

TEMPORAL PATTERNS OF ACIDIFICATION OF RIVERS IN
NOVA SCOTIA AND NEWFOUNDLAND AND THEIR
RELATIONSHIP TO SULPHATE EMISSIONSG.D. Howell¹, P.E.J. Green², C.A. Field³ and B. Freedman⁴

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ABSTRACT

Twenty-eight rivers in Atlantic Canada are sampled monthly, and have periods of record dating back as far as 1965. Statistical analysis of water chemistry for rivers in areas of Nova Scotia and Newfoundland that are believed to be sensitive to acidification has revealed that pH was significantly lower during the late 1960's and early 1970's. Annual hydrogen ion export for selected rivers was also greater during this period. This period of relatively low pH and large hydrogen ion export corresponds to a peak of North American sulphur dioxide emission, suggesting that these rivers may be responding to atmospheric loading of anthropogenic mineral acids.

INTRODUCTION

The Atlantic provinces are downwind of large sources of emission of SO₂ and NO_x (Shaw, 1979), and they receive acidic precipitation due to the long-range transport (LRTAP) of these atmospheric pollutants. The bedrock and glacial till of much of Atlantic Canada is comprised of hard siliceous and granitic minerals, which resist chemical weathering. This fact coupled with a thin overburden of soil, results in dilute surface waters which are sensitive to acid precipitation. Clair *et al.* (1981) used a limited set of surface water data to prepare maps of LRTAP-related variables which indicated that southwestern Nova Scotia and much of insular Newfoundland are sensitive to acidification. This suggests that even though the atmospheric deposition of sulphate is less than an advocated target loading of 20 kg SO₂(wet)/ha.yr (MOI, 1983), there may nevertheless be a great potential for acidification of surface waters in Atlantic Canada.

Previous studies of water chemistry in Atlantic Canada have indicated that the acidity of certain lakes (Watt *et al.*, 1979) and rivers (Clair and Whitfield, 1983; Thompson, 1986) may have increased as a result of acidic deposition. However, these studies only examined relatively short time-records for a few surface waters, in contrast to the present study in which time series of up to 21 years were examined for 28 rivers throughout Atlantic Canada. This is the largest, most comprehensive set of chemical data for surface waters in Atlantic Canada, and it is

therefore important for the determination of regional acidification.

METHODS

The water quality samples were collected at 28 gauged rivers in the four Atlantic provinces (Figure 1), at variable but approximately monthly intervals. The period of record ranges up to 21 years. The chemical analyses were performed at the Water Quality Branch laboratory in Moncton, New Brunswick, using standard methods (pH method code 10301) described in the NAQUADAT Analytical Methods Manual (Environment Canada, WQB, 1979).

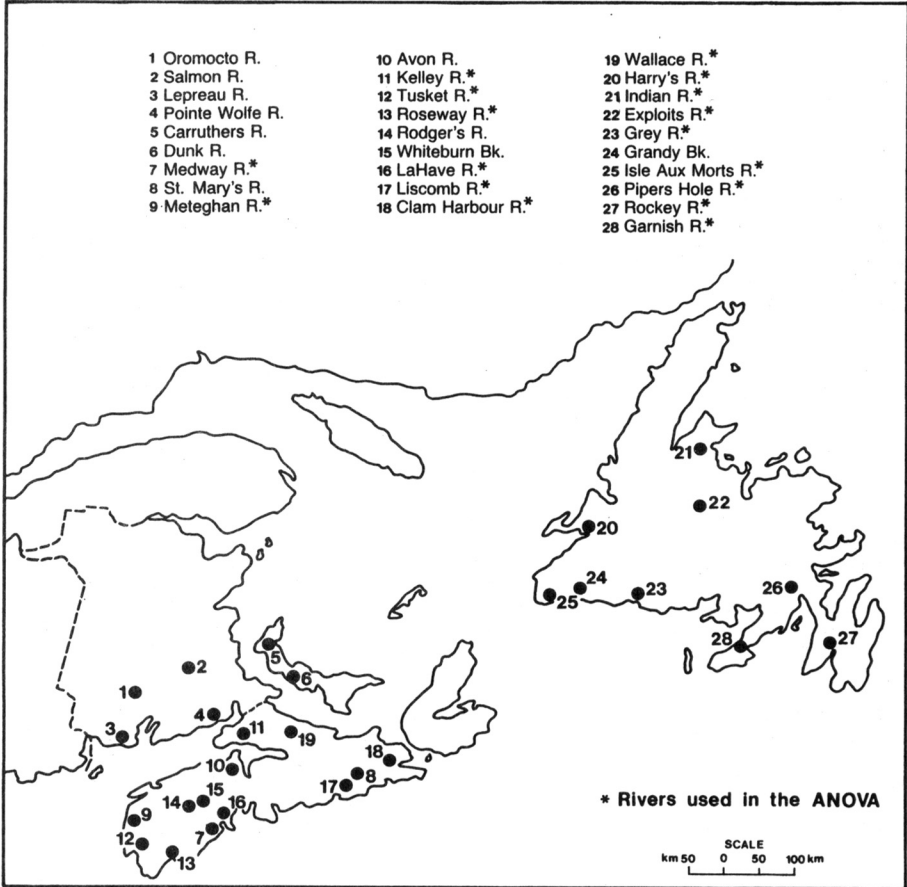


FIGURE 1: Locations of the twenty-eight study rivers which were considered in the analysis.

Our primary approach was to employ statistical analysis as an exploratory tool rather than for model-fitting or hypothesis testing. Temporal patterns which were observed graphically were submitted to more detailed statistical modelling, in order to compute statistical parameters which describe the data and to test whether there was evidence that the patterns could be due to random temporal variation. The results of the graphical analyses and any resulting hypotheses were linked by linear models. These models were basically two-way ANOVA's of median values that were weighted according to the number of observations used in their calculation. The two factors used were river and year, thus enabling an estimate of year effects after accounting for river effects, using the variance model given below:

$$y_{ij} = \text{mean} + \text{river } i \text{ effect} + \text{year } j \text{ effect} + \text{error}$$

The appropriate F-statistic was computed and the corresponding P-value was determined. For this analysis a small value of P indicates that there is a year effect and a large r^2 indicates a good fit of the model to the data. The estimate of the year effect divided by the standard error was used to determine which particular years had statistically significant year effects, using an arbitrarily chosen t-statistic cut-off point of 2. For the purposes of the present report, the analysis was carried out on nine Nova Scotia rivers and eight Newfoundland rivers, using the entire data set as well as three subsets of spring, summer and winter data. These particular rivers were chosen for consideration here, as they drain watersheds that are believed to be susceptible to acidification.

Annual hydrogen ion exports were calculated for selected rivers using several different methods. Annual mean concentrations were weighted using either daily or monthly mean discharge, and then multiplied by the annual discharge to calculate the annual export, using the formula given below:

$$\left(\begin{array}{c} i=1 \\ \sum [C_i \times (Q_i / \sum Q_i)] \\ n \end{array} \right) \times Q_{\text{annual}}$$

In addition, individual daily values were calculated and scaled to annual exports using either daily and monthly mean discharge, and all the annual estimates were then used to calculate the annual median and interquartile range.

RESULTS

Although the statistical analysis investigated several water quality variables, only the results of the pH data set will be considered here. Statistical methods used and the results obtained are reported by Green *et al.* (1986).

Running medians of pH for selected Nova Scotia and Newfoundland rivers (Figure 2) indicate that relatively low median pH values were frequent during the late 1960's and early 1970's. After 1973 the pH tended to increase to a level approximately equal to or greater than that observed at the beginning of the data record. The ANOVA tables for the Nova Scotia and Newfoundland river pH data are presented in Table 1, and indicate that periods of low pH were most frequently observed during 1967 to 1983. The Newfoundland rivers appear to have a strong seasonal component, with significantly lower spring pH values from 1967 to 1973 (Table 1).

TABLE 1: Statistically Significant Year Effects for pH of Selected Nova Scotia (9) and Newfoundland (8) Rivers

Year	NOVA SCOTIA				NEWFOUNDLAND			
	All Data	Spring ¹ Data	Summer ² Data	Winter ³ Data	All Data	Spring Data	Summer Data	Winter Data
1966								
1967								
1968						-.31		
1969						-.40		
1970			-.25		-.27	-.24		
1971			-.31			-.35		-.31
1972	-.18 ⁴		-.41		-.30	-.22	-.42	-.70
1973	-.24			-.43	-.34	-.34		-.32
1974					-.23	.27		
1975	.29							
1976								
1977								
1978	.60		-.40					
1979								
1980								
1981								
1982			-.30					
1983								
1984	.13							
1985								
P	.001	.05	.001	.05	.001	.001	.001	.001
RSquare	.98	.95	.97	.93	.88	.81	.68	.73

- 1 March to May
- 2 June to September
- 3 December to February
- 4 Direction and magnitude of change in median pH relative to 1965

Plots of the fitted yearly pH values from the ANOVA model for the Nova Scotia and Newfoundland rivers are given in Figure 3. It should be noted that the pH values on these figures are provincial composites and as such represent generalized temporal patterns. The pH of the Nova Scotia rivers decreased slowly from 1966 and reached a minimum in 1973. After 1973, the pH began to increase and there was a period of highly variable values between 1975 and 1980. Following this, the median pH values appeared to stabilize at levels similar to those observed during the early part of the data record. The temporal pattern of pH in Newfoundland rivers is similar to that observed for the Nova Scotia rivers.

Figures 4 and 5 present estimates of hydrogen ion export for two rivers in Newfoundland, using the four alternate methods of calculation. Regardless of the method used, the mean and/or median hydrogen ion exports were highest during the early part of

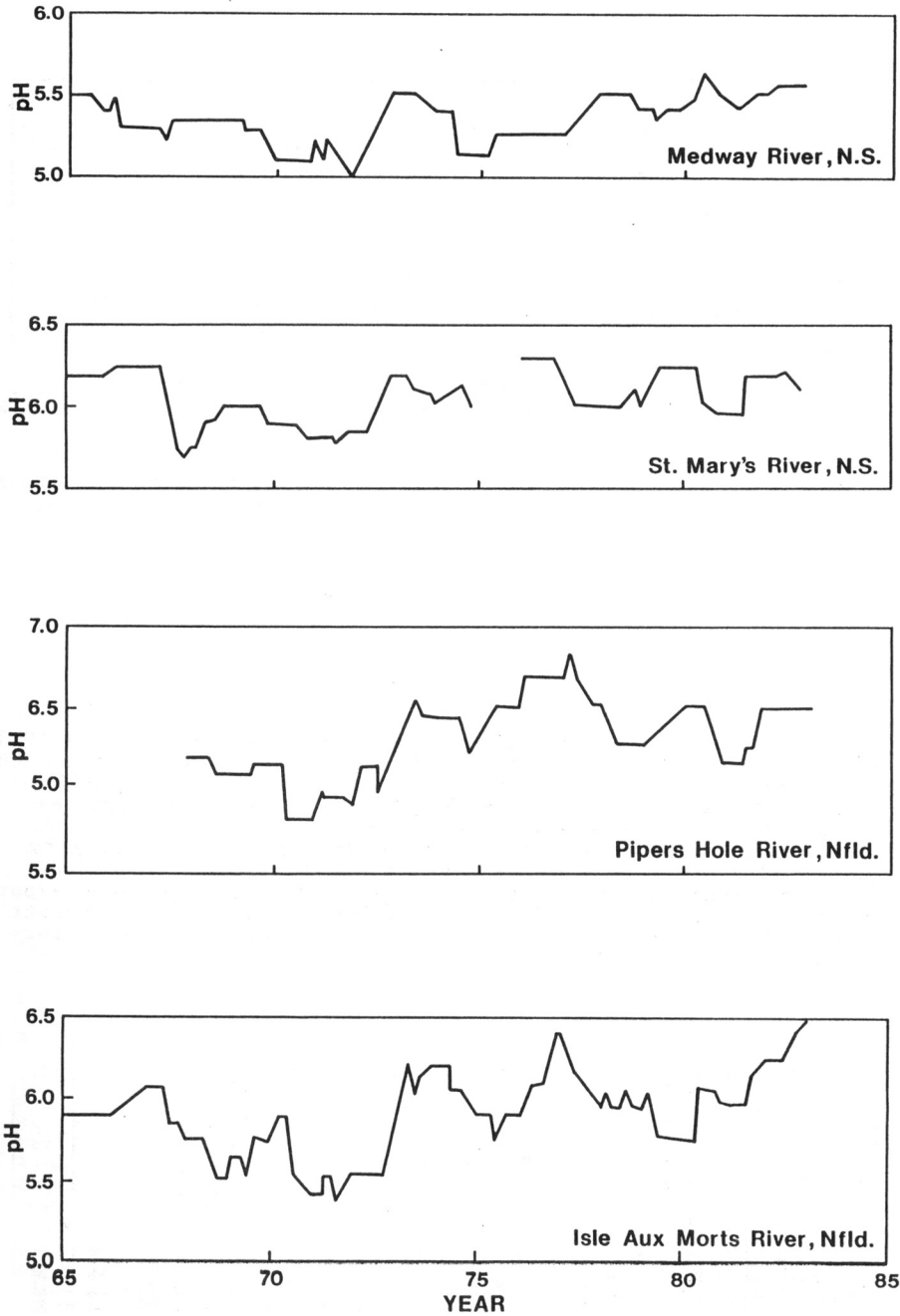


FIGURE 2: Running median pH values over the twenty year sampling period for four selected rivers.

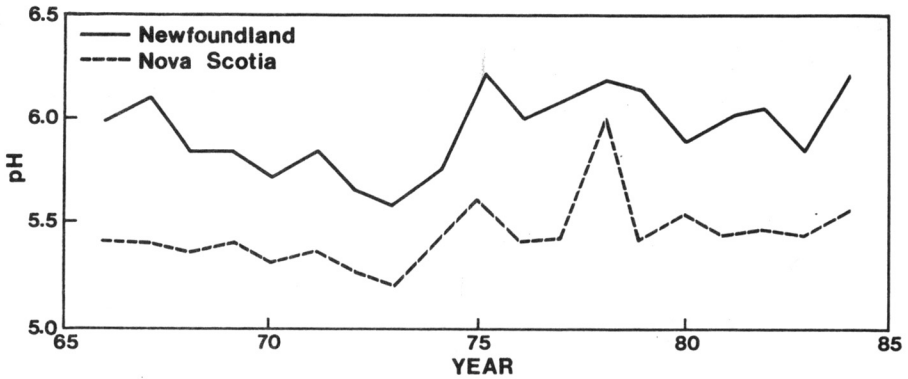


FIGURE 3: The annual fitted median pH values from the ANOVA model for the Nova Scotia and Newfoundland rivers.

the data record, and they generally peaked during 1972 and 1973. From 1975 to 1984 hydrogen ion exports decreased, with the exception of slightly elevated values observed during 1982 and 1985. In addition, the interquartile ranges of the export estimates were considerably larger during the early portion of the record. Although some of this decrease in variability is undoubtedly the result of improved analytical quality control, it may also indicate a higher frequency of high hydrogen export events during 1969 to 1974. Similarly, larger interquartile ranges observed during 1982–1983 may also be indicative of larger hydrogen export events.

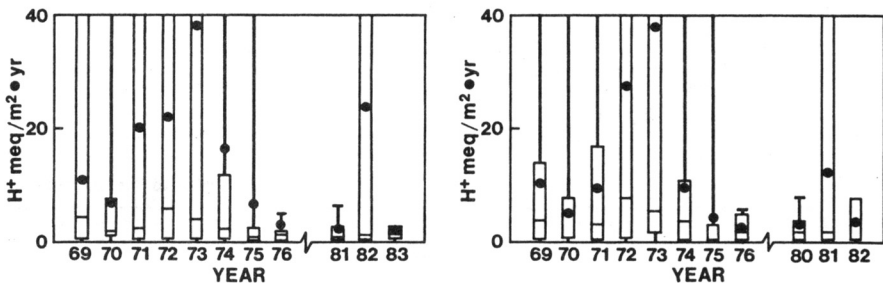


FIGURE 4: Annual hydrogen ion export estimates for the Isle Aux Mort River, Newfoundland, displayed as boxplots of individual sample estimates and as the mean thaw-weighted estimate (●).

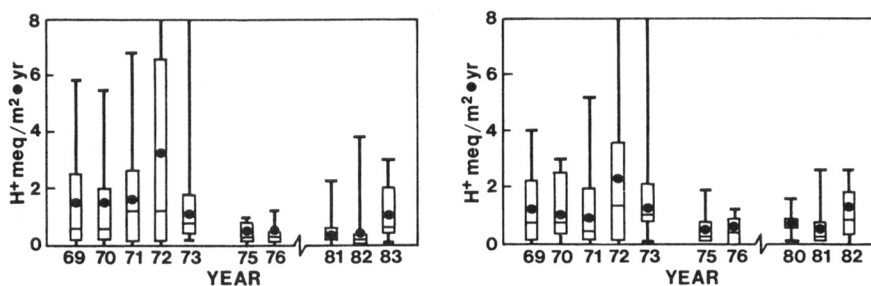


FIGURE 5: Annual hydrogen ion export estimates for the Pipers Hole River, Newfoundland, displayed as boxplots of individual sample estimates and as the mean flow-weighted estimate (●).

DISCUSSION

The running medians and the ANOVA model results for pH indicate that rivers in geologically sensitive portions of Nova Scotia and Newfoundland have been acidified, with the lowest pH values occurring during the late 1960's and early 1970's. These findings confirm those given by Thompson (1986) who observed lower mean pH values during 1971-1973 than in 1982-1984 for several rivers in Atlantic Canada. The ANOVA of the seasonal data shows that there is a strong seasonal component to the acidification pattern, with the Newfoundland rivers having significantly more acidic spring pHs from 1967 to 1973.

A major concern with the statistical results of temporal pH changes, is that by ignoring discharge some of the observed patterns could reflect changes in hydrology rather than changes in atmospheric deposition. For this reason it is useful to consider the changes in hydrogen ion export as well as changes in pH. However, due to the relatively low sampling frequency and the inherent variability in much of the water quality data, annual estimates of ionic export can be expected to be highly variable, and thus use of discharge-weighted mean values may not give the best estimate of central tendency. Similarly, the use of monthly mean discharge may not be adequate, particularly when calculating ionic exports for rivers on the south coast of Newfoundland, since these respond rapidly to precipitation events. To overcome these difficulties annual exports were calculated using mean and median estimates and daily and monthly mean discharges. Regardless of the method of calculation, the temporal patterns of hydrogen export are similar to those of pH depression and the results of the ANOVA model. This suggests that the lower pH values observed in Nova Scotian and Newfoundland rivers during the early 1970's were not the result of changes in the hydrologic regime. Furthermore, analysis of variance of monthly mean discharge for the two rivers indicates that there are no significant annual differences in discharge. Figure 6 presents the annual pattern of sulphur emissions in the U.S.A. and eastern Canada. This indicates that the periods of

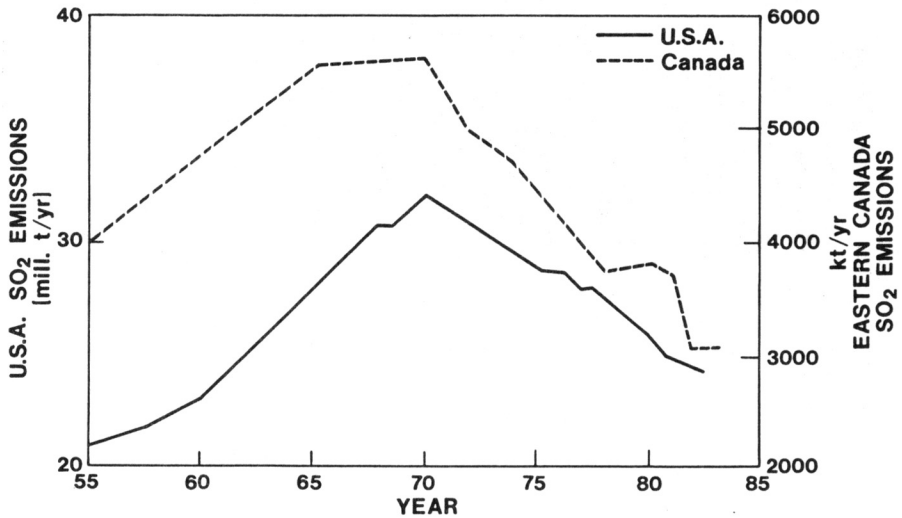


FIGURE 6: Annual estimates of SO₂ Emissions in Canada and the USA for the period 1955-1985.

the greatest sulphur dioxide emissions generally coincide with the lowest pH values and highest hydrogen ion exports for our study rivers in Nova Scotia and Newfoundland. This putative linkage between sulphur emissions and water chemistry indicates that these sensitive receptor systems in Atlantic Canada have not only experienced acidification due to anthropogenic mineral acid loading, but they can also possibly be employed as monitors of the aquatic response to future emission control strategies.

CONCLUSIONS

Statistical analysis of pH data indicated that rivers in sensitive portions of Newfoundland and Nova Scotia experienced significantly lower pH values during the late 1960's and early 1970's. Hydrogen ion exports were also higher and more variable during this period, which indicates that the reduced pH values were not solely a reflection of annual changes in hydrology. This period of apparently reduced pH levels corresponds to the peak in sulphur dioxide emissions in eastern Canada and the United States.

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