ONTARIO REGION

Water Quality Investigations in Ontario's Arctic Watershed

by

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ABSTRACT

A water quality sampling network was established in the major rivers of Ontario's arctic watershed to provide baseline information. Based on data generated by the network sampling, several short-term studies were carried out to address concerns particular to these basins. More specifically, these studies were conducted to (1) identify and enumerate the benthic macroinvertebrate communities; (2) investigate the distribution of heavy metals and organic contaminants in water, sediment and fish; (3) examine the relative mobility of various elements through the analyses of sorbed and lattice-bound sediment fractions; (4) assess atmospheric depositions of organic pollutants in the region by sampling the wetlands; and (5) characterize the major colloid types in these northern waters and determine the relative binding capacity of the dissolved and colloidal fractions. These follow-up studies have provided information for assessing the source and fate of contaminants and for describing ambient environmental conditions. Selected results are presented.

INTRODUCTION

The Ontario arctic watershed, with a combined drainage area of 552 000 km^2, extends over substantial portions of two major physiographic regions, the Canadian Shield and the Hudson Bay Lowland. The Shield portion of the watershed is composed of ancient crystalline granites interspersed with metasedimentary and metavolcanic rocks. Outcrops of bedrock are common, since much of the overlying material was stripped away by glacial action (Hutton and Black 1975). The Hudson Bay Lowland (HBL) is a vast and gently sloping coastal plain, located between the Canadian Shield and the south and west shores of Hudson and James Bay. This region is of particular national importance as a nesting and feeding area for many species of geese, ducks and shorebirds, and represents a unique wetland environment which is sparsely populated and supports few resource-based activities. It is characterized by a sedimentary limestone bedrock overlain with marine clay. Virtually the entire Lowland area is poorly drained, and features extensive bog and fen complexes in combination with a myriad of pools, ponds and lakes. The Ontario portion (265 000 km^2) of this immense peat complex is dissected by five major rivers: the Moose, Albany, Attawapiskat, Winisk and Severn. Except during spring freshet, these highly coloured waters are generally shallow and slow moving. River beds and banks are widened and deepened in many areas by the scouring action of ice and spring flood waters (Hutton and Black 1975). The resulting riverbanks commonly rise 5 to 15 m to forested levees.

As part of a multi-disciplinary baseline program, the Water Quality Branch, Ontario Region (WQB-OR), has undertaken a study to establish baseline water quality conditions in the five major rivers. This is largely being achieved by a water quality network. Several other studies, however, have been carried out to provide information on the source, fate and compartmentalization of contaminants in these northern watersheds. In this paper, the development of a multi-phase environmental sampling program (Fig. 1) and selected results are presented. Detailed descriptions of the sampling sites and methods can be obtained from previous reports.

PILOT STUDY

Prior to the establishment of the Northern Water Quality Network, a pilot study was conducted in the Moose River basin. This watershed is located in the northeast sector of the Province of Ontario, and drains an area of approximately 109 000 km^2. The three main tributaries, the Missinaibi, Mattagami and Abitibi, descend approximately 500 m over a distance of 500 km from their source on the Shield to the mouth of the Moose River on James Bay (Fig. 2). The lower reaches of the Moose River and estuary present a complex pattern of islands and channels. Langford (1963) suggests that salt water enters the Moose River and travels upstream to a point just north of Moosonee, while tidal movements can be observed upstream from the south end of Bushy Island (Fig. 3). The maximum range of tides at the mouth of the Moose River is approximately 3 m. Water levels in several of the headwater streams are also regulated to maximize hydroelectric generation. This

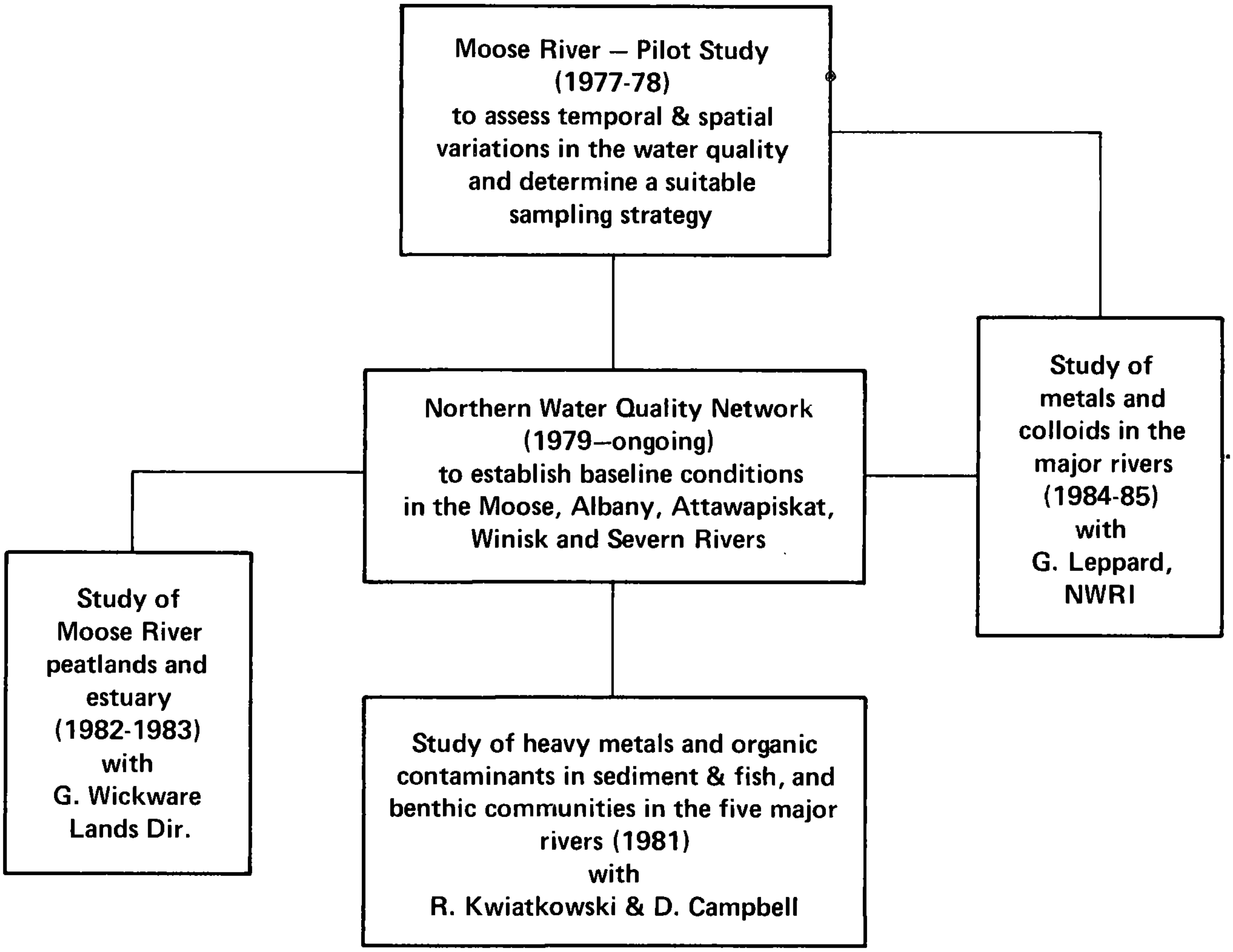


Figure 1. Development of a multi-phase sampling program in Ontario's arctic watershed.

regulation results in substantial changes in the discharge of both the Abitibi and Mattagami rivers.

The main objectives of the pilot study were to assess spatial and temporal variations, and to design a suitable sampling strategy for determining seasonal variations and long-term trends in the water quality of the lower Moose River. The approach adopted was to sample the Moose River upstream from Moosonee on a transect located at the south end of Bushy Island. Four sampling sites were selected (Fig. 3), and eight surveys were carried out between March 1977 and March 1978. Because of dangerous ice conditions the river could not be sampled during spring break-up and fall freeze-up.

Each survey was scheduled to consist of two consecutive days of sampling; unpredictable events such as adverse weather conditions and equipment failure, however, sometimes altered the schedule. During each day of sampling, six samples (three at low tide and three at high tide) were collected from all stations at a depth of 1 m. In the

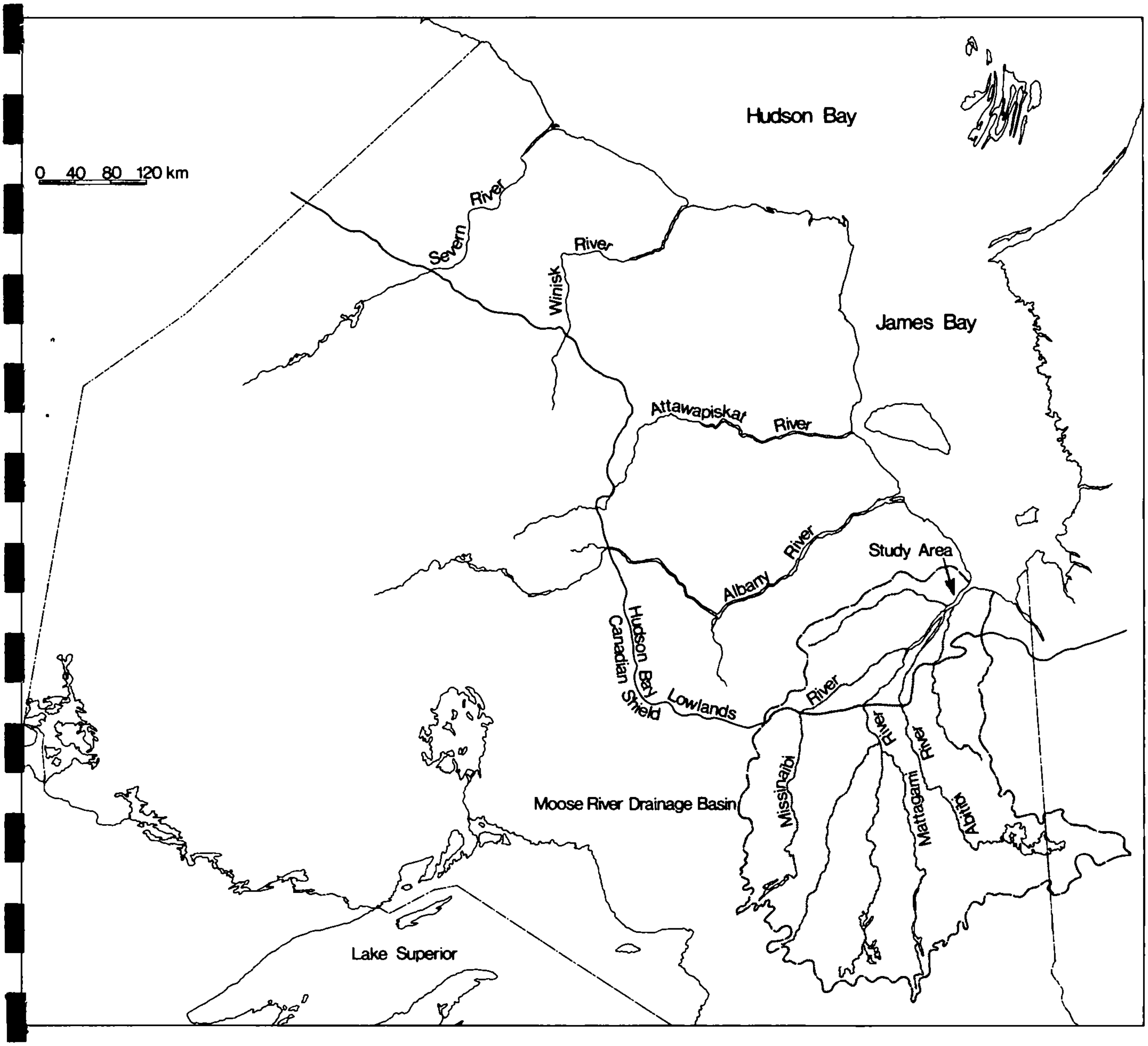


Figure 2. Moose River drainage basin.

winter months, a hole was drilled through the ice and after the stagnant water and ice chips had been removed, a sampling device was lowered into the free-flowing water (below the ice) to collect the water samples. All sample preparation such as filtering and preserving was completed within 8 h of collection. The samples were then returned to the Water Quality Branch laboratory in Burlington for the analysis of major ions, nutrients and trace metals (Environment Canada 1979).

A two-way analysis of variance was performed on data from the four most complete surveys to determine whether short-term variations (T), those differences observed at any station over the two-day sampling periods, and/or lateral variations (L) were significant (Table 1). The

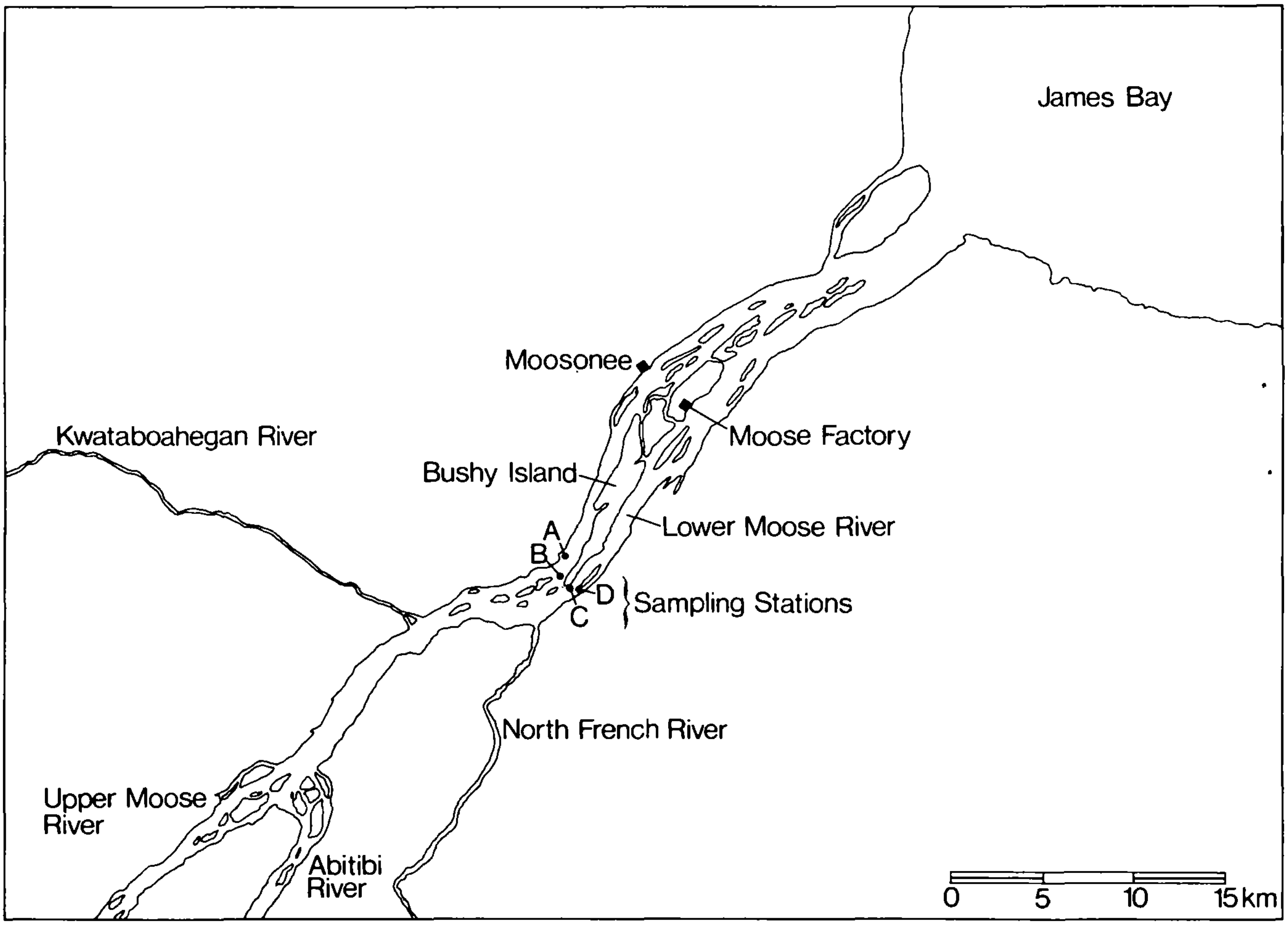


Figure 3. Moose River and tributaries.

UCLA Biomedical computer program BMD OV8 (Dixon 1971) was used to calculate the F-values. If the calculated F-value exceeded the critical F-value, then the observed changes were considered to be significant.

Short-Term Variation

Less than 20% of the cases tested for temporal variation (T) had F-values greater than the critical F-value (at the 95% confidence level). Those cases showing significant concentration difference with time ($P > 0.05$) usually varied by only 5%-10% from the mean value of samples collected at that station during the two-day surveys. Although statistically significant, this magnitude of short-term variation was relatively unimportant when compared with the large seasonal variation exhibited by most parameters.

Lateral Variation

As a result of reconnaissance survey carried out in 1976, it was postulated that distinct channels of differing water quality might

Table 1. Temporal and Lateral Variance in the Lower Moose River Water Quality

Parameter	Survey 2 May 10-11, 1977 L	 T	Survey 4 July 9-10, 1977 L	 T	Survey 5 August 30-31, 1977 L	 T	Survey 6 October 18-19, 1977 L	 T
Alkalinity, total	148.0	2.10	88.0	1.71	41.0	2.35	417.0	0.20
Calcium	82.0	2.77	21.0	1.68	100.0	1.89	57.0	1.18
Chloride	65.0	1.38	147.0	1.19	43.0	1.02	40.0	0.44
Magnesium	218.0	1.50	436.0	11.3	77.0	1.95	107.0	0.45
Potassium	10^{11}	10^{-9}	47.0	1.50	45.0	1.00	11.4	1.00
Sodium	308.0	1.00	167.0	2.25	92.0	2.62	17.6	0.55
Sulphate	14.7	5.61	7.1	0.41	2.3	6.08	14.6	2.17
Carbon, diss. organic	0.7	3.88	4.8	0.27	43.0	5.04	1.8	0.50
Carbon, part. organic	21.1	0.58	1.4	4.70	-	-	23.1	2.56
Nitrogen, part.	10.4	1.70	0.2	2.74	-	-	37.5	1.81
Nitrogen, total Kjeldahl	39.0	0.58	11.8	1.32	6.0	0.10	15.4	0.97
Phosphorus, total	50.0	5.96	1.9	2.14	29.0	9.60	16.7	0.54
Turbidity	134.0	4.57	26.0	7.41	20.0	1.79	7.5	1.56
Conductivity	68.0	2.66	61.0	4.69	1.5	1.08	1870.0	1.00

L = Variance between sampling locations (calculated F-values).
T = Variance between sampling times (calculated F-values).
95% Critical F-value: L = 3.86, T = 3.86
99% Critical F-value: L = 6.99, T = 6.99

occur in the lower Moose River owing to the convergence of the Kwataboahegan, upper Moose, Abitibi and North French rivers (Fig. 3). The four sampling sites A, B, C and D were selected to reflect the water quality of these rivers. Results of analysis of variance (Table 1) showed that 88% of the cases tested had significant lateral (L) variations ($P > 0.05$). Physical evidence such as sharp changes in colouration and distinct differences in turbidity across the river also indicated strong channelization of flow. Although lateral variations were significant throughout the year, they were at a minimum in the summer and maximum in the winter for many of the parameters investigated. Figure 4 illustrates relative concentrations across the Moose River for calcium.

Seasonal Variation

The largest variations in the water quality of the lower Moose River occurred on a seasonal basis, with some parameter concentrations showing flow-related changes. Discharge of the Moose River into James Bay, as derived from the summation of the tributary discharges, varied greatly during the study period (Fig. 5). Maximum values approaching 10 000 $cm.s^{-1}$ were found during spring freshet, April 23-25, 1977;

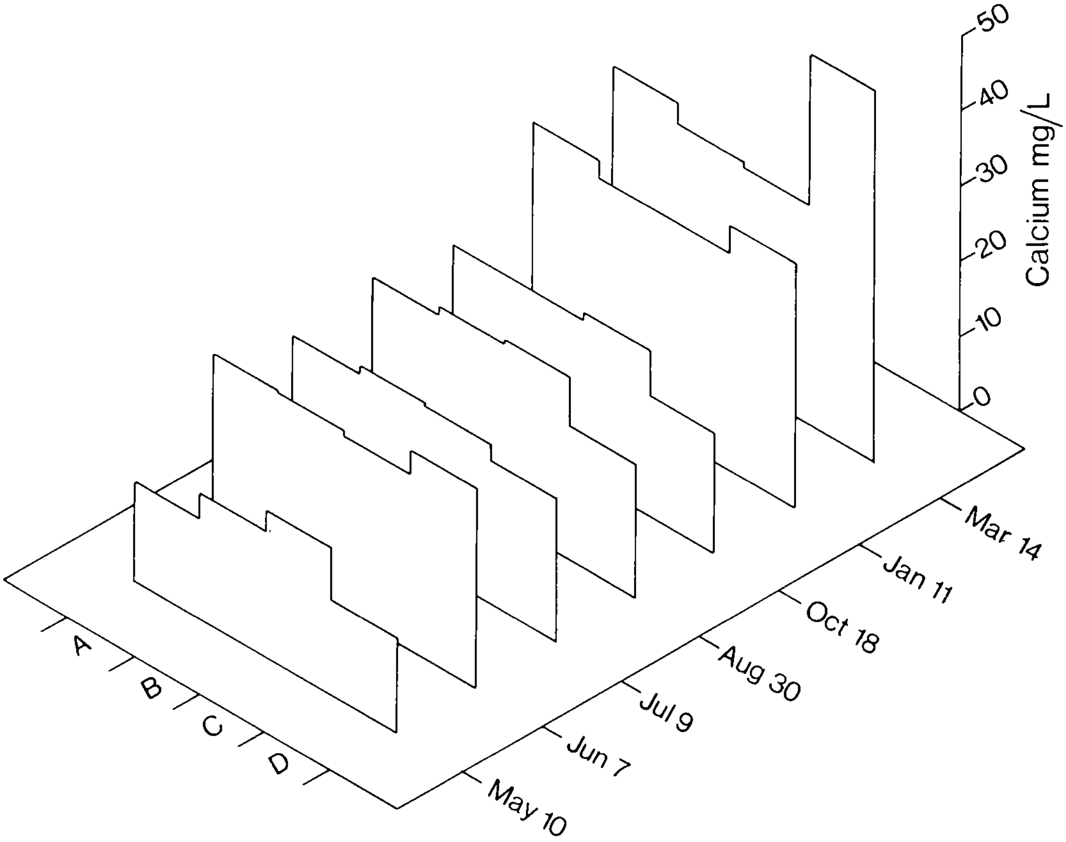


Figure 4. Lateral variation in the concentration of calcium across the lower Moose River, May 1977 to March 1978.

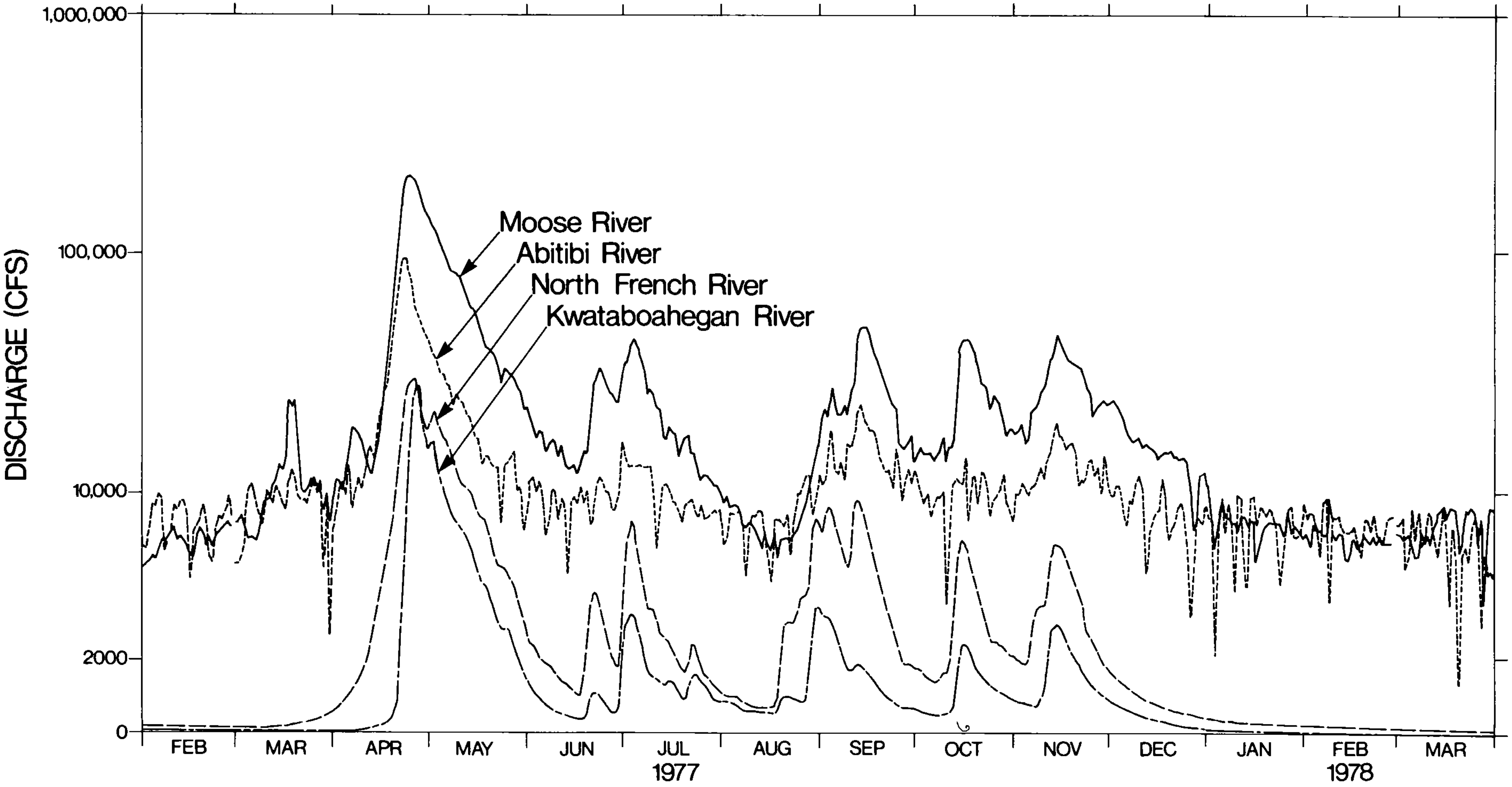


Figure 5. Hydrographs of the lower Moose River tributaries, February 1977 to March 1978.

minimum discharge levels averaging 420 cm.s^{-1} were observed during the winter months, January to March 1978. The sharp fluctuations in the discharge of the Abitibi and upper Moose rivers were due to hydroelectric dams upstream holding back or impounding the water to maximize electrical generation. The North French and Kwataboahegan rivers were undammed and had natural flow regimes.

The maximum seasonal variation in the major ion chemistry was found in the side channels. Conductivity, a measure of the ionic constituents, varied by 200% at stations B and C, and up to 600% at stations A and D. Individual ions such as sodium, potassium and chloride were extremely variable; concentrations of the latter element were found to vary up to 2800% at station D. In general, the major ion concentrations varied inversely with flow. A six-year record of discharge and conductivity for the Moose River at Moose River Crossing typifies this relationship (Fig. 6).

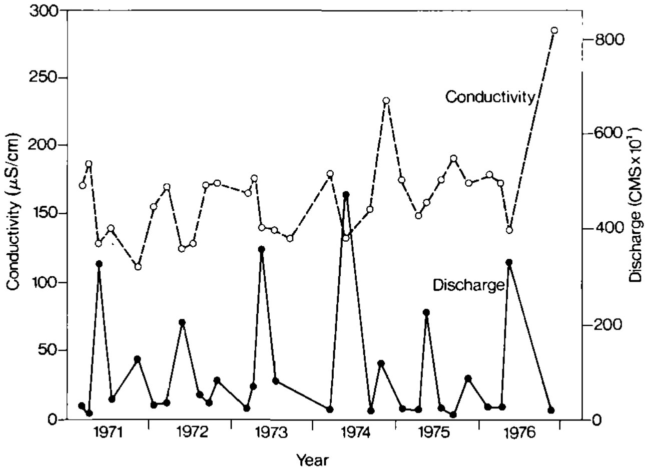


Figure 6. Seasonal discharge and conductivity of the upper Moose River.

Concentrations of nutrients and trace metals, which in many cases reflected both dissolved and particulate species, did not vary directly with flow but were strongly affected by flow. While spring runoff tended to dilute the concentration of dissolved species, severe erosion of the banks and river bottom tended to increase total concentrations. Of the various metals investigated, iron and aluminum were the most noteworthy, as concentrations approaching 1 ppm were not uncommon. Elevated levels of total iron in May 1977 reflected the high suspended sediment load associated with freshet (Fig. 7).

Dissolved organic carbon (DOC), a measure of aquatic humic substances, was a major component of these northern waters. Concentrations were commonly found in the range of 15 to 25 mg.L^{-1} and exceeded levels of all riverborne constituents except calcium and bicarbonate. Relatively low levels in May and June 1977 reflected the dilution effect of spring runoff, whereas the decrease found during the winter months was likely due to the freeze-up of creeks that drain the peatlands (Fig. 8). Concentrations of particulate organic carbon, which average 0.8 $mg.L^{-1}$, were a small fraction of the total organic carbon.

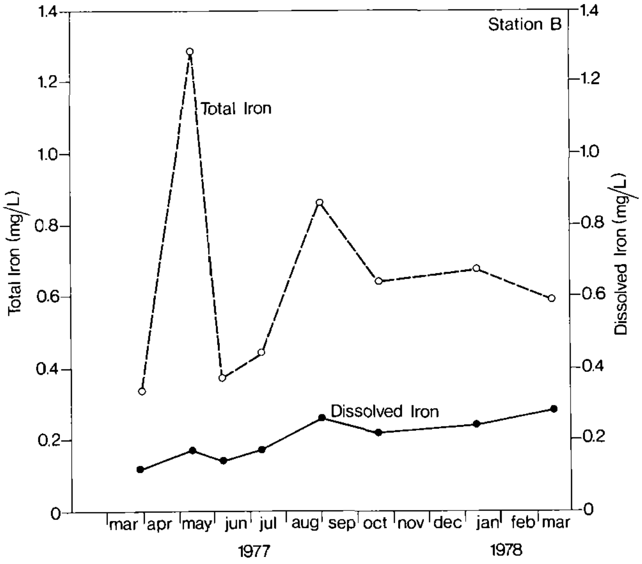


Figure 7. Total and dissolved iron in Moose River.

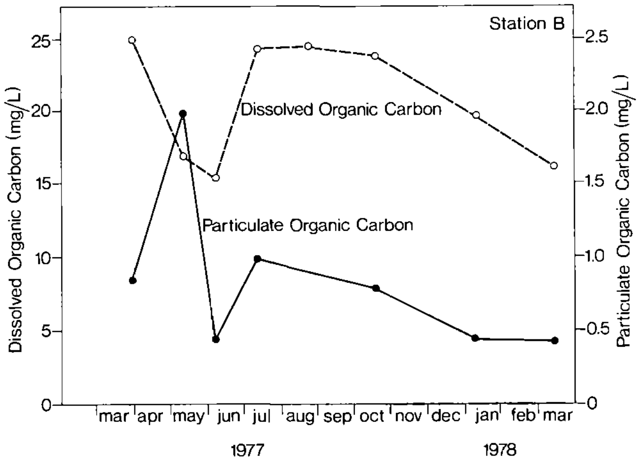


Figure 8. Dissolved and particulate organic carbon in the Moose River.

In summary, results from this study revealed the following information about the lower Moose River:

1. Short-term (temporal) variations in the water quality were insignificant, and therefore, water quality sampling at the Bushy Island transect could be conducted independent of time of day.

2. Lateral variations in the water quality across the lower Moose River were very significant throughout the year for most parameters. These differences in water quality resulted from the channelized flow in the lower Moose River.

3. The greatest single factor affecting the major ion concentration of the Moose River was the annual flow cycle. Highest concentrations occurred during periods of lowest flow (fall and winter) and lowest chemical concentrations were found during spring runoff. Both flow and major ion concentrations were highly variable. In any single year, flow may vary up to 2000%, while chemical concentrations may vary up to 2800%.

4. The high suspended sediment load associated with spring runoff caused substantial increases in the concentration of total iron, extractable aluminum and particulate organic carbon, whereas the concentration of dissolved organic carbon decreased as a result of the dilution effect of spring runoff.

Since there was insignificant variation in the short-term and substantial concentration changes between surveys carried out on a five- to six-week time interval, it was felt that bi-weekly sampling would be suitable for establishing baseline water quality conditions. Sampling in two midstream channels (B and C), which accounts for 90% of the total discharge of the lower Moose River, would be most cost-effective.

Based on this study, a native resident of Moosonee was offered a contract to collect water samples from the two midstream stations.

NORTHERN WATER QUALITY NETWORK

Following a reconnaissance survey in 1979, a water quality sampling program was established to provide baseline information on all major rivers of Ontario's arctic watershed. Samples for nutrient, major ion and trace metal analyses were collected on a bi-weekly basis 10 to 20 km upstream from the mouths of the Moose, Albany, Attawapiskat, Winisk and Severn rivers (Fig. 2). Aliquots for organochlorine pesticides and PCBs were collected on a monthly basis. Results of the network data will be discussed along with fish and sediment data in the next section.

AN INVESTIGATION OF CONTAMINANTS AND BENTHIC COMMUNITIES

A study was undertaken in 1981 to investigate various inorganic and organic contaminants in water, fish and sediment, and provide information on the benthic macroinvertebrate communities for assessing ambient environmental conditions. The approach adopted was to sample the five major rivers of Ontario's arctic watershed just upstream from their mouths near the northern water quality network sampling stations.

A field crew of five was flown to the sampling areas, and surveys were conducted from freighter canoes. Macroinvertebrate samples were collected in replicates of five at four to nine sites in each river using a 15 cm by 15 cm mini-Ponar. Visual estimates of the bottom substrate type were made as a percentage of pebble, sand, silt, clay and organic matter. Contents of each grab sample were hand-sieved using a standard No. 30 (0.59-mm mesh) sieve bucket. The sieved material was transferred to 2-L bottles and kept in river water until the live macroscopic organisms could be hand-picked. All samples were sorted and preserved within 24 h of collection.

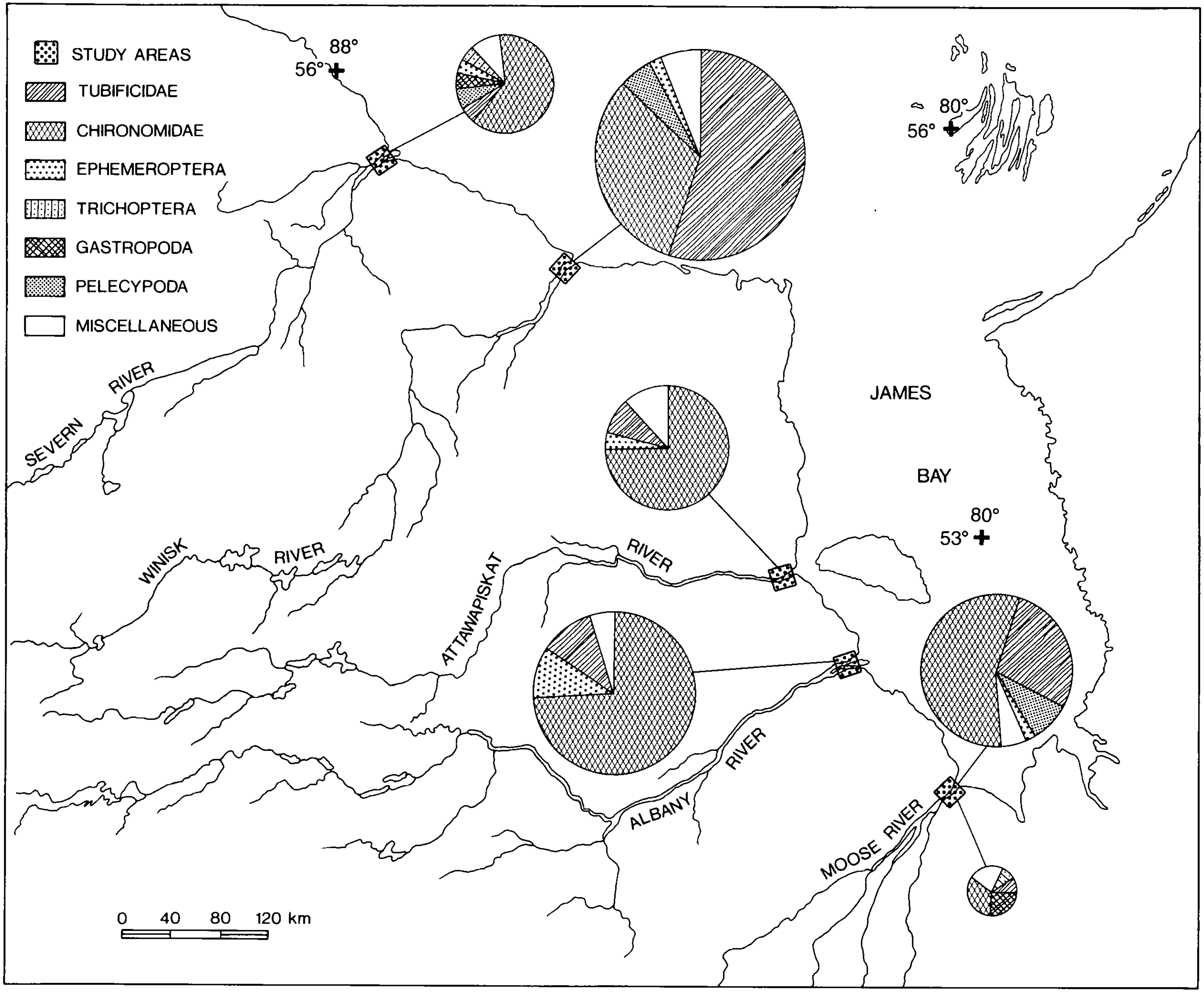
Bottom sediment grab samples for trace contaminant analyses were also collected with a mini-Ponar. The top 1 cm of sediment was carefully removed and stored at -20°C in polyethylene bags and tin-plated containers for metal and organic analyses, respectively. Two species of freshwater fish common to the five rivers were captured using gill nets near the network sampling stations. The species chosen represent two trophic levels: northern pike, a top carnivore, and common white sucker, a bottom scavenger. Immediately after collection, each fish was wrapped in solvent-washed aluminum foil, placed in polyethylene bags and stored at -20°C. Ages of the northern pike and common white sucker were established by counting cleithral and opercular annuli. The fish were homogenized and aliquots of the homogenate stored in acid-washed and acetone-hexane rinsed glass containers for trace metal and trace organic contaminant analyses, respectively.

Benthic Communities

The benthic communities were primarily dominated by chironomids and oligochaetes in each river except in the east channel of the Moose River where gastropods were also a common taxon (Fig. 9). Despite the harsh conditions associated with long winters and intense spring break-up periods, 126 species of macroinvertebrates were collected.

Diversity, as measured by the Shannon-Weiner diversity index for the individual stations, was found to range from 0 to 4.3. A one-way analysis of variance at the 5% level showed that there was no significant difference between station means among the five rivers. Species richness of the five rivers was also insignificantly different as determined by Q-statistics (Hendrickson 1978). Analysis of the individual station data showed that species richness was related to substrate composition, river velocity and water depth but not to any of the water chemistry variables measured.

Community structure analysis was performed using three indices: Coefficient of Community, Jaccard's coefficient and Percent Similarity of Community (Jaccard 1908; Whittaker and Fairbanks 1958; Sanders 1960). These indices showed that rivers geographically closest together resembled each other the most (Fig. 10).



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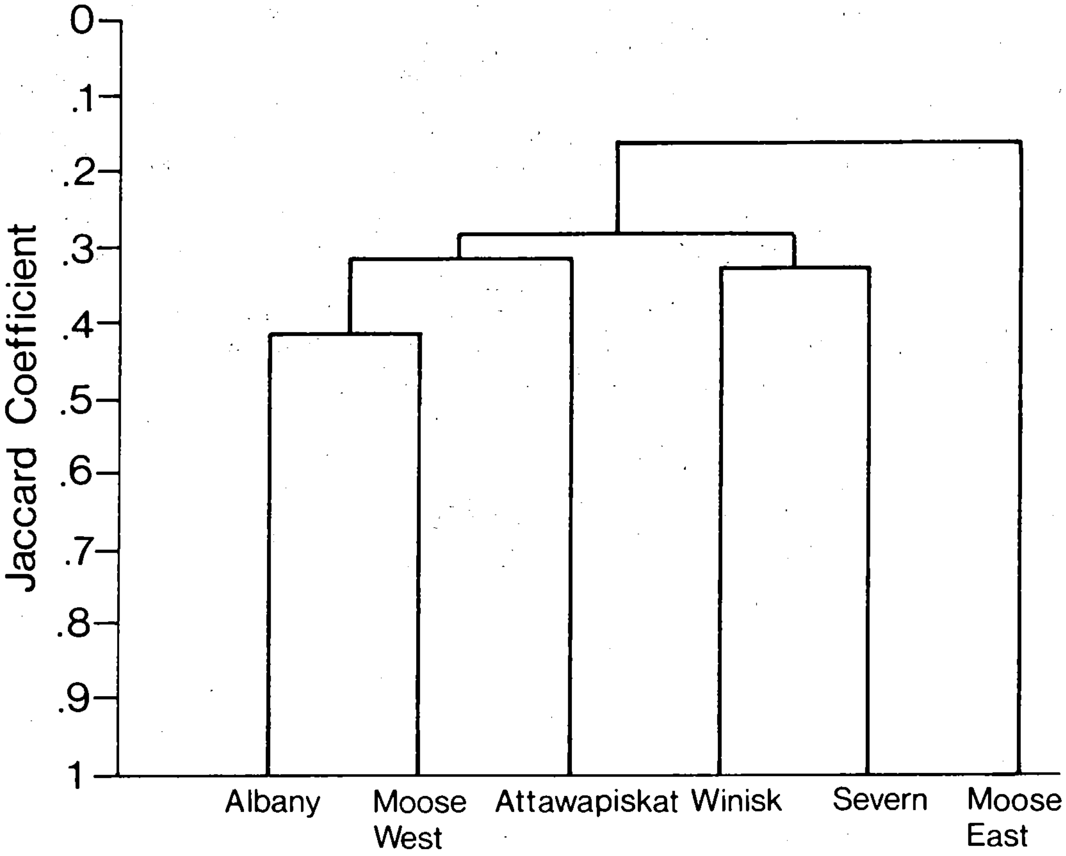

Figure 10. Results of cluster analysis on the benthic communities of the Hudson Bay Lowland rivers using the Jaccard coefficient and simple weighted pair groups.

Cluster analysis tended to confirm results of the three community structure indices. The east channel of the Moose River did not cluster strongly with the other rivers, whereas the Moose West, Albany and Attawapiskat clustered as did Winisk and Severn. Although there are obvious similarities and differences in the benthic communities, these northern rivers appeared to have the same level of diversity. Most of the values fell within the category (D = 1 to 3) for moderately stressed environments (Wilhm and Dorris 1968). Factors such as pH, dissolved oxygen and suspended sediment load, which normally limit species diversity and numbers of individuals, did not appear to limit the occurrence of macroinvertebrates. The low diversity indices were likely due to the natural processes of these harsh environments.

Water

Major ion analyses of the network samples showed that these waters are of the alkaline-earth-bicarbonate type, with conductivities ranging from 100 to 350 µS on a seasonal basis in each river. These northern waters were often highly coloured and had elevated levels of dissolved organic carbon, which ranged from 10.1 to 14.5 $mg.L^{-1}$ (Table 2). Heavy metal analyses indicated the presence of high levels of total iron in each river; mean concentrations ranged from 260 to

860 $\mu g.L^{-1}$. Individual iron values often exceeded the Ontario Ministry of Environment (MOE) objective of 300 $\mu g.L^{-1}$ for the protection of aquatic life (MOE 1978). The percentage of exceedances in the five rivers ranged from 45% to 100%, with a greater proportion occurring in the Moose and Severn rivers. Overall, exceedant concentrations were found in 79% of the samples collected from the five watersheds.

Table 2. Mean Concentration of Selected Elements ($\mu g.L^{-1}$) and Organochlorine Contaminants ($ng.L^{-1}$) Present in Raw Water Samples Collected from Rivers of the Hudson Bay Lowland, June 1980 to December 1981

Parameter	Moose	Albany	Attawapiskat	Winisk	Severn
Aluminum[1]	450	470	100	60	330
Arsenic	0.7	0.3	0.6	0.2	0.4
Copper	5	4	5	2	3
Iron	860	260	380	350	840
Lead	2	1	1	1	1
Nickel	2	1	1	-	1
Zinc	-	3	4	4	5
α-BHC	5.0	5.5	8.4	6.0	7.2
γ-BHC	0.6	0.9	0.9	0.4	1.5
Cis-chlordane	0.5	0.4	0.1	0.1	0.1
Trans-chlordane	0.2	0.1	0.2	0.1	0.1
p,p'-DDE	0.1	0.1	0.1	0.1	0.1
Dieldrin	0.4	0.1	0.1	0.3	0.1
HCB	0.2	0.2	0.1	0.6	0.2
PCBs	8	9	11	6	16
DOC[2]	14.5	12.7	11.6	10.1	11.2

[1] All heavy metal analyses are total, with the exception of aluminum which is extractable.

[2] Refers to dissolved organic carbon; concentrations are expressed in milligrams per litre.

The major inorganic species of iron in natural waters is ferric hydroxide. However, it has a very low solubility in the pH range of 5 to 8 (Wetzel 1975). Sholkovitz and Copeland (1980) have demonstrated that the solubilities of Fe, Ca, Ni, Cd, Co and Mn are opposite to those predicted by inorganic solubility considerations, and that complexation with humic substances is an important process. Weathering of mineral soils and sediments is often enhanced by naturally occurring organic acids and may increase the concentration of these soil constituents in aqueous solutions to levels far in excess of their normal solubilities (Schnitzer 1981). Owing to the elevated levels of DOC, which is a measure of aquatic humic substances, it is likely that a significant proportion of total iron in each river was complexed to humic fraction.

Previous water quality investigations of the Moose River have shown that on average 200 $\mu g.L^{-1}$ of iron was present in the dissolved phase, which accounted for 25% of total concentrations. The high non-filterable iron concentrations were largely due to suspended sediments, as the Moose River is shallow and resuspension of bottom sediments is common.

Of the various organochlorine pesticides and metabolites detected in water, α-BHC was by far the most concentrated with levels ranging from 5.0 to 8.4 $ng.L^{-1}$. Trace amounts of γ-BHC, cis-chlordane, trans-chlordane, dieldrin, p,p'-DDE and HCB were also detected in each river (Table 2). Polychlorinated biphenyls (PCBs), which are a group of industrial chemicals, were found at higher concentrations than any of the organochlorine pesticides. Mean concentrations ranged from 6 to 16 $ng.L^{-1}$. The hydrophobic contaminants were likely maintained in these northern waters due to binding capacity of humic substances.

In view of the remoteness of the study areas, concentrations of organochlorine contaminants found in these northern waters were indeed elevated. In fact, these concentrations were similar to levels found in the Niagara River, which is impacted by major municipal and industrial discharges as well as leachates from chemical waste dumps. Since these northern rivers are essentially free from direct contaminant inputs and the same contaminants were present in all rivers and comparable levels, the probable source of these compounds was atmospheric.

Sediment

Bottom sediment grab samples for elemental analyses were subjected to a two-part analytical scheme for 1 N HCl extractable and residual determinations. The 1 N HCl extractable fraction is an estimation of the sorbed or non-lattice bound component and is indicative of past and potential mobilization in the environment. Extractable analyses of the river sediments showed that sorbed concentrations were in the following order: Ba>Pb>Co=Zn>Cu=Ni>V>Cr>Cd>Be (Table 3). Several elements, such as Cr, V, Be, were relatively inert, as by far the greater proportion was found in the lattice bound fraction. Other elements, which include Pb, Co, Ba and Cu, exhibited a less conservative behaviour, as the percentage present in the sorbed fraction ranged from 20% to 40%. The most striking feature of the data was the high percentage of Cd (88%-100%) in the non-lattice bound fraction, which indicated that this element has a relatively high mobility in these northern watersheds.

Total concentrations of various elements investigated were similar in all five rivers. In many cases, these concentrations ranged between the high calcium granitic and deep-sea carbonate data reported by Turekian and Wedepohl (1961).

Table 3. Mean 1 N HCl Extractable (ex) and Total (t) Concentrations ($\mu g.g^{-1}$, dry weight) for 12 Elements in Bottom Sediments from the Five Major Rivers of Ontario's Arctic Watershed, 1981

Location	Ba	Be	Cd	Cr	Co	Cu	Pb	Mo	Ni	P	V	Zn
Moose (ex)	32	0.04	0.25	1.6	3.0	1.3	3.5	-	1.8	-	1.2	4.1
Albany (ex)	80	0.05	0.21	1.0	3.1	3.6	6.5	-	1.8	-	1.8	5.7
Attawapiskat (ex)	55	0.05	0.31	0.2	3.1	1.4	4.5	-	1.2	-	0.7	2.2
Winisk (ex)	60	0.05	0.42	0.2	3.3	1.6	4.0	-	1.3	-	0.5	3.2
Severn (ex)	45	0.05	0.25	0.2	3.2	1.0	4.3	-	1.3	-	1.3	2.0
Moose (t)	220	0.9	0.25	29	9.3	8.0	11	1.8	11	230	35	34
Albany (t)	230	1.2	0.24	27	9.4	9.0	12	1.2	12	340	42	29
Attawapiskat (t)	130	1.1	0.35	23	9.5	8.3	12	1.5	14	320	40	35
Winisk (t)	340	1.2	0.48	24	9.3	6.5	10	1.7	12	310	34	25
Severn (t)	170	1.0	0.25	29	9.0	8.1	13	1.5	13	260	39	25
Granitic*	420	2	0.13	22	7	30	15	1	15	920	88	60
Carbonate*	190	2	0.13	11	7	30	9	3	30	350	20	35

*Mean elemental concentrations in granitic and deep sea carbonate rocks; Turekian and Wedepohl (1962).

Note: Total concentrations are the sum of the 1 N HCl extractable and residual determinations.

Composite bottom sediment samples were prepared for each river, and analyzed for a wide range of organochlorine pesticides, chlorobenzenes, phthalates and polyaromatic hydrocarbons. Results indicated that the river sediments were free from these classes of compounds, and only trace amounts of PCBs were detected in samples collected from the Moose and Severn rivers. The virtual absence of organochlorine contaminants indicated that the accumulation of hydrophobic contaminants in bottom sediments was a relatively unimportant fate in these northern rivers. Hassett and Anderson (1982) have demonstrated that dissolved organic matter in natural waters can reduce the sorption of hydrophobic compounds by riverborne particulates. Previous water quality sampling of the Moose River has also shown that the concentration of dissolved organic carbon was approximately 20 times greater than particulate organic carbon (McCrea and Merriman 1981). In view of the binding capacity of humic substances, and the relative abundance of dissolved and particulate carbon, sorption of organic contaminants to sediments may not readily occur.

Fish

Mercury was found in all of the 46 fish analyzed with mean concentrations ranging from 0.14 to 0.28 $ng.g^{-1}$ in northern pike and 0.16 to 0.32 $ng.g^{-1}$ in common white sucker (Tables 4 and 5). Concentrations in the largest pike (68 cm) and white sucker (46 cm) collected from the Moose River were found to approach the 0.50 $ng.g^{-1}$ limit for consumption with concentrations of 0.40 and 0.45 $ng.g^{-1}$, respectively. Sources of mercury to these fish are not known; elevated levels of this element in fish from the many tributaries of the Moose River, however, indicated that mercury contamination is widespread in the watershed (Johnson 1984). Even though the Moose River basin has major pulp and paper, and mining operations, which may have contributed to mercury levels in the past, natural sources of this element should not be disregarded. Concentrations of mercury in fish collected from the other four rivers were considerably lower and corroborate the provincial consumption guide (MOE 1978).

Organic analyses showed that only trace amounts of a few contaminants were detected in the whole fish tissue of either species. The most prominent contaminant was PCBs with mean concentrations ranging from 0.01 to 0.06 $ng.g^{-1}$ in pike and 0.01 to 0.09 $ng.g^{-1}$ in white sucker. Trace amounts of α-BHC, p,p'-DDE and HCB were occasionally detected; mean concentrations were less than 0.0005 $ng.g^{-1}$.

Little or no information is available regarding the bioaccumulation of organochlorine contaminants in humic waters. However, a significant reduction in the biological uptake of petroleum hydrocarbons from seawater containing 3.0 $mg.L^{-1}$ of dissolved organic carbon was reported by Boehm and Quinn (1976). In this study, bioaccumulation factors showed that there was a low level of uptake in both species (Table 6).

Table 4. Mean Concentrations ($\mu g.g^{-1}$) of Selected Contaminants in Northern Pike Collected from Five Ontario Rivers of the Hudson Bay Lowland, 1981

Parameter	Moose	Albany	Attawapiskat	Winisk	Severn
Age	13 +	10 +	8 +	13 +	13 +
Length (cm)	63	58	50	68	68
Weight (kg)	1.74	1.29	0.83	2.16	2.22
Mercury	0.28	0.21	0.14	0.18	0.20
α-BHC	-	0.003	-	-	-
p,p'-DDE	-	0.003	-	0.004	-
HCB	-	-	-	0.001	-
PCBs	0.04	0.06	0.01	0.01	0.01

Table 5. Mean Concentrations ($\mu g.g^{-1}$) of Selected Contaminants in Common White Sucker Collected from Five Ontario Rivers of the Hudson Bay Lowland, 1981

Parameter	Moose	Albany	Attawapiskat	Winisk	Severn
Age	10 +	6 +	10 +	10 +	11 +
Length (cm)	44	38	42	41	45
Weight (kg)	1.10	0.67	0.86	0.82	0.109
Mercury	0.32	0.16	0.19	0.24	0.18
α-BHC	0.002	0.003	-	-	0.002
p,p'-DDE	0.002	-	0.001	-	0.001
HCB	-	-	-	-	0.001
PCBs	0.09	0.06	0.01	0.01	-

Table 6. Bioaccumulation Factors (fish/water) for Various Organochlorine Contaminants in Fish from the Major Ontario Rivers of the Hudson Bay Lowland

Organochlorine contaminant	Northern pike	Common white sucker
α-BHC	2×10^2	3×10^2
p,p'-DDE	2×10^4	1×10^4
PCBs	2×10^3	3×10^3

In summary, the presence of humic substances appeared to play an important role in the water chemistry of these northern aquatic systems. Elevated levels of iron and aluminum indicated that high molecular weight organic acids can enhance the mobilization and solubilization of various heavy metals to levels far above their normal solubilities in inorganic waters. In addition, the data suggested that dissolved organic matter can alter the solubility, partitioning and bioaccumulation of organochlorine contaminants.

AN INVESTIGATION OF SEVERAL PEATLANDS AND ESTUARY SITES OF THE MOOSE RIVER BASIN

As a follow-up to the discovery of organochlorine contaminants in the major rivers of Ontario's arctic watershed, a survey was conducted in the Moose River basin to provide additional information regarding the source and fate of these toxic substances.

The Moose River basin drains an area of 109 000 km^2 and extends over substantial portions of three physiographic regions (Fig. 11). The upper portions of the basin are characterized by rolling to rugged uplands typical of the Canadian Shield. Wetlands cover approximately 20% of this area, primarily as small open bogs and spruce swamps. The central portion of the basin, referred to as the Great Clay Belt, represents the largest physiographic region, 50% of which is covered by extensive deposits of peat. In all, 58 000 km^2, or 53%, of the entire Moose River basin is covered by peatland terrain. Of the various wetland types, peat bogs are of particular interest, as they receive all of their water input from atmospheric sources and are thus excellent indicators and accumulators of airborne pollutants.

Moose River water has typically a yellow-brown colour, which is largely derived from the seepage of humic matter originating in the surrounding wetlands. Dissolved organic carbon, a measure of aquatic humic substances, has been found to be a major constituent of these northern waters having a mean concentration of 14.5 $ng.L^{-1}$. With the exception of spring runoff, discharge of these coloured waters into James Bay occurs primarily at ebb tide (Langford 1963) and provides an important source of nutrients to the adjacent coastal marshes. These salt marshes are periodically covered and uncovered by tidal waters, which have a maximum range of 3.1 m (Fisheries and Oceans Canada 1985). Contours of surficial waters at the southern extent of James Bay indicate that salinity is between 22% and 25% (Prisenberg 1982). Several studies have suggested that a portion of the riverborne humic matter may precipitate on contact with seawater (Sholkovitz 1976; Sieburth and Jensen 1968).

Since atmospheric deposition was considered a potential source of organochlorine contaminants to the northern watersheds, water from several peatland types common to the Moose River basin was sampled in August 1982. The water samples were collected from five peatland sites near Cochrane, Ontario (Fig. 11) by submerging solvent-washed glass bottles into existing bog-pools or small pits dug into the organic mat. In addition, sediment and vascular plants were collected from six

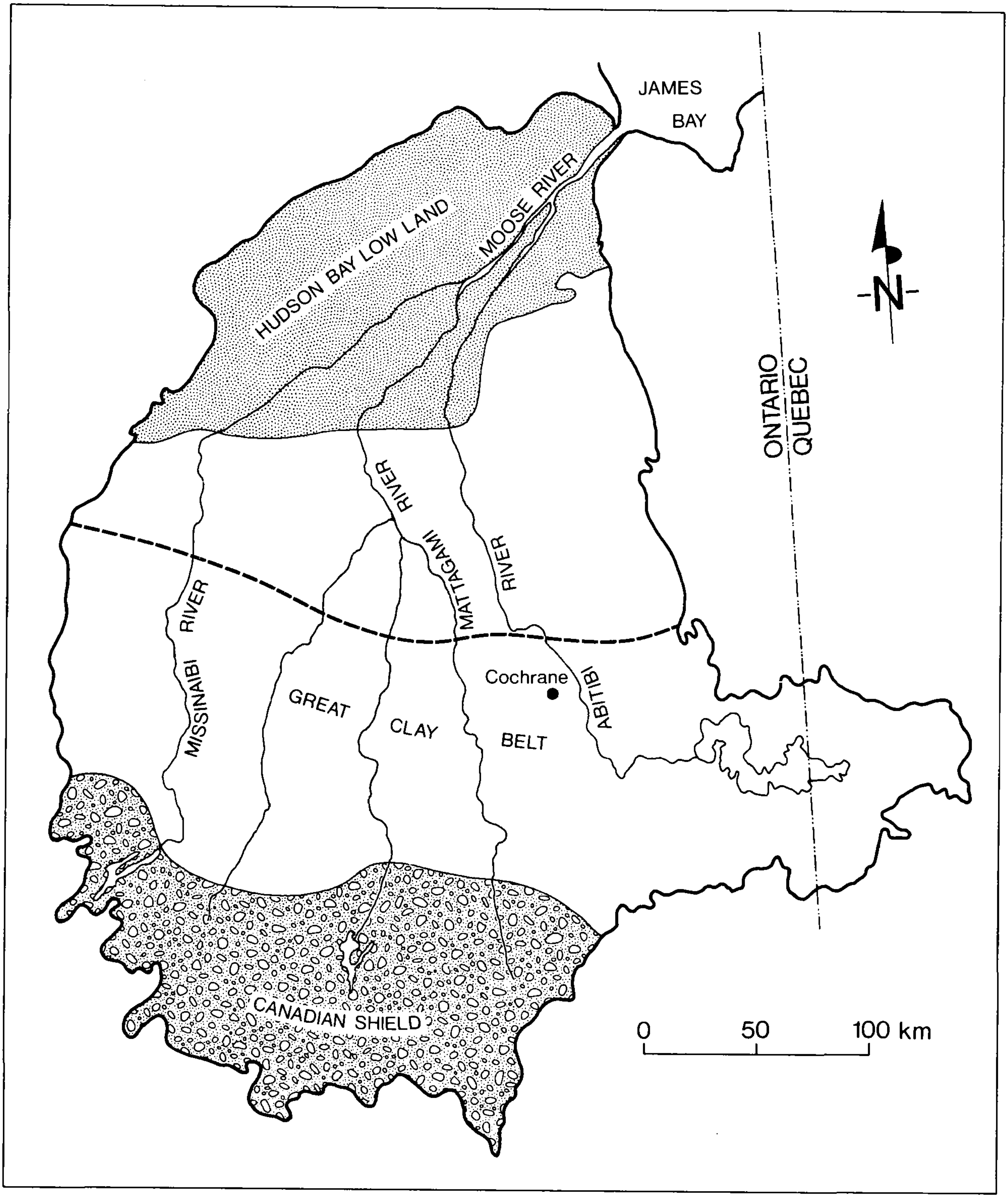

Figure 11. Major physiographic regions of the Moose River basin.

coastal marsh and tidal flat sites of the Moose River estuary to assess the deposition and accumulation of riverborne organochlorine contaminants which may result from estuarine mixing. At each estuary site, exposed sediment from the top 1-cm layer was carefully removed during ebb tide with a steel trowel and transferred into solvent-washed jars. Estimates of sediment texture and organic matter content were noted using a hand texture classification (Ontario Institute of Pedology 1982). Seed heads of Triglochin maritima L., an important food source for migrating geese (Thomas and Prevett 1980; Prevett et al. 1979), were collected at four marsh sites. Roots of Typha latifolia L. were obtained along a small tidal creek.

Analyses of the unfiltered peatland water samples showed that PCBs were present at each site with concentrations ranging from 28 to 65 ng.L^{-1}. These levels were indeed elevated, as concentrations were several times greater than had been reported for the Moose River. Of the various pesticides studied, the hexachlorohexane isomer α-BHC was the most concentrated, with values ranging from 0.5 to 12.1 ng.L^{-1}. An investigation of organic compounds in Canadian surface waters has also revealed that of the 27 sites sampled, the highest concentrations of PCBs were present in a fen located 80 km west of Moose River (Lawrence 1978). These data further substantiate the atmospheric deposition of organochlorine contaminants in the region and demonstrate the importance of peatlands as accumulators of toxic substances. In view of the extensive peatland area in he Moose River basin, and the concentration of contaminants found, it is likely that water draining from the peatlands was an important source of PCBs and α-BHC to the Moose River.

Sediment texture at the six estuary sites ranged from silty clay with humus in the upper marsh to fine and medium sand in the tidal flats. Analyses of nine sediment samples showed that organochlorine pesticides and PCBs were not present in either the tidal flats or coastal marsh sites. Samples of Triglochin maritima and Typha latifolia were also free from PCBs. Although significant amounts of several contaminants have been transported into the Moose River estuary, no evidence of deposition or accumulation has been found.

AN INVESTIGATION OF HEAVY METALS AND COLLOIDS

Elevated levels of several metals have been found in raw water samples collected from all five major rivers of Ontario's arctic watershed. In particular, the northern network data have shown that concentrations of iron and aluminum are commonly above the MOE objectives of 300 and 100 μg.L^{-1} for the protection of aquatic life. Overall, the mean percentage of exceedances of total iron and extractable aluminum in these watersheds was 79% and 60%, respectively.

Previous investigations of the Moose River have also shown that the major portion of these heavy metals was due to the suspended sediment load. Nevertheless, concentrations of iron and aluminum in the dissolved phase ($\lesssim$0.45 μm) were indeed elevated and far above their normal solubilities with mean concentrations of 200 and 70 μg.L^{-1}, respectively. In view of the levels of aquatic humic substances and their binding capacity, it was felt that complexation and/or adsorption of heavy metals to the humic fraction was an important process in these northern rivers. With this in mind, a study was undertaken with Dr. G. Leppard, NWRI, to investigate the compartmentalization of heavy metals in the dissolved and colloidal phase, characterize the major colloid types, and determine the relative binding capacity of each fraction.

Two-litre samples reflecting the water quality in the various seasons were collected from the northern rivers and subjected to a two-part fractionation technique yielding several fractions (Fig. 12). Raw, aqueous, dissolved and colloidal water fractions were analyzed for total iron, extractable aluminum, dissolved and/or particulate organic carbon. Aliquots of each of the four fractions were precipitated with ruthenium red and later examined with an electron microscope (Burnison and Leppard 1983). At the time of preparation of this document, sampling and analyses was on-going.

Preliminary results have shown that the fractionation process, outlined in Figure 12, has been effective in isolating colloids, and that the colloidal fraction is an important component. Analyses of Severn River water, collected as part of the first sample set, showed that by far the greater proportion of the non-particulate iron and aluminum was associated with the colloidal fraction (Table 7).

Table 7. Distribution of Iron and Aluminum in Severn River Water Collected in March 1984

Fraction	POC ($mg.L^{-1}$)	DOC ($mg.L^{-1}$	Iron ($mg.L^{-1}$)	Aluminum ($mg.L^{-1}$)
Raw	0.65	-	0.43	0.082
Aqueous	-	10.5	0.13	0.017
Dissolved	-	10.1	0.021	0.001
Colloidal	-	0.5	0.096	0.011

CONCLUSION

The network data have provided an effective means for establishing baseline water quality in Ontario's arctic watershed. More important, it has provided a basis for recognizing environmental issues particular to these basins and for developing short-term goal-specific studies to address these concerns. The follow-up studies, which account for only a small fraction of the entire sampling effort, combined with the network data have yielded information for assessing ambient environmental conditions as well as the source, distribution and fate of heavy metals and organic contaminants in these watersheds.

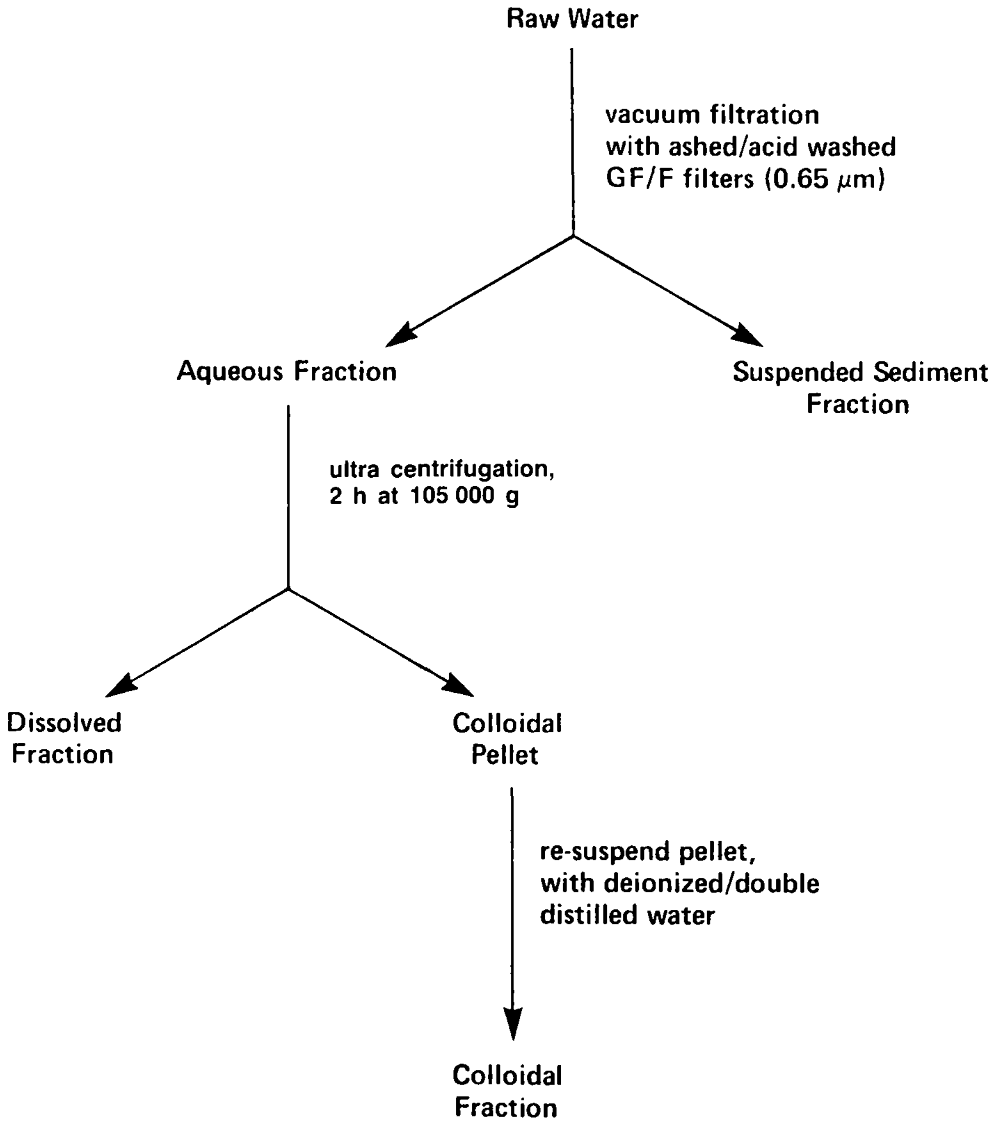

Figure 12. Flow diagram of the procedures used to separate the particulate dissolved and colloidal fractions.

ACKNOWLEDGMENTS

The material presented in this document was liberally drawn from several published and unpublished reports identified by asterisks in the bibliography. In particular, I would like to thank D. Campbell, J. Fischer, G. Leppard, K. Lum, R. Kwiatkowski, P. McCarthy, J. Merriman, T. Norris and G. Wickware for their participation in these studies.

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ONTARIO WORKING GROUP SESSION

Attendees

T. Pollock (Chairman)	Atlantic (WQB)
L. Désilets (Recorder)	Headquarters (WQB)
R. McCrea (Presenter)	Ontario (WQB)
U. Borgmann	Great Lakes Fisheries Research Branch (DFO)
W. Glooschenko	Aquatic Ecology Division (NWRI)
G. Leppard	Aquatic Ecology Division (NWRI)
W. Strachan	Environmental Contaminants Division (NWRI)

NWRI - National Water Research Institute, Department of the Environment
WQB - Water Quality Branch, Department of the Environment
DFO - Department of Fisheries and Oceans

The meeting began with discussion on the need for monitoring, surveys and special studies, and where interaction between WQB and NWRI could occur. It was agreed that WQB had the responsibility to carry out monitoring, but that NWRI should become more involved in surveys and special studies. Communication was identified as the key to this involvement. Only with a thorough knowledge of what is required or expected can the research community respond in an effective manner to the needs of the monitoring group. Historically, this communication has not occurred, and when it has, the requests were too broad in scope and not well defined. Personal contacts were considered preferable to a coordinating committee.

The working group then decided to describe a generic river basin monitoring program, outlining the various levels of planning and providing a checklist of activities that should be addressed by the project leader. Comments on when and where NWRI assistance would be best incorporated were also added.

Stage 1 Discovery

The group discussed the need to obtain as much information as possible on the river basin to be monitored, prior to any design considerations. Information should be acquired on the following areas:

geology
hydrology
meteorology
land use (forestry, agricultural, industrial, urban)
water chemistry
sedimentology
aquatic biology (benthos, algae, fish)
the dominant aquatic food web
terrestrial predators of aquatic life (birds, muskrats, mink, etc.)
present and predicted water uses
chemical use (from sources such as Commercial Chemicals Branch of EPS and/or Pest Control products Act)
available water quality objectives or guidelines.

It was recognized that information on all of these areas would not always be available; an effort to obtain as much information as possible, however, should be made. Sources for the information include previous studies, other government agencies (federal and provincial), universities, colleges, newspapers, local citizens and consulting firms.

All too often baseline studies are carried out on river basins when a substantial amount of information already exists. This results in a duplication of effort and the potential loss of acquiring valuable new insight into the major issues within the river basin. The information gathered during the discovery stage provides the project leader with initial answers to these questions: are there any problems/issues or potential problems/issues within the river basin; where are they located; when in the hydrological cycle is the problem/issue most acute; is there a need for a pilot study, survey, special study, or can a routine monitoring program be designed? Without this baseline ecology information there is no rational way to establish station location, sample parameter lists, or sampling frequency. Gaps in knowledge should be identified and assistance from NWRI requested. If no information gaps exist, and problems/issues are identified, routine monitoring for the identification and determination of levels, concentrations, trends and natural variations of chemical compounds in water, sediments, and biota can be carried out.

Stage 2 Program Development

Once the problems/issues within the basin have been identified, the project leader should actively seek the participation of scientists for the establishment of a scientifically defensible hypothesis, and a statistically sound sampling program. Again, the group stressed the importance of having a holistic program, and therefore expert advice should also be sought from provincial or other federal departments. A written proposal, or preferably an oral presentation, should be made to the research community, outlining as thoroughly as possible the objectives of the study and the baseline/background information available. For their part, it is mandatory that NWRI management or management of other agencies encourage staff participation in both program development and implementation.

Concern was expressed by the group that these efforts, which may consume a considerable amount of time, may go unrecognized, or be considered inappropriate for research scientists. The working group, however, felt that unless the scientist is involved at these early levels of monitoring development, participation at a later date is difficult and often useless. The entire group stressed the importance of effective communication and timeliness. NWRI work plans are done in the fall for the following year, and thus requests for assistance must be made prior to this. The concept of developing an expertise directory, within both WQB and NWRI, was discussed. It was felt that at the early stage of development, direct contact with the research scientists to determine the work load would be a superior route to follow, rather than the historically traditional project leader to management WQB, to management NWRI to scientist. This formal route could be established once the project leader and scientist had made some preliminary estimates of the need for, and resource requirements of, the research component of the monitoring program.

Stage 3 Monitoring for Problem Identification

Discussions revolved around the need to have ecological (holistic, ecosystem) information. Multimedia sampling was identified as mandatory for all studies. Some discussion was held on community structure analyses versus biomass measurements, studying energy flow through the food web, etc. It was concluded that each river basin had to be studied individually and the information requirements established on a case by case basis. Table 1 was produced as a general guide for project leaders to follow. Due to the high costs often associated in travelling to a sampling site, it was also recommended that as wide a range of measurements as possible be taken at each site.

Table 1. Parameter Matrix to Consider for Monitoring Programs

		Medium	
Parameter set	Water	sediment	Biota
Major ions	+	-	-
Nutrients	+	+	-
Total metals	+	+	+
Organic carbon	+	+	-
Physical parameters	+	+	-
OCs and PCBs	+	+	+
Local pesticides	+	+	?
Radionuclides	+	+	+
GC/MS scan	+	+	+

The use of biotic indicators as a monitoring tool for problem identification was discussed by the group. Both functional (within an individual) and structural (within the community) biomonitoring were considered as valuable monitoring tools. Forage and large fish, benthic invertebrates, periphyton, microbes, and plankton (lakes) were all considered. Again, depending on the issues to be addressed, some of the above lists are more appropriate for monitoring than others. The group also identified the need to set objectives for biological organisms or biotic communities.

Also the importance of establishing a statistically valid sampling program received a great deal of discussion. Sites representative of the river basin, and based on the identified problems/issues, should be established. Review of historical data to ensure adequacy with respect to the number of stations, their location, parameters to be measured and sampling frequency, to provide statistical sound results, must be done.

Stage 4 Evaluation

The value of any monitoring program can only be assessed after the data have been collected and interpreted. No monitoring program should have data collection as a sole objective. Timely interpretation with review of the network, with respect to station location, measured parameters and sampling frequencies is a step that must be taken annually to ensure that routine monitoring does not degrade to a data gathering exercise. NWRI staff can play a large role in the interpretation and review process. Information gaps can be identified at this stage and interaction of NWRI researchers with WQB coordinated so that the monitoring program naturally evolves to meet its objectives.