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Niagara River Chemical Loading
1975–1977

C.H. Chan

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Abstract

Detailed analyses of chemical data collected daily over a 29-month period from August 1975 to December 1977 at Niagara-on-the-Lake have identified short-term trends in some of the water quality parameters. The pH, phosphorus and nitrogen concentrations remained relatively stable. Seasonal variation in major ions concentrations was observed to occur inversely to the outflow of the Niagara River. Due to a 9% decline in water supply to Lake Erie during 1977, there was a significant decrease in calcium, magnesium and sulphate concentrations, but sodium and chloride concentrations were higher. The annual phosphorus load for 1977 was 11.78 metric tons per day compared with 13.53 metric tons per day in 1976, a 13% decrease. Results computed from different sampling frequencies suggested that a sampling frequency of once per week for phosphorus would yield results to within 5% of daily sampling.

Résumé

L'analyse détaillée, d'août 1975 à décembre 1977, à Niagara-on-the-Lake, de données chimiques recueillies quotidiennement pendant 29 mois a permis de déterminer dans quels sens évoluaient, à court terme, certains des paramètres de la qualité des eaux. Les teneurs en phosphore et en azote ainsi que le pH sont demeurés relativement stables. La variation saisonnière de la concentration des principaux ions s'est révélée inversement proportionnelle au débit de la rivière Niagara. La baisse de 9 % d'apport d'eau au lac Érié en 1977 a eu pour effet de faire diminuer sensiblement les concentrations de calcium, de magnésium et de sulfates, tandis que celles de sodium et de chlorures augmentaient. En 1977, la charge de phosphore a été de 11,78 t/j, comparativement à 13,53 en 1976, soit une baisse de 13 %. Selon les résultats compilés après variation de la fréquence des échantillonnages, il suffirait, pour le phosphore, d'en effectuer un seul par semaine pour obtenir des données qui s'écarteraient tout au plus de 5 % de celles d'un échantillonnage quotidien.

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INTRODUCTION

The adverse environmental changes within the Great Lakes owing to accelerated and excessive material inputs into the lower Great Lakes have been widely documented (Beeton, 1965). As a result, present water quality research programs focus on relationships between water quality and loads to determine how the physical, biological and chemical systems of the Great Lakes operate. Many predictive mathematical models for various water quality parameters have been developed for the Great Lakes, and comprehensive water quality data are needed for their calibration and verification. Concern for preservation and restoration of Great Lakes water quality has also led to the legislative regulation of phosphorus detergents and the implementation of various remedial and pollution abatement programs. Monitoring material loads into the Great Lakes has become a useful method to assess the effectiveness of these remedial programs and the validity of mathematical water quality models.

The Surveillance Subcommittee of the Great Lakes Water Quality Board of the International Joint Commission (IJC) has identified the need to monitor tributary loadings into the Great Lakes and has recommended that tributary loadings be part of an overall strategy in Great Lakes surveillance (IJC, 1976).

The Water Quality Branch of the Department of the Environment has established a water quality monitoring station at Niagara-on-the-Lake. It has been in operation since August 1975 for the purposes of obtaining detailed estimates of annual Niagara River loading into Lake Ontario, establishing long-term loading trends of the Niagara River, developing sampling methodology on tributary loadings and quantifying long-term trends in various water quality parameters.

This report summarizes a number of water quality parameters sampled on a daily basis over a 29-month period. Seasonal variations in Niagara River water quality are discussed in relation to Lake Erie outflow. Annual loading estimates are computed and different sampling frequencies for Niagara River monitoring are examined.

EXPERIMENTAL

A 2-L sample of water is routinely collected midstream near the mouth of the Niagara River on a daily basis. The sampling station is located at the pumping station for the town of Niagara-on-the-Lake (Fig. 1). Sample collection is initiated by pumping water from midstream in the Niagara River to an automatic sampler housed inside the pumping station.
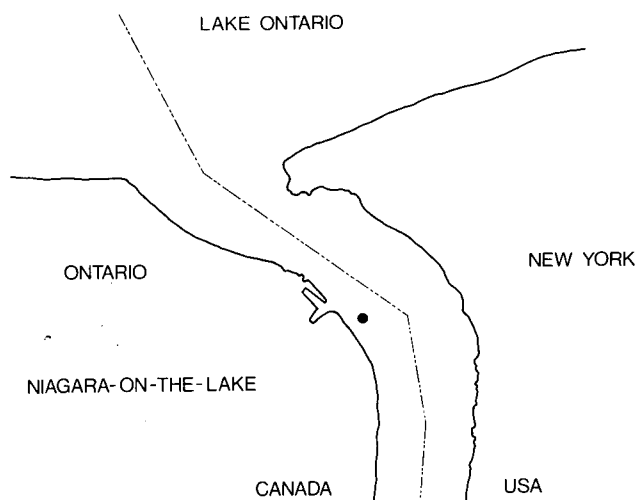
Figure 1. Sampling location at Niagara-on-the-Lake.

The sample pump, installed near the riverbank, continuously draws water through a 100-ft polyethylene hose which extends into the river. By means of an anchor and a float, the end of the sample intake hose floats about 15 m from shore and about 10 m below the water surface. Through the control of a timer, the sampler system is capable of routing the water into one of 24 2-L polyethylene bottles. The sampler is programmed to collect a water sample between 11:00 and noon everyday. At the beginning of each week, the water samples collected during the previous week are taken to a laboratory in Burlington for chemical analysis. During winter, the water intake is insulated with heating cables, making sample collection possible year-round.

Water samples are analyzed for pH, specific conductance, total phosphorus, Kjeldahl nitrogen, nitrate, alkalinity, potassium, calcium, magnesium, sodium, chloride, sulphate and heavy metals. Nutrient analyses are performed on every sample, whereas dissolved minerals analyses are performed once a week. Methods of analysis are described in the *Analytical Methods Manual* (Department of the Environment, 1974).

RESULTS AND DISCUSSION

The Niagara River accounts for over 85% of the water inflow to Lake Ontario and contributes a large proportion of the total material load to the lake. Its physical characteristics are ideal for long-term automatic monitoring experiments because the water at the sampling location is well mixed and the flow is gauged and regulated.

One of the major criticisms regarding water quality monitoring is the arbitrary nature of the sampling design and a general failure to account for the temporal and spatial background variability in water quality resulting from the variabilities of hydrological and meteorological phenomena.

Studies carried out in 1974 and 1975 (Chan, 1977) showed that the water at Niagara-on-the-Lake is chemically homogeneous, although significant spatial variations existed in the upper Niagara River (IJC, 1978). In 1975 and 1976, four seven-day periods of intensive hourly sampling detected no significant diurnal cycles in any of the parameters being studied (Chan and Clignett, 1978). The chemical composition of the water samples collected in this study is considered to be representative of the outflowing water of the Niagara River.

The number of water samples collected monthly from 1975 to 1977 is shown in Table 1. Of a total of 833 days, approximately 12% of the data are missing due either to sampler malfunction or to power disruption primarily during severe winter conditions. Even though missing data have not been estimated, the data set is of sufficient length and detail to provide reliable estimates of the material loads into Lake Ontario. These are used to give an indication of significant changes in water quality during the 29-month period from 1975 to 1977.

Flow

Water is the medium in which materials or wastes are being transported. Generally, a large river has a greater capacity to dilute or assimilate wastes than a small river and is consequently less susceptible to degradation. River flow is perhaps the most important factor governing the time and space variability in water quality.

As indicated previously, the flow of the Niagara River is regulated. Water is stored and diverted through two reservoirs, the regulation being done on an hourly basis. As expected, this results in a cyclic pattern over a 24-h period (Fig. 2). Previous studies (Chan and Clignett, 1978) have shown that the chemistry of the river at the downstream end is not affected by such regulation.
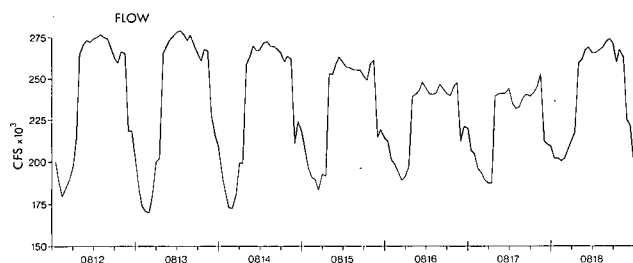
Figure 2. Niagara River flow at Queenston, August 12-18, 1975.

Figure 3 is a plot of the monthly average river discharge and the 12-month moving average river discharge measured at Queenston from August 1975 to December 1977. Average flow for 1975 was 245 000 cfs, 237 000 cfs in 1976 and 215 000 cfs in 1977. There is a gradual overall decrease in the outflow of the Niagara River from 1975 to 1977. This downward trend in river discharge is also demonstrated in the 12-month moving average plot. The changes in river discharge significantly affect the material loads of the river.

Figure 3. Monthly average flow of Niagara River at Queenston, August 1975 to December 1977. Closed circles represent the monthly average river discharge; open circles represent the 12-month moving average river discharge. The *r* is the correlation coefficient.

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Table 1. Number of Water Samples Collected from August 1975 to December 1977

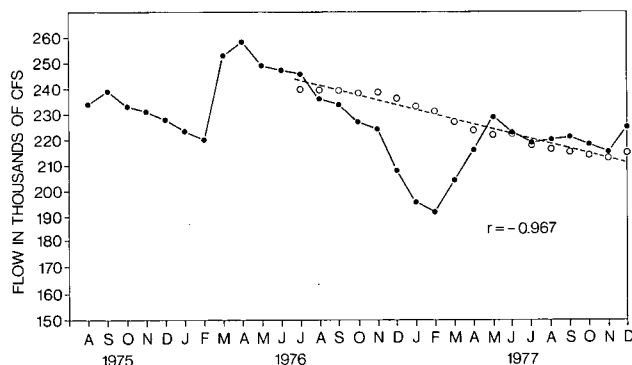| Month	1975		1976		1977	
	Nutrients	Major ions	Nutrients	Major ions	Nutrients	Major ions
January	–	–	26	4	18	2
February	–	–	19	3	28	5
March	–	–	25	5	30	4
April	–	–	30	4	30	4
May	–	–	23	3	29	5
June	–	–	22	4	30	4
July	–	–	27	4	24	3
August	31	4	25	5	31	5
September	30	5	30	4	29	4
October	31	4	22	3	30	5
November	30	4	20	5	29	4
December	31	5	28	4	21	4
Total	153	22	297	48	329	49

Table 2. Monthly Average Phosphorus and Nitrogen Concentrations (mg/L), 1976-1977

Month	1976				1977			
	TP	TKN	NO_3	TN	TP	TKN	NO_3	TN
January	0.022	0.272	0.297	0.576	0.018	0.274	0.191	0.465
February	0.022	0.255	0.295	0.551	0.019	0.289	0.216	0.494
March	0.025	0.294	0.322	0.616	0.023	0.282	0.233	0.515
April	0.029	0.284	0.343	0.624	0.022	0.324	0.240	0.565
May	0.023	0.318	0.315	0.639	0.021	0.291	0.188	0.479
June	0.019	0.229	0.296	0.522	0.018	0.328	0.158	0.486
July	0.018	0.239	0.177	0.419	0.018	0.292	0.148	0.440
August	0.024	0.278	0.139	0.417	0.015	0.302	0.108	0.410
September	0.014	0.286	0.085	0.372	0.033	0.282	0.101	0.382
October	0.018	0.306	0.108	0.409	0.020	0.280	0.108	0.388
November	0.029	0.298	0.188	0.486	0.021	0.228	0.136	0.364
December	0.035	0.254	0.181	0.440	0.040	0.278	0.278	0.554
Mean	0.023	0.276	0.220	0.497	0.022	0.288	0.173	0.460

TKN–Total Kjeldahl nitrogen.

Phosphorus

The time plot for total phosphorus concentration in the lower Niagara River is shown in Figure 4. This figure displays a seasonal cycle and some rapid and large fluctuations which are indicated by the sharp peaks in the diagram. Such random fluctuations in total phosphorus concentration would make detection of any real significant changes in total phosphorus concentration difficult. The observed seasonal cycle of phosphorus, lower values in summer and fall and higher in winter and spring, is consistent with observations made in 1974 and 1975. This pattern is probably closely related to the nutrient cycles in Lake Erie where the formation of nutrient-depleted epilimnetic water in the summer creates a partition of nutrients between surface and bottom water. Lake turnover in the fall mixes epilimnetic and hypolimnetic water and the isothermal condition in winter tends to raise the phosphorus concentration in the whole water column.

Mean phosphorus concentrations for 1976 and 1977 were 0.023 mg/L and 0.022 mg/L, respectively (Table 2). Unlike dissolved major ions (to be discussed later) phosphorus concentration seemed to be unaffected by changes in Lake Erie outflow. Trend analysis, by calculating the linear correlation coefficients of the 12-month moving average concentrations, shows that pH and total phosphorus were least correlated with time, exhibiting no significant
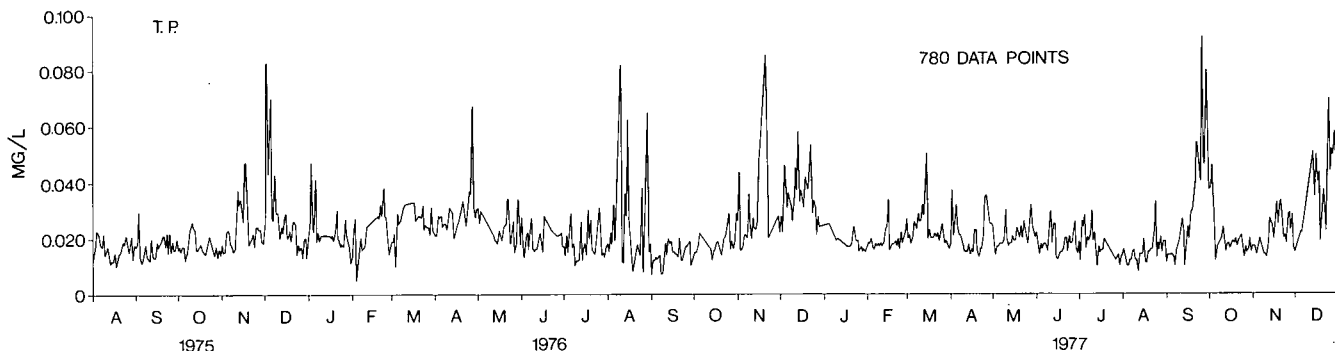
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Figure 4. Time-series plot of total phosphorus.

changes over the 29-month period (Fig. 5). This observation could be an indication of the complexity of phosphorus cycles in which physical, biological and chemical interactions are major controlling factors. It could also suggest that the response of total phosphorus concentration in Great Lakes water quality to remedial programs is slow. It will likely be much longer before any real significant changes in total phosphorus concentration can be established.
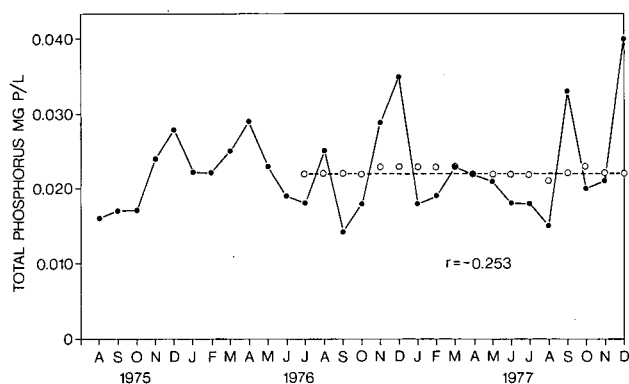

Figure 5. Monthly average plot of total phosphorus concentration .

Nitrogen

Nitrogen is measured as three fractions: Kjeldahl nitrogen, nitrate + nitrite, and ammonia. Because of the time lapse between the time of sampling and the chemical analysis, some decomposition and transformation may take place. Consequently, it is possible that each fraction of the values may not be entirely representative of the values at the time of sampling. Total nitrogen (organic nitrogen plus ammonia) is taken as an overall measure of nitrogen.

A time series plot of total nitrogen is shown in Figure 6, and the average monthly concentrations of Kjeldahl nitrogen, nitrate + nitrite and total nitrogen showed similar seasonal variations in concentrations with peak values in April and May and low values in August and September (Figs. 7, 8 and 9). Mean annual Kjeldahl nitrogen increased slightly from 0.276 mg/L in 1976 to 0.288 mg/L, whereas nitrate nitrogen decreased from 0.220 mg/L in 1976 to 0.173 mg/L in 1977. This can be interpreted as organic nitrogen or biomass being on the increase, resulting in lower inorganic nitrate concentration. In 1976, Kjeldahl nitrogen showed two main peaks, one in spring and the
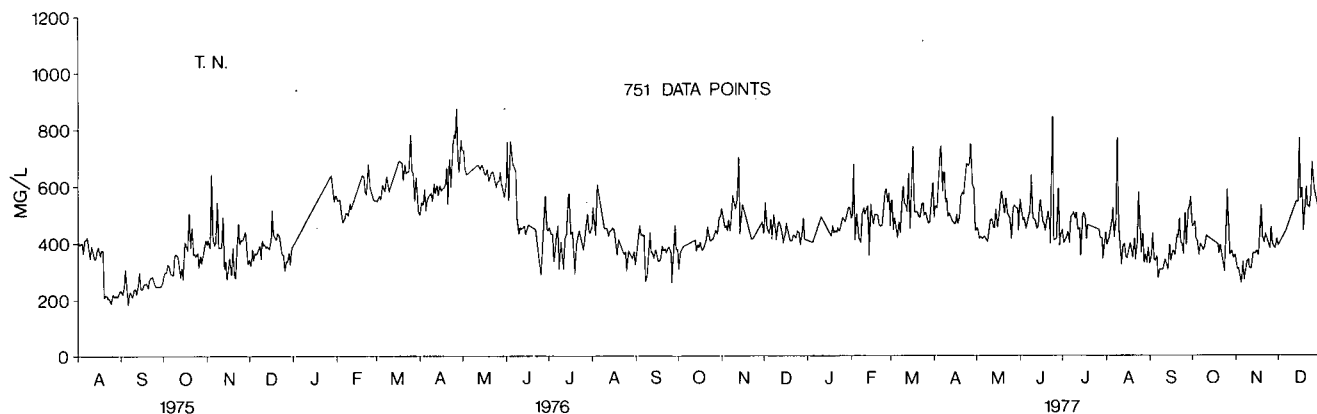

Figure 6. Time-series plot of total nitrogen.

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other in fall, whereas in 1977, Kjeldahl nitrogen remained fairly high from March until September. Average annual total nitrogen, on the other hand, was lower in 1977 (0.460 mg/L) than in 1976 (0.497 mg/L). Trend analysis showed this change to have low significance (Fig. 9 and Table 3).
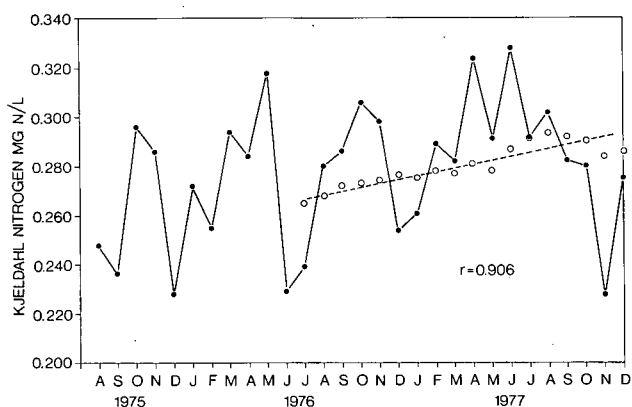

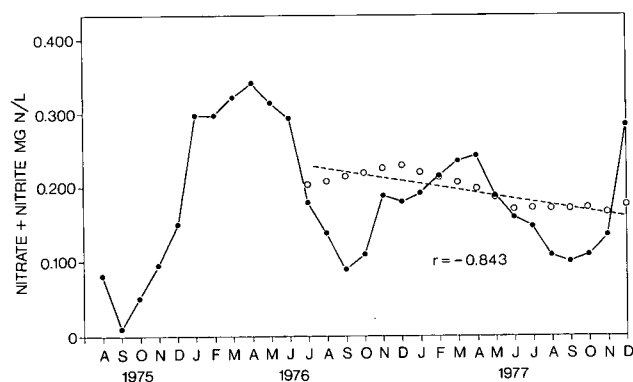Figure 7. Monthly average plot of Kjeldahl nitrogen concentration.

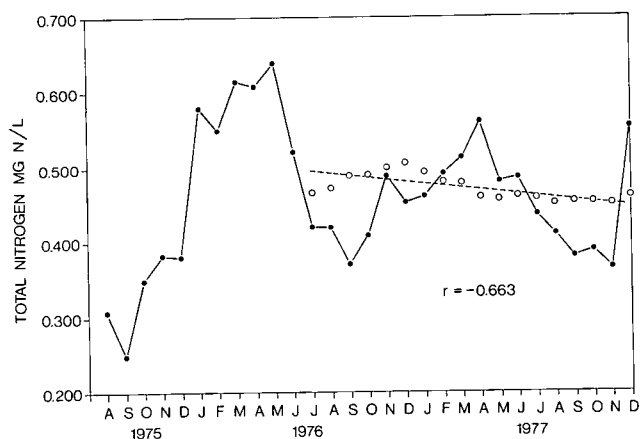Figure 8. Monthly average plot of nitrate + nitrite concentration.

Figure 9. Monthly average plot of total nitrogen concentration.

Table 3. Time Trend Analysis Linear Correlation Coefficients*

Parameter	Concentration	Loading
pH	−0.283	−
Specific conductance	0.926	−
Phosphorus	−0.253	−0.836
Kjeldahl nitrogen	0.906	−0.773
Nitrate + nitrite	−0.843	−0.896
Total nitrogen	−0.663	−0.890
Alkalinity	−0.987	−
Calcium	−0.719	−0.986
Magnesium	−0.940	−0.986
Potassium	−0.746	−0.914
Sodium	0.898	−0.973
Chloride	0.946	−0.986
Sulphate	−0.968	−0.981
Flow	−0.967	−

*Twelve-month moving averages of linear correlation coefficients for parameter vs. concentration and loading.

Nitrogen is considered an uncontrollable nutrient in the Great Lakes ecosystem. The many sources of nitrogen plus the complexity of the nitrogen cycle make a nitrogen mass balance much more difficult.

Major Ions

Average monthly concentrations of major dissolved mineral constituents are tabulated in Tables 4 and 5. With the exception of potassium, they all exhibit a seasonal pattern marked by lower values in the summer and a gradual increase in concentrations in the fall until February and a decline until April. This annual cyclic pattern is also observed in conductivity measurements (Fig. 10). An anomaly recorded in specific conductance was the peak in July, which could not be accounted for by increases in dissolved ions; the reason for this is not known.
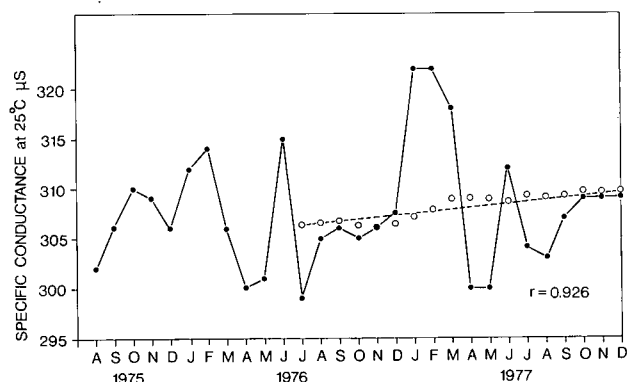

Figure 10. Monthly average plot of specific conductance.

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Table 4. Monthly Average Dissolved Major Ions Concentrations (mg/L), 1976

Month	pH*	Specific conductance†	Alk.	Ca	Mg	K	Na	Cl	SO₄
January	8.09	312	96.2	40.0	8.4	1.4	11.3	22.8	26.7
February	7.94	315	94.5	39.9	8.3	1.4	10.9	23.1	26.5
March	8.07	306	92.1	37.8	7.8	1.3	10.5	20.4	26.4
April	8.07	301	90.8	36.4	7.8	1.3	10.2	20.6	25.3
May	8.22	302	94.2	37.0	8.0	1.3	10.3	21.1	25.0
June	8.15	315	89.3	37.2	7.9	1.3	10.5	21.7	24.6
July	8.10	296	94.0	37.5	7.7	1.3	10.2	20.7	24.1
August	8.35	305	90.6	38.2	7.8	1.3	10.0	20.8	24.5
September	8.22	306	90.9	37.4	8.0	1.3	10.3	21.5	25.2
October	8.18	305	92.8	38.5	8.1	1.3	10.0	20.2	25.5
November	8.06	306	93.6	40.1	8.2	1.3	10.2	22.3	25.1
December	8.04	310	93.9	39.2	8.2	1.3	10.9	23.4	25.0
Mean	8.12	306	92.6	38.3	8.0	1.3	10.4	21.5	25.3

*pH unit.
†Microsiemens per square centimetre.

Table 5. Monthly Average Dissolved Major Ions Concentrations (mg/L), 1977

Month	pH*	Specific conductance†	Alk.	Ca	Mg	K	Na	Cl	SO₄
January	7.97	322	95.5	380	8.3	1.3	10.6	23.6	25.4
February	8.03	322	93.8	39.7	8.2	1.4	11.4	24.7	26.0
March	8.03	318	91.8	38.4	7.8	1.4	11.2	23.9	25.5
April	8.11	300	87.9	36.4	7.6	1.4	10.2	21.9	23.9
May	8.25	306	89.4	36.5	7.8	1.4	10.5	22.6	24.2
June	8.20	312	92.6	37.0	7.9	1.3	10.6	22.2	24.3
July	8.14	304	91.9	36.6	7.8	1.4	10.7	22.9	24.0
August	8.32	303	88.8	36.8	8.0	1.4	10.6	20.7	25.1
September	8.29	307	91.3	37.1	7.8	1.4	10.4	20.2	24.4
October	8.28	309	91.0	37.3	7.9	1.4	10.4	21.8	23.9
November	8.25	309	92.5	36.9	8.2	1.5	10.5	20.8	24.5
December	8.11	309	92.2	36.8	8.1	1.5	10.6	21.7	24.9
Mean	9.17	309	91.3	37.3	7.9	1.4	10.6	22.2	24.6

*pH unit.
†Microsiemens per square centimetre.

Changes in major ions were also obvious from 1976 to 1977. Mean annual concentrations for calcium, magnesium and sulphate were all lower in value, while sodium and chloride were higher. The annual mean calcium concentration in 1976 was 38.2 mg/L compared with 37.3 mg/L in 1977. The annual average magnesium concentration was 8.0 mg/L in 1976 and 7.9 mg/L in 1977, and sulphate, which measured 25.3 mg/L in 1976, was 24.6 mg/L in 1977. In contrast, sodium increased by 0.2 mg/L from 10.4 mg/L in 1976 to 10.6 mg/L in 1977. Chloride showed an increase of 0.7 mg/L (21.5 mg/L to 22.2 mg/L) during the same period. Changes in potassium concentration are within the detection limit of the method. These changes, although small in magnitude, are detectable and considered to be real. Trend analysis by calculating linear correlation coefficients on 12-month moving averages indicated the level of significance is high (Table 3).

The decrease in calcium, magnesium and sulphate concentrations from 1976 to 1977 and the increase of sodium and chloride concentrations seem to indicate that the two groups of ions may have different mechanisms of transport and origins. Most dissolved minerals, which originate from weathering of bedrock, are carried into water bodies by runoff within the whole drainage basin. Thus their sources are diffuse and their loading is dependent

Table 6. Linear Correlation Coefficients, Concentrations vs. Discharge

Parameter	Conc. vs. discharge	Conc. vs. log (discharge)	Log (conc.) vs. log (discharge)
pH	0.240	0.259	0.260
Specific conductance	-0.621	-0.635	-0.633
Phosphorus	0.026	0.024	0.037
Kjeldahl nitrogen	0.066	-0.064	-0.073
Nitrate + nitrite	0.204	0.181	-0.024
Total nitrogen	0.164	0.146	0.080
Alkalinity	-0.155	-0.160	-0.158
Calcium	-0.308	-0.308	-0.307
Magnesium	-0.292	-0.289	-0.288
Potassium	-0.426	-0.414	-0.415
Sodium	-0.595	-0.609	-0.607
Chloride	-0.695	-0.706	-0.700
Sulphate	-0.025	-0.036	-0.037

on the runoff and the amount of rainfall. The smaller outflow of Lake Erie in 1977, a result of lower tributary inflow, would lower the concentration because of reduced load.

For sodium and chloride, whose sources are found in all urban and industrial centres, however, the cultural inputs are probably many times higher than the natural inputs. The total load is relatively constant and does not depend on runoff and rainfall. Therefore a smaller inflow of water into Lake Erie would elevate the salt concentration.
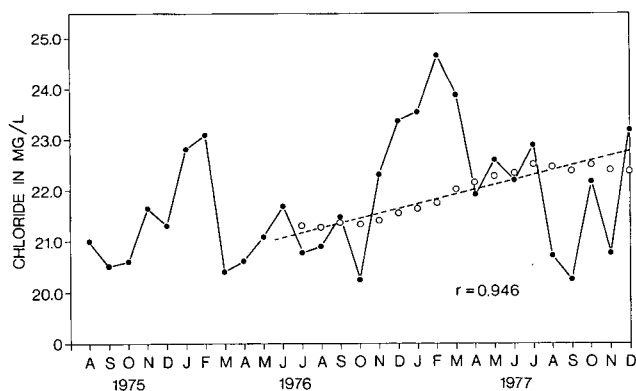
The seasonal variation in major ions concentrations and the year to year changes are related to the outflow of Lake Erie. Although linear correlation analysis (Table 6) failed to demonstrate any simple linear relationship between concentration and river discharge, the relationship could be found by examining the seasonal variations in chloride concentration and flow. As discussed before, the outflow of the Niagara River is the highest in March and April and the lowest in December and January (Fig. 3). The opposite is true for chloride (Fig. 11), being the lowest in March and April and the highest in January and February. The same can also be said of sodium (Fig. 12), calcium (Fig. 13) and other ions. This inverse relationship between concentration and river discharge is a result of dilution. Another factor

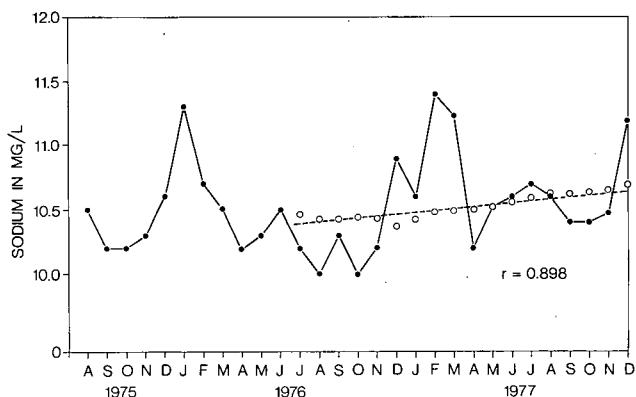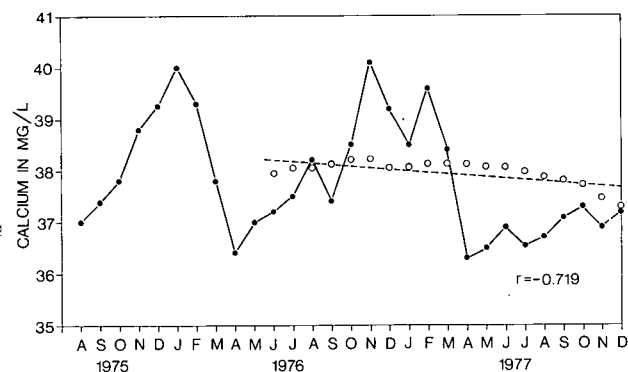Figure 11. Monthly average plot of chloride concentration.

Figure 12. Monthly average plot of sodium concentration.

Figure 13. Monthly average plot of calcium concentration.

Table 7. Niagara River Annual Loading

Parameter	1975	1976	1977
Phosphorus (metric tons per day)	11.69	13.59	11.78
Kjeldahl nitrogen (metric tons per day)	147.6	160.8	152.6
Nitrate + nitrite (metric tons per day)	44.5	130.8	91.5
Total nitrogen (metric tons per day)	189.7	292.5	24.38
Calcium (metric tons X 10^3 per day)	22.18	22.33	19.76
Magnesium (metric tons X 10^3 per day)	4.76	4.67	4.21
Potassium (metric tons X 10^3 per day)	0.78	0.78	0.74
Sodium (metric tons X 10^3 per day)	6.05	6.09	5.67
Chloride (metric tons X 10^3 per day)	12.24	12.56	11.76
Sulphate (metric tons X 10^3 per day)	14.60	14.79	13.08
Flow (cfs X 10^3)	247	237	215

which would explain this relationship is the seasonal input of salt in the winter months, thus raising the salt concentration in January and February.

Loadings

Tributary loadings are highly variable due to large fluctuations in flow and concentration. The concentration of chemicals in tributaries often varies with flow and depends on specific chemicals, season and tributary hydrology. Consequently, reliable measurement of tributary loadings would require very frequent sampling.

In estimating Niagara River loading into Lake Ontario, previous attempts have been based on a few water samples collected either on a quarterly basis or at irregular intervals, mostly between spring and late fall (Casey and Selbach, 1974). These loading data are usually subjected to statistical criticism because of the scarcity of data points and a lack of background variability. A biological and chemical understanding of the hydrology of the river and seasonal variation of the river is essential to reliable loading estimates.

Annual loading estimates for phosphorus, nitrogen and the main dissolved major ions are tabulated in Table 7. Loading figures for 1975 are based on the period from August to December. Mainly owing to a 9.3% reduction in outflow from 1976 to 1977, all chemical parameters show a significant reduction in loads, although not at the same degree as flow. Plots of 12-month moving averages of loading show a decreasing trend for all chemical parameters (Figs. 14, 15, 16 and 17). Total phosphorus load decreased by 13.4% from 13.59 metric tons per day to 11.77 metric tons per day. The total nitrogen load was reduced by 16.7%.

The IJC Great Lakes Water Quality Board (IJC, 1975) reported Niagara River phosphorus loading from 1967 to 1974 as follows:

	1967	1968	1969	1970	1971	1972	1973	1974
P (metric tons per day)	19.03	18.19	19.14	18.37	18.64	18.6	21.5	20.96
Flow (cfs X 10^3)	202	214	227	217	220	236	255	251

The IJC figures are considerably higher than the loading figures obtained from this study. According to these figures, phosphorus loading remained fairly constant, ranging between 18 and 21 metric tons per day from 1967 to 1974.

For the purpose of estimating material loadings, both the flow and the concentration terms have to be measured. Depending on the relative magnitude of fluctuations in flow and concentration, river loading can roughly be estimated from either one of the variables. Table 8 shows correlation of loading with river flow and concentrations. It is evident that there are two types of correlations. For nutrients, loading shows more correspondence with concentration than with flow, whereas the reverse is true for

Table 8. Linear Correlation Coefficients for Niagara River Loading

Parameter	Flow	Concentration
Phosphorus	0.263	0.966
Kjeldahl nitrogen	0.502	0.820
Nitrate + nitrite	0.358	0.980
Total nitrogen	0.447	0.949
Calcium	0.834	0.181
Magnesium	0.862	0.119
Potassium	0.812	0.126
Sodium	0.821	0.075
Chloride	0.573	0.135
Sulphate	0.874	0.383

dissolved major ions. This is because fluctuation in nutrient concentration is much higher than that of flow; the river flow is almost constant relative to the concentration term. The opposite is true for dissolved major ions.
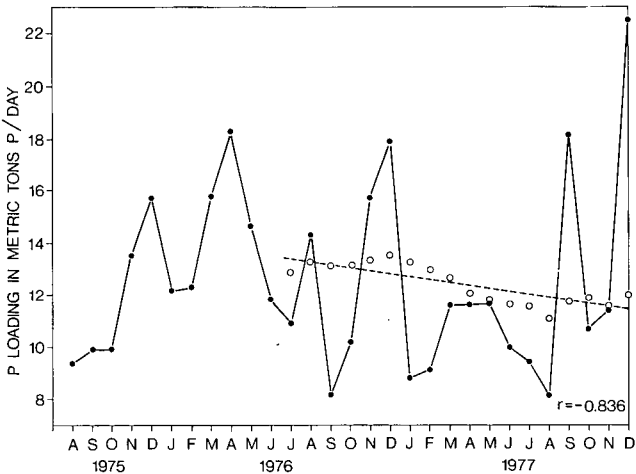

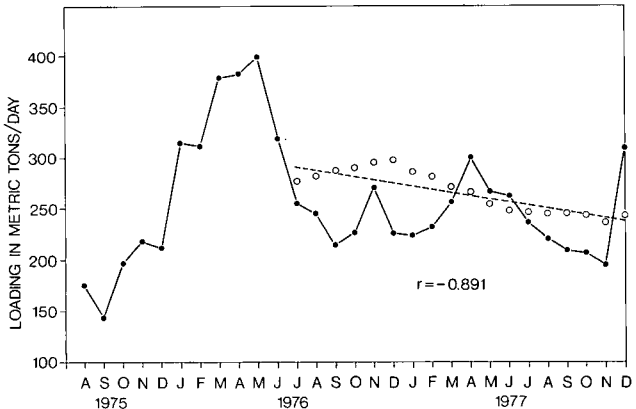Figure 14. Niagara River monthly phosphorus loading.

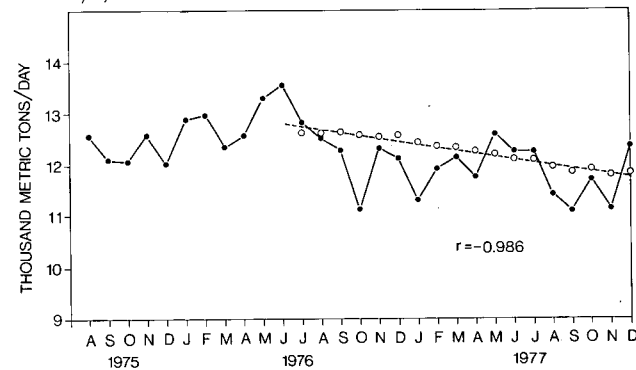Figure 15. Niagara River monthly nitrogen loading.

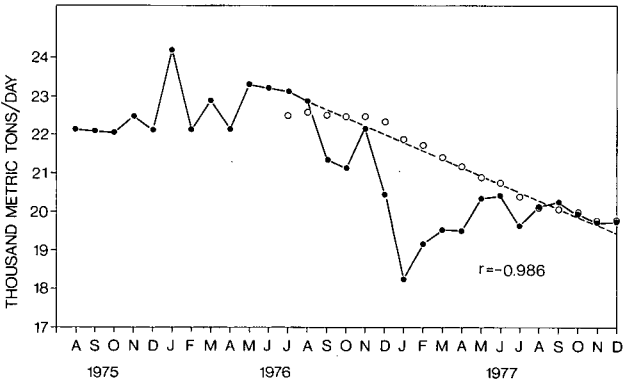Figure 16. Niagara River monthly chloride loading.

Figure 17. Niagara River monthly calcium loading.

Sampling Frequency

The design of river water quality sampling programs is a subject of considerable interest, since logistical and cost limitations make continuous measurement in both time and space impractical. The number of measurements must be balanced against the accuracy required for a particular study.

Intensive hourly sampling carried out in 1975 and 1976 at the same location has led to the recommendation that systematic sampling be adopted for Niagara River loading estimation; it indicated that phosphorus loading from daily sampling is accurate to about 10% to 15% of the hourly sampling program and major ions are accurate to about 3% (Chan and Clignett, 1978; El-Shaarawi and Whitney, in press). For most purposes, a sampling frequency of once per day is considered high unless the program objectives warrant such an effort. Sampling at a weekly, biweekly or monthly interval would be practical. To evaluate such sampling schemes, results were simulated and computed from the daily record and comparisons were made between the various frequencies of sampling. Since major ions are already measured on a weekly basis, only the nutrients were considered here.

Figure 18 graphically depicts the means and standard deviations of total phosphorus data for the three different sampling frequencies conducted for the 1977 data set. Seven sets of results are possible for sampling at weekly intervals, 14 sets for sampling at biweekly intervals and 28 sets for one sample every 28 days. It is obvious that sampling the same day every week gives the results closest to the annual mean concentration and standard deviation to within 5%. As expected, when the sampling frequency is reduced to once every four weeks, there is a much wider spread of the results, making them less reliable. For total nitrogen (Fig. 19) even at a sampling frequency of once every two weeks, the result is still within 3%.
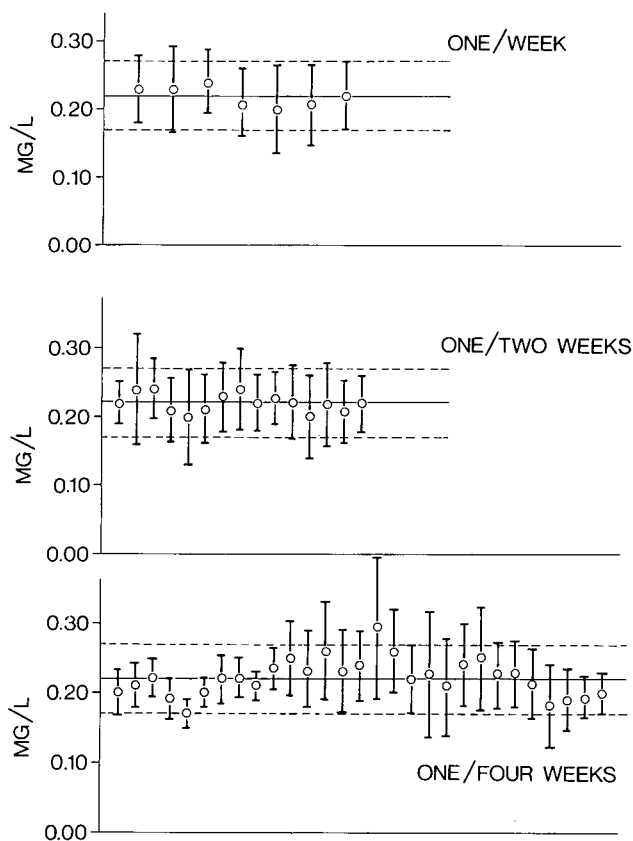
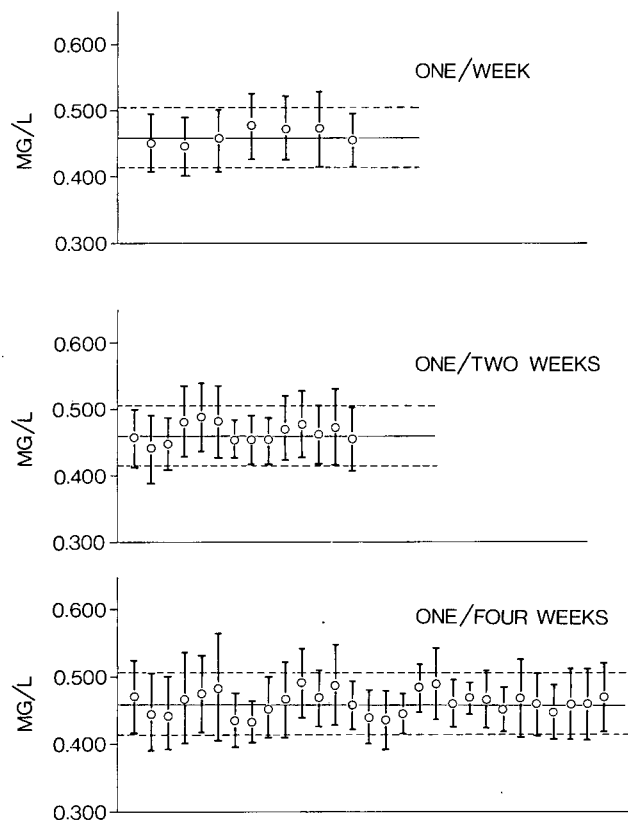Figure 18. Expected means and standard deviations for total phosphorus from reduced sampling frequencies.

Figure 19. Expected means and standard deviations for total nitrogen from reduced sampling frequencies.

SUMMARY AND CONCLUSION

Detailed analysis of the water quality data collected daily for 29 months at Niagara-on-the-Lake has identified short-term trends in some of the water quality parameters. These trends have been shown to be related to the annual outflow of Lake Erie. Refined loading estimates of the Niagara River into Lake Ontario have been computed. Different sampling frequencies for monitoring Niagara River loading and water quality are examined.

The 12-month moving average technique indicates that pH, phosphorus and nitrogen concentrations in the lower Niagara River have remained relatively stable. Dissolved major ions, calcium, magnesium and sulphate concentrations are decreasing, whereas specific conductance, sodium and chloride concentrations are increasing. Seasonal variation in major ions concentration has been observed to vary inversely to the outflow of the Niagara River, but the relationship is complex and not a simple linear one. The decrease in concentrations of calcium, magnesium and sulphate, whose origins are mostly natural, was caused by a decline in water supply to Lake Erie during 1977 when the outflow was reduced by 9% from the previous years. Sodium and chloride concentrations, owing to additional cultural inputs, have increased despite the decrease in natural load.

The annual phosphorus load for 1977 was 11.78 metric tons per day compared with 13.53 metric tons per day in 1976, a 13% decrease. This decrease is largely explained by a 9% reduction in the flow of the Niagara River. This figure is about 50% of the values reported by the IJC. Similar reductions in chemical loadings have also been detected in all the other parameters. For monitoring nutrient loadings, concentration is the determining factor, whereas for major ions loadings, flow is the dominant factor.

Results computed from different sampling frequencies suggest that a sampling frequency of once per week would yield results to within 5% of those from daily sampling. Any sampling frequencies less than one sample per week would adversely affect the reliability of the results.

ACKNOWLEDGMENTS

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