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Contaminants in Bottom Sediments of the St. Lawrence River in June 1975

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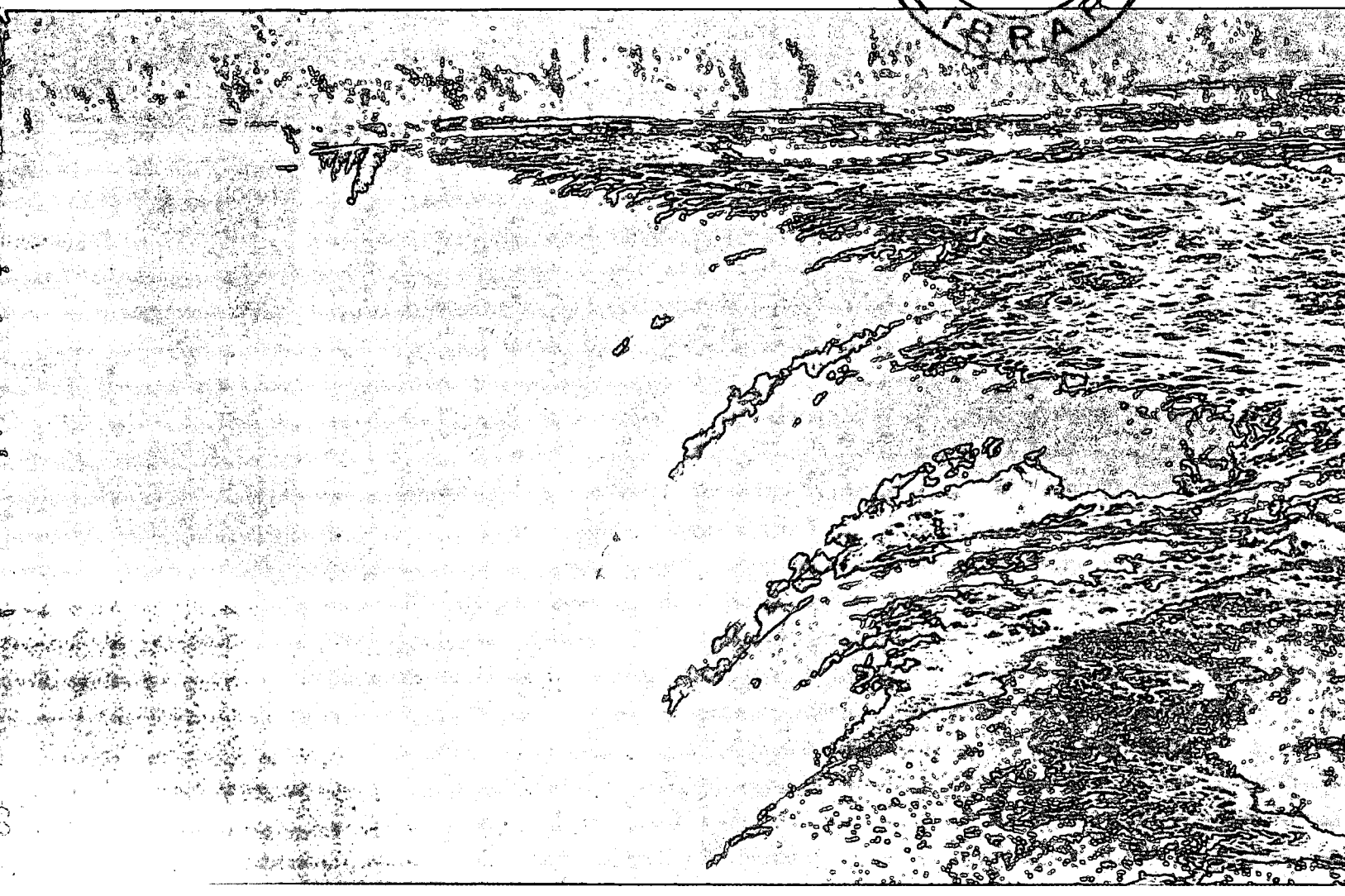

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WATER QUALITY BRANCH
BURLINGTON, ONTARIO, 1988

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Abstract

Results from a survey of bottom sediments conducted at 59 stations along the international section of the St. Lawrence River between Lake Ontario and the Quebec border in June 1975 are discussed. Summaries of trace organic and trace metal data are compared with various criteria, and possible municipal, industrial, and tributary sources of contaminants are identified.

Résumé

Les résultats d'une campagne sédimentologique réalisée à 59 stations le long du bief international du Saint-Laurent, entre le lac Ontario et les limites du Québec, en juin 1975, font l'objet d'une discussion. Les données sommaires relatives aux matières organiques et aux métaux à l'état de traces sont comparées à divers critères. Enfin, les villes, les industries et les affluents, qui sont une source possible de contaminants et qui ne respectent pas ces critères, sont identifiés.

Contaminants in Bottom Sediments of the St. Lawrence River in June 1975

K.W. Kuntz

INTRODUCTION

In June 1975, the Water Quality Branch, Ontario Region (WQB-OR), undertook a survey of bottom sediments in the international section of the St. Lawrence River between Lake Ontario and the Quebec border. The purpose of this survey was to characterize the bottom sediments in terms of their chemical composition and to look for major sources of toxic contaminants (both trace metals and organics) along the course of the river. Samples were collected at 59 stations in this section of the river. Attempts to collect samples at 11 more stations failed because of the type of bottom materials present.

SAMPLING METHODS

Samples of bottom sediments were collected with a US BM-54 sampler (Fig. 1) at the station locations identified in Figure 2. This sampler is equipped with tail fins to maintain its position in the current. When supported by a cable or rope, the sampler is in the open position for taking a bed sample. When tension on the cable is released by resting the sampler on the river bottom, the top 2.5 cm (approximately) of sediment is collected. The bucket surrounds and encloses the sample so that it is not washed out when the sampler is raised to the water surface.

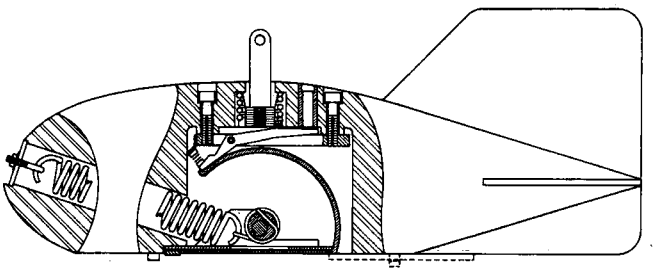

Figure 1. Bottom sediment sampler (US BM-54).

The bottom sediments collected are described in Table 1. Metals and organic contaminants listed in Table 2 were analyzed according to methods contained in the *Analytical Methods Manual* (Environment Canada, 1979). All samples were collected in prewashed plastic bottles (for metals) and prewashed aluminum cans (for organics). Samples were immediately frozen with dry ice and stored frozen until analyzed.

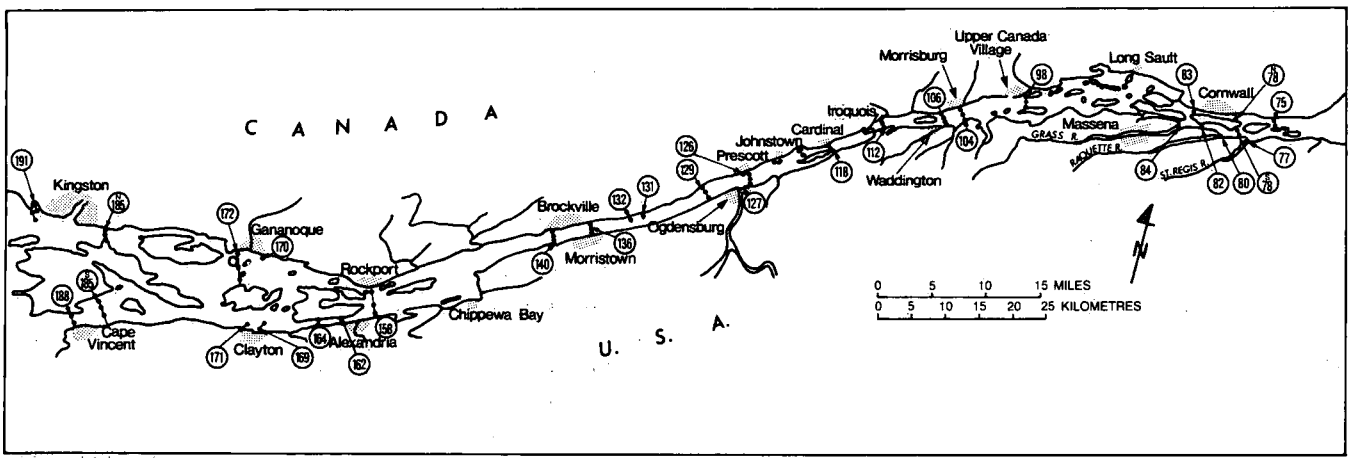

Figure 2. Sampling ranges and stations.

Table 1. Bottom Sediments in the St. Lawrence River

Station	Date	Description
191A	75-11-06	fine silty clay
191B	75-11-06	fine silty clay
191C	75-11-06	NS
191D	75-11-06	grey fine silty clay
188A	75-05-06	NS
188B	75-05-06	fine silty clay
185-NA	75-10-06	black mud
185-NB	75-10-06	clay mud
185-NC	75-10-06	clay mud
185-SA	75-05-06	sand
185-SB	75-05-06	sand
185-SC	75-05-06	sand
172A	75-10-06	mud
172B	75-10-06	mud
172C	75-10-06	mud
171A	75-10-06	sand and mud
170A	75-10-06	mud, weeds, and organics
169A	75-10-06	NS
169B	75-10-06	rocks and shells
164A	75-10-06	clay and mud
164B	75-10-06	mud
162A	75-10-06	NS
158A	75-10-06	muddy clay and clam shells
158B	75-10-06	muddy clay and clam shells
158C	75-10-06	muddy clay and clam shells
140A	75-07-06	silty clay
140B	75-07-06	NS
140C	75-07-06	silty clay
136A	75-07-06	sand and gravel
136B	75-07-06	sand and gravel
136C	75-07-06	NS
132A	75-07-06	fine sand
131A	75-07-06	fine sand
129A	75-07-06	silty clay
129B	75-07-06	NS
129C	75-07-06	organic debris
127A	75-07-06	coarse gravel

NS = no sample collected.
ND = no description.

Table 1. Continued

Station	Date	Description
126A	75-07-06	silty clay
126B	75-07-06	NS
126C	75-07-06	sand, silt, and roots
126D	75-07-06	sand, silt, and roots
118A	75-07-06	sand
118B	75-07-06	gravel
118C	75-07-06	gravel
112A	75-08-06	fine sand
112B	75-08-06	coarse sand
112C	75-08-06	sand and mud
106A	75-08-06	sand and gravel
106B	75-08-06	NS
106C	75-08-06	sand
106D	75-08-06	clay and till
104A	75-08-06	silty clay and sand
104B	75-08-06	NS
104C	75-08-06	sand
98A	75-08-06	silty sand
98B	75-08-06	NS
98C	75-08-06	sand and organics
84A	75-09-06	ND
83A	75-09-06	fine sand and rock
82A	75-09-06	mud
82B	75-09-06	mud
80A	75-09-06	black mud
78-NA	75-09-06	mud
78-NB	75-09-06	mud
78-SA	75-09-06	gravel and shells
78-SB	75-09-06	mud
77A	75-09-06	ND
77B	75-09-06	brown coarse sand
75A	75-09-06	sand
75B	75-09-06	ND

RESULTS

Criteria

Various criteria have been suggested by several different Canadian and U.S. government agencies for dredge spoil disposal of bottom sediments, including criteria established by the Ontario Ministry of the Environment (MOE) (1976), Thomas and Mudroch (1979), and the United States Environmental Protection Agency (EPA) (1975). These criteria are given in Table 3, and will be used as references thoughout this report.

Table 2. Parameters Analyzed

Trace metals	Organics	Others
Cadmium	Lindane	Cyanide
Chromium	Heptachlor	Phenols
Copper	Aldrin	Total chemical oxygen demand
Iron	Heptachlor epoxide	Inorganic phosphorus
Lead	p,p'-DDE	Total phosphorus
Manganese	Dieldrin	Loss at 105°C
Mercury	p,p'-TDE (DDD)	Loss on ignition (550°C)
Nickel	p,p'-DDT	Oil and grease
Arsenic	o,p'-DDT	
Selenium	Endrin	
Zinc	α-Chlordane	
	γ-Chlordane	
	α-Endosulfan	
	β-Endosulfan	
	p,p'-Methoxychlor	
	Total PCB	
	HCB	
	α-BHC	
	Mirex	

Trace Metals

Cadmium

Cadmium concentrations in bottom sediments were generally at or below the analytical detection limit of 10 $\mu g\ g^{-1}$. Five of the 56 samples analyzed for cadmium were above the detection limit. The highest value was 14 $\mu g\ g^{-1}$ at station 82A, just downstream from the Grass River. A likely source of this high cadmium concentration is the Reynolds Metals Co. industrial and sanitary sewers, which discharge just upstream from this station. The MOE dredge spoil objective is 1 $\mu g\ g^{-1}$, an order of magnitude below the detection limit.

Chromium

The distribution of chromium in the bottom sediments of the St. Lawrence River (see Fig. A-1 in the Appendix) showed a rather even pattern throughout the river system. Nearly all samples were above the MOE dredge spoil objective of 25 $\mu g\ g^{-1}$. Several stations had levels above 100 $\mu g\ g^{-1}$, i.e., 191A, 170A, 106A, 171A, and 158C. All of these stations, except 171A and 106A, are located downstream from municipal or industrial sources. Twelve stations were designated as being heavily polluted because they were above the EPA heavily polluted category of 75 $\mu g\ g^{-1}$ (Table 3). Four of these stations were also above Thomas and Mudroch's revised guidelines of 120 $\mu g\ g^{-1}$.

Copper

Thirty-seven of the stations sampled had copper concentrations higher than the MOE dredge spoil objective of 25 $\mu g\ g^{-1}$ (Fig. A-2). Seven stations (191A, 170A, 132A, 126A, 171A, 158C, and 82A) had concentrations above 60 $\mu g\ g^{-1}$ in their bottom sediments. Thirteen stations were classified as heavily polluted when compared with the 1977 EPA guidelines. Most of these locations are downstream from possible municipal or industrial sources.

Iron

Concentrations of total iron (Fig. A-3) in bottom sediments were quite evenly distributed between 12 and 42 $mg\ g^{-1}$ (12 000–42 000 $\mu g\ g^{-1}$). Every sample violated the

Table 3. Bottom Sediment Criteria

Parameter	MOE dredge spoil objective	Thomas and Mudroch's guidelines	EPA heavily polluted category
Cadmium ($\mu g\ g^{-1}$)	1	1.5	>6
Chromium ($\mu g\ g^{-1}$)	25	120	>75
Copper ($\mu g\ g^{-1}$)	25	45	>50
Iron ($\mu g\ g^{-1}$)	10 000	45 500	>25 000
Lead ($\mu g\ g^{-1}$)	50	50	>60
Manganese ($\mu g\ g^{-1}$)	–	1 625	>500
Mercury ($\mu g\ g^{-1}$)	0.3	0.3	>1.0
Nickel ($\mu g\ g^{-1}$)	25	90	>50
Arsenic ($\mu g\ g^{-1}$)	8	8	>8
Zinc ($\mu g\ g^{-1}$)	100	105	>200
PCBs ($\mu g\ g^{-1}$)	0.05	0.05	>10
Cyanide ($\mu g\ g^{-1}$)	0.1	0.1	>0.25
COD ($mg\ g^{-1}$)	50	50	>80
Oil and grease ($mg\ g^{-1}$)	1.5	1.5	>2.0
Percentage loss on ignition (%)	6	6	>8
Total P ($\mu g\ g^{-1}$)	1 000	1 000	>650

MOE dredge spoil objective of 10 000 $\mu g\ g^{-1}$. Sixteen of the stations sampled were classified as heavily polluted when compared with the 1977 EPA guidelines.

Lead

Lead concentrations (Fig. A-4) varied from the detection limit of 50 $\mu g\ g^{-1}$ to a high of 190 $\mu g\ g^{-1}$ at station 127A in the Oswegatchie River at Ogdensburg, N.Y. Twenty-seven of the stations were above the EPA heavily polluted category of 60 $\mu g\ g^{-1}$. Eight stations (170A, 131A, 106A, 78-NA, 171A, 169B, 164B, and 127A) were above 120 $\mu g\ g^{-1}$, more than twice the objective. Most of these locations are downstream from probable sources.

Manganese

Manganese concentrations (Fig. A-5) ranged from 240 $\mu g\ g^{-1}$ to 1000 $\mu g\ g^{-1}$ at station 185-SB, just downstream from Cape Vincent. Sixteen of the stations sampled were classified as heavily polluted when compared with the 1977 EPA guidelines.

Mercury

Most of the samples collected showed mercury concentrations below the MOE dredge spoil objective of 0.3 $\mu g\ g^{-1}$. However, stations 170A, 169B, 164A, and 78-NA (Fig. A-6), where the highest concentration of 4.9 $\mu g\ g^{-1}$ was found, were above this criterion. These "hot spots" indicate small sources of mercury at Gananoque and Clayton, and a larger source at Cornwall.

Nickel

Thirty-four of the 59 samples collected violated the MOE dredge spoil objective for nickel concentrations of 25 $\mu g\ g^{-1}$ (Fig. A-7). A high of 87 $\mu g\ g^{-1}$ was observed at station 171A just upstream from Clayton. Other stations with concentrations of nickel above 50 $\mu g\ g^{-1}$, and thus in the EPA heavily polluted category, were 185-NA, 172A, 172C, 170A, 106A, and 158C. None of the stations sampled had nickel concentrations as high as Thomas and Mudroch's revised guideline of 90 $\mu g\ g^{-1}$.

Arsenic

Only two of the samples collected violated the MOE dredge spoil objective for arsenic concentrations of 8 $\mu g\ g^{-1}$ (Fig. A-8). Station 185-SB (48 $\mu g\ g^{-1}$) and station 118C (8 $\mu g\ g^{-1}$) equaled or exceeded the objective. Other stations with somewhat higher arsenic concentrations, but below the objective, were stations 185-NA, 188B, 158B, and 112C.

Selenium

Selenium concentrations (Fig. A-9) ranged from 0.03 $\mu g\ g^{-1}$ at station 77B to 1.5 $\mu g\ g^{-1}$ at station 172C. Stations 172C, 106A, and 171A had elevated concentrations of selenium.

Zinc

Twenty-six of the 57 samples collected (Fig. A-10) were in violation of the MOE dredge spoil objective for zinc concentrations of 100 $\mu g\ g^{-1}$. Values above the 200 $\mu g\ g^{-1}$ EPA heavily polluted category were observed at stations 191A, 172A, 170A, 78-NA, 171A, and 126C.

Organics

Of the 19 organic contaminants analyzed for in the bottom sediments (Table 2), nine compounds (lindane, α-BHC, heptachlor, heptachlor epoxide, aldrin, endrin, o,p′-DDT, α-endosulfan, and mirex) were not detected in any of the samples at the 0.001 $\mu g\ g^{-1}$ detection limit. Two compounds, p,p′-methoxychlor and β-endosulfan, were detected once at the 0.002 $\mu g\ g^{-1}$ level. Dieldrin was detected at only five stations at the 0.001 $\mu g\ g^{-1}$ level. α-Chlordane and γ-chlordane were detected three and five times respectively at the 0.001 $\mu g\ g^{-1}$ level. Hexachlorobenzene was detected five times at the 0.001-0.002 $\mu g\ g^{-1}$ level.

DDT and Metabolites

The o,p′-DDT metabolite was not found in any of the 57 samples analyzed.

Generally, values of p,p′-TDE were low throughout the river system. This compound was found in 13 of the 57 samples collected. Several values above the detection limit in the 0.003-0.011 $\mu g\ g^{-1}$ range were observed at ranges 172 and 158 in the Gananoque-Rockport area.

Concentrations of p,p′-DDE were normally below the detection limit of 0.001 $\mu g\ g^{-1}$ as this compound was detected at only 5 of the 57 stations sampled. High values of this compound were found at station 84 in the Grass River (0.090 $\mu g\ g^{-1}$) and at stations 82 (0.060 $\mu g\ g^{-1}$) and 78S (0.057 $\mu g\ g^{-1}$) immediately downstream from the Grass River. This would indicate that there has been a source of either this compound or p,p′-DDT that has been transformed in the biological system to p,p′-DDE in the Grass River.

The parent compound, p,p′-DDT, was observed in low concentrations at the detectable level of 0.001 $\mu g\ g^{-1}$ at

five of the stations sampled. It was also observed at higher levels at station 126A (0.005 $\mu g\ g^{-1}$) and at station 132A (0.021 $\mu g\ g^{-1}$). These levels indicate probable sources of p,p'-DDT at Maitland and Prescott.

PCBs

Low levels of PCBs were detected at most of the stations sampled (Fig. A-11). Levels above the 0.05 $\mu g\ g^{-1}$ MOE dredge spoil objective occurred at 10 of the 57 stations sampled. Highest values occurred at stations 84A (1.51 $\mu g\ g^{-1}$) in the Grass River and at station 82B (1.59 $\mu g\ g^{-1}$) downstream from the Grass River. Station 78-SB, farther downstream from the Grass River source, was also quite high at 0.64 $\mu g\ g^{-1}$. Other small local sources of PCBs would appear to be present at Gananoque, Alexandria Bay, and the Raquette and St. Regis rivers.

Other Analyses

Cyanide

Every sample collected (52) (Fig. A-12) violated the MOE dredge spoil objective for cyanide concentrations of 0.1 $\mu g\ g^{-1}$, and only one sample would not be classified as heavily polluted using the EPA guideline of 0.25 $\mu g\ g^{-1}$. Values ranged up to 3.3 $\mu g\ g^{-1}$ at stations 185-SA and 191D. No sample was found with less than 0.2 $\mu g\ g^{-1}$, twice the MOE dredge spoil objective. Stations 191D, 172B, 185-SA, and 82A were above 2.0 $\mu g\ g^{-1}$.

Phenols

Concentrations of total phenols (Fig. A-13) above the 2.0 $\mu g\ g^{-1}$ level were found at stations 185-SA, 169B, and 164B. Most other stations were in the 0.0–1.0 $\mu g\ g^{-1}$ range.

Chemical Oxygen Demand

Chemical oxygen demand (COD) (Fig. A-14) ranged from 0.0 to 350 mg g^{-1}. The MOE dredge spoil objective of 50 mg g^{-1} was violated at numerous stations. Many stations were classified as heavily polluted when compared with the 1977 EPA guidelines. Highest values occurred at stations 170A (223 mg g^{-1}) and 164B (354 mg g^{-1}).

Oil and Grease

All samples were considerably higher than the MOE dredge spoil objective of 1.5 mg g^{-1} (Fig. A-15). The highest values recorded were at stations 191A (1125 mg g^{-1}) and 78-NA (1147 mg g^{-1}). Both of these stations have local inputs from Kingston and Cornwall respectively. All of the stations sampled were classified as heavily polluted when compared with the 1977 EPA guidelines.

Percentage of Loss at 105°C

The loss on ignition test at 105°C gives an indication of how compressed the sediment is at each location. Generally, the samples varied from about 20% to about 75% water (Fig. A-16). Highest values were found at stations 191A (75%), 171A (73%), and 164B (74%). Perhaps this is one of the reasons that the contaminants are often highest at these stations. Since the analyses were done on dry samples, those with highest water content would have highest concentrations of contaminants on a dry weight basis as well.

Percentage of Loss on Ignition

Twenty-two samples were above the MOE dredge spoil objective for loss on ignition of 6% (Fig. A-17). Seventeen of the stations sampled were classified as heavily polluted when compared with the EPA guidelines. Values as high as 27% were found at station 164B. Other stations with high values of organic content were stations 191A (17%), 170A (17%), 171A (13%), 164A (13%), and 77A (13%).

Total, Inorganic, and Organic Phosphorus

Total phosphorus concentrations were in violation of the MOE dredge spoil objective of 1000 $\mu g\ g^{-1}$ at nine of the stations sampled (Fig. A-18). Most of the stations sampled were classified as heavily polluted when compared with the 1977 EPA guidelines. Highest values were measured at stations 191A (1260 $\mu g\ g^{-1}$), 158B (1310 $\mu g\ g^{-1}$), and 129C (1470 $\mu g\ g^{-1}$).

Inorganic phosphorus concentrations were somewhat lower than total phosphorus and ranged from about 140 $\mu g\ g^{-1}$ to 1050 $\mu g\ g^{-1}$ (Fig. A-19). Highest values of inorganic phosphorus were found at station 158B (1050 $\mu g\ g^{-1}$).

Organic phosphorus, the difference between total and inorganic phosphorus, had highest values at stations 171A (450 $\mu g\ g^{-1}$), 170A (340 $\mu g\ g^{-1}$), 164B (410 $\mu g\ g^{-1}$), and 77A (340 $\mu g\ g^{-1}$) (Fig. A-20).

SUMMARY

When compared with several criteria for dredge spoil disposal of bottom sediments, it was found that the sediments at many of these stations were not suitable for open

Table 4. **Possible Municipal, Industrial, and Tributary Sources of Contaminants**

Source	Contaminants and other analyses
Grass River	p,p′-DDE (or p,p′-DDT), PCBs
St. Regis River	PCBs, organic P, percentage loss on ignition
Raquette River	PCBs
Oswegatchie River (Ogdensburg)	Pb, Zn
Cataraqui Bay	Cr, Cu, CN, Ni, Zn, TP, oil and grease, percentage loss at 105°C, percentage loss on ignition
Lake Ontario	Mn, As
Kingston	Ni, As
Gananoque	Cr, Cu, Hg, Ni, Pb, Zn, COD, PCBs, p,p′-TDE, percentage loss on ignition, organic P
Cornwall	Hg, Pb, Zn, oil and grease
Clayton	Phenols, percentage loss at 105°C, organic P, Pb, COD, Cr, Cu, Ni, Zn, percentage loss on ignition
Rockport	p,p′-TDE
Alexandria Bay	PCBs, TP, Cu, Ni, As, Cr, inorganic P
Prescott	p,p′-DDT, Cu
Cape Vincent	As, CN, Mn, phenols
Reynolds Metals Co.	CN, Cd, Cu
Maitland (Dupont)	Pb, Cu, p,p′-DDT

water disposal. A summary of the possible municipal, industrial, or tributary sources of contaminants found in sediments in the river near their discharges is given in Table 4. Many of these sources appear to be significant.

All samples collected violated the MOE objectives for iron, cyanide, and oil and grease. Numerous samples violated the MOE objectives for chromium, copper, lead, nickel, zinc, chemical oxygen demand, and loss on ignition. Cornwall appears to be a significant source of mercury, and the Grass River a significant source of p,p′-DDE and PCBs. Transboundary pollution may be occurring downstream from these sources in Quebec and U.S. waters.

Since many of these objectives are consistently violated, it would appear that either the objectives are too low and need to be revised, or the sources are not controlled enough and inputs need to be reduced so that further degradation of the bottom sediments does not occur.

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Appendix

Bottom Sediment Survey Results, St. Lawrence River, June 1975

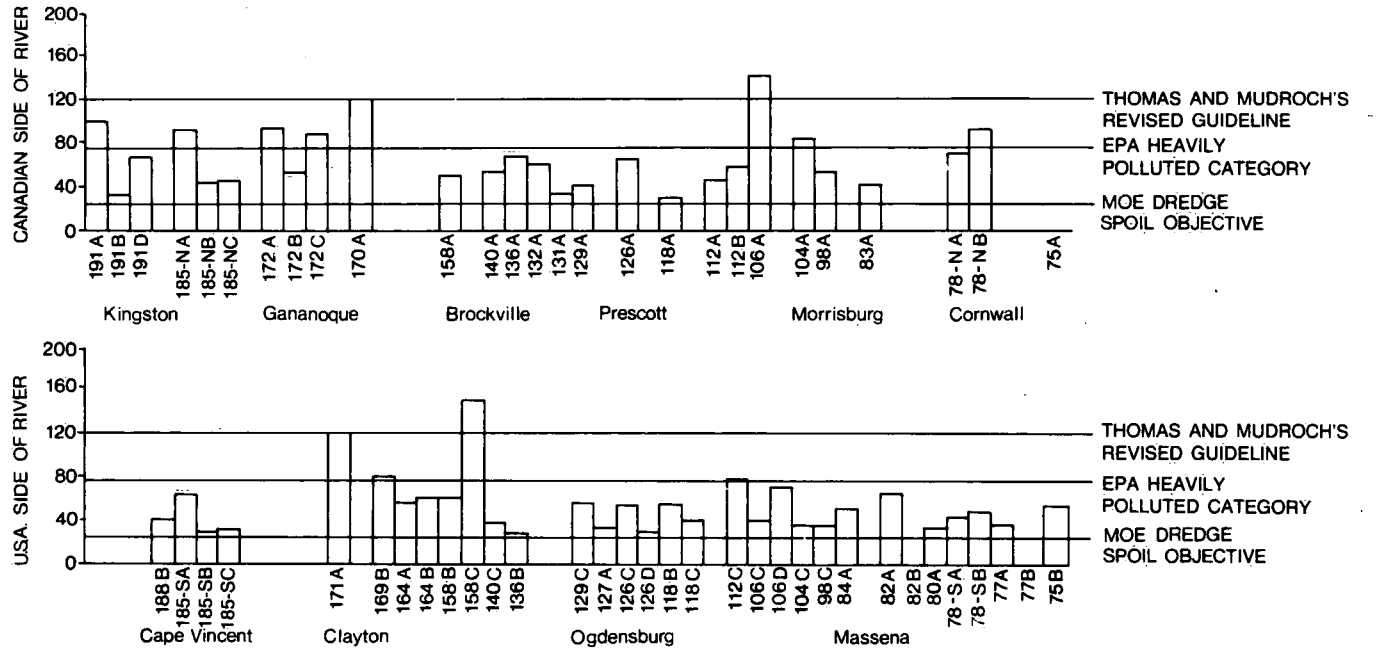

Figura A-1. Chromium ($\mu g\ g^{-1}$).

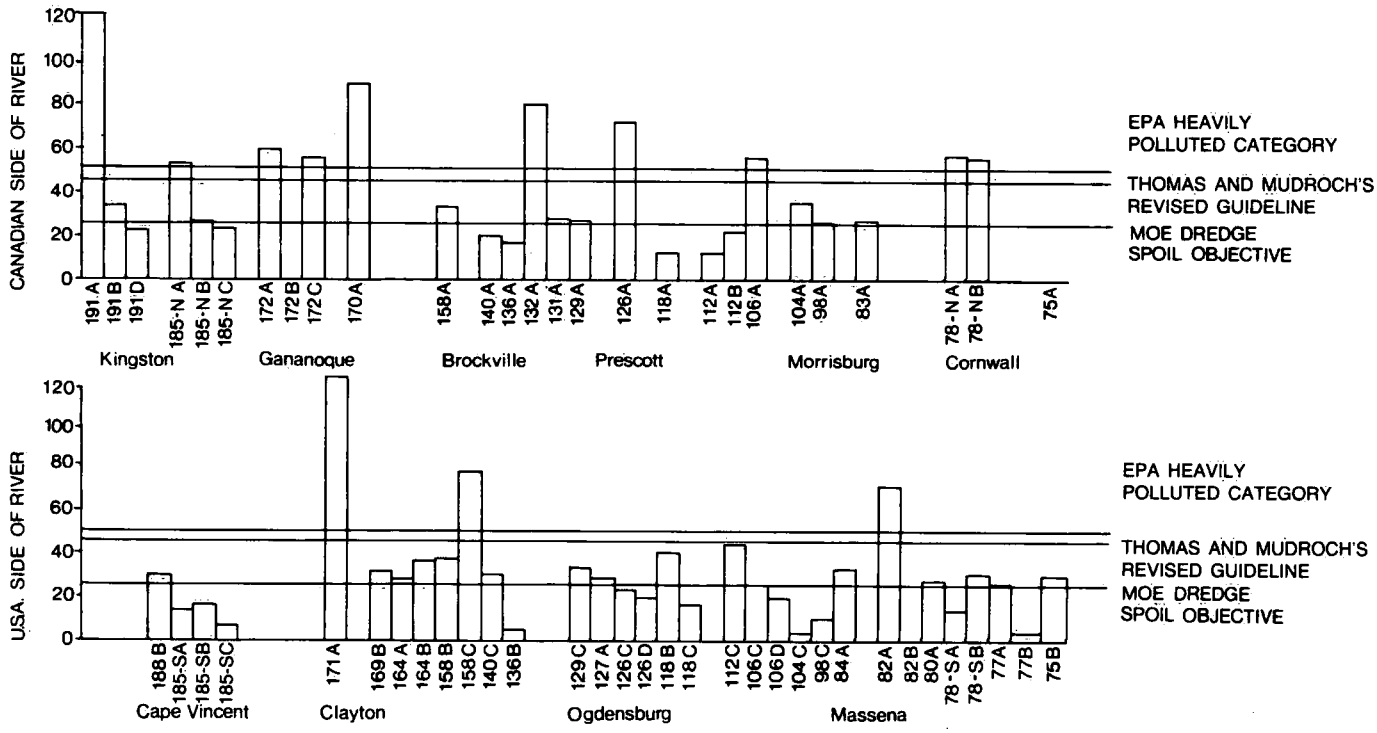

Figure A-2. Copper ($\mu g\ g^{-1}$).

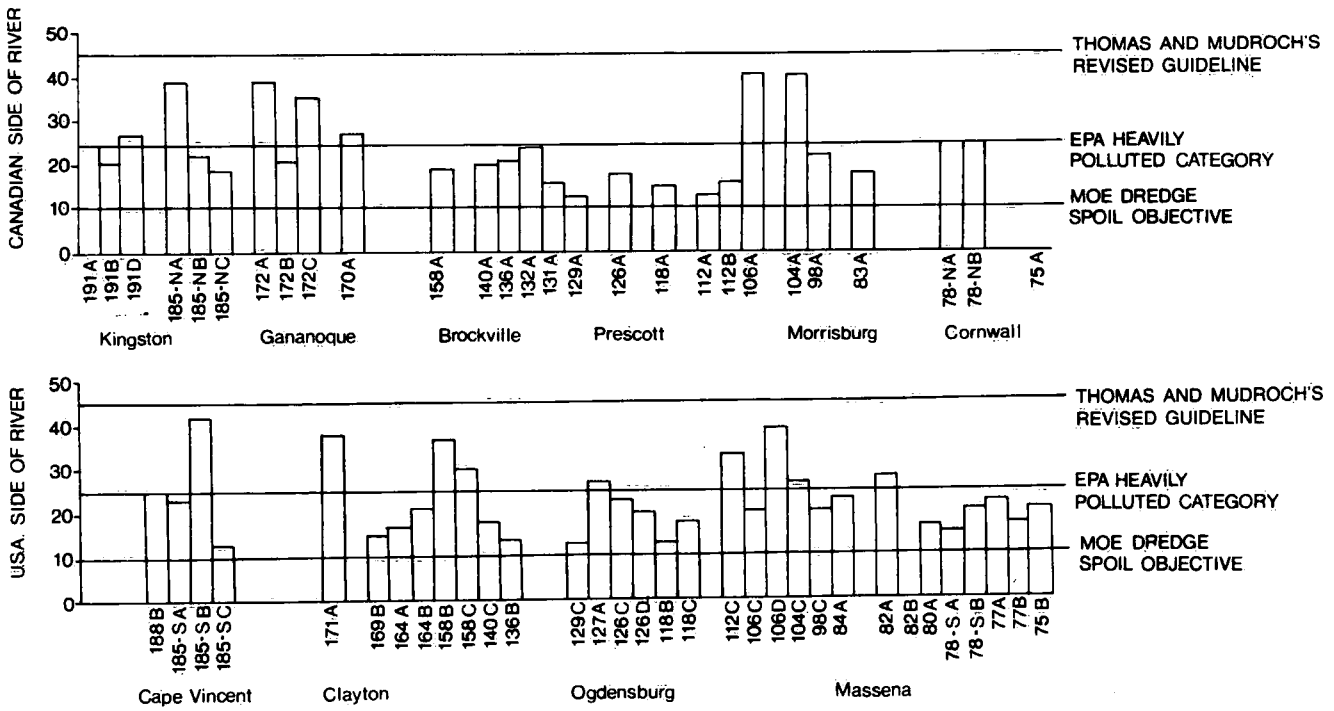

Figure A-3. Iron (mg g^{-1}).

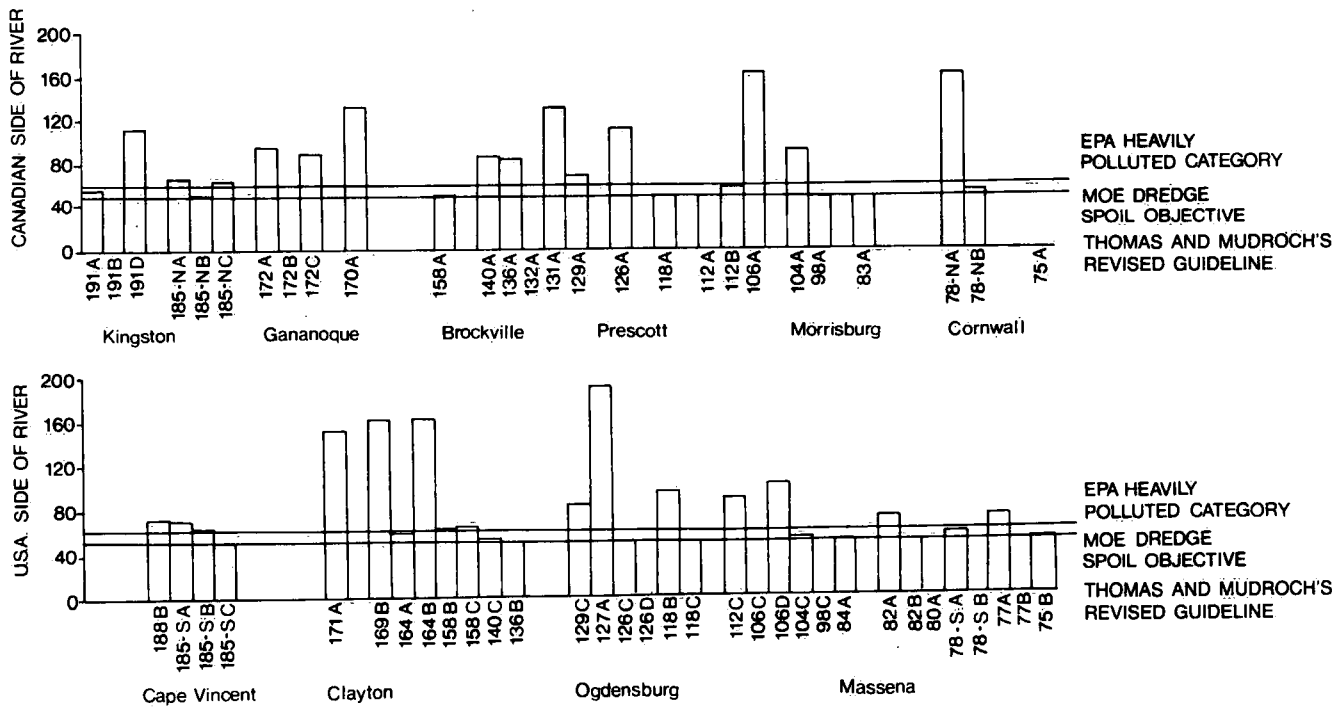

Figure A-4. Lead (μg g^{-1}).

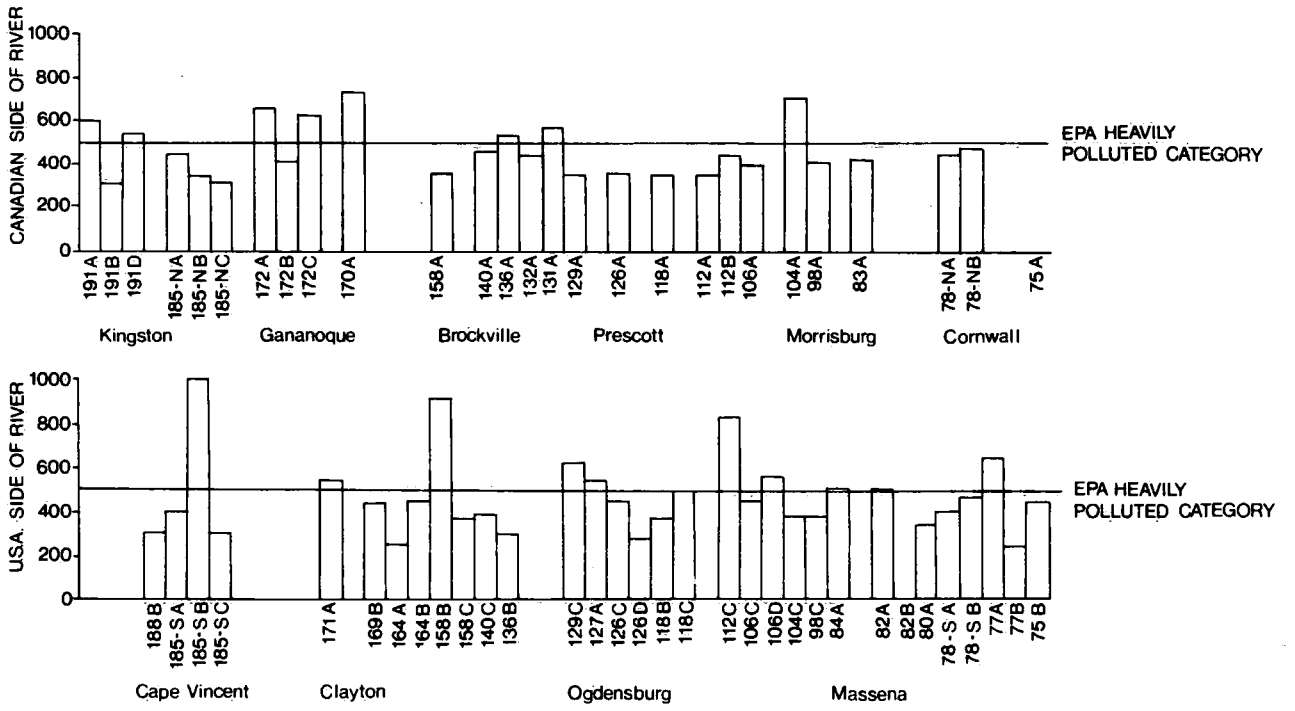

Figure A-5. Manganese ($\mu g\ g^{-1}$).

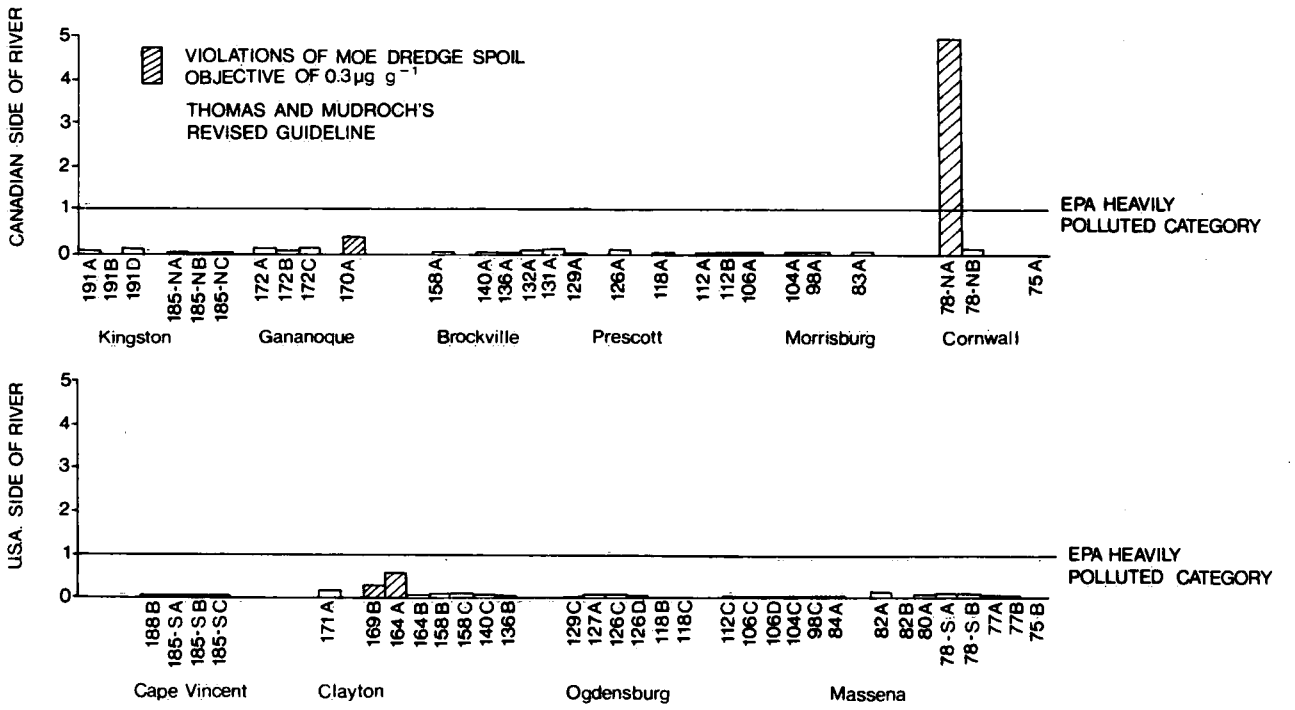

Figure A-6. Mercury ($\mu g\ g^{-1}$).

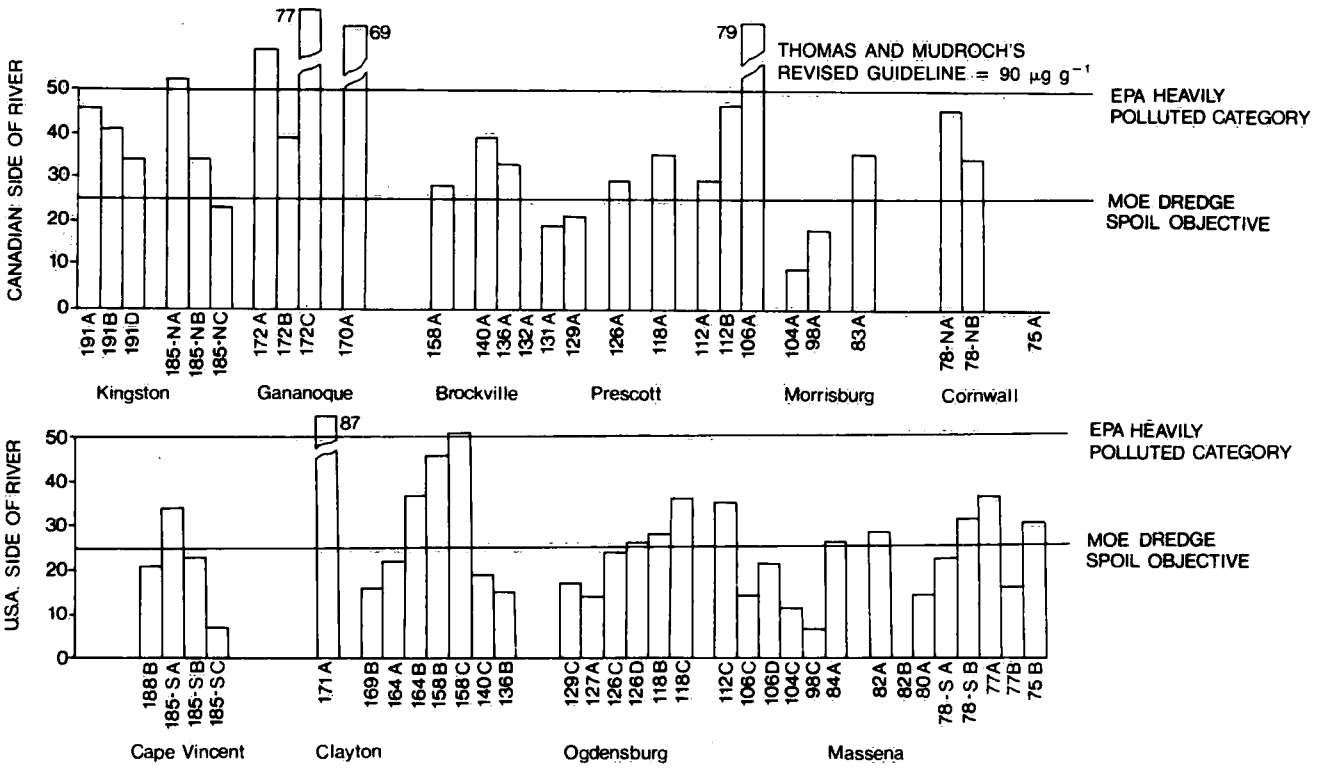

Figure A-7. Nickel ($\mu g\, g^{-1}$).

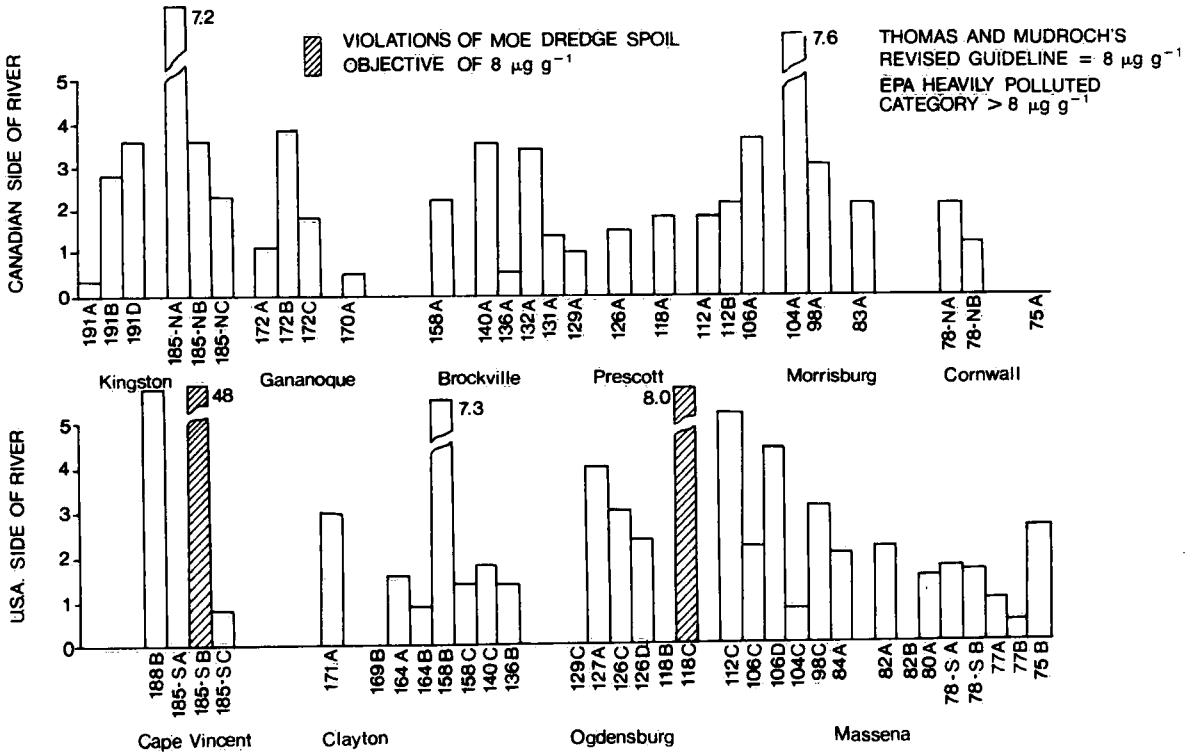

Figure A-8. Arsenic ($\mu g\, g^{-1}$).

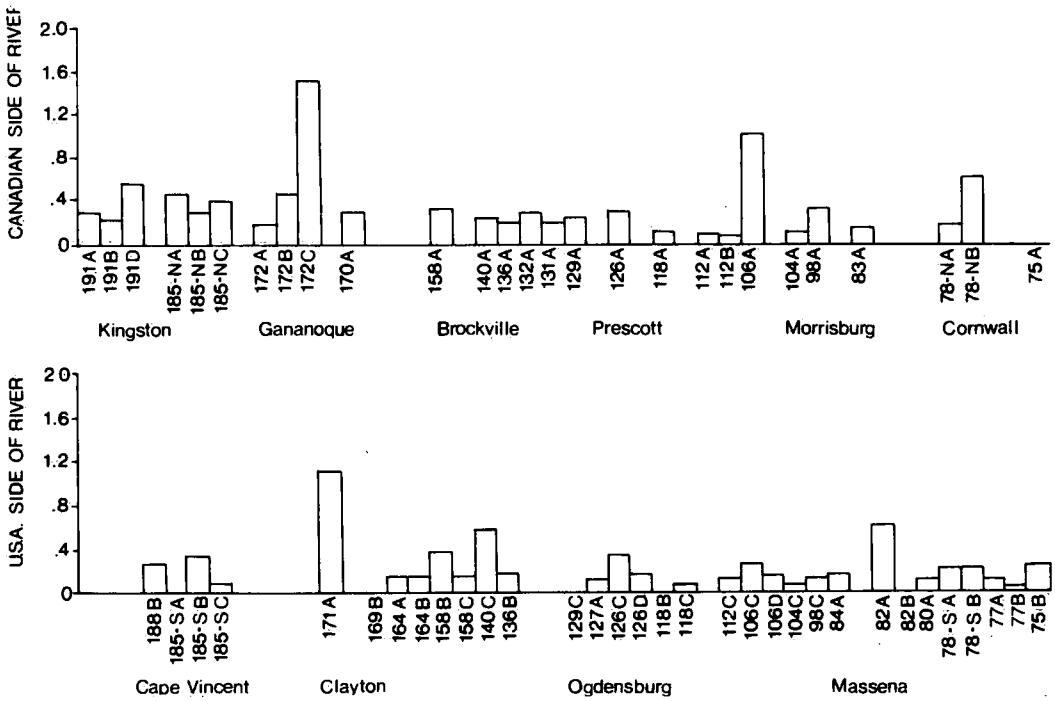

Figure A-9. Selenium ($\mu g\ g^{-1}$).

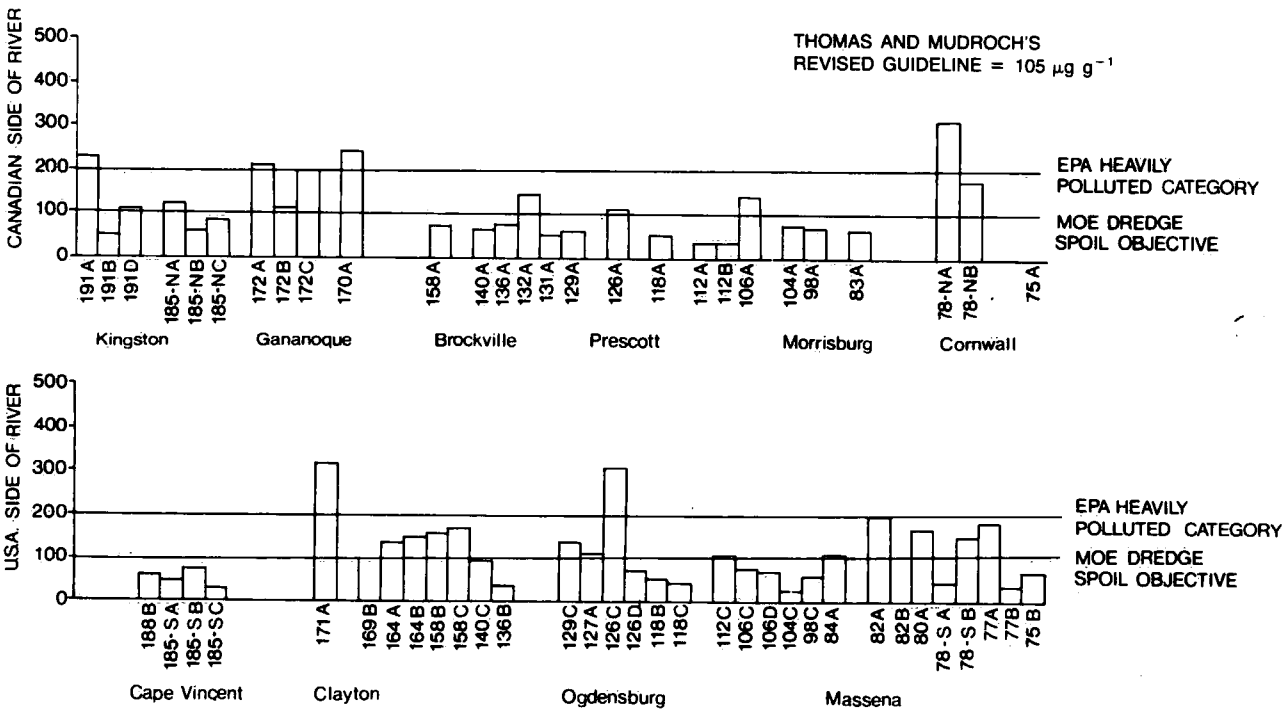

Figure A-10. Zinc ($\mu g\ g^{-1}$).

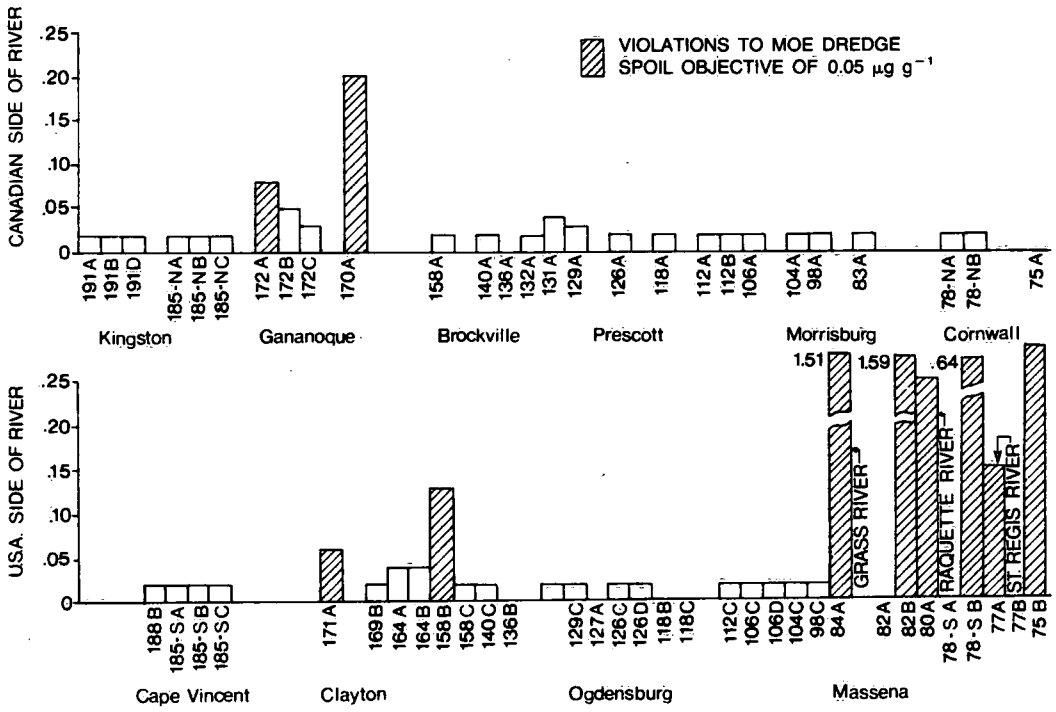

Figure A-11. PCBs ($\mu g\ g^{-1}$).

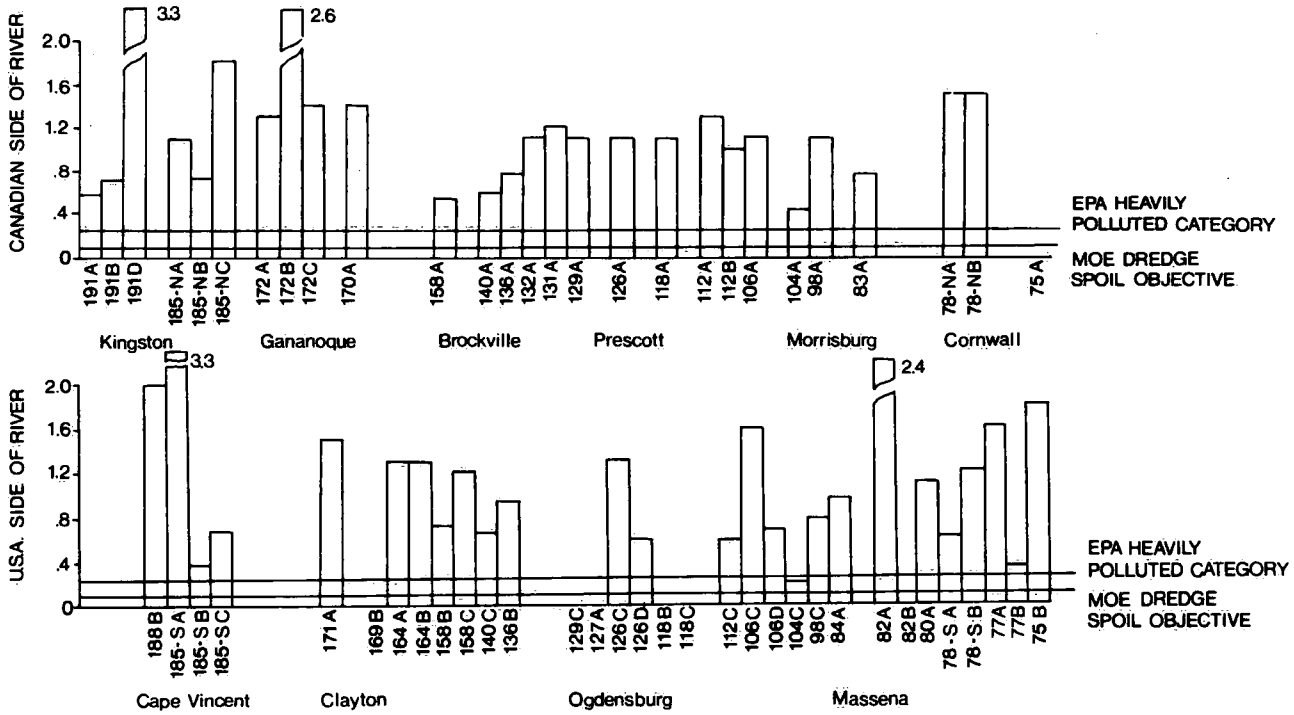

Figure A-12. Cyanide ($\mu g\ g^{-1}$).

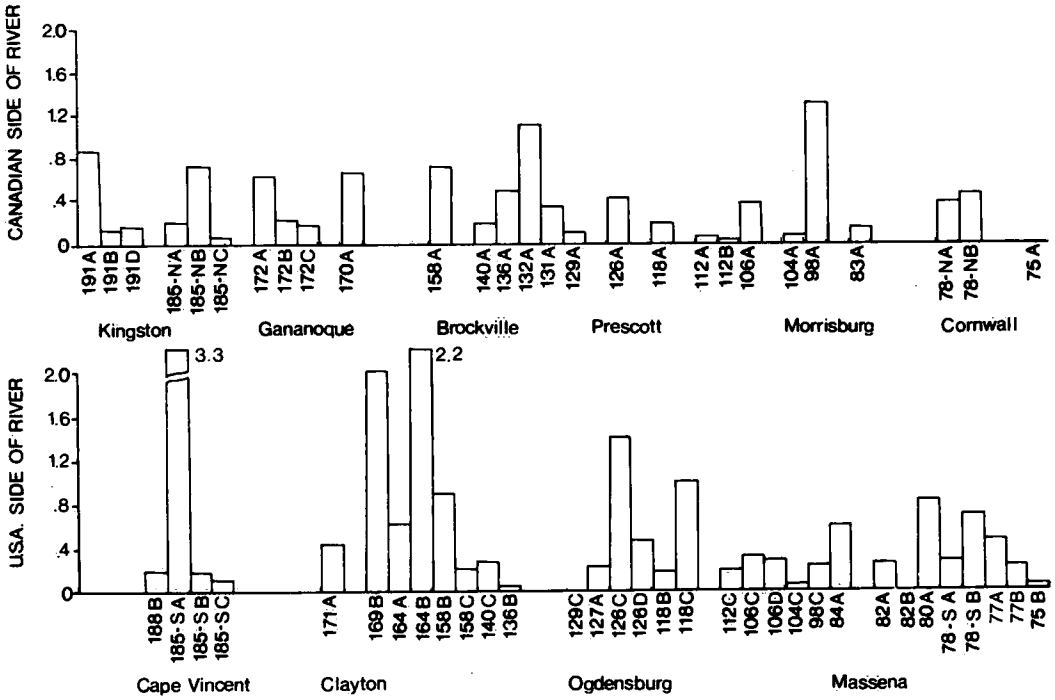

Figure A-13. Phenols ($\mu g\ g^{-1}$).

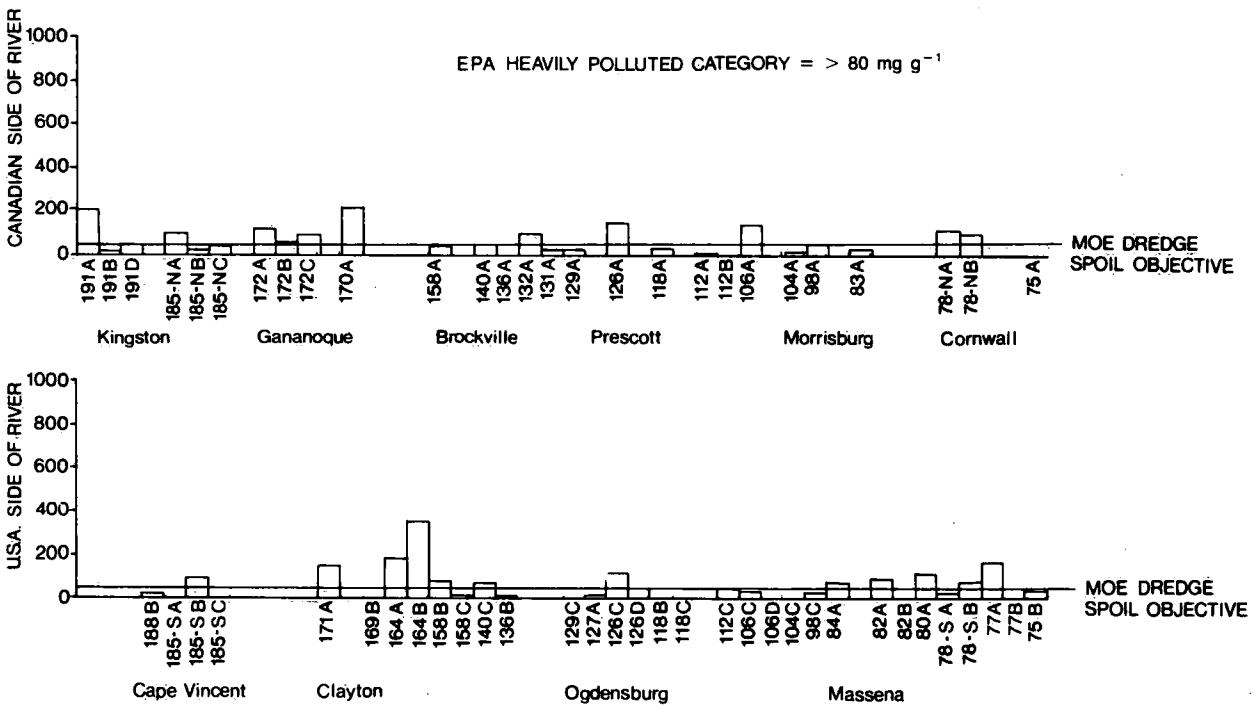

Figure A-14. Chemical oxygen demand ($mg\ g^{-1}$).

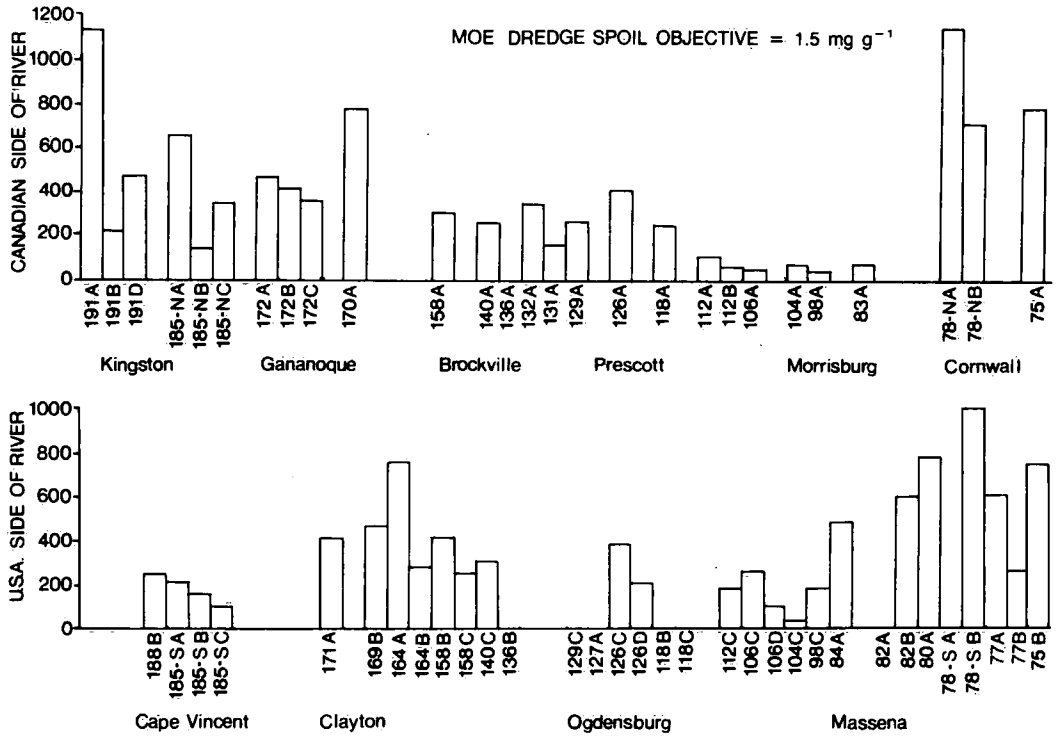

Figure A-15. Oil and grease (mg g^{-1}).

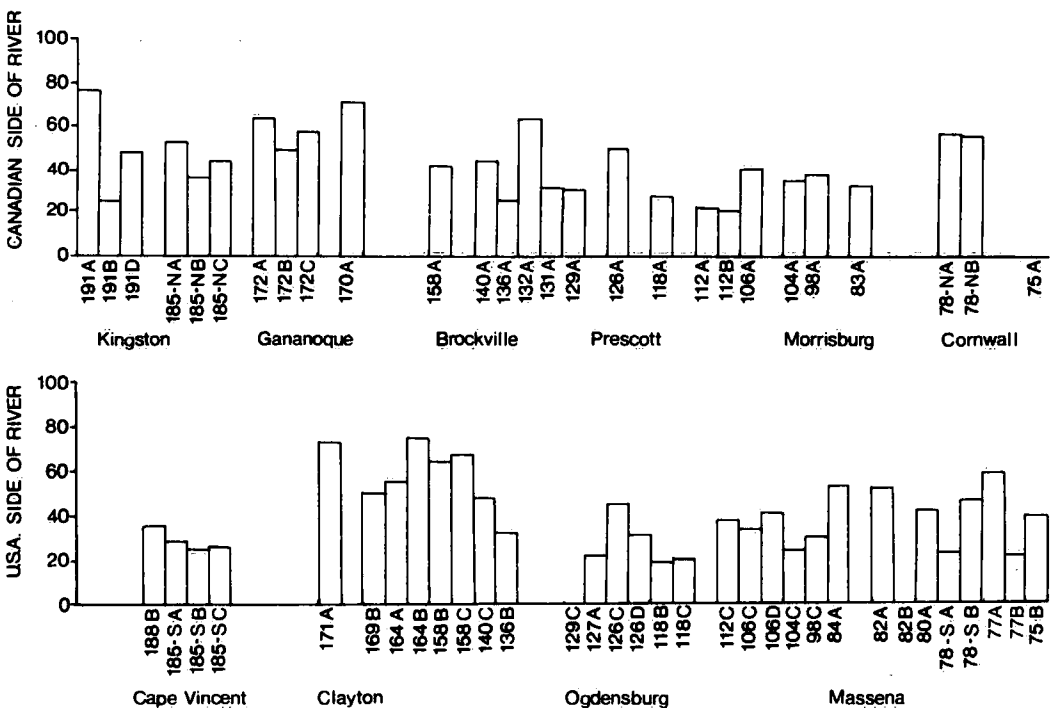

Figure A-16. Percentage of loss at 105°C.

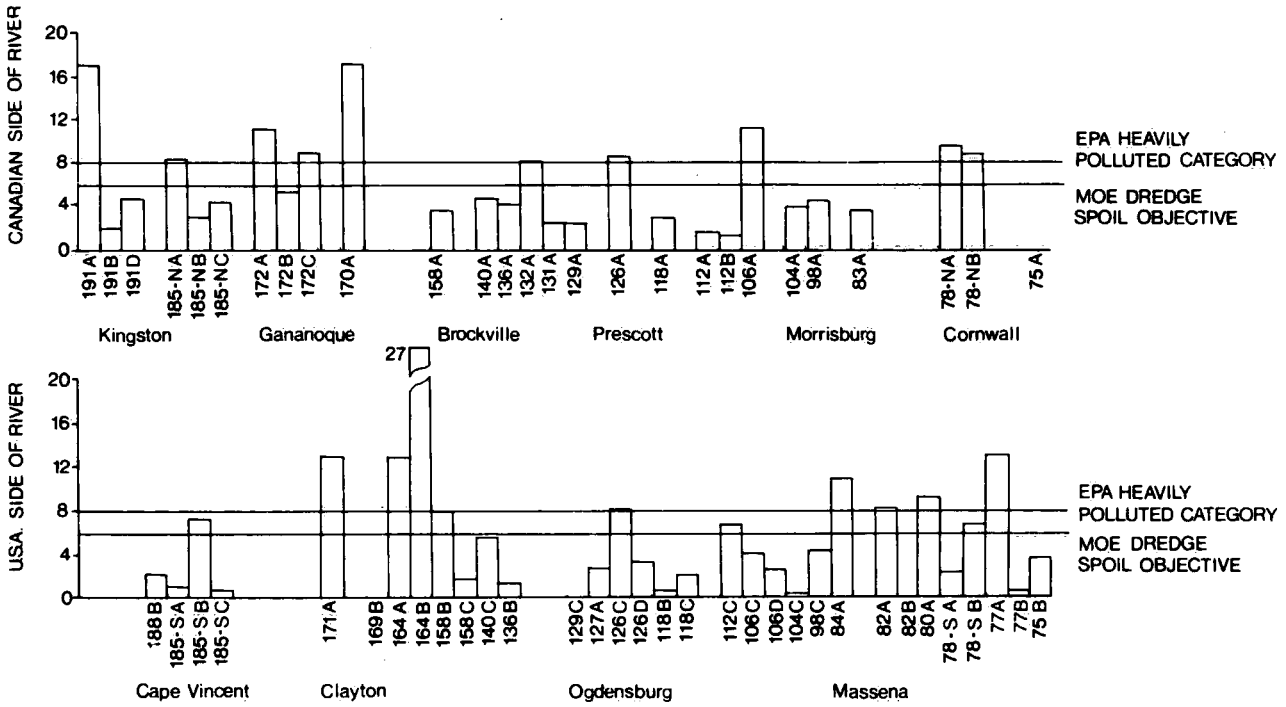

Figure A-17. Percentage of loss on ignition.

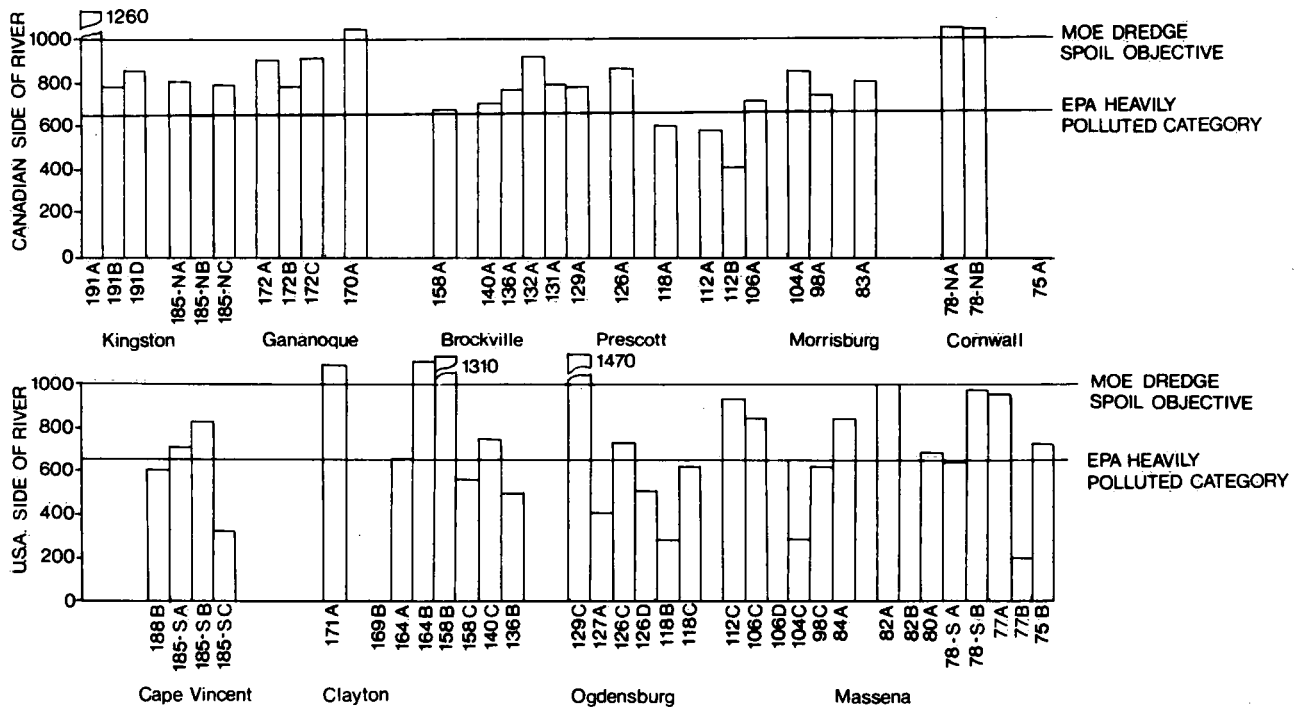

Figure A-18. Total phosphorus ($\mu g\ g^{-1}$).

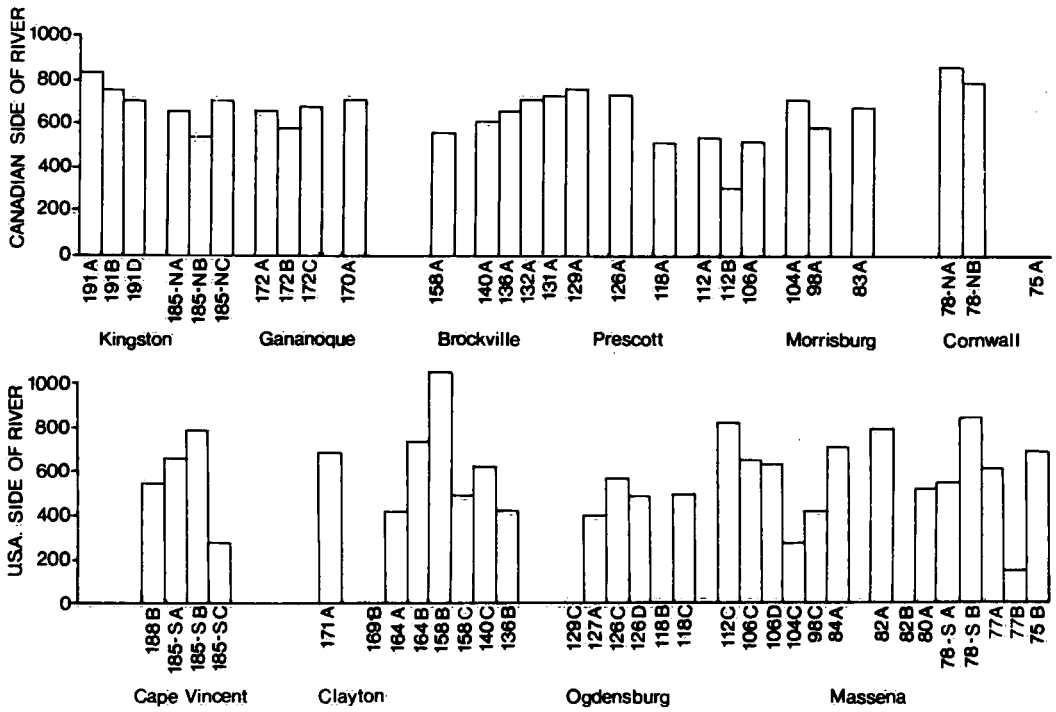

Figure A-19. Inorganic phosphorus ($\mu g\ g^{-1}$).

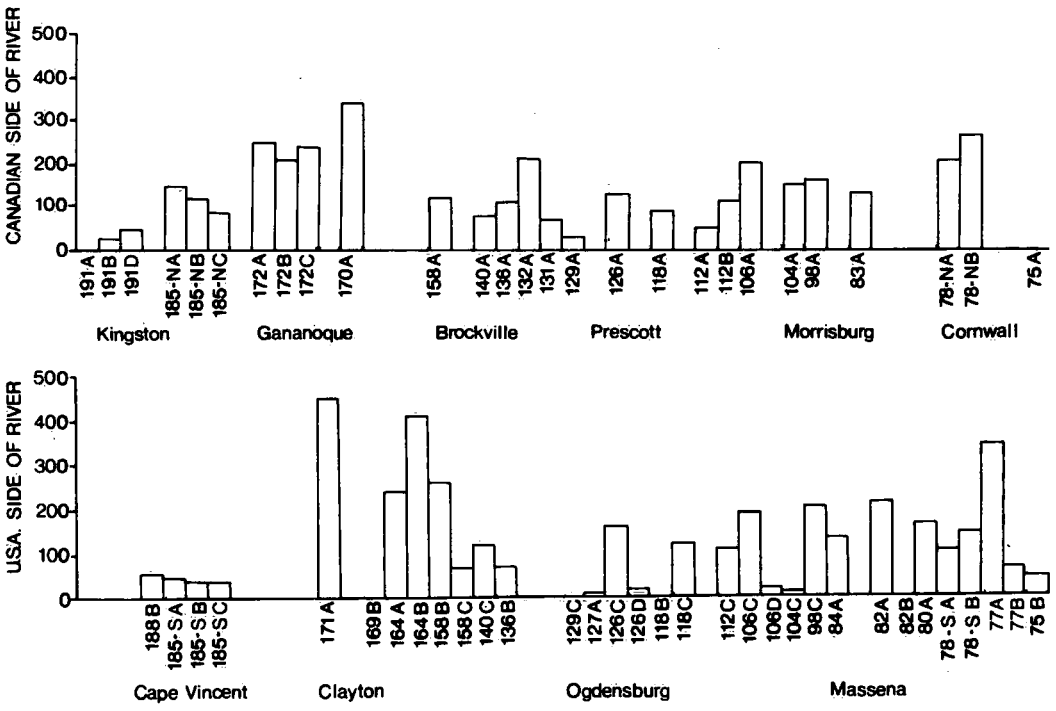

Figure A-20. Organic phosphorus ($\mu g\ g^{-1}$)

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