Fisheries and Environment Canada
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Water Quality Surveys on the Niagara River—1974

C. H. Chan

REPORT SERIES No. 48
(Résumé en français)

INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
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Abstract

Five water quality surveys were carried out from July to December of 1974 at Niagara-on-the-Lake to examine the cross-sectional, downstream and seasonal variation of the water chemistry of the mouth of the Niagara River. Sixteen surface water samples were collected for three consecutive days on each survey. The water samples were analyzed for nutrients, dissolved major ions, heavy metals and organic contaminants. Variance analysis of the results indicates that there is no lateral or cross-sectional variation in the water chemistry and that the variability in the water quality of the Niagara River is both parameter and season dependent.

Résumé

On a effectué de juillet à décembre 1974 cinq études de la qualité des eaux à Niagara-on-the-Lake pour examiner les variations transversales, en aval, et saisonnières des propriétés chimiques de l'eau à l'embouchure de la rivière Niagara. On a prélevé seize échantillons d'eau de surface trois jours de suite pour chaque étude et on les a analysés afin de déterminer la concentration des substances nutritives, des principaux ions, des métaux lourds et des contaminants organiques. L'analyse de variance des résultats indique qu'il n'y a pas de variations latérales ou transversales des propriétés chimiques de l'eau et que la qualité des eaux de la rivière varie selon les paramètres et les saisons.

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INTRODUCTION

The Niagara River receives municipal and industrial wastes from one of the greatest concentrations of population and industries within the Great Lakes Basin. The pollution of the Niagara River and its pollution abatement program have been the focus of attention of the International Joint Commission in 1961 and 1971. Different agencies from various levels of government have carried out intermittent surveillance programs on the water quality of the Niagara, but few data have been published.

The Water Quality Branch of the Ontario Region has conducted five river surveys at Niagara-on-the-Lake from mid-July to early December in 1974. The prime objective of these surveys is to determine the water quality of the Niagara River as it enters Lake Ontario. These water quality data provide input to the International Joint Commission in its annual assessment of the Great Lakes water quality, for material balance calculations in the Lake Ontario Basin and for other water management studies of the Great Lakes Basin.

This report summarizes the results from these surveys.

EXPERIMENTAL

On each survey 16 surface water samples were collected each day from three ranges located at the mouth of the Niagara River at Niagara-on-the-Lake (Fig. 1). Sampling was carried out for three consecutive days during each of the five surveys between July and December of 1974. The three ranges are approximately 1.0, 1.3 and 1.5 mi from Mississauga Point. The dates of the surveys were July 17-19, August 20-22, October 1-3, November 12-14 and December 3-5. The parameters measured are listed in Table 1.

Detailed methods of analysis are described in the *Analytical Methods Manual* from Inland Waters Directorate, Water Quality Branch, Ottawa, Canada, 1974.

Table 1. Parameters Measured

Physical	Temperature, pH, specific conductance, Secchi depth
Nutrients	Total phosphorus, total filtered phosphorus, orthophosphate, nitrate and nitrite, ammonia, reactive silicate, and total Kjeldahl nitrogen
Major ions	Sodium, potassium, calcium, magnesium, chloride, sulphate and alkalinity
Heavy metals	Iron, manganese, nickel, copper, lead, zinc, cadmium, chromium, arsenic, selenium and mercury
Others	Phenol, cyanide, NTA, PCB and pesticides

STATISTICAL TREATMENT OF DATA

A three-factor design analysis of variance was performed to evaluate the temporal (D), cross-sectional (T), and downstream (S) variation, in each parameter for each survey. The computer program used was the UCLA Biomedical computer program 08 V. The F value calculated for each factor is tabulated in Table 2 and the critical F values are obtained from mathematical tables. F values which exceed the critical F value indicate that the observed changes are significant at the 95% level and F values smaller than the critical F mean that the observed changes probably are not significant.

Confidence intervals for the mean concentration at 90% level for each parameter are calculated from Student (t) distributions using the following formula:

$$\left(\bar{x} - \frac{(s)\quad(t)}{\sqrt{n-1}}\right) \leq \bar{x} \leq \left(\bar{x} + \frac{(s)\quad(t)}{\sqrt{n-1}}\right)$$

where $\bar{x}$ = sample mean, s = standard deviation, t = statistics (t), n = number of samples.

Loading estimates are the product of the overall survey mean concentration and the mean daily flow data

Table 2. F Ratio for Three-factor Analysis of Variance

	July 17-19			August 20-22			October 1-3			November 12-14			December 3-4		
Parameter	D	T	S	D	T	S	D	T	S	D	T	S	D	T	S
pH	–	–	–	6.23	1.39	0.45	108.4	1.42	4.54	–	–	–	–	–	–
Conductance	–	–	–	0.06	0.92	1.11	4.44	0.10	1.03	2.56	0.52	0.98	45.85	1.30	0.22
Orthophosphate	14.57	8.33	3.76	0.41	4.30	3.35	4.15	0.46	1.00	17.18	3.24	0.20	0.99	1.00	1.00
Total P	48.09	1.36	3.03	19.99	1.65	0.94	0.93	1.02	1.00	586.9	0.11	2.68	1.08	1.03	1.04
TFP	114.5	1.33	3.53	1.07	0.99	0.99	1.03	0.99	0.99	29.97	0.85	0.10	1.04	0.97	1.00
NO_3	197.6	20.44	7.23	477.7	160.6	5.79	145.9	53.34	17.89	24.06	0.23	0.89	295.8	95.25	5.02
NH_3	156.2	4.42	21.70	2.74	1.64	2.91	10.92	3.95	5.65	2.16	4.22	0.13	10.32	2.69	1.14
TKN	50.89	3.05	0.84	7.08	0.22	1.35	4.30	1.68	2.83	1.35	2.38	0.68	1.55	0.60	0.61
Total N	52.39	11.44	1.48	10.29	1.39	1.44	63.86	2.44	4.40	3.35	2.28	0.62	0.79	1.11	0.61
SiO_2	14.81	0.21	0.39	97.72	26.59	3.96	0.61	6.38	2.19	0.60	7.68	9.48	17.31	8.00	3.06
Ca	55.54	9.85	0.33	118.70	1.85	0.69	–	–	–	1.06	0.87	1.11	0.89	1.03	0.98
Mg	–	–	–	11.39	12.55	0.30	–	–	–	–	–	–	0.99	0.90	0.96
K	5.19	6.16	0.11	5.90	6.18	2.57	–	–	–	3.96	4.98	2.35	0.92	1.21	1.10
Na	4.33	0.16	0.50	9.85	19.22	0.82	–	–	–	0.14	0.62	0.31	1.14	1.02	1.10
Cl	7.14	1.86	1.29	18.81	0.06	0.72	–	–	–	1.19	1.22	1.12	0.69	1.23	1.11
SO_4	13.21	2.29	0.78	7.21	1.91	0.98	–	–	–	4.96	0.89	0.56	0.81	1.02	1.00
Alkalinity	1.94	2.80	0.55	2.09	0.40	0.21	–	–	–	1.08	0.97	0.82	0.82	1.21	0.96

95 % Critical value D, 3.63; T, 3.63; S, 3.01
99 % Critical value D, 6.23; T, 6.23; S, 4.77

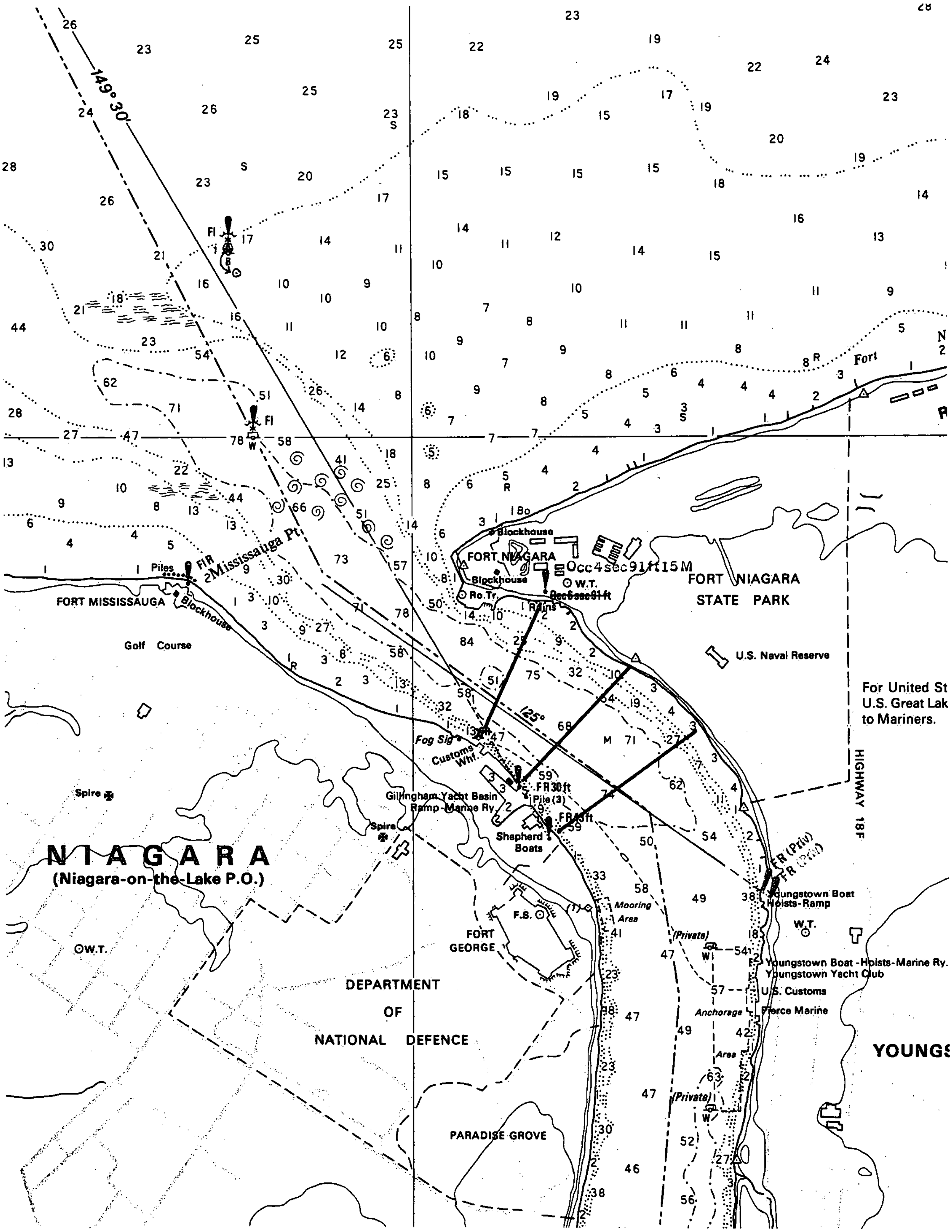

Figure 1. Location of survey sites.

for the corresponding month. The average annual load is the arithmetic mean of the five monthly figures.

RESULTS AND DISCUSSION

Variance Analysis

Results of the variance analyses are summarized in Table 2. F values for factor D are used to evaluate the changes in water quality from day to day during each survey, and F values for factors T and S are used for evaluating downstream and cross-sectional variations.

Most F values for downstream and cross-sectional variation (T and S) are less than the critical F values, indicating homogeneous or uniform distribution of the parameters.

Most of the F values for daily variation (D) which exceed the critical F occur in July and August, suggesting that changes in the chemical constituents of the Niagara River are more rapid in the summer than the fall and winter. The more rapid fluctuation in water quality in July is probably associated with the higher productivity in the water.

The largest variabilities are exhibited by nitrate + nitrite and reactive silicate, whose F values consistently exceed the critical F. These large variabilities are also reflected in the estimation of confidence intervals for the mean concentrations. Thus, it seems for the Niagara River, the degree of variability in water quality is seasonally as well as parameter dependent.

Confidence Intervals

The 90% confidence intervals for the mean concentrations for each parameter are shown in Table 3. For most of the parameters, the intervals are close to or within the detection limits of the analysis, with the exception of total Kjeldahl nitrogen, total nitrogen, and reactive silicate. The confidence interval for both total Kjeldahl nitrogen (TKN) and total nitrogen in November is .030 μg/l, about 8-10% of the estimated mean concentrations. Similarly, reactive silicate has a confidence interval of .014 μg/l in November, 10.6% of the estimated mean concentration. These large confidence intervals reflect the inherent variabilities associated with these parameters under the conditions in the Niagara River.

Nutrients

Table 4 shows the overall mean concentrations of the five surveys, while Table 5 shows the daily mean concentrations. The confidence interval for the mean concentrations at the 90% level and loading estimates are shown in Tables 3 and 7, respectively.

Most of the nutrient parameters showed considerable seasonal variation. Generally, nutrients were lower in summer and higher in fall and winter. Mean orthophosphate concentrations ranged between .002 and .007 mg/l and mean soluble phosphorus (TFP) concentrations were .008 to .012 mg/l. Total phosphorus concentrations were low in summer (.016-.018 mg/l) and higher in fall and winter (.021-.024 mg/l). Mean concentration for nitrate and nitrite decreased from .264 mg/l in July to .077 mg/l in October and increased to .169 mg/l in December. The summer mean value for ammonia was .028 mg/l and increased to .014-.048 mg/l in November and December. On the contrary, reactive silicate was high in July and August (.225-.291 mg/l) and lower in November and December (.114-.131 mg/l).

These observed seasonal variations in the nutrient parameters are attributed to the nutrient cycle in Lake Erie. Nutrient uptake or depletion in the summer months in the surface water of Lake Erie when productivity is high results in low nutrient concentration in the Niagara River in the summer months. During fall and winter when the lake water turns over, most of the nutrients are recirculated, resulting in a more even distribution of nutrients throughout the water column, thus explaining the higher nutrient concentrations in the fall and winter months in the river.

Dissolved Major Ions

Dissolved major ions show little variation within each survey; however, some seasonal variations are observed in calcium, chloride and sulphate. The mean concentrations for calcium in November and December, 37.87 mg/l, are about 1.0 mg/l higher than for July and August, 38.96 mg/l. For chloride and sulphate, the fall and winter mean concentrations are lower than in summer. The mean fall and winter concentrations for chloride are 22.21-22.56 mg/l and 23.22-23.39 mg/l in summer. The mean fall and winter concentrations for sulphate are 24.69-25.19 mg/l and 26.16-26.55 mg/l in July and August. Alkalinity shows a gradual increase from summer and winter. The lower

Table 3. Ninety Percent Confidence Mean Concentration Limits for Lower Niagara, 1974

Parameter	July 17-19	August 20-22	October 1-3	November 12-14	December 3-5
pH	–	7.98-8.01	8.22-8.31	7.76-7.86	8.14-8.24
Conductance (μmho/cm^2)	–	301-304	329-331	310-314	312-313
Orthophosphate (mg/l)	.003-.004	.002-.003	.002-.002	.006-.008	.007-.008
Total P (mg/l)	.017-.020	.016-.017	.021-.021	.021-.023	.023-.024
TFP (mg/l)	.009-.011	.007-.008	.007-.008	.010-.011	.012-.013
TKN (mg/l)	.206-.226	.199-.210	.271-.287	.298-.328	.268-.288
NO_3, NO_2 (mg/l)	.261-.267	.104-.108	.076-.079	.133-.140	.166-.170
Total N (mg/l)	.470-.490	.305-.316	.347-.366	.433-.464	.436-.457
NH_3 (mg/l)	.028-.029	.024-.024	.033-.035	.040-.043	.047-.049
SiO_2 (mg/l)	.222-.228	.287-.295	.134-.167	.124-.138	.107-.120
Ca (mg/l)	37.75-38.02	37.76-37.98	–	38.65-38.88	38.87-39.04
Mg (mg/l)	8.36-8.36	7.67-7.87	–	–	8.07-8.09
K (mg/l)	1.10-1.12	1.32-1.35	–	1.40-1.40	1.30-1.31
Na (mg/l)	10.92-11.00	10.52-10.65	–	10.48-10.54	10.29-10.34
Cl (mg/l)	23.13-23.30	23.29-23.50	–	21.84-22.57	22.41-22.71
SO_4 (mg/l)	26.27-26.83	26.08-26.25	–	24.61-24.77	25.07-25.23
Alkalinity (mg/l)	92.53-93.23	93.70-94.31	–	94.69-95.31	95.54-96.26

Table 4. Mean Concentrations for Niagara River Survey, 1974

Parameter	July 17-19	August 20-22	October 1-3	November 13-14	December 3-5
Temperature (°C)	22.2	23.0	15.3	10.3	4.6
pH	–	7.99	8.27	7.81	8.19
Conductance (μmho/cm^2)	–	303	330	312	312
Orthophosphate (mg/l)	0.003	0.002	0.002	0.007	0.007
Total P (mg/l)	0.018	0.016	0.021	0.022	0.024
TFP (mg/l)	0.010	0.008	0.008	0.011	0.012
TKN (mg/l)	0.216	0.205	0.279	0.313	0.278
NO_3, NO_2 (mg/l)	0.264	0.106	0.077	0.136	0.168
Total N (mg/l)	0.480	0.310	0.356	0.449	0.446
NH_3 (mg/l)	0.028	0.024	0.034	0.041	0.048
SiO_2 (mg/l)	0.225	0.291	0.150	0.131	0.114
Ca (mg/l)	37.88	37.87	–	38.76	38.96
Mg (mg/l)	8.37	7.77	–	–	8.08
K (mg/l)	1.11	1.33	–	1.40	1.31
Na (mg/l)	10.96	10.58	–	10.51	10.32
Cl (mg/l)	23.22	23.39	–	22.21	22.56
SO_4 (mg/l)	26.55	26.16	–	24.69	25.15
Alk. (mg/l)	92.88	94.00	–	95.00	95.9

Table 5. Daily Mean Concentrations for Niagara River Survey, 1974

	July			August			October			November			December		
	17	18	19	20	22	23	1	2	3	12	13	14	3	4	5
pH	–	–	–	8.07	8.02	7.96	8.44	8.08	8.29	7.73	–	7.89	–	8.07	8.31
Conductance*	–	–	–	.303	303	303	332	331	329	312	316	310	315	313	310
Orthophosphate (mg/l)	.004	.003	.004	.002	.003	.002	.002	.002	.003	.011	.006	.005	.007	.008	.008
Total P (mg/l)	.018	.012	.025	.018	.016	.014	.023	.021	.020	.018	.019	.030	.025	.024	.023
TFP (mg/l)	.009	.066	.016	.009	.008	.006	.007	.008	.008	.009	.010	.012	.013	.012	.011
TKN (mg/l)	.182	.216	.251	.215	.193	.206	.309	.267	.261	.316	.294	.328	.271	.271	.292
NO_3, NO_2 (mg/l)	.209	.255	.268	.112	.109	.097	.084	.075	.073	.126	.130	.152	.175	.167	.163
Total N (mg/l)	.451	.471	.519	.326	.302	.303	.393	.342	.335	.442	.424	.480	.446	.438	.455
NH_3 (mg/l)	.027	.026	.032	.025	.023	.024	.036	.033	.034	.040	.041	.043	.050	.046	.049
SiO_2 (mg/l)	.219	.238	.219	.307	.290	.276	.219	.134	.098	.155	.117	.122	.133	.106	.103
Ca (mg/l)	37.62	37.61	38.42	37.64	37.55	38.42	–	–	–	39.06	38.44	38.80	38.75	39.06	39.07
Mg (mg/l)	8.36	8.37	8.39	8.04	8.06	7.21	–	–	–	–	–	–	8.07	8.08	8.08
K (mg/l)	1.14	1.12	1.09	1.35	1.32	1.32	–	–	–	1.40	1.40	1.40	1.30	1.30	1.30
Na (mg/l)	10.88	10.97	11.03	10.54	10.49	10.73	–	–	–	10.39	10.61	10.54	10.31	10.31	10.29
Cl (mg/l)	23.09	23.12	23.44	23.37	23.77	23.05	–	–	–	22.64	21.96	22.03	22.51	22.44	22.74
SO_4 (mg/l)	25.83	26.38	27.43	25.94	26.41	26.15	–	–	–	24.77	24.80	24.50	25.14	25.05	25.27
Alkalinity (mg/l)	92.35	93.22	93.07	93.82	94.49	93.70	–	–	–	94.50	95.52	94.97	94.43	96.81	96.49

*μmho/cm^2 at 25°C

summer alkalinity concentration results from photosynthetic CO_2 update.

Changes in major ion concentration except for alkalinity are usually related to changes in inputs, runoff and flow, but are seldom a result of changes in aquatic productivity because of their abundance.

Heavy Metals

Metal analyses are divided into total and soluble forms. Determinations of mercury, selenium and arsenic are performed on unfiltered water samples only. Their mean, maximum, and minimum concentrations are summarized in Table 6. Over 50% of copper, iron, lead and zinc occur in particulate form. Almost all of the manganese is in particulate form. Cadmium and lead levels are about 1 μg/l. Mercury concentrations are less than the analytical detection limit of <.05 μg/l. Mean concentrations of selenium and arsenic are 0.05 μg/l and 0.44 μg/l, respectively.

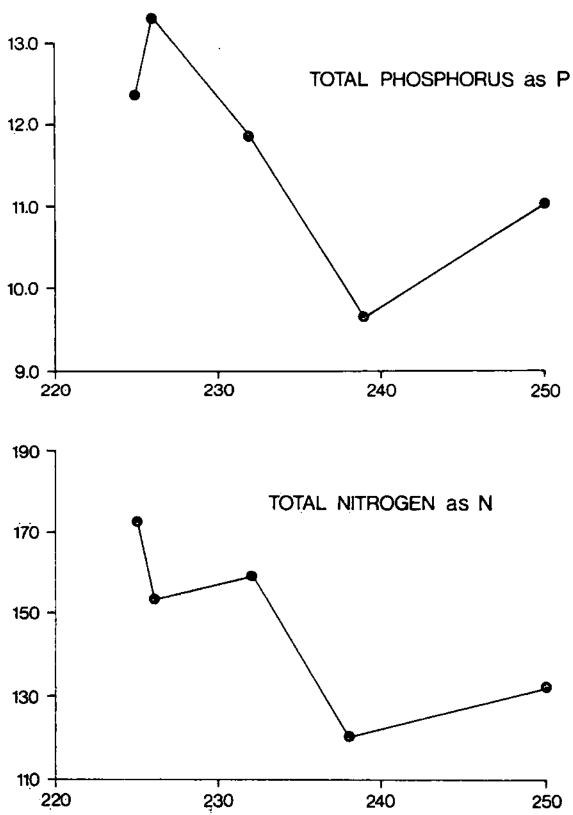

Figure 2. Niagara River loading (metric tons per day) vs. discharge (cfs x 10^3).

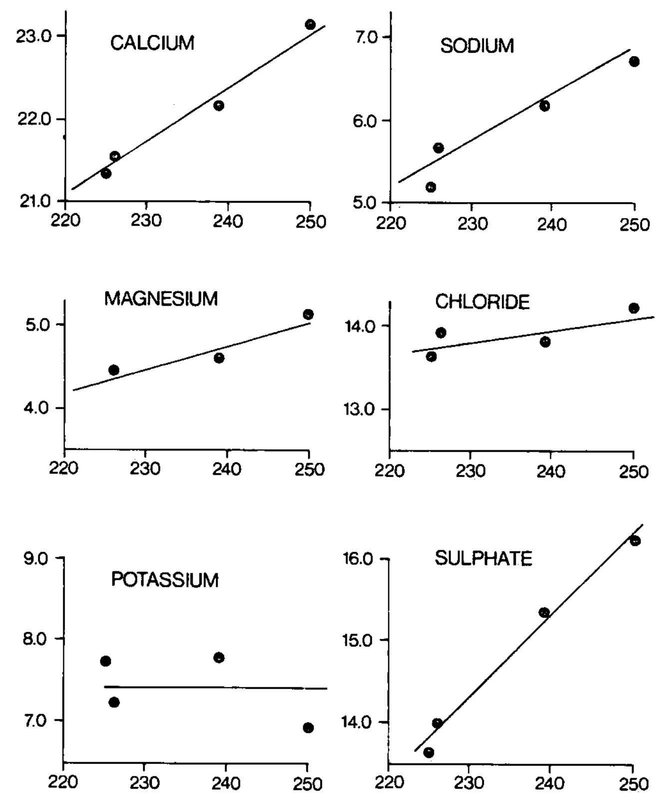

Figure 3. Niagara River loading (metric tons x 10^3 per day) vs. discharge (cfs x 10^3).

NTA, PCB and Pesticides

Concentrations of nitrilotriacetic acid (NTA), polychlorinated biphenyl (PCB) and organochlorine pesticides are below the detection limits (0.01 mg/l for NTA and 0.001 μg/l for PCB and pesticides) of the analytical methods.

Loadings

Loading figures are tabulated in Table 7. Total phosphorus loads vary from 10 metric tons per day in August to 13 metric tons per day in December, while total nitrogen loads range from 120 metric tons per day in August to 172 metric tons per day in December. Dissolved major ion loads are constant.

The variation of loading with flow (Figs. 2 and 3) showed that no predictable relationship exists between nutrient loads and flow, whereas major ion loads are linearly related to flow. The flow of the Niagara River is

Table 6. Mean Metal, Cyanide and Phenol Concentration ($\mu g/l$) in the Lower Niagara River, 1974

		Number of Observations	Mean	Max.	Min.
Cadmium	Total	40	1.0	2.0	<1.0
	Dissolved	60	0.2	12.0	<1.0
Copper	Total	44	4.7	33.0	1.0
	Dissolved	60	1.6	3.0	1.0
Iron	Total	44	147.0	400.0	3.0
	Dissolved	58	6.2	60.0	<1.0
Lead	Total	45	0.8	7.0	<1.0
	Dissolved	60	0.2	1.0	<1.0
Manganese	Total	30	17.6	140.0	4.0
	Dissolved	30	< 1.0	< 1.0	<1.0
Nickel	Total	45	2.8	14.0	1.0
	Dissolved	60	1.2	2.0	<1.0
Zinc	Total	45	7.8	18.0	4.0
	Dissolved	55	3.5	8.0	<1.0
Mercury		73	< .05	.05	< .05
Selenium		62	0.05	0.3	<0.05
Arsenic		62	0.44	0.7	<0.05
Cyanide		144	4.0	29.0	<1.0
Phenol		221	1.0	4.0	<1.0

Table 7. Niagara River Loading, 1974

	Metric tons per day of:		Thousands of metric tons per day of:						
	Total P	Total N	Ca	Mg	K	Na	Cl	SO_4	Flow (10^3 cfs)
July 17-19	11.01	132.13	23.16	5.12	0.69	6.70	14.22	16.2	250
August 20-22	9.59	119.88	22.15	4.54	0.78	6.19	13.69	15.3	239
October 1-3	11.92	158.38	–	–	–	–	–	–	232
November 12-14	12.17	172.32	21.34	–	0.77	5.18	13.59	13.59	225
December 3-4	13.24	153.73	21.54	4.47	0.72	5.71	13.91	13.91	226
Mean	11.59	147.29	22.05	4.71	0.73	6.10	13.85	14.15	234.4

closely regulated for optimal power generation, and for this reason its flow cannot be considered "natural." Nutrient loadings to Lake Ontario are primarily dependent on seasonal nutrient cycles in Lake Erie and not on the discharge of the Niagara River. Conversely, major ion loads can be estimated from flow measurements in the Niagara River.

CONCLUSIONS

1. Water samples collected at Niagara-on-the-Lake are representative of the water flowing into Lake Ontario. There is no lateral or cross-sectional variation in the water chemistry at the mouth of the Niagara River.
2. The variability in the water quality of the Niagara River is both parameter and season dependent. Phosphorus and nitrogen concentrations are low in summer and high in fall and winter. Variations in concentrations of all major ions are small. Variability is greater in summer than during fall and winter.
3. Heavy metal concentrations are generally low. Over 50% of the heavy metals are found in the particulate fraction of the water samples.
4. Concentrations of NTA, PCB and organochlorine pesticides are below the detection limits of the analytical methods.
5. Nutrient loadings are related to the seasonal variation in concentration, whereas dissolved major ion loadings are a linear function of flow.

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