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St. Lawrence River Water Quality Surveys, 1977

C. H. Chan

SCIENTIFIC SERIES NO. 113

INLAND WATERS DIRECTORATE
ONTARIO REGION
WATER QUALITY BRANCH
BURLINGTON, ONTARIO, 1980

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Cat. No. En 36-502/113E

ISBN 0-662-11178-8

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Abstract

Six water quality surveys were carried out in 1977 on the international section of the St. Lawrence River. Results compared with 1973-1974 data showed no apparent change in the water quality of the river.

Nutrient concentrations (nitrate and phosphorus) increased progressively downstream, especially downstream from Brockville. High inputs of metals from United States tributaries were found in areas of the St.Lawrence below Massena. High levels of PCBs were detected in the Grass River.

Résumé

Six relevés de qualité des eaux ont été effectués dans la partie internationale du fleuve Saint-Laurent en 1977. Une comparaison des résultats avec ceux de 1973-74 n'a pas mis en évidence de changement de qualité des eaux.

Les concentrations de substances nutritives (nitrate et phosphore) augmentaient progressivement vers l'aval, surtout en aval de Brockville. Les tributaires des États-Unis fournissaient les plus forts apports de métaux aux eaux du Saint-Laurent, en aval de Massena. Les teneurs en BPC étaient élevées dans la rivière Grass.

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INTRODUCTION

The St. Lawrence River is one of the most important rivers in North America. Since the opening of the St. Lawrence Seaway in 1959, it has not only become a vital transportation link to the North American interior but also is a major factor contributing to the economic development of both Canada and the United States. The St. Lawrence is used for municipal and industrial supplies, recreation, navigation, commercial fisheries and wildlife as well as for domestic and industrial waste disposal.

The international section of the St. Lawrence River extends from Lake Ontario to Cornwall, a distance of 180 km (112 mi). The rapid deterioration in the water quality of Lake Ontario, which supplies over 95% of the river's water, led to the establishment of the International Lake Ontario-St. Lawrence River Water Pollution Board by the International Joint Commission (IJC) in 1964. The Board concluded that the effects of accelerated eutrophication in Lake Ontario were being carried into the St. Lawrence River (IJC, 1966, 1969). Since then various government agencies have maintained periodic water quality surveillance of the St. Lawrence River (Department of Fisheries and Forestry, 1970, 1971; IJC, 1970; Environment Canada, 1972). These surveys included those of the Water Quality Branch (WQB) of the Canadian Department of Fisheries and the Environment in 1973 and 1974 and of the Ontario Ministry of the Environment in 1968 and 1970. Findings from these surveys were published in the IJC Great Lakes Water Quality Board Fourth Annual Report (IJC, 1976). Since in most of these intermittent river surveys the data collected were scanty, data interpretation was limited. Six intensive water quality surveys were conducted in 1977 to provide a comprehensive, detailed set of water quality data for an assessment of the current water quality conditions in the St. Lawrence River and to provide a comprehensive base-line data set for future reference. This report summarizes the data and discusses some of the changes in water chemistry throughout the course of the river.

METHODS

The field programs in 1977 were intended to assess the current water quality condition in the river, evaluate any changes in the water quality condition of the river relative to earlier surveys, and establish the seasonal variation in the water quality parameters for future reference.

To ensure that data comparisons would be possible, the sampling locations remained similar to those visited in previous IJC studies. Most of these stations were located above and below major inputs to the river (Fig. 1). Additional stations were sampled around the Wolfe Island channels where previous data had suggested that the two channels could be chemically different. Sampling started in late April as soon as the river was ice free and ended in late October. Each survey was spaced about four weeks apart.

The list of parameters for the 1977 surveys was more extensive than in 1973 and 1974. This was due largely to the need for a comprehensive data base to establish a chemical base line. Most of the extra parameters relate to the biomass production of the river and to toxic contaminants.

Six surveys were conducted on the international section of the St. Lawrence River between Kingston and Cornwall, Ontario, during the periods April 27-May 2, June 13-16, July 11-14, August 15-19, September 15-19 and

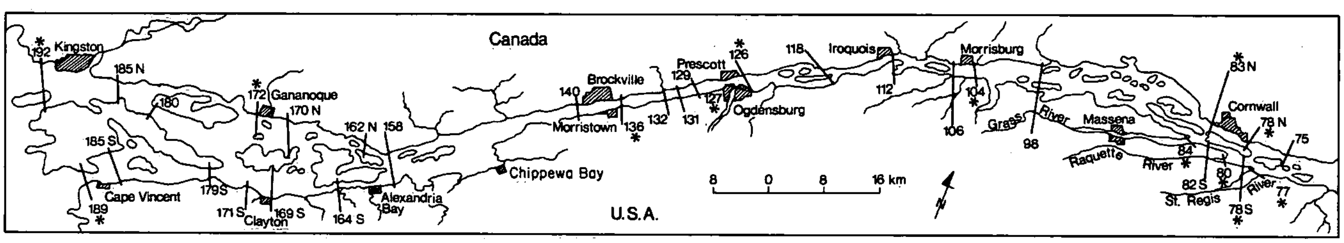


Figure 1. Sampling locations on the St. Lawrence River (*organic sampling stations).

October 24-28. In each survey, 74 water samples were collected on 33 transects (Fig. 1). Each survey took four days to complete. The river was divided into four sections, one section for each day of the survey. The sections were (1) the Wolfe Island channels, (2) the Thousand Islands, (3) Brockville to Morrisburg, and (4) Cornwall.

At each station, a 7.6-L surface water sample was collected for analysis (Table 1) in a polyethylene bottle using a manual guzzler pump mounted aboard an 18-ft motor boat. Separate water samples were collected for parameters requiring special treatment, such as phenol, pesticides, chlorophyll and bacteria. Phenol samples were collected in 100-mL glass bottles and treated with 1 mL of 50% $CuSO_4$ solution. Chlorophyll samples were treated by adding 1 mL of saturated $Mg(HCO_3)_2$ solution and stored in a cooler. Samples were taken to a mobile laboratory in Kingston for processing and analysis. Alkalinity, ammonia, silica (reactive), orthophosphate, and nitrate and nitrite were analyzed in the mobile laboratory. Aliquots of samples were split, treated wth preservatives as required and sent to the laboratory in Burlington for the remaining analyses. The methods of analysis are described in the *Analytical Methods Manual* (Environment Canada, 1974).

RESULTS AND DISCUSSION

The data summarized in the tables do not include data collected at stations located in major tributaries which have chemistry quite different from the mainstream of the St. Lawrence River. The stations are 127 on the Oswegatchie River, 84 on the Grass River, 80 on the Raquette River, and 77 on the St. Regis River. These river waters are characterized by low conductance, high turbidity and high organic and metal content. Annual mean concentrations from each transect are plotted downstream from Kingston to Cornwall to show the change in water quality with distance from the lake. Rigorous statistical analysis could not be undertaken because of the lack of detailed knowledge regarding the background variabilities and seasonal variations of each parameter. The bacteriological data have been summarized by Rao *et al.* (Canada Centre for Inland Waters, 1978) and are not discussed here.

NUTRIENTS

Phosphorus

A plot of the average phosphorus concentration in the St. Lawrence River in each survey between 1973 and 1977 shows no apparent change in concentration (Fig. 2). Apart from three observations of high concentration in July and August of 1977, the average phosphorus concentration remained about 0.020 mg/L over the four-year period.

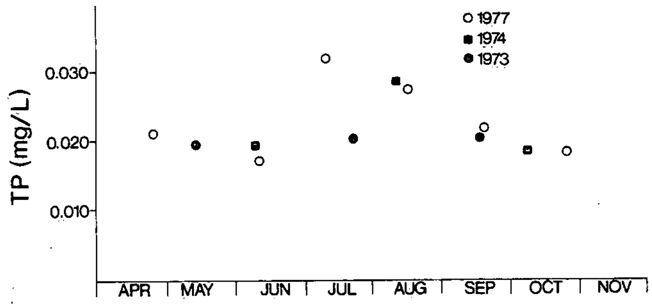


Figure 2. Seasonal variation in total phosphorus, St. Lawrence River.

Phosphorus concentrations exhibited spatial variations along the length of the river. The two most notable observations were that phosphorus concentrations in the north channel of Wolfe Island were higher than in the south channel by about 0.002 mg/L and that phosphorus concentrations downstream from Brockville to Cornwall were generally higher than upstream values (Fig. 3). This spatial distribution was observed in every survey carried out during 1977.

Average phosphorus concentrations in the south channel of Wolfe Island were in the range of 0.014 mg/L to 0.018 mg/L (discounting the July value), about the same as those in the surface waters of eastern Lake Ontario (unpublished data). Average phosphorus concentrations in the north channel ranged between 0.016 mg/L and 0.022 mg/L. The high phosphorus content of the north channel waters likely originated from Kingston and the Bay of Quinte, the primary water input to this channel of the river.

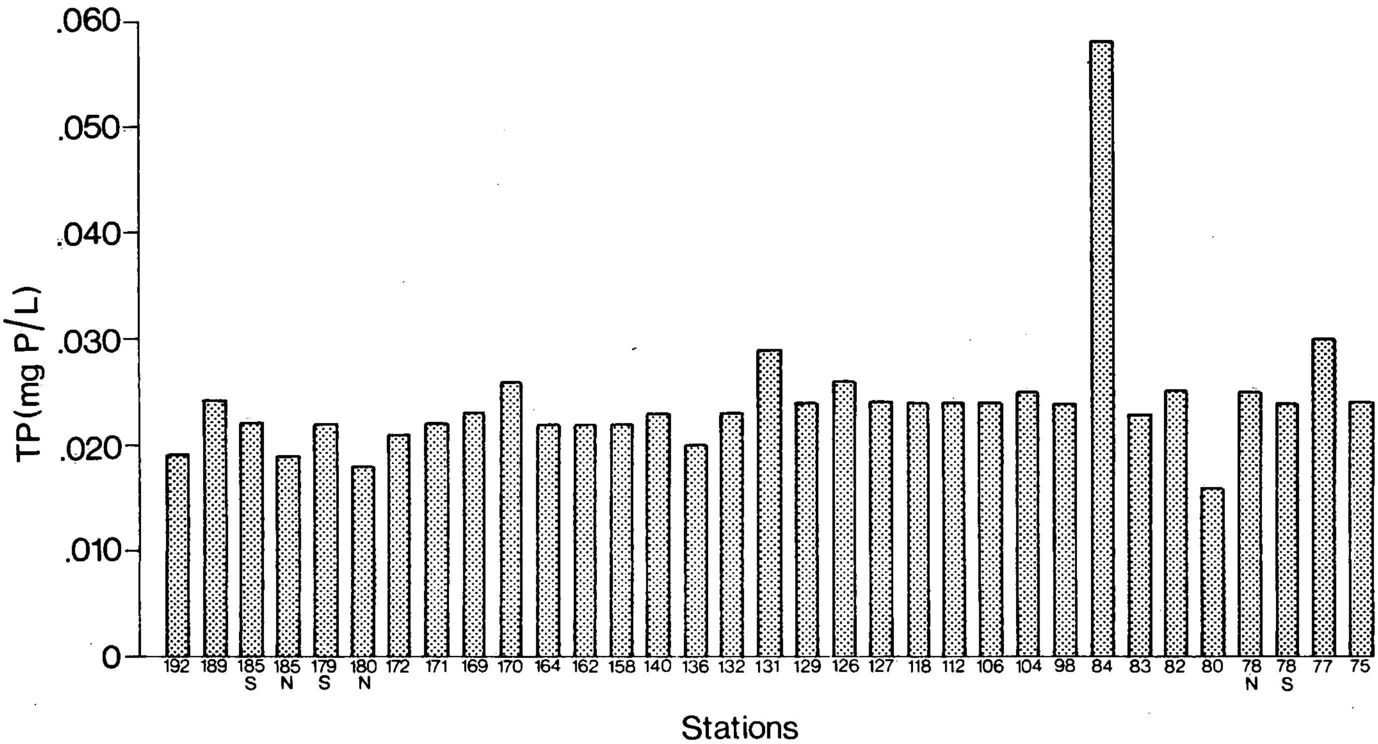
Total phosphorus concentration downstream from Maitland was higher than upstream. Downstream average phosphorus concentration was 0.025 mg/L compared with 0.019 mg/L and 0.022 mg/L measured around Wolfe Island. Most of the increase occurred near station 131 just downstream from Maitland where the maximum concentration of phosphorus for the entire river was recorded in three of the six surveys. The sewage treatment plant located upstream may account for the high phosphorus measurements. High concentrations (0.030-0.100 mg/L) of phosphorus were also recorded at the mouth of the Grass River (station 84) and the St. Regis River (station 77). Such high phosphorus readings are not uncommon from these tributaries where the flows are low and bed loads are high.

Total filtered phosphorus (phosphorus fractions which pass through 0.45-μm filter paper) and reactive orthophosphate showed the same spatial and temporal distributions as total phosphorus. Their ratio, however, varied with the seasons. Total filtered phosphorus was 43% of the

Table 1. Mean Concentrations of Nutrients (mg/L) and Physical Parameters in the St. Lawrence River, 1977

Parameter	April 27–May 2	June 13–16	July 11–14	August 15–19	September 15–19	October 24–28
Temperature*	3.14	11.33	18.44	21.08	18.14	11.02
pH†	7.86	8.40	8.29	8.37	8.25	8.31
Specific conductance‡	310.0	327.0	316.0	307.0	313.0	320.0
Total phosphorus	0.021	0.017	0.032	0.027	0.021	0.017
Total filtered phosphorus	0.009	0.008	0.017	–	0.012	0.010
Orthophosphate	0.001	0.001	0.006	0.008	0.006	0.005
Particulate organic carbon	0.553	0.426	0.455	0.408	0.488	0.372
Dissolved organic carbon	3.92	3.64	3.05	3.53	3.71	2.83
Particulate nitrogen	0.092	0.064	0.079	0.060	0.060	0.055
Ammonia	0.009	0.010	0.040	0.034	0.026	0.008
Nitrate	0.251	0.179	0.097	0.060	0.064	0.151
Total Kjeldahl nitrogen	0.262	0.228	0.393	0.315	0.316	0.305
Total nitrogen	0.513	0.408	0.490	0.375	0.380	0.456
Silica	0.343	0.275	0.445	0.496	0.476	0.358
Chlorophyll	5.97	4.25	3.83	3.91	3.76	5.19

*Temperature in °C
†pH in pH units
‡Specific conductance in microsiemens per square centimetre



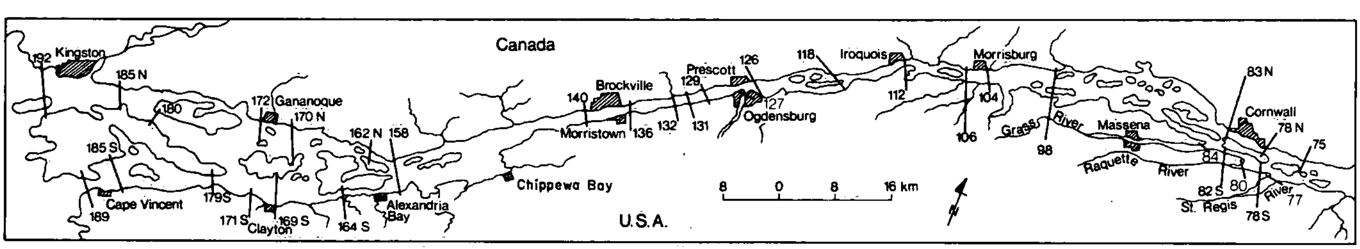


Figure 3. Variation in total phosphorus concentration, St. Lawrence River.

total phosphorus in May and increased to 55% in October. Orthophosphate was 5% to 9% in May and June and increased to 27% in October.

Nitrogen

The concentration of nitrate in water is highly variable, since this fraction of nitrogen is readily available for biological growth. Generally, at the peak of biomass production, nitrate concentration is lowest and can under certain conditions become a limiting nutrient. The seasonal cycle of nitrate in the St. Lawrence River is illustrated in Figure 4, which shows that the concentration declines from 0.250 mg/L in April to 0.060 mg/L in August, returning to 0.150 mg/L in late October. Although data from 1973 and 1974 are less numerous, they fit well into the annual cyclic pattern. There is no evidence that nitrate concentration has changed over the years from 1974 to 1977.

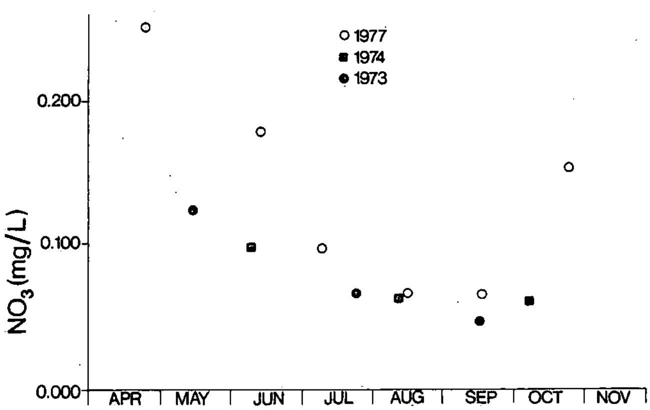


Figure 4. Seasonal variation in nitrate, St. Lawrence River.

Total Kjeldahl nitrogen, a measure of organic nitrogen, shows much less fluctuation than nitrate. Except for a peak July concentration of 0.390 mg/L, Kjeldahl nitrogen concentrations remain around 0.220 mg/L in spring and at 0.300 mg/L through August to November (Fig. 5).

Ammonia, a product in the decomposition of most nitrogenous compounds, is another parameter which exhibits a very strong seasonal variation (Table 1). Average ammonia concentrations in spring and fall were about 0.010 mg/L, but average summer concentrations were between 0.026 and 0.040 mg/L. The high ammonia concentrations in summer are probably a result of the faster rate of bacterial decomposition of nitrogenous waste at this time.

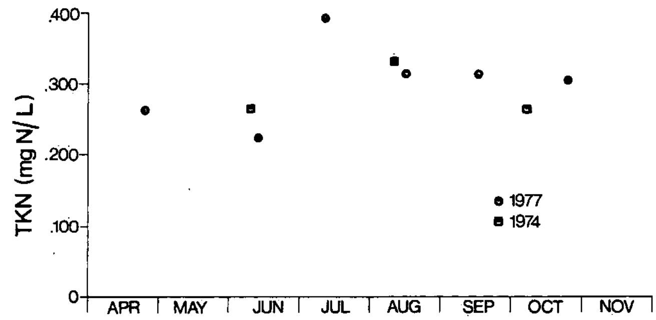


Figure 5. Seasonal variation in total Kjeldahl nitrogen, St. Lawrence River.

All three fractions of nitrogen showed identical spatial distribution (Figs. 6, 7, 8) similar to those observed in phosphorus. At Wolfe Island, the north channel nitrogen concentration was higher than that of the south channel, and the biggest increase in nitrogen occurred downstream in the vicinity of Maitland at stations 129, 131 and 132. Mean nitrate concentrations for these stations were about 0.200 mg/L, with a maximum reading of 0.500 mg/L compared with the overall river average of 0.133 mg/L. Highest ammonia was 0.300 mg/L compared with the overall river average of 0.021 mg/L. The maximum Kjeldahl nitrogen at these locations was 0.068 mg/L with an average Kjeldahl nitrogen level of 0.370 mg/L, about 0.070 mg/L higher than the average of the entire river. Data collected in 1974 and 1973 also identified high nitrogen concentration at these locations. It appeared that the area downstream from Maitland was a source of nitrogen.

Biomass

The problem of algal growth in the international section of the St. Lawrence River has been cited in several reports to the IJC (Department of Fisheries and Forestry, 1970; Canada Centre for Inland Waters, 1978). There is no simple technique or procedure available for quantifying algal growth. Chemical parameters such as chlorophyll *a*, particulate and dissolved organic carbon and particulate nitrogen can give an indication of biomass production in the water, although there are no well-defined relationships between biological productivity and any one of these parameters.

Particulate organic carbon, dissolved organic carbon, particulate nitrogen and chlorophyll *a* all showed similar downstream distributions. Concentrations of these parameters gradually declined from Wolfe Island to Brockville, and then increased gradually from Brockville to Cornwall (Figs. 9, 10, 11). Their spatial distributions did not correspond to the spatial distribution of nutrients, indicating that biomass production does not necessarily increase with higher nutrient concentrations. It appeared that there was a reduction in productivity as the water flowed from Lake Ontario into the river. This partial reduction in productivity could be attributed to the changes in physical morphology from a large lake to a river when the river is flowing north and the flow is swifter. As the water reached Brockville, a new equilibrium may have been re-established, and with nutrient enrichment, biomass production was on the rise again.

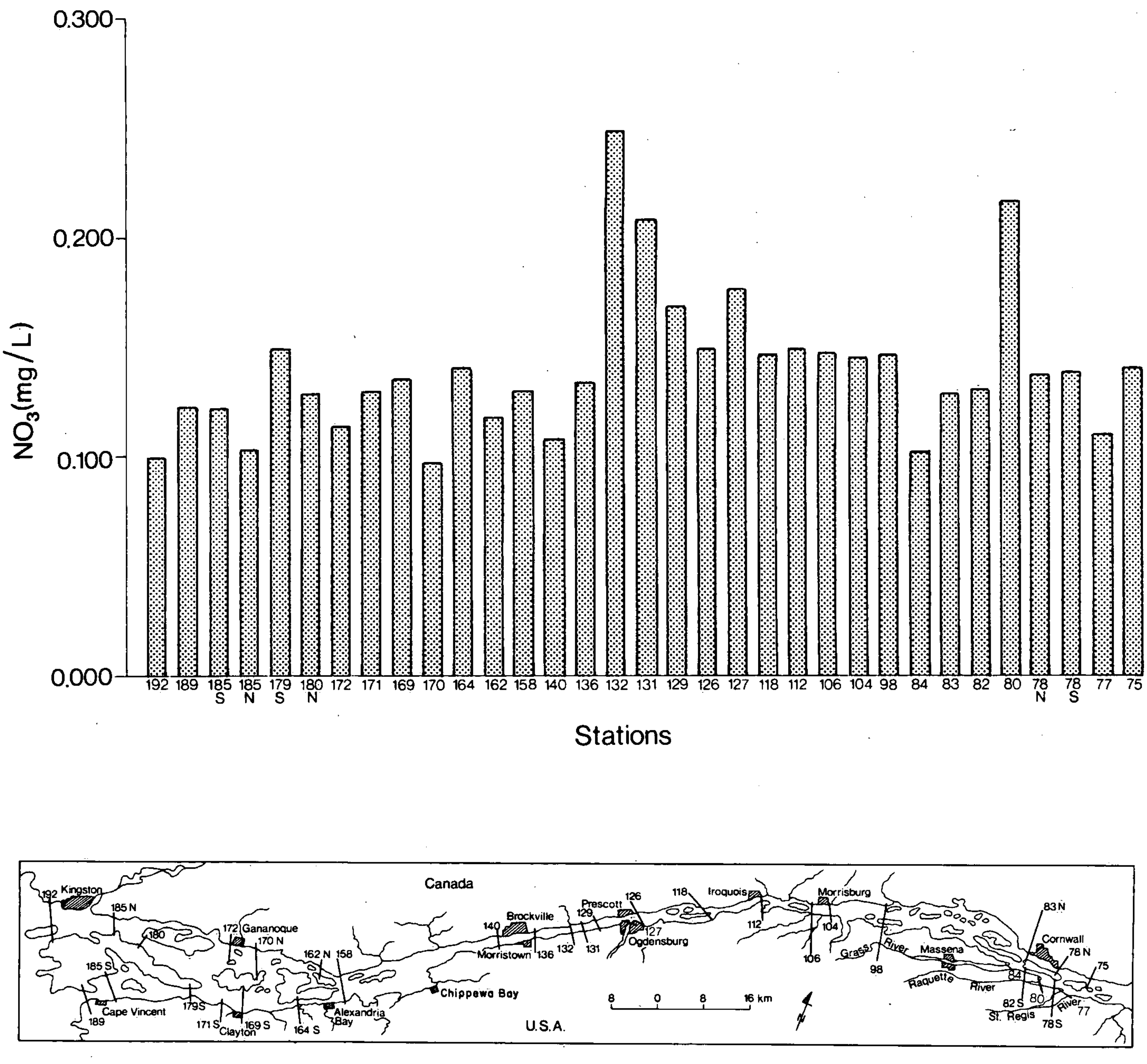


Figure 6. Variation in nitrate concentration, St. Lawrence River.

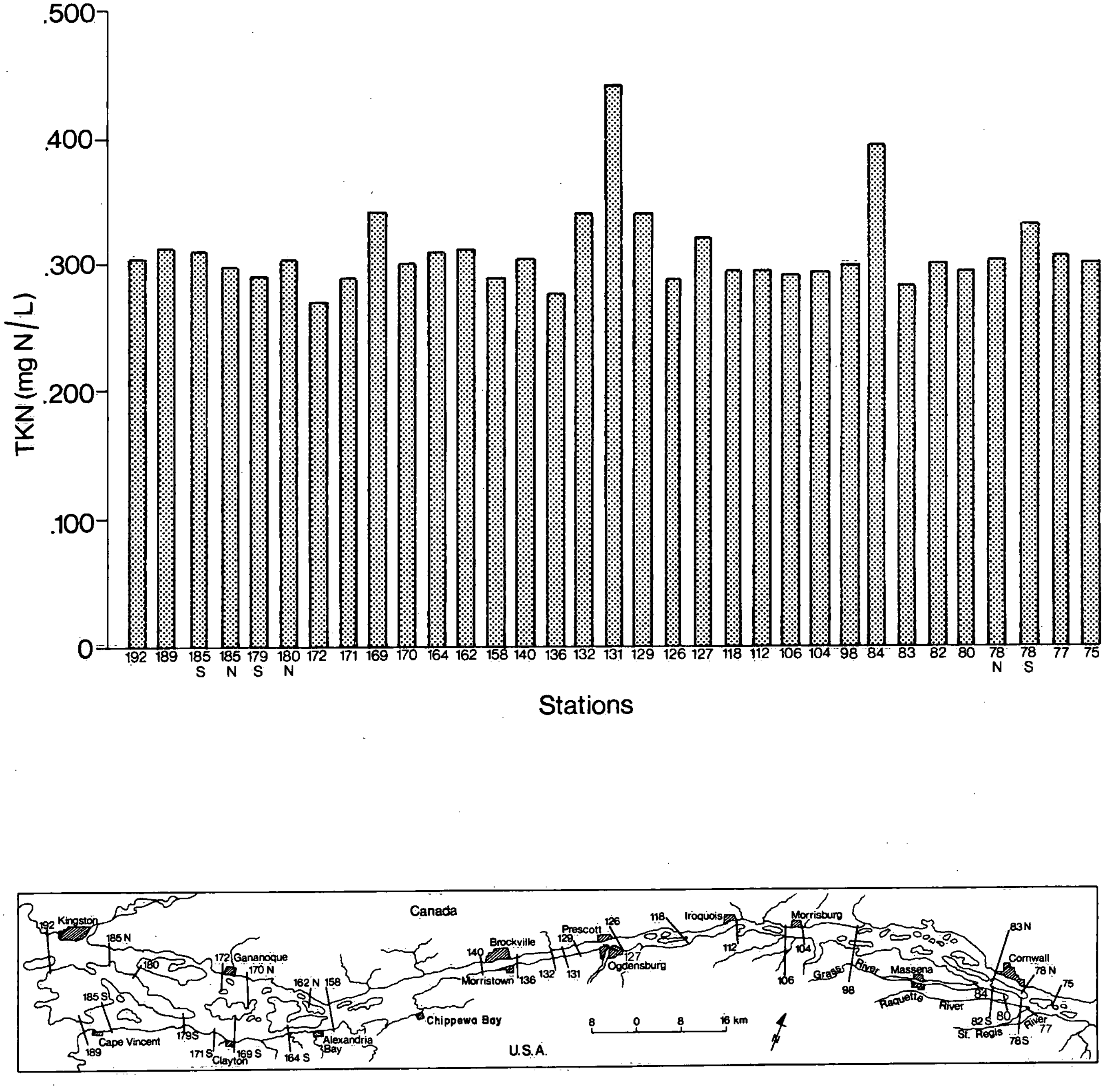
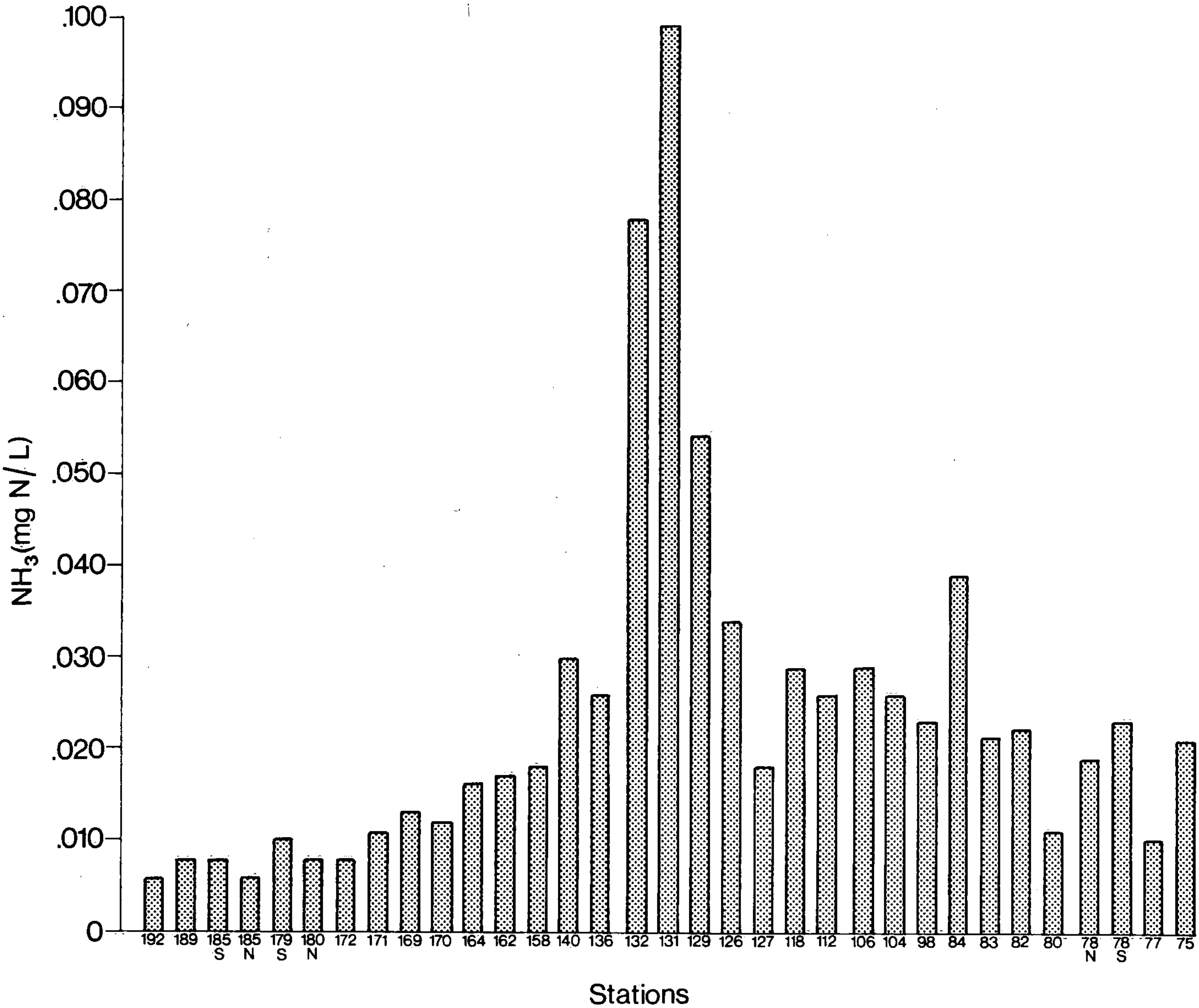


Figure 7. Variation in Kjeldahl nitrogen concentration, St. Lawrence River.



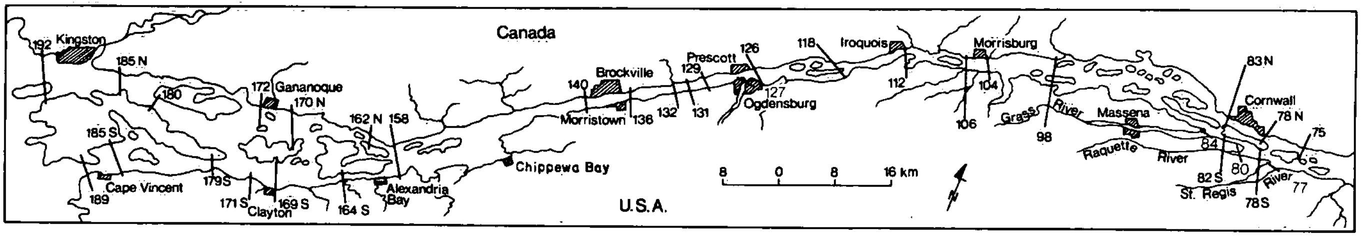
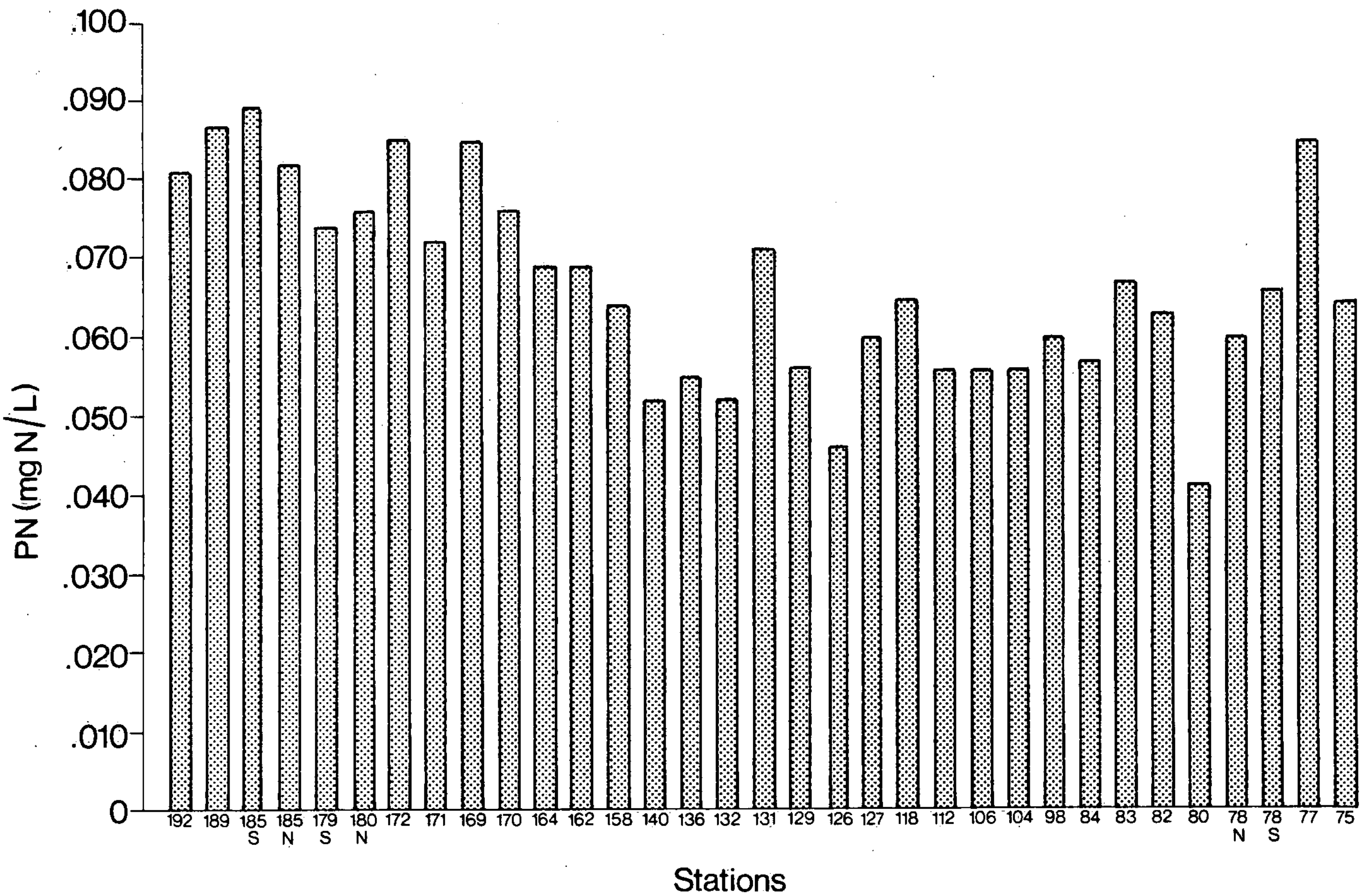


Figure 8. Variation in ammonia concentration, St. Lawrence River.



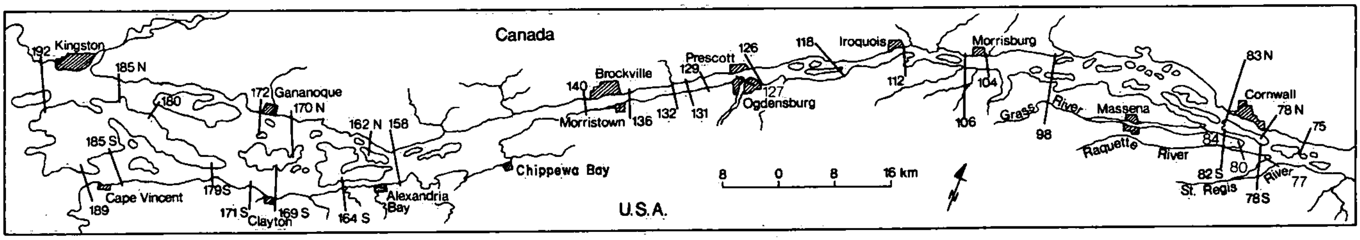
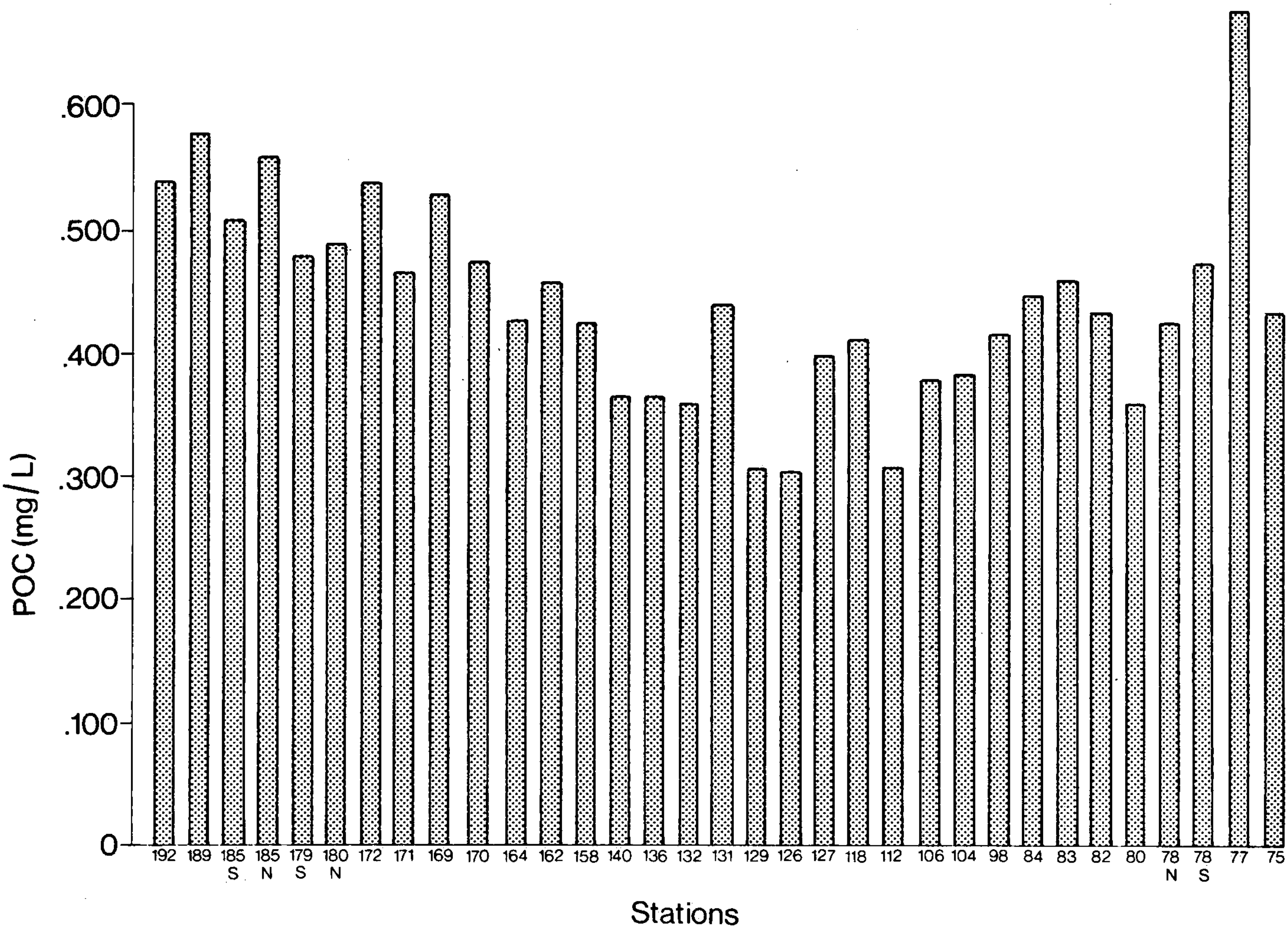


Figure 9. Variation in particulate nitrogen concentration, St. Lawrence River.



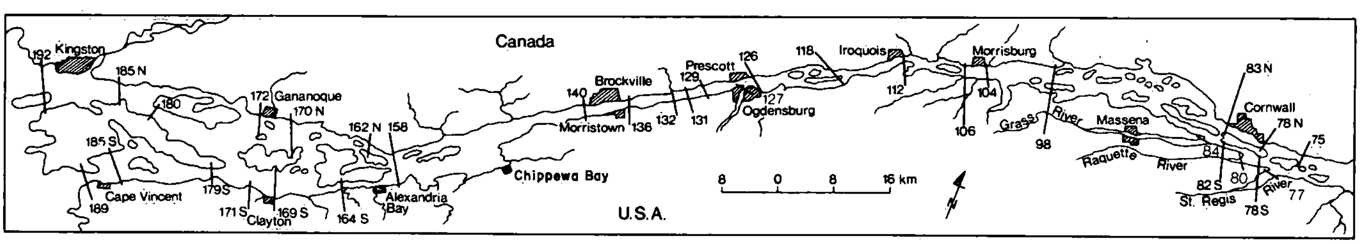


Figure 10. Variation in particulate organic carbon concentration, St. Lawrence River.

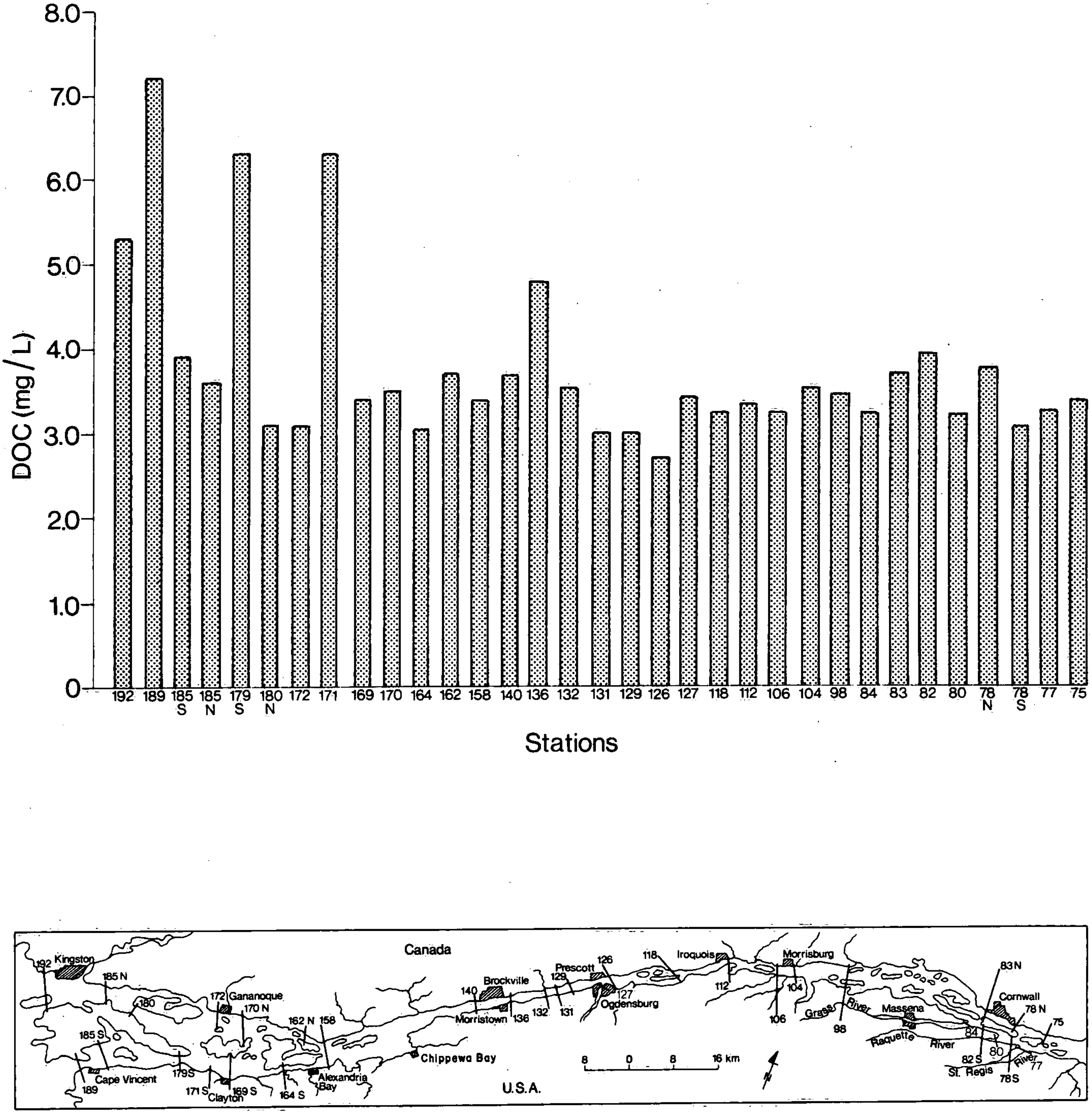


Figure 11. Variation in dissolved organic carbon concentration, St. Lawrence River.

Dissolved Solids

The pH of the St. Lawrence River centred on 8.3, based on 1973–1977 data (Fig. 12). An abnormally low pH of 7.86 was recorded in April of 1977. Average pH measurements in rain and snow samples collected in Kingston from 1974 and 1977 ranged from 4.5 to 5.3. The thawing of the accumulated "acidic" snow cover during winter in April could account for the low pH in April. The river also showed a downstream decrease in pH (Fig. 13), accompanied by a corresponding downstream decrease in alkalinity.

There was no apparent change in specific conductance of the St. Lawrence River (Fig. 14). Averaged specific conductance in 1977 was 314 $\mu S/cm^2$. Specific

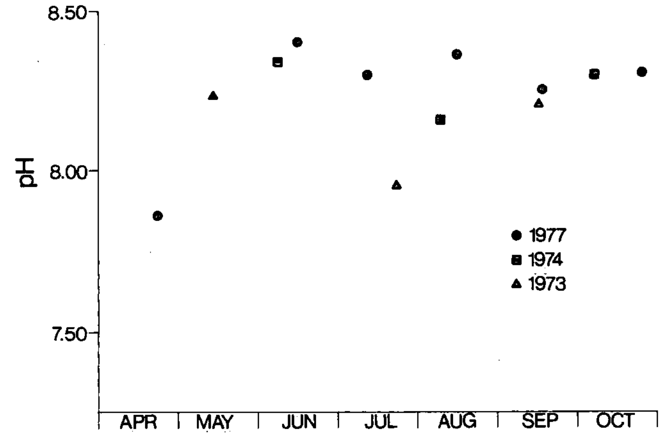


Figure 12. Seasonal variation in pH, St. Lawrence River.

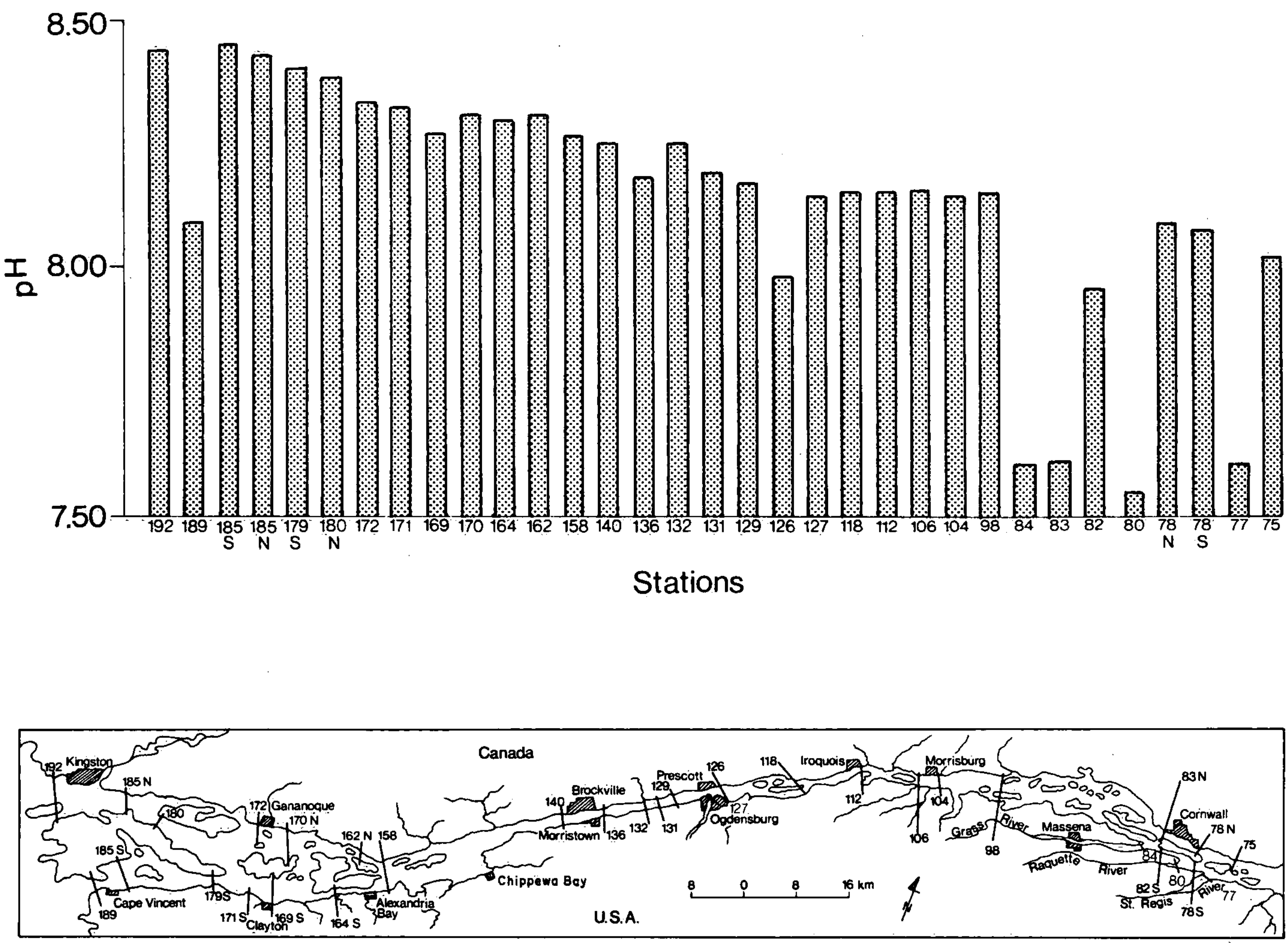


Figure 13. Variation in pH, St. Lawrence River.

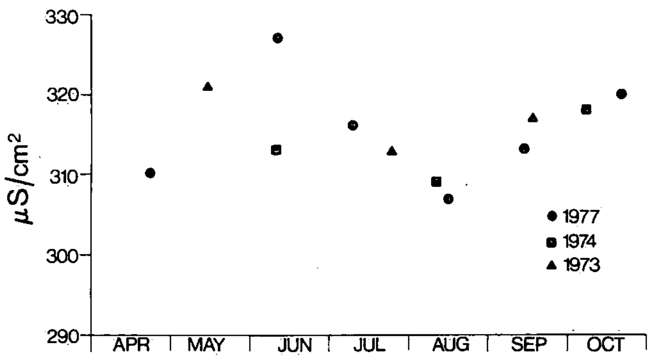


Figure 14. Seasonal variation in specific conductance, St. Lawrence River.

conductance was generally lower in July and August at a time when the flow of the St. Lawrence River was highest. There was no noticeable downstream pattern in specific conductance, although some river stations located immediately downstream from tributaries registered lower readings on account of dilution.

Concentrations of major ions and heavy metals are shown in Tables 2 and 3. These major ion concentrations

Table 2. Mean Concentrations of Major Ions (mg/L) in the St. Lawrence River, 1977

Major ions	April 27–May 2	July 11–14	September 15–19
Alkalinity	87.17	89.27	84.95
Potassium	1.40	1.40	1.40
Sodium	11.95	12.91	12.96
Calcium	37.32	37.95	36.44
Magnesium	7.37	7.82	7.89
Chloride	25.77	28.15	26.75
Sulphate	25.00	25.39	26.24

Table 3. Mean Concentrations of Metals (µg/L) in the St. Lawrence River, 1977

Metals	April 27–May 2	July 11–14	September 15–19
Aluminum	35.15	32.73	48.77
Cadmium	N.D.	N.D.	N.D.
Chromium	1.21	1.68	–
Iron	103.70	68.27	61.98
Lead	0.50	1.01	0.62
Manganese	5.62	10.57	5.97
Nickel	1.37	1.94	2.09
Zinc	2.55	4.38	3.52
Mercury	0.001	0.004	–
Selenium	0.01	0.06	0.09
Arsenic	0.55	0.56	0.73

N.D. – Not detected.

were comparable with those found in previous years with no detectable changes, indicating that they have remained relatively unchanged over five years. Chloride concentration increased slightly from Kingston to Cornwall. Calcium, which is closely related to alkalinity, tended to decrease going downstream. There were no visible spatial differences in the other ions.

Metals

The metal data presented here were anlayzed on unfiltered water samples using the acid digestion method (solvent extraction for aluminum). Since past metal analyses were performed on filtered water samples using solvent extraction, there were little historic data for comparison.

Most of the metals detected in the St. Lawrence River were in trace quantities (Table 3). There were, however, spatial differences in the levels of aluminum, iron and zinc. One common feature was the high concentration of metals found downstream from Cornwall by the Grass, Raquette and St. Regis rivers. The average aluminum concentration found downstream from the Grass River station 84 was 0.090 mg/L, about three times higher than the background upstream concentration (Fig. 15). The maximum aluminum concentration detected was 0.200 mg/L at the mouth of the Grass River. Spatial distribution of iron was almost identical with that of aluminum. Average iron concentration downstream from the Grass River was about 0.160 mg/L, while the upstream concentration was about 0.060 mg/L (Fig. 16). Concentrations of 0.400 mg/L to 0.440 mg/L of iron were also recorded just downstream from the Grass and Raquette rivers, respectively. A similar spatial pattern was also observed for zinc (Fig. 17). The high metal concentrations found at the mouth of these tributaries suggest that these rivers were sources of metal contamination.

Organics

Water samples were collected at 12 selected locations in June and August for analysis of persistent organic contaminants, polychlorinated biphenyls (PCBs), mirex, organochlorine pesticide residues and some chlorinated hydrocarbons. Of those tested, only lindane, hexachlorocyclohexane and PCBs were detected. Lindane (γ-BHC) and hexachlorocyclohexane (α-BHC) were detected over the stretch of the river. Lindane concentrations ranged from 0.003 to 0.007 µg/L and the levels of α-BHC were in the range from 0.003 to 0.008 µg/L. Polychlorinated biphenyls were detected only at the mouth of the Grass River (station 84) at concentrations of 0.18 µg/L and 0.06 µg/L. Levels of

PCBs in water, if present, were normally near or below the detection limits of the analytical method. The presence of PCBs in quantifiable quantities confirms a source of PCB contamination.

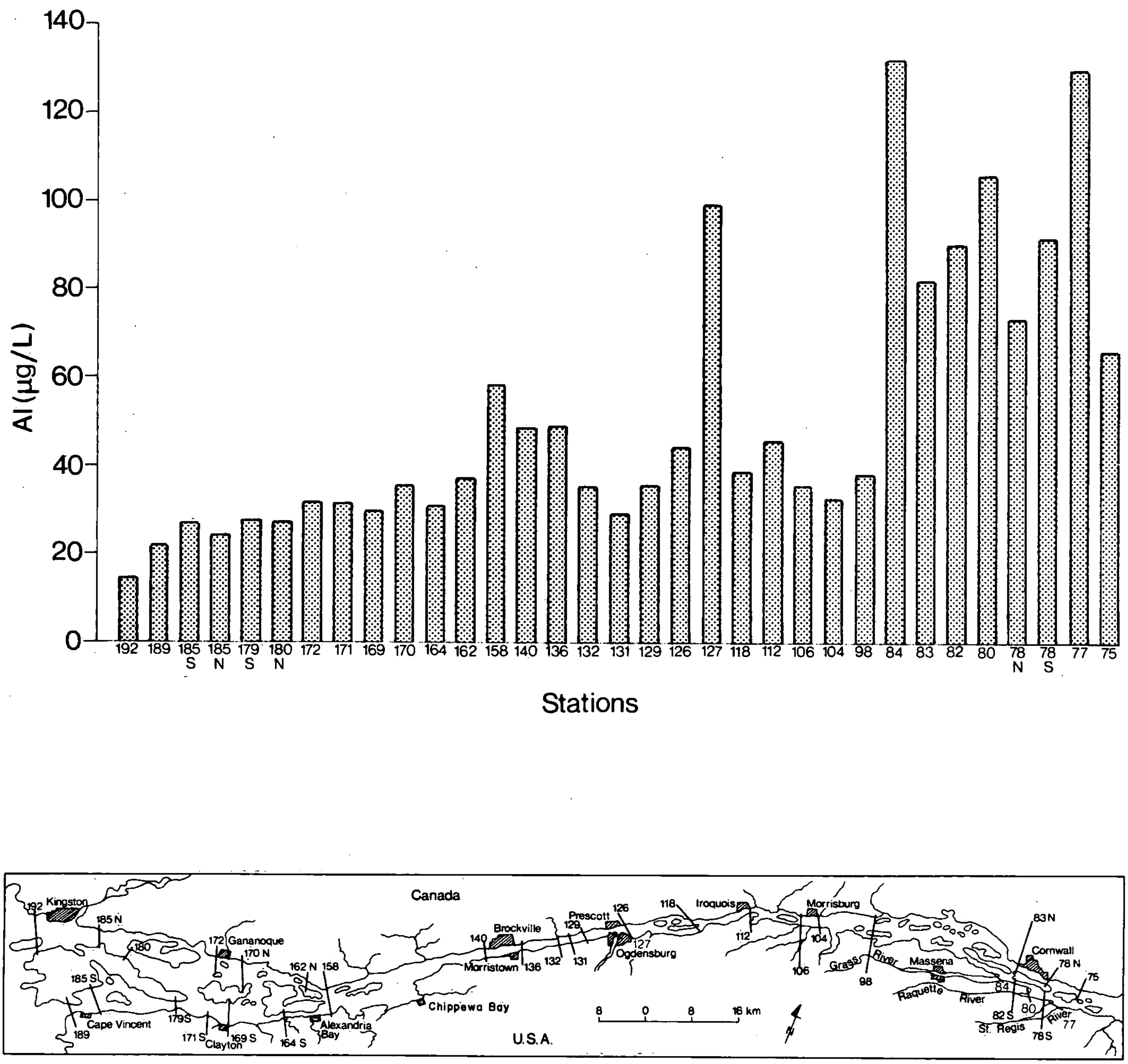


Figure 15. Variation in aluminum (extractable), St. Lawrence River.

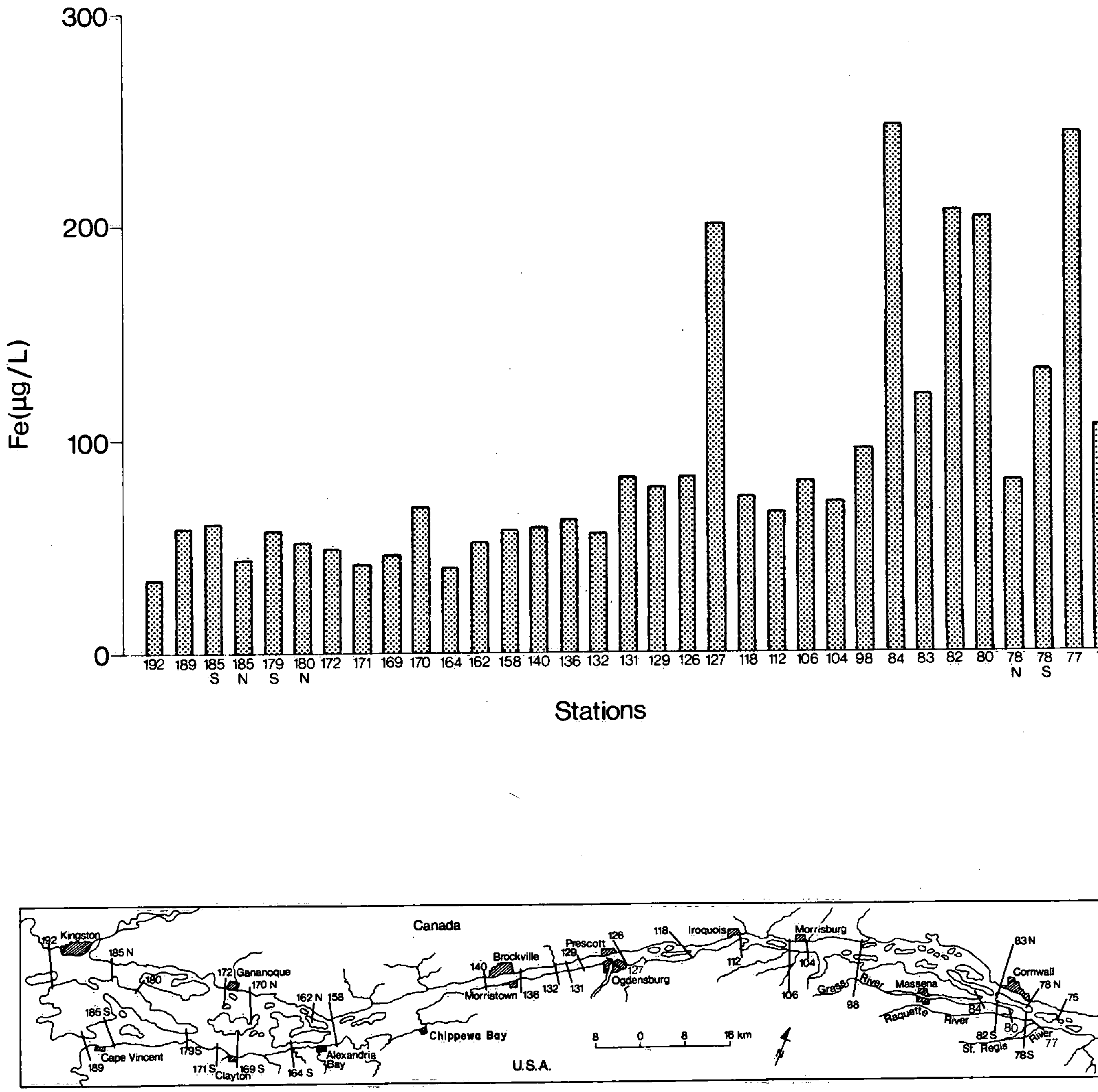


Figure 16. Variation in iron concentration, St. Lawrence River.

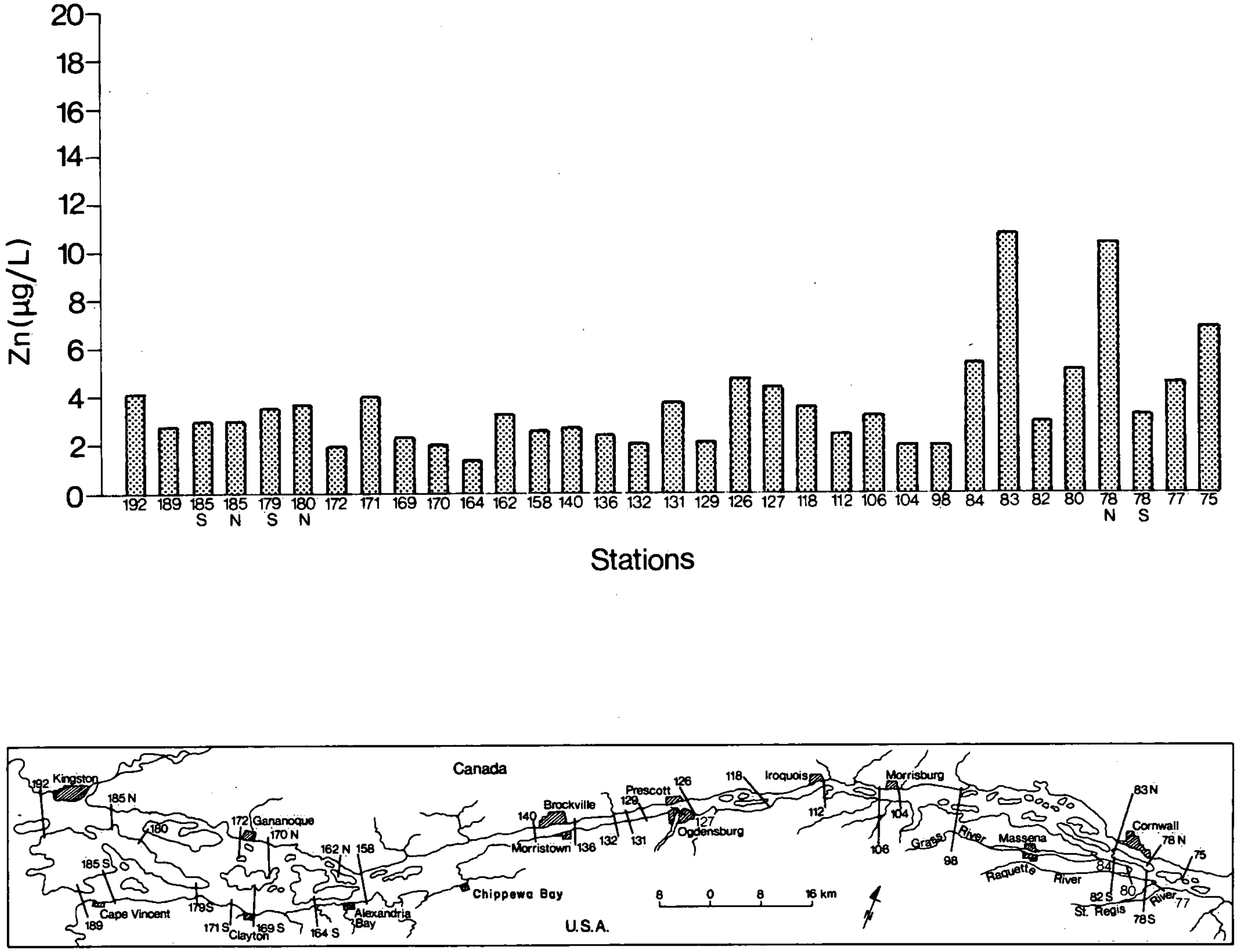


Figure 17. Variation in zinc concentration, St. Lawrence River.

SUMMARY AND CONCLUSION

There is no apparent change in nutrient concentrations (phosphorus and nitrogen) in the international section of the St. Lawrence River during the period 1974 to 1977.

In general, proceeding downstream there was a progressive increase in nutrient concentration, and the north channel of Wolfe Island was slightly more enriched than the south channel. Average phosphorus concentration for the entire river was 0.022 mg/L. Average phosphorus concentration downstream from Brockville was 0.025 mg/L compared with the upstream value of 0.020 mg/L. Seasonal nitrate concentrations varied between 0.060 mg/L and 0.250 mg/L. Large increases in nitrogen concentrations occurred in the vicinity of Maitland. These spatial differences are consistent with those observed in 1973 and 1974.

Biomass production seemed to be lower at the river source than in Lake Ontario. Downstream from Brockville, however, biomass production increased.

Total dissolved solids, as indicated by specific conductance and major ion measurements, were comparable with those found in previous years with no detectable change.

High inputs of metals and PCBs were found in areas downstream from Cornwall along the United States shore. Metal concentrations found near the tributaries of the Grass River, Raquette River and St. Regis River were three to four folds higher than upstream concentrations. The Grass River was the only location where quantifiable PCBs were found.

ACKNOWLEDGMENTS

The author wishes to thank Messrs. K.W. Kuntz, A.H. Clignett and R.C. McCrea for their assistance in collecting the water samples, and the staff of the Technical Operations Section at the National Water Research Institute in Burlington for providing the field support.

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