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NATIONAL INVENTORY OF NATURAL ORGANIC COMPOUNDS - AN INTERIM REPORT

J. Lawrence

September 1978

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EXECUTIVE SUMMARY

NATIONAL INVENTORY OF NATURAL ORGANIC COMPOUNDS: AN INTERIM REPORT

J. Lawrence

A preliminary inventory of 27 rivers and lakes across Canada for natural organic compounds indicates that humic acid, fulvic acid, tannins and lignins account for the major part of soluble organics in surface waters (visually assessed by the brown colour of water). Fulvic acid usually occurs in larger quantities (x10) than humic acid. The chloroform potential (chlorination by-product previously reported on by Oliver and Lawrence) roughly follows the concentration of these two acids. Stable amino acids (proline, alanine and glycine) were found in high concentrations in areas of livestock farming. The amino acids form only a small part of Kjeldahl nitrogen and therefore it must be concluded that the bulk of the nitrogen comes from agricultural fertilizers. Relatively low concentrations of oil, grease and PCBs were recorded from the localities samples.

INTRODUCTION

Most developed countries of the world have on-going water quality monitoring programs[1,2] to determine both the current state and trends in aquatic environmental quality. Such information is required for assessment of water bodies for uses such as drinking water, industrial application, recreation, irrigation, shipping, fishing, etc. These surveys usually include general parameters such as turbidity, colour, hardness, conductivity, pH, dissolved organic carbon (DOC) and suspended solids as well as detailed measurement of inorganic ions: the only specific organic data usually included are those relating to pesticides and polychlorinated biphenyls (PCBs). Organic compounds of natural origin have been mostly omitted - presumably because they have not been regarded as having a deleterious effect on water quality. However, recent investigations have shown that humic and fulvic acids react with chlorine to form chloroform and other halogenated organics during water disinfection[3], the organic content of water and sediments can have pronounced effects on the mobility and fate of pesticides[4], and natural organics combine with heavy metals to form highly toxic complexes[5].

The aim of this study was to collect background information on specific classes of natural organic compounds (most natural organics cannot be identified in terms of single, well defined molecules) and to assess the data in terms of geographic, geological and climatic regimes. Parameters measured include humic acid, fulvic acid, tannins, lignins, amino acids, carbohydrates, phenols, oil and grease, DOC, Kjeldahl nitrogen (KN) and potential for forming halomethanes during chlorination (Chloroform potential). Samples from most stations were also analysed for pesticides and PCBs. Two river stations in each province were selected for the initial phase of the study and a few other locations of special interest have since been added. Where possible, the sampling sites were chosen to coincide with NAQUADAT* stations of the Water Quality Branch so that general and inorganic data were readily available.

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* National Water Quality Data Bank operated by Water Quality Branch, Inland Waters Directorate of Environment Canada.

EXPERIMENTAL

The sampling stations selected for the study are listed in Table 1. Some general climatic and vegetation data is also included for each station. These data were obtained from The National Atlas of Canada[6] so will not reflect any local deviations from the area average. Where possible, local descriptions have been obtained and these are listed in Table 2.

Samples were collected as one-time, grab samples during July - September 1977. From each station the following sample containers were filled:

1. Pesticides, PCB, Oil and Grease:
   Three solvent-cleaned, 1.2 ℓ glass bottles fitted with inert caps. These were stored in the dark at 4°C as soon after sampling as possible.

2. Phenols:
   One 100 ml glass bottle, preserved with 0.1% $CuSO_4$ and 1.6% ortho-phosphoric acid.

3. DOC/KN:
   Two 100 ml glass bottles, preserved with 0.2% sulfuric acid.

4. Humic, Fulvic, Amino Acids, Tannins, Lignins, etc.:
   One 2 gal. polyethylene jug preserved with 0.2% sulfuric acid.

Once samples were returned to C.C.I.W. (which sometimes took 1 - 2 weeks), they were stored at 2°C until analyses were completed.

Analyses for pesticides, PCBs, oil and grease, phenols, DOC and KN were carried out by the Water Quality Branch of Environment Canada using their standard procedures[7]. Tannins and lignins were determined by the phospho-molybdic acid method[8], using lignosulfonic acid as standard. Humic and fulvic acids were measured by determination of DOC at pH 9 and pH 2[9]: results are expressed as mg ℓ^{-1} DOC. Amino acids were analyzed by a gas chromatographic method developed by Roach & Gehrke[10]. A commerically available reference mixture of amino acids (Type H, Hamilton Co., Reno, Nevada) was used as the calibration standard. The concentration of total carbohydrates in each sample was measured by the phenol-sulfuric acid method[9]. The detection limits of these analyses are shown in Table 3.

TABLE 3

Analysis	Detection Limit
Total Pesticides	0.01* μg ℓ^{-1}
PCBs	0.1 μg ℓ^{-1}
Oil and Grease	1 mg/ℓ^{-1}
Phenols	1-2 μg ℓ^{-1}
DOC	0.2 mg ℓ^{-1}
KN	0.1 mg ℓ^{-1}
Tannins & Lignins	0.1 mg ℓ^{-1}
Humic Acid	0.1 mg ℓ^{-1}
Fulvic Acid	0.1 mg ℓ^{-1}
Amino Acids	0.1 μg ℓ^{-1}
Carbohydrates	10 μg ℓ^{-1}

* of any individual component (see footnotes on page 6 and Table 4)

Analyses for tanins, lignins, humic acid, fulvic acid and carbohydrates were done on filtered samples only, whereas all other analyses were done on whole (i.e., unfiltered) samples.

RESULTS AND DISCUSSION

The results of the analyses are presented in Table 4 for the 27 stations included in this phase of the study. Blank spaces in the table indicate samples that were lost or broken in transit or otherwise unintentionally destroyed. Specific conductance, total hardness, pH, relative colour and turbidity data have also been included where these were available from NAQUADAT listings[1].

Inspection of the data indicates that humic acid, fulvic acid, tannins and lignins (the refractory organics) account for the major part of the soluble organic content of the water and in fact, the sum of these parameters agrees reasonably well with the measured DOC. From this one can infer that no major organic components are being neglected, unless they are of such a nature that they have been included in the humic and fulvic acid results. An improved analytical procedure for these two acids is currently being developed by the author and it is hoped to have this operational for the 1978 sampling season. With the exception of Nipigon, Mississagi and Moose Rivers, concentration of fulvic acid is usually at least a factor of 10 greater than that for humic acid. This ratio of 10 has been observed by other workers[9] but one might have expected it to have been less in cases where the pH is relatively high (pH ≈ 8). At this stage it is not suggested that any significance should be attached to the fact that the three rivers with much lower fulvic/humic ratios are all in Ontario.

The 24 hour chloroform and bromodichloromethane potentials roughly follow the concentrations of humic and fulvic acids as would be expected from previous work in which humic and fulvic acids were identified as the predominant chloroform precursors in natural waters.[3] The bromodichloromethane potential seems abnormally high for the Red River at Emerson and the two sampling sites near Tuktoyaktuk. This could be due to high bromide ion concentrations at these locations. ($C\ell_2$ oxidises Br^- to Br_2 which will then react to form bromo-methanes.)

In general, the concentrations of tannins and lignins were lower than those of fulvic acid by a factor of between 3 and 30. Most of those rivers with the higher ratios are either fed from forested drainage basins or have known local sources such as pulp mills upstream of the sampling location. The phospho-molybdic acid method used for the determination of tannins and lignins gives only a combined result but it is hoped that by the 1978 sampling season an improved method (currently under development by the author) will be perfected that will determine the concentrations of tannins and lignins separately.

Phenols were essentially absent ($< 1\ \mu g\ \ell^{-1}$) in all the rivers which were tested except the St. Lawrence River at Levis. The $3\ \mu g\ \ell^{-1}$ reported for this station is presumably due to the large volumes of industrial and domestic effluents which are discharged into the river upstream from Levis.

The concentrations of amino acids fall within a range of < 0.1 to $0.9\ mg\ \ell^{-1}$ with the major part being in the combined form. These values are somewhat higher than those reported by Telang *et al.*[9] in waters of the Marmot Creek[9] but most of the difference is probably because the results presented in this report refer to whole water samples whereas those reported by Telang *et al.* were for filtered samples. Of the 11 amino acids separated*, proline, alanine, glycine, and ornithine occurred in the highest abundance. Proline, alanine and glycine are three of the more stable amino acids in solution so it is perhaps not surprising that these three occurred in high concentrations. It is interesting to note that of the seven rivers exhibiting a higher free/combined amino acid ratio, two are northern rivers and the other five are in areas with considerable livestock farming.

Since the concentrations of Kjeldahl nitrogen (KN) (0.2 - 1.2 mg ℓ^{-1}N) are much higher than the concentrations of amino acids, one must conclude that the latter is only a minor source of KN (the major contribution presumably being from agricultural nitrogen). The ratio of DOC/KN is >20, with three exceptions. The three rivers with lower ratios, Battle, Qu'Appelle and Assiniboine, are all prairie rivers where the application of nitrogenous fertilizer is likely to be extensive. Typical KN values for oligotrophic and eutrophic lakes are of the order of 0.2 and 2.0 mg ℓ^{-1} respectively, therefore, in terms of this parameter, many of the prairie rivers included in this survey are eutrophic.

Carbohydrates, as determined by the phenol-sulphuric acid method, ranged in concentration from 20 - 190 μg ℓ^{-1}, which is about the same range as has been reported for seawater by Lewis & Rakestraw[12]. The method does not distinguish between mono-, di- and polysaccharides but it is probable that a combination of all these are present. Carbohydrates are introduced into surface water by the degradation of vegetation, soil and aquatic organisms and also from groundwater. Areas in which precipitation or groundwater leaches through vegetative matter can be expected to show relatively high carbohydrate concentrations. Carbohydrates are non-volatile compounds so the contribution from atmosphere is likely to be small, except in areas where excessive dust fallout occurs.

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* Proline, Alamine, Glycine, Threonine, Serine, Leucine, Ornithine, Hydroxy-Proline, Phenylalanine, Glutamic acid and Lysine.

Oil, grease and PCBs were essentially absent from all the rivers studied and the concentrations of total pesticides* were also relatively low, except for the Exploits River at Bishops Falls (Nfld.) which exhibited 0.25 μg ℓ^{-1}. The high total pesticide concentration at Bishops Falls was due to 0.248 mg/ℓ of hexachlorobenzene recorded at this location. Since no abnormalities were observed at Millertown dam (80 km upstream from Bishops Falls) it must be concluded that a localized discharge is responsible.

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* Includes hexachlorobenzene, α-BHC, lindane, heptachlor, aldin, heptachlor epox., γ-chlordane, α-chlordane, dieldrin, p,p'-DDD, o,p'-DDT, p,p'-DDT, endrin, α-endosulfan, β-endosulfan, p,p'-methoxychlor, mirex, p,p'-DDE.

FUTURE PLANS

During the summer of 1978 it is planned to resample at, or near, most of the 27 stations included in this report. All samples will be filtered within a few hours of collection and both the filtrate and residue analyzed for organics. In this way a more detailed understanding of the role of suspended matter on organic loadings will be obtained. This will also lead to better estimates of organic transport under varying conditions and will supply background information for future studies on organic/pesticide interactions and the ability of natural organics to 'buffer' anthropogenic inputs. A more detailed discussion of the results (especially in terms of geological, geographical and climatic regimes) will be included in next year's report.

ACKNOWLEDGMENTS

A sampling program of this nature could not be undertaken in a country the size of Canada without the cooperation of personnel in numerous regional offices. I am very grateful to Mr. K. Reid, Dr. A. Caille, Mr. D. Cullan and Dr. W. Erlebach and their staffs of the Regional Water Quality Laboratories, Mr. M. Guilcher, EPS Regional Office, St. John's and Mr. W. Whitley, Pollution Control Laboratory, Indian and Northern Affairs, Whitehorse, for so willingly collecting, preserving and shipping samples to NWRI.

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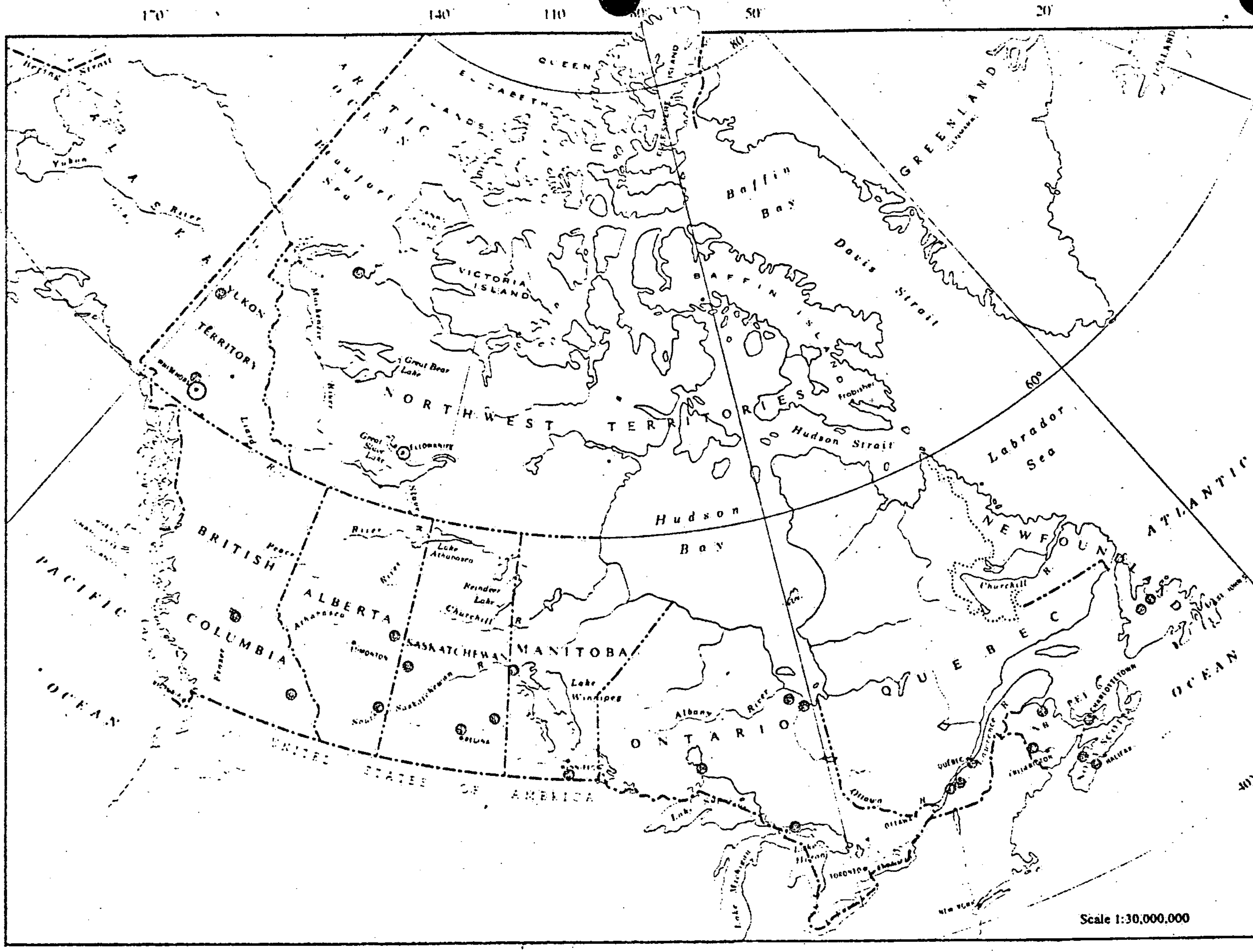

SAMPLING STATIONS.

TABLE 1

NAQUADAT Station No.	River & Location of Station	Latitude	Longitude	Snow Cover 28 Feb. (cm)	Average Runoff (cm)	Annual Precipitation (cm)	Soil **	Predominant Vegetation	Agricultural Practices
00AL05CR0001	Red Deer River near Bindloss	51	110	0-20	0-10	30-50	A1	Grassland	Cattle, wheat
00AL06AD0001	Beaver River at Beaver Crossing	54	110	20-40	0-10	30-50	H1	Spruce/Boreal broadleaf-forest	Cattle, wheat
00BC08LF0008	Thompson River,200 yds above Savona T.C.H. Bridge	51	121	40-76	0-10	30-50	A1	Sub-alpine forest, grassland	Cattle, mixed farming
00BC08NG0002	Kootenay River at Wardner	49	116	20-40	50-100	80-160	E3	Softwood forest	---
00MA05KH0001	Saskatchewan River above Carrot River	54	101	40-76	0-10	30-50	C2	Black Spruce, Tamarack, Jackpine, swamp	Grain, mixed livestock
00MA05OO0001	Red River at Emerson	49	97	20-40	10-50	30-50	A2	Grassland	Grain, mixed livestock
00NB01BO0019	Bartibog River at Hwy. 8, Bartibog	47	65	20-40	50-100	80-160	D3	Softwood/hardwood forest	Potatoes, dairy products
00NB01AJ0014	St. John River at Grafton Br. Woodstock	46	68	20-40	50-100	80-160	D3	Softwood/hardwood forest	Potatoes. dairy products
00NF02YO0009	Exploits River at Bishops Falls	49	55	40-76	50-100	80-160	D3	Boreal/spruce, balsam, fir	---
00NF02YO0004	Exploits River at Millertown Dam	49	57	20-40	50-100	80-160	D3	Boreal Spruce, balsam, fir	----
00NS01EH0003	Little East River, Lunenburg County	45	64	0-20	100-200	80-160	D3	Softwood/hardwood forest	Poultry, pigs
00NS01DC0001	Annapolis River at Wilmot	45	65	0-20	50-100	80-160	D3	Softwood/hardwood forest	Mixed livestock
	Lake near Tuktoyaktuk	69	132	20-40	0-10	0-30	G3	Arctic sedges, grasses, shrubs	----
	Estuary near Tuktoyaktuk	69	132	20-40	0-10	0-30	G3	Arctic sedges, grasses shrubs	----

/continued

TABLE 1 (continued)

NAQUADAT Station No.	River & Location of Station	Latitude	Longitude	Snow Cover 28 Feb. (cm)	Average Runoff (cm)	Annual Precipitation (cm)	Soil **	Predominant Vegetation	Agricultural Practices
00ON02AD0001	Nipigon River at Pine Portage	49	88	40-76	10-50	50-80	D3	Softwood - spruce	---
00ON02CC0001	Mississagi River at TCH Bridge	46	83	40-76	10-50	80-160	D3	Softwood/hardwood	Dairy products
	Moose River near mouth	52	81	40-76	10-50	50-81	G2	Boreal forest	---
	Hudson Bay Lowlands (Fen Drainage)	52	81	40-76	10-50	50-81	G2-H3	Bogs	---
00PE01CC0002	North Yorke River, Milton Station	46	63	20-40	50-100	80-160	D3	Softwood/hardwood	Potatoes, mixed livestock
00QU020A0036	St. Lawrence River at Ice Boom above Champlain Bridge	45	74	40-76	10-50	80-160	E1-G1	Broadleaf forest	Vegetable/Dairy products
00QU020J0003 *	Richelieu River at Hwy. 9, St. Hilaire	46	73	40-76	10-50	80-160	G1-D3	Broadleaf forest	Dairy products
00QU02PH0001	St. Lawrence River at Levis	47	71	40-76	50-100	80-160	D3	Broadleaf forest	Mixed livestock
00SA05MD0002	Assiniboine River, Hwy 8 Bridge below Kamsack	52	102	20-40	10-50	30-50	A4	Aspen & spruce forest	Wheat, cattle, barley
00SA05FE0001	Battle River near Unwin	53	110	20-40	0-10	30-50	A3-A4	Aspen & spruce forest	Wheat, cattle
00SA05JM0014	Qu'Appelle River, South of Welby	50	102	20-40	0-10	30-50	A2	Grassland	Wheat
00YT09AC0001	Takhini River near mouth	61	136	20-40	10-50	0-30	E2	Boreal forest, barren areas	----
00YT09EB0001	Yukon River above Klondike at Dawson	64	139	40-76	10-50	0-30	E2	Boreal forest, barren areas	----

* NAQUADAT station downstream of sampling site

** Dominant Soil Classifications

A - Chernozemic:
A1 - Brown
A2 - Dark Brown
A3 - Black
A4 - Dark Grav

C - Luvisolic:
C1 - Gray-brown
C2 - Gray

D - Podezolic:
D3 - Humo-ferric

E - Brunisolic:
E1 - Melanic
E2 - Eutric
E3 - Dystric

G - Gleysolic:
G1 - Humic
G2 - Gleysol
G3 - Cryic

H - Organic
H1 - Fibrisol
H3 - Cryic Fibrisol

TABLE 2

River and Location of Station	Local Description
Red Deer near Bindloss	River approximately 50 meters wide, low-moderate current, very turbid. Banks of sparse grass or barren. Downstream of badlands.
Beaver River at Beaver Crossing	
Thompson River, 200 yds above Savona T.C.H. Bridge	At mouth of Kamloops Lake. Bottom predominantly gravel. Current low-moderate. Approximate width 75 meters. Vegetation at site sparse, but forested on shores of lake upstream.
Kootenay River at Wardner	
Saskatchewan River above Carrot River	
Red River at Emerson	River approximately 100 meters wide. Low current, meandering, very turbid. Vegetation along banks, grass, further back, predominantly grain and livestock.
Bartibog River at Hwy 8, Bartibog	River approximately 6 meters wide, 15-60 cm deep. Rambling, rocky river of moderate flow. Small farms along banks.
St. John River at Grafton Br., Woodstock	River approximately 300 meters wide and falls within the upper reaches of Mactaquac Headpond which extends another 20 km upstream. Very light flow. Sampling site above town of Woodstock.
Exploits River at Bishops Falls	
Exploits River at Millertown Dam	
Little East River, Lunenburg County	River approximately 10 cm wide with very light flow - meandering over large rocks. Largely influenced by seepage from treatment lagoons of a wood panelling plant.
Annapolis River at Wilmot	River approximately 12 meters wide, 15-60 cm deep. Bottom mainly bedrock. Influenced by heavy agriculture and a number of towns and villages upstream.

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TABLE 2 (continued)

River and Location of Station	Local Description
Lake near Tuktoyaktuk	Arctic lake
Estuary near Tuktoyaktuk	Arctic estuary
Nipigon River at Pine Portage	River approximately 30 meters wide. Location just below dam. Vegetation predominantly softwood forest.
Mississagi River at TCH Bridge	River approximately 50 m wide and 2 m deep. Current moderate. Vegetation predominantly softwood forest.
Moose River near mouth	
Hudson Bay Lowlands (Fen drainage)	North bog; vegetation predominantly grass.
North Yorke River, Milton Station	River approximately 5 m wide and up to 1 m deep. On estuary with ~30 cm tide. Bottom clay to sand to gravel. Heavy algal bloom covering 80% of bottom. Flow light. Not aesthetically appealing. Vegetation, mixed agriculture.
St. Lawrence River at Ice Boom above Champlain Bridge	Mid-stream of main St. Lawrence channel between 29th and 30th pillars of Champlain Bridge. Appears relatively free of local sources of pollution.
Richelieu River at Hwy 9, St. Helaire	Numerous cottages and private docks on river banks and one public marina just upstream. A CIL plant is located 2 miles upstream.
St. Lawrence River at Levis	Sample collected from raw water inlet pipe of Levis water treatment plant. Golden Eagle Wharf is possible source of contamination of organics (oil tanker terminal).
Assiniboine River, Hwy 8, Bridge below Kamsack	Quite turbid. Wooded along banks - mixed grain agriculture in immediate area.
Bottle River near Unwin	
Qu'Appelle River south of Welby	River approximately 6-10 m wide. Turbid. Vegetation - grain with rough grass in immediate banks
Takhini River near Mouth	
Yukon River above Klondike at Dawson	

TABLE 4

River & Location of Station	Humic Acid mg ℓ^{-1}	Fulvic Acid mg ℓ^{-1}	Tannin &Lignin mg ℓ^{-1}	Phenols mg ℓ^{-1}	KN mg ℓ^{-1}	DOC mg ℓ^{-1}	Oil & Grease mg ℓ^{-1}	Carbo-hydrate mg ℓ^{-1}	Amino Acids µg ℓ^{-1} Free	Amino Acids µg ℓ^{-1} Combined	Total Pesticides µg ℓ^{-1}	PCB µg ℓ^{-1}	Pot $CHCl_3$ µg ℓ^{-1}	Pot $CHBrCl_2$ µg ℓ^{-1}	Spec. Cond. µ mho cm^{-1}	Total Hardness mg ℓ^{-1}	Turb. JTU	Rel. Colour (Col. units)	pH
Red Deer River near Bindloss	0.6	7.8	1.2	<0.001	0.45	10	0.004 W	0.05	Low		0.003	0.007	54	3.7	450	196	25	10	8.0
Beaver River at Beaver Crossing	0.3	16.3	1.4	<0.001	0.80	18	0.002 W	0.11	High		0.001	ND	109	4.4	350	170	8.3	35	7.8
Thompson River, 200 yds above Savona T.C.H. Bridge	ND	2.1	0.4	<0.001		6		0.03	ND	172	0.006 T	0.001			107	44	1.0	17	7.6
Kootenay River at Wardner	ND	1.9	0.8			6		0.07	ND	899	0.005 T	0.002			290	140	3.3	7	8.1
Saskatchewan River above Carrot River	1.7	8.0	1.3	<0.001	0.54	13	0.001 W	0.10	High		0.006 T	ND	58	4.4	370	165	16	10	8.0
Red River at Emerson	0.1	14.5	1.8	<0.001	0.90	20	ND	0.10	High		0.007 T	ND	152	72	615	248	23	20	7.9
Bartibog River at Hwy. 8, Bartibog	ND	7.6	1.7			7	0.800 W	0.14	ND	168	0.001 T	ND	124	3.7	54	26	0.8	30	7.2
St.John River at Grafton Br. Woodstock	ND	12.6	4.0	<0.001		14	ND	0.10	54	149	0.001 T	ND	123	0.7	110	42	1.7	30	7.0
Exploits River at Bishops Falls	ND	9.1	3.9	<0.001	0.22	14	ND	0.06	ND	226	0.250	ND	83	2.7					
Exploits River at Millertown Dam	0.6	5.5	1.4	<0.001	0.20	7	ND	0.11	ND	100	0.004 T	ND	104	5.7					
Little East River Lunenburg County	1.2	15.6	6.3	<0.001		25	ND	0.02	ND	238	0.0003 W	ND	147	1.6					
Annapolis River at Wilmot	0.6	5.2	1.2	<0.001		7	0.500 W		37	216	ND	ND	85	10.3	95	30			6.8

..../continued

TABLE 4 (continued)

River & Location of Station	Humic Acid mg ℓ^{-1}	Fulvic Acid mg ℓ^{-1}	Tannin &Lignin mg ℓ^{-1}	Phenols mg ℓ^{-1}	KN mg ℓ^{-1}	DOC mg ℓ^{-1}	Oil & Grease mg ℓ^{-1}	Carbo-hydrate mg ℓ^{-1}	Amino Acids μg ℓ^{-1} Free	Amino Acids μg ℓ^{-1} Combined	Total Pesticides μg ℓ^{-1}	PCB μg ℓ^{-1}	Pot $CHCl_3$ μg ℓ^{-1}	Pot $CHBrCl_2$ μg ℓ^{-1}	Spec. Cond. μ mho cm^{-1}	Total Hardness mg ℓ^{-1}	Turb.	Rel. Colour (col. units)	pH
Lake near Tuktoyaktuk	ND	7.2	0.4										83	32					
Estuary near Tuktoyaktuk	ND	9.7	0.3										31	17					
Nipigon River at Pine Portage	2.6	4.0	0.6			5		0.03	ND	ND	0.006 T	ND	63	3.5					
Mississagi River at TCH Bridge	1.7	3.5	1.0			5		0.08	Low		0.004 T	ND	97	3.1	57	24	1.3	20	7.2
Moose River near mouth	7.1	11.3	4.0			18		ND	31	260	0.017 T	0.006 W	216	4.3					
Hudson Bay Low-lands (Fen drainage)	1.7	23	4.7	<0001	0.75	25	ND		ND	214	ND	0.018 W							
North Yorke River Milton Station	0.1	6.2	0.5	<0.001		8	ND	0.11	33	84	0.003 T	ND	16	6.4	226	105	1.3	5	8.1
St. Lawrence River at Ice Boom above Champlain Bridge	0.2	2.5	0.2	<0.001		3	ND		67	194	0.007 T	ND	13	4.5					
Richelieu River at Hwy 9, St. Helaire	ND	7.7	0.3	<0.001		8	ND	0.09	ND	189	0.006 T	ND	48	3.5	154	60	3.8	10	7.5
St. Lawrence River at Levis	0.3	6.8	0.7	0.003				0.08	Low		0.004 T	0.001 W	34	13	267	103	4.8	10	7.6
Assiniboine River, Hwy. 8 Bridge near Kamsack	1.7	16	1.3	<0.001	1.0	15	ND	0.15	High		0.008 T	ND	109	23	970	492	10.5	30	8.0
Battle River near Unwin	0.4	17	1.4	<0.001	1.2	15		0.19	180	206	0.008 T	ND	110	30					

..../continued

TABLE 4 (continued)

River & Location of Station	Humic Acid mg ℓ^{-1}	Fulvic Acid mg ℓ^{-1}	Tannin & Lignin mg ℓ^{-1}	Phenol mg ℓ^{-1}	KN mg ℓ^{-1}	DOC mg ℓ^{-1}	Oil & Grease mg ℓ^{-1}	Carbo-hydrate mg ℓ^{-1}	Amino Acids $\mu g\ \ell^{-1}$ Free	Amino Acids $\mu g\ \ell^{-1}$ Combined	Total Pesticides $\mu g\ \ell^{-1}$	PCB $CHCl_3$ $\mu g\ \ell^{-1}$	Pot $CHBrCl_2$ $\mu g\ \ell^{-1}$	Pot $\mu g\ \ell^{-1}$	Spec. Cond. μ mho cm^{-1}	Total Hardness mg ℓ^{-1}	Turb.	Rel. Colour (col. units)	pH
Qu'Appelle River South of Welby	0.8	12	1.4	<0.001	0.8	12	0.002 W	0.07	Low		0.004 T	ND	50	46	1480	470	16	20	8.3
Takhini River near mouth	0.2	2.0	0.7			3	0.10 W	0.11	ND	288	0.002 T	ND	5						
Yukon River above Klondike at Dawson	ND	2.7	0.6	<0.001		5		0.19	105	571	0.002 T	ND	42	1.6					

ND - Not Detectable

* Due to difficulties with some analyses, detailed quantitative results could not be obtained. The following are estimates from the data:

Low Free <20, Combined <60
High Free >50, Combined >100

T - Confirmed positive response but below statistical detection limit of instrument.

W - Positive response that cannot be confirmed by other methods.

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