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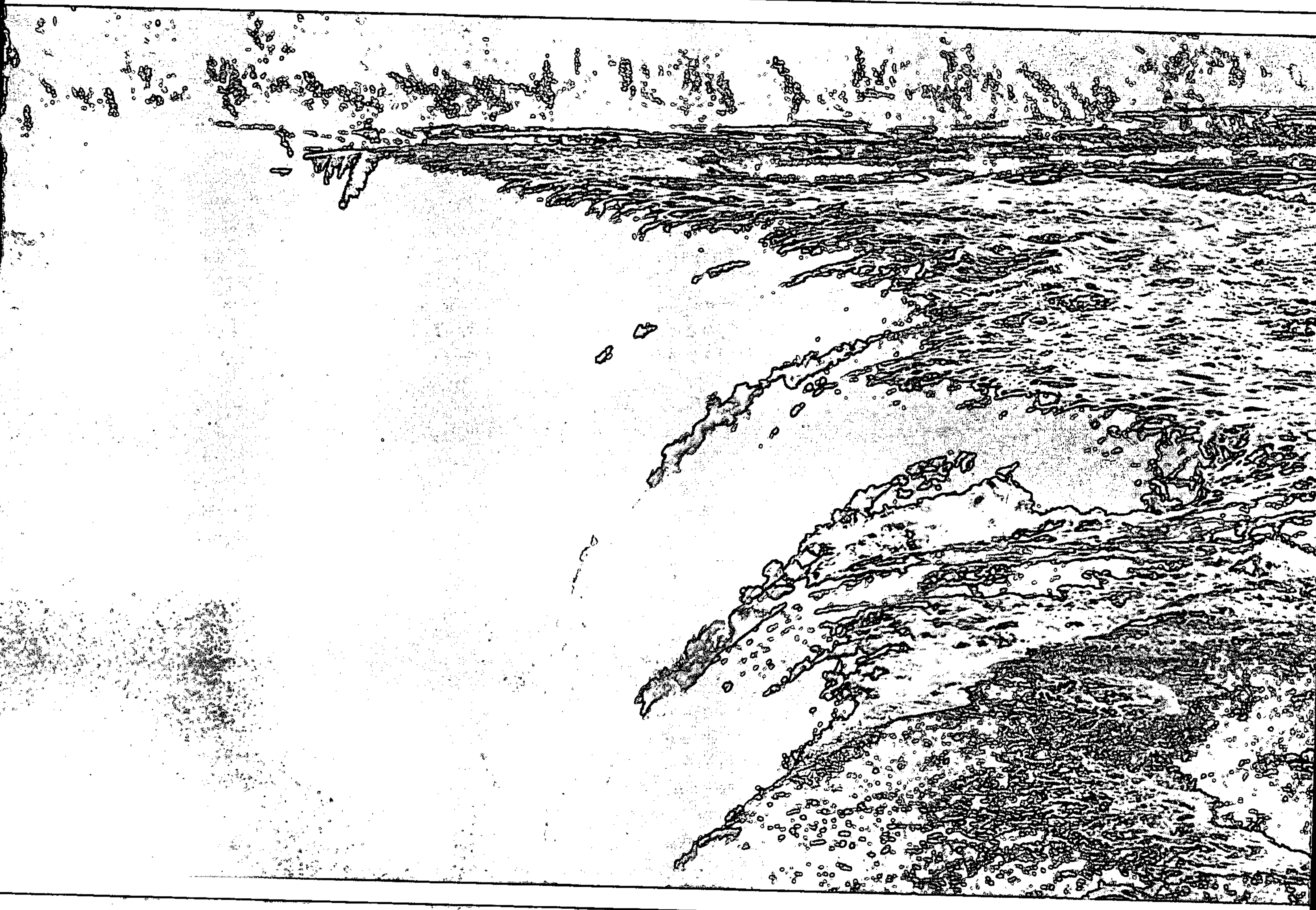
# Recent Trends in Water Quality of the Niagara River

K.W. Kuntz



## TECHNICAL BULLETIN NO. 146

*INLAND WATERS DIRECTORATE*
*ONTARIO REGION*
*WATER QUALITY BRANCH*
*BURLINGTON, ONTARIO, 1988*

*(Disponible en français sur demande)*

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# Abstract

Results from Niagara River water samples collected at Niagara-on-the-Lake over the period 1976 to 1983 are discussed. Annual mean concentrations and estimated annual mean loadings for selected physical parameters, nutrients, major ions, and trace metals are presented. Monthly mean values have also been included to indicate seasonal changes. Annual loadings are compared to historic loading estimates. The observed long-term trend for selected parameters and compliance with the 1978 Great Lakes Water Quality Agreement specific objectives are discussed.

# Résumé

Les résultats de l'analyse des échantillons d'eau prélevés dans la rivière Niagara à Niagara-on-the-Lake au cours de la période de 1976 à 1983 sont examinés. Les moyennes annuelles de la concentration et de l'apport estimatif sont présentées pour divers paramètres physiques, substances nutritives, ions importants et métaux à l'état de traces. Les moyennes mensuelles sont également données pour faire voir les variations saisonnières. Les apports annuels calculés sont comparés aux estimations historiques. La tendance à long terme observée pour les paramètres choisis est analysée, ainsi que le respect des objectifs établis dans l'Accord relatif à la qualité de l'eau dans les Grands Lacs de 1978.

# Recent Trends in Water Quality of the Niagara River

### K.W. Kuntz

## INTRODUCTION

The chemical characteristics of the Great Lakes have changed primarily because of the rapid increase in material loadings to their basins, due mainly to increased populations within their boundaries since 1900 (Beeton, 1965). Accurate estimates of the changes in the amount of material being loaded into the Great Lakes are required for trend evaluation, model development, future planning, and successful management of Great Lakes water resources.

The Niagara River is the major tributary to Lake Ontario, accounting for more than 85% of the total input water budget and about 50% of the nitrogen and phosphorus input to the lake from all sources (Casey and Salbach, 1974). It is the only outflow for Lake Erie and accounts for 50% of all incoming fine-grained sediment material (silt- and clay-sized fractions) to Lake Ontario (Kemp and Harper, 1976).

Because of the importance of Niagara River loadings to the water quality of Lake Ontario, the Water Quality Branch of the Inland Waters Directorate, Ontario Region (WQB-OR), established a daily monitoring station at the mouth of the Niagara River at Niagara-on-the-Lake in 1975. One of the primary objectives of this program was to provide annual estimates of chemical loading and trends in water quality in the Niagara River. This report will provide information on changes in concentrations and loadings in the Niagara River for the period from 1976 to 1983.

## SAMPLING METHODS

### Location and Sampling Apparatus

Samples were collected at the water treatment plant of the Regional Municipality of Niagara in Niagara-on-the-Lake about 1.6 km upstream from Lake Ontario on the Ontario side of the Niagara River. This location was chosen because water quality surveys conducted in this area during 1974 indicated that the river is chemically homogeneous at this location, exhibits no cross-sectional variation in water chemistry (Chan, 1977), and is therefore representative of the water flowing into Lake Ontario.

Daily water samples were collected by means of an intake line, submersible pump, and daily water sampler. The intake line, composed of a 1.9-cm I.D., black polyethylene tube, was placed in the river, anchored to shore with a 0.6-cm steel cable, and weighted so as to settle onto the bottom of the river. The polyethylene tube was connected to an anchored spar buoy, which allowed the sample intake to float freely up from the river bottom. The intake line extended to a point approximately 60 m from shore and was located in the main current of the Niagara River. This intake line extended up the spar buoy to about 6 m from the river bottom and 13 m below the river surface. The end of the intake line was then extended about 2 m from the spar buoy with a piece of polyethylene tube, plugged at the end. A series of 0.3-cm holes were drilled from the end towards the spar buoy for about 1 m. The small holes act like a coarse filter, preventing fish and weeds from entering the intake pipe. Complete details of this system can be found in Kuntz *et al*. (1982).

### Chemical Analysis

Chemical analyses were completed on these water samples as described in the *Analytical Methods Manual* (Environment Canada, 1979). Daily measurements were made for physical parameters (turbidity, discharge, and specific conductance at 25°C) and nutrients (total phosphorus, total Kjeldahl nitrogen, nitrate + nitrite nitrogen, and soluble reactive silica). Weekly analyses were completed for major ions (total alkalinity, calcium, sulphate, chloride, sodium, magnesium, and potassium) and total trace metals (iron, aluminum, manganese, copper, zinc, nickel, chromium, cadmium, lead, arsenic, and mercury).

## DISCUSSION

### Physical Parameters

Monthly mean discharge during the eight-year period from 1976 to 1983 varied from a low of 5950 $m^3\ s^{-1}$ during February to a high of 6721 $m^3\ s^{-1}$ during May (Fig. 1), a variation of about 13%. Peak flow occurred during April, May, and June as a result of spring runoff conditions. The winter minimum occurred during January and February as a result of winter freeze-up. Annual average discharges (Table 1) varied from a high of 6714 $m^3$ $s^{-1}$ in 1976 to a low of 6102 $m^3$ $s^{-1}$ in 1977, a variation of about 10%.

Monthly mean specific conductance at 25°C ranged from a low of 295 $\mu$S $cm^{-1}$ in April, during the peak flow period, to a high of 314 $\mu$S $cm^{-1}$ in February, during the low flow period. Elevated chloride and sodium concentrations during this low flow period, the result of winter road salting activities, may have caused part of this increase in specific conductance. Since these data have been collected, specific conductance at 25°C has dropped from a mean of 310 $\mu$S $cm^{-1}$ in 1977 to about 298 $\mu$S $cm^{-1}$ in 1983 (Table 1). The long-term rate of change, as calculated from the 12-month moving average plot (Fig. 2), is about

**Table 1. Physical Parameters**

| Year | Discharge ($m^3 s^{-1}$) | Specific conductance at 25°C ($\mu$S $cm^{-1}$) | Turbidity (JTU) |
|---|---|---|---|
| 1976 | 6714 | 306 | – |
| 1977 | 6102 | 310 | – |
| 1978 | 6190 | 308 | – |
| 1979 | 6303 | 310 | – |
| 1980 | 6574 | 300 | – |
| 1981 | 6265 | 300 | 2.9 |
| 1982 | 6296 | 297 | 4.7 |
| 1983 | 6473 | 298 | 4.5 |

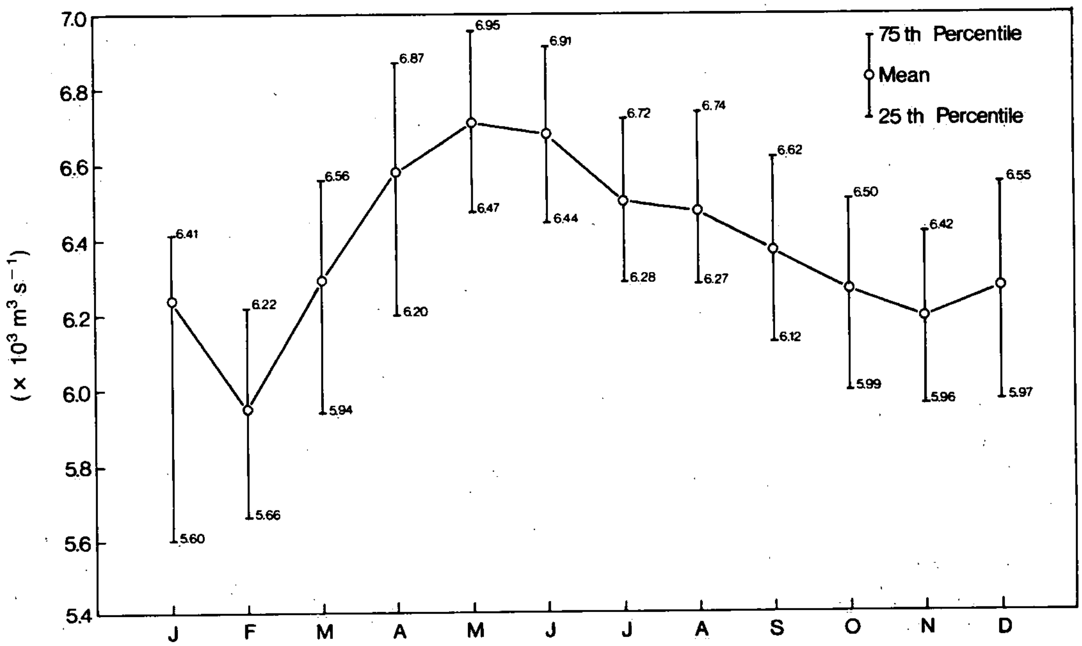

Figure 1. Monthly discharge from 1976 to 1983.

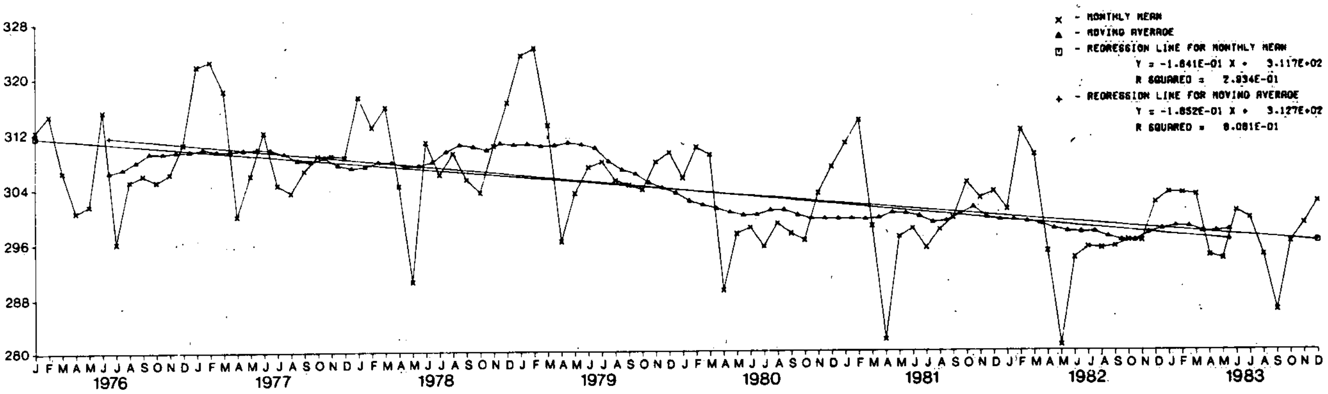

Figure 2. Monthly mean and 12-month moving average plot of specific conductance (25°C).

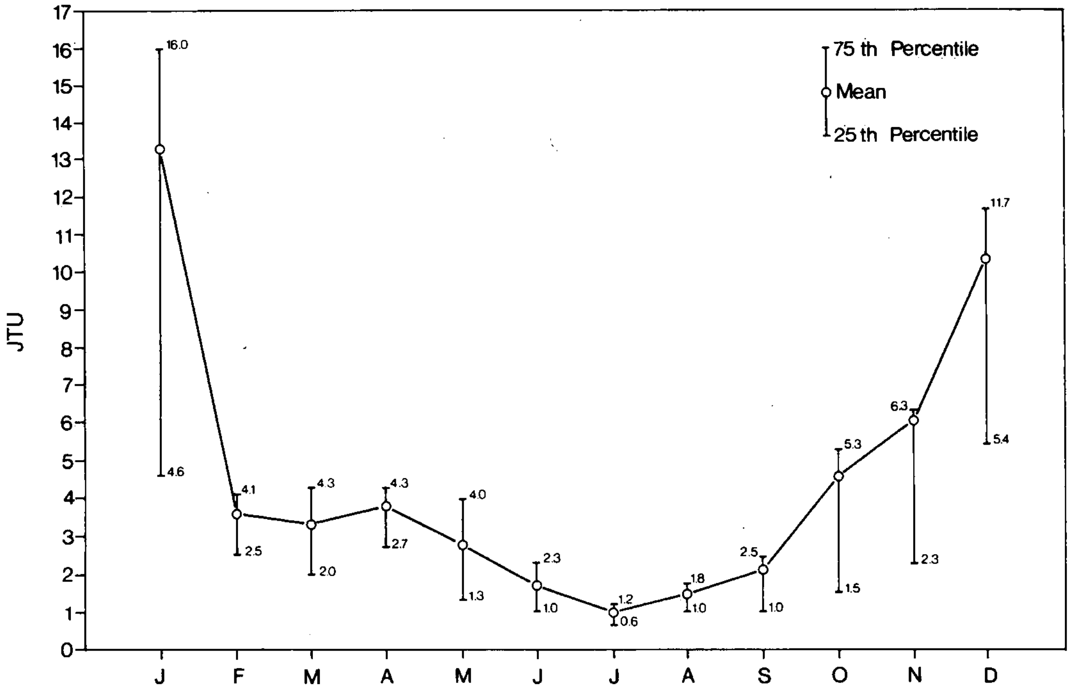

Figure 3. Monthly turbidity from 1981 to 1983.

2.2 μS $cm^{-1}$. The r value for the moving average line is -.90, indicating a good fit, and is significant at the 1% level. The F value for the analysis of variance is 345, indicating a significant decrease at the 99% confidence level. Most of this decrease in specific conductance can be explained by the decrease in sodium and chloride concentrations observed during this period.

Turbidity data, collected only from 1981 to 1983, showed a distinct seasonal increase in November, December, and January (Fig. 3). Monthly mean values for these three months were in the 6.1- to 13.2-JTU range, while values in the 1.0- to 1.7-JTU range were measured in June, July, and August. The winter increase in turbidity is believed to be related to increased erosion and resuspension of sediments in Lake Erie due to increased wind velocity in fall and winter.

## Nutrients

### *Total Phosphorus*

Monthly mean concentrations of total phosphorus during the eight-year period from 1976 to 1983 varied from a low of 0.016 mg $L^{-1}$ during July to a high of 0.032 mg $L^{-1}$ during December (Fig. 4). Winter values were higher because of increased levels of suspended sediments in the water as evidenced by the higher turbidity values also recorded at this time. This would also be expected as a result of the biological cycle in the eastern basin of Lake Erie, where high epilimnion values of phosphorus are observed during the well-mixed winter period and depleted epilimnion values are observed during the summer after algal uptake and its subsequent sedimentation (Rathke and Edwards, 1984).

Concentrations of total phosphorus in Lake Ontario have decreased substantially since the data reported for 1972 (Casey and Salbach, 1974). This decrease in total phosphorus in the Niagara River is shown well by the 12-month moving average plot in Figure 5. These data show a decrease from about 0.026 mg $L^{-1}$ to about 0.016 mg $L^{-1}$, for a yearly decrease of 0.001 mg $L^{-1}$ $a^{-1}$ during the eight-year period from 1976 to 1983. However, this decrease was not significant at the 95% confidence level (El-Shaarawi *et al.*, 1983) for 1975-80. A similar decrease of 0.0011 mg $L^{-1}$ $a^{-1}$ in total phosphorus concentrations in Lake Ontario has been reported by Neilson (1983) for spring surface water data. The r value for the moving average line for 1976-83 is -.71, indicating a good fit, significant at the 1% level. The F value is 85, indicating significance at the 99% level.

There are several reasons for this decrease in total phosphorus concentration in the Niagara River. As shown in Figure 6, the municipal phosphorus load to Lake Erie has decreased significantly since 1966-67 (data from International Joint Commission, 1969). This decrease is primarily due to the upgrading of sewage treatment plant facilities on Lake Erie and the Detroit River. At the same time, however, a significant decrease in the use of phosphorus in detergents was also realized in Canada and some of the Great Lakes states (Fig. 6). Since 1973, phosphorus levels in detergents have decreased from 11% in 1968 to 2.2%. This decrease may also have had an effect on the municipal load and in turn the water quality of Lake Erie and the Niagara River.

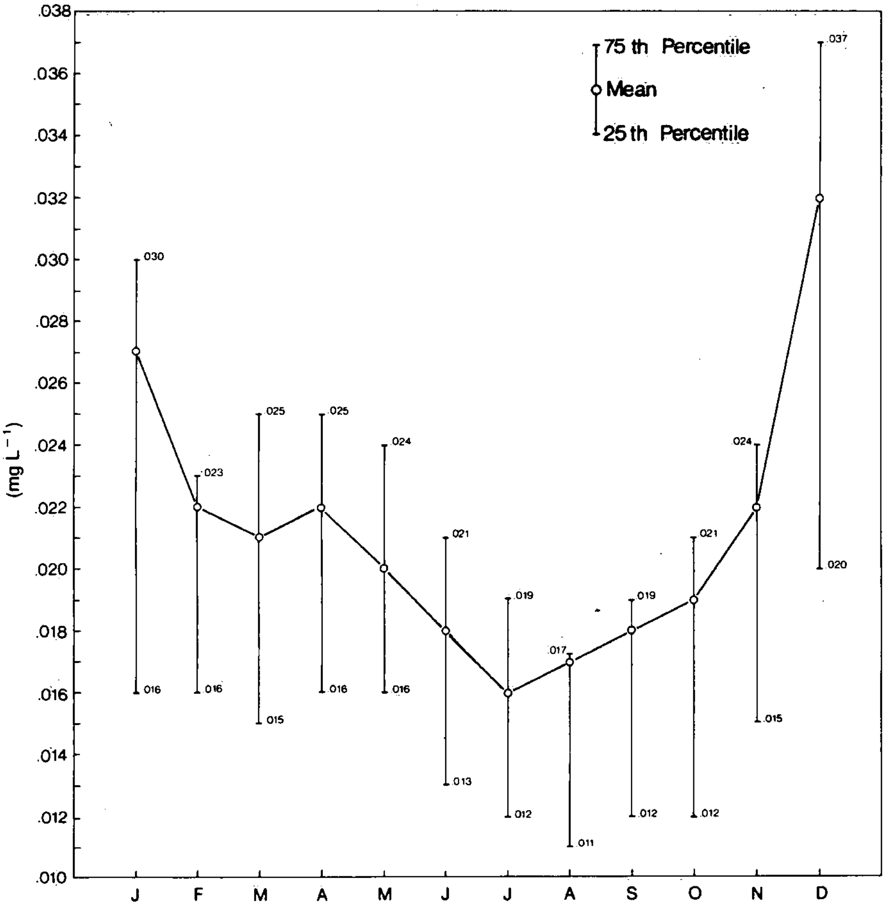

**Figure 4.** Monthly total phosphorus concentrations from 1976 to 1983.

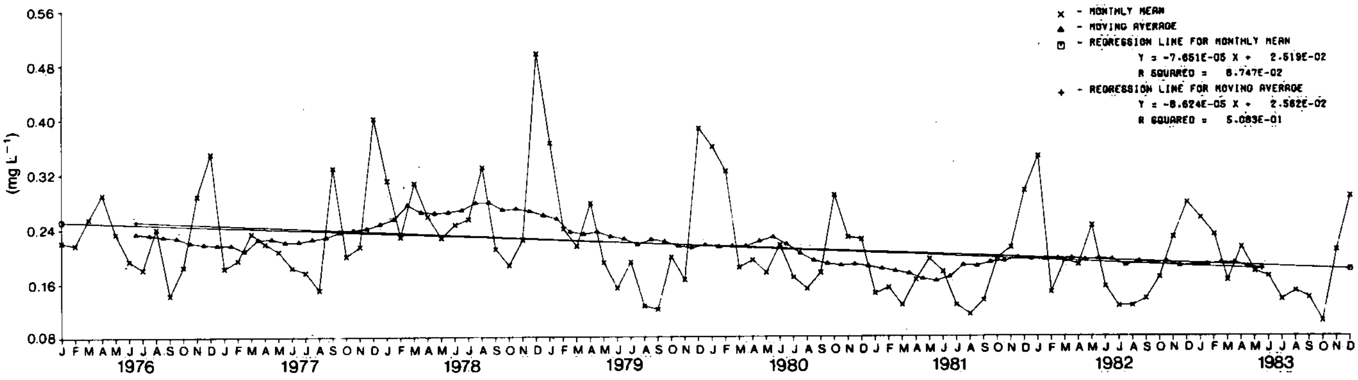

**Figure 5.** Monthly mean and 12-month moving average plot of total phosphorus concentrations.

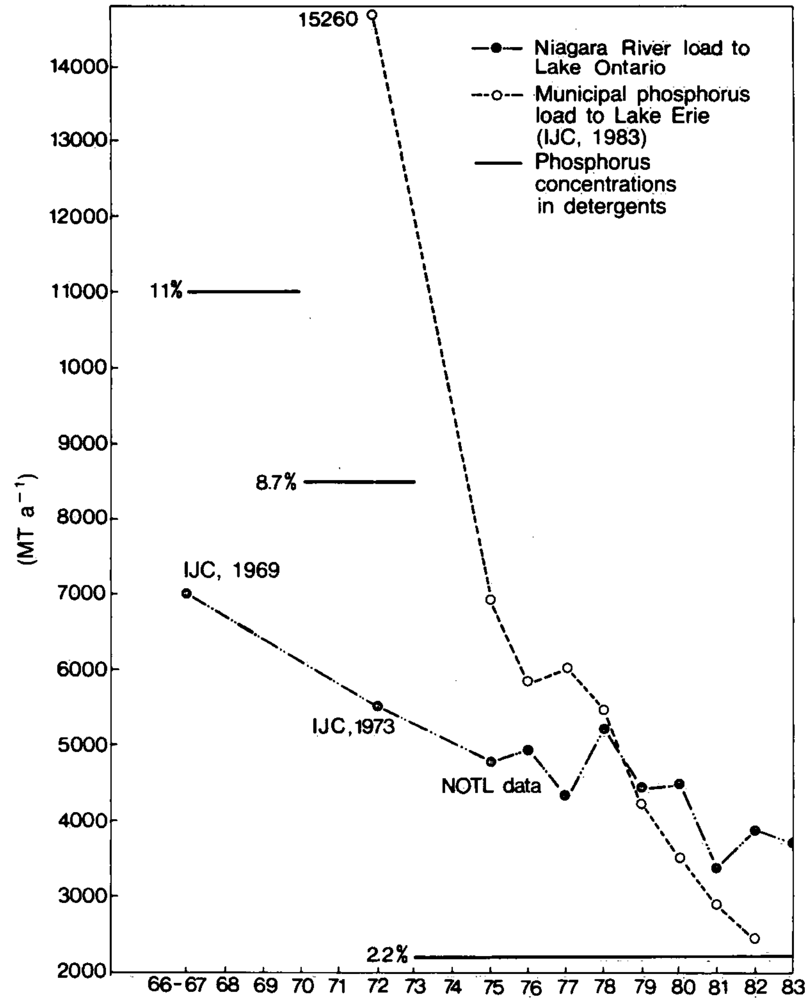

**Figure 6.** Annual total phosphorus loadings.

Other researchers have also reported a decrease in total phosphorus in Lake Erie. El-Shaarawi (1984) developed a statistical model for the variation of total phosphorus in each of the basins of Lake Erie. Using surface data (1 m) collected by the Canada Centre for Inland Waters (CCIW) from 1968 to 1980, he found the trend component to be highly significant ($P \geqslant .01$) in the western and central basins and significant ($P \geqslant .05$) in the eastern basin of Lake Erie. His data showed a decrease from 0.018 mg L$^{-1}$ in 1970 to 0.0129 mg L$^{-1}$ in 1980 (about 34%) during this 10-year period for the eastern basin of Lake Erie. Rosa (1985) also observed a decrease of 0.000 56 mg L$^{-1}$ a$^{-1}$ in the epilimnion waters of the central basin of Lake Erie from 1968 to 1982.

### *Nitrate + Nitrite Nitrogen*

Monthly mean concentrations of nitrate nitrogen from 1976 to 1983 showed the typical nitrogen uptake cycle in late summer, with a minimum monthly average value of 0.122 mg L$^{-1}$ in September. Winter and spring monthly average values were considerably higher and ranged up to 0.314 mg L$^{-1}$ in May. Monthly variations in nitrate nitrogen, as measured at this station since 1975 (Fig. 7), exhibit the typical nitrogen uptake cycle with high values in winter and spring and low depleted nitrate nitrogen concentrations in August, September, and October.

The monthly mean and 12-month moving average plots for nitrate nitrogen are given in Figure 8. These data show the distinctive yearly cycle very well. In addition, these data show a continuous increase in nitrate nitrogen concentrations since 1976. The r value for the moving average line is +.77, indicating a good fit, and is significant at the 1% level. The F value for the analysis of variance is 116, and is significant at the 99% level. The rate of increase from the 12-month moving average regression line is 0.010 mg L$^{-1}$ a$^{-1}$. An identical increase was reported for the

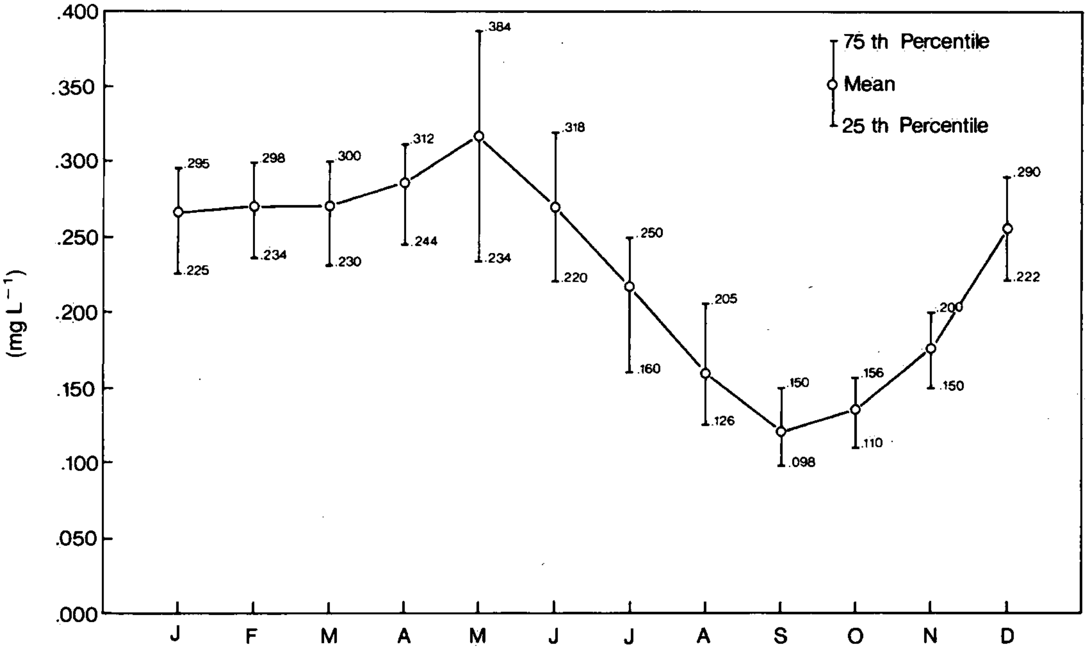

**Figure 7. Monthly nitrate nitrogen concentrations from 1976 to 1983.**

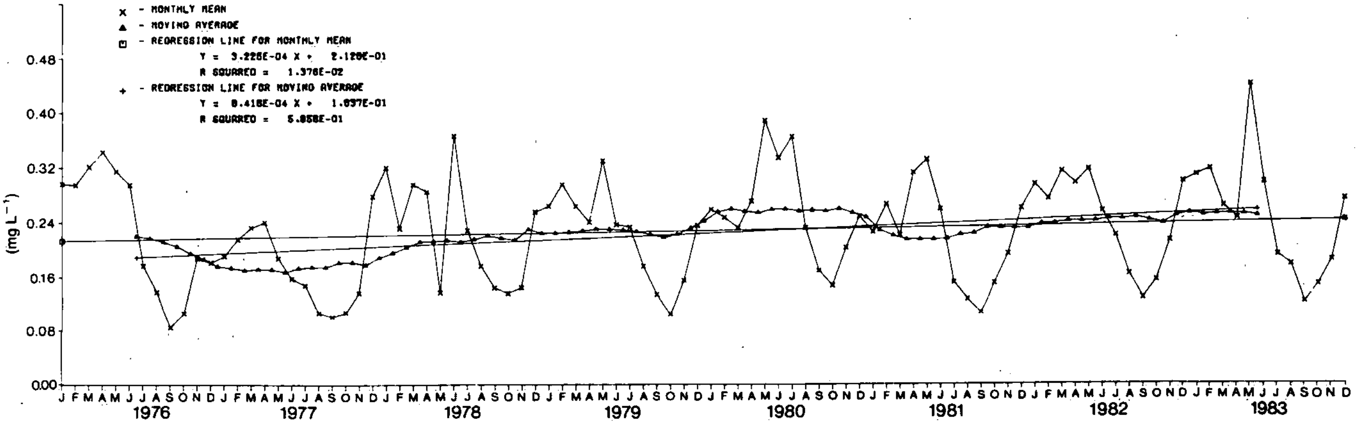

**Figure 8. Monthly mean and 12-month moving average plot of nitrate nitrogen concentrations.**

whole of Lake Ontario for 1969–77 in the annual report on the status of the open waters of Lake Ontario prepared by WQB-OR (Neilson, 1983) for the annual Water Quality Board report.

### *Reactive Silica*

Reactive silica concentrations from 1981 to 1983 showed the typical seasonal depletion of silicate during spring and summer (Fig. 9). Higher values were measured in fall and winter. This type of seasonal cycle was also observed for Lake Erie data by Rathke and Edwards (1984).

### *Loadings*

Annual loadings of nutrients (TP and $NO_3$) from the Niagara River to Lake Ontario are given in Table 2.

Loadings of total phosphorus to Lake Ontario (Fig. 6) have decreased substantially since the data reported for 1972 (Casey and Salbach, 1974). Monthly mean loadings of total phosphorus varied from 6.8 MT $d^{-1}$ in July and August to 18.6 MT $d^{-1}$ in January. These loadings do not appear to be directly related to the discharge cycle, which had highest flows in June and lowest in October.

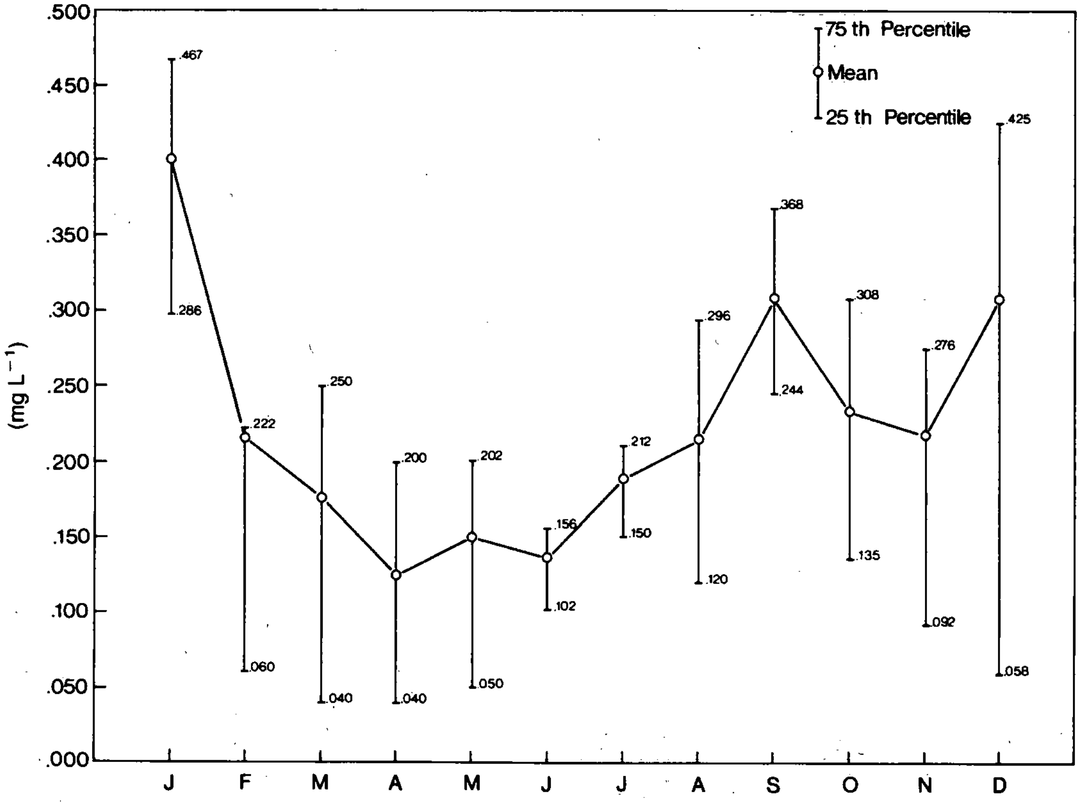

Figure 9. Monthly reactive silica concentrations from 1981 to 1983.

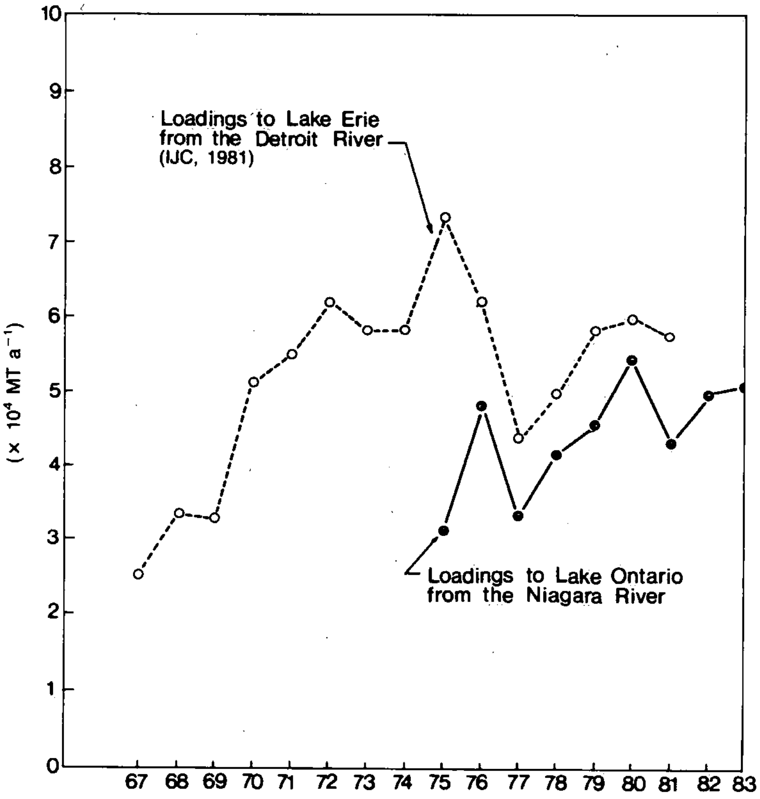

Figure 10. Annual nitrate loadings.

Nitrate loadings to Lake Ontario (Fig. 10) have shown a substantial increase since 1975 from about 3 x $10^4$ MT $a^{-1}$ to about 5 x $10^4$ MT $a^{-1}$, an increase of about 40%. El-Shaarawi (1984) applied a statistical model to a limited number of annual data sets during 1971-80. These data showed not only that the level of $NO_3 + NO_2$ was increasing each year at a statistically significant level ($P \geqslant .05$), but also that the amplitude of the seasonal cycle was also changing. A similar increase is also shown for the Detroit River load to Lake Erie (International Joint Commission, 1981) (Fig. 10).

Table 2. Annual Loadings of Nutrients (× $10^4$ MT $a^{-1}$)

| Year | TP | $NO_3$ |
|---|---|---|
| 1975* | 0.478 | 3.14 |
| 1976 | 0.493 | 4.78 |
| 1977 | 0.431 | 3.32 |
| 1978 | 0.522 | 4.16 |
| 1979 | 0.441 | 4.53 |
| 1980 | 0.449 | 5.44 |
| 1981 | 0.336 | 4.27 |
| 1982 | 0.387 | 4.93 |
| 1983 | 0.376 | 5.11 |

* Incomplete data set.

## Major Ions

Annual mean concentrations of the seven major ions measured since 1975 are given in Table 3. Annual major ions loadings from the Niagara River to Lake Ontario since 1975 are given in Table 4.

A plot of seasonal variations during 1982 shows that there is little seasonal variability for Ca, Cl, $SO_4$, Na,

Table 3. Annual Mean Concentrations of Major Ions (mg $L^{-1}$)

| Year | Total alkalinity | Ca | $SO_4$ | Cl | Na | Mg | K |
|---|---|---|---|---|---|---|---|
| 1975* | 92.3 | 37.4 | 25.1 | 21.1 | 10.4 | 8.1 | 1.3 |
| 1976 | 92.6 | 38.2 | 25.3 | 21.5 | 10.4 | 8.0 | 1.3 |
| 1977 | 91.3 | 37.3 | 24.7 | 22.2 | 10.6 | 7.9 | 1.4 |
| 1978 | 90.2 | 36.2 | 24.5 | 22.0 | 10.5 | 8.1 | 1.4 |
| 1979 | 91.0 | 36.0 | 24.6 | 21.4 | 10.4 | 8.0 | 1.4 |
| 1980 | 88.7 | 35.1 | 24.7 | 19.7 | 9.9 | 8.1 | 1.4 |
| 1981 | 93.6 | 36.2 | 24.3 | 19.0 | 9.6 | 8.0 | 1.3 |
| 1982 | 99.4 | 36.5 | 24.7 | 18.2 | 9.3 | 8.0 | 1.3 |
| 1983 | 97.1 | 35.5 | 26.0 | 17.2 | 9.0 | 8.2 | 1.4 |

* Incomplete data set.

Table 4. Annual Loadings of Major Ions (× $10^6$ MT $a^{-1}$)

| Year | Total alkalinity | Ca | $SO_4$ | Cl | Na | Mg | K |
|---|---|---|---|---|---|---|---|
| 1975* | 19.9 | 8.06 | 5.41 | 4.56 | 2.26 | 1.76 | 0.284 |
| 1976 | 19.8 | 8.16 | 5.40 | 4.59 | 2.22 | 1.71 | 0.284 |
| 1977 | 17.7 | 7.22 | 4.78 | 4.30 | 2.06 | 1.54 | 0.271 |
| 1978 | 18.0 | 7.22 | 4.89 | 4.39 | 2.09 | 1.61 | 0.272 |
| 1979 | 18.4 | 7.27 | 4.96 | 4.32 | 2.11 | 1.62 | 0.275 |
| 1980 | 18.6 | 7.38 | 5.20 | 4.15 | 2.08 | 1.71 | 0.287 |
| 1981 | 18.8 | 7.28 | 4.87 | 3.81 | 1.93 | 1.62 | 0.255 |
| 1982 | 19.9 | 7.32 | 4.95 | 3.65 | 1.87 | 1.60 | 0.272 |
| 1983 | 20.1 | 7.35 | 5.38 | 3.54 | 1.85 | 1.70 | 0.280 |

* Incomplete data set.

Mg, and K (Fig. 11). A somewhat larger variation occurred in total alkalinity. It appears that some of the decrease in alkalinity in April, May, and June may have been caused by dilution as a result of the high spring runoff conditions during these months. In addition, some of this alkalinity decrease was caused by the decrease in calcium concentrations in April and May of each year (Fig. 12). Specific conductance also shows the same yearly pattern.

In recent years, concern has increased regarding the buildup of salt within the Great Lakes. This increase has usually been blamed on the use of road salt for deicing purposes during the winter (Fraser, 1981). Recent information, however, shows that chloride concentrations have decreased in Lakes Erie and Ontario during the last ten years. Fraser (1981) reported that chloride concentrations were decreasing in Lakes Erie and Ontario, especially from 1974 to 1976. Further data by Sonzogni *et al.* (1983) indicated a similar decrease in chloride concentrations in Lake Erie and the Detroit River. The authors gave further data indicating that the major reason for the decrease in Lake Erie was the large reduction in industrial source loading to the Detroit River. A 40% decrease in chloride discharge was reported by the U.S. Environmental Protection Agency (1972) for several major industries along the Detroit River from 1971 to 1973. This Detroit-Windsor complex is a major source of chloride loading to the Detroit River and therefore to Lake Erie. Because this load has been reduced significantly since 1971, it should only be a matter of time before chloride decreases become evident in the Niagara River at Niagara-on-the-Lake. Since 1977, the chloride

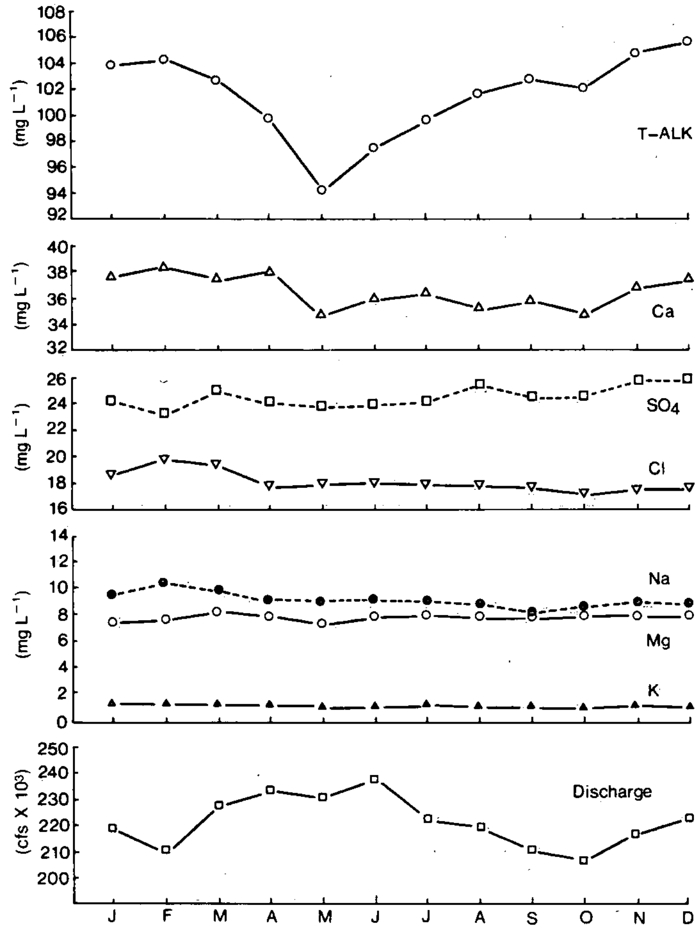

**Figure 11.** Monthly mean concentrations of major ions and discharge in 1982.

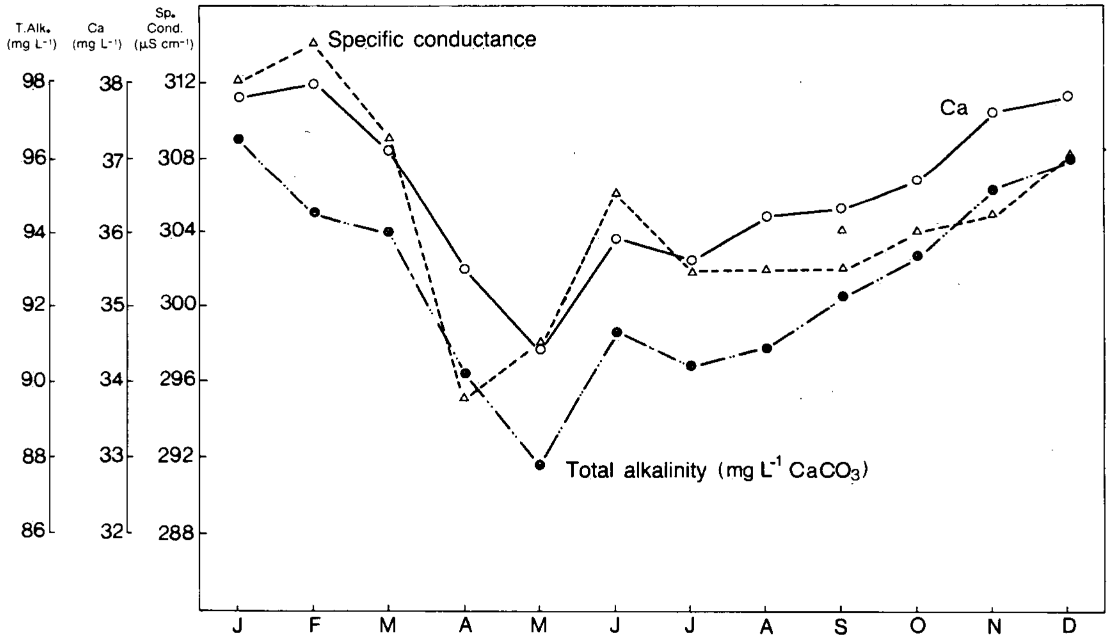

**Figure 12.** Relationship of total alkalinity, calcium, and specific conductance from 1975 to 1982.

concentration in the Niagara River has decreased by about 5 mg $L^{-1}$, a decrease of about 22% (Fig. 13). This would indicate that it has required about six or seven years to flush through Lake Erie. This is about two to three times longer than the flushing rate for Lake Erie of 2.6 years predicted by Rainey (1967).

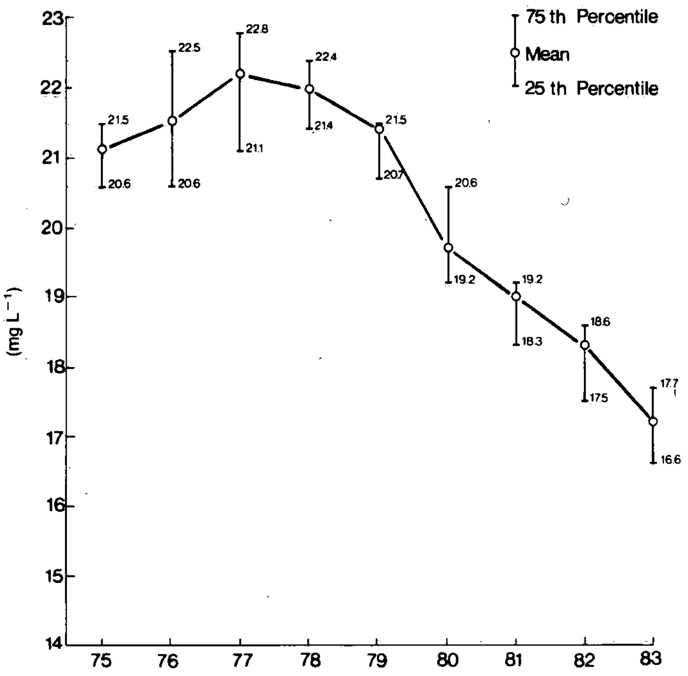

**Figure 13. Annual chloride concentrations from 1975 to 1983.**

Some of the other major ions, especially calcium and sodium (Fig. 14), have also shown a considerable decrease in concentration since 1975 (Table 3). Annual average sodium concentrations have decreased by 1.7 mg $L^{-1}$ since 1977, and annual average calcium concentrations have decreased about 2.7 mg $L^{-1}$ since 1976.

The change with time for chloride and sodium concentrations is shown very well by the 12-month moving average plots (Figs. 15 and 16). The r values for these moving average lines are -.96 and -.95, respectively, indicating a fit significant at the 99% level. The F value for analysis of variance was significant at the 99% level for both parameters. Chloride and sodium are both decreasing, at rates of 0.79 mg $L^{-1}$ $a^{-1}$ and 0.25 mg $L^{-1}$ $a^{-1}$, respectively. Calcium concentrations (Fig. 17) are also decreasing at a rate of 0.23 mg $L^{-1}$ $a^{-1}$, while total alkalinity concentrations are increasing at a rate of 1.15 mg $L^{-1}$ $a^{-1}$ (Fig. 18). The r value for the moving average line for calcium was -.55, while for alkalinity it was +.67, still significant at the 99% level. The F values for analysis of variance were 35 and 68, respectively, also significant at the 99% level. Using these rates of change, the net change in specific conductance over the period, due to sodium, chloride, and calcium concentration decreases and the alkalinity increase, was calculated as 1.8 $\mu$S $cm^{-1}$ $a^{-1}$. This is nearly the same as the 2.2-$\mu$S $cm^{-1}$ change in specific conductance indicated in the moving average plot (Fig. 3).

This decrease in chloride concentration has resulted in a substantial decrease in chloride loadings to Lake Ontario from 1976 to 1983. The chloride loadings to Lake Ontario from the Niagara River decreased from 4.6 x $10^6$ MT $a^{-1}$ to about 3.5 x $10^6$ MT $a^{-1}$, a decrease of about 23% (Fig. 19). A larger decrease of 42% was shown by the Detroit River from 1967 to 1980 (data from International Joint Commission, 1981).

Other major ions, such as magnesium, potassium, and sulphate, are not showing significant changes. The change for sulphate is significant at the 95% level, but not at the 99% level.

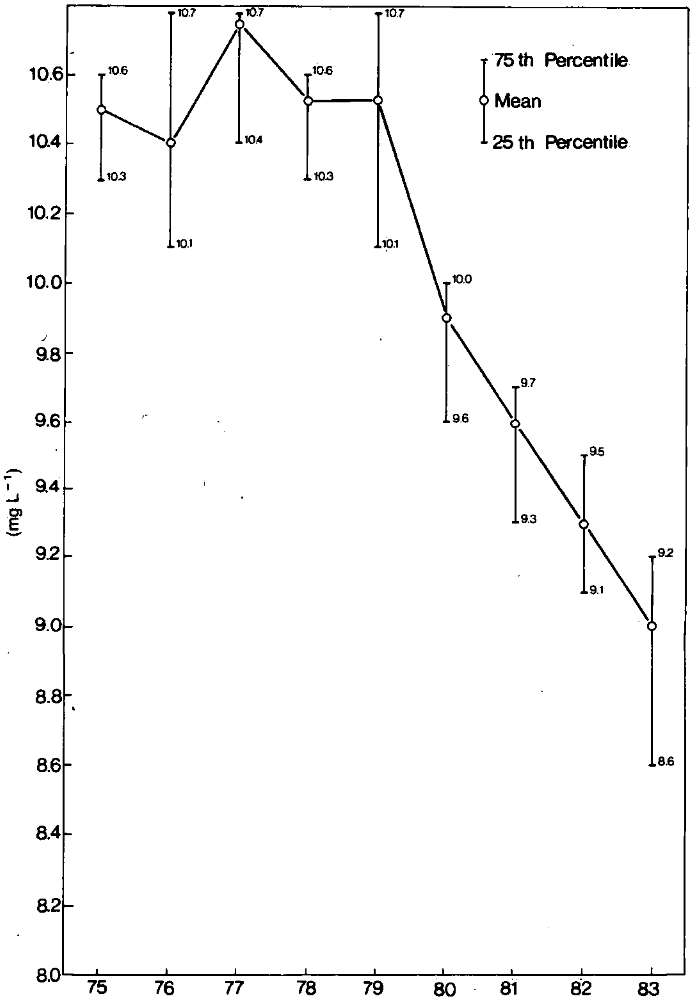

**Figure 14. Annual sodium concentrations from 1975 to 1983.**

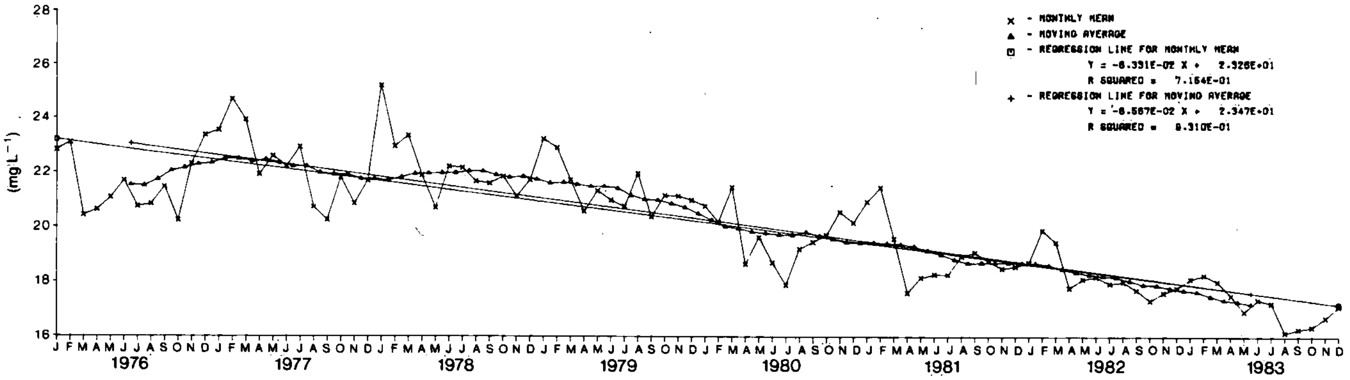

**Figure 15.** Monthly mean and 12-month moving average plot of chloride concentrations.

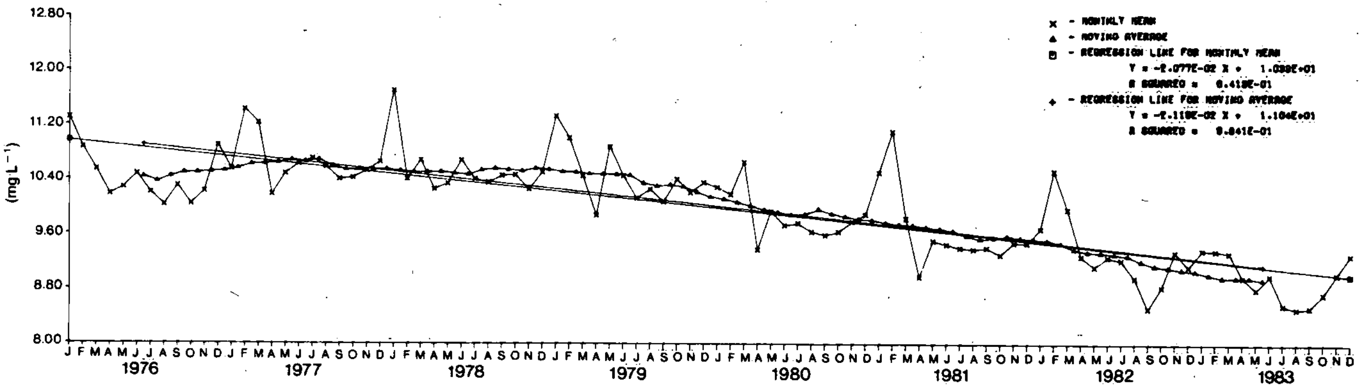

**Figure 16.** Monthly mean and 12-month moving average plot of sodium concentrations.

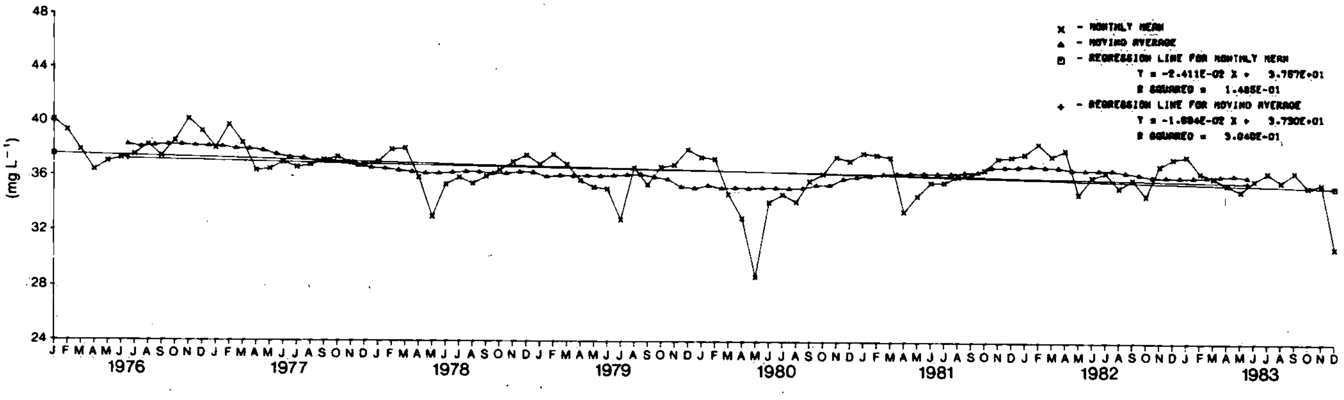

**Figure 17.** Monthly mean and 12-month moving average plot of calcium concentrations.

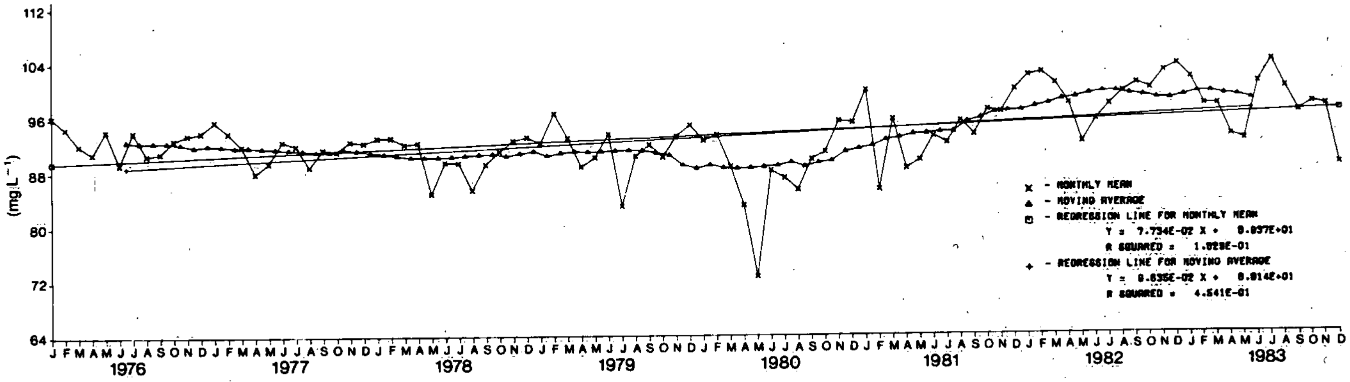

**Figure 18. Monthly mean and 12-month moving average plot of total alkalinity concentrations.**

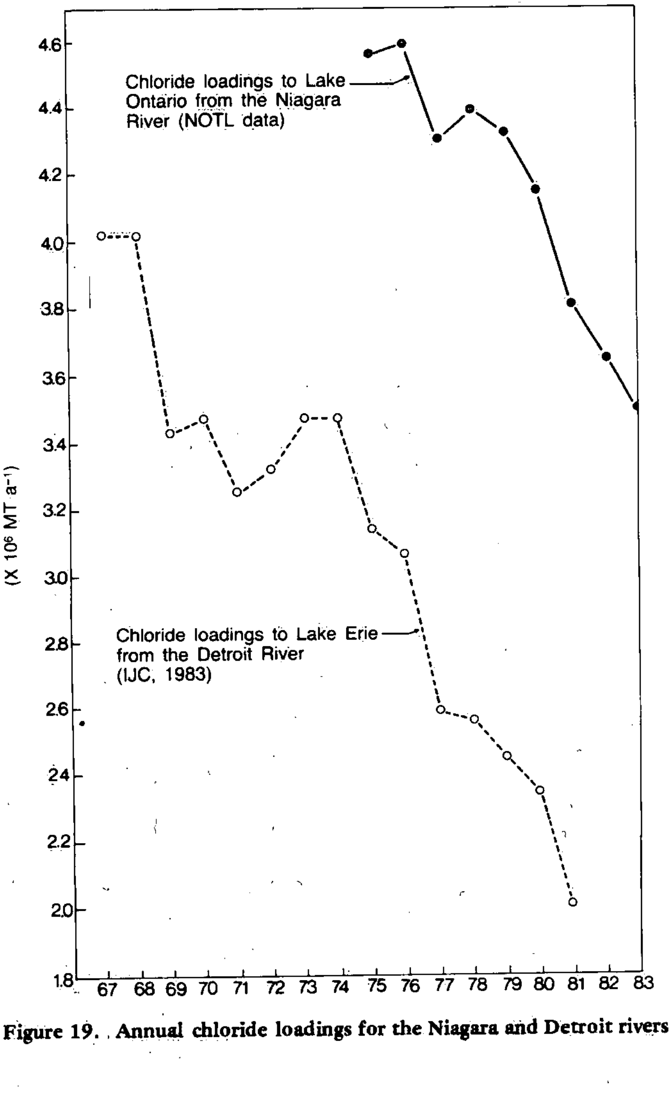

**Figure 19. Annual chloride loadings for the Niagara and Detroit rivers.**

### Trace Metals

Annual median concentrations of the 11 trace metals measured since 1975 are given in Table 5. These samples were collected approximately once a week. The percentage of weekly water samples violating the 1978 Agreement objectives is given in Table 6. Annual loadings to Lake Ontario by the Niagara River from 1975 to 1983 are given in Table 7.

Twelve-month moving average plots for total iron and extractable aluminum concentrations (Figs. 20 and 21) indicate that substantial increases in these parameters have occurred from 1976 to 1983. From the moving average regression line, the rate of increase in total iron concentration is 0.045 mg $L^{-1}$ $a^{-1}$ since 1976. The rate of increase for extractable aluminum during this period is 0.008 mg $L^{-1}$ $a^{-1}$. The r values for the moving average lines for aluminum and iron are +.49 and +.79, respectively, both significant at the 99% level. The F values for analysis of variance were 26 and 132, respectively, also both significant at the 99% levels. These increases are believed to be related to the frequency of occurrence of natural climatic events such as heavy rainfall or wind events.

An analysis of the National Oceanic and Atmospheric Administration data collected at the Buffalo airport revealed that the frequency of days with average daily winds above 20 mph (≈ 32 km/h) was lower in 1981 than in 1979 and 1980. During 1979 and 1980, there were 12 and 10 days, respectively, with average wind speeds greater than 20 mph. In 1981, however, there were only six days with average winds of this magnitude, while in 1982 there were 33 days with average winds above 20 mph. In 1983, there were 11 days with average winds above 20 mph.

Another factor is the timing of the sample collection. If the sample is collected the day of one of these wind events, or even the day after one of these wind events, the iron and aluminum concentrations are likely to be high. In 1982, the year with the highest median iron concentrations measured to date, 12 of the sampling dates occurred

Table 5. Annual Median Concentrations of Trace Metals (mg $L^{-1}$)

| Year | No. observations | Fe | Al | Mn | Ni | Zn | Cu | Cr | Pb | Cd | Hg | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1975* | 19 | 0.110 | 0.040 | 0.004 | 0.002 | 0.003 | 0.003 | 0.002 | 0.002 | <0.001 | – | – |
| 1976 | 51 | 0.110 | 0.060 | 0.010 | 0.003 | 0.005 | 0.006 | 0.001 | 0.002 | <0.001 | – | – |
| 1977 | 48 | 0.140 | 0.050 | 0.006 | 0.003 | 0.005 | 0.010 | 0.001 | 0.001 | <0.001 | – | – |
| 1978 | 43 | 0.160 | 0.050 | 0.009 | 0.002 | 0.004 | 0.004 | 0.001 | 0.001 | <0.001 | – | – |
| 1979 | 41 | 0.200 | 0.100 | 0.008 | 0.003 | 0.003 | 0.003 | 0.001 | 0.001 | <0.001 | <0.00005 | – |
| 1980 | 62 | 0.380 | 0.150 | 0.024 | 0.003 | 0.004 | 0.002 | 0.003 | 0.002 | <0.001 | <0.00005 | 0.0005 |
| 1981 | 47 | 0.140 | 0.050 | <0.010 | 0.001 | 0.002 | 0.002 | 0.001 | 0.001 | <0.001 | <0.00005 | 0.0005 |
| 1982 | 52 | 0.390 | 0.070 | <0.020 | 0.001 | 0.003 | 0.002 | 0.002 | <0.001 | <0.001 | <0.00005 | 0.0006 |
| 1983 | 50 | 0.220 | 0.055 | 0.010 | 0.002 | 0.004 | 0.007 | 0.001 | 0.001 | <0.001 | <0.00002 | 0.0011 |

*Incomplete data set.
< = less than detection limit.

Table 6. Percentage of Trace Metals Samples Violating 1978 Agreement Objectives

| Year | Fe (0.300)* | Cu (0.005)* | Ni (0.025)* | Zn (0.030)* | Cd (0.0002)* | Cr (0.100)* | Pb (0.025)* |
|---|---|---|---|---|---|---|---|
| 1975† | 0 | 16 | 0 | 0 | 0 | 0 | 0 |
| 1976 | 20 | 61 | 0 | 0 | 6 | 0 | 0 |
| 1977 | 14 | 79 | 2 | 2 | 6 | 0 | 0 |
| 1978 | 21 | 40 | 0 | 0 | 0 | 0 | 0 |
| 1979 | 42 | 33 | 0 | 0 | 5 | 0 | 0 |
| 1980 | 55 | 11 | 0 | 0 | 2 | 0 | 0 |
| 1981 | 17 | 19 | 0 | 0 | 2 | 0 | 0 |
| 1982 | 54 | 27 | 2 | 0 | 0 | 0 | 0 |
| 1983 | 39 | 65 | 0 | 0 | 0 | 0 | 0 |

*1978 IJC objective (mg $L^{-1}$).
† Incomplete data set.

Table 7. Annual Loadings of Total Trace Metals (MT $a^{-1}$)*

| Year | Fe | Al | Mg | Ni | Zn | Cu | Cr | Pb | Cd | Hg | As |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1975† | 23 490 | 8 540 | 850 | 430 | 640 | 640 | 430 | 430 | 215 | – | – |
| 1976 | 23 300 | 12 710 | 2120 | 635 | 1060 | 1270 | 210 | 420 | 210 | – | – |
| 1977 | 26 945 | 9 620 | 1155 | 580 | 960 | 1925 | 385 | 190 | 190 | – | – |
| 1978 | 31 245 | 9 765 | 1760 | 390 | 780 | 780 | 195 | 195 | 195 | – | – |
| 1979 | 39 770 | 19 885 | 1590 | 595 | 595 | 595 | 200 | 200 | 200 | 10 | – |
| 1980 | 78 815 | 31 110 | 4980 | 620 | 830 | 415 | 620 | 415 | 205 | 10 | 105 |
| 1981 | 27 670 | 9 885 | 1975 | 200 | 395 | 595 | 200 | 200 | 200 | 10 | 100 |
| 1982 | 76 475 | 13 905 | 3970 | 200 | 595 | 395 | 395 | 200 | 200 | 10 | 120 |
| 1983 | 44 930 | 11 230 | 2040 | 410 | 815 | – | 410 | 205 | 205 | 4 | 225 |

*Derived from product of yearly median concentration and average daily discharge for each year.
†Incomplete data set.

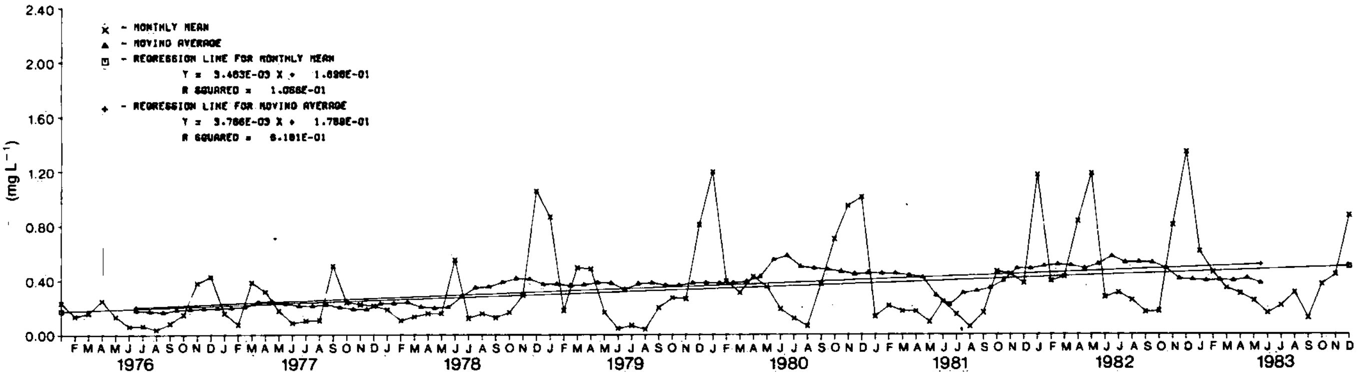

Figure 20. Monthly mean and 12-month moving average plot of total iron concentrations.

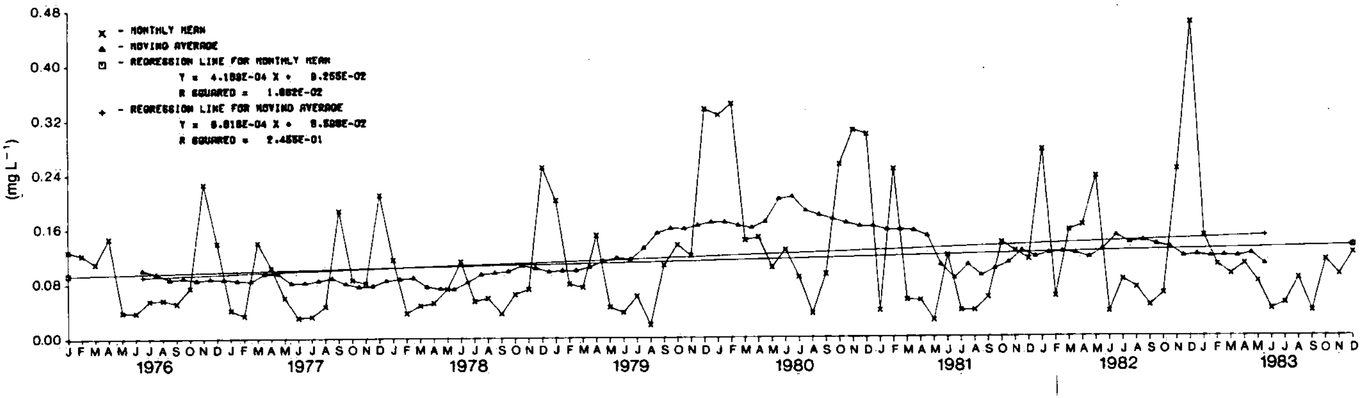

Figure 21. Monthly mean and 12-month moving average plot of extractable aluminum concentrations.

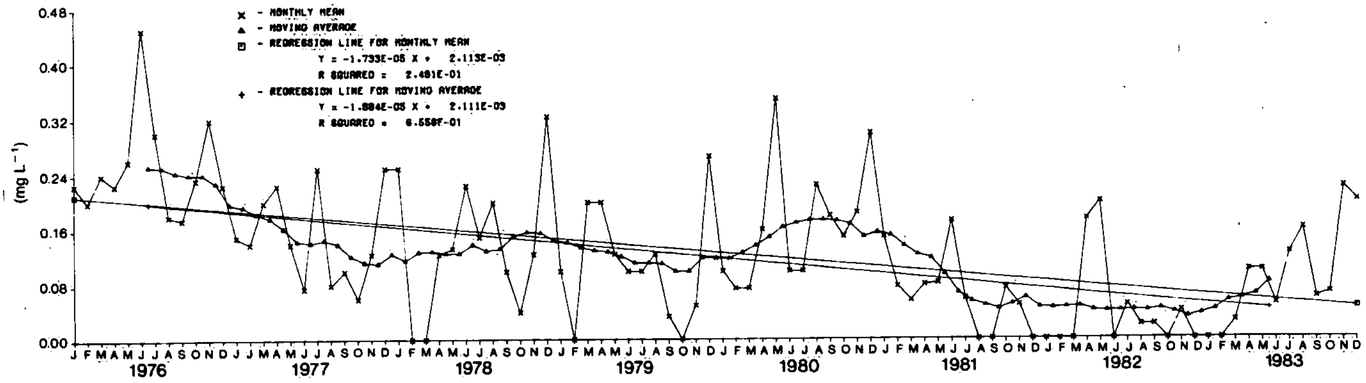

Figure 22. Monthly mean and 12-month moving average plot of total lead concentrations.

either on the day of or the day after an average wind speed of 20 mph or greater was recorded at Buffalo. Since the concentration of total iron in the water column appears to be related to the amount of resuspension of bottom sediments caused by the wind energy, it follows that the percentage of violations to the IJC objective of 0.300 mg $L^{-1}$ for total iron also increased in 1980 and 1982 to 55% and 54%, respectively.

The 12-month moving average plot for total lead concentrations (Fig. 22) seems to be showing a decrease in lead concentrations in the Niagara River since 1976. The r value for this moving average line is -.81 and is significant at the 99% level. The F value for analysis of variance is 156, and is also significant at the 99% level. Although this decrease is a small one, it may be related to increasing use of unleaded gasoline in automobiles, particularly in the U.S. part of the Lake Erie basin.

## SUMMARY

Since 1975, WQB-OR has been collecting water quality samples from a single station near the mouth of the Niagara River. A complete set of water quality parameters, including physical parameters (daily), nutrients (daily), major ions (weekly), and trace metals (weekly), have been analyzed.

Since 1975 there have been significant changes in the water quality of the Niagara River at Niagara-on-the-Lake. Some parameters have been increasing in concentration, and therefore loading to Lake Ontario has increased. These parameters are nitrate nitrogen, total iron and aluminum, total alkalinity, and possibly sulphate (only at the 95% level). Some parameters have been decreasing in concentration, and therefore loading to Lake Ontario has decreased. Those parameters that are decreasing significantly are specific conductance, total phosphorus, chloride, sodium, calcium, and lead. Other parameters, namely magnesium and potassium, have remained the same over this period.

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