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Ionic Constituents and Interparameter Relationships of Ottawa River Water at Lemieux Island

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IONIC CONSTITUENTS AND INTERPARAMETER RELATIONSHIPS OF OTTAWA RIVER WATER AT LEMIEUX ISLAND

PERFORMED AT
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by

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Job Title:	Chemical Data Analyst
Co-op Work Assignment:	Water Quality data gathered in the National Capital Region was analysed and the following report was prepared. Since the results presented within are confidential to Environment Canada, WQB, this report is not for circulation.

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ABSTRACT

In September, 1984 a Water Quality Monitoring Station was established on the Ottawa River at Lemieux Island. The study was designed to establish baseline conditions, monitor heavy metals and toxic contaminants and to assess microbiological and radionuclide concentrations in the National Capital Region. The study took place between September 1984 and March 1986.

This report discusses the general major ion chemistry and interparameter relationships during the study period. With the exception of the February 1985 to May 1985 period, major ion concentrations were constant over the life of the study. During the four months of change, concentrations were seen to first increase and then decrease, before returning to normal values. Linear correlations between parameters suggested a common cause for the observed concentration increases. These were determined to result from increased ground water input over the winter. Negative correlation which exhibited hysteresis was also observed between total dissolved solids and discharge.

INTRODUCTION

The Ottawa River descends a total height of 366 m from Lake Temiskiming to Pointe Fortune, at an average annual flow just under 2000 m^3/s. Its drainage basin is 146,000 square kilometers and is largely covered by igneous and metamorphic rock of the Canadian shield. A small area of limestone, dolomite, gypsum and other sedimentary rock makes up the remaining part of the basin. The hydrology of the Ottawa River is not typical of most rivers in Ontario. This is due to the fact that the Ottawa River is highly regulated by 834 dams located throughout the basin. These dams control discharge rates and water levels, thus maximizing hydroelectric power and minimizing flood damage to surrounding municipalities.

The Ottawa River provides water to 38 municipalities, including the Ottawa-Hull area, the 4th largest metropolitan area in Canada. Many industries also use water from the river, the most dominant is the pulp and paper industry with six mills located directly on the mainstem of the river. Not only is the water essential to industry, it also provides hydroelectric power, supports a nuclear energy facility at Chalk River and is vital to agriculture and forestry.

In September 1984 a study of the Ottawa River at Lemieux Island (700 m upstream of Chaudiere Falls) was initiated to establish baseline conditions, monitor heavy metals and toxic organic contaminants and to assess microbiological and radionuclide levels in the National Capital Region. This report discusses the general water classification and chemistry and also studies the influence of surface and ground water draining the carbonate rock of this area. Interparameter relationships and the effects of freshet (spring run-off) were also studied over this 18 month survey.

METHODOLOGY

Sampling

The monitoring station was established at Lemieux Island on the Ottawa River because it provided midstream sampling and ensured well mixed samples (Fig. 1). Water samples were collected on a weekly basis from September 1984 to September 1985 and then bi-weekly to March 1986.

A triple line intake system was secured on a stainless steel frame, 3 to 4 meters deep, in midstream. Three lines ran from the intake structure to a trailer which was equipped with a continuous flow centrifuge and various controls for the collection of raw and centrifuged water. All samples were transported back to the Water Quality Branch Laboratory in Burlington and analysed in accordance with methods outlined in Analytical Methods Manual, Environment Canada (1979).

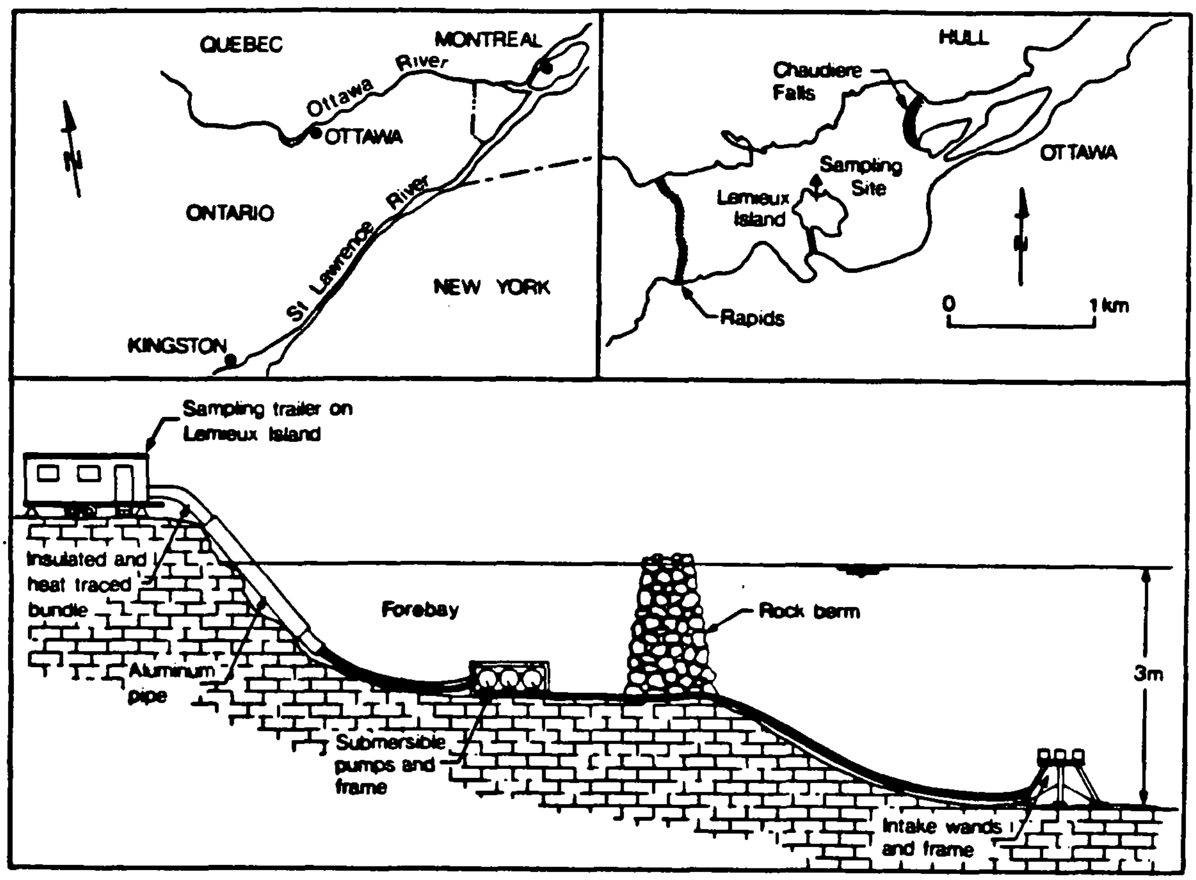


Figure 1. Lemieux Island monitoring station location

Data Interpretation

Arithmetic means and standard deviations were calculated for each parameter over one hydrological cycle (Sept./84-Sept./85) and not for the entire 18 months of the survey. This elminated possible skewing of the data caused by having two winter periods in the calculations. Total dissolved solid (TDS) was calculated by summing all the dissolved ionic species. This provided a method of measuring the total ionic constituents in the water sample.

Linear regressions, interparameter relations, time plots and relative percent abundance plots were done using the IBM microcomputer to identify any trends that existed.

RESULTS AND DISCUSSION

Discharge

During one hydrological cycle (Sept./84-Sept./85) it was noticed that the average winter discharge was greater than the average summer discharge. This trend seemed representative of historical discharge data and can be attributed to the reservoirs drain down period between December and April. The drain down is completed just prior to spring run-off, thus reducing flooding and maximizing hydro-electric power.

For the period September 1984 to September 1985 drain down at the Temiskaming Reservoir was from December 31, 1984 to April 8, 1985 (Fig. 3) and spring run-off occurred April 1, 1985 to June 5, 1985. The maximum discharge (4400 m^3/s) occurred during run-off, while the minimum discharge of 480 m^3/s recorded on September 26, 1985. A summer storm on July 31, 1985 caused discharge to jump from 792 m^3/s to 1830 m^3/s, but returned to normal summer rates within a week (Fig. 4).

Both discharge and water levels can effect the overall water chemistry, so it is important to observe their influence closely.

General Chemistry

Conductance

The mean conductivity value of the Ottawa River water sampled at Lemieux Island between September 1984 and September 1985 was 75 USIE/cm, with 80% of the values in the range of 56-96 USIE/cm. Higher conductivity values were found during the winter months due to the influx of ground water (Fig. 2). Total conductivity rose 37% between February and April 10, 1985. This rapid increase resulted from a constant ground water input coupled with low water conditions at the Temiskaming Reservoir causing a significant increase in the proportion of total water volume coming from ground water.

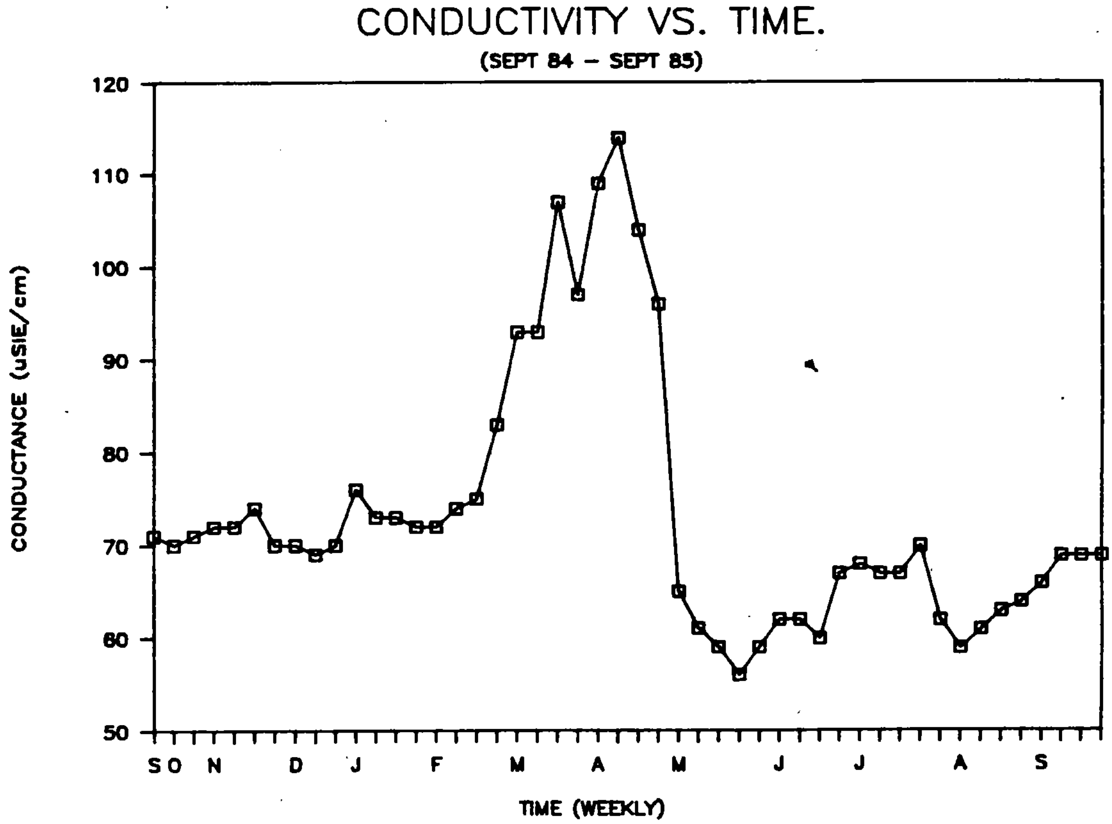
Following the maximum conductivity value (114 USIE/cm) on April 10, 1985, a 50% decrease occurred over the six week span of spring run-off. A 12% decrease also occurred after a summer storm on July 31, 1985. Both these decreases were due to an increase in discharge which flushed out the river system with low conductivity rain water causing dilution of the dissolved species in the river.

pH

The pH of Ottawa River water at Lemieux Island remained relatively constant with 80% of the values ranging between 6.7 and 7.5. There were no identifiable trends observed and no relationship existed between alkalinity and pH.

Alkalinity

Alkalinity is a measure of carbonate (CO_3) and bicarbonate (HCO_3) in water and is commonly expressed as concentration of calcium carbonate ($CaCO_3$). Alkalinity as in the case of conductivity is highly influenced by ground water. In the Ottawa River at Lemieux Island the river drains an area largely covered by carbonate-type rocks such as limestone and dolomite. During the winter months the influx of ground water was evident by the large increase in Alkalinity (18.2 - 36.6).



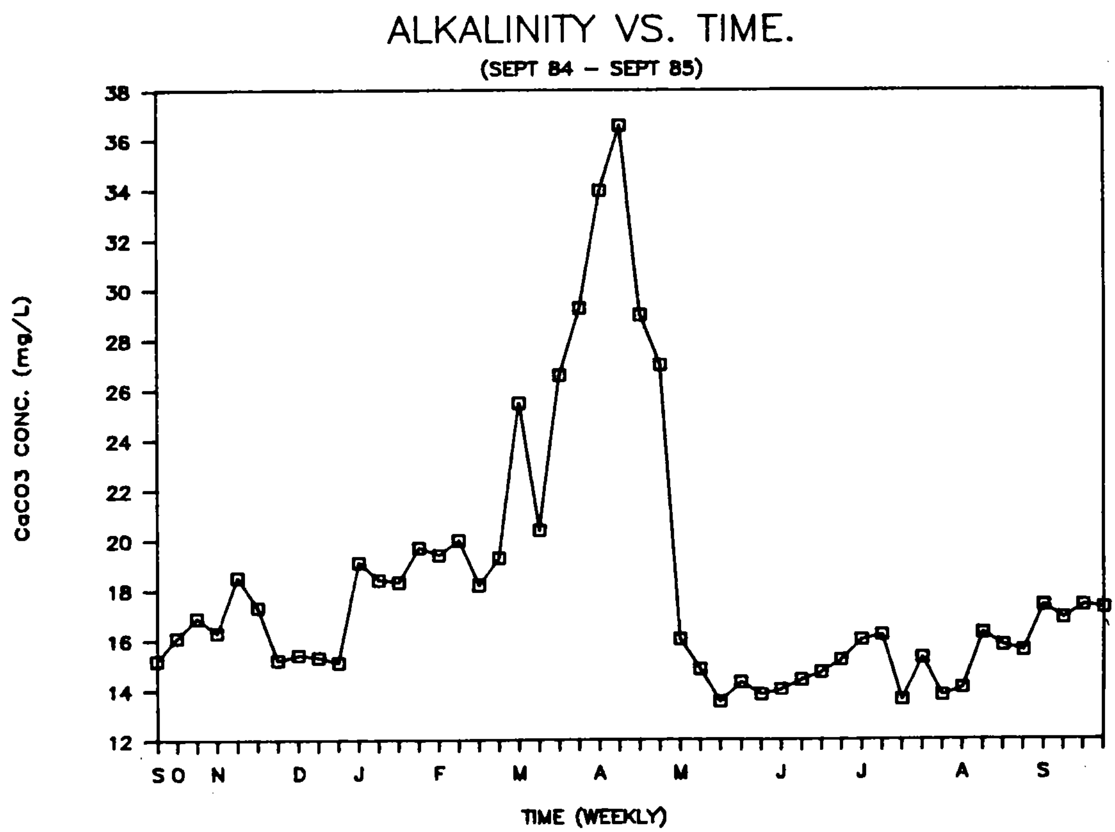


Figure 2. Conductance and Alkalinity vs. time

This increase was followed by a sharp decrease of 23.1 units over a five week period during freshet (Fig. 2). The summer storm on July 31/85 only marginally decreased alkalinity values.

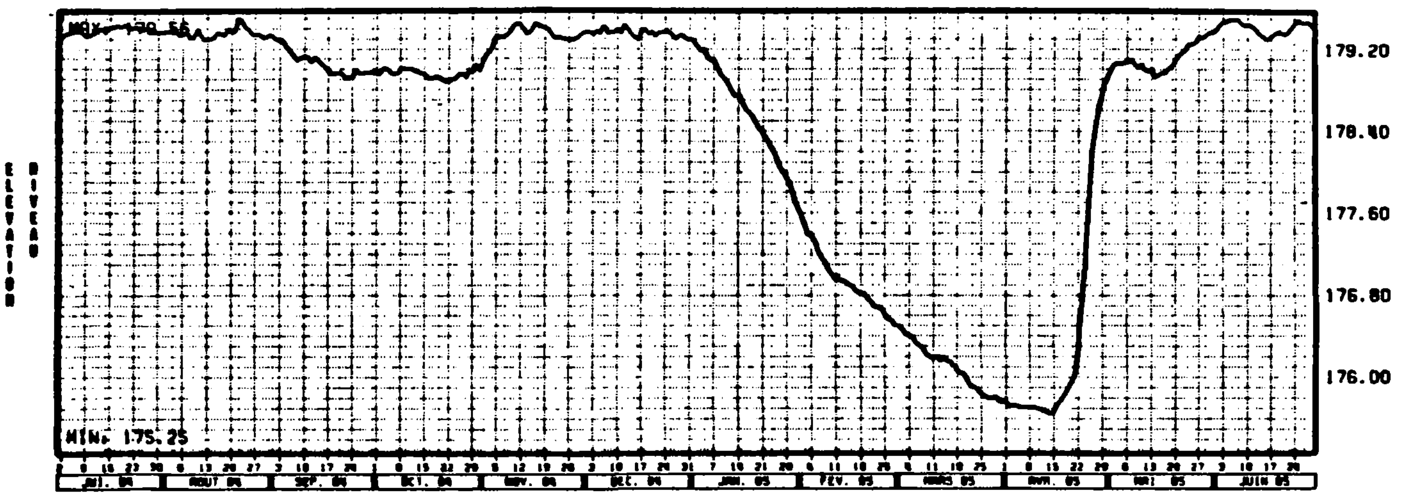


Figure 3. Water levels at Temiskaming Reservoir

Water Type

Water classification is done to convey general information about the predominant cations and anions in the water. When naming the water type if no one cation or anion represents 50% of the total major ions, then the water is recognized as a mixed type and is named according to the major constituents. Ottawa River water is classified as calcium bicarbonate sulphate water, since 80% (by mass) of the total ions are of the preceeding species. The remaining 20% of the major ions in decreasing abundance, are: Na, Cl, Mg and K (Table 1). Ottawa River water is also considered soft water (Hem, 1970), as the mean calcium carbonate concentration is 18.3 mg/L.

When Ca, HCO_3, and SO_4 were analysed individually with respect to time, Ca and HCO_3 appeared to respond similarly, while SO_4 concentration fluctuated independently (Fig. 4). Both Ca and HCO_3 concentration increased over the winter months while SO_4 values varied between 9.0 - 10.8. All three parameters did, however, decrease during freshet, HCO_3 decreased 63%, calcium 55%, and SO_4 24%. Another interesting event occurred in the summer during the storm on July 31, 1985. Calcium and bicarbonate concentrations decreased slightly while SO_4 decreased 19%. Both the decrease during freshet and the summer storm can be attributed to flushing out of the river and dilution as discussed earlier. The fact that Ca and HCO_3 only showed minor decreases indicated that the storm water had Ca and HCO_3 concentrations just slightly less than the river water, while SO_4 concentration must have been much lower. The minimum concentrations for the three predominant ions occurred during June-August and were in the following ranges: Ca (6.2-7.2), HCO_3 (8.3-9.9), and SO_4 (7.5-9.4).

The three major constituents were also analysed as percentages of total ions. The relative percent abundance of Ca, HCO_3, SO_4 and the remaining ions were calculated and plotted against time (Fig. 5). The percent bicarbonate remained relatively constant (30.9 $\pm$ 2.8%) except during the time period March 6, 1985 to April 24, 1985 when an 8% increase occurred. This 8% increase in bicarbonate was balanced by a corresponding decrease in percent sulphate. This relative change was attributed to an influx of water with higher HCO_3 and lower SO_4 concentrations than the river water. As a result of a shift in the equilibriums of $CaCO_3$ (limestone) and $CaSO_4$ (gypsum) no relative change in percent Ca occurred (22.2 $\pm$ 1.1%) over the period.

TABLE 1. STATISTICAL SUMMARY OF THE MAJOR IONS. (SEPT 84 - SEPT 86)

	HCO3	Ca	Cl	K	Mg	Na	SO4	pH	ALK
MEAN	11.2	7.93	2.2	0.8	2	2.2	9.4	7.1	16.3
STANDARD DEV.	3.2	1.69	0.7	0.1	0.4	0.5	0.9	0.3	5.3
10th PERCENTILE	8.5	6.3	1.5	0.7	1.6	1.7	8	6.7	14
90th PERCENTILE	16.2	10.71	3.2	0.9	2.6	2.8	10.4	7.5	26.6
% ABUNDANCE (mass)	30.9	22.2	6.1	2.3	5.7	6.2	26.7	--	--
% ABUNDANCE (mileq)	24.5	26.7	8.4	2.7	11.3	13.1	13.2	--	--

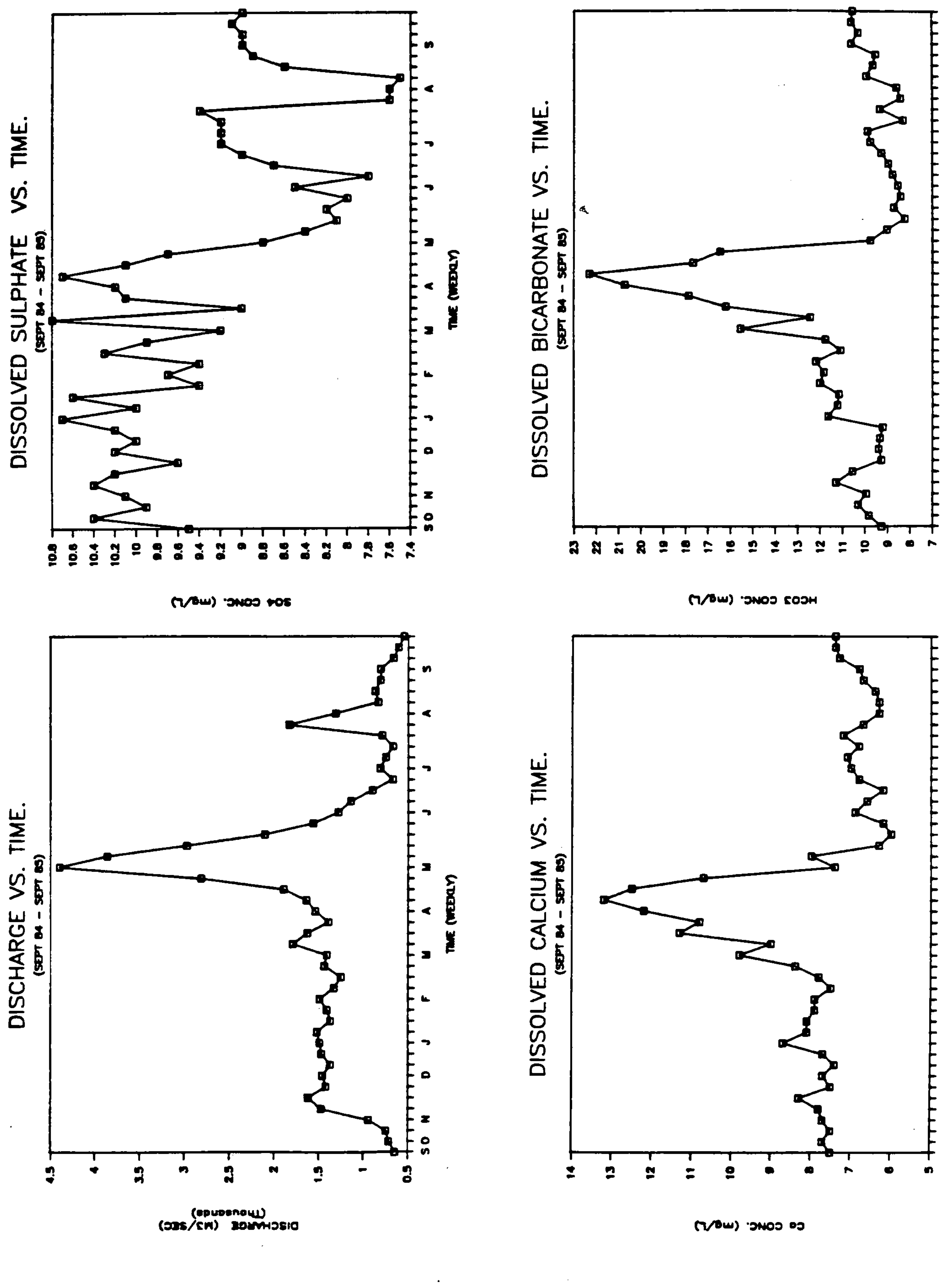


Figure 4. Hydrographs and chemographs for the Ottawa River

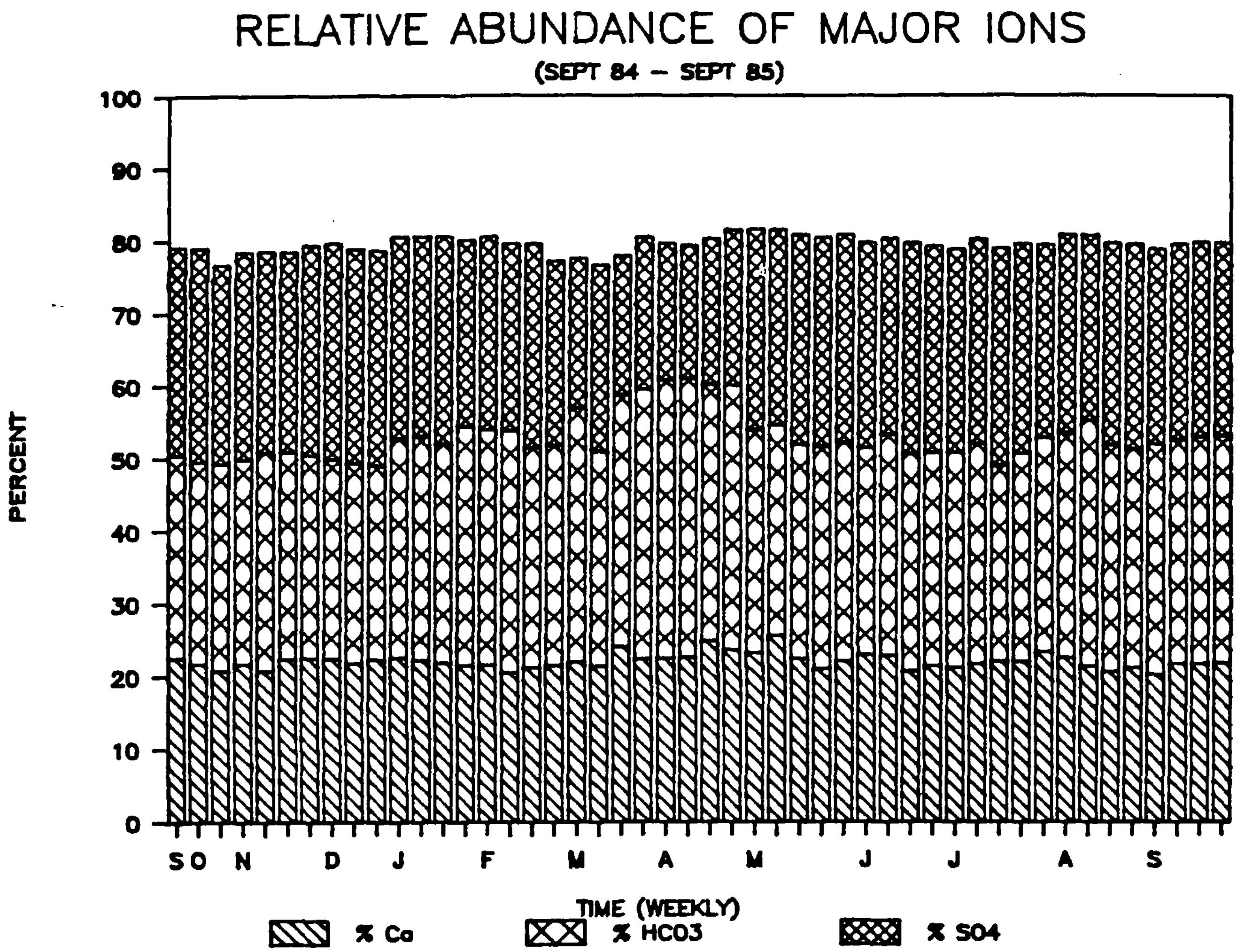


Figure 5. Percent relative abundance of the major ions

Interparameter Relationships

This section will discuss linear and non-linear interparameter relationships. A linear interparameter relationship exists when one parameter increases or decreases with respect to a corresponding parameter. The quantity R^2 is called the coefficient of correlation and is a measure of positive or negative linear correlations. A relatively strong linear correlation exists when the coefficient of correlation approaches 1.0. A non-linear interparameter relationship is any relationship existing between two parameters that can be described mathematically but not using the relationship $y = ax + b$ (a + b equal constants). Correlation coefficients were studied to establish baseline conditions on how the dissolved species are interrelated, which in turn, will help identify any cause in change of the water chemistry in the future.

In the Ottawa River, calcium and magnesium had a correlation coefficient of 0.95. This was not surprising as both ions are members of the alkaline earth metals and have similar chemical and physical properties, therefore, they should respond similarily in the same environment. On the other hand, sodium and potassium are both elements of the alkali metals and had a poor correlation coefficient (R^2 = 0.50). This poor relationship may be attributed in part to the consistency of potassium concentration and the fact that Na can be artifically changed by man.

Conductivity is often used as a measure of Total Dissolved Solids (TDS). This relationship holds true for the Ottawa River as the correlation coefficient for conductivity and TDS was equal to 0.94. Conductivity also showed a good positive correlation with alkalinity, calcium, magnesiuim and sodium. Other parameters with high correlation coefficients were alkalinity vs. calcium and magnesium and sodium vs. chloride. Sulphate and potassium had poor correlation coefficients with all other parameters, which indicated little or no interparameter linear relationships existed (Table 2).

Discharge showed no correlation with any of the major ions. The highest coefficient was 0.03 which was between discharge and calcium. On further analysis of discharge vs major ions (TDS) it was discovered that a non-linear relationship did exist. Figure 6 shows this non-linear relationship existing between TDS and discharge over one hydrological cycle (Sept./84-Sept./85). This relationship known as a hysteresis loop was due to the lagging (in time) of a physical effect (concentration change) in relation to its cause (discharge).

In Figure 6, point A represents the start of one hydrological cycle September 25, 1984 (TDS conc. 33.2 mg/L). From point A to B concentrations increased from 33.2 mg/L to 38.9 mg/L due to the influx of ground water during the winter. Discharge also increased over this period from 647 m^3/s to 1440 ,^{3}/s. From point B to C water levels reached a minimum at the Temiskaming Reservoir, thus amplifying the effects of ground water input and increasing the concentration 33% to a maximum.

Freshet occurs from C to E with a maximum discharge (4400 m^3/s) occurring at point D. From point C to D a 45% decrease in concentration occurred but due to the lag in time the minimum concentration did not occur at maximum discharge. The minimum concentration (27.9 mg/L) occurred at point E 4 weeks after maximum discharge, thus creating the hysteresis loop. After spring run-off a very slow and marginal increase in TDS concentration (29.9 mg/L to 33.8 mg/L) occurred between point E and F. A summer storm was evident at point G as discharge increased from 792 m^3/s to 1830 m^3/s and concentration decreased 13% following the hysteresis loop pattern.

TABLE 2. R SQUARED VALUES FOR MAJOR ION INTERRELATIONSHIPS. (SEPT 84 - MAR 86)

PARAMETERS	ALK	Ca	Cl	Mg	K	Na	SO4	T.D.S	COND.
ALKALINITY	=========								
CALCIUM	0.9	=========							
CHLORIDE	0.62	0.66	=========						
MAGNESIUM	0.87	0.95	0.65	=========					
POTASSIUM	0.35	0.36	0.38	0.32	=========				
SODIUM	0.65	0.65	0.74	0.63	0.5	=========			
SULPHATE	0.18	0.27	0.4	0.33	0.21	0.31	=========		
TOTAL DIS. SOLIDS	0.93	0.95	0.77	0.93	0.43	0.76	0.38	=========	
CONDUCTIVITY	0.89	0.81	0.66	0.76	0.31	0.66	0.29	0.94	=========
FLOW	0.01	0.03	0.001	0.01	0.002	0.03	0.003	0.006	0.002

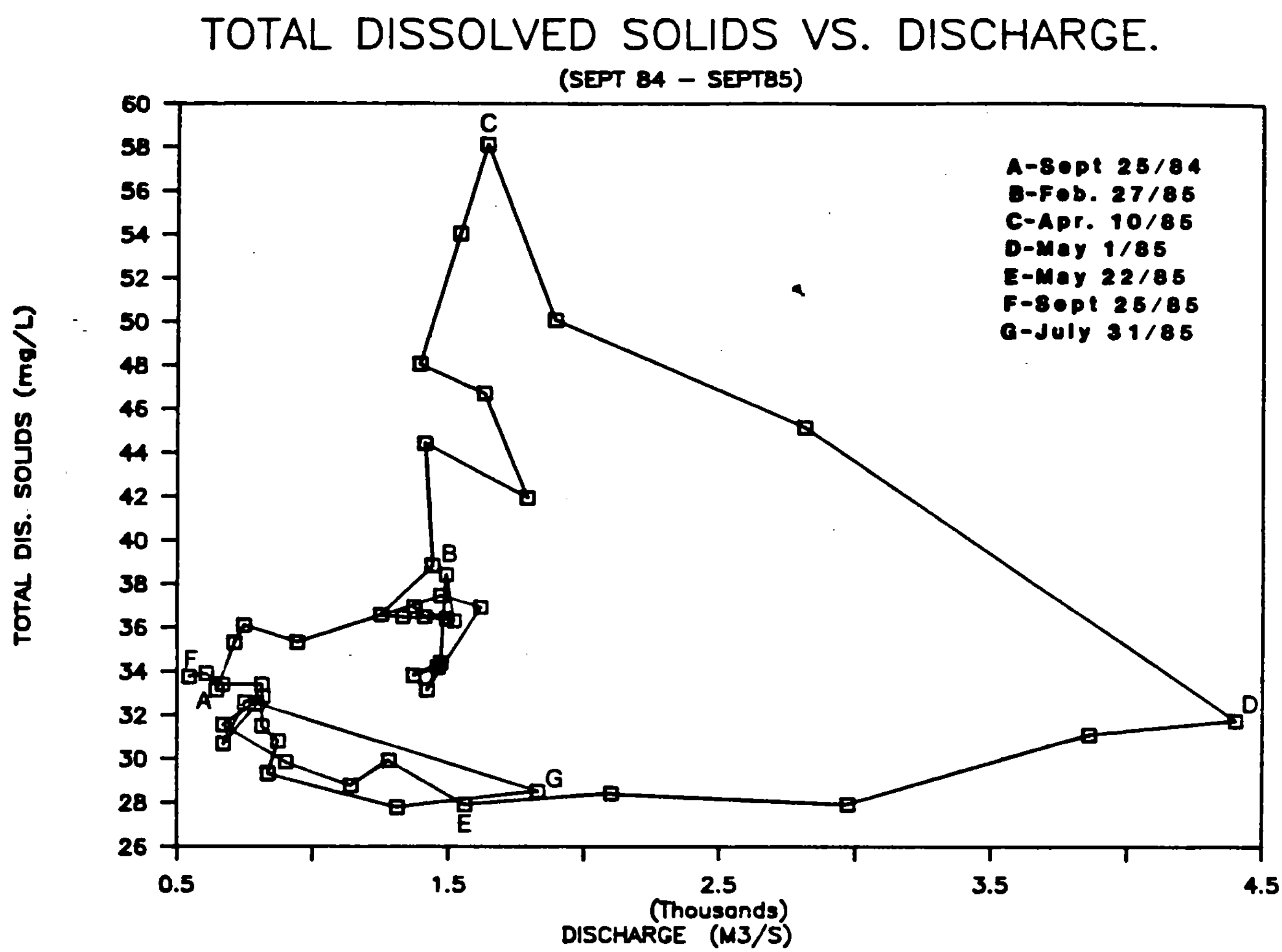


Figure 6. Non-linear relationship between t.d.s. and discharge over one hydrological cycle

SUMMARY

The water classification of the Ottawa River water at Lemieux Island was soft calcium, bicarbonate sulphate water.

The water chemistry was relatively constant throughout the year, except during the period of February to May. Over the winter months all major ion concentrations (except K, SO_4) increased 35 to 50%. Freshet and the summer storm event also influenced the dissolved ion concentrations, decreasing values up to 63% during spring run-off and up to 19% after the summer storm. Even with these large deviations in concentrations the relative abundance of the three major ions (Ca, HCO_3, SO_4) still remain constant (80%).

Linear interparameter relationships were identified and a non-linear relationship between total dissolved solids (major ion except K, SO_4) and discharge was observed. The relationship illustrates a lag (in time) between cause and effect which creates the hysteresis loop and explained why the minimum concentrations did not occur at the maximum discharge.

RECOMMENDATIONS

1. Owing to the fact that the hydrology of the Ottawa River varies substantially from year to year, sampling should be continued over a five year period to better define seasonal trends, interparameter relationships and the effects of run-off.

2. Future sampling should be conducted on a biweekly basis except during the period of large variation (February-May), when sampling should be increased to weekly to better monitor the effects o the deviations.

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