged from 0.3 pg/g at the reference site to 2.5 pg/g in the reach below the Weldwood pulp mill (Pastershank and Muir, 1995; Crosley, 1996a). In depositional sediments, the range of 2,3,7,8-TCDF concentrations was 0.4 to 2.2 pg/g in the reach downstream of Hinton. Both 2,3,7,8-TCDD and 2,3,7,8-TCDF were detected in suspended sediment samples collected downstream of the Weyerhaeuser pulp mill on the Wapiti/Smoky River (Swanson *et al*., 1993). These results suggested that bleached kraft mills represented the primary sources 2,3,7,8-TCDF and in suspended and depositional sediments downstream of the bleached kraft mills (Crosley, 1996b).

In January 1994, the Canadian Environmental Protection Act (CEPA), created a new regulation requiring “non-measurable” concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in final effluent discharged by BKMs (Pastershank and Muir, 1995). To achieve this goal, the pulp and paper industry reduced the use of molecular chlorine, substituting chlorine dioxide (Pastershank and Muir, 1995). During 1993, the Weldwood mill at Hinton went to complete substitution of molecular chlorine with chlorine dioxide (Pastershank and Muir, 1995). Analysis of mill effluents from 1989 to1994 indicated that the levels of contaminants discharged by seven mills in the NRBS study area were reduced throughout this time frame. These decreases were attributed to changes in the bleaching processes (Carey *et al.,* 1997).

A corresponding decline in pulp mill-related PCDD/PCDF concentrations in sediments downstream of pulp mills was also observed. 2,3,7,8-TCDF on sediment downstream from Hinton decreased from 7 pg/g in 1989 to 2 pg/g in 1992 to <1 pg/g in 1995 (Carey *et al.,* 1997). In the Wapiti River near the Smoky River confluence, concentrations of 2,3,7,8-TCDF in sediment decreased from 36 ng/g in 1989 to <2 pg/g in 1994 and 1995 (Carey *et al.,* 1997). The increased use of chlorine dioxide substitution resulted in a reduction of PCDD/F compounds detected in suspended sediment samples collected downstream of the Weyerhaeuser pulp mill on the Wapiti/Smoky River (Swanson *et al*., 1993). Decreases in PCDD/PCDF concentrations in fish in both Wapiti and Athabasca rivers downstream from BKM were also observed (Carey *et al.,* 1997).

A similar decrease was observed in the Slave River study. 2,3,7,8-TCDF was detected in nine of 11 samples in SREQMP (1990-1995) and only one of nine samples in Follow-Up Study (2000-2010). However, additional sampling should be conducted to confirm this apparent decrease.

Several of the NRBS studies concluded that 2,3,7,8-TCDF was a good sediment marker for bleached kraft effluent (Crosley, 1996c; Brownlee *et al*., 1997). The compound was detected in sediment from Hinton combined effluent (HCE) and concentrations in suspended sediment samples remained above control levels to Wood Buffalo National Park (Crosley, 1996c). Concentrations of 2,3,7,8-TCDF in bottom sediments were also highest downstream of Hinton, but eventually returned to upstream levels (Brownlee *et al*., 1997). Bottom sediment samples collected from both the Peace and Athabasca rivers in 1994 and 1995 found 2,3,7,8-TCDF as one of the most commonly detected congeners and results suggested that it was mainly from bleached kraft mill sources (Crosley, 1996b). The presence of 2,3,7,8-TCDF in sediment cores from Lake Athabasca were considered to have a bleached kraft mill (BKM) effluent origin; 2,3,7,8-TCDF was also detected in surficial sediment samples from the lake (Bourbonniere *et al*., 1996).

Although at lower levels, 2,3,7,8-TCDF was also detected in the suspended sediment samples collected from the Slave River at Fort Smith and in core and surficial sediment samples from Great Slave Lake, which could be an indication of downstream transport of these contaminants.

Recommendation

It is recommended that further sampling on the Slave River should continue to include 2,3,7,8-TCDF, as it appears to be a good sediment marker for bleached kraft effluent. In addition, further monitoring is necessary to confirm the apparent decrease in PCDD/PCDF concentrations.

Mono, Di and Tri Dioxin and Furan Congeners

Background

Another class of dioxin and furan congeners are the mono, di and tri-substituted PCDD/Fs, which are formed in softwood bleaching (Crosley, 1996c). Due to their low toxicity and limited tendency to bioaccumulate, they are not often included in sampling programs as was the case for the SREQMP and Follow-Up Study.

However the mono-, di- and tri-chlorodibenzofurans were the most prominent PCDD/Fs detected in the water effluent from the Weldwood bleached kraft mill at Hinton (Crosley, 1996c) and these compounds have been demonstrated to be persistent in sediments (Crosley, 1996a). They have also proved to be excellent markers of BKM effluent downstream of the Weldwood mill at Hinton because they were present in all abiotic samples collected downstream of the mill (Pastershank and Muir, 1995). Crosley (1996a) found the lower chlorinated dioxins and furans above detection in depositional sediments at most sites downstream of Hinton. Mono, di and tri- substituted dioxins and furans were detected more frequently than most highly substituted congeners in Peace and Athabasca depositional sediments (Crosley 1996b). Crosley (1996c) found a longitudinal trend in concentration of D_2CDF in both suspended and depositional sediment samples along the Athabasca River, with levels remaining detectable in water for up to 250 km downstream from Hinton, making it an excellent tracer of BKM effluent.

Recommendation

The detection of these compounds in the cores and surficial sediments collected in Great Slave Lake indicates that they are transported long distances in particle and dissolved phases (Evans *et al.,* 1996). For these reasons, it is recommended that future monitoring include these parameters. Further, it would be beneficial to access updated information with respect to the levels of dioxins and furans throughout the Basin to confirm these observed decreases.

Total Toxicity Equivalents

Background

As dioxins and furans each display a different level of toxicity, International Toxicity Equivalent factors (I-TEFs) have been developed for 17 of the most toxic congeners (Crosley, 1996a). The most toxic isomer, 2,3,7,8-TCDD, has been assigned an I-TEF of 1 (Safe and Phil, 1990). I-TEF values have been assigned to the remaining 16 PCDD/F congeners, based on their relative toxicity compared to 2,3,7,8-TCDD. For example, the I-TEF for 2,3,7,8-TCDF is 0.1, since this compound is 10 times less toxic than

2,3,7,8-TCDD. I-TEF values allow the total toxicity level of a sample to be expressed as a single Toxic Equivalent (TEQ) value.

TEQs are calculated by multiplying the measured concentration of a congener by the 2,3,7,8-TCDD toxic equivalency factor (TEF) for that congener. Since the congeners are thought to have a similar mode of toxicity, the TEQs for each congener are then added to calculate a total TEQ for that sample. The I-TEFs values for the 17 congeners have changed over the years (NATO, World Health Organization (WHO) 1998, Van den Berg *et al*; WHO 2005, Van den Berg *et al*; Appendix 9-5). The WHO 1998 TEFs were used to determine the TEQs for the samples collected in this study, as these TEFs were used to determine the Sediment Quality Guidelines (CCME, 1999).

Due to the limited number of values above the detection limit and the large variation in detection limits, the methodology cited in the CESI Water Quality Indicator Technical document was followed (Government of Canada, 2008). Accordingly, only the results from congeners which were detected more than 50% of the time were included in the TEQ calculation. This method has been used to prevent the presence of high detection limits from unduly influencing the TEQ value.

Results

During both the SREQMP and the Follow-Up Study, only three of the six detected dioxin and furan congeners were above detection at least 50% of the time, namely 2,3,7,8-TCDF (detected in 10 of 20 samples), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (H_7CDD; 14 of 20), OCDD (18 of 20). TEQs for each suspended sample were calculated based on these three congeners and are included in Table 9.10. When calculating TEQs for these three congeners, any results that were reported as less than detect have been replaced by the whole detection limit. Results reported as NDR have been treated as the reported value.

All TEQ values for suspended sediment samples from this study were well below the Interim Sediment Quality Guideline of 0.85 pg TEQ/g and the PEL of 21.5 pg TEQ/g (CCME, 2002; Table 9.10).

Table 9.10: Dioxin and furan TEQ values for suspended sediment samples collected from the Slave River at Fort Smith (SREQMP and Follow-Up Study).

Sample Date	TEQ [1,2]
6/11/1992	0.0409
9/17/1992	0.0515
1/13/1993	0.0264
6/10/1993	0.0285
8/23/1993	0.0182
1/13/1994	0.0110
3/8/1994	0.0142
6/15/1994	0.0423
9/22/1994	0.0295
1/10/1995	0.0296
3/7/1995	0.1474
9/11/2000	0.0471
2/20/2001	0.0438
6/19/2001	0.0278
6/9/2003	0.0114
6/14/2006	0.0165
8/29/2006	0.0170
3/6/2007	0.0142
5/29/2007	0.0146
9/28/2010	0.0255

[1] calculated based on three congeners where more than 50% of the results were above the detection limit (Government of Canada, 2008).

[2] NDR and less than detect values treated as reported value.

9.5 Summary – Suspended Sediment

Suspended sediment samples collected from the Slave River at Fort Smith have been tested for particle size, metals, chlorinated phenolics, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated benzenes and dioxins and furans.

Particle Size and TOC

The suspended sediment samples collected from the Slave River below Rapids of the Drowned were composed of sand, silt and clay particles, the proportions of which vary with the seasons. Sand was found to be highest in the winter, likely a result of the under ice frazil slush scouring the river bed and re-suspending bottom sediments. During the remaining open water seasons, the sand fraction was minimal and the majority of the particles were of the clay/silt size. Clay particles were highest during the open water season, particularly in the fall, and silt particles remained relatively constant over the year.

The total organic carbon (TOC) content of the Slave River suspended sediments was low, averaging only 1.23%. The organic carbon content in the Slave River is considered to be at the lower end of the natural range for rivers of the boreal forest region.

As metals and organic compounds adsorb strongly to finer suspended particulates, their concentrations should be highest when silt and clay are at a maximum. This was observed, as statistically significant correlations were noted between many metals and clay with r_s values ranging from 0.44 to 0.68. However, the most significant correlations were observed between metal concentrations and total organic carbon, with r_s values ranging from 0.7 to 0.86.

Metals

Statistically significant differences in metal concentrations between the suspended sediments samples collected during the SREQMP and the Follow-Up study (other than boron) were not observed. Therefore, the metal data from the two time frames were combined and assessed together.

For those metals with Canadian Draft Interim Freshwater Bottom Sediment Quality Guidelines, concentrations of lead and mercury were consistently below the threshold effect level (TEL). On occasion, arsenic, cadmium, chromium, copper and zinc exceeded the TEL, but all of these metals had concentrations that were below the probable effect level (PEL). As there are no national guidelines for nickel and manganese, the Ontario SQGs were used. Nickel exceeded the lowest effect level

(LEL) guideline in almost every sample but the severe effect level (SEL) guideline was not exceeded. Manganese exceeded the LEL on eight of 24 occasions and the SEL twice.

As the suspended sediment data can only be compared to bottom sediment guidelines (due to a lack of guidelines specifically for suspended sediments), definitive conclusions could not be made with respect to the potential for adverse effects on biota. Given the conservative nature of the guidelines and the infrequent exceedances of the upper effect levels, it is unlikely that the metal concentrations in the Slave River would have adverse impacts on aquatic life. However, it is recommended that monitoring metals in suspended sediment should continue to be able to compare to past results. Furthermore, the frequency of suspended sediment sampling should be augmented to be able to generate enough data to examine trends over time.

Chlorophenols

During the SREQMP (1990-1995), 20 chlorophenol compounds were detected in suspended sediment samples at very low levels. Within the Follow-Up Study (2000-2010), none of these compounds were detected; however, the very low detection limits obtained during the earlier study are not available today due to changes in laboratory reporting requirements. The only compounds detected in the Follow-Up Study were two compounds which had not been part of the earlier study: p-cresol and phenol. As more chlorinated phenolic compounds were detected in the suspended sediments than in the centrifugate water samples, it is recommended that monitoring of chlorophenols, including p-cresol and phenol, in suspended sediment should continue, with the lowest detection limits possible.

Organochlorine Pesticides

Organochlorine pesticides were below detection limits in all suspended sediment samples tested during the SREQMP and the Follow-Up Study. As the detection limits in both the SREQMP and the Follow-Up Study were sometimes higher than the sediment quality guidelines and upstream studies, comparisons could not always be made. It is recommended that lower detection limits be utilized in future monitoring. Given the agricultural activity in the upstream portion of the catchment, it is recommended that monitoring for organochlorine pesticides should continue. Lastly, it is recommended that additional pesticides, focussing on in-use compounds, also be evaluated for inclusion in future monitoring.

PAHs

During the SREQMP, 13 suspended sediment samples were analyzed for up to 17 PAH parent compounds. All of the substances tested for, with the exception of acenaphthylene, were present in at least one sample, with concentrations varying between <3 to 580 ng/g. During the Follow-Up Study, eight suspended sediment samples were analyzed for up to 22 PAH parent compounds, with concentrations ranging between 3 and 180 ng/g. Of all the substances tested for, chrysene, naphthalene and phenanthrene were detected at the highest concentrations.

During the Follow-Up Study (2000-2010), the PAH values in the suspended sediment were lower than in the SREQMP (1990-1995), and fewer values exceeded the TEL and LEL guidelines. All results were well below the levels at which adverse effects are predicted to occur frequently (CCME/PEL), and those levels at which remediation is required (Ont. MOE/SEL). Concentrations of total PAHs, estimated by summing the concentrations of 16 individual parent PAHs, were much lower than the Ontario sediment quality guideline for the protection of aquatic life.

In 2007, alkylated PAHs were added to the suspended sediment monitoring program and detected at low levels in the two samples collected (<4 to 250 ng/g). Although there are currently no Canadian guidelines for alkylated PAHs, the results were well below the United States Environmental Protection Agency (USEPA) benchmark established for the protection of bottom dwelling aquatic animals.

Given the increased oil sands developments occurring upstream, continued monitoring for parent and alkylated PAHs, as well as naphthenic acids, is recommended, with the lowest detection limits available.

PCBs

During the SREQMP (1990-1995), 14 suspended sediment samples were analyzed for total PCBs and all values were below detection limits (2-300 ng/g). During the Follow-Up Study (2000-2010), suspended sediment samples were analyzed for total PCBs and/or a suite of nine Aroclors. Concentrations were also below the detection limit (2-50 ng/g and 2-10 ng/g, respectively). In May, 2007, for the first time, the suspended sediment sample was analyzed for a wide list of individual PCB congeners with very low detection limits. Few were detected (0.011-0.03 ng/g), and all were well below existing guidelines.

Chlorinated Benzenes

During the SREQMP (1990-1995), and in February 2001, suspended sediment samples were analyzed for up to 11 chlorinated benzenes. Levels for all samples were below the detection limits (1-10 ng/g). There are no sediment quality guidelines against which to evaluate the data.

Dioxins and Furans

Over the period of record, 20 suspended sediment samples were analyzed for a suite of 17 dioxins and furans. The most toxic isomer, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), was not detected in any of the suspended sediment samples collected from the Slave River . All TEQ values for suspended sediment samples from this study met the Interim Sediment Quality Guideline of 0.85 pg TEQ/g and the PEL of 21.5 pg TEQ/g.

Of the seven congeners that were detected, only three were above detection more than two times; 2,3,7,8-TCDF (detected in 10 of 20 samples), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (H_7CDD; 14/20), and OCDD (18/20).

Several of the NRBS studies concluded that 2,3,7,8-TCDF was a good sediment marker for effluent discharged from bleached kraft pulp mills. This congener was detected in nine of 11 samples in SREQMP and only one in nine samples collected during the Follow-Up Study. This apparent decrease may be due to changes made by the pulp mills to the bleaching process. It is recommended that further sampling be conducted to confirm these results.

Of the six higher congeners that were detected in this study, only H_7CDD and OCDD were detected more than twice. Although these compounds have been detected in pulp mill and wastewater effluent, their presence is often indicative of combustion sources. Further monitoring should also include these congeners.

Although mono, di and tri -substituted PCDD/Fs are not as toxic as other congeners, they are considered good markers of pulp mill effluent, so consideration should be given to including these congeners in future monitoring, as well.

10.0 RECOMMENDATIONS

10.1 Water Quality

- Increase the frequency of water quality sampling in the Slave River at Fort Smith and the Mouth.
- Increase the suite of total metals analyzed at Fort Smith to include antimony, mercury and vanadium, at minimum.
- Initiate the analysis of dissolved metals at Fort Smith and the Mouth.
- Strive to obtain lower detection limits for total cadmium, PCBs, pesticides and chlorinated phenolics analyses.
- Reinstate the analysis of total and methyl mercury at Fort Smith.
- Conduct long-term trend analyses for dissolved metals and the remaining total metals, once an adequate amount of data is available.

10.2 Suspended Sediment

- Increase the frequency of suspended sediment sampling at Fort Smith to better characterize the annual variability in the suspended sediments and allow for statistical trend assessments of compounds of concern.
- Strive to obtain lower detection limits for pesticides analysis.
- Reintroduce toxicological tests on Slave River suspended sediment. These tests measure the toxicity of the sediment samples to lower trophic levels of the aquatic environment and are considered standard protocols for toxicity testing by Environment Canada.
- Consider archiving suspended sediment samples. Archival of these samples will allow for the re-analysis should new contaminants emerge or if lower detection limits can be obtained.

10.3 General Recommendations

- Continue to work with the Slave River Partnership to ensure local and traditional knowledge is incorporated into all aspects of the program including program objectives, identification of community concerns, field sampling and presentation of results.

- Conduct under-ice transect sampling to assess the vertical and horizontal variability of the current sampling site during the winter. Confirm that the current sampling site at Fort Smith is representative of mainstem winter river conditions.

- Support the development of site-specific water quality objectives.

- Monitor for pesticides that are currently being used in the Slave River Catchment (including pyrethroid insecticides) and ensure that these are included along with legacy pesticides in future monitoring.

- Initiate discussions with community members regarding the collection of samples following large rain events. It is during these times that levels of TSS and therefore metals concentrations are high.

- Work with the jurisdictions of the Mackenzie River Basin to develop a consistent approach to assessing water quality and quantity conditions so that regional comparisons can be made. This will allow for a common understanding of potential changes to water quality throughout the watershed, and specifically in the Slave River.

10.4 Future Research Needs

- Studies to understand the causes and impacts of the long-term trends identified in the water quality of the Slave River.

- Compare Slave River suspended sediment data to bottom sediment data from the Slave River Delta.

- Studies to determine if the increasing trend in winter water flows and the decreasing trend in summer and fall water flows are having an impact on the water quality and biological receptors of the Slave River.

- Studies to determine if the trends in flow are the result of upstream regulation and/or climate change.

- Identify and sample natural bitumen seeps along the banks of the Slave River. Analyse samples for PAHs (parent and alkylated), metals and naphthenic acids. This work may help to differentiate natural versus anthropogenic sources.

- Encourage studies which help to determine the sources of any contaminants found in the Slave River.

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Tembec – Chetwynd: http://tembec.com
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http://www.ec.gc.ca/pdb/websol/querysite/facility_substance_summary_e.cfm?opt_npri_id=0000000001&opt_report_year=2010

Base Map Sources:

Figure 1.1:
Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Figure 3.1:
Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:2 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 3.2:
Place Names: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:2 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 3.3:
Place Names: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Canadian Place Names.

Hydrology (Lakes and Rivers): Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Network (Cartographic).

Hydrology (Wetlands): Government of Canada, Natural Resources Canada, Centre for Topographic Information. National Topographic Data Base (NTDB) 1:250,000 scale.

Figure 3.4:
Hydrology: Government of Canada, Natural Resources Canada, Centre for Topographic Information. National Topographic Data Base (NTDB) 1:50,000 scale.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 3.5:
Industrial Activity: Environment Canada.

Oil Sands Area: Digitized from map from Wikipedia created by Norman Einstein, May 10, 2006.

Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Place Names: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 3.7:
Industrial Activity: Environment Canada.

Oil Sands Area: Digitized from map from Wikipedia created by Norman Einstein, May 10, 2006.

Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Place Names: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 4.1:
Industrial Activity: Environment Canada.

Oil Sands Area: Digitized from map from Wikipedia created by Norman Einstein, May 10, 2006.
Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Place Names: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

Figure 5.1:
Monitoring Sites: Water Resources Division.

Hydrology: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. 1:7.5 million scale National Atlas digital base map data for Canada.

Provincial/Territorial Boundaries: Government of Canada, Natural Resources Canada, Legal Surveys Division. GeoBase, Canadian Geopolitical Boundaries.

Watershed Boundaries: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Hydrology - Drainage Areas.

Wood Buffalo National Park: Government of Canada, Natural Resources Canada, Earth Sciences Sector, Mapping Information Branch, Data Dissemination Division, The Atlas of Canada. Atlas of Canada 1,000,000 National Frameworks Data, Protected Areas.

12.0 APPENDICES

Appendix 5-1: Participating Laboratory Information

Laboratory	Contact Person
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National Laboratory for Environmental Testing Environment Canada Canada Centre for Inland Waters 867 Lakeshore Road, P.O. Box 5050 Burlington , ON L7R 4A6 Tel.: (905) 336-4563 Fax: (905) 336-6404	Pat Falletta A/Manager Tel.: (905) 336-4563 Email: Pat.Falletta@ec.gc.ca

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	**Surface Water**		**Centrifugate Water**	**Suspended Sediment**
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
Physicals				
pH - Field	x	x		
pH - Lab	x	x	x	
Specific Conductance - Field	x	x		
Specific Conductance - Lab	x	x		
Temperature Water - Field	x	x	x	
Total Suspended Solids	x	x	x	
Turbidity	x	x	x	
Total Dissolved Solids	x	x	x	
Total Dissolved Solids (Calcd.)	x			
Oxygen Dissolved	x	x		
Alkalinity Total $CaCO_3$	x	x	x	
Colour Apparent	x	x	x	
Colour True	x	x	x	
Stability Index (Calcd.)	x			
% Moisture				x
% Clay				x
% Sand				x
% Silt				x
Major Ions				
Bicarbonate (Calcd.)	x			
Calcium Total	x	x		x
Chloride Dissolved	x			
Chloride Total		x	x	
Fluoride Dissolved	x	x	x	
Phosphorous Total	x	x	x	x
Potassium Dissolved/Filtered	x	x	x	
Potassium Extractable/Unfiltered	x			
Potassium Total	x	x	x	x
SiO_2/Reactive Silica	x			
Sodium Dissolved/Filtered	x			
Sodium Extractable/Unfiltered	x			
Sodium Percentage (Calcd.)	x			
Sodium Total	x	x	x	x
Sulfate Dissolved	x			
Sulfate Total		x	x	
Sulphide		x	x	
Calcium Dissolved/Filtered	x	x	x	
Calcium Extractable/Unfiltered	x			
Calcium Total	x	x	x	
Hardness Total (Calcd.) $CaCO_3$	x	x	x	
Magnesium Dissolved/Filtered	x			
Magnesium Extractable/Unfiltered	x			

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
Magnesium Total	x	x	x	x
Nutrients				
Ammonia Dissolved	x			
Ammonia Total		x	x	
BOD		x		
BOD_5		x		
COD		x		
Dissolved Inorganic Carbon	x			
Dissolved Organic Carbon	x	x	x	
Nitrate - as N		x	x	
Nitrite - as N		x	x	
Nitrate & Nitrite Filtered	x	x	x	
Nitrogen Dissolved	x			
Nitrogen Dissolved Nitrite	x			
Nitrogen Particulate	x			
Nitrogen Total	x			
Nitrogen Total Dissolved	x			
Nitrogen Total Kjeldahl	x	x		
Ortho-Phosphate as P		x	x	
Phosphate Dissolved Inorganic	x			
Phosphate Dissolved Ortho	x	x		
Phosphate Total Inorganic	x			
Phosphorous Dissolved	x	x		
Phosphorous Particulate (Calcd.)	x			
Phosphorous Total	x	x	x	
Particulate Organic Carbon	x			
Total Inorganic Carbon	x			x
Total Organic Carbon	x	x		x
Metals				
Aluminum Dissolved	x			
Aluminum Extractable	x			
Aluminum Total	x	x	x	x
Antimony Dissolved	x			
Antimony Total	x	x	x	x
Arsenic Dissolved	x			
Arsenic Total	x	x	x	x
Barium Dissolved	x			
Barium Extractable	x			
Barium Total	x	x	x	x
Beryllium Dissolved	x			
Beryllium Extractable	x			
Beryllium Total	x	x	x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
Bismuth Dissolved	x			
Bismuth Total	x	x	x	x
Boron Dissolved	x			
Boron Extractable	x			
Boron Total	x	x	x	x
Cadmium Dissolved	x			
Cadmium Extractable	x			
Cadmium Total	x	x	x	x
Cerium Dissolved	x			
Cerium Total	x			
Cesium Dissolved	x			
Cesium Total	x			
Chromium Dissolved	x			
Chromium Extractable	x			
Chromium Total	x	x	x	x
Cobalt Dissolved	x			
Cobalt Extractable	x			
Cobalt Total	x	x	x	x
Copper Dissolved	x			
Copper Extractable	x			
Copper Total	x	x	x	x
Gallium Total	x			
Gallium, Dissolved	x			
Iron Dissolved	x			
Iron Extractable	x			
Iron Total	x	x	x	x
Lanthanum Total	x			
Lanthanum, Dissolved	x			
Lead Dissolved	x			
Lead Extractable	x			
Lead Total	x	x	x	x
Lithium Dissolved	x			
Lithium Extractable	x			
Lithium Total	x			
Manganese Dissolved	x			
Manganese Extractable	x			
Manganese Total	x	x	x	x
Mercury Total	x	x	x	x
Molybdenum Dissolved	x			
Molybdenum Extractable	x			
Molybdenum Total	x	x	x	x
Nickel Dissolved	x			
Nickel Extractable	x			
Nickel Total	x	x	x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
Niobium Dissolved	x			
Niobium Total	x			
Platinum Dissolved	x			
Platinum Total	x			
Rubidium Dissolved	x			
Rubidium Total	x	x	x	
Selenium Dissolved	x			
Selenium Total	x	x	x	x
Silver Dissolved	x			
Silver Total	x	x	x	x
Strontium Dissolved	x			
Strontium Extractable	x			
Strontium Total	x	x	x	x
Thallium Dissolved	x			
Thallium Total	x	x	x	x
Tin Dissolved	x			
Tin Total	x	x	x	x
Titanium Total		x	x	x
Tungsten Dissolved	x			
Tungsten Total	x			
Uranium Dissolved	x			
Uranium Total	x	x	x	x
Vanadium Dissolved	x			
Vanadium Extractable	x			
Vanadium Total	x	x	x	x
Yttrium Dissolved	x			
Yttrium Total	x			
Zinc Dissolved	x			
Zinc Extractable	x			
Zinc Total	x	x	x	x
Bacteriological				
Coliforms, Fecal	x	x	x	
Coliforms, Total	x	x	x	
E-COLI	x			
Polycyclic Aromatic Hydrocarbons				
1,2,3,4-Tetrahydronaphthalene	x			
1-Methylnaphthalene	x			
2-Chloronaphthalene	x			
2-Methylnaphthalene	x		x	x
Acenaphthene	x		x	x
Acenaphthylene	x		x	x
Anthracene	x		x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
Benzo(A)Anthracene	x		x	x
Benzo(A)Anthracene/Chrysene			x	x
Benzo(A)Pyrene	x		x	x
Benzo(B or K)Fluoranthene			x	x
Benzo(B)Fluoranthene	x		x	x
Benzo(E)Pyrene	x			x
Benzo(G,H,I)Perylene	x		x	x
Benzo(K)Fluoranthene	x		x	x
Biphenyl			x	x
C2 sub'd B(a)A/chrysene			x	x
C2 sub'd B(b&k)F/B(a)P			x	x
C2 sub'd biphenyl			x	x
C2 sub'd dibenzothiophene			x	x
C2 sub'd fluorene			x	x
C2 sub'd naphthalene			x	x
C2 sub'd phenanthrene/anthracene			x	x
C3 sub'd dibenzothiophene			x	x
C3 sub'd naphthalene			x	x
C3 sub'd phenanthrene/anthracene			x	x
C4 sub'd dibenzothiophene			x	x
C4 sub'd naphthalene			x	x
C4 sub'd phenanthrene/anthracene			x	x
Chrysene	x		x	x
Dibenzo(A,H)Anthracene	x		x	x
Dibenzothiophene			x	x
Fluoranthene	x		x	x
Fluorene	x		x	x
Indene	x			
Indeno(1,2,3-C,D)Pyrene	x		x	x
Methyl Acenaphthene			x	x
Methyl B(A)A/Chrysene			x	x
Methyl B(B&K)F/B(A)P			x	x
Methyl Biphenyl			x	x
Methyl Dibenzothiophene			x	x
Methyl Fluoranthene/Pyrene			x	x
Methyl Fluorene			x	x
Methyl Phenanthrene/Anthracene			x	x
Methylnaphthalenes			x	x
Naphthalene	x		x	x
Perylene	x		x	x
Phenanthrene	x		x	x
Phenanthrene/Anthracene			x	x
Pyrene	x		x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
Chlorinated Benzenes				
Hexachlorobenzene	x		x	x
Hexachlorobutadiene	x			
Pentachlorobenzene	x		x	x
OC Pesticides				
Aldrin	x		x	x
Alpha-Benzenehexachloride or Alpha-1,2,3,4,5,6-Hexachlorocyclohexane	x		x	x
Alpha-Chlordane	x			
Alpha-Endosulfan or Endosulfan I	x		x	x
Beta-Endosulfan or Endosulfan II	x		x	x
Endosulfan I & II			x	
Beta-HCH	x		x	x
Carbathin	x			
Chlorpyrifos (Dursban)	x			
Cis-Chlordane			x	x
Cis-Nonachlor	x			
Nonachlor			x	x
Cyanazine	x			
Delta-Benzenehexachloride	x			
Diazinon	x			
Dieldrin	x		x	x
Endrin	x		x	x
Gamma-Benzenehexachloride or Gamma-1,2,3,4,5,6-Hexachloroclohexane (G-HCH or G-HCB or Lindane)	x		x	x
Gamma-Chlordane	x			
Heptachlor	x		x	x
Heptachlor Epoxide	x			
Imazethapyr	x			
Malathion	x			
Methoxychlor (P,P'-Methoxychlor)	x		x	x
Mirex	x		x	x
O,P'-DDD	x			
O,P'-DDE	x			x
O,P'-DDT - 1,1,1-Trichloro-2-(O-Chlorophenyl)-2-(P-Chlorophenyl)Ethane	x			x
Oxychlordane	x		x	
P,P'-Ddd (TDP or 2,2-Bis(P-Chlorophenyl)-1,1-Dichloroethane)	x		x	x
P,P'-DDE - 1,1-Dichloro-2,2-Bis(P-Chlorophenyl)Ethylene	x		x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
P,P'-DDT - 1,1,1-Trichloro-2,2-Bis(P-Chlorophenyl)Ethane	x		x	x
Pentachloroanisole	x			
Photomirex			x	x
Pyridaben	x			
Quintozine (Pcnb)			x	x
Ronnel				x
Sum of PP DDT & OP DDT	x		x	
Sum of PP'DDD & OP'DDD	x		x	
Total Chlordanes			x	
Total Hexachlorocyclohexane - Total			x	
Toxaphene			x	x
Trans-Chlordane			x	x
Trans-Nonachlor	x			
OC Herbicides				
2,3,6 TBA	x			
2,4,5-T	x		x	x
2,4,5-TP			x	x
2,4-D	x		x	x
2,4-DB	x			
Atrazine	x			
Bromacil	x			
Bromoxynil	x		x	x
Clopyralid	x		x	x
Desethyl Atrazine	x			
Desisopropyl Atrazine	x			
Dicamba	x		x	x
Dichlorprop (2,4 DP)	x			
Diclofop-Methyl	x		x	x
Diuron	x			
Ethalfluralin	x			
Fenoprop (Silvex)	x		x	
Fenoxaprop-P-Ethyl	x			
Fluazifop-P-Butyl			x	x
Imazamethabenz-Methyl	x			
MCPA	x		x	x
MCPB	x			
MCPP (Mecoprop)	x		x	x
Picloram	x		x	x
Quinclorac (Quinolinecarboxylic Acid)	x			
Triallate	x		x	x
Triclopyr			x	x
Trifluralin	x		x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
OP Pesticides				
Dimethoate	x			
Disulfoton (Disyston)	x			
Ethion	x			
Guthion	x			
Phorate	x			
Terbufos	x			
Polycyclic Chlorinated Biphenyls				
% Moisture				x
All Aroclors				x
AROCLOR	x			
Aroclor 1016			x	x
Aroclor 1221			x	x
Aroclor 1232			x	x
Aroclor 1242	x		x	x
Aroclor 1248	x		x	x
Aroclor 1254	x		x	x
Aroclor 1260	x		x	x
Aroclor 1262			x	x
Aroclor 1268			x	x
PCB 1				x
PCB 100				x
PCB 102				x
PCB 103				x
PCB 104				x
PCB 105				x
PCB 106				x
PCB 108/86/125				x
PCB 11				x
PCB 110				x
PCB 111/117				x
PCB 112				x
PCB 113				x
PCB 114				x
PCB 115				x
PCB 116				x
PCB 118				x
PCB 12				x
PCB 120				x
PCB 122				x
PCB 123/107/109				x
PCB 124				x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
PCB 126				x
PCB 127				x
PCB 128/162				x
PCB 13				x
PCB 130				x
PCB 131/142/133				x
PCB 132				x
PCB 134				x
PCB 135				x
PCB 136				x
PCB 137				x
PCB 138				x
PCB 139/143				x
PCB 14				x
PCB 140				x
PCB 141				x
PCB 144				x
PCB 145				x
PCB 146				x
PCB 147/149				x
PCB 148				x
PCB 15				x
PCB 150				x
PCB 151				x
PCB 152				x
PCB 153/168				x
PCB 154				x
PCB 155				x
PCB 156				x
PCB 157				x
PCB 158/129				x
PCB 159				x
PCB 16				x
PCB 160/163				x
PCB 161				x
PCB 164				x
PCB 165				x
PCB 166				x
PCB 167				x
PCB 169				x
PCB 17				x
PCB 170				x
PCB 171				x
PCB 172				x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
PCB 173				x
PCB 174				x
PCB 175/182				x
PCB 176				x
PCB 177				x
PCB 178				x
PCB 179				x
PCB 18				x
PCB 180				x
PCB 181				x
PCB 183				x
PCB 184				x
PCB 185				x
PCB 186				x
PCB 187				x
PCB 188				x
PCB 189				x
PCB 19				x
PCB 190				x
PCB 191				x
PCB 192				x
PCB 193				x
PCB 194				x
PCB 195				x
PCB 197				x
PCB 198				x
PCB 199				x
PCB 2				x
PCB 200				x
PCB 201/204				x
PCB 202				x
PCB 203/196				x
PCB 205				x
PCB 206				x
PCB 207				x
PCB 208				x
PCB 209				x
PCB 21/20/33				x
PCB 22				x
PCB 23				x
PCB 24				x
PCB 25				x
PCB 26				x
PCB 27				x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
PCB 28				x
PCB 29				x
PCB 3				x
PCB 30				x
PCB 31				x
PCB 32				x
PCB 34				x
PCB 35				x
PCB 36				x
PCB 37				x
PCB 38				x
PCB 39				x
PCB 4/10				x
PCB 40/68				x
PCB 41				x
PCB 43/52				x
PCB 44				x
PCB 45				x
PCB 46				x
PCB 47				x
PCB 48/49				x
PCB 5				x
PCB 50				x
PCB 51				x
PCB 53				x
PCB 54				x
PCB 55				x
PCB 56				x
PCB 57				x
PCB 58/67				x
PCB 59/42				x
PCB 6				x
PCB 60				x
PCB 61				x
PCB 63/76				x
PCB 64				x
PCB 66				x
PCB 69				x
PCB 7				x
PCB 70				x
PCB 71				x
PCB 72				x
PCB 73				x
PCB 74				x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
PCB 75/65/62				x
PCB 77				x
PCB 78				x
PCB 79				x
PCB 8				x
PCB 80				x
PCB 81				x
PCB 82				x
PCB 83/119				x
PCB 84/89				x
PCB 85				x
PCB 87				x
PCB 88/121				x
PCB 9				x
PCB 90/101				x
PCB 91				x
PCB 92				x
PCB 93				x
PCB 94				x
PCB 95				x
PCB 96				x
PCB 97				x
PCB 98				x
PCB 99				x
PCB-TOTAL			x	x
SUM OF MEASURED AROCLORS			x	
Total HeptaCB				x
Total HexaCB				x
Total Mono-TriCB				x
Total Nona/DecaCB				x
Total OctaCB				x
Total PCB			x	x
Total PentaCB				x
Total TetraCB				x
Cholorophenols				
1,1,3-Trichlorodimethyl sulfone			x	x
1,1-Dichlorodimethyl sulfone			x	x
1,2,3 - Trichloro-4,5,6-trimethoxybenzene			x	
2,3,4,5-Tetrachlorophenol			x	x
2,3,4,6-Tetrachlorophenol			x	x
2,3,4-Trichlorophenol			x	x
2,3,5,6-Tetrachlorophenol			x	x
2,3,5-Trichlorophenol			x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	**Surface Water**		**Centrifugate Water**	**Suspended Sediment**
Station	**Fitzgerald**	**Fort Smith**	**Fort Smith**	**Fort Smith**
Chemical Class / Analyte				
2,3,6-Trichlorophenol			x	x
2,3-Dichlorophenol			x	x
2,4 & 2,5-Dichlorophenol			x	x
2,4,5-Trichlorophenol			x	x
2,4,6-Trichlorophenol			x	x
2,4-Dichlorophenol			x	x
2,4-Dimethylphenol			x	x
2,4-Dinitrophenol			x	x
2,6-Dichlorophenol			x	x
2,6-Dichlorosyringaldehyde			x	x
2-Chlorophenol			x	x
2-Chlorosyringaldehyde			x	x
2-Nitrophenol			x	x
3,4,5-Trichlorocatechol			x	x
3,4,5-Trichloroguaiacol			x	x
3,4,5-Trichlorophenol			x	x
3,4,5-Trichloroveratrole			x	x
3,4,6-Trichlorocatechol			x	x
3,4,6-Trichloroguaiacol			x	x
3,4-Dichlorocatechol			x	x
3,4-Dichloroguaiacol			x	x
3,4-Dichlorophenol			x	x
3,5-Dichlorocatechol			x	x
3,5-Dichlorophenol			x	x
3,6-Dichlorocatechol			x	x
3-Chlorophenol			x	x
4,5,6-Trichloroguaiacol			x	x
4,5,6-Trichlorosyringol			x	x
4,5-Dichlorocatechol			x	x
4,5-Dichloroguaiacol			x	x
4,5-Dichloroveratrole			x	x
4,6-Dichloroguaiacol			x	x
4,6-Dinitro-2-methylphenol			x	x
4-Chloro-3-methylphenol			x	x
4-Chlorocatechol			x	x
4-Chloroguaiacol			x	x
4-Chlorophenol			x	x
4-Nitrophenol			x	x
5,6-Dichlorovanillin			x	x
5-Chloroguaiacol			x	x
5-Chlorovanillin			x	x
6-Chloroguaiacol			x	x
6-Chlorovanillin			x	x
EOCL			x	x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
m-Cresol			x	x
NITROBENZENE-d5			x	
o-Cresol			x	x
p-Cresol			x	x
Pentachlorophenol			x	x
Phenol			x	x
Tetrachlorocatechol			x	x
Tetrachloroguaiacol			x	x
Tetrachloroveratrole			x	x
Trichloromethoxybenzene			x	x
Dioxins and furans				
% Moisture				x
1234678 HpCDD				x
1234678 HpCDF				x
123478 HxCDD				x
123478 HxCDF				x
1234789 HpCDF				x
123678 HxCDD				x
123678 HxCDF				x
12378 PeCDD				x
12378 PeCDF				x
123789 HxCDD				x
123789 HxCDF				x
234678 HxCDF				x
23478 PeCDF				x
2378 TeCDD				x
2378 TeCDF				x
OCDD				x
OCDF				x
Total Homologues				x
Total HpCDD				x
Total HpCDF				x
Total HxCDD				x
Total HxCDF				x
Total PCDDs				x
Total PCDFs				x
Total PeCDD				x
Total PeCDF				x
Total TCDD				x
Total TCDF				x
Total TEQ (ND=0) (NATO Calc)				x
Total TEQ (ND=0.5DL) (NATO Calc)				x
Total TEQ (ND=DL) (NATO Calc)				x

Appendix 5-2: Summary of parameters sampled over the periods of record at Slave River at Fitzgerald and Fort Smith

Media Type	Surface Water		Centrifugate Water	Suspended Sediment
Station	Fitzgerald	Fort Smith	Fort Smith	Fort Smith
Chemical Class / Analyte				
Total TEQ (ND=DL) (NATO Calc)				x

Appendix 5-3: Methods and changes in methods at ALS Laboratory Group (formerly Envirotest Inc.) during the water and suspended monitoring at the Slave River, 1990 and 2007.

	Instrumentation				Analytical Methodology					Data Calculations			
Parameters	**Sample Matrix**	**Original**	**Changed to**	**Year of Change**	**Sensitivity**	**Original**	**Sample Matrix**	**Changed to**	**Year of Change**	**Sensitivity**	**Original**	**Changed to**	**Year of Change**
Chlorophenols	Water and sediment	GC/MS (HP5890/5971)	GC/MS (Agilent 6890/5973)	Sept. 1999	Increased 3-5x			No Change***				No Change***	
EPA PAHs	Water and sediment	GC/MS (HP5890/5971)	GC/MS (Agilent 6890/5973)	Feb-00	Increased 3-5x			No Change***				No Change***	
Chlorinated and Non-Chlorinated Phenols	Water and sediment	GC/MS (HP5890/5971)	GC/MS (Agilent 6890/5973)	Sept. 1999	Increased 3-5x			No Change***				No Change***	
Herbicide Screen	NA	****	****	****	****	****		****	****	****	****	****	****
OC Screen	NA	*****	*****	*****	*****	*****		*****	*****	*****	*****	*****	*****
ICPMS Metals - Prep	Sediment	Microwave	Hot-Block	2005	Comparable	EPA3051	Sediment	EPA3050	2005	Comparable			
ICPMS Metals - Analysis		ICPOES + AAS (Hydride and Cold-Vapour)	ICPMS	~1996	Comparable LORs from a single instrument	EPA6010, EPA7062, EPA7471, EPA7742	Water and sediment	EPA6020	~1996	Comparable LORs from a single instrument	Instrument Software	Excel Macro	1998
Dioxins & Furans	Water and sediment	Kratos Concept	Thermo DFS	2007	Increased 5x	EPA 1613		No Change			EPA 1613	*	
Total PCBS	Water and sediment	GC/ECD (HP5890)	GC/microECD (Agilent 6890)	Sept. 2003	Increased 10x			No Change***				No Change***	
Congener PCBs	Water and sediment	Kratos Concept	Thermo DFS	2007	Increased 5x	EPA 1668		No Change			EPA 1668	**	

*TEQ Calculations were based on the NATO TEF values until about 2006, when the were switched to WHO TEFs.
When the client has requested reports using NATO TEFs, we have complied and re-issued the reports based on NATO calculations

**We increased the list of analytes form 54 to 209 in 2003.

***Changes in detection limit were based on available sample size and changes to the concentration of the sample extract, not to changes in methodology or instrumentation.

****No major changes were made with the methods or instruments that would impact the DL's.
Any D.L. variance would most likely have been caused by limited sample size provided. We require 2 L of sample to reach the 0.002-0.9.

*****No major changes were made with the methods or instruments that would impact the DL's.
The D.L. for the OC's should have remained fairly consistent as that is our regular DL.
Any D.L. variance would most likely have been caused by limited sample size provided.

Appendix 5-4: Data Compilation and Handling

Data Compilation

The compiled data was entered into a relational database in MS Access format. INAC provided hard copies of a number of reports that contained candidate data sets, along with electronic versions of the underlying data.

1) Slave River Environmental Quality Monitoring Program (SREQMP) and Follow-Up Study

Data from the Slave River at Fort Smith (mid-river) site consisted of two data sets that provided information on environmental quality conditions for the Slave River at Fort Smith. The historical data from SREQMP (1990-1995) had been previously compiled into MS Excel files and these were brought into the MS Access database. The follow-up study (2000-2007) data were received from ALS and Taiga in electronic format. The original field sheets and analytical reports from the labs were also available. Data were initially verified and formatted in MS Excel (to facilitate any unit conversions, or arrangement of data into columns that match database fields) and then transposed into separate worksheets for each chemical class (i.e., metals, PAHs, etc.) and for each media type. Subsequently, final incorporation into the project database was completed. The list of parameters is presented in Appendix 5-1.

2) Slave River at Fort Smith (shore) Monitoring Program

Data from the Fort Smith (shore) site sampled by INAC were received in an MS Excel format from the Fort Smith Sub-District office. The files were processed and an initial verification of the data was performed as described above. The original field sheets and analytical reports from the labs were all also available to support verification. Subsequently, these data were translated into MS Access database format. The list of parameters is presented in Appendix 5-1.

3) Slave River at Fitzgerald Monitoring Program

Data from the Environment Canada monitoring program for the Slave River at Fitzgerald consisted of the results from grab water samples collected at the site since 1960. These data were compiled from a database maintained by Environment Canada (ACBIS, 2008). The list of parameters is presented in Appendix 5-1. Data for this site were provided by Environment Canada in two formats, the national database and a database that was maintained in the Yellowknife Environment Canada office. Some analytical reports from the laboratories were available at the Yellowknife office and these were photocopied for future reference. These external databases were translated into MS Access using the verification and formatting procedures as described above. Data from the two external databases were crosschecked and any discrepancies were verified against the hard copies when possible. Otherwise, validation of the data was requested from the Environment Canada office in Saskatchewan.

Data Handling

The surface water quality data, centrifugate water quality data, and suspended sediment quality data used in this study were generated by various governments and contract laboratories. These data were initially compiled in spreadsheets in MS Excel format by INAC staff. Subsequently, these data were translated into a relational database in MS Access format by MacDonald Environmental Sciences Limited (MESL).

The database structure made it possible to retrieve data in several ways, including by media type (i.e., suspended sediment, surface water), by sampling station (i.e., Slave River at Fort Smith or Fitzgerald), and by date, to name a few. As such, the dataset facilitated a variety of data analyses.

1) Censored Data (Values reported as "less than the detection limit")

Trace contaminants in water, including metals and organics, often are measured at sufficiently low concentrations to be reported only as values below the instrument detection limit. Interpretation of these "less thans" is complicated when multiple detection limits occur. When calculating basic statistics (mean, median, max, min), "less than" values were treated as results equal to the detection limit.

2) Replicates

In this project database, duplicate and triplicate samples were averaged to support subsequent data analysis. The means of the duplicates and/or triplicates were entered in the project database. In cases where values were below detection, to present a worst case scenario to identify parameters that could be of concern for humans or aquatic life, the data was handled using the following rules:

i) When the triplicate values were below detection, the mean was reported as less than detection. For example, the triplicate values result in <1, <1 and <1 ug/L, the mean is <1 ug/L. The value would be counted as a value "less than detection" but for the basic stats the value would have been entered as 1 ug/L.

ii) When two replicates were above detection (measurable results) and one value was at detection, the following was undertaken, for example: total barium values for a triplicate collected on March 11, 1991 are 0.121, 0.130 and <0.080 ug/L, the mean would be reported as 0.110 ug/L ((0.121+0.130+0.080)/3).

iii) When two replicates were at detection, the mean was reported as being at detection. For example, the extractable aluminium values (Slave/Fitz) on April 18, 1994 were 60, <50 and <50 ug/L, the mean was reported as <50 ug/L for a particular compound. The value would be counted as a value "less than detection" but for the basic stats computations, the value would have been entered as 50 ug/L.

3) Duplicates and Triplicates for Organic Compounds

It should be noted that during the SREQMP (1990-1995), data were summarized to present a worst case scenario, to identify compounds that could be a concern for humans or aquatic life. Therefore, when there were triplicate values, the highest value was reported. For the follow-up study (2000-2007), a different approach was taken. Rather than report the highest value from a set of replicates from the SREQMP data, the average of the set of replicates was reported. As comparisons are being made between the SREQMP and the follow-up study, it is more conservative to represent the old data as an average value, to ensure that we are not overestimating the original data. Therefore, in this report when there are triplicate values, the average value is reported.

4) Non detectable ratios for Organic Compounds

Concentrations of dioxins, furans and chlorinated phenolics obtained from chromatographs were sometimes reported as Anon detectable ratios@ (NDR). NDRs are conservative estimates of the total concentration in a sample and were included in the A# of samples@ and A# of detected values@ columns. However since they are only approximate concentrations, they were not included in the range of values (minimum and maximum) presented in the summary tables.

Replicates for which NDR values were reported were handled as follows:

i) in the cases where a value (real or NDR) and a detection limit were reported, the value was retained, since NDR values are approximate concentrations;

ii) when a real value and an NDR value were reported, the real value was used as the maximum value since the NDR value, although a valid value, is not totally reliable and cannot be used for statistical analyses; and

iii) in the case where only NDR values appeared, the highest value was kept, and labelled as NDR. The comment column of the summary tables shows that a NDR value was reported for a particular compound.

The number of NDR values was recorded in the comment column of the summary tables, thus the following situation may arise: if the maximum value was an NDR value, it will not appear in the maximum column of the summary table (e.g. octachlorodibenzodioxin (OCDD) in sediment). Instead, the reliable maximum value is presented and the number of NDRs is recorded in the comment column.

5) Spiked samples

During the SREQMP (1990-1995), the chlorophenol results from spiked samples were included in the results and discussion chapter. Only the results for the spike itself and its two breakdown compounds were removed from the database. However, for this follow up study, it was deemed prudent to exclude all results from spiked samples. This however impacts that number of hits (measurable values) for the chlorophenol analyses.

All of the data were carefully reviewed to determine their applicability to the assessment of the status and trends of water quality in the Slave River catchment. Where relevant, specific approaches take to deal with censored data for basic statistical computations and detailed statistical analyses are discussed in the results and discussion chapter.

Appendix 5-5: Analytical Methodologies

The information included in this appendix is a summary provided by the analytical chemists from the participating laboratories (Appendix 5-1). As many of the analytical methods were already documented in detail in the SREQMP report (1990-1995), the present report focuses on those variables that were not included in the SREQMP report or for which the methodologies have changed (Sanderson et al., 1998). Minor changes in methods to improve efficiency and reduce analysis time, which would not affect the results, have not been described. The quality assurance and quality control (QA/QC) procedures employed by each of the laboratories are also presented. However, all of the laboratories employed standard operating procedures throughout the sampling record.

A complete summary of the range of detection limits for each method and each laboratory is not available. The production of such a summary requires an investigation of all the raw data reports which are not available in all cases. However, ranges of detection limits are presented in the results section. These were reproduced from the databases and may not represent the full range of detection limits especially for those compounds that are often above detection. The following sections are organized by laboratory and include analytical methodologies for the selected parameters as well as details on the QA/QC protocols.

Taiga Environmental Laboratory Analytical Methods

For samples collected prior to 1990, Taiga followed the analytical methodologies outlined in American Public Health Association Standard Methods 18th edition (Greenburg et al. 1992), and Environment Canada's (1979a; 1979b) Analytical Methods Manual. The lab also maintained an intensive QA/QC program. Although detailed methodologies are not included in this report, the methodology codes are referenced in the raw data and are available upon request. Since 1993, Taiga has been accredited by the Canadian Association for Laboratory Accreditation (CALA) for the various types of tests listed in the scope of accreditation (Appendix 5-6). Taiga Environmental Laboratory is also involved in proficiency studies offered by National Laboratory for Environmental Testing twice a year.

Taiga Environmental Laboratory does not report to the client until the results fall within their standards. Results may be adjusted according to the performance of the QA/QC analyses or samples may be reanalyzed until the results fall within the acceptable performance standards of the laboratory. Taiga does not provide the detailed QA/QC results to their client, unless requested by the client.

Analytical methods from the SREQMP (1990-1995) have been summarized in Sanderson *et al*., (1998). The following section includes only those methods that were not in the SREQMP report, or for which the methodologies have changed.

Surface Water Samples

Major Ions

The methodologies and the ion chromatography method described below were both in use between January 2004 and October 2004 at Taiga. Starting in October 2004, ions were strictly analyzed by ion chromatography normally using ICS1500 (cations) or ICS 2000 (anions) equipment. An IC 3000 apparatus was used as back-up. An aliquot of a filtered or unfiltered sample is transported through the ion chromatograph in a liquid phase and forced through a stationary phase. The target ions are compared to a set of standard to determine the concentration (TEL055: SM4110:B). The results are for total concentrations.

For the ion chromatography method, very turbid samples are filtered to protect the equipment lines from clogging. In these cases, Taiga considers the data as “total ions” even if there is a filtration step prior to testing. Taiga also considers that dissolved results are comparable to total results as the vials used on all the IC equipments are capped with special filters caps and all the samples end up being filtered before testing. Hardness results are therefore also comparable. Results from both methods are considered to be comparable during the accreditation period.

Hardness (total $CaCO_3$): Hardness results are calculated from the calcium and magnesium results using the following formula: 2.497 x Ca (mg/L) + 4.117 x Mg (mg/L).

Starting in March 2005, results are given as total ions. Results were previously reported as dissolved values but are considered comparable (see comment in the above section for further details).

Nutrients

Nitrate/nitrite: Effective January 2004, Nitrate as N, Nitrite as N and Nitrate+Nitrite as N were measured by a Segmented Flow Analysis system manufactured by OI Analytical. Prior to that date, analyses were done using a Technicon, which is also segmented flow analysis instrumentation. The method is based on Standard Method 4500N:D (TEL014A) and is the same method that was used during the SREQMP (1990-1995).

Total and Dissolved Organic Carbon (TOC and DOC): Total and dissolved organic carbon were determined by high-temperature combustion coupled with a non-dispersive infrared detector (TEL 033, Method SM5310:B). The sample was acidified and sparged (purged using purified gas) to remove inorganic carbon. The sample was then injected into a combustion tube filled with platinum catalyst and heated to 680 ˚C. The organic carbon was oxidized to CO_2 and was then detected. DOC is filtered prior to analysis.

Metals

Taiga was first accredited for metals in water in 1993 and has maintained accreditation since that time. Quality control has been maintained by analyzing a method blank to monitor contamination; blank spikes and sample spikes to monitor recovery; control standard independent of calibration standards and reagent blanks to monitor calibration accuracy/stability, and a certified reference samples to monitor accuracy/recovery.

Between 1982 and 2007, INAC samples sent to Taiga were not filtered prior to analysis. As a result, all metal values reported refer to total metals, which include both dissolved and particulate metals.

Total Iron: Between 1993 and January 2004, total iron was determined by flame atomic absorption. Thereafter, the ICP-MS method was used. Taiga was accredited by CAEAL for iron by atomic absorption and are now accredited by CALA for iron by ICP-MS so the results should be comparable over the years (Glen Hudy 2009, Pers. Comm.)

Total Arsenic: Until 2001, total arsenic was measured by flameless atomic absorption with hydride generation, as described in the SREQMP report. From 2001 to January 2004, total arsenic was determined by Graphite Furnace atomic absorption. In this method, a light beam was directed through a sample. The atoms in the sample absorb light energy. As the amount of energy absorbed is proportional to the concentration of the element in the sample, the concentration can be estimated. Starting in January 2004, arsenic was determined using the ICP-MS method described in the “Other metals” section below. Taiga was accredited for all methods therefore the results between 1993 and 2007 should be comparable. Taiga is also confident that metals results between pre-1993 and 1993 – 2007 are also comparable (Glen Hudy 2009, Pers. Comm.).

Suspended Sediment Samples

Taiga laboratory determined the particle size, % moisture, total organic carbon, and total inorganic carbon in suspended sediment samples. These analyses were performed by different laboratories during the SREQMP.

Nutrients

Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC): Prior to January 2003, the methods used to measure TOC and TIC could not be easily identified. Between 2003 and 2007, the method used to measure total organic carbon and total inorganic carbon was based on Method TEL 033, 5310A- B, a combustion-infrared method (Sparks 1996). Carbon components are separated from each other with the aid of specific adsorption columns and determined in succession with a thermal conductivity detector. The samples are ignited for 2 hours at 500˚C to burn off organic carbon. The ignited soil is then analyzed for carbon to give inorganic carbon values. The organic carbon may then be calculated as the difference between total carbon and inorganic carbon. The detection limit for this method is 0.05% (i.e., 500 ppm).

The SREQMP methods and the Standard Methods utilize heat and oxygen which convert all organic carbon to carbon dioxide. The methods may differ in the ways they measure the carbon dioxide, but the results are considered to be comparable (Pers. comm. A. Ruzindana 2009).

Particle Size

Particle size was determined on a Malvern Masterisizer-S laser particle size analyser using method TEL 042. The Matersizer uses the volume of the particle to measure its size. The percentages of clay (0.01-3.90 um), silt (3.90-62.5 um), and sand (62.6 and 900 um) were estimated from a frequency curve. The peak of the curve gave the modal diameter - the most commonly occurring particle diameter. A good fit is indicated by a residual of under 1%. This method uses a different instrumentation that the one used during the SREQMP, but the methods are based on the same general principles.

ALS Laboratory Group Analytical Methods

ALS Laboratory Group (ALS) in Edmonton, formerly Envirotest (ETL), became a member of CAEAL in June 1990 and has participated in CAEAL proficiency testing since 1990, when it was first offered. The lab received accreditation in 1993. Previous to 1990, ETL participated in proficiency testing programs for EPA and AIHA (Pers. comm. ALS October 2009).

ALS analyzed centrifuged water and suspended sediment samples from the Slave River at Fort Smith (mid-river). ALS performed the organic analyses during the SREQMP (1990-1995) and the Follow-Up study (2000-2007). The analytical methodologies for samples collected between 1990 and 1995 are presented in Section 4.2 (centrifuged water) and 4.3 (suspended sediments) of the SREQMP Report (Sanderson et al. 2008). Efforts were made to document the changes in methodology and ascertain the comparability of the recent results to the results obtained during the earlier years of the SREQMP. Methods used between 2000 and 2007 are documented below.

Appendix 5-3 presents the changes in instrumentation, methodology, and calculation introduced during the course of the Follow-Up study (2000-2007) for the various analyses. Changes in instrumentation resulted in an increase in detection sensitivity by 3 to 10 times. Analytical methodology change for metals and the calculations of detection limits remained the same for most analysis:

$$\text{Detection Limit} = \text{lowest std response} \times \frac{\text{final volume (mL)}}{\text{sample volume (L)}}$$

The changes in detection limits reported were based on available sample size and changes to the concentration of the sample extract. Changes in methodology or instrumentation were not considered to be primary determinants of DL changes. Data calculation for dioxins, furans and PCBs were adjusted to standards.

The number of polycyclic aromatic hydrocarbons, organochlorinated herbicides and pesticides, and metals analyzed varied over the years. Changes are due to improvements in technology, changes in regulatory requirements over time, requirements of jurisdictions, and changes in the basic list of compounds the lab provides as efforts are made to combine reporting lists in the interest of simplification (Pers. comm. ALS October 2009).

To ensure the quality of the environmental data presented in this report, ALS performed seventeen (17) QA/QC procedures. Appendix 5-8 gives a brief summary of each QA/QC performed and lists the quality assurance manuals that ALS follows. Certain types of QC procedures are performed on each batch of samples, which may contain samples from several clients. The resultant QC data is considered to be applicable to all of the samples in the batch. More detailed methods and the exact quality control checks used for each type of analysis are available in the appropriate standard operating procedures.

The detection limits presented in the sections below are representative of the analyses performed by ALS between 2000 and 2007. The following explanation was offered by the lab manager from ALS regarding the higher detection limits in 2000 to 2007 than in the SREQMP (1990-1995):

> "It should be noted that the lab's policies regarding acceptable changes to methodology have changed over the years. The extremely low detection limits reported in the past were based on one-time, custom changes to approved methods, and while theoretically capable of seeing the reported DLs, they were not based on rugged, validated methodology. Since regulations have changed in the 2000s to place greater emphasis on method uncertainty, laboratory practices have responded by being much more conservative in modifications to established methods, to ensure the best and most consistent data quality possible. As a result, we can report only our validated, default detection limits for the tests we offer."

S. Johnston, Analytical Laboratory Services (ALS). Edmonton, Alberta, Pers. Comm.

Centrifugate Water Samples

Extractable Organochlorines (EOCL)

Extractable organochlorines (EOCL) were analyzed in 2000 and 2001 using 12 L samples that were cold spiked or preserved with methanol. The EOCL analysis was subcontracted to SRC Analytical laboratories, who determined the concentration by standard operating procedure Number: Rad-357. The extraction is based on US EPA Method 9023 and the determination is based on US EPA method 9022.

After fortification with the 2,4,6–tribromophenol surrogate, samples were extracted with a solution of methyl-t-butylether:cyclohexane in a ratio of 1:1. The resulting extract was concentrated after the addition of iodine in toluene (to transfer surrogate). The extracts were then submitted to the University of Alberta Slowpoke Reactor Facility for neutron activation analysis. Quality control was maintained by analyzing method blanks (4), glassware proofs (3), and a spiked sample. The spike used was Aroclor 1254 in 2001. No QA/QC data were provided by the lab.

Chlorinated and Non-chlorinated Phenolics

The ALS chlorinated/non-chlorinated list of compounds is designed to meet the Municipal and Industrial Strategy for Abatement (MISA) requirements. MISA was designed to address the common pollutants of nine major industries, namely petroleum, pulp and paper, metal mining, industrial minerals, metal casting, organic chemical manufacturing, inorganic chemical, iron and steel, and electric power generation.

The methodology used to determine the concentrations of chlorinated and non chlorinated phenolics in the centrifuged water samples is based on EPA 3510 for extraction and EPA 8270 for analysis (ALS MSOP71.03, MSOP71.04, MSOP71.07). Aqueous samples were fortified with acidic surrogates and serially extracted with dichloromethane (DCM) by either separatory funnel or Erlenmeyer flask/stir techniques, depending on sample volume. The solvent aliquots were collected, dried through baked, acidified with sodium sulfate and concentrated to low, discrete final volume. The extract was derivatized by dry acetylation then analyzed by gas chromatograph/mass spectrometer (GC/MS) in selected ion monitoring (SIM) mode. Detection limits varied between 0.008 and 3 µg/L between 2000 and 2007.

Up to three surrogates, 2-fluorophenol, phenol d5, and 2,4,6-tribromophenol, were used for quality control. The ranges of surrogate recoveries along with the quality control results for field and method blanks, field spikes, and lab control samples provided by the ALS are available upon request.

Chlorophenols

The ALS chlorophenol list is designed specifically for evaluating pulp and paper mill effluents in accordance with licensing regulations in Alberta, which require the use of Alberta Environment Method AE130 for chlorophenol determination.

Surrogates were added to the aqueous samples. The samples were then adjusted to neutral pH and extracted serially with methyl-t-butyl-ether (MTBE). The extracts were exchanged to hexane, derivatized by dry acetylation and analyzed by GC/MS in selected ion monitoring (SIM) mode.

Method references are Alberta Environment AE130 and EPA 1653 (ALS MSOP 63.05 and MSOP 42.17). Detection limits ranged between 0.0004 and 0.2 µg/L between 2000 to 2007.

Eight surrogates were used between June 2001 and May 2007. Surrogate recoveries and results for field and method blanks, field spike, and lab control samples provided by the laboratory are available upon request.

Polycyclic Aromatic Hydrocarbons (PAHs)

For PAHs, extraction was based on EPA3540 and analysis was based on EPA 8270 (ALS MSOP5.05, 5.07, 5.10 and 5.13). Aqueous samples were fortified with neutral surrogates and serially extracted with DCM by either separatory funnel or Erlenmeyer flask/stir techniques, depending on sample volume. The solvent aliquots were collected, dried through baked sodium sulfate and concentrated to low, discrete final volume. The extract was analyzed by GC/MS-SIM. Detection limits achieved between 2000 and 2001 were of 0.01 µg/L, and ranged from 0.001 to 0.005 µg/L between 2003 and 2007.

The number of PAH compounds analyzed increased during the course of the monitoring program. In 2001, chrysene and benzo(b)fluoranthene were added. In addition, phenanthrene and anthracene results were reported independently instead of a combined result. Perylene was measured in February 2001 and March 2007 only. 2-methyl naphthalene results were available in March 2007, while fluorene was not analyzed in the routine analysis. In addition to the routine PAHs analysis normally performed, the May 2007 sample was analyzed a second time for an extended series of alkylated PAHs using the same method. Nitrobenzene d5, 2-fluorobiphenyl, p-Terphenyl d14 were used as surrogates. The ranges of recovery percentages as well as quality control data for field and lab method blank, field spike, matrix spike and lab control samples are available upon request.

Naphthenic Acids

Dissolved naphthenic acids were solvent extracted from acidified aqueous samples using dichloromethane (DCM) prior to quantitation by Fourier Transform Infra-Red spectroscopy (FTIR; Syncrude, 1994). Note that FTIR is not uniquely selective to naphthenic acids. If present, other carboxylic acids (e.g. humic acids, fulvic acids) may also be detected by this method.

Organochlorine Pesticides and Herbicides

Nineteen organochlorine pesticides were targeted throughout the monitoring program, except in 2001 and 2003, when a few more substances were added to the list. The list of herbicides of concern increased from five to thirteen compounds between 2000 and 2007.

Organochlorine pesticides and herbicides concentrations were determined by a method similar to the one used during the SREQMP, which utilized gas chromatography electron capture detection GC/ECD. Between 2000 and 2007, aqueous samples were fortified with appropriate surrogates and serially extracted with DCM by separatory funnel. Acidic compounds such as phenoxy acid herbicides were extracted under acidic conditions; neutral compounds were extracted under neutral pH conditions. The solvent aliquots were collected, dried through baked sodium sulphate and concentrated to low, discrete final volume. Acidic compounds were derivatized by methylation with diazomethane. The extract was analyzed by GC/MS-SIM. The extraction method was based on EPA 3540 and the analysis method was based on EPA 8151 and EPA 8081 (ALS PSOP 100.00, 100.01, 100.04, and 101.03). Detection limits for pesticides ranged from 0.001 to 1 µg/L, while those for herbicides varied between 0.002 and 0.1 µg/L. Any detection limit variance was most likely caused by differences in sample size.

Quality control samples for water analyses include surrogates in each sample to measure extraction efficiency; an internal glassware proof to ensure that glassware does not contaminate samples; method blank to account for any possible contamination from reagents and extraction procedures; a laboratory control spike to prove method validity; and internal standard compounds in the extracts to ensure instrument consistency. Surrogates were not used for the pesticide analyses. However data for field blank, field spikes, lab method blank and lab control samples for pesticide analysis are available upon request. For herbicides, the QC data is also available upon request/. The surrogate used between June 2001 and May 2007 were 2,4-D d5 and Treflan d14. No surrogate data was available for samples analyzed in February 2001.

Polychlorinated Biphenyls (PCBs and Aroclors)

PCBs were measured in water in 2001, 2006, and 2007. In 2001, PCBs were evaluated as a total concentration with a detection limit of 1 µg/L as part of the organochlorine pesticides scan (see above section). In 2006 and 2007, nine Aroclors groups were quantified along with total PCBs, using a method based on EPA 3540 and EPA 8082 (method MSOP4.13) for extraction and analysis, respectively. Aqueous samples were fortified with neutral surrogates and serially extracted with DCM by either separatory funnel or Erlenmeyer flask/stir techniques, depending on sample volume. The solvent aliquots were collected, dried through baked sodium sulfate and concentrated to low, discrete final volume. The extract was analyzed by GC/ECD. Detection limits for total PCBs were 0.05 µg/L and 0.01 µg/L for individual Aroclor groups.

The method changed from a GC/ECD (HP5890) to a GC/micro ECD (Agilent 6890) instrumentation which increased the sensitivity by 10 times. Changes in detection limits are based on available sample size and changes to the concentration of the sample extract, not to changes in methodology or instrumentation.

The quality control procedures for these analyses included twelve different quality control samples and standards. Recoveries of the surrogate used, decachlorobiphenyl, and data for field and method blank and lab controls samples are available upon request.

Suspended Sediment Samples

Moisture

The percent moisture of the samples were estimated using a gravimetric method. Samples were oven dried at 105˚C.

Metals

A list of 15 to 30 metals was targeted each year. In 2000 and 2001, metals were extracted by method SW 3051 and EPA6010, which involved microwave-assisted digestion and analysis by ICP-OES and atomic absorption spectrometry (AAS) using method EPA 6010. In 2001, extraction was by strong acid digestion. Starting in 2003, digestion was conducted by method EPA 3050 (hot–block method) and metals were measured by inductively coupled plasma mass spectrometry (ICP/MS; EPA 6020). In 2006 and 2007, mercury and antimony were measured in separate analytical runs with method based on SW3051 and EPA 6010. Detailed methods and a complete list of quality controls are described in ALS ISOP 100.07, 107.01, 108.05, 12.09, 52.05, and 53.05. Detection limits varied between individual metals, ranging from 0.05 to 200 mg/kg. Mercury and antimony had detection limits of 0.05 and 0.1 mg/kg, respectively.

No surrogate is used in this analysis. The quality control data provided by the lab including data for laboratory method blanks, matrix spikes, and certified, standard, and internal reference materials (ICP standard) are available upon request.

Chlorinated and Non-chlorinated Phenolics

A list of 6 to 28 chlorinated and non chlorinated phenolics were targeted in suspended sediment samples each year. The method used to measure the chlorinated and non-chlorinated phenolics in the suspended sediment samples are based on the Environmental Protection Agency (EPA) 3540 and EPA 8270 methods (ALS MSOP 70.04, 70.05, and 70.07). A wet soil sample was weighed and a surrogate solution was added. It was acidified and mixed with acidic sodium sulfate until a dry, free-flowing powder is achieved. Extraction is by soxhlet extraction for a minimum of 16 hours using DCM as the extraction solvent. The extract was dried with acidified sodium sulphate, concentrated, and derivatized by dry acetylation. The extract is analyzed by Gas Chromatography/Mass Spectroscopy- Selective Ion Monitoring (GC/MS-SIM). Detection limits ranged between 0.002 and 2 mg/kg between 2000 and 2007.

Each year, eight to nine quality control checks were included in the lab procedures for this group of parameters. The data available for lab method blanks and lab control samples along with the recoveries of the three surrogates used, including 2-fluorophenol, phenol d5, and 2,4,6-tribromophenol are available upon request.

Chlorophenols

For each suspended sample, 28 to 38 chlorophenols were targeted. Solid samples were weighed, surrogate compounds added, acidified with 6N sulfuric acid, then shaken with acetone to remove water. They were then extracted by soxhlet extraction with an acetone:hexane solvent mix for a minimum 16 hours. The solvent was concentrated by evaporation of the acetone, leaving hexane and any residual water. The solvent/aqueous layer was transferred to a separatory funnel and acidified, then serially extracted with methyl-t-butyl ether. The extracts were dried with sodium sulphate, exchanged to hexane, derivatized by dry acetylation and analyzed by GC/MS-SIM. Method references are Lee et al. (1987) and EPA 1653 (MSOP 43.06 and 43.07). Detection limits varied between 0.0004 to 0.08 mg/kg between 2000 and 2007.

Seven quality control checks were used for this method. Lab method blank, lab control samples and the surrogate recovery results for the eight surrogates used from June 2001 and later are available upon request.

Organochlorine Pesticides and Herbicides

The number of pesticides targeted during the course of the study was 19 except in February 2001, where 27 compounds were measured. For herbicides, the number of target analytes increased from 9 to 13 compounds between 2000 and 2007.

Organochlorine pesticides and herbicides in sediments were measured using methods EPA 8081 and EPA 8151 (ALS PSOP 102.00). Solid samples were weighed, a surrogate solution was added then extracted with an acetone:water at various specific pH levels. The various liquid extracts were collected into a separatory funnel and extracted under base/neutral/acidic conditions to separate the three pH-specific chemical classes of compounds. The extracts were concentrated and the acidic fraction was derivatized with diazomethane. 2,4-D d5 and Treflan d14 were used as surrogates for the herbicide analyses; no surrogates were used for the pesticides analyses. Analyses were by GC/MS. For pesticides, detection limits varied between 0.001 and 0.01 mg/kg; while detection limits ranged between 0.001 and 0.005 mg/kg for herbicides.

Quality control for soil analyses include internal glassware proofs, method blanks, and duplicates and/or spikes (matrix or laboratory control), plus the aforementioned surrogates and internal standards are available upon request.

Polycyclic Aromatic Hydrocarbons (PAHs)

A total of 14 to 19 PAHs were targeted in suspended sediment samples collected between 2000 and 2007. PAHs were extracted using a method based on the EPA 3540 modified for use of rotary evaporator and for ETL glassware and analyzed based on EPA 8270 modified for SIM analysis (MSOP143.01 and 143.04, 143.08). Solid samples were fortified with neutral surrogates and extracted with DCM by soxhlet extraction for a minimum 16 hours. The solvent aliquots were dried through baked sodium sulphate and concentrated to low, discrete final volume. The extract was analyzed by GC/MS-SIM. Detection limits ranged from 0.003 and 0.01mg/kg between 2000 and 2007.

In 2007, 38 alkylated PAHs were investigated using similar methods. Detection limits varied between 0.003 and 0.012 mg/kg. These compounds were included as research has shown that a wide variety of alkyl-substituted PAHs can contribute to PAH toxicity (USEPA 2003).

The quality control results available, including surrogate recoveries, lab duplicates, lab method blanks and lab control spikes, are available upon request. Surrogates used for the PAHs analyses are nitrobenzene d5, 2-fluorobiphenyl, and p-Terphenyl d14.

Naphthenic Acids

Naphthenic acids were Soxhlet extracted from soils using dichloromethane prior to quantitation by Fourier Transform Infra-Red spectroscopy (FTIR; Syncrude, 1994). Note that FTIR is not uniquely selective to naphthenic acids. If present, other carboxylic acids (e.g. humic acids, fulvic acids) may also be detected by this method.

Polychlorinated Biphenyls (PCBs)

PCBs results were obtained using different methods and instrumentation between 2000 and 2007. In 2001, total PCBs were measured in conjunction with the screen for organochlorine pesticides (using the method described for this group of compounds in the section above). Between 2003 and May 2007, total PCB, total Aroclors, and various Aroclor mixtures were measured based on EPA 3550 for extraction and EPA 8082 for analysis (MSOP7.06, MSOP 7.07, and MSOP 7.12). Solid samples were fortified with surrogates and extracted with acetone/hexane by either soxhlet extraction or shake/sonication techniques. The extraction solvent was dried through baked sodium sulfate and concentrated to low, discrete final volume. Cleanup was achieved by charring with concentrated sulfuric acid and column cleanup by using florisil and acid silica, if necessary. If sulfur contamination was seen, additional cleanup was done using mercury or activated copper techniques. The extract was then analyzed by GC/ECD. The quality control procedure included nine quality control checks and decachlorobiphenyl was used as surrogate for these analyses.

In May 2007 a more elaborate scan was performed on the suspended sediment by method EPA 1668 (ALS UTCSOP# 18.10), and 185 congeners and total PCBs were measured using an isotope dilution procedure. Twenty-one isotopically-labeled analogues were added to 10 grams of suspended sediment sample which was then soxhlet extracted, concentrated, cleaned up and analyzed by high-resolution gas chromatography-mass selective detector. Results are corrected for surrogate recoveries and reported on a dry-weight basis. Detection limits obtained between 2000 and 2007 ranged between 0.002 to 0.05 mg/kg for both total PCBs and individual Aroclor groups, and from 0.0021-0.11 mg/kg for congener-specific or coplanar PCBs.

The quality control results including surrogate recoveries, lab duplicates, method blanks and lab control samples are available upon request.

Polychlorinated Dibenzo Dioxins (PCDD) and Polychlorinated Dibenzo Furans (PCDF)

The conventional series of PCDD and PCDF congeners and homologues were measured using EPA Method 1613 (MSOP 89.03 and 89.04, UTCSOP18.09 and 18.10).

Suspended sediment samples were fortified with 15 isotopically-labelled surrogate compounds, mixed with sodium sulfate to dry until a free-flowing powder was achieved. It was then extracted by soxhlet with dichloromethane (DCM) for at least 16 hours. Extracts were concentrated, cleaned by column chromatography, and analyzed by high-resolution gas chromatography-mass selective detector. A Kratos concept high-resolution mass spectrometer was used until 2007, when a Thermo-DFS system was introduced, which provided a five fold increase in sensitivity. The analytical methodology did not change over the years. Toxic equivalent quotients were calculated by multiplying the concentration obtained for each dioxin and furan congener (total of 17 congeners) by the appropriate toxic equivalency factor. The toxic equivalency factors include NATO (1988a&b), WHO (1998) and WHO (2005). NATO was used prior until about 2006. Detection limits ranged from 0.1 to 3.6 pg/g between 2000 and 2007. Results are corrected for surrogate recovery and reported by ALS on a dry-weight basis.

Quality control data available, including surrogate recoveries, lab duplicates, lab method blanks (sodium sulfate) and lab control spikes are available upon request.

Appendix 5-6: Taiga Environmental Laboratory – Accreditation

The Taiga Environmental Laboratory is accredited by the Canadian Association for Laboratory Accreditation (CALA), for the specific tests listed in the scope of accreditation published by CALA. The laboratory was first granted accreditation in 1993, the full scope of accreditation can be viewed on the CALA website (CALA) under laboratory # 2635.

The Accreditation Program provides formal recognition of the competence of a laboratory to manage and perform specific tests or types of tests listed in the scope of accreditation. As part of the accreditation process, laboratories must undergo a site assessment where conformance to ISO/IEC 17025 (*General Requirements for the Competence of Testing and Calibration Laboratories*) is assessed. Accreditation itself is based on satisfactory participation in an assessment plus satisfactory compliance with the CALA Proficiency Testing Requirements for accreditation. Following the initial assessment, regular reassessments are carried out every two years. Accreditation of additional tests or matrices or methods changes in the interval between regularly scheduled site assessments, proceeds by scope extensions application that imply an abbreviated site-assessment, supporting method validation data and proficiency testing results.

Proficiency testing is a special type of inter-laboratory comparison study. It is a powerful quality assurance tool that enables laboratories to monitor their performance and compare their results against similar laboratories.

CALA's Proficiency Testing Program is accredited to ILAC:G13 (and ISO Guide 43) and consists, in general, of four samples per study, two studies per year. The analyte concentrations in these samples are unknown to the participating laboratory, which analyses the samples and reports the results for evaluation. A successful participation results in the laboratory obtaining proficient status for the analytes analysed and is used as one of the surveillance tools in support of laboratory accreditation to ISO/IEC 17025. CALA offers two Proficiency testing per year for each analytical method. Taiga Environmental Laboratory is also involved in Proficiency Studies offered by National Laboratory for Environmental Testing twice a year. This initiative is not a CALA requirement but the laboratory evaluations provided by NLET are additional tools to demonstrate Taiga Environmental Laboratory competence and maintain a high level of assurance in test data.

As part of the accreditation requirements, Taiga Environmental Laboratory have to continually improve the effectiveness of its Quality Management System through the use of the quality policy, quality objectives, audit results, analysis of data, corrective and preventive actions and management reviews. The Laboratory seeks feedback, both positive and negative from its customers and identifies all opportunities for improvements. That's why methods used by Taiga Environmental Laboratory have been changed through the years to:

1) increase the accuracy and precision of the analytical data
2) increase analytical range and achieve a lower detection limit (if possible)
3) minimize sources of error (automation)
4) increase samples turn-around-time (laboratory productivity/efficiency)

Each new analytical method is validated and accredited to ensure its fitness for purpose before put in use.

Appendix 5-7: Taiga Environmental Laboratory Quality Assurance/Quality Control Protocols

Quality Assurance/Quality Control Protocols

The Quality Control (QC) data are produced to measure bias and variability of the analytical method. Without QC data, the magnitude of errors and thus the quality of the environmental data are not known.

The following section describes the quality control samples incorporated into analytical methods and how they are to be used to assess the method performance on a daily and continuous basis. Refer to analytical methods for specific details (Section 9 for each specific method) on:

(1) Which quality control samples are used,
(2) The level of quality control effort, and
(3) The control limits.

Taiga Environmental Laboratory uses several types of QC to validate the tests results (PRO 026, PRO 043, PRO 063 and Quality Manual for more details):

Reagent Blank

Definition
A reagent blank consists of an aliquot of purified water (Type I, de-onized, or Type I UV$^+$ that is devoid of the parameter being measured) that is analyzed in exactly the same manner as a sample if the sample undergoes no pre-treatment prior to analysis.

Purpose
It is used to establish the calibration baseline, i.e. to monitor for contamination from reagents employed in the analysis. Reagent blanks can also be used to reduce carryover from standards or samples of high concentration.

Frequency
With each analytical run, analyze at least two reagent blanks, once at the beginning of the run, and at least once during the run. Repeat analysis of a reagent blank throughout the run at a minimum rate of 5% of the sample load. Also include the analysis of reagent blanks when new reagents are used, if calibration is repeated, and when contamination from sample carryover is encountered.

Assessment
The concentration of the blanks should not exceed the method detection limit. Higher values for reagent blanks indicate possible contamination with the reagents. Prepare new reagents and repeat the analysis.

Method Blank

Definition
A method blank consists of an aliquot of purified water (Type I, deionized, or Type I UV$^+$ that is devoid of the parameter being measured) that is carried through all steps of the analysis (including any preparatory procedures such as filtration, digestion, extraction, or autoclaving).

Purpose
It is used to monitor for contamination from equipment employed in the analysis.

Frequency
At least one method blank should be prepared with every batch of samples being prepared. At the beginning of each analytical run, analyze at least one method blank.

Assessment
The values of the method blanks should not exceed the method detection limit. High or erratic values indicate possible problems with the method or the equipment.
Identify possible areas of contamination and rectify, if possible.

- ***If the method blank is less than twice the method detection limit, a blank correction may be applied to all sample readings in the same batch.***
- ***Re-prepare or re-analyze the method blanks and samples if the value of the method blank is greater than twice the method detection limit.***

Note: If the value is below the detection limit, no blank correction is required.

Duplicate Samples

Definition
A laboratory duplicate sample is a separate aliquot of sample, prepared and analyzed in identical fashion to the original sample aliquot. Both aliquots are removed from the same sample container. In contrast, field duplicates consist of a sample that is collected twice and placed into two different sample containers, and are usually analyzed as two separate samples.

Purpose
Precision of a method is monitored by the analysis of laboratory duplicate samples. If the entire sample is consumed for one analysis, use field duplicates if available to assess precision.

Frequency
Perform a duplicate analysis on every 10th sample, regardless of the sample matrix or expected concentration, with a minimum of one duplicate analysis per run. Analyze at least one sample in between the duplicate samples being analyzed to avoid errors in reading or calculating concentrations (see example of typical analysis set-up below).

Calculations

Calculate the % <u>Relative Percent Difference (% RPD</u>) between the duplicate values:

$$\% \text{ RPD} = \frac{|\text{original sample value - duplicate sample value}|}{\text{Average of the two values}} \times 100\%$$

Assessment

- For sample concentrations greater than or equal **3** times the Method Detection Limit (MDL), the basic criteria for acceptance (for inorganic analyses) is <u>RPD</u> ≤ 20%.
- For sample concentrations greater than or equal 3 times the Method Detection Limit (MDL), the basic criteria for acceptance (for organic analyses) is <u>RPD</u> ≤ 30%.
- For sample concentrations less than 3xMDL, the acceptance is <u>RPD</u> ≤ 30%.
- If available, use Range-Ratio charts to assess duplicate data (see below). Non-conformances are to be addressed by corrective actions (see below and Procedure 044).

Spiked Samples (Analyte Spike)

Definition

Known amounts of an analyte (standard) are added to an aliquot of sample, and measured.

Purpose

Effects of sample matrix on analyte measurements are determined by the use of spiked samples.

Frequency

Perform spike analyses on samples representative of the matrix analyzed routinely in the laboratory, on every 20th sample, with a minimum of one spike analysis per run.

Preparation

- If the original (unspiked) sample concentration is known beforehand, prepare the spike at a concentration that is 1 to 2 times higher.
- If the original (unspiked) sample concentration is unknown, prepare spikes at three different concentrations: one at the estimated concentration, and one each at an order of magnitude above and below the estimated concentration. After the sample concentration has been determined, use the spiked sample that is closest in concentration to the original sample for calculating recovery.

Calculations

$$\% \text{ Recovery} = \frac{\text{Actual Value}}{\text{Theoretical Value}} \times 100\%$$

$$\text{Where: Theoretical Value} = \frac{(\text{spike vol. x stock conc.}) + (\text{sample vol. x sample conc.})}{\text{Total volume of spike \& sample}}$$

Use the original sample concentration value, not the average of the original sample and its duplicate concentrations, when calculating the theoretical value.

In spikes in which there is no dilution of the original sample, an alternate calculation for spike recovery is available:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

WhereSSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Assessment
Recoveries should fall within the range of ***80 - 120%*** for inorganic analyses, and between ***70 - 130%*** for organic and metals analyses. Non-conformances are to be addressed by corrective action (see below and Procedure 044).

Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

Definition
Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MSD analyses are performed for soil/sediments samples.

Purpose
The MS and MSD samples are prepared and/or analyzed exactly like field samples. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for back-ground concentrations.

Frequency
Perform MSD analyses on samples representative of the matrix analyzed routinely in the laboratory, on every 20th sample, with a minimum of one MSD analysis per run
Assessment
Recoveries should fall within the range of ***80 - 120%***. Non-conformances are to be addressed by corrective action (see below and Procedure 044)

Control Standard
Definition
A Control Standard is a solution which contains the same analyte (s) as the calibration standards. It is prepared from a source that is independent of the source used to prepare the calibration standards.

Purpose
A Control Standard is used to monitor calibration accuracy and stability during an analytical run.

Frequency
Perform calibration check analyses at a rate of 10% of the sample load, or at a minimum of twice during the analytical run.

Preparation
It is prepared from a source that is independent of the source used to prepare the calibration standards. It may be prepared from a different stock solution, or purchased. The concentration of the control standard should fall within the range of the calibration standards.

Assessment
If the solution is prepared from an independent stock calibration standard, the control standard should read between 95 - 105% of the theoretical value of the standard.

If the control standard is purchased from an external source, the control standard should read within the 95% confidence interval (mean ± two standard deviations) as determined by the supplier. These values should be revised or established using (in-control) laboratory data on the materials.

The use of Shewhart control charts is required. If the value obtained is outside of the acceptable range, re-calibrate the instrument and repeat the last samples analyzed after the previous in-range control standard.

Reference Sample

Definition
The Reference Sample is a reference material, of matrix that is equivalent to that of the test samples, obtained from an external supplier. It has been analyzed by a technically valid procedure, and is accompanied by a certificate (CRM) or documentation of traceability to a certifying body (SRM). When used in the laboratory, the reference sample undergoes similar processing (including any preparatory steps) as the test samples.

Purpose
The Reference Sample is used to establish the accuracy and recovery of a measurement method.

Frequency
A Reference Sample is to be analyzed at least twice in each analytical run, once at the beginning and once at the end.

Assessment

The values and control limits are provided by the supplier or stated in the preparation instructions. Values should fall within the established control limits. The values may be revised or established using (in-control) laboratory data on the materials. Values are to be plotted on a Shewhart or X-Bar control chart; non-conformances are to be addressed by corrective actions (see below and Procedure 044).

Detection Limit Verification Sample

Definition

The detection limit verification sample is a sample with matrix similar to the samples being analyzed routinely, containing the analyte of interest at a concentration equal to the method detection limit.

Purpose

This is used to verify that the method is still capable of reading samples at the stated method detection limit.

Frequency

The detection limit verification sample is analyzed at least once during each analytical run.

Preparation

Use a sample known to contain the analyte of interest at a concentration equal to the method detection limit. If a sample is not available, a standard may be prepared (fresh daily), using a stock solution independent of the calibration standards.

Assessment

The concentration reading obtained from the detection limit verification sample (or standard) must be equal to the stated method detection limit, with an error of ± 10%. Non-conformances are to be addressed by corrective action (see below and Procedure 044). Re-assessment of the method detection limit may also be required.

Calibration Check Standard

Definition

Calibration check standards are standards prepared like the calibration standards, but analyzed as samples.

Purpose

Calibration check standards are used to monitor the stability of the calibration throughout the analytical run. The calibration check standard(s) may also be used to apply a drift correction, or be incorporated into a new calibration curve.

Frequency

A calibration check standard should be analyzed after every 20 samples.

Preparation:
Prepare as per the calibration standard (same stock solutions); the concentration(s) should fall around the mid-point of the calibration curve.

Assessment
The concentration of the standard(s) should not deviate from the nominal value of the standard(s) by more than 10%. If the value is outside of the acceptable range, apply a drift correction if possible, or re-calibrate by re-analyzing the complete set of calibration standards. All samples analyzed prior to the deviating calibration check standard should be re-analyzed after the new calibration.

Dilution Verifications

Definition:
Dilution verifications are either
- Method 1: duplicates of analyzed dilutions (for methods that are not linear outside of the working calibration range), or
- Method 2: comparisons of diluted and undiluted sample data for methods that have been validated to be linear outside of the working range (e.g. atomic absorption, ICP methods).

Purpose:
Dilution verifications confirm that the correct dilution factors are used in the calculations of the final reported sample values.

A. Method 1 Dilution Duplicates

A.1 Frequency

- In each analytical batch, at least one dilution must be duplicated for each (final) dilution factor used within that batch of samples;

e.g. If the batch contains samples requiring 2x and 1000 x dilutions (in order to bring the original samples within the working calibration range of the method), at least one duplicate dilution must be performed on a sample that required a 2x dilution, and at least one duplicate dilution must be performed on a sample that required a 1000x dilution.

- For each (final) dilution factor used, at least one dilution for every five dilutions must be verified;

e.g. If ten samples required a final dilution of 5x, at least two of the sample dilutions must be verified by preparing and analyzing 5x duplicate dilutions.

A.2 Assessment:

The final concentrations (i.e. dilution factor applied) of the duplicate diluted sample and the original diluted sample should have a difference of less than 10%.

Note: Indicate dilutions and verification duplicates clearly in the sample descriptions; e.g. Original Sample: "264444 x5", Dilution Verification: "#264444 x5 dil dup". On the data print-outs, indicate values not being used by marking "↑" beside the values for samples/dilutions that are higher than the calibration range, and "↓" for dilutions that should be repeated at a lower level (i.e. dilution factor used was too high, diluted sample value is too low).

B <u>Method 2 Dilution Verifications</u>

B.1. Frequency

Comparisons of undiluted and diluted samples should be made for every diluted sample.

B.2 Assessment

The magnitude of the dilution must correlate with the original and subsequent dilution values;
e.g. :
(i) A sample that appears to read slightly outside of the linear range, should read close to mid-range of the linear range at a 2x dilution;
(ii) A 100x dilution should read 10x lower than a 10x dilution, if readings for both dilutions are within the linear working range.

Note: The final diluted values being reported and the dilution verifications must be clearly marked; e.g. mark "↑" beside the values for samples/dilutions that are higher than the linear range, mark "↓" for dilutions that should be repeated at a lower level (i.e. dilution factor used was too high, diluted sample value is too low).

Quality Control Charting

Control charts are used to determine whether measurement equipment or procedures are functioning properly or are "in-control", and to identify trends of positive or negative bias.

Shewhart Control Charts

These are used for monitoring equipment performance as well as method recoveries on control standards and certified reference materials. At the end of each month, the charts will be checked by the Quality Assurance Officer for approval. If the Control Charts are not available, the Laboratory Information Management System (LIMS)-generated and maintained lists/databases with values, limits, and trending are used to monitor method quality control.

Equipment Monitoring:

Equipment data (including refrigerators, walk-in coolers, ovens, and water purification systems) is plotted on Shewhart control charts on a daily basis. Charts are changed monthly. Initial operating limits are prescribed by equipment specifications and laboratory requirements. Deviations outside of these limits are to be addressed by adjustments, repairs, or replacement.

Recovery Monitoring:
Analytical data is plotted on Shewhart control charts with each analytical run. For spikes (inorganic analyses), the initial control limits are between 80 and 120% recovery. The initial warning and/or control limits for control standards and reference samples are as stated on accompanying certificates of analysis, in literature, or as determined by the laboratory from previous testing.

Criteria for evaluating Shewhart Control Charts:

- A chart is considered valid if 68% of the data fall within one standard deviation of the mean value.

Control Limits

- represent the 99% confidence interval.
- calculated as the mean (or true) value ± 3 s.d.
- NO DATA should exceed these limits

Warning Limits

- represent the 95% confidence interval.
- calculated as the mean (or true) value ± 2 s.d.
- NO TWO CONSECUTIVE POINTS should exceed these limits

Central Line (Mean)

- represents the mean value.
- NO SEVEN VALUES to be CONSECUTIVELY INCREASING OR DECREASING.
- If data is deemed out of control by any of the above criteria, take corrective action (see Procedure 044).
- To calculate new limits, or to revise existing limits, compile at least 20 sets of data deemed valid by the previous criteria. Obtain the mean and standard deviations to calculate the new warning and control limits.

X-Bar/Range Control Chart
The X-Bar/Range Control Chart is used to assess both the accuracy and precision of the analysis of a chosen reference material. For each analytical run, the average of a pair of duplicate data is plotted on the X-Bar portion of the chart while the absolute difference between the duplicate values (range) is plotted on the corresponding range portion of the chart.

- The X-Bar portion of the chart is utilized as a Shewhart chart (see above).
- The Range portion of the chart shows the precision of the reference material on a per-run basis.
- Initial statistics on the average range between duplicate values for the reference material are obtained from at least 10 pairs of data
- calculate the range (R) for n pairs of in-control reference data, with n ≥ 10.
- using only valid range (R) values (ie. <10%), calculate the average range:
    - For pairs of data numbered 1 to n : average range = (R1 + R2 + ... Rn)/n

* the upper control limit = 3.27 * average range
* the upper warning limit = 2.51 * average range

- If data is deemed out of control for either the accuracy or precision of the reference material, take corrective action (see Procedure 044).

Range-Ratio Control Charts

Range-Ratio charts are to be used to assess sample duplicate data. The differences between the paired results are averaged for various concentrations, and critical range (Rc) values are obtained. Subsequent duplicate differences (hereafter referred to as the observed range, Ro) are then compared to the critical range for the corresponding concentration, and Range Ratios (Rr) are calculated:

Rr = Ro/Rc

- The Upper Control Limit (UCL) for Rr = 3.27
- The Upper Warning Limit (UWL) for Rr = 2.51
  - *If Rr is within the warning limits, accept the data.*
  - *If Rr is outside the control limit, reject the data.*
  - *If Rr is greater than the warning limit, but less than the control limit (ie. between 2.51 and 3.27), accept the measurements, but monitor the next duplicates.*
  - *If the next Rr is greater than the warning limit, reject the data since the system was last in control, and take corrective action. If the next Rr is less than the warning limit, accept the data.*

- Critical Ranges (Rc) should be updated as method or instrument changes are made, or at least annually. *At least 20 pairs of duplicate results should be used to calculate each critical range value.*
- Take corrective action (see below and Procedure 044) to determine causes of out-of-control data.
-

Corrective Action Protocol

Routine, on-the-spot corrective actions are to be documented as normal operating procedure, and noted in the parameter quality control record books and/or on the control charts as such. The Procedure 044 details the corrective actions and root-cause analysis of the deviations. Such actions include, followed in a step-wise fashion:

- re-running the quality control sample.
- re-preparing a spike or duplicate.
- re-preparing standards and/or standard curve; if the curve is significantly different (>5%) from the previous curve, repeat analysis of samples.
- re-running the samples using methods of addition to compensate for interferences; checking procedures, reagents, instrument for malfunction.

- if the system is still not in control, contacting the area supervisor.
- decision being made by the Quality Assurance Officer to edit, flag, or delete the data,
- Laboratory Manager or designate to make proper notification to the clients.

Data approval

The Section Supervisors check percent accuracies, recoveries and differences between duplicates. Data is acceptable if the control values fall within the prescribed range as determined by the range charts for particular reference materials.

The Section Supervisors approve the quality control and data files contained in the Laboratory Information Management System before the results are released.

Final Reports are checked by the Quality Assurance Officer, the Laboratory Manager or Client Services Officer. If for any reason it is suspected that non-conforming data may have been reported (*i.e.,* as a result of audit findings, proficiency testing, client feedback or any other circumstance) the Laboratory Manager shall immediately notify any client whose data may have been affected.

Appendix 5-8: Types of quality control protocols used by ALS Laboratory Group, 2000-2007.

Term	Abbreviation	Type	Definition - Direct Quote	Reference	Frequency ** which QC performed is dependent on the method**
Calibration Verification Standard	CVS	Quality Control - Component	A standard used as a basis for comparison with calibration standards, prepared independently from the calibration standards, and which undergoes sample processing identical to that carried our for the calibration standards. (Control Standard)	CAEAL P07	with every new batch of working standards
Control Limits	CL	Quality Control - Other	Control limits define the area three standard deviations on either side of the centerline, or mean, of data plotted on a control chart. Control limits reflect the expected variation in the data.		-
Certified Reference Material	CRM	Quality Control - Component	Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each ce	CAEAL P07	Once per batch if available
Reference Material	RM	Quality Control - Component	Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.	Eurachem 1998	*See also Certified Reference Material and Internal Reference Material.*
Internal Reference Material	IRM	Quality Control - Component	*See Reference Material*	-	A Reference Material developed within the laboratory or company whose characteristics are sufficienctly established to be used for the assessment of a test method. Characteristics may be established by comparison of results achieved with another method o
Standard Reference Material	SRM		*A standard reference material is similar to a certified reference material but is not accompanied by a certificate which is traceable to a certified value accompanied by an uncertainty at a stated level of confidence.*		
Continuing Calibration Verification	CCV	Quality Control - Component	A standard solution (or set of solutions) analyzed periodically to verify that the instrument is analyzing and calculating a known value correctly and consistently i.e. a 0.2 ppm CVS standard when analyzed gives a reported result of 0.2ppm +/- 2%.		every 10 samples & end of run
Duplicate Samples	DUP	Quality Control - Component	Two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analy	EPA TRS	1 per batch, if sufficient sample available
Internal Reference Material	IRM	Quality Control - Component	*See Reference Material*	-	
Laboratory Control Sample	LCS	Quality Control - Component	A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.	EPA 1992	1 per batch

Appendix 5-8: Types of quality control protocols used by ALS Laboratory Group, 2000-2007.

Term	Abbreviation	Type	Definition - Direct Quote	Reference	Frequency ** which QC performed is dependent on the method**
Laboratory Control Sample Duplicate	LCSD	Quality Control - Component	*See Duplicate Sample and Laboratory Control Sample*	-	with every LCS when a duplicate is not done
Matrix Spike	MS	Quality Control - Component	A sample prepared by adding a known mass of a target analyte to a specified amount of matrix sample for which an independent estimate of the target analyte concentration is available. Spiked samples are used, for example, to determine the effect of the ma	EPA QA/G-5	1 per batch
Matrix Spike Duplicates	MSD	Quality Control - Component	Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.	EPA 1992	-
Method Blank	MB	Quality Control - Component	A blank prepared to represent the sample matrix as closely as possible and analyzed exactly like the calibration standards, samples, and quality control (QC) samples. Results of method blanks provide an estimate of the within batch variability of the blan	EPA QA/G-5	1 per batch
Relative Percent Difference	RPD	Quality Control - Other	RPD = {(sample result - duplicate result) / [(sample result + duplicate result)/2]} x 100	APHA 2005	-
Standard Reference Material	SRM	Quality Control - Component	*See Certified reference material.*		quarterly
Limit of Quantitation	LOQ	Test Method - Characteristic	The lowest concentration of an analyte that can be determined with acceptable precision (repeatability) and accuracy under the stated conditions of the test. - The 'limit of quantitation' (LoQ) is strictly the lowest concentration of analyte that can be d	Eurachem 1998	-
Limit of Reporting	LOR	Test Method - Characteristic	The lowest concentration that will be reported for a specific method. (Method Reporting Limit)	CAEAL P07	-
Limit of Reporting, Minimum	LOR$_{Minimum}$	Test Method - Characteristic	*See Limit of Reporting*	CAEAL P07	-
Limit of Reporting, Instrument	LOR$_{Inst.}$	Test Method - Characteristic	*See Limit of Reporting*	CAEAL P07	-
Average Desorption Efficiency	ADE	Test Method - Characteristic	The average efficiency of carbon tube desorption over the range of sensitivity of the test	NIOSH	-
Data Quality Objective	DQO	Quality Control - Component	The qualitative and quantitative statements derived from the DQO Process that clarify study's technical and quality objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis f	EPA QA/G-5	-

The quality control performed is dependent on the method, the availability of standards, the amount of sample received and the method of analysis. The QC limits reported are based on the internal control charts generated from results

The following documents are also part of the QA protocols:

1. Environment Canada (1992). Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents. EPS 1/RM/19
2. Environment Canada (1992). Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples. EPS 1/RM/23
3. United States Environmental Protection Agency (1994). Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. EPA 821-B-94-005

Appendix 6-1: Mann-Kendall test results for 1972-2010 trends in medians of annual and seasonal flows in the Slave River at Fitzgerald, with the corresponding parameters for linear regressions on the median flows.

	Annual	Winter	Spring	Summer	Fall	Parameter Description
Mann-Kendall Statistical Test	-117	152	-80	-216	-306	S, Mann-Kendall test statistic from data
	6832	6829	6831	6833	6833	VAR(S), variance of S (zero ties in the data sets)
	-1.403	1.827	-0.956	-2.601	-3.690	Z-score, normalized Mann-Kendall test statistic S
	-10.000	8.958	-9.118	-34.167	-28.125	Sen's Slope estimate for M-K test (m^3/s·year)
	0.920	0.966	0.830	0.995	1.000	Significance level from Mann-Kendall test
	NO	YES	NO	YES	YES	Significant at 0.95 confidence level?
Linear Regression	0.0679	0.0942	0.0201	0.1484	0.1596	Linear Regression R^2 value
	-12.552	10.496	-7.587	-31.814	-24.747	Linear Regression slope estimate (m^3/s·year)
	3230.13	2337.18	3521.67	4715.64	3488.97	Mean 39-year Flow, 1972-2010 (m^3/s)
	-489.51	409.34	-295.89	-1240.74	-965.13	Mean change over 39 years (m^3/s)
	-15.15%	17.51%	-8.40%	-26.31%	-27.66%	percent change over 39 years

Appendix 7-1: Significant Long Term Temporal Water Quality Trend Results for the Slave River at Fitzgerald (from Zajdlik, 2011a and 2011b). All trends are significant at the 95% confidence level unless otherwise denoted with an asterisk (*). Trends denoted with an asterisk are significant at the 90% confidence level.

		Non-flow adjusted trend results (full dataset)						Non-flow adjusted trend results (truncated dataset: 1989-2006)	
Parameter	**Period of Record**	**Model**	**spring (p-value)**	**summer (p-value)**	**fall (p-value)**	**winter (p-value)**	**annual (p-value)**	**Model**	**annual (p-value)**
pH	1972-2010	S	NA	NA	NA	NA	↔ (p > 0.1)	Y +S	↑ (0.0044)
Specific conductance	1972-2010	Y + S + Y*S	↔ (0.1832)	↔ (0.6035)	↔ (0.8328)	↔ (0.1779)	↔ (0.8331)		
Total dissolved solids	1993-2010	Y + S	NA	NA	NA	NA	↓ (p=0.0340)		
Total suspended solids	1972-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Turbidity	1972-2010	Y + S + Y*S	↔ (0.8041)	↔ (0.5924)	↔ (0.6558)	↔ (0.6651)	↔ (0.6571)		
Alkalinity	1972-2010	NMP							
Dissolved calcium	1972-2010	Y + S	NA	NA	NA	NA	↓* (p=0.0947)		
Dissolved magnesium	1978-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Water hardness	1972-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Dissolved sodium	1972-2010	Y + S + Y*S	↑ (0.0352)	↑ (0.0097)	↑* (0.0572)	↔ (0.7595)	↑* (0.0572)	S	↔ (p > 0.1)
Dissolved potassium	1972-2010	Y + S + Y*S	↓ (p=0.0002)	↔ (0.5798)	↔ (0.7294)	↔ (0.1401)	↔ (0.7317)	S	↔ (p > 0.1)
Dissolved sulphate	1972-2010	Y + S	NA	NA	NA	NA	↑ (p=0.0011)		
Dissolved ammonia	1993-2010	NMP							
Total phosphorus	1974-2010	S	NA	NA	NA	NA	↔ (p > 0.1)	S	↔ (p > 0.1)
Dissolved phosphorus	1978-2004	Y + S + Y*S	↑ (p=0.005)	↔ (p=0.3113)	↔ (p=0.3408)	↑ (p=0.018)	↔ (p=0.3408)		
Dissolved organic carbon	1978-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Particulate organic carbon	1978-2010	S	NA	NA	NA	NA	↔ (p > 0.1)	S	↔ (p > 0.1)/↑ (p<0.1) ☝
Total aluminum	1993-2010	Y + S + Y*S	↔ (p=0.4347)	↓* (p=0.0839)	↔ (p=0.5229)	↔ (p=0.5983)	↔ (p=0.5389)		
Total chromium	1993-2010	Y + S + Y*S	↔ (p=0.7019)	↓ (p=0.0362)	↔ (p=0.5418)	↔ (p=0.2609)	↔ (p=0.5161)		
Total cobalt	1980-2010	NA	NA	NA	NA	NA	NA		
Total copper	1980-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Total iron	1972-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Total lead	1980-2010	Y + S + Y*S	↔ (p=0.4828)	↔ (p=0.2896)	↔ (p=0.2432)	NA	↔ (p=0.2408)		
Total manganese	1993-2010	Y + S + Y*S	↔ (p=0.3511)	↔ (p=0.2762)	↔ (p=0.9696)	↔ (p=0.6828)	↔ (p=0.9805)		
Total molybdenum	1993-2010	Y + S + Y*S	↓ (p=0.0314)	↓* (p=0.0866)	↔ (p=0.1313)	↔ (p=0.7343)	↔ (p=0.1435)		
Total nickel	1980-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Total vanadium	1980-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Total zinc	1980-2010	S	NA	NA	NA	NA	↔ (p > 0.1)		
Dissolved arsenic	1978-2010	NA	NA	NA	NA	NA	NA		

☝ Two models fit the particulate organic carbon data: one model revealed a significant trend, while the other model did not. The model with the significant increasing trend is a contending model but was not selected as the final model because it did not fit the data as well as the model with only season as an explanatory variable (Zajdlik, 2011a).

Appendix 7-1: Significant Long Term Temporal Water Quality Trend Results for the Slave River at Fitzgerald (from Zajdlik, 2011a and 2011b). All trends are significant at the 95% confidence level unless otherwise denoted with an asterisk (*). Trends denoted with an asterisk are significant at the 90% confidence level.

		Flow-adjusted trend results (full dataset)					
Parameter	**Period of Record**	**Model**	**spring (p-value)**	**summer (p-value)**	**fall (p-value)**	**winter (p-value)**	**annual (p-value)**
pH	1972-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Specific conductance	1972-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Total dissolved solids	1993-2010	F+ Y	NA	NA	NA	NA	↓ (p=0.0264)
Total suspended solids	1972-2010	F + S	NA	NA	NA	NA	↔ (p > 0.1)
Turbidity	1972-2010	F + Y + S + Y*S	↔ (0.9832)	↔ (0.1522)	↔ (0.2708)	↔ (0.4352)	↔ (0.2663)
Alkalinity	1972-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Dissolved calcium	1972-2010	F + S	NA	NA	NA	NA	↔ (p > 0.1)
Dissolved magnesium	1978-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Water hardness	1972-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Dissolved sodium	1972-2010	F + Y + S	NA	NA	NA	NA	↑ (p=0.0228)
Dissolved potassium	1972-2010	F + S	NA	NA	NA	NA	↔ (p > 0.1)
Dissolved sulphate	1972-2010	F + Y + S + Y*S	↔ (p=0.5022)	↑ (0.0010)	↑* (0.0788)	↑ (0.0165)	↑* (0.0788)
Dissolved ammonia	1993-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Total phosphorus	1974-2010	F + Y + S	NA	NA	NA	NA	↑ (p=0.0255)
Dissolved phosphorus	1978-2004	F + Y + S + Y*S	↑ < 0.0001	↔ (p=0.9322)	↔ (p=0.3986)	↑ (p=0.0027)	↔ (p=0.4550)
Dissolved organic carbon	1978-2010	F	NA	NA	NA	NA	↔ (p > 0.1)
Particulate organic carbon	1978-2010	F+S	NA	NA	NA	NA	↔ (p > 0.1)
Total aluminum	1993-2010	F+S	NA	NA	NA	NA	↔ (p > 0.1)
Total chromium	1993-2010	F + Y + S + Y*S	↔ (p=0.8329)	↔ (p=0.3242)	↔ (p=0.9860)	↑* (p=0.0529)	↔ (p=0.9752)
Total cobalt	1980-2010	NA	NA	NA	NA	NA	NA
Total copper	1980-2010	F + S	NA	NA	NA	NA	↔ (p > 0.1)
Total iron	1972-2010	F + S	NA	NA	NA	NA	↔ (p > 0.1)
Total lead	1980-2010	NA	NA	NA	NA	NA	NA
Total manganese	1993-2010	F + S + F*S	NA	NA	NA	NA	↔ (p > 0.1)
Total molybdenum	1993-2010	NFE	no flow effect	no flow effect	no flow effect	no flow effect	no flow effect
Total nickel	1980-2010	F+S	NA	NA	NA	NA	↔ (p > 0.1)
Total vanadium	1980-2010	F + Y + S	NA	NA	NA	NA	↔ (p=0.1990)
Total zinc	1980-2010	F+S	NA	NA	NA	NA	↔ (p > 0.1)
Dissolved arsenic	1978-2010	NA	NA	NA	NA	NA	NA

Appendix 7-1: Significant Long Term Temporal Water Quality Trend Results for the Slave River at Fitzgerald (from Zajdlik, 2011a and 2011b). All trends are significant at the 95% confidence level unless otherwise denoted with an asterisk (*). Trends denoted with an asterisk are significant at the 90% confidence level.

MODEL	
S:	no interaction, no temporal trend. Therefore no p-value for year is provided or season within year is provided.
NMP:	No model possible, none of the terms described a significant proportion of the variability. Consequently, no model was fit.
NFE:	No flow effect.
F + S:	model includes only flow and season (similar to season only model), no interaction, no temporal trend. Therefore no p-value for year is provided.
Y + S:	model includes only year and season (similar to season only model), no interaction. Therefore there will be only 1 p-value and this is for year.
F + Y:	model includes only flow and year (similar to season only model), no interaction. Therefore there will be only 1 p-value and this is for year.
Y + S + Y*S:	model includes year, season and year * season interaction. Therfore there will be a p-value for each season that tests for a trend within season.
F + Y + S + Y*S:	model includes flow, year, season and year * season interaction. Therefore there will be a p-value that accounts for flow for each season and that tests for a trend within season.
F + Y + S:	model includes flow, year and season . Therefore there will be a p-value that accounts for an overall trend, only.
F:	model includes flow only . Therefore there will be no p-value for trend or trend within season.
F + S + F*S:	model includes flow, season and flow * season interaction . Therefore there will be no p-value that accounts for a trend or within-season trend.

Note: Due to data quallity criteria not being met, total cobalt and dissolved arsenic (non-flow adjusted and flow adjusted) as well as total lead (flow adjusted) were not assessed for long term trends.

Appendix 8-1: Physical parameters, major ions, nutrients and metals in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at Fort Smith, NWT, 1990-2007

Parameter	Units	Missing Sample Dates	# of Samples	# of Non-Detects	Detection Limits	Mean	Median	Minimum	Maximum
Physicals									
pH	pH units		6	0		7.66	7.97	5.99	8.14
Specific Conductance	µS/cm		6	0		212	217	157	243
Turbidity	NTU		6	0		12.75	4.60	1.97	31.60
Total Suspended Solids	mg/L		6	1	3	3.6	3.5	3.0	4.3
Total Dissolved Solids	mg/L		6	0		150	136	100	254
Major Ions									
Calcium Total	mg/L		6	0		26.4	25.7	19.0	32.1
Magnesium Total	mg/L		6	0		6.2	6.2	4.1	7.5
Sodium Total	mg/L		6	0		5.8	5.5	5.1	6.9
Potassium Total	mg/L		6	0		0.99	0.74	0.69	1.63
Chloride Total	mg/L		6	0		5.03	4.96	2.10	7.21
Sulphate Total	mg/L		6	0		19	19	17	22
Hardness Total (CALCD.) CACO3	mg/L		6	0		92	90	64	111
Alkalinity Total CACO3	mg/L		6	0		84.9	82.8	58.5	123.0
Nutrients									
Nitrate/Nitrite	mg/L	6/9/2003	5	1	0.008	0.054	0.063	0.008	0.104
Ammonia Total	mg/L		6	2	0.003-0.005	0.011	0.007	0.003	0.026
Phosphorus Total	mg/L		6	1	0.004	0.021	0.011	0.006	0.055
Metals									
Aluminum Total	µg/L	9/22/1994, 3/7/1995, 2/20/2001	3	0		441	320	46	957
Arsenic Total	µg/L	6/29/2003	5	2	0.2	0.9	0.7	0.3	2.1
Cadmium Total	µg/L		6	5	0.1	0.1	0.1	0.1	0.3
Chromium Total	µg/L		6	3	0.2-0.3	10.4	1.3	0.2	56.1
Cobalt Total	µg/L		6	3	0.1	0.4	0.2	0.1	1.0
Copper Total	µg/L		6	1	0.3	2.1	1.8	0.7	4.1
Iron Total	µg/L		6	0		478	165	0	1660
Lead Total	µg/L	3/6/2007	5	1	0.1	0.8	0.7	0.3	1.4
Manganese Total	µg/L	2/20/2001	5	0		9.1	7.0	5.2	15.7
Nickel Total	µg/L		6	1	0.1	1.9	1.2	0.9	3.9
Zinc Total	µg/L		6	5	0.5-10	8	10	1	10

Notes: Data from the centrifugate samples collected on the following dates are included in the above table (9/22/1994, 3/7/1995, 2/20/2001, 6/9/2003, 3/6/2007, 5/29/2007). Missing sample dates are noted. This table was produced using the mean of the triplicate analyses. The means were calculated considering the less than values to be at detection limit (<0.5 was considered 0.5), when one of the triplicates was above detection.

Appendix 8-2: EXTRACTABLE ORGANOCHLORINES and CHLORINATED PHENOLICS (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at FORT SMITH, NWT (2000-2012)

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	CCME GUIDELINES***		COMMENTS
							Drinking Water*	Freshwater Aquatic Life	
EOCL									
EOCL	00	1	1	30-30	<30	<30			**All non-detects
PHENOLS									
Phenol	00,06	2	2	0.2-1	<0.2	<1			**All non-detects
2-Chlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1	7.0*		**All non-detects
3-Chlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5	7.0*		**All non-detects
4-Chlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1	7.0*		**All non-detects
2,3-Dichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5	0.2*		**All non-detects
2,4-Dichlorophenol	03,06,07,07,10	5	5	0.0004-0.01	<0.0004	<0.01	0.2*		**All non-detects
2,4 & 2,5-Dichlorophenol	00,01,06	3	3	0.008-0.5	<0.008	<0.5	0.2*		**All non-detects
2,6-Dichlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1	0.2*		**All non-detects
3,4-Dichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5	0.2*		**All non-detects
3,5-Dichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5	0.2*		**All non-detects
2,3,4-Trichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		18	**All non-detects
2,3,5-Trichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		18	**All non-detects
2,3,6-Trichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		18	**All non-detects
2,4,5-Trichlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1		18	**All non-detects
2,4,6-Trichlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1		18	**All non-detects
3,4,5-Trichlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		18	**All non-detects
2,3,4,5-Tetrachlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		1.0	**All non-detects
2,3,4,6-Tetrachlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1		1.0	**All non-detects
2,3,5,6-Tetrachlorophenol	00,06	2	2	0.1-0.5	<0.1	<0.5		1.0	**All non-detects
Pentachlorophenol	00,01,03,06,07,07,10	7	7	0.0004-0.1	<0.0004	<0.1		0.5	**All non-detects
2,4-Dimethylphenol	00,01,03,06,07,07	6	6	0.008-1	<0.008	<1			**All non-detects
4-Chloro-3-methylphenol	00,01,03,06,07,07	6	6	0.008-0.5	<0.008	<0.5			**All non-detects
2-Nitrophenol	00,01,03,06,07,07	6	6	0.008-1	<0.008	<1			**All non-detects
4-Nitrophenol	00,01,03,06,07,07	6	6	0.008-5	<0.008	<5			**All non-detects
2,4-Dinitrophenol	00,01,03,06,07,07	6	6	0.008-3	<0.008	<3			**All non-detects
4,6-Dinitro-2-methylphenol	00,01,03,06,07,07	6	6	0.008-3	<0.008	<3			**All non-detects
CATECHOLS									
4-Chlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4-Dichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,5-Dichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,6-Dichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
4,5-Dichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4,5-Trichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4,6-Trichlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
Tetrachlorocatechol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects

Appendix 8-2: EXTRACTABLE ORGANOCHLORINES and CHLORINATED PHENOLICS (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at FORT SMITH, NWT (2000-2012)

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	CCME GUIDELINES***		COMMENTS
							Drinking Water*	Freshwater Aquatic Life	
GUAIACOLS									
4-Chloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
5-Chloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
6-Chloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4-Dichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
4,5-Dichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
4,6-Dichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4,5-Trichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
3,4,6-Trichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
4,5,6-Trichloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
Tetrachloroguaiacol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
VERATROLES									
4,5-Dichloroveratrole	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
3,4,5-Trichloroveratrole	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
Tetrachloroveratrole	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
VANILLINS									
5-Chlorovanillin	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
6-Chlorovanillin	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
5,6-Dichlorovanillin	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
SYRINGOLS, SYRINGALDEHYDE, METHOXYBENZENE AND METHYLSULFONES									
4,5,6-Trichlorosyringol	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
2,6-Dichlorosyringaldehyde	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
2-Chlorosyringaldehyde	01,03,06,07,07,10	6	6	0.0008-0.1	<0.0008	<0.1			**All non-detects
Trichloromethoxybenzene	01,03,06,07,07,10	6	6	0.0004-0.1	<0.0004	<0.1			**All non-detects
1,1-Dichlorodimethyl sulfone	01,03,06,07,07,10	6	6	0.004-5	<0.004	<5			**All non-detects
1,1,3-Trichlorodimethyl sulfone	01,03,06,07,07,10	6	6	0.004-5	<0.004	<5			**All non-detects
CRESOLS									
m-Cresol	00,06	2	2	0.2-1	<0.2	<1			**All non-detects
o-Cresol	00,06	2	2	0.2-1	<0.2	<1			**All non-detects
p-Cresol	00,06	2	2	0.2-1	<0.2	<1			**All non-detects

*Values denote the aesthetic objectives
*** Guidelines values are for TOTAL mono-, di-, tri-, tetra-, and pentachlorophenols.
Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010

Appendix 8-3: ORGANOCHLORINE PESTICIDES (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at Fort Smith, NWT, 2000-2010

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	CCME GUIDELINES Freshwater Aquatic Life	COMMENTS
PESTICIDES								
Aldrin	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Alpha-BHC	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Beta-BHC	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Cis-Chlordane	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Dieldrin	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Endosulfan I	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1	0.02	** All non-detects
Endosulfan I & II	00,01,03,07,07	5	5	0.04-0.2	<0.04	<0.2		** All non-detects
Endosulfan II	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Endrin	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
gamma-BHC (Lindane)	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1	0.01	** All non-detects
Heptachlor	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Hexachlorobenzene	01,03	2	2	0.1-1	<0.1	<1		** All non-detects
Methoxychlor	00,01,03,06,07,07	6	6	0.02-0.2	<0.02	<0.2		** All non-detects
Mirex	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Nonachlor	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Oxychlordane	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
p,p'-DDD	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
p,p'-DDE	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
p,p'-DDT	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Pentachlorobenzene	01,03	2	2	0.1-0.1	<0.1	<0.1		** All non-detects
Photomirex	01	1	1	0.1	<0.1	<0.1		** All non-detects
Quintozine (PCNB)	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Trans-Chlordane	00,01,03,06,07,07	6	6	0.02-0.1	<0.02	<0.1		** All non-detects
Toxaphene	01	1	1	1	<1	<1		** All non-detects
HERBICIDES								
2,4,5-T	01,03,06,07,07	5	5	0.002-0.1	<0.002	<0.1		** All non-detects
2,4-D	01,03,06,07,07	5	5	0.002-0.1	<0.002	<0.1	4.0	** All non-detects
MCPA	01,03,06,07,07	5	5	0.002-0.1	<0.002	<0.1	2.6	** All non-detects
Bromoxynil	03,06,07,07	4	4	0.005-0.1	<0.005	<0.1	5.0	** All non-detects
Clopyralid	03,06,07,07	4	4	0.005-0.1	<0.005	<0.1		** All non-detects
Dicamba	03,06,07,07	4	4	0.005-0.1	<0.005	<0.1	10	** All non-detects
Diclofop-methyl	03,06,07,07	4	4	0.005-0.1	<0.005	<0.1	6.1	** All non-detects
Fenoprop (Silvex)	03	1	1	0.005	<0.005	<0.005		** All non-detects
Fluazifop-p-butyl	06,07,07	3	3	0.02-0.1	<0.02	<0.1		** All non-detects
Mecoprop	03,06,07,07	4	4	0.005-0.1	<0.005	<0.1		** All non-detects
Picloram	03,06,07,07	4	4	0.02-0.1	<0.02	<0.1	29	** All non-detects
Triallate	01,03,06,07,07	5	5	0.002-0.1	<0.002	<0.1	0.24	** All non-detects
Triclopyr	06,07,07	3	3	0.02-0.1	<0.02	<0.1		** All non-detects

Appendix 8-3: ORGANOCHLORINE PESTICIDES (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at Fort Smith, NWT, 2000-2010

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	CCME GUIDELINES	COMMENTS
							Freshwater Aquatic Life	
Trifluralin	01,03,06,07,07	5	5	0.002-0.1	<0.002	<0.1	0.2	** All non-detects
				PCBs				
Aroclor 1016	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1221	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1232	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1242	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1248	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1254	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1260	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1262	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Aroclor 1268	06,07,07	3	3	0.01-0.01	<0.01	<0.01		** All non-detects
Total PCBs	01,06	2	2	0.05-1	<0.05	<1		** All non-detects

Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010

Appendix 8-4: POLYCYCLIC AROMATIC HYDROCARBONS (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at Fort Smith, NWT, 2000-2010

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	GUIDELINES CCME Freshwater Aquatic Life	COMMENTS
Acenaphthene	00,01,03,06,07,07,10	7	7	0.001-0.01	<0.001	<0.01	5.8	**All non-detects
Acenaphthylene	00,01,03,06,07,07,10	7	7	0.001-0.01	<0.001	<0.01		**All non-detects
Anthracene	01,03,06,07,07,10	5	5	0.001-0.01	<0.001	<0.01	0.012	**All non-detects
Benzo(a)anthracene/Chrysene	00,01,03,06,07,07	6	6	0.003-0.01	<0.003	<0.01		**All non-detects
Chrysene	01,03,06,07,07,10	6	6	0.001-0.01	<0.001	<0.01		**All non-detects
Benzo(a)anthracene	07,10	2	0	0.001	0.001	0.001	0.018	-
Dibenzo (a,h) anthracene	00,01,03,06,07,07	6	6	0.001-0.01	<0.001	<0.01		**All non-detects
Benzo(b or k)fluoranthene	00,01,03,06,07,07	6	6	0.003-0.01	<0.003	<0.01		**All non-detects
Benzo (b) fluoranthene	01,03,06,07,07	5	5	0.001-0.01	<0.001	<0.01		**All non-detects
Benzo (k) fluoranthene	07,10	2	2	0.001	<0.001	<0.001		**All non-detects
Benzo(b&j)fluoranthene	10	1	1	0.001	<0.001	<0.001		**All non-detects
Benzo(ghi)perylene	00,01,03,06,07,07,10	7	7	0.001-0.01	<0.001	<0.01		**All non-detects
Benzo (a) pyrene	00,01,03,06,07,07,10	7	7	0.001-0.01	<0.001	<0.01	0.015	**All non-detects
Benzo(e)pyrene	10	1	1	0.001	<0.001	<0.001		**All non-detects
Fluoranthene	00,01,03,06,07,07,10	7	5	0.001-0.01	0.001	<0.01	0.04	-
Fluorene	00,01,03,06,07,10	6	4	0.001-0.01	0.001	<0.01	3	-
Indeno(1,2,3-c,d)pyrene	00,01,03,06,07,07,10	7	7	0.001-0.01	<0.001	<0.01		**All non-detects
Naphthalene	00,01,03,06,07,07,10	7	5	0.001-0.01	0.002	<0.01	1.1	-
Perylene	01,07,10	3	2	0.001-0.01	0.001	<0.01		-
Phenanthrene	01,03,06,07,07,10	6	4	0.001-0.01	0.001	<0.01	0.4	-
Phenanthrene/Anthracene	00,07	2	2	0.005-0.01	<0.005	<0.01		**All non-detects
Pyrene	00,01,03,06,07,07,10	7	5	0.001-0.01	0.001	<0.01	0.025	-
Biphenyl	07,10	2	0	0.001	0.001	0.001		-
Dibenzothiophene	07	1	1	0.001	<0.001	<0.001		**All non-detects
Acridine	10	1	1	0.001	<0.001	<0.001	4.4	**All non-detects
Quinoline	10	1	1	0.001	<0.001	<0.001	3.4	**All non-detects
Retene	10	1	0	0.001	0.001	0.001		
C1 Acenaphthenes	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Benz(a)Anthracenes/Chrysenes	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Benzofluoranthenes/Benzopyrenes	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Biphenyls	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Dibenzothiophenes	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Fluoranthenes/Pyrenes	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C1 Phenanthrenes/Anthracenes	07,10	2	1	0.004	<0.004	0.00867		-
Methylnaphthalenes	00,01,03,06,07,07	6	6	0.003-0.01	<0.003	<0.01		**All non-detects
1-Methylnaphthalene	07,10	2	0	0.001	0.001	0.003		-

Appendix 8-4: POLYCYCLIC AROMATIC HYDROCARBONS (µg/L) in CENTRIFUGATE WATER samples collected from the SLAVE RIVER at Fort Smith, NWT, 2000-2010

PARAMETER	YEARS OF RECORD	# OF SAMPLES	# OF NON DETECTS	DETECTION LIMITS	MINIMUM	MAXIMUM	GUIDELINES CCME Freshwater Aquatic Life	COMMENTS
2-Methyl naphthalene	07,10	2	1	0.0001-0.005	0.001	<0.005		-
C1 fluorene	07	1	1	0.004	<0.004	<0.004		**All non-detects
C2 Benzofluoranthenes/Benzopyrenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C2 Fluoranthenes/Pyrenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C2 Fluorenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C2 sub'd B(a)A/chrysene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C2 sub'd B(b&k)F/B(a)P	07	1	1	0.004	<0.004	<0.004		**All non-detects
C2 sub'd biphenyl	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C2 sub'd dibenzothiophene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C2 sub'd fluorene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C2 sub'd naphthalene	07,10	2	1	0.004	<0.004	0.00567		-
C2 sub'd phenanthrene/anth.	07,10	2	1	0.004	<0.004	0.00733		-
C3 Benzanthracenes/Chrysenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C3 Fluoranthenes/Pyrenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C3 Fluorenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C3 sub'd dibenzothiophene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C3 sub'd naphthalene	07,10	2	0	0.004	0.004	0.00667		-
C3 sub'd phenanthrene/anth.	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C4 Benzanthracenes/Chrysenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C4 Fluoranthenes/Pyrenes	10	1	1	0.004	<0.004	<0.004		**All non-detects
C4 sub'd dibenzothiophene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C4 sub'd naphthalene	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
C4 sub'd phenanthrene/anth.	07,10	2	2	0.004	<0.004	<0.004		**All non-detects
Naphthenic Acids	10	1	1	1000	<1000	<1000		**All non-detects
Total PAH	07	1	0	-	0.0117	0.0117		-

NOTE: Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010.

Appendix 8-5

Chlorinated Phenolics

Phenolics such as phenols, guaiacols, and syringols are commonly produced by pulp mills and may become chlorinated during the bleaching process with elemental chlorine (Carey *et al*., 1997). As chlorophenols consist of both polar and non-polar portions, they are transitioned between hydrophobic and hydrophilic (Woolley *et al*., 2000). The tendency of chlorophenols to dissociate in aqueous solutions increases as the number of chlorine atoms increases (Woolley *et al*., 2000). Many chlorophenolics are water soluble and are ionised at ambient pH, properties which do not favour partitioning to sediments (Carey *et al*., 1997). Methylation of chlorophenols by microorganisms however, can produce anisoles, guaiacols, catechols, and veratroles, which tend to be more hydrophobic and have higher bioaccumulation potential than their phenolic analogues (Neilsen *et al*., 1983; 1984). Generally, the lipophilicity and toxicity of chlorinated phenolics increases with increasing chlorine substitution (CCREM, 1987).

Polycyclic Aromatic Hydrocarbons - Parent PAH Compounds

As the number of rings increase, there are rapid declines in natural abundance, solubility in water, volatility and rate of microbial degradation. Heavier PAHs are relatively immobile because of their larger molecular volumes and extremely low volatility and solubility (Eisler, 1987). The tendency of these compounds to partition into the solid phase, and to bioaccumulate in organisms, is also greatest for the larger, multi-ring compounds (Southworth, 1979; MacKay *et al*., 1980; Herbes, 1981).

Polycyclic Aromatic Hydrocarbons - Alkylated PAHs

Alkylated PAHs are another class of PAH compounds that were recently added to the monitoring program at Fort Smith. PAH compounds containing a straight carbon side chain are referred to as alkylated PAHs (AXYS website, 2010a). The alkyl groups generally have one to four saturated carbon atoms and thus can produce many different structural isomers and homologs for each aromatic hydrocarbon family (Irwin et al., 1997). The most abundant aromatic hydrocarbon families have two or three fused rings with one to four carbon atom alkyl group substitutions (denoted C1-, C2-, C3-, and C4). The naming convention for reporting total C1-, C2-, C3-, or C4- alkyl homologues is C1-, C2-, C3-, or C4- followed by a PAH name. For example, C1- naphthalene reported concentrations represent the total concentration of all C1 naphthalenes. C1-compounds differ from C2- compounds in that the former would have one carbon group attached, while the latter would have two (Irwin et al., 1997).

Alkylated PAHs are more abundant, persist for a longer time, and are sometimes more toxic than the parent PAH compounds (Irwin et al., 1997). They also tend to bioaccumulate to a greater degree. Within an aromatic series, acute toxicity increases with increasing alkyl substitution on the aromatic nucleus (Irwin et al., 1997). For example, there is an increase in toxicity as alkylation of the naphthalene structure increases. Alkylation also causes regular changes to the biological activity of the compound and increases lipophilicity, which often appears as increased absorption. Alkyl substitution usually decreases water solubility (Irwin et al., 1997) in fresh petroleum products. Alkyl PAHs are often more abundant in fresh petroleum products than their parent compounds, and the proportion of alkyl PAHs to parent compound PAHs increases as the oil ages (Irwin et al., 1997). The parent compound naphthalene degrades before the alkyl naphthalenes, therefore as petroleum products age, the percentage of alkyl PAHs vs. parent PAHs increases (Irwin et al., 1997). Therefore it is very important to analyze oil spill samples for alkyl PAHs any time that biological effects are a concern.

As mentioned, PAH compounds are associated with the effluents from hydrocarbon developments, including oil sands and mining operations. Samples from the Suncor process effluent collected from 1989 to 1994 were found to contain a mixture of alkylated PAHs as well 164 as naphthenic acids13 (Carey et al., 1997). Generally, petrogenic PAHs are characterized by alkylated forms of their parent PAHs (Timoney, 2007). Further, low temperature change processes (diagenesis) of naturally occurring PAHs in bituminous rocks such as coal and crude oil deposits favors the formation of alkylated PAHs over the parent PAH compounds (NRCC, 1983). Petroleum PAHs have abundant alkyl group substitution on their ring structures (Irwin et al., 1997) and crude oils contain primarily the alkyl homologs of aromatic compounds and relatively small quantities of the unsubstituted "parent" aromatic structures. Generally, therefore, PAHs and the alkylated homologs are important target analytes when assessing impacts to the environment from oil spills and tailings leaks (Irwin et al., 1997).

Polychlorinated Biphenyls (PCBs)

PCBs were typically synthesized by chlorinating biphenyl with chlorine gas, substituting chlorine atoms for hydrogen atoms on the biphenyl molecule. Individual chlorinated biphenyl molecules are called congeners. Individual congeners are identified by the number and position of the chlorine atoms around the biphenyl rings (Columbia Analytical Services website, 2010). There are 209 possible PCB congeners ranging from the mono-substituted 2-chlorobiphenyl to the fully-substituted decachlorobiphenyl (Cook, 1972; Hutzinger et al., 1974). Varying the conditions of the chlorination process produced different mixtures of congeners with different physical properties. These mixtures were sold as products called Aroclors followed by a 4 digit number (Columbia Analytical Services website, 2010). The first two digits generally refer to the number of carbon atoms in the biphenyl skeleton (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture. Thus, Aroclor 1260 has 12 carbon atoms and contains 60% chlorine by mass. An exception is Aroclor 1016, which also has 12 carbon atoms, but has 42% chlorine by mass. Different Aroclors were used at different times and for different applications (Columbia Analytical Services website, 2010).

Appendix 9-1: EXTRACTABLE ORGANOCHLORINES (µg/kg) and CHLORINATED PHENOLICS (µg/kg) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	Comments
EOCL	00	1	0	300	2200	2200	
2-Chlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
3-Chlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
4-Chlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
2,3-Dichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,4 & 2,5-Dichlorophenol	00,01,06,06	4	4	2-100	<2	<100	** All Non-detects
2,4-Dichlorophenol	01,03,06,06,07,07,10	7	7	0.4-10	<0.4	<10	** All Non-detects
2,6-Dichlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
3,4-Dichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
3,5-Dichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,3,4-Trichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,3,5-Trichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,3,6-Trichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,4,5-Trichlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
2,4,6-Trichlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
3,4,5-Trichlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,3,4,5-Tetrachlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
2,3,4,6-Tetrachlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
2,3,5,6-Tetrachlorophenol	00,06,06	3	3	5-50	<5	<50	** All Non-detects
Pentachlorophenol	00,01,01,03,06,06,07,07,10	9	9	0.4-50	<0.4	<50	** All Non-detects
Phenol	00,06,06,10	4	2	10-50	10	<50	-
2,4-Dimethylphenol	00,01,01,03,06,06,07,07	8	8	2-100	<2	<100	** All Non-detects
4-Chloro-3-methylphenol	00,01,01,03,06,06,07,07	8	8	2-50	<2	<50	** All Non-detects
2-Nitrophenol	00,01,01,03,06,06,07,07	8	8	2-400	<2	<400	** All Non-detects
4-Nitrophenol	00,01,01,03,06,06,07,07	8	8	2-2000	<2	<2000	** All Non-detects
2,4-Dinitrophenol	00,01,01,03,06,06,07,07	8	8	2-2000	<2	<2000	** All Non-detects
4,6-Dinitro-2-methylphenol	00,01,01,03,06,06,07,07	8	8	2-2000	<2	<2000	** All Non-detects
4-Chlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,4-Dichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,5-Dichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,6-Dichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4,5-Dichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects

Appendix 9-1: EXTRACTABLE ORGANOCHLORINES (µg/kg) and CHLORINATED PHENOLICS (µg/kg) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	Comments
3,4,5-Trichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,4,6-Trichlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
Tetrachlorocatechol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4-Chloroguaiacol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
5-Chloroguaiacol	01,01,03,06,07,07,10	7	7	0.4-10	<0.4	<10	** All Non-detects
6-Chloroguaiacol	01,01,03,06,07,07,10	7	7	0.4-10	<0.4	<10	** All Non-detects
3,4-Dichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4,5-Dichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4,6-Dichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,4,5-Trichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
3,4,6-Trichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4,5,6-Trichloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
Tetrachloroguaiacol	01,01,03,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
4,5-Dichloroveratrole	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
3,4,5-Trichloroveratrole	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
Tetrachloroveratrole	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
5-Chlorovanillin	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
6-Chlorovanillin	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
5,6-Dichlorovanillin	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
4,5,6-Trichlorosyringol	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
2-Chlorosyringaldehyde	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
2,6-Dichlorosyringaldehyde	01,01,03,06,06,07,07,10	8	8	0.8-10	<0.8	<10	** All Non-detects
Trichloromethoxybenzene	01,01,03,06,06,07,07,10	8	8	0.4-10	<0.4	<10	** All Non-detects
1,1-Dichlorodimethyl sulfone	01,01,03,06,07,07,10	8	8	2-200	<2	<200	** All Non-detects
1,1,3-Trichlorodimethyl sulfone	01,01,03,06,07,07,10	8	8	2-200	<2	<200	** All Non-detects
m-Cresol	00,06,06	3	3	10-100	<10	<100	** All Non-detects
o-Cresol	00,06,06	3	3	10-100	<10	<100	** All Non-detects
p-Cresol	00,06,06,10	4	1	10-100	90	700	-
Nitrobenzene	10	1	1	20	<20	<20	** All Non-detects

No guidelines are available for chlorinated phenolics in sediment at the present time.

Appendix 9-1: ORGANOCHLORINE PESTICIDES and TOTAL PCBs (µg/kg or µg/kg OC or %) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	CCME Interim Freshwater Sediment Quality Guidelines		Comments
							TEL	PEL	
PESTICIDES									
Hexachlorobenzene	01	1	1	1	<1	<1			** All non-detects
Pentachlorobenzene	01	1	1	1	<1	<1			** All non-detects
Quintozine(PCNB)	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
cis-Chlordane	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Oxychlordane	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	4.50[1]	8.87[1]	** All non-detects
trans-Chlordane	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	4.50[1]	8.87[1]	** All non-detects
p,p'-DDD	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	3.54[2]	8.51[2]	** All non-detects
p,p'-DDE	01	1	1	2	<2	<2	1.42[2]	6.75[2]	** All non-detects
p,p'-DDE	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	1.42[2]	6.75[2]	** All non-detects
o,p'-DDT	01	1	1	1	<1	<1	1.19[2]	4.77[2]	** All non-detects
p,p'-DDT	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	1.19[2]	4.77[2]	** All non-detects
Heptachlor	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Methoxychlor	00,01,01,03,06,06,07,07	8	8	1-10	<1	<10			** All non-detects
Nonachlor	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Ronnel	01	1	1	1	<1	<1			** All non-detects
alpha-BHC	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
beta-BHC	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
gamma-BHC (Lindane)	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	0.94	1.38	** All non-detects
Aldrin	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Dieldrin	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	2.85	6.67	** All non-detects
Endrin	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5	2.67	62.4	** All non-detects
Endosulfan I	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Endosulfan I & II	00,01,01,03,06,06,07,07	8	8	2-10	<2	<10			** All non-detects
Endosulfan II	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Mirex	00,01,01,03,06,06,07,07	8	8	1-5	<1	<5			** All non-detects
Photomirex	01	1	1	1	<1	<1			** All non-detects
Toxaphene	01	1	1	1	<1	<1	0.1	-	** All non-detects
HERBICIDES									
2,4-D	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
2,4,5-T	01,03,06,06,07,07	6	6	1-5	<1	<5			** All non-detects
MCPA	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Clopyralid	03,06,06,07,07	5	5	1-5	<1	<5			** All non-detects
Picloram	01,03,06,06,07,07	6	6	1-5	<1	<5			** All non-detects
Triclopyr	06,06,07,07	4	4	1-5	<1	<5			** All non-detects

Appendix 9-1: ORGANOCHLORINE PESTICIDES and TOTAL PCBs (µg/kg or µg/kg OC or %) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	CCME Interim Freshwater Sediment Quality Guidelines		Comments
							TEL	PEL	
Bromoxynil	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Dicamba	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Diclofop-methyl	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Fenoprop (Silvex)	03	1	1	5	<5	<5			** All non-detects
Fluazifop-p-butyl	06,06,07,07	4	4	1-5	<1	<5			** All non-detects
Mecoprop	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Triallate	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
Trifluralin	01,01,03,06,06,07,07	7	7	1-5	<1	<5			** All non-detects
PCBs									
All Aroclors	00,01	2	2	50-50	<50	<50			** All non-detects
Aroclor 1016	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1221	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1232	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1242	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1248	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1254	06,06,07,10	4	4	2-10	<2	<10	60	340	** All non-detects
Aroclor 1260	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1262	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Aroclor 1268	06,06,07,10	4	4	2-10	<2	<10			** All non-detects
Total Mono-TriCB	07	1	0	-	0.03	0.03			-
Total TetraCB	07	1	0	-	0.055	0.055			-
Total PentaCB	07	1	0	-	0.012	0.012			-
Total HexaCB	07	1	0	-	0.011	0.011			-
Total HeptaCB	07	1	1	0.005	<0.005	<0.005			** All non-detects
Total OctaCB	07	1	1	0.005	<0.005	<0.005			** All non-detects
Total Nona/DecaCB	07	1	1	0.005	<0.005	<0.005			** All non-detects
Total PCBs	01,03,07,10	4	3	0.01-50	0.11	<50	34.1	277	-

TEL: Threshold Effect Level

PEL: Probable effect level

[1] Guideline is for Chlordane

[2] Guideline is for total DDD, total DDE or total DDT

Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010

Appendix 9-1: POLYCYCLIC AROMATIC HYDROCARBONS (µg/kg) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	CCME Interim Freshwater Sediment Quality Guidelines		Ontario Sediment Quality Guidelines		Comments
							TEL	PEL	LEL	SEL	
Acenaphthene	00,01,01,03,06,06,07,07,10	9	6	1-10	2	10	6.71	88.9			-
Acenaphthylene	00,01,01,03,06,06,07,07,10	9	8	1-10	<1	<10	5.87	128			-
Anthracene	01,01,03,06,06,07,07,10	8	6	1-10	<1	10	46.9	245			-
Benzo(a)anthracene/Chrysene	00	1	0	10	30	30					-
Benzo(a)anthracene	01,01,03,06,06,07,07,10	8	3	1-10	5	20	31.7	385			-
Chrysene	01,01,03,06,06,07,07,10	8	0	1-10	7	50	57.1	862			-
Dibenzo(a,h)anthracene	00,01,01,03,06,06,07,07,10	9	6	1-10	4	10	6.22	135			-
Benzo(b or k)fluoranthene	00	1	0	20	10	10					-
Benzo(b)fluoranthene	01,01,03,06,06,07,07	7	2	3-10	<10	33					-
Benzo(k)fluoranthene	01,01,03,06,06,07,07,10	8	6	3-10	3	10			240	1340[1]	-
Benzo(b+k)fluoranthene	07	1	0	3	32	32					-
Benzo(b&j)fluoranthene	10	1	0	1	20	20					-
Benzo(ghi)perylene	00,01,01,03,06,06,07,07,10	9	1	1-10	8	40					-
Benzo(a)pyrene	00,01,01,03,06,06,07,07,10	9	5	1-10	<6	10.5	31.9	782			-
Benzo(e)pyrene	10	1	0	1	16	16					-
Fluoranthene	00,01,01,03,06,06,07,07,10	9	2	1-10	8	20	111	2355			-
Fluorene	00,01,01,03,06,06,07,07,10	9	4	1-10	<6	20	21.2	144			-
Indeno(1,2,3-c,d)pyrene	00,01,01,03,06,06,07,07,10	9	5	1-10	<6	10			200	320[1]	-
Naphthalene	00,01,01,03,06,06,07,07,10	9	0	3-10	10	50	34.6	391			-
Perylene	01,07	3	1	1-10	<81	160					-
Phenanthrene	01,01,03,06,06,07,07,10	8	0	1-10	28	100	41.9	515			-
Phenanthrene/Anthracene	00	1	0	10	30	30					-
Pyrene	00,01,01,03,06,06,07,07,10	9	1	1-10	<10	40	53.0	875			-
Biphenyl	07,10	2	0	1-3	10	20					-
Dibenzothiophene	07,10	2	0	1-3	6	11					-
Acridine	10	1	1	1	<1	<1					** All non-detects
Quinoline	10	1	1	1	<1	<1					** All non-detects
Retene	10	1	0	1	60	60					-
C1 Acenaphthenes	07,10	2	1	4-12	<4	20					-
C1 Benz(a)Anthracenes/Chrysenes	07,10	2	0	4-12	61	70					-
C1 Benzofluoranthenes/Benzophyrenes	07,10	2	0	4-12	43	100					-
C1 Biphenyls	07,10	2	0	4-12	23	40					-
C1 Dibenzothiophenes	07,10	2	0	4-12	17	30					-
C1 Fluoranthenes/Pyrenes	07,10	2	0	4-12	44	70					-
C1 Fluorenes	07,10	2	0	4-12	15	30					-
C1 Phenanthrenes/Anthracenes	07,10	2	0	4-12	108	200					-
Methylnaphthalenes	00,01,01,03,06,06,07,07,10	9	0	1-10	25	180					-
2-Methyl naphthalene	07, 10	2	0	1-6	31	33	20.2	201			-

Appendix 9-1: POLYCYCLIC AROMATIC HYDROCARBONS (µg/kg) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	CCME Interim Freshwater Sediment Quality Guidelines		Ontario Sediment Quality Guidelines		Comments
							TEL	PEL	LEL	SEL	
C2 Benzofluoranthenes/Benzophyrenes	10	1	0	4	29	29					-
C2 Fluoranthenes/Pyrenes	10	1	0	4	59	59					-
C2 sub'd B(a)A/chrysene	07,10	2	0	4-12	60	68					-
C2 sub'd B(b&k)F/B(a)P	07	1	0	12	50	50					-
C2 sub'd biphenyl	07,10	2	0	4-12	16	30					-
C2 sub'd dibenzothiophene	07,10	2	0	4-12	27	40					-
C2 sub'd fluorene	07,10	2	0	4-12	27	60					-
C2 sub'd naphthalene	07,10	2	0	4-12	121	250					-
C2 sub'd phenanthrene/anth.	07,10	2	0	4-12	113	160					-
C3 Benzanthracenes/Chrysenes	10	1	0	4	32	32					-
C3 Fluoranthenes/Pyrenes	10	1	0	4	56	56					-
C3 Fluorenes	10	1	0	4	35	35					-
C3 sub'd dibenzothiophene	07,10	2	0	4-12	34	40					-
C3 sub'd naphthalene	07,10	2	0	4-12	97	170					-
C3 sub'd phenanthrene/anth.	07,10	2	0	4-12	84	120					-
C4 Benzanthracenes/Chrysenes	10	1	0	4	11	11					-
C4 Fluoranthenes/Pyrenes	10	1	0	4	48	48					-
C4 sub'd dibenzothiophene	07,10	2	0	4-12	10	41					-
C4 sub'd naphthalene	07,10	2	0	4-12	64	120					-
C4 sub'd phenanthrene/anth.	07,10	2	0	4-12	120	164					-
Naphthenic Acids	10	1	1	5000	<5000	<5000					** All non-detects
Total PAH	01,01,03,06,06,07,07	7	0	-	125	300	4000				-

TEL: Threshold Effect Level

PEL: Probable effect level

[1] Need to convert bulk sediment values by multiplying by TOC

Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010

Appendix 9-1: DIOXINS AND FURANS (ng/kg /%) in SUSPENDED SEDIMENT samples collected from the Slave River at Fort Smith, NWT, 2000-2010

Parameter	Years of Record	# of Samples	# of Non-Detects	Detection Limits	Minimum	Maximum	Comments
Dioxins							
2,3,7,8-TCDD (Tetrachlorodibenzo-p-dioxin)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.49	<0.1	<0.49	** All non-detects
12378 Pentachlorodibenzo-p-dioxin (P5CDD)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.72	<0.1	<0.72	** All non-detects
1,2,3,4,7,8 Hexachlorodibenzo-p-dioxin (H6CDD)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.88	<0.1	<0.88	** All non-detects
1,2,3,6,7,8 Hexachlorodibenzo-p-dioxin (H6CDD)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.96	<0.1	<0.96	** All non-detects
1,2,3,7,8,9 Hexachlorodibenzo-p-dioxin (H6CDD)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.92	<0.1	<0.92	** All non-detects
1,2,3,4,6,7,8 Heptachlorodibenzo-p-dioxin (H7CDD)	00,01,01,03,06,06,07,07,10	9	1	0.1-1.1	<0.1	1.44	** NDR's: 1
Octachlorodibenzo-p-dioxin (OCDD)	00,01,01,03,06,06,07,07,10	9	0	0.3	3.1	11	** NDR's: 2
Furans							
2,3,7,8-TCDF (Tetrachlorodibenzofuran)	00,01,01,03,06,06,07,07,10	9	8	0.1-0.38	<0.1	<0.38	** EMPC: 1
1,2,3,7,8 Pentachlorodibenzofuran (P5CDF)	00,01,01,03,06,06,07,07,10	9	8	0.1-0.81	<0.1	<0.81	-
2,3,4,7,8 Pentachlorodibenzofuran (P5CDF)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.94	<0.1	<0.94	** All non-detects
1,2,3,4,7,8 Hexachlorodibenzofuran (H6CDF)	00,01,01,03,06,06,07,07,10	9	8	0.1-1.2	<0.1	<1.2	-
1,2,3,6,7,8 Hexachlorodibenzofuran (H6CDF)	00,01,01,03,06,06,07,07,10	9	8	0.1-1.3	<0.1	<1.3	-
1,2,3,7,8,9 Hexachlorodibenzofuran (H6CDF)	00,01,01,03,06,06,07,07,10	9	9	0.1-1.4	<0.1	<1.4	** All non-detects
2,3,4,6,7,8 Hexachlorodibenzofuran (H6CDF)	00,01,01,03,06,06,07,07,10	9	9	0.1-1.1	<0.1	<1.1	** All non-detects
1,2,3,4,6,7,8 Heptachlorodibenzofuran (H7CDF)	00,01,01,03,06,06,07,07,10	9	9	0.1-0.79	<0.1	<0.79	** All non-detects
1,2,3,4,7,8,9 Heptachlorodibenzofuran (H7CDF)	00,01,01,03,06,06,07,07,10	9	9	0.1-1.2	<0.1	<1.2	** All non-detects
Octachlorodibenzofuran (OCDF)	00,01,01,03,06,06,07,07,10	9	7	0.1-1.9	<0.1	<1.9	-
Homologues							
Tetrachlorodibenzo-p-dioxin (TCDD) homologues	00,01,01,03,06,06,07,07,10	9	5	0.1-0.49	<0.1	16	-
Pentachlorodibenzo-p-dioxin (P5CDD) Homologs	00,01,01,03,06,06,07,07,10	9	4	0.1-0.72	<0.1	12	-
Hexachlorodibenzo-p-dioxin (H6CDD) homologues	00,01,01,03,06,06,07,07,10	9	2	0.1-0.92	<0.1	8.8	-
Heptachlorodibenzo-p-dioxin (H7CDD) Homologues	00,01,01,03,06,06,07,07,10	9	3	0.1-1.1	<0.1	1.72	-
Total Polychlorinated Dibenzo-p-dioxin (PCDD) homolgues	00,01,01,03,06,06,07,07,10	9	1	0.1-0.3	<DL	42	no DL provided
Tetrachlorodibenzofuran (TCDF) Homologs	00,01,01,03,06,06,07,07,10	9	8	0.1-0.38	<0.1	<0.38	-
Total Pentachlorodibenzofuran (P5CDF) Homologues	00,01,01,03,06,06,07,07,10	9	8	0.1-0.88	<0.1	<0.88	-
Hexachlorodibenzofuran (H6CDF) homologues	00,01,01,03,06,06,07,07,10	9	8	0.1-1.2	<0.1	<1.2	-
Heptachlorodibenzofuran (H7CDF) homologues	00,01,01,03,06,06,07,07,10	9	9	0.1-1	<0.1	<1	** All non-detects
Total Polychlorinated dibenzofuran (PCDF) homologues	00,01,01,03,06,06,07,07,10	9	6	0.1-0.2	<0.1	0.95	3 DLs not provided
% Moisture	00,01,01,03,06,06,07	7	0	-	2.4	48	-
Total TEQ (ND=0) (NATO Calc)	00,01,01,03,06,06,07,07,10	9	0	-	0	0.06	-
Total TEQ (ND=0.5DL) (NATO Calc)	00,01,01,03,06,06,07,07,10	9	0	-	0.15	1	-
Total TEQ (ND=DL) (NATO Calc)	06,06,07,07,10	5	0	-	0.29	0.36	-

Notes: No guidelines are available for dioxins and furans in sediment at the present time.

NDR - Non Detectable Ratio; EMPC - Estimated Maximum Possible Concentration

Samples were collected on the following dates: 9/11/2000, 2/20/2001, 6/9/2003, 8/29/2006, 3/6/2007, 5/29/2007, 9/28/2010

Appendix 9-2: Dioxins and Furans NATO and WHO toxic equivalency factors for calculating 2,3,7,8-TEQ-TEF

Chlorinated dibenzo-p-dioxins	NATO	WHO 1998 TEF	WHO 2005 TEF
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	0.5	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
OCDD	0.001	0.0001	**0.0003**
Chlorinated dibenzofurans			
2,3,7,8-TCDF	0.1	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,6,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.001	0.0001	**0.0003**
Non-ortho substituted PCBs			
3,3’,4,4’-tetraCB (PCB 77)		0.0001	0.0001
3,4,4’,5-tetraCB (PCB 81)		0.0001	**0.0003**
3,3’,4,4’,5-pentaCB (PCB 126)		0.1	0.1
3,3’,4,4’,5,5’-hexaCB (PCB 169)		0.01	**0.03**
Non-ortho substituted PCBs			
2,3,3’,4,4’-pentaCB (PCB 105)		0.0001	**0.00003**
2,3,4,4’,5-pentaCB (PCB 114)		0.0005	**0.00003**
2,3’,4,4’,5-pentaCB (PCB 118)		0.0001	**0.00003**
2’,3,4,4’,5-pentaCB (PCB 123)		0.0001	**0.00003**
2,3,3’,4,4’,5-hexaCB (PCB 156)		0.0005	**0.00003**
2,3,3’,4,4’,5’-hexaCB (PCB 157)		0.0005	**0.00003**
2,3’,4,4’,5,5’-hexaCB (PCB 167)		0.00001	**0.00003**
2,3,3’,4,4’,5,5’-heptaCB (PCB 189)		0.0001	**0.00003**

Source: Van den Berg et al (2006). Toxicological Sciences, 93: 223-241