LIARD RIVER ENVIRONMENTAL QUALITY MONITORING PROGRAM

SUMMARY REPORT

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Table of Contents

Page

Table of Contents (Continued)

List of Tables

List of Figures

List of Photographs

Acknowledgements

The Liard River Environmental Quality Monitoring Program was a complex undertaking requiring more than three years of effort and co-operation from many dedicated individuals. A list is given below of people who participated in various phases of the study, and while an attempt has been made to include everybody, there are undoubtedly others who contributed to the success of the project in ways large and small. The contributions of everyone are appreciated. Affiliations are given in the list as they were when the people worked on the Program.

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The Liard River Environmental Quality Monitoring Program was implemented and directed by Juanetta Sanderson of the Water Resources Division, Indian and Northern Affairs Canada, Yellowknife. Caroline Lafontaine compiled and verified the data and reviewed the study report. Barry Taylor wrote this report.

Abbreviations and Special Terms

>	Greater than
<	Less than
Acute	Affecting an organism over a relatively short period, usually a few hours to a few days, relative to the length of the live cycle.
Anthropogenic	Produced by humans or human activities.
Benzene	A common, stable organic compound consisting of six carbon atoms, bonded into a hexagonal ring. Benzene is a component of gasoline. Two or more benzene rings may be bound together in various ways and are the foundation of a great many natural organic compounds.
Bile	A solution of chemicals that aid digestion, produced by the liver and stored and concentrated in the gall bladder. Bile is released into the intestines of fish through the bile duct, and is the principal route by which the liver removes water-soluble contaminants from the body.
Bioaccumulation	The uptake of contaminants into living tissues at concentrations greater than those in the surrounding environment.
Bioavailability	The degree to which a substance in the environment is in a chemical or physical form in which it may be taken up by organisms and incorporated into their tissues. Generally, the bioavailability of substances in solution is much greater than that of substances attached to particles.
Biomagnification	The accumulation of contaminants in fish or other predatory organisms through the food they eat.
Biota	Living organisms generally; e.g., “aquatic biota” refers to all species that live in water.

Carcinogenic	Describes a chemical that causes tumours.
CCREM	Canadian Council of Resource and Environment Ministers
Chronic	Affecting an organism over a long period relative to the length of the life cycle, usually months or years.
Centrifuge	A machine that spins water samples at very high speed to separate water from suspended sediments.
Centrifugate Water	River water from which suspended sediments have been removed by passage through a centrifuge
Contaminant	Any substance that accumulates in an ecosystem from outside sources and which is harmful to humans or aquatic life at low concentrations.
DDT	Dichlorodiphenyltrichloroethane, an insecticide
Detection Limit	The lowest concentration of a substance that an instrument or analytical method can measure reliably.
DIAND	Department of Indian Affairs and Northern Development
Ecosystem	A distinct unit of the landscape, such as a river, forest or lake, together with all the interacting plants and animals that live there.
Effective Concentration	The lowest concentration of a substance that has measurable biological effects on living organisms
Enzyme	Any of a great number of complex organic chemicals produced by living cells that perform all metabolic processes.
Hydrological Cycle	The annual cycle of high river flow in spring, declining to low flow in fall and winter, that rivers pass through each year
Hydrophobic	Describes substances that do not dissolved in water, and which tend to migrate into other materials, especially sediments and animal or plant tissues.
Ion	A molecule or element that carries a charge when dissolved in water. Cations carry a positive charge. Anions carry a negative charge.
Lipophilic	Describes substances that tend to accumulate in fats, including animal tissues
N	Nitrogen
Non-Detect	A concentration of a substance so low that it cannot be measured
NWT	Northwest Territories
OMOE	Ontario Ministry of Environment
Organic	Refers to chemical compounds composed mostly of carbon and hydrogen, sometimes with oxygen and smaller amounts of other elements
P	Phosphorus

PAH	Polyaromatic hydrocarbons, natural organic chemicals found in petroleum
Parameter	Any contaminant or other aspect of the aquatic ecosystem that can be measured. Suspended sediments, PCBs, and water temperature are all parameters.
PCB	Polychlorinated biphenyl
Suspended Sediments	Particles of sand, silt and clay suspended in the water column and carried along by the current. Also called Total Suspended Solids (TSS) and Nonfilterable Residue (FR)
TCDD	Tetrachlorodibenzo-*p*-dioxin
TDS	Total Dissolved Solids, the mass of salts carried in solution in river water. Also called Filterable Residue (FR)
Toxicity	The capacity of a substance to cause harm to an exposed organism, such as slowed growth, reduced reproduction, or death. Acute toxicity occurs quickly and is usually fatal. Chronic toxicity occurs over a longer period, and usually causes more subtle effects such as stunted growth
Volatility	The rate at which a substance evaporates when exposed to the air. Gasoline is an example of a highly volatile chemical.

The Liard River Environmental Quality Monitoring Program

The Liard River Environmental Quality Monitoring Program was a comprehensive sampling program measuring the current condition of the Liard River at the boundary between British Columbia and the Northwest Territories. The Liard River Program measured important contaminants in water, suspended sediments and fish over a three-year period. The purpose of the Program was to assess the present status of the river, discover any hazards to human health or the aquatic environment, and to define a solid baseline to see if conditions change in the future.

The Liard River, a major tributary of the Mackenzie River, arises in the Pelly Mountains of southern Yukon and flows southeast through a broad plain into British Columbia (see Figure 1). At Nelson Forks, the river is joined by the Fort Nelson River, and swings abruptly northward, crossing the 60th parallel into the Northwest Territories near the intersection of British Columbia, Yukon and NWT. The river then continues northward to eventually join the north-flowing Mackenzie River at Fort Simpson. The Liard is a big river; at Fort Liard, just north of the NWT boundary, average river flow is almost 2000 m^3/s.

Most of the Liard River basin outside of the mountains is northern boreal forest or muskeg. Population density in the basin is low and so far there is little intense industrial development. However, there are rich mineral deposits in the headwaters, forestry is an important industry in British Columbia and Alberta, and oil and gas extraction is beginning in the basin. Construction of hydroelectric reservoirs on the upper Liard River has been contemplated (see Photographs 1 to 6). These developments could degrade environmental quality in the Liard River, particularly by adding contaminants to water or sediments, which may accumulate in fish or other species. The Liard River Environmental Quality Monitoring Program assessed the status of the Liard River at the NWT boundary by measuring concentrations of important pollutants in water, in sediment particles suspended in the water column, and in resident fish. The Liard River Program was a companion to a larger monitoring program on the Slave River, and shared many of its objectives and features.

The large quantity of technical data produced by the Liard River Program has been digested and interpreted in a final Study Report and a series of data appendices that are available from the Department of Indian Affairs and Northern Development in Yellowknife. This Summary Report presents the main findings of the Program in a concise format and provides an integrated summary of the status of the Liard River. A list of special terms and abbreviations is provided to help clarify technical terms. The interested reader is encouraged to consult the Study Report for details omitted here.

Participants in the Liard River Program

The Liard River program was a large and complicated undertaking, requiring dedicated contributions from many people. The entire Program was part of the "Action on Water" portion of the federal Arctic Environmental Strategy, and was undertaken and funded by the Water Resources Division, Department of Indian Affairs and Northern Development (DIAND).

DIAND was the lead organization in the Liard River Program. Personnel from the Water Resources Division, led by Ms Juanetta Sanderson were chiefly responsible for designing the Program, carrying out three years of intense and often difficult sampling, and interpreting the resulting data. Other federal and territorial departments assisted with sampling design and field work, and took responsibility for particular aspects of the program that fell within their specialties. In particular, experts in laboratories of the Department of Fisheries and Oceans in Edmonton, Alberta, Winnipeg, Manitoba (Freshwater Institute) and Burlington, Ontario (Canada Centre for Inland Waters) were responsible for measuring many contaminants in fish tissues. Commercial laboratories also performed many of the analyses of trace-level contaminants that required special equipment or methods because of the extremely low concentrations involved.

Development of the Liard River Program

A variety of industrial activities in the upstream part of the Liard River basin, especially mining, logging, oil and gas extraction and construction of big dams could potentially degrade environmental quality of the Liard River in the NWT. The Liard River Environmental Quality Monitoring Program included a large number of samples of water, sediments and fish from the Liard River just north of the NWT boundary. The sampling measured the present condition of the aquatic ecosystem and set a baseline for comparison with future conditions.

Concerns about the possibility of development and industry upstream polluting the rivers of the NWT have been prominent in the public mind for many years. As early as 1983, DIAND (Yellowknife) and the government of the NWT began discussions with the government of Alberta about protecting rivers in the vast Mackenzie River Basin that cross provincial boundaries. The main rivers of concern are the Slave, Hay and Liard rivers, all of which flow through Alberta or British Columbia before entering the Northwest Territories. Transboundary negotiations to protect the Liard River are especially complex because parts of the river basin lie in Yukon, British Columbia and Alberta, as well as the NWT (see Figure 1).

Potential effects of upstream industry on rivers downstream, particularly as related to the subsistence lifestyle, were quickly identified as the single most important issue in transboundary negotiations. Water bodies in the NWT are important as direct sources of drinking water and as habitat for many wildlife species that local people harvest by hunting, fishing or trapping. In particular, domestically harvested fish are vital food sources for people who live off the land. The river has spiritual importance for many people too, as northerners generally have a strong sense of connection with the land.

To ensure that any transboundary water management agreements are based on a sound base of facts, a background assessment of the Liard River basin was undertaken (MacDonald 1993). That report had three objectives: (1) to summarize everything presently known about environmental conditions in the Liard River Basin; (2) to inventory human uses of the river, along with its flora and fauna, to establish what uses needed protection; and (3) to identify present or potential human activities that could pollute or disturb the Liard River as it enters the Northwest Territories. Information for the report was obtained from federal, provincial and territorial agencies, native groups, industry and local residents.

MacDonald (1993) found that the Liard River basin was a healthy and exceptionally diverse ecosystem still largely in its pristine state. The river is used for many purposes, but in-stream uses, especially harvesting of fish and other aquatic or semi-aquatic life, is of top economic and social importance, especially in the NWT. The river supports more than a dozen species of harvestable fish, at least half of which are targets of domestic and sport fishing. To protect these important fish populations, both water flow and water quality must be maintained. Moreover, fish and other aquatic biota tend to be sensitive to changes in environmental conditions. Measures sufficient to protect aquatic life are generally sufficient to protect other water uses in the basin.

A number of present and forthcoming land uses in the Liard River basin have the potential to alter the river. Among the current activities, metals mining, logging, and oil and gas developments in British Columbia are seen as having the greatest potential effect on the Liard River in the NWT (see Photographs 1 to 5). Many of these activities, especially mining and oil and gas extraction, are currently expanding and will probably increase further in the future. Finally, the British Columbia portion of the Liard River has been studied as a potential site for one or more hydroelectric reservoirs (see Photograph 6). Large reservoirs have profound effects on the hydrology, chemistry and ecology of rivers for hundreds of kilometres downstream, and would have major consequences for the Liard River and many of the species it supports.

The basin assessment report (MacDonald 1993), which was distributed to a wide audience, became the basis from which the Liard River Environmental Quality Monitoring Program was developed. Under this Program, a large number of samples were collected from the Liard River just north of the NWT boundary. The sampling measured the present condition of the aquatic ecosystem and set a baseline for comparison with future samples. The various parameters chosen for analysis emphasized those that could potentially be affected by upstream developments. At the same time, the Program provided baseline data on contaminant levels in Liard River fish, water and sediment to ensure that any present hazards were known, and to support transboundary water negotiations.

Collecting and Analysing Water, Sediments and Fish

The Liard River Program used a new "multi-media" or "ecosystem-based" design. Instead of sampling water alone, sampling included suspended sediments, fish, raw water, and water with suspended sediments removed. Water and sediment samples were collected about 10 km upstream from Fort Liard, just north of the NWT/BC boundary. Collections of fish were made over a slightly larger area. The River was sampled for three years.

Grab water samples, containing both water and suspended sediments, were analysed for routine water chemistry and trace metals. A portable centrifuge was used to separate river water and suspended sediments. The sediment-free water was analysed for the same parameters as grab water samples. The sediment samples were analysed for particle size, trace metals, PAH, PCBs, pesticides and toxicity. Five species of fish (walleye, burbot, northern pike, mountain whitefish and longnose sucker) were analysed for metals, PCBs, PAH, dioxins and furans, and activity of detoxifying enzymes. Analysis used muscles, bile, whole-fish or burbot livers, depending upon where a particular contaminant was deemed most likely to accumulate.

The Ecosystem Approach

Currently, rules and criteria to protect a particular water use specify concentrations of chemicals not to be exceeded in water. However, many organic contaminants that are harmful to aquatic life may not be detected by conventional sampling of the water column. In fact, many such contaminants can cause harm to aquatic life or pose a health hazard to people eating fish well before their concentrations in water indicate there is a problem.

Therefore, monitoring water alone was considered insufficient for the protection of the Liard River ecosystem. Contaminants had to be monitored in the environmental compartments (water, sediment, fish) where they could be expected to migrate, accumulate and possibly cause harm. The Liard River Environmental Quality Monitoring Program was designed as a "multi-media" monitoring program. This is a new and evolving field. Suspended sediments, fish, and two types of water samples (raw water and water with suspended sediments removed) were collected and analysed for a wide range of organic and inorganic contaminants. The Program gave special attention to contaminants likely to result from industrial activities upstream from the NWT portion of the basin, particularly metal mining and oil and gas development.

The Liard River Program included measurements of basic physical parameters, dissolved salts, nutrients and metals on raw water samples and on water from which sediments had been removed. Sediments and fish were analysed for metals, pesticides, and two important groups of organic contaminants, polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCBs). Toxicity of sediment extracts to aquatic life was also measured directly. Dioxins and furans, another group of persistent organic chemicals, were also measured in fish. The significance of each of these parameters, and the results from the monitoring program, are discussed below.

Selection of Fish Species

Fish sampling was included as a part of the monitoring program for several reasons. Many of the contaminants of concern are *hydrophobic* and *lipophilic*; that is, they do not dissolve well in water but tend to accumulate in lipids (fats), including those in living organisms. Fish are particularly susceptible to accumulation of these lipophilic substances. Fish have a relatively high content of fatty tissues, and they often feed on other organisms which may themselves contain contaminants. Thus, fish tend to bioaccumulate these pollutants to a greater degree than other organisms. Fish serve as a good signal of contamination in an aquatic environment, and may be the first species to show signs of ill health if contaminant loads are high.

Fish species to be sampled were chosen based on their presence and residency time in the Liard River, their importance as food for humans, their potential to accumulate contaminants, their place in the aquatic food chain, and their degree of sediment exposure. Five common species were selected according to these criteria:

Common Name	**Scientific Name**
burbot	*Lota lota*
mountain whitefish	*Prosopium williamsoni*
walleye	*Stizostedion vitreum vitreum*
northern pike	*Esox lucius*
longnose sucker	*Catostomus catostomus*

Walleye, burbot and longnose sucker are valuable species as food and are used extensively by residents of the Liard River basin. Longnose suckers are used both for people to eat and for dog food. The large liver of burbot is eaten preferentially by the native population, so the health of that species and the quality of that organ are important. Mountain whitefish and northern pike are popular as sportfish and the former species is very abundant in the Liard River. All five selected species are common in the Liard River, and complete most or all of their life cycles within the basin.

In this Program, mesh sizes of capture nets were chosen to catch fish of sizes similar to those caught by local fishers. The sampling program thus concentrated on fish of the size most likely to be caught, and eaten, by people.

Sampling Sites

Water and sediment samples for the Liard River program were collected at a site about 10 km upstream from Fort Liard, between the confluence with the Kotaneelee River to the north and the NWT/BC boundary to the south (Figure 2). The site was positioned as near as possible to the boundary with British Columbia, which ensured that water and sediment quality were measured just as the river enters the Northwest Territories. Furthermore, all water and sediment sampling was done upstream from the mouth of the Kotaneelee River. Active oil and gas developments in the upper reaches of that river, and in the Fisherman Lake area, could conceivably affect water quality in the Liard River. Such an occurrence would confound inferences about the source of petroleum-derived contaminants, should any be found.

Water and sediment samples were collected at the same location on each sampling trip (60˚09'17.5"N, 123˚44'33"W). Collections of fish were made over a slightly larger area, bounded by the Muskeg River to the north and the Kotaneelee River to the south. Because fish roam widely and some are migratory there is no point in attempting to confine sampling to a single point. Instead, fishing sites were chosen according to where river conditions (eddies, backwaters) suggested that a particular species would likely be found. Finding the best fishing sites was greatly aided by experience from local people who regularly fish the river.

To obtain a useful baseline of river conditions and to allow for annual variation, the Liard River was sampled for three years, beginning in June 1992 and ending in March 1995. Water sampling began in August 1991. As far as possible sampling took place on approximately the same dates each year.

Sample Collection and Analysis

Grab Water Samples

Water samples collected in bottles dipped into the river are called grab samples. Grab samples contain both water and suspended sediment from the river. These samples were collected 15 times over a period of four years, beginning in August 1991 and concluding in March 1995. The Liard River was sampled three times or more in most years. Samples were collected throughout the year to cover all phases of the hydrological cycle. Unsafe river ice prevent sample collections in November through January, but March samples should be representative of winter conditions.

Different sampling procedures were used throughout the year depending on river conditions. In the summer, samples were collected from a boat by submerging the bottles beneath the surface of the water. In the winter, the sampling site could only be reached by helicopter. Winter grab samples were taken through holes drilled through the ice with a hand auger (see Photographs 7 and 8). In all cases care was taken to ensure that the bottles were kept clean and free from accidental contamination. Samples were shipped to the laboratory by air the day after they were collected.

Grab water samples were analysed by DIAND's Northern Analytical Laboratory in Yellowknife for routine water chemistry and trace metals. These parameters provide basic information on water quality and ecosystem health, and are required for interpretation of other results. This sampling also ensured that each component of the aquatic ecosystem was studied.

Centrifugate Water and Suspended Sediments

The Liard River carries a heavy load of suspended sediments in the ice-free season, and measurements of water quality can be affected when suspended sediments concentrations are high. Many of the variables included in this monitoring program, especially heavy metals and organic contaminants, tend to bind to solid particles in the water column. Therefore, the Liard River Program included both raw water samples (grab samples) that contained suspended sediment, and special "centrifugate" water samples from which virtually all suspended particles had been removed. A portable centrifuge was used to remove suspended particles from the water. A centrifuge is a machine that uses a gasoline-powered engine to spin a covered metal bowl at high speed. The spinning motion creates centrifugal force (the same force created by a spinning top or by twirling a weight on a string) that forces the sediments to the bottom of the bowl and clean water to the top (see Photograph 9). A submersible pump placed below the surface of the river pumped water into the centrifuge where the suspended sediment was continuously removed. The water collected after centrifuging, called centrifugate water, did not contain any appreciable sediment (see Photograph 10). Centrifugate samples and grab water samples were taken on the same day, to make comparisons easier.

Centrifugate samples were collected on seven occasions from 1992 through 1994. Sampling was spread over the year (March, June and September) to sample at different stages of the annual flow regime. It turned out to be impossible to collect good sediment-free water samples in June because sediment concentrations in the river were so high. The sediment accumulating in the bottom of the bowl was analysed as well, except in winter, when suspended sediment concentrations were so low that almost no material accumulated in the centrifuge.

Centrifugate water samples were analysed for the same physical parameters, major ions, nutrients and metals as grab samples, to establish background information on the quality of the water. Comparisons of centrifugate samples with grab water samples reveals which parameters are associated with suspended sediments. Furthermore, by separating out the sediment using the centrifuge, it was possible to study each component of the aquatic ecosystem.

Four groups of potential contaminants were measured in suspended sediments: trace metals, PAH, PCBs and pesticides. In addition, the particle size distribution of sediment samples was measured. Toxicity tests on a few samples were included to provide a direct measure of acute toxic effects from any contaminants which the sediments might contain.

Fish

Fish sampling sites were located in areas used for domestic and sport fishing near the town of Fort Liard. Mountain whitefish, northern pike, walleye and longnose sucker were sampled in Sept-ember and October, during the open-water season. Fall sampling was done upstream, near the Kotaneelee River, downstream, at the mouth of the Muskeg River, and near town on each side of the Liard River. Walleye, northern pike and mountain whitefish were principally collected just below the Kotaneelee River, across from the Petitot River outlet (Figure 2), in eddies that were fished by the local people. Burbot were collected in early December, under ice. Sampling for burbot was centred just outside town on both sides of the river. Collections of fish were made from the same areas each year.

Fish were captured during the open-water season in 23-m or 46-m gill nets. Mesh sizes of 89 mm (3.5") and 114 mm (4.5") were used, to catch fish of sizes similar to those caught by the local fishers. Nets and set lines were generally set overnight and left in the water for 18-24 hours before they were checked and reset. Angling was used to catch some of the northern pike. Set lines, made of a lead sinker and a large hook baited with a piece of lake whitefish, mounted on a pole, were used in the winter to catch burbot (see Photograph 11). Lines were checked and bait replaced twice each day.

Standard biological information on each fish collected was obtained in the field, including length, weight and liver weight. The sex and stage of maturity were determined by looking at the sex organs. The age of each fish was determined by examining scales or other markers in the laboratory.

Contaminants were measured in whole fish or in any of three tissues: muscle, liver and bile. More than one tissue was sampled from most fish. Contaminant analysis on whole fish provides an indication of the availability of contaminants to other species in the ecosystem. Fish muscle is consumed by people and fed to dogs. Burbot livers were analysed because they are eaten by local people and because they tend to accumulate organic contaminants.

Bile is a solution of digestive acids produced by the liver. Bile is stored in the gall bladder and excreted into the digestive system through the bile duct. The liver of fish is chiefly responsible for clearing foreign substances from the body. Many of these substances are pumped into the bile, which then carries them into the digestive tract and out of the body. Concentrations of some organic contaminants, notably PAH, are often much higher in bile than in muscle, liver or other tissues. For this reason, bile was collected from Liard River fish and analysed for PAH.

A drawback of sampling bile is that good samples cannot always be obtained. The quantity of bile stored in the gall bladder of an adult fish is at most only a few millilitre. Often the gall bladder is empty (see Figure 12).

All the elements or organic compounds analysed in fish tissues were chosen because they are known to bioaccumulate. The list included metals, PCBs, PAH and dioxins and furans. Analysis used muscles, bile, whole-fish or burbot livers, depending upon where a particular contaminant was deemed most likely to accumulate. The species and tissues analysed were revised continually over the course of the Program based on experience and results as they were obtained. In addition, the activity of certain liver enzymes called *mixed-function oxygenases* that are involved in the removal of contaminants like PAH was assayed as a indication of recent contaminant exposure.

The Present State of the Liard River

Units of Measurement and Detection Limits

Before we begin to examine the results of the Liard River Program, a few comments are warranted about how environmental data are presented. Concentrations of ordinary substances like natural dissolved salts in fresh water are measured in milligrams per litre (mg/L) or *parts per million*. A milligram per litre is equivalent to about one second in ten days; a few grains of table salt in a bowl of soup makes a salt solution of a few hundred parts per million. A part per million in a solid, like sediments or fish tissues, is expressed as micrograms per gram (µg/g), a microgram being one millionth of a gram.

Less abundant substances, such as trace metals, are measured at *parts per billion* levels. In water, parts per billion measurements have units of micrograms per litre (µg/L), and in solids, nanograms per gram (ng/g). A part per billion is roughly equivalent to a second in three years. Finally, for a very few contaminants that are significant at extremely low concentrations, measurements are reported in *parts per trillion*: nanograms per litre (ng/L) in water or picograms per gram (pg/g) in sediments and fish. A part per trillion is equivalent to one second in more than 3000 years.

The table below summarizes the units used to report contaminant concentrations.

Concentration	Water	Sediments and Fish
parts per million (ppm)	mg/L	µg/g
parts per billion (ppb)	µg/L	ng/g
parts per trillion (ppt)	ng/L	pg/g

The Liard River Program used state-of-the-art instruments and the latest laboratory methods to measure trace contaminants in water, sediments and fish even at extremely low concentrations. Merely finding a contaminant does not necessarily mean there is any cause for concern. Many persistent organic contaminants are carried in the upper atmosphere and may be found in minute quantities almost anywhere on the globe. Similarly, very low concentrations of metals are natural in all aquatic ecosystems because running water gradually erodes the bedrock it flows over. The important point is the concentration of a contaminant relative to the *effective concentration*, which is the level at which it begins to have harmful effects on aquatic life or people. Ordinary dissolved substances in water may not affect its suitability for drinking or washing unless concentrations reach hundreds of milligrams per litre. Heavy metals and some organic compounds may be toxic at parts per billion concentrations; very few compounds are significant at the parts per trillion level.

Even with the best analytical instruments available, there will always be a limit to how low a concentration can be measured. The lowest concentration of a substance that can be measured reliably by a given method is called the *detection limit*. Samples with contaminant concentrations below the detection limit are called *non-detects*. In the Liard River Program, non-detects were very common for most trace contaminants, despite the remarkably low detection limits used in the analysis. This is an indication that the river is clean and essentially free of contamination.

Water Quality

Background

These parameters were included in the analyses of grab water samples:

Physical Parameters	Major Ions	Nutrients	Metals
pH	Calcium	Nitrate+Nitrite	Arsenic
Conductivity	Magnesium	Nitrate	Cadmium
Turbidity	Sodium	Ammonia	Chromium
True Colour	Potassium	Total Kjeldahl Nitrogen	Cobalt
Nonfilterable Residue	Chloride	Total Phosphorus	Copper
Filterable Residue	Sulphate	Orthophosphorous	Iron
	Total Hardness		Lead
	Alkalinity		Manganese
			Mercury
			Nickel
			Zinc

Results for metals in water are discussed in a later section along with metals in sediments and fish.

The Canadian Council of Resource and Environment Ministers (CCREM 1987) has established a set of water quality guidelines for drinking water and for protection of freshwater life that can be used to assess the data from the Liard River. The CCREM guidelines are based on a thorough review of information on toxicity and health implications of different parameters, and have been adapted to suit Canadian conditions. These are national guidelines, however, and may not reflect local conditions, especially those in northern ecosystems. A few guidelines have been set on the basis of aesthetic considerations of taste and appearance of the water, as opposed to human health or environmental concerns. Nevertheless, the CCREM guidelines provide a general reference for comparison with field and laboratory data.

River Flow and Water Quality

Volume of flow in the Liard River at Fort Liard varies from about 200-400 m^3/s in winter to 4000 to 8000 m^3/s in late June. The river carries an enormous load of suspended material in spring and summer but almost none under winter ice. Concentrations of many water quality variables are tightly linked to flow and thus vary widely over the year.

Any evaluation of chemistry and biology in the Liard River must take into account the wide variations in river discharge (by ten times or more) that occur over the year (Figure 3). Discharge is lowest and most constant during the long winters, when surface water is locked up as ice and snow. During the winter, the river is fed solely by ground water. At Fort Liard, discharge in late winter is typically 200-400 m^3/s. Discharge increases dramatically at the time of ice-melt in spring, reaching peak discharges of 4000 to 8000 m^3/s by the end of June. Flow declines steadily for the remainder of the summer and fall until ice returns in November. Discharge was typical on the days when grab and centrifugate water samples were taken in the Liard River Program (Figure 3). Hence, results from this Program should reflect the usual condition in the river.

Because of the spectacular variation in flow in the Liard River, many of the water quality parameters measured varied markedly throughout the year. Suspended solids and related parameters such as turbidity and metals (often bound to particles) showed the most dramatic annual pattern. Suspended solids concentrations were remarkably high in spring, but barely detectable in winter (see Photograph 13). Smaller trends were apparent for dissolved materials as well. Statistical analysis of discharge data and water quality parameters showed that levels of many parameters are tightly linked to flow, and that the relationship is *nonlinear*. This means that when discharge begins to increase in spring, concentrations of suspended materials increase even faster, leading to extremely high concentrations during peak flows.

The annual pattern in suspended solids loads in the Liard River reflects the erosive power of water and the availability of particles for transport. High flows of fast-moving water are very energetic; they erode the river banks and scour particles off the river bottom. In addition, the surface area of the river and its many tributaries is greatest when the channels are full, exposing a larger area of ground to erosion. Discharge, and therefore river power, is lowest under ice, when surface water sources are frozen and the surface area of the river system is also least.

The effect of discharge on dissolved substances, on the other hand, is negative. As discharge increases, concentrations of dissolved solids tend to decline. This is a common observation in large rivers. In winter, deep ground water, which has accumulated dissolved salts as it percolates downward through the soil, is the major source of water to the river. Overland runoff from rain or snow-melt tends to be low in dissolved material compared with ground water. Thus, high flows in spring dilute solute-rich ground water, leading to lower TDS concentrations than in winter, when deep ground water predominates.

Relationships with flow extend to most of the water quality parameters measured. They provide a means of discovering whether a particular parameter is transported in solution (concentrations decline with increasing flow) or attached to particles (concentrations increase with flow). The graph in Figure 4 displays typical examples of these relationships.

Based on the annual hydrograph and the progression of temperatures in the NWT, water quality data were summarized by season. Seasons were defined as follows: spring comprises May and June and corresponds to the period of increasing discharge; summer (July and August) corresponds to the period of rapidly declining flows; fall (September and October) corresponds to a period of lower and more slowly declining flow; and winter (November to April) is the six-month period of low, stable flows under ice (Figure 3). Breaking the data into seasons based on climate and flow allows for easier evaluation of the data and allows patterns attributable to the flow regime to be easily seen.

Water Quality of Grab and Centrifugate Water

Background water quality in the Liard River is good. Concentrations of suspended solids vary dramatically over the course of the year, from 1000 to 10 000 mg/L in spring to less than 5 mg/L in winter. The water is very murky in spring and summer, but as clear as glass in winter. Liard River water is hard and alkaline, but nutrient concentrations are moderate. All physical conditions in the river are normal and within the ranges that support abundant aquatic life. CCREM water quality guidelines for protection of aquatic life or drinking water are never exceeded for pH, total dissolved solids, calcium, magnesium, sulphate or ammonia.

pH

The pH measures the acid-base balance of the water on a scale ranging from about 4 (very acid) through 7 (neutral) to 11 (very basic) in natural waters. Aquatic life is most productive in moderately basic water (pH 7 to 9). Mean pH of the Liard River varied over a narrow range, from 7.8 in winter to 8.1 in summer and fall. Variation within seasons was also small. All pH measurements in the Liard River were well within CCREM guidelines (6.5 to 9.0) for protection of aquatic life and drinking water.

Turbidity

Water that is high in suspended solids tends to be murky, and this characteristic is quantified by turbidity, which is defined as the capacity of a water sample to scatter light. Turbidity in the Liard River is strongly flow dependent. In winter, turbidity falls to near the detection limit, indicative of water as clear as glass. In spring, the river carries extremely murky water. As river flow declines throughout the warm seasons, turbidity gradually falls as well, to return to extremely low winter values once ice cover has formed again.

The high turbidity of the Liard River in summer has implications for human safety, because underwater hazards are hard to see, and for aquatic life. High turbidity is the natural condition of the Liard River, however, and species living there would be adapted to it. The CCREM drinking water guideline for turbidity is virtually always exceeded in the Liard River during the open-water season, sometimes by 200 times. Except in winter, water from this river is not suitable for drinking without being clarified.

Total Suspended Solids

Total suspended solids is a measure of all the suspended particulate matter in a water sample, which mostly consists of fine silts and clay. As discussed earlier, suspended solids concentrations in the Liard River are dramatically flow-dependent and range over more than three orders of magnitude in the course of a year (Figure 4). Highest concentrations occur during the high, erosive flows of the spring freshet, following break-up of the ice layer. Seasonal mean concentrations in spring routinely exceed 1000 mg/L and individual samples may approach 10 000 mg/L. Concentrations drop off sharply as flow declines later in the season, to an average concentration below 30 mg/L in the fall and below 5 mg/L in winter. Similar patterns are common in other northern rivers, although the trends in the Liard River are extreme.

On average, Liard River suspended sediments are about 15% sand, 35% silt and 50% clay. The high proportion of silts and clays is significant because most metals and hydrophobic organic compounds tend to attach mostly to smaller particles. In the Liard River, water samples with a greater proportion of silts and clays carry higher metals concentrations. This is why suspended sediment sampling was included in the Liard River Program. The high proportion of clay also contributes to the very high turbidity of the water, because smaller particles scatter light more effectively than larger ones.

Total Dissolved Solids (Filterable Residue)

Total dissolved solids (TDS) is the quantity of all material in solution in a water sample, which is mostly small quantities of natural salts. As a broad generalization, the productivity of most aquatic ecosystems, from algae up to fish, is correlated with the total dissolved solids content of the water.

As remarked earlier, total dissolved solids concentrations in the Liard River bear a strong negative relationship with discharge, a common observation in large rivers. Nevertheless, the annual range in TDS for the Liard River is not large: the mean for spring (150 mg/L) is 65% of the mean for winter (226 mg/L). Fresh waters range in TDS from about 50 mg/L to more than 1000 mg/L. TDS levels in the Liard River are typical of rivers draining the Rocky Mountains. CCREM (1987) has set an aesthetic guideline of 500 mg/L of TDS in water used for domestic supply, and the Liard River is always well below that limit.

Major Ions

A relatively small group of dissolved, inorganic ions are found in all fresh waters and are therefore referred to as the major ions. The mass and proportions of major ions define critical water quality parameters such as pH, alkalinity and hardness. In the Liard River, the cations (positively charged ions) are dominated by calcium, followed by magnesium; sodium and potassium are minor ions. This sequence of cations is almost universal among inland fresh waters of North America. The Liard River is unexceptional in ion composition.

Calcium concentrations ranged mostly 30-40 mg/L in the open water seasons, but sometimes exceeded 60 mg/L in winter. High calcium interferes with domestic use of water, but calcium in the Liard River always remained well below the CCREM aesthetic guideline of 75 mg/L. Average magnesium concentrations ranged 8-16 mg/L, and always remained far below the CCREM aesthetic guideline of 150 mg/L. Sulphate ranged roughly 20-40 mg/L, comparable with calcium, but far below the CCREM aesthetic guideline of 500 mg/L, at which concentration it begins to produce off-flavours in drinking water. Chloride concentrations were always low, seldom exceeding 1 mg/L. The background concentrations of dissolved ions in the Liard River are typical of a clean, unpolluted river.

Hardness

Hardness, which is principally determined by the sum of calcium and magnesium in solution, is an important modifying factor of water quality since it influences the toxicity of many organic and inorganic chemicals, especially heavy metals. Water hardness also affects the effectiveness of soaps and the convenience of water for domestic use. Water in the Liard River would be considered moderately hard by CCREM guidelines. Hardness approached or exceeded 100 mg/L throughout the open-water season, and averaged over 200 mg/L under winter ice. Those levels of hardness are sufficient to confer considerable protection against toxicity of metals and organic toxicants, but would not limit the use of the water domestically.

Alkalinity

Alkalinity is a measure of the capacity of water to neutralize an acid and is expressed as an equivalent concentration of calcium carbonate. Alkalinity is an indication of the buffering capacity of the water body, and naturally tends to be greater in alkaline than in neutral or acid waters. Alkalinity in the Liard River is moderately high. Mean values in the open-water season were all close to 100 mg/L, and alkalinity in wintertime routinely exceeds 150 mg/L. These high alkalinity values speak of a strong buffering capacity and are probably responsible for the small seasonal variation in pH in the river. They also strongly reduce the toxicity of heavy metals and are therefore beneficial to aquatic life.

Nutrients

In most seasons the Liard River is low in nutrients. Nitrogen (N) and phosphorus (P) are commonly the nutrients that limit growth by algae and rooted plants and hence by all the other organisms in the ecosystem which ultimately depend on plant production. Total P includes all forms of phosphorus, whether attached to, or part of, suspended particles, or in various dissolved forms. Total P concentrations in the Liard River were very high in summer and very low in winter, following the pattern of suspended solids. This relationship strongly suggests that most of the P in the river is bound to suspended sediments, in which form it is generally considered unavailable to aquatic life. Total P in centrifugate water, in which virtually all particulate matter had been removed, ranged only 0.005 to 0.018 mg/L, even during the highest flows in June. These concentrations are typical of unproductive or moderately productive ecosystems.

Ammonia (NH_3) is the reduced form of nitrogen excreted in animal wastes and released from decaying organic matter. It also has anthropogenic sources such as treated sewage and commercial fertilizers. Ammonia is rapidly oxidized to nitrate under aerobic conditions, which would account for the low and more or less constant ammonia concentrations in the Liard River. Most N in the Liard River is present as dissolved organic N. All forms of nitrogen in the river were far below guidelines from CCREM or other agencies (Nordin and Pommen 1986) for protection of aquatic life or drinking water. From the perspective of aquatic productivity, the Liard River is very N-poor in most seasons.

Metals

Background

Metals were measured in grab water samples, centrifugate water, suspended sediments and fish in the Liard River Program. Ten metals that can be toxic to people or aquatic life were examined in detail: arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc. Most of these metals can arise from natural sources, especially bedrock erosion. They can also be produced by human activities anticipated in the basin, particularly mining, and to a lesser extent oil and gas extraction. In small quantities many metals are essential nutrients for all living things. Their presence in detectable quantities does not necessarily pose a hazard. But in larger quantities metals can be harmful to aquatic life and to people who drink river water or feed on fish.

Metals concentrations in water are reported as total concentrations, which includes both metals dissolved in water and metals attached to suspended sediments. Much of the metal associated with suspended particles is tightly bound or even a part of the internal structure of the sediment, so its availability for biological uptake would be very low. CCREM guidelines for drinking water or for protection of aquatic life assume that all of the metal is bioavailable. Still, these guidelines provide useful benchmarks against which to evaluate metals concentrations.

Metals concentrations in suspended sediments are compared with the interim quality guidelines for freshwater sediment, which were developed by Environment Canada (1995) for bottom sediments. Toxic effects of contaminants in sediments depend heavily on the physical structure and chemical composition of the sediments. Effective concentrations vary widely among places and species. Therefore, the guidelines do not attempt to set a single threshold of effect for each metal. Instead, two guidelines are presented: the *Threshold Effect Level* is the lower limit where harm to aquatic life is observed only rarely; the *Probable Effects Level* is the limit above which negative effects occur frequently. Metals concentrations between the two effect levels sometimes prove harmful to aquatic life.

For metals that have no national guideline, data were compared against similar guidelines from the Ontario Ministry of Environment (OMOE 1992). Both sets of guidelines were developed for bottom sediment, not suspended sediment. They are included here only as a reference for comparison.

Metals were measured in muscle or whole-fish samples from all five fish species sampled because these elements are known to accumulate in fish tissues. For mercury, there are also human health consumption guidelines against which to compare concentrations. Metals were also measured in burbot livers because many metals accumulate in the liver to substantially higher concentrations than in muscle. Burbot livers are also an important food item for residents along the River.

Metals and Suspended Sediments

Heavy metals in Liard River water are largely associated with suspended sediments. These particle-bound metals are not taken up by aquatic organisms and therefore are not toxic. Metals concentrations in some samples of whole fish may also be inflated by the inclusion of sediments in the stomach.

Before considering concentrations of metals individually, it is instructive to examine the relationship between metals and suspended sediments. Most trace metals are present in the environment as inorganic ions that are not highly soluble. Where suspended sediment concen-trations are high, these ions will rapidly leave the water and bind to the surfaces of suspended particles. Thus, it might be expected that most metals in the Liard River would be bound to suspended particles in the ice-free season. A comparison of grab water samples and centrifugate samples shows that this is so.

Concentrations of all metals were sharply reduced in most centrifugate water samples, in parallel with the suspended sediments that were removed by centrifugation. For examples, cadmium ranged 1-13 µg/L in grab water samples but only 1-3 µg/L in centrifugate water; zinc ranged 2-47 µg/L in grab water but only 1-4 µg/L in centrifugate water. A similar reduction in the range appeared for all the other metals. The greatest reductions in concentration in centrifugate water occurred in June samples, when suspended sediment concentrations were highest, and the least were usually in September.

It is clear then that heavy metals in the Liard River are largely associated with suspended sediments. This is an important conclusion because particle-bound metals are largely unavailable to organisms and therefore are not toxic. This fact must be kept in mind when individual metal concentrations are considered.

Particle-bound metals may also be responsible for some apparently high metals concentrations in fish. Concentrations of all metals were dramatically higher in whole longnose sucker from the Liard

River than in any other species or tissue. Suckers are bottom-feeders. They consume detritus and bottom sediments along with their food, and in the passage of this material through the gut, metals could be absorbed into fish tissues. Metals concentrations in whole-fish longnose sucker samples may also be inflated by the inclusion of sediments in the stomach.

Metals in Water, Suspended Sediments, and Fish

Most metals in grab water samples from the Liard River exceed CCREM guidelines for protection of aquatic life in spring, but these high concentrations reflect inert metals attached to suspended particles and are not a hazard to aquatic life. Concentrations in sediment-free water are always well below guidelines. Arsenic and nickel in suspended sediments sometimes exceed thresholds for biological effects. These metals are apparently not available to aquatic life and do not appear to be causing toxic effects. In fish, metals concentrations are generally higher in burbot liver than in other tissues or species. Mean mercury concentration in walleye muscle exceeds the Health Canada guideline of 0.2 μg/g for subsistence consumption. All metals concentrations in fish are comparable with those in fish from other clean water bodies of the western NWT.

Arsenic

Arsenic occurs both naturally as a result of the weathering of rocks and soils, and from human sources. Although data on total arsenic in Canadian waters are limited, values ranging from less than 1 to 47 μg/L have been recorded. Arsenic in minute amounts stimulates growth, but in large amounts it may be toxic. This metal accumulates mainly in the liver but also concentrates in muscle cells, where it interferes with enzyme activity.

Arsenic concentrations in Liard River grab water were strongly seasonal with values at or near the detection limit in winter and late in the open-water season, but sharply higher during the period of spring high flow. Nevertheless, even the most extreme arsenic concentrations fell well below guidelines for drinking water or protection of aquatic life.

On the other hand, arsenic was one of only two metals (the other is nickel) that occurred in high concentrations in suspended sediments. Arsenic exceeded the Environment Canada threshold effects concentration in every sample, and the probable effects level in two samples. A remarkably similar pattern was observed in the Slave River (Sanderson et al. 1997). It is unlikely, however, that arsenic creates a risk to aquatic life in the Liard River because concentrations in centrifugate water, the best indicator of available forms, were very low (0.3-0.5 μg/L), compared with the CCREM guideline for protection of aquatic life (50 μg/L).

As expected, arsenic concentrations were higher in burbot livers than in whole fish samples of that species. In muscle samples, and whole fish of northern pike and burbot, arsenic concentrations were very low and the majority of samples were less than the detection limit of 0.01 μg/g. Higher concentrations were observed in whole mountain whitefish and longnose suckers, probably because these species feed on insects from the river bottom. In absolute terms these amounts were still small; the highest concentration observed was less than 0.5 μg/g. Arsenic levels in all Liard River fish lie toward the lower end of the range observed in other lakes and rivers of the NWT.

Cadmium

Cadmium is usually present in natural water in the range of 0.1 to 10 μg/L. Cadmium in solution may be both acutely and chronically toxic to aquatic biota. Cadmium toxicity is much less in hard water than in soft water. Cadmium bioaccumulates in fatty tissues, especially the kidney, liver and gill, and to a lesser extent in the muscle. Higher levels of this metal are usually found in forage fish than in predatory species such as walleye or northern pike.

Cadmium concentrations in Liard River grab water samples were always below detection in the winter, but briefly rose to concentrations in excess of 0.5 μg/L in the spring. The high concentrations quickly subsided again when flows declined later in the season. None of the cadmium concentrations exceeded the guideline for drinking water (5 μg/L) but some samples during spring peaks were above the guideline for protection of aquatic life (0.8-1.8 μg/L). However, concentrations in centrifugate water never exceeded 0.2 μg/L, well below the CCREM guideline. In suspended sediments, cadmium exceeded the threshold effect level in three samples, but the excess was small, and none of these samples even approached the probable effects level.

Cadmium concentrations in the majority of fishes from the Liard River were extremely low, rarely above 0.05 μg/g and frequently below detection. Accumulation in burbot liver was somewhat greater, with a mean arsenic concentration above 0.25 μg/g, and peak concentrations almost three times that. All cadmium measurements in Liard River fish fall within the range of concentrations reported in fish muscle and liver from other lakes and rivers in the NWT.

Chromium

Chromium is generally found at low concentrations in Canadian surface waters, with levels in Canadian rivers ranging between 1.0 and 23 µg/L. Liard River grab water data mostly matched that general range. A few replicates in June of 1992 and 1994, when suspended solids concentrations were very high, exceeded the guideline for freshwater aquatic life of 20 µg/L, and approached the drinking water guideline of 50 µg/L. In other seasons chromium concentrations fell below 1 µg/L. Again, these figures are exaggerated by the inclusion of particulate metal; in the two centrifugate samples in which it was measured, chromium concentrations were 1.0 and 4.9 µg/L. Very similar concentrations and seasonal patterns were observed in the Slave River at the NWT boundary (Sanderson et al. 1997).

Chromium concentrations in suspended sediment were well below the threshold effects concentrations in every sample. Chromium concentrations were always below the detection limit in all fish tissues of every species, except whole longnose sucker, in which it ranged 0.5-1.1 µg/g. Contamination with sediment particles in the gut probably account for the trace amounts of chromium in this species.

Copper

Copper is essential for all living organisms and has both natural and human sources. Nevertheless, in excess amounts copper may be very toxic. Like many other metals, its toxicity is increased by decreases in water hardness and dissolved oxygen, and reduced in the presence of suspended solids.

Total copper in Liard River grab water samples ranged from less than 1 µg/L to a little over 20 µg/L in most samples. Samples in June 1992 were exceptional, however, in that they averaged near 100 µg/L with little variability. Total suspended solids concentration on this date was higher than on any other sampling date in the Liard River Program.

The CCREM guideline for protection of aquatic life for copper is .2 to 0.4 µg/L for the range of water hardness found in the Liard River. That guideline was always exceeded during the period of peak concentrations in the spring, but rarely in other seasons. Most of the copper in the spring would be bound to suspended particles and therefore would not be toxic to aquatic organisms: copper ranged only 1-3 µg/L in centrifugate water. Concentrations of copper in suspended sediments were always well below threshold effects concentrations in every sample.

Copper concentrations in almost all fish species and tissues varied over a narrow range, from 0.2 to 1.0 µg/g, except for a few samples of whole longnose sucker. Copper concentrations in burbot liver, however, were an order of magnitude greater than any of the other tissues, undoubtedly reflecting the tendency of metals to be stored in the liver. Similar concentrations of copper have been found in fish muscles and burbot livers in a number of other lakes in the NWT, as well as the Slave River.

Iron

Iron is an essential nutrient, but can be toxic at high concentrations. The Liard River is rich in iron. Concentrations in grab water samples ranged from 46 µg/L in a few winter samples to as much as 20 mg/L during spring peak flows. Even more exceptional was the sample collected in June 1992, which contained an average of 70 mg/L of total iron. A comparison with Environment Canada monitoring data from Fort Liard (mean 2.0 mg/L, maximum 22 mg/L in 49 samples) confirms that high iron concentrations are not uncommon in the lower Liard River. By comparison, most surface waters contain less than 0.5 mg/L of total iron. The CCREM water quality guideline for both drinking water and protection of aquatic life is 0.3 mg/L.

There are two likely forms of these high iron levels. Most of this iron is evidently particulate, probably common iron hydroxides contained in fine silt and clay particles. Particulate iron is not biologically active and is not a concern for water quality. Centrifugation removed up to 95% of the total iron in grab samples.

Of the remaining, dissolved iron, much of this is probably chemically bound to dissolved organic matter, a common occurrence in northern rivers. This complexed iron imparts the tea-brown colour so often seen in streams draining northern forests. Iron-organic matter complexes are highly stable and very soluble compared with inorganic iron. Because of the stability of the complexes, iron in this form is largely inert and is not assimilated by aquatic organisms. High iron concentrations have been observed for many years in the Slave River.

Except for longnose sucker, iron concentrations in fish muscles and whole fish varied over a rather narrow range, with means not far from 10 µg/g. Burbot liver was richer in iron than other tissues, but the difference was not as great as for many other metals. Whole-fish samples of longnose sucker are again exceptional both in the mean iron concentration (greater than 100 µg/g) but also the extremely wide range of individual values. Iron hydroxides in ingested sediment are probably responsible for the high iron levels in whole suckers. Iron levels in all the remaining fish tissues are entirely comparable to values from other lakes and rivers of the region.

Lead

Lead is a toxic metal which generally occurs in low concentrations (trace to 40 µg/L) in natural waters. Unlike many other metals, lead is not required as a micronutrient by aquatic organisms, and is toxic at comparatively low concentrations. The toxicity of lead depends on water hardness and pH of the water. Lead does not biomagnify in aquatic food chains nor do concentrations in tissues typically increase with body size or age.

Lead in grab water samples displayed the familiar seasonal pattern, with high to extremely high concentrations during the high flow period in spring, declining concentrations in summer and fall and lowest concentrations in winter. About 23% of the observations were below detection limits. Yet the June 1992 grab samples, which had exceptionally high suspended solids concentrations had a lead concentration an order of magnitude greater than the highest peaks in other years, and 100 times greater than concentrations in other seasons.

The CCREM lead guideline for protection of aquatic life (2 to 7 µg/L, depending on water hardness) was exceeded in all the spring grab samples and occasionally in other seasons as well. Most samples in spring also exceeded the drinking water guideline of 10 µg/L. However, lead concentrations in centrifugate water never exceeded 2 µg/L and were usually much less. In suspended sediments, concentrations of lead were always well below the Environment Canada threshold effects concentrations in every sample.

Lead concentrations in Liard River fish were low and very similar among species and tissues. In every species except longnose suckers, 70% or more of all samples returned values below the detection limit. The remaining samples ranged upward to 0.07 µg/g. The maximum concen-tration in longnose sucker was only 0.15 µg/g. Similar lead concentrations occur in fish from other NWT lakes and rivers.

Manganese

Manganese seldom reaches concentrations of 1000 µg/L in natural surface waters and is usually present in concentrations of 200 µg/L or less. In the environment it behaves like iron in chemistry, distribution and biological effects. Manganese has low toxicity at concentrations found in the environment so no guideline for protection of aquatic life has been established. The CCREM aesthetic guideline of 50 µg/L protects against off-flavours.

Manganese concentrations in grab water samples from the Liard River were highest, exceeding 200 µg/L, during peak flow in spring, and lowest under winter ice. Most spring and summer concentrations exceeded the aesthetic guideline. Treatment of domestic water to remove sediments would also relieve the excess of manganese. There are no Environment Canada guidelines for manganese in sediments, but this metal exceeded the OMOE lowest effect level in one sample only.

The distribution of manganese among fish sample types from the Liard River generally parallelled that of iron, but concentrations were much lower. Average manganese concentrations for most species and tissues were less than 1 µg/g, up to 2.8 µg/g in longnose sucker. All the manganese concentrations in Liard River fish are low in absolute terms, and very similar to values reported for the Slave River and nearby lakes.

Mercury

Mercury is a special concern in natural waters because it is acutely and chronically toxic, and unlike most other metals, mercury concentrations tend to increase up the food chain (biomagnification). Highest concentrations are usually found in top predators, including most sportfish. High mercury levels may pose a health hazard in the long term to people who regularly consume fish, as well as terrestrial predators such as fish-eating birds.

All grab water samples collected in the Liard River Program had mercury concentrations at or below the detection limit of 0.02 µg/L. Concentrations of mercury in suspended sediments were always well below threshold effects concentrations in every sample. It was only in fish tissues that significant mercury accumulations were found.

Mercury was detected in every sample of fish taken from the Liard River (Figure 5). With the exception of walleye muscles, average concentrations were similar for all species. Mercury concentrations in walleye muscles were both higher and more variable than in other species and tissues. In contrast to other metals, mercury concentrations in burbot liver were markedly lower than in whole fish, indicating that the liver is not the primary site of storage for mercury. Mercury concentrations in Liard River fish are entirely typical of other lakes and rivers in the region.

In Canada, the maximum allowable level of mercury in the edible portion of commercial fish is 0.5 µg/g (Health and Welfare Canada 1969), while a tolerance concentration of 0.2 µg/g has been set by the Medical Services Branch of Health Canada for frequent consumption (Health and Welfare Canada 1984). In the Liard River samples, only walleye muscles exceeded the 0.5 µg/g limit for commercial fish harvesting, and the mean is below this guideline. Mean mercury concentrations for walleye were above the guideline of 0.2 µg/g for subsistence consumption. Health Canada is currently assessing these data. Further monitoring of mercury in Liard River fish in future may be warranted.

Nickel

Nickel is a toxic metal at low concentrations, especially in acid, soft water and in the presence of other metals. Natural concentrations of nickel are very low compared with biologically effective concentrations, but it is a frequent contaminant from mine discharges or other activities that disturb and expose bedrock. Like most metals, nickel does not biomagnify.

Nickel was detectable in every grab water sample in the Liard River Program, with concentrations ranging from 1 µg/L to more than 225 µg/L. Concentrations remained well below the guideline for protection of aquatic life (85 to 150 µg/L) on every sampling date, except for one unusually high concentration observed in 1992. Suspended solids concentrations and discharge were both greater on that date than on any other day in the Program, suggesting that such peaks are an occasional event. In centrifugate water, nickel concentrations ranged only 1-3 µg/L, far below the CCREM guideline.

Nickel was one of only two metals that occurred in suspended sediments at high concentrations relative to Environment Canada guidelines. Nickel concentrations exceeded the threshold effects concentration in four out of five samples, and exceeded probable effects level in two samples. But it is apparent from the centrifugate samples that virtually none of this nickel is migrating into the water, so it is very unlikely that it is a hazard to aquatic life in the Liard River.

Figure 5: Mercury in fish

Nickel was not even detected in the majority of fish samples from the Liard River, including burbot livers. A few concentrations above the detection limit were reported for walleye muscles, whole mountain whitefish and whole longnose sucker. These extremely low concentrations are typical of fish in the region.

Zinc

The concentration of zinc in natural waters is usually below 50 µg/L. At low concentrations it is an essential nutrient, but high concentrations can be acutely toxic. Zinc is often found in water along with nickel and copper.

In grab water samples from the Liard River, highest zinc concentrations, usually in the range of 30-90 µg/L, were observed in spring (June). Concentrations in fall and winter were commonly below detection. June 1992 is again an exception: in this month total zinc concentrations averaged over 300 µg/L. Grab water samples exceeded the zinc guideline for protection of aquatic life (30 µg/L) on five of the 15 sampling dates. Like the other metals, zinc concentrations were reduced by as much as 97% when suspended sediments were removed by centrifugation, illustrating that most of the zinc was adsorbed to suspended particles. This particulate zinc does not pose a hazard to aquatic life.

In suspended sediments, there were two samples in which zinc exceeded the threshold effect level, but none that exceeded the severe effect level. The great majority of fish samples from the Liard River had zinc concentrations in the range 5-20 µg/g, which is typical of other northern water bodies. The exception this time was whole northern pike, in which zinc concentrations were higher than in all other species and tissues (25-58 µg/g).

Source of Metals

Metals in Liard River fish appear to come from natural sources.

Where do the metals, especially mercury, in Liard River fish, come from? All the evidence presently suggests that these metals are derived from natural sources, especially weathering of rocks in the drainage basin. Two lines of reasoning lead to this conclusion.

First, there are no active mines or industrial developments in the Liard River basin from which metals might be derived. Abandoned and potential mine sites are all far upstream, in the Rocky Mountains, and the contribution from current oil and gas exploration is too small and too diffuse to be felt in a large river like the Liard. Second, metals concentrations in water, sediments and fish in the Liard River are always similar to those in other regional lakes and rivers in both concentration and patterns among species or seasons. Metals have been thoroughly sampled in the Slave River as part of the Slave River Environmental Quality Monitoring Program (Sanderson et al. 1997). That program always found metals concentrations comparable with those in the Liard River, including the high mercury concentrations. Numerous other studies have examined metals in lakes and rivers of the western NWT, especially in fish (see references in Sanderson et al. 1997), and have always found similar metals levels. Only a natural, regional source like bedrock erosion could produce such a consistent pattern.

The highly erodible headwaters in the Eastern Slopes of the Rocky Mountains may be the ultimate source of most metals; the very fact that mining is being considered in this region illustrates that the bedrock is relatively rich in these metals. High mercury concentrations are a common problem in the southwest portion of the NWT. The mercury appears to arise from a geological source. Within the southern NWT, there are several geological zones known to have relatively high mercury contents, including the area around Great Slave Lake. High mercury concentrations are also common in fish from more southern rivers draining the eastern slopes of the Rocky Mountains.

Polyaromatic Hydrocarbons

Background

Polyaromatic hydrocarbons (PAH) are a very large group of stable organic molecules composed of two to seven fused benzene rings. They are a common component of petroleum and are therefore associated with extraction and processing of fossil fuels. Naphthalene, the most generally familiar PAH, is the active ingredient in mothballs.

The PAH of environmental concern vary in molecular weight from 128.2 (naphthalene, two benzene rings) to 300.4 (coronene, seven rings). As the number of rings increases there are rapid declines in natural abundance, solubility in water, volatility, and rate of microbial degradation. The heaviest PAH are relatively immobile because of their large molecular volumes and extremely low volatility and solubility.

The tendency of these compounds to bind to particles, and to bioaccumulate in organisms, is also greatest for the larger, multi-ring compounds. The lower molecular weight PAH containing two or three rings, such as naphthalenes, fluorenes, phenanthrenes and anthracenes, may be acutely toxic to aquatic organisms, especially in the presence of ultraviolet light, whereas heavier compounds containing four to seven rings are not. However, all known PAH with carcinogenic properties are in the high-molecular-weight group.

PAH were measured in sediments and fish in the Liard River Program. The solubility in water of most PAH is so low that there is little point in looking for them there. PAH were measured in nine suspended sediment samples from the Liard River over 1992-1994. PAH analysis usually measured a set of 15 key compounds prevalent in industrial waste waters and which are known or suspected carcinogens. A more complete scan, including 26 individual PAH considered "priority pollutants" by the U.S. Environmental Protection Agency, was performed on a single sample collected 16 March 1993. Analyses for 24 or 27 PAH were carried out on all five fish species collected from the Liard River. In each species, separate scans were run on muscles and bile, and for mountain whitefish, on whole fish samples as well.

Sediments

Concentrations of PAH in suspended sediments of the Liard River are low and unlikely to be harmful to aquatic life.

Of the 15 common PAH measured in suspended sediments, two were never detected and two others were detected only once, despite detection limits in the low parts per billion range. Concentrations of the remaining 11 compounds were always highest in spring and least in fall, probably as a result of microbial breakdown over the summer. The average total PAH concentration in Liard River suspended sediments was 1.2 µg/g. This concentration is low in relation to biologically important concentrations, but it is still significantly greater than in surrounding lakes or the Slave River.

PAH concentrations in Liard River sediments are compared against sediment quality guidelines from Environment Canada (1995) and Ontario Ministry of Environment (OMOE 1992) in Table 1. There are no sediment quality criteria for lighter PAH such as naphthalene which seldom persist long enough to be harmful to aquatic life. Among the compounds for which sediment quality criteria do exist, only four ever exceeded the threshold effects level defined by Environment Canada (1995), and only three exceeded the lowest effect level of Ontario's sediment quality guidelines (OMOE 1992). Concentrations of all these compounds remained far below the probable effects level in every sample. It is very unlikely that these PAH levels pose a threat to biota in the Liard River.

Table 1. Comparison of PAH concentrations in suspended sediments from the Liard River against sediment quality guidelines from Environment Canada (1995) (threshold effects levels) and Ontario Ministry of Environment (1992) (lowest effect levels).

PAH	Range of Conc. (ng/g)	Threshold Effects Level	N of Samples Above Guideline (Total)	Lowest Effect Level	N of Samples Above Guideline (Total)
Fluorene	8.3-500			1.2	8 (9)
Phenanthrene	43-320	42	8 (8)	8.4	8 (8)
Chrysene	27-140	32	5 (8)		
Dibenzo(a,h) anthracene	<5-8			37	0 (8)
Fluoranthene	9.1-60	111	0 (9)	465	0 (9)
Benzo(a)pyrene	<5-50	32	3 (9)	229	0 (9)
Pyrene	15-90	53	3 (9)	735	0 (9)
Benzo(g,h,i)perylene	17-140			105	3 (9)

Fish

Only smaller PAH with two to four rings are found in Liard River fish. Cancer-causing PAH were never detected. PAH profiles are similar in all fish species; the general trend is one of rapidly declining concentration with increasing molecular weight, even though sediments contain relatively equal amounts of light and heavy PAH. Flesh concentrations of PAH in Liard River fish are at the low end of the range for uncontaminated sites elsewhere in North America and are typical of fish from other NWT water bodies. PAH levels in Liard River fish are not presently a concern.

Despite the large number of PAH analyses performed on fish tissues, results for the Liard River are highly uniform across species and sample types. Virtually all the PAH measured in fish tissues were at the light end of the spectrum, especially two-ring and three-ring compounds such as naphthalene, phenanthrene and fluorene. Fluoranthene and pyrene were the only four-ring compounds regularly detected, and with very few exceptions none of the target compounds with five, six or seven rings were ever detected in fish. Thus, none of the compounds with known carcinogenic properties were ever detected. Evidently any hazard from PAH in Liard River fish relates to acute toxicity and not induction of tumours.

A comparison of PAH profiles in bile and muscle samples showed that almost exactly the same compounds were found in both. Only fluoranthene and pyrene were found regularly in bile but not in muscle. Hence, either sample type is adequate to gauge contamination levels in Liard River fish. However, the PAH profile in the five whole-fish samples of mountain whitefish was different from that for either bile or muscle. Almost all the PAH compounds found in muscle or bile were also found in whole fish, but in addition whole fish contained four other PAH that were never detected in the other samples. PAH appear to accumulate in other pools besides muscles and bile, which are only detected when the whole fish is analysed. Concentrations and frequencies of detection tended to be higher in whole fish samples of mountain whitefish too, but it cannot be said whether this applies to the other species.

Total PAH concentrations were highly variable for muscle and especially so for bile (Table 2). Measurements in bile must be viewed cautiously because the volume of bile retrieved from many fish was very small. Nevertheless, there is surprisingly little difference in average total PAH concentrations among species, when similar sample types are compared. This uniformity of total

PAH concentrations suggests that uptake is independent of feeding habits, which range from feeding strictly on other fish (northern pike) to mixed open-water predation (mountain whitefish) to bottom-feeding (longnose sucker). Hence, whatever the ultimate source, PAH appear to be generally distributed in the environment of the Liard River. Direct uptake from sediments may be an important route of PAH acquisition by fish in this river, given the very high sediment loads, but uptake from water and food may also be significant.

The general trend of PAH concentrations in Liard River fish is illustrated in Figure 6, which shows average concentrations in bile of each fish species of the ten most common PAH compounds. The species are plotted in order from greatest concentrations (walleye) to least (burbot) but the apparent differences are not large relative to the variance within each species. Moreover, the relative proportions of each individual compound are virtually identical from one species to the next. All samples are dominated by naphthalene, and to a lesser extent the substituted naphthalenes (those with methyl groups, $-CH_3$, attached), with relatively small contributions from all other compounds. The general trend is one of rapidly declining concentration with increasing molecular weight, a trend interrupted only by phenanthrene, and sometimes pyrene (Figure 6).

The PAH profile in fish is a highly selective portion of the PAH in sediments. Concentrations of various PAH in sediments are much more similar, and do not show the rapid declines with increasing molecular weight that were observed in fish tissues. For examples, mean concentration of 1-methyl naphthalene in sediments (0.120 µg/g) is nearly identical to that for naphthalene (0.129 µg/g); concentrations of pyrene (0.044 µg/g), fluorene (0.079 µg/g) and phenanthrene (0.16 µg/g) were relatively much greater in sediments than in fish, the last even exceeding concentrations of naphthalene. Moreover, there were a number of heavy, multi-ring PAH that were detected in sediments at significant concentrations but seldom or never detected in fish. The evidence indicates that PAH in Liard River fish are strongly biased toward light, mobile compounds and against heavier, hydrophobic compounds. Similar bias has been observed in laboratory studies.

PAH may be taken up by fish from water, sediments or food. If passage of water over the gills is a major pathway of PAH uptake in the Liard River, then either the heavier PAH are too strongly bound to suspended particles to cross into fish lipids, or uptake is primarily of compounds dissolved in water. The latter explanation would account for the heavy bias toward naphthalene, the only PAH that is freely soluble in water at milligrams per litre concentrations (Eisler 1987). It is also possible that other PAH are assimilated by fish but are cleared so quickly that significant tissue concentrations never accumulate.

Table 2. Total PAH in tissues of five fish species from the Liard River. Units in bile are picograms of PAH per gram of whole fish wet weight. SD = standard deviation. n = number of samples.

	Burbot		Mountain Whitefish		Walleye		Northern Pike		Longnose Sucker	
Tissue (units)	Mean	SD (n)	Mean	SD (n)	Mean	SD (n)	Mean	SD (n)	Mean	SD (n)
Muscle (µg/g)	3.1	1.6 (21)	4.7	1.6 (15)	3.9	1.6 (33)	3.6	2.3 (21)	4.0	2.8 (28)
Bile (pg/g)	13.8	11.7 (11)	32.9	20.4 (7)	34.9	20.2 (14)	25.9	27.1 (11)	24.7	11.7 (16)
Whole Fish (µg/g)			14.1	8.6 (5)						

Based on data from the Slave River Program, the PAH concentrations in Liard River fish do not appear to be elevated above levels found in fish from other water bodies of the western NWT, once differences in species and analytical methods are accounted for. Extensive data on PAH in fish and other invertebrates compiled in Eisler (1987) show that flesh concentrations in Liard River fish are at the low end of the range for uncontaminated sites elsewhere in North America, and 50 to more than 100 times less than at sites with known sources of contamination. Hence, while the PAH data collected in this program provide a strong data base for future monitoring, the PAH levels are not presently a concern.

Organochlorine Pesticides

Pesticide residues were never detected in suspended sediments from the Liard River. Some samples of whole fish or burbot liver contain a few pesticide residues, almost always at concentrations near the detection limit. Concentrations are always below Health Canada guidelines for fish consumption.

The Liard River Environmental Quality Monitoring Program included analyses of 19 organochlorine pesticides and their breakdown products in suspended sediments, and 23 pesticides, pesticide breakdown products, and related chlorinated organic compounds in fish. The fish samples included whole-fish samples of northern pike, mountain whitefish, longnose sucker and burbot. In addition, pesticides were measured in muscle samples from walleye, northern pike and mountain whitefish, as well as in burbot livers.

None of the pesticides was detected in any sample of suspended sediment. None of the pesticides was ever detected in fish muscle samples, whether from walleye, northern pike or mountain whitefish. Furthermore, no pesticides were detected in any whole-fish sample of mountain whitefish.

Pesticides were only detected in whole fish samples and burbot liver. Some of these samples contained a few detectable pesticide residues, almost always at concentrations near the detection limit. The higher concentrations (more frequent detects) in whole-fish samples compared with muscle samples is probably due to the inclusion of the liver, which is high in fatty tissue and tends to accumulate persistent, hydrophobic compounds. This is evidenced by the substantially higher concentrations of many pesticides measured in samples of burbot liver.

Originally, the maximum residue limit for agricultural chemicals in foods sold in Canada was set at 0.1 µg/g for all organochlorine pesticides other than DDT and its stable breakdown products, which was set at 5 µg/g (Pastershank and Muir 1996). These limits were developed as a result of pesticide use in Canada, but were applied to imported foods to protect Canadian consumers once the pesticides were no longer in use. Therefore, the default maximum residue limit for pesticides in fish can be considered to be 0.1 µg/g (Department of Health 1996). Concentrations of all organochlorine pesticides in fish from the Liard River were well below this guideline, except for toxaphene, for which Health Canada has established a separate Tolerable Daily Intake for residues in food.

If toxaphene in the non-detect samples is assumed to be at the detection limit, the most conservative assumption, the mean concentration of toxaphene in burbot livers is 0.075 µg/g. By contrast, in the Slave River, toxaphene was found in walleye, northern pike, lake whitefish and burbot, with a mean concentration in burbot liver of 0.90 µg/g. Hence, toxaphene concentrations in the Liard River are low relative to fish from the Slave River. Health Canada is currently completing a human health assessment of all pesticide residues in Liard River fish, based on the data collected in the Liard River Program. An interim assessment, based on data from 1992 and 1993, concluded that these levels of toxaphene and other organochlorines pose no health hazard to consumers. Concentrations in the third year of the study are similar to those from the first two years.

Toxaphene has been detected in several other studies of northern fish, commonly at levels higher than those detected in the Liard River. This general distribution in the absence of known usage strongly suggests that atmospheric deposition is the source of contamination. Atmospheric deposition is implicated as the source of the trace quantities of other pesticides as well, most of which have not been used in Canada for many years.

Polychlorinated Biphenyls

Background

PCBs are a group of synthetic organic compounds which contain a biphenyl molecule (two benzene rings bonded at one carbon), on which a varying number of chlorine atoms are attached. Chlorinated organic compounds are almost unknown in nature, so micro-organisms are not adapted to decompose them. As a result, PCBs are among the most persistent pollutants in the global ecosystem. They were widely used in industrial applications because of their stability, resistance to both acids and bases, inertness, solubility in organic solvents, dielectric properties and nonflammability. However, because of their toxicity and persistence in the environment, in 1980 the use and importation of PCBs was totally prohibited in Canada.

In theory, there are 209 different PCBs, depending on the number and arrangement of the chlorine atoms, and commercially prepared PCBs were always complex mixtures. For simplicity, individual PCBs are identified by a number from 1 to 209. Individual PCBs vary widely in their physical and chemical properties according to the number of chlorine atoms and their position on the molecule.

PCBs enter the environment through accidents and improper use or disposal, including incomplete burning of PCB-containing wastes, spills, and leaching from dumps and landfills. Evaporation and atmospheric transport are probably responsible for the global dispersion of PCBs. PCBs are only slightly soluble in water and have a strong tendency to bind to sediment particles. PCBs are also soluble in the lipids of biological systems, and tend to accumulate in fatty tissues. Very low levels of PCB contamination in aquatic ecosystems can result in the accumulation of relatively high PCBs levels in biota.

The PCB analysis in the Liard River Program was extremely thorough. The total concentrations of PCBs were measured in suspended sediments and in whole fish samples from all five species over the three years of the Program. Total PCBs were also measured in muscles of walleye, pike and mountain whitefish, and in burbot livers. Along with total PCBs, a set of 10, 16 or 54 important PCB compounds was analysed in each tissue type of each species. Some samples were also analysed separately for PCBs 77, 81, 126 and 169, the most toxic of all PCBs. The analysis for these PCBs in burbot liver in 1994 used a new analytical method that pushed detection limits to the parts per *trillion* level.

Sediments and Fish

PCBs were never detected in any sediment sample. PCB concentrations in all fish samples from the Liard River Program fell far below the Health Canada limit for commercial fish sale and export, and therefore should not be considered hazardous to consumers.

Among muscle and whole fish samples, none of the individual 10, 16 or 54 PCBs was ever detected in any sample from any species. Similarly, none of the potent PCBs 77, 81, 126 or 169 was ever above detection limits in any sample of muscle or whole fish from any species of fish from the Liard River. Any PCB residues that may occur in Liard River fish clearly include only the less potent compounds.

The concentration of total PCBs was below the detection limit (10 ng/g) in every sediment sample. Total PCBs were undetectable in whole northern pike or muscles of mountain whitefish from the Liard River. Among the other species and tissues, above-detection concentrations of total PCBs were found in roughly half of all samples. Concentrations of total PCBs varied over a relatively narrow range in all samples, from about 10 to 125 ng/g, except in burbot liver, which ranged from 20 to 400 ng/g.

Burbot livers were the only tissues in which individual PCB compounds were ever detected. Only six out of a possible 54 compounds were detected, and those only in one or two samples out of 20. Approximate concentrations ranged from 3 to 16 ng/g. Higher concentrations of PCBs in burbot liver than in other fish or other tissues have been observed elsewhere in the region and are a reflection of the high lipid content of the liver.

Some or all of the four most potent PCBs were detected in every burbot liver sample from the Liard River because an improved analytical method allowed concentrations to be measured in the low parts per trillion range. Even so, these concentrations were all very near the detection limit. Measured concentrations ranged from 0.0003 to 0.087 ng/g.

In Canada, a limit for commercial fish sale and export of 2000 ng/g total PCBs in the edible portion of fish has been established by Health Canada (Health and Welfare Canada 1998). All of the samples from the Liard River program fell far below this limit, and therefore should not be considered hazardous to consumers. The British Columbia Ministry of Environment recommends a guideline of 100 ng/g of total PCBs in whole fish to protect wildlife dependent on aquatic life for food (Nagpal 1992). All whole fish samples from the Liard River were well below this strict guideline, except for a single burbot. Again, no impairment of the health of wildlife would be expected from consumption of fish from the Liard River.

PCB concentrations in Liard River fish are lower than those from the Slave River program, in which all samples had detectable PCBs, and comparable with or lower than samples taken from other lakes and rivers in the NWT and elsewhere in Canada. The presence of trace levels of PCBs in samples from both the Liard River and other lakes and rivers throughout the NWT strongly suggests an airborne source. Atmospheric deposition of PCBs in remote areas is well documented.

Dioxins and Furans

Background

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are large families of chlorinated hydrocarbons with one (furans) or two (dioxins) oxygen atoms connecting two benzene rings. There are some 75 polychlorinated dioxins and 135 polychlorinated furans, each having a different number and arrangement of chlorine atoms attached to the carbon atoms of the benzene rings. Dioxins and furans are by-products of various processes from chemical, pulp and paper, metallurgical and dry-cleaning industries. Forest fires are evidently the largest natural source.

Dioxins and furans are structurally similar to PCBs, and behave in much the same way in the environment. However, dioxins and furans are toxic at extremely low concentrations compared with other groups of organic compounds. A limit of 20 pg/g of the most toxic dioxin, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), in the edible portion of fish has been set by Health Canada for commercial fish sale and export (Department of Health 1996).

Fish

Dioxins and furans are present only in minute quantities in Liard River fish, far below levels considered a hazard to animal or human health.

A set of the most potent dioxins and furans was measured in livers from ten burbot collected in the Liard River in 1994. The liver is the most sensitive tissue for monitoring because dioxins and furans are extremely hydrophobic and tend to accumulate in fatty tissues. The analytical method produces detection limits at the parts per trillion level. Nevertheless, 2,3,7,8-TCDD was never detected in any sample. A number of other dioxins and furans, never the most toxic varieties, were detected in some or all liver samples, at concentrations ranging from 0.06 pg/g (detection limit) to 2.8 pg/g.

While dioxins and furans are evidently present in these samples, the absolute values are low, so low in fact that the exact values of the measurements cannot be certain. Samples that were split and analysed twice often produced quite different results, a common problem when ultra-trace compounds are being measured near the detection limit. However, it can be concluded that dioxins and furans are present in minute quantities in Liard River fish, far below levels considered a hazard to animal or human health.

There are no pulp mills or other industrial sources of dioxins upstream in the Liard River, so atmospheric deposition is the most likely source of the low levels found in fish there. The very low dioxin and furan levels in Liard River burbot livers suggest that these fish are essentially free of contamination from sources in the basin, and these data can be used as a baseline against which to gauge any changes in future.

Sediment Toxicity and Enzyme Induction

Laboratory tests on water extracts of Liard River sediments indicate no acute toxicity to aquatic life. Activities of mixed-function oxygenase enzymes in fish livers from the Liard River are similar to those in fish from clean water bodies in Canada, and are considered indicative of an unpolluted environment.

Two other minor tests were undertaken to evaluate the health of the Liard River ecosystem. Toxicity tests were used to assess whether any elements or compounds weakly bound to sediments might prove harmful to aquatic life. The activities of certain enzymes in the liver of fish, that are known to increase in response to contamination, were also measured.

Sediment toxicity was measured by mixing Liard River sediments with water in a 1:10 ratio, and shaking the mixture overnight to release any available chemicals from the surfaces of the sediment particles. The sediments were then removed by centrifugation. Any toxic substances available to aquatic life would then be in the water. Toxicity was measured by placing 10 water fleas (*Daphnia*) a small, free-swimming crustacean abundant in Canadian fresh water, in the extracted water and seeing how many survived for 48 h. Sediment toxicity was measured twice with this method and on both occasions all the *Daphnia* survived the full duration of the test.

A similar test was run on three occasions using a stronger 1:1 mixture of sediments and water and using a strain of naturally light-emitting (bioluminescent) bacteria as the test agent. Light production by the bacteria declines when they are exposed to toxic substances. Results of the bacterial test agree closely with tests on fish or other organisms, but require only a small sample. Again there was no indication of toxicity in any of these tests. It may be concluded from these simple, direct tests that suspended sediments from the Liard River are not acutely toxic to aquatic life.

The liver of fish contains a special group of enzymes, called mixed-function oxygenases, that aid in the removal of certain toxic substances, notably PAH and similar organic compounds. Liver cells manufacture more of these enzymes when the fish is exposed to toxic substances in the environment, so measuring the activity of these enzymes is a quick way to tell if fish are exposed to toxicants. Mixed-function oxygenase activity was measured in extracted liver cells from all five fish species from the Liard River.

Enzyme activities in fishes from the Liard River were low and very similar to those of the same or closely related species in the Slave River and nearby lakes reported in the Slave River Program (Sanderson et al. 1997). These levels of enzyme activity are considered indicative of an unpolluted environment. Enzyme activities were also similar to those from clean water bodies in other regions of the Northwest Territories and elsewhere in Canada.

Conclusions:
The Liard River is Healthy and Uncontaminated

DIAND had three objectives when the Liard River Environmental Quality Monitoring Program was undertaken:

(1) to characterize the conditions of water, suspended sediment and fish of the Liard River at the NWT boundary;

(2) to provide baseline data on contaminant levels in the Liard River in support of transboundary water negotiations; and

(3) to address concerns of the local people regarding possible effects on water uses and fish from upstream developments in the basin.

The Program achieved these objectives. A broad, detailed and reliable base of information on the river and its biota was collected. From this data base it becomes apparent that the river is presently pristine and unimpaired by upstream industrial activity. Any contaminants in fish are either naturally derived or globally distributed. Concentrations of most organic contaminants are extremely low and only measurable with sophisticated instrumentation. With the possible exception of mercury, which is naturally high in fish of this region, none of the measured contaminants pose a hazard to aquatic biota or people living along the river.

The dramatic seasonal pattern of discharge and suspended solids concentrations in the Liard River dominates all aspects of water quality. When allowance is made for this annual cycle, water quality in the Liard River is quite good. The water is hard and alkaline. Proportions of inorganic ions are typical of inland fresh waters in Canada. Nutrient supplies are indicative of a clean, moderately productive ecosystem. High turbidity in the Liard River may impede some recreational uses of the river, and in most seasons the water certainly could not be used domestically without treatment. The high turbidity is also something to which fish and other organisms must adapt. But physical and chemical conditions in the Liard River are otherwise within ranges considered supportive of freshwater life.

The Liard River carries an enormous load of suspended sediments in spring and summer. The suspended material is dominated by fine particles, silts and clay, with a relatively small contribution from sand. PCBs and organochlorine pesticides are not a concern in suspended sediments. A few metals, notably arsenic and nickel, sometimes exceed sediment quality guidelines. There is no evidence, however, that these metals, or other contaminants, are causing toxic effects on the biota of the river. On the other hand, low but potentially significant concentrations of a few PAH were detected in sediments. These low background levels do not constitute a threat to the environment, but a solid baseline of compounds and their concentrations is necessary if anthropogenic increases in PAH levels are to be detected in the future.

Fish sampling in the Liard River program was thorough, and included a large number and variety of fish and fish tissues. With very few exceptions, analyses indicated that Liard River fish are essentially free of hazardous contaminants, including PAH, PCBs, pesticides, metals and dioxins and furans. Those elements or compounds that were present were mostly detected only by virtue of the extremely sensitive analytical methods brought to bear on the samples. Tissue concen-trations are for the most part typical of fish from pristine regions. These concentrations represent the trace residues spread globally by the atmosphere or generated by erosion or other natural processes within the basin.

The Liard River Program provides a strong argument for the multi-media approach to environmental monitoring. For example, mercury is naturally high in muscles of Liard River fish, even though concentrations were low in sediments and undetectable in water. Had sampling relied on conventional parameters in water and sediments alone, the accumulation of mercury in fish would have gone unnoticed. Similarly, while PAH were detected at low concentrations in sediments and fish, the proportions of different compounds in fish tissues could not be predicted from those in sediments. Relying on sediment sampling alone could have lead to concerns about tumour-inducing PAH that were not borne out by fish samples. Sampling of all the major compartments in the ecosystem is clearly justified in a program of this kind.

The information obtained in the Liard River Environmental Quality Monitoring Program provides a strong data base to carry forward into transboundary negotiations to protect the Liard River and the northern people who depend upon it. DIAND can use the experience gained in this Program to streamline future sampling, by measuring potential contaminants in the ecosystem compartment where they are most readily detected. The Liard River Program is an important first step toward ensuring that the Liard River ecosystem remains clean and uncontaminated into the future.

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