

**CATION DENUDATION RATES OF
RIVERS IN NOVA SCOTIA,
1971-1974 AND 1977-1982**

by

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EXECUTIVE SUMMARY

The validation of the Cation Denudation Rate (CDR) Model is an essential activity as over six years have elapsed since its formulation and the CDR Model was used by the Work Group on the Aquatic Effects of Acid Precipitation to arrive at an acceptable target load of sulfate deposition. This report considers such a validation by applying the CDR Model to eleven rivers in Nova Scotia, using data for the early 1980s and testing whether the Model accurately predicts pH.

The CDR Model was developed using data from rivers in Nova Scotia and Newfoundland. Since the Model was developed it has been learned that the methyl thymol blue (MTB) method for sulfate analysis includes some organic anion as well, especially in the more strongly colored rivers. This report shows that in only two of the most acid rivers in southern Nova Scotia is there more reactive organic anion than there is excess (non-marine) sulfate.

The excess sulfate yields of the Nova Scotia rivers have decreased in more recent years, and the pHs have increased, as predicted by the CDR Model. The CDR Model predicts the pHs of the rivers well, if the sum of excess sulfate and reactive organic anion are plotted on the x axis of the Model plot.

RÉSUMÉ ADMINISTRATIF

La validation du modèle du taux de la dénudation des cations (TDC) est une activité de grande importance. Mis au point il y a six ans, le modèle a été utilisé par le Groupe de travail sur l'incidence des pluies acides sur les systèmes aquatiques pour fixer la charge acceptable des retombées de sulfate dans les cours d'eau. Le présent rapport est consacré à la validation du modèle en l'appliquant à l'analyse des données recueillies au début des années 1980 dans onze cours d'eau de la Nouvelle-Écosse pour déterminer l'exactitude des prévisions du modèle en matière de pH.

Le modèle du taux d'apport en cations a été mis au point à l'aide des données prélevées dans les cours d'eau de la Nouvelle-Écosse et de Terre-Neuve. Depuis, on a découvert que la méthode d'analyse du sulfate à l'aide du bleu de thymol réagit à la présence de certains anions organiques surtout dans les cours d'eau plus fortement colorés. Le rapport montre que la proportion d'anions organiques réactifs dépasse celle de la teneur excessive en sulfate (d'origine non océanique) dans seulement deux des cours d'eau les plus acides.

La teneur excessive en sulfate des cours d'eau de la Nouvelle-Écosse a regressé depuis quelques années et le pH a remonté comme le prévoyait le modèle. Le modèle du taux d'apport en cations permet de prévoir le pH des cours d'eau avec exactitude si l'on porte sur l'axe des x du modèle le total du sulfate excédentaire et des anions organiques réactifs.

ABSTRACT

Cation denudation rates for 11 rivers in Nova Scotia are compared for the two periods 1971 - 1974 and 1977 - 1982. Deposition rates of sulfate are presumed to have been lower during the latter period because the excess sulfate yields of the rivers have decreased. A striking change in the mean ratio Na^+/Cl^- between the two periods was found, especially for the more strongly coloured rivers. The colorimetric method for Cl^- , used until mid-1978, is affected by colour unless corrected for it, and apparently falsely high values of Cl^- were reported, resulting in too great a seasalt correction. The change in the mean discharge-weighted sum of cations was found to correlate strongly with the change in the mean ratio Na^+/Cl^- . It is concluded that, within the limits of the data available, there is little difference in the mean discharge-weighted sum of cations for the two time periods. The cation denudation rates, therefore, vary only as a function of runoff. The cation denudation rate model is validated by the observation that as the sulfate yields of the rivers have decreased, the pH values have risen, as the model predicts.

RÉSUMÉ

On compare les taux d'apport en cations dans onze cours d'eau de la Nouvelle-Écosse entre la période allant de 1971 à 1974 et celle allant de 1977 à 1982. On suppose que les taux d'apport en sulfate durant la deuxième période ont été inférieurs à ceux de la première période à la suite d'une baisse des teneurs excessives de sulfate dans les cours d'eau. On a constaté une différence marquée entre les rapports moyens de $\text{Na}^+ : \text{Cl}^-$ d'une période à l'autre, surtout dans le cas des rivières fortement colorées. La mesure du Cl^- par colorimétrie, employée jusque vers le milieu de 1978, est influencée par la couleur initiale de l'eau à moins que l'on en tienne compte dans les résultats. Ainsi, il semble qu'on a signalé des valeurs de Cl^- trop élevées ce qui a entraîné une rectification trop importante pour le sel marin. On a trouvé une étroite corrélation entre les fluctuations du total moyen de cations pondéré en fonction du débit et celles du rapport moyen $\text{Na}^+ : \text{Cl}^-$. À la lumière des données limitées dont on dispose, on peut conclure que le total moyen de cations pondéré en fonction du débit est presque le même pour les deux périodes. Les taux d'apport en cations ne varient donc qu'en fonction de l'importance des eaux de ruissellement. On a observé qu'une baisse de la teneur en sulfate se traduit par un p^{H} plus élevé, comme le prévoit le modèle, ce qui a permis de la valider.

INTRODUCTION

The purpose of this report is to compare cation denudation rates (CDRs) of 11 rivers in Nova Scotia in the early 1970s, when the excess sulfate yields of the rivers were higher, with CDRs in a more recent period (1977-1982), during which the excess sulfate yields were lower. The lower excess sulfate yields of the rivers are in accord with the report of reduced emission rates in the United States (United States Environmental Protection Agency, 1984).

Cation denudation rates are calculated as mean discharge-weighted, seasalt-corrected sum of cations ($\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^{+} + \text{K}^{+}$) in $\mu\text{eq L}^{-1}$, times runoff. Runoff is calculated from the mean annual flow, converted from $\text{m}^3 \text{s}^{-1}$ to $\text{m}^3 \text{yr}^{-1}$, and divided by the drainage area of the watershed above the gauge.

The best available set of data for such an exercise is for rivers in Nova Scotia and Newfoundland, which have been monitored for a number of years, generally by regularly spaced monthly samples. The samples were analyzed at the Water Quality Branch of Environment Canada, Atlantic Region, in Moncton, New Brunswick. The data are stored in NAQUADAT, Canada's national water quality storage system (Demayo, 1970), and the rivers are gauged by the Water Survey of Canada (Environment Canada, 1983). Table 1 shows by year the number of samples for which data on the four major cations, (Ca^{++} , Mg^{++} , Na^{+} , and K^{+}), Cl^{-} , and mean daily discharge (Q) are available for 11 rivers in Nova Scotia. Because many of these rivers are flashy, that is,

given to rapid increases in flow in response to rainstorms, and rapid decreases in flow after rainfall ceases, 7 to 12 samples per year are not sufficient to permit reliable calculations of CDRs. Therefore, the data are grouped into two time periods, 1971 - 1974, and 1977 - 1982. As can be seen in Table 1, for many of the rivers, the latter time period is actually 1980 - 1982.

DISCHARGE DATA

In Table 2, the mean flow for the sample dates, \bar{Q}_{SD} , is compared with the mean annual flow, \bar{Q}_{ANN} , actually the mean for the years for which there are data, and the percent difference between the two means, calculated as:

$$\frac{(\bar{Q}_{SD} - \bar{Q}_{ANN})}{(\bar{Q}_{SD} + \bar{Q}_{ANN})} \times 100 = \% \Delta,$$

are shown. If plus or minus 10% is taken as an acceptable difference, then in the period 1971-1974 only the Mersey River below Mill Falls (MERSEY MF) is outside the limits of acceptability. In the period 1977 - 1982, four rivers are outside the limits. The choice of sampling days in the period 1977 - 1982 resulted in consistent over sampling at times of low flow, except for the Mersey River at George Lake (MERSEY GL) as indicated by the negative %Δ values in Table 2.

If the sum of cations (SUM^+) should correlate either directly or inversely with $\log Q$, then the result of \bar{Q}_{SD} being very different from \bar{Q}_{ANN} could mean a bias in the sample data toward a higher or lower mean SUM^+ than the true mean. This effect is illustrated schematically in Figure 1. If, for example, SUM^+ correlates inversely with $\log Q$, then if \bar{Q}_{SD} is much higher than \bar{Q}_{ANN} , a bias toward low values of SUM^+ will exist. Conversely, if \bar{Q}_{SD} is much lower than \bar{Q}_{ANN} , a bias toward high values of SUM^+ will exist. For direct correlations of SUM^+ with $\log Q$, the effects are similar but of opposite sign. If the correlations with $\log Q$ are significant ($P < 0.001$), however, it is possible to calculate a mean SUM^+ by applying the regression equation to the daily discharge data.

REGRESSIONS

Linear regression analyses were obtained on several properties of the data. The results of regression between Cl^- and Na^+/Cl^- are listed in Table 3, which shows mean Cl^- , mean Na^+/Cl^- , the correlation coefficient, r , for the regression, and P , the probability that the regression is not significant. The regressions are all inverse, that is, for higher values of Cl^- , the ratio Na^+/Cl^- tends to be lower. As the ratio Na^+/Cl^- is in every case higher than the seasalt ratio (0.556), the results suggest that there is some Na^+ produced by chemical weathering in each watershed, but that when a

large input of seasalt occurs, the ratio drops towards the seasalt ratio. The results of the converse regressions, between Na^+ and Na^+/Cl^- (not shown) were both direct and inverse and generally of low significance. In other words, the ratio Na^+/Cl^- is not particularly dependent on Na^+ , but is dependent upon the amount of seasalt.

In evaluating the data from these regressions for the two time periods, a striking change in the ratio Na^+/Cl^- was found. The amount of seasalt received by these rivers depends upon the vagaries of the weather so that there is no reason to expect to find identical mean Cl^- concentrations for the two time periods. But, as can be seen on Figure 2, there is, in general, no striking difference in the mean Cl^- concentrations in the two time periods. The case is different, however, for Na^+ . The mean seasalt-corrected Na^+ concentrations are shown on Figure 3. The rivers are plotted, from left to right, according to decreasing "mean" colour concentrations for 1971 - 1974. (The true mean colour concentrations cannot be calculated, because, until quite recently, colour values greater than 100 were reported as 100G.) There is an obvious, colour-related increase in the mean seasalt-corrected Na^+ in the more recent data set. Figure 4 shows the same kind of colour-related change in the mean ratio Na^+/Cl^- .

Regressions were also obtained between SUM^+ and $\log Q$. Table 4 shows r , the correlation coefficient for the regression, \bar{Q}_{SD} , \bar{Q}_{ANN} , the direction of bias in the mean SUM^+ due to the

sampling scheme, the arithmetic mean SUM+, AMSU+, the discharge-weighted mean SUM+, DWSU+, and for some rivers the mean SUM+ obtained by applying the regression equation to the daily discharge data, REGSU+. The nature of the possible bias in the mean SUM+ is determined by comparing \bar{Q}_{SD} with \bar{Q}_{ANN} and referring to Figure 1.

As can be seen in Table 4, for rivers whose SUM+ data correlate strongly with log Q, whether directly or inversely, there is a distinct difference between AMSU+ AND DWSU+. In fact, the sign of the difference (DWSU+ - AMSU+) is an accurate predictor of the sign of r, the correlation coefficient, and the magnitude of the difference is a good estimator of the value of r. Figure 5 is a plot of % Δ ($\Delta = [(DWSU+ - AMSU+)/ (DWSU+ + AMSU+)] \times 100$) versus r, the correlation coefficient for the regression between SUM+ and log Q. Linear regression analysis of 34 paired values of Δ and r gave $r^2 = 0.896$, $r = -0.043 + 0.066 \Delta$, $F = 275.6$, and P, the probability that the regression is not significant, 0.0000.

DISCUSSION

The various analytical methods used between 1971 and 1982 are briefly described by species in Table 5. For most species, the methods are similar, the main change being the introduction of automated methods in place of manual ones. A major change was made in mid 1978 in the analytical method for Cl^- : the change from a colori-

metric method on an autoanalyser to a specific ion electrode. The colorimetric method for Cl^- , NAQUADAT code 17203L, is affected by colour, resulting in falsely high results unless a correction is made. It is possible, therefore, that at least some of the earlier Cl^- data are too high. This may explain, in part, the observed, colour-related changes in seasalt-corrected Na^+ and in Na^+/Cl^- (Figures 3 and 4).

In late 1981, at the Water Quality Branch Laboratory in Moncton, New Brunswick, a problem associated with the methyl thymol blue (MTB) method for sulfate was recognized, when the results were compared with data from the newly installed ion chromatograph (IC) (Kerekes et al. 1984). In the MTB method, after allowing the sulfate to react with excess BaCl_2 , the pH is raised to 11 or 12 to facilitate the development of the blue colour. At such a high pH much of the excess Ba^{++} is present as $\text{Ba}(\text{OH})_2$. According to Schnitzer and Hahn (1972) $\text{Ba}(\text{OH})_2$ addition is one of the most widely used methods to measure the total acidity of humic materials. It seems likely, therefore, that the large positive interference of the organic material on the MTB sulfate measurement is due to the high pH reached during the procedure. Before mid 1973, however, sulfate was measured by a different procedure, during which the pH was always low (~pH 4). For this procedure the organic interference should have been much less, if any. Therefore, a comparison of the 1971-1973 excess sulfate (non-MTB) yields of the rivers was made with the

1981-1983 excess sulfate (IC) yields. The results are shown on Figure 6 showing generally lower yields of excess sulfate in the latter time period.

As can be seen in Table 4, there are rather large differences in DWSU+, with all the rivers except the Wallace having higher DWSU+ in 1977 - 1982 than in 1971 - 1974. The % change in DWSU+, calculated as described earlier, and the % change in the mean Na^+/Cl^- are plotted on Figure 7. Because of the obvious relationship for the first nine rivers (Roseway to Kelley) linear regression analyses were applied to the % changes for these rivers. The results were: $r = 0.909$, $n = 9$, $\% \Delta \text{DWSU}^+ = 3.28 + 1.40 \% \Delta (\text{Na}^+/\text{Cl}^-)$, $F = 33.15$, and P (exceeding F under $H:0$) is <0.001 .

The sums of squares from the regression were partitioned to those due to the regression and those due to deviations from the regression, in order to calculate F . The partition showed, however, that only 17% of the sums of squares were due to deviations from the regression. Thus, it can be concluded that, on the average, 83% of the changes in $\% \Delta \text{DWSU}^+$ are due to changes in Na^+/Cl^- , that is, to the seasalt correction. On the average, therefore, only 17% of the changes in $\% \Delta \text{DWSU}^+$ are due to causes other than the seasalt correction. This change, calculated as a %, ranges from 0.4 to 3.6% change in DWSU+. All of the changes are positive, except for the Wallace River, but are very small.

One can conclude, therefore, on the basis of the data available, that there have been no striking changes in the CDRs of these rivers, keeping in mind that the CDR is very much a function of flow. CDRs will be higher during years of higher flow and lower during years of lower flow.

THE CDR MODEL AND ORGANIC ANIONS

Since mid-1982, dissolved organic carbon (DOC) has been measured in these rivers, and since December 1982, IC sulfate as well as MTB sulfate has been reported. This makes it possible to calculate the concentration of A^- by the method of Oliver et al. (1983) from DOC and pH, with 10 or 11 samples from each river, and to compare the calculated A^- with the difference between MTB and IC sulfate. There is considerable variation among individual samples, so mean values only are shown in Table 6, which includes the mean pH, mean calculated A^- , the mean difference between MTB and IC sulfates and the percent that the mean difference between the two sulfate is of the MTB sulfate. It can be seen that the calculated concentration of A^- is always greater than the difference between the MTB and IC sulfates. As the difference between the MTB and IC sulfates represents the amount of A^- that has reacted with excess Ba^{++} in the MTB method, it might be termed soluble reactive A^- , or SRA^- and, conversely, the portion of A^- that does not react might be termed soluble unreactive

A⁻, or SUA⁻. It is likely that the latter is either complexed with Fe and Al, or that it is polymerized.

CDRs calculated for the period, December 1982 to December 1983 are compared with MTB excess sulfate yields for the same period on the CDR Model Plot on Figure 8, and it can be seen that the mean pH values, shown beside the data points, are reasonably close to the values predicted by the model. The data are presented in Table 7, in which it may more easily be seen that the model pH agrees with the mean measured pH within 0.2 pH units or better.

By plotting the MTB excess sulfate yields on the X axis of the CDR model plot, one is actually plotting excess sulfate plus SRA⁻, and the results fit the model well. Just as in the case where the yield of nitrate ion is quantitatively significant, and it would be necessary to plot the sum of the excess sulfate and nitrate yields to make the data fit the model, that is, to make the model an accurate predictor of pH, in organic waters, it is necessary to plot the sum of the excess sulfate and SRA⁻ yields (as measured by MTB excess sulfate yields), for the model to predict pH accurately.

The proportion of SRA⁻ in the MTB excess sulfate yields is greatest in the more acid rivers, as shown in Table 6. In only two of the rivers, however, the Roseway and the Liscomb, is the percentage of SRA⁻ more than half of the MTB excess sulfate yields. All of these rivers should benefit, therefore, if sulfate depositions should be further reduced.

SUMMARY AND CONCLUSIONS

1. The mean discharge weighted sums of cations have not changed significantly between the periods 1971-1974 and 1977-1982; the cation denudation rates, therefore, are primary functions of runoff.
2. The excess sulfate yields of the rivers have decreased between 1971-1973 and 1981-1983, and the mean pHs of the rivers have risen, as the CDR model predicts.
3. For rivers whose sums of cations correlate with flow, discharge-weighted data provide more reliable estimates of CDR; the sign of the difference between discharge-weighted mean sum of cations and arithmetic mean sum of cations is an accurate predictor of the sign of the correlation coefficient r in the regression between sums of cations and log flow, and the size of the percent difference is a good predictor of the magnitude of r .
4. The 1981-1983 CDRs, mean pHs, and MTB sulfate yields of the rivers fit the CDR model plot, implying charge balance, and suggesting that the difference between MTB and IC sulfate, which is always smaller than A^- calculated by the method of Oliver et al. (1983), is a measure of the reactive part of A^- , or SRA^- (soluble reactive A^-), and that the difference between A^- and SRA^- , that is, SUA^- (soluble unreactive A^-) does not contribute to charge balance because it is either complexed with iron and aluminum or is polymerized.

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TABLE 1. By year, the number of samples for which data are available on the four major cations (Ca^{++} , Mg^{++} , Na^+ , K^+), on Cl^- , and on mean daily discharges (Q)

	71	72	73	74	Total	77	78	79	80	81	82	Total
Meteghan	11	12	19	2	35	0	0	0	7	12	8	37
Kelley	10	12	10	5	37	4	0	0	7	12	9	32
Wallace	10	10	9	3	32	2	3	5	9	11	10	40
Tusket	12	12	12	1	37	0	0	0	5	14	8	27
Roseway	9	12	7	2	30	0	0	0	7	11	8	26
Mersey GL	11	11	13	4	39	3	1	2	23	47	56	132
Mersey MF	0	8	12	4	24	4	1	6	150	211	151	523
Medway	10	12	12	4	38	4	4	5	18	12	9	52
La Have	9	11	12	1	33	0	0	0	15	19	8	42
Liscomb	9	12	12	2	35	2	0	0	15	11	8	36
St. Marys	12	12	12	3	39	3	3	5	10	12	9	42
Clam Harbour	12	11	12	2	37	0	0	0	7	12	9	28

TABLE 2. A comparison of the mean flow from sample dates and from annual means, for 1971 - 1974 and 1977 - 1982, in m^3s^{-1}

	\bar{Q}_{SD}	\bar{Q}_{ANN}	% Δ	\bar{Q}_{SD}	\bar{Q}_{ANN}	% Δ
	1971 - 1974			1977 - 1982		
Meteghan	5.29	5.34	-0.5	3.85	4.40	-6.7
Kelley	2.28	2.09	4.4	1.68	2.20	-13.4
Wallace	8.65	9.87	-6.6	8.24	10.1	-10.1
Tusket	42.7	37.9	6.0	32.8	35.8	-4.4
Roseway	15.6	18.5	-8.5	13.9	17.8	-12.3
Mersey GL	26.8	23.8	5.9	20.8	19.7	2.7
Mersey MF	7.69	9.67	-11.4	8.60	9.20	-3.4
Medway	46.6	46.1	0.5	41.2	42.6	-1.7
La Have	44.6	42.2	2.8	28.5	32.8	-7.0
Liscomb	15.8	17.9	6.2	12.6	15.3	-9.7
St. Marys	52.7	52.4	0.3	37.0	45.3	-10.1
Clam Harbour	1.91	1.86	1.3	1.39	1.69	-1.7

TABLE 3. By river, the results of the regression between Cl^- and Na^+/Cl^- , showing mean Cl^- , mean Na^+/Cl^- , the correlation [coefficient from the regression, r , and P (exceeding F under $H:90$), for 1971 - 1974 and 1977 - 1982]

River	Cl^- mgL^{-1}	Na^+/Cl^-	r	P
1971 - 1974				
Meteghan	8.91	0.560	-0.632	0.0000
Kelley	3.20	0.858	-0.196	0.2454
Wallace	5.02	0.743	-0.394	0.0255
Tusket	6.45	0.579	-0.536	0.0006
Roseway	5.22	0.582	-0.215	0.2542
Mersey GL	4.63	0.603	-0.666	0.0000
Mersey MF	4.86	0.590	-0.442	0.0346
Medway	4.32	0.617	-0.574	0.0002
La Have	4.06	0.644	-0.642	0.0000
Liscomb	3.83	0.621	-0.644	0.0000
St. Marys	4.33	0.644	-0.733	0.0000
Clam Harbour	5.57	0.636	-0.899	0.0000
1977 - 1982				
Meteghan	9.49	0.622	-0.725	0.0000
Kelley	3.36	0.838	-0.119	0.5180
Wallace	7.70	0.653	-0.565	0.0001
Tusket	6.02	0.696	-0.777	0.0000
Roseway	4.11	0.751	-0.499	0.0094
Mersey GL	4.74	0.659	-0.722	0.0000
Mersey MF	5.34	0.671	-0.578	0.0000
Medway	4.80	0.656	-0.625	0.0000
La Have	4.22	0.705	-0.647	0.0000
Liscomb	3.55	0.709	-0.862	0.0000
St. Marys	4.74	0.661	-0.729	0.0000
Clam Harbour	5.34	0.683	-0.814	0.0000

TABLE 4. By river, the correlation coefficient, r , from the regression between SUM+ and log Q, QSD, QANN, the inferred bias in mean SUM+, AMSU+, DWSU+, and for six rivers, REGSU+, the mean SUM+ obtained from applying the regression equation to the daily Q, for 1971 - 1974 and 1977 - 1982

River	Regression Correlation Coefficient	\bar{Q}_{SD} $m^3 s^{-1}$	\bar{Q}_{ANN} $m^3 s^{-1}$	BIAS	AMSU+ μeqL^{-1}	DWSU+ μeqL^{-1}	REGSU+ μeqL^{-1}
1971 - 1974							
Meteghan	0.034	5.29	5.34	N	116	118	
Kelley	-0.835	2.28	2.09	L	115	88.6	80.8
Wallace	-0.855	8.65	9.87	H	243	201	185
Tusket	-0.233	42.7	37.9	L	64.0	60.2	62.0
Roseway	0.124	15.6	18.5	L	43.6	46.4	
Mersey GL	0.026	26.8	23.8	H	62.1	62.5	
Mersey MF	0.195	7.69	9.67	L	63.3	66.7	
Medway	-0.247	46.6	46.1	L	77.7	73.7	
La Have	-0.248	44.6	42.2	L	118	110	
Liscomb	-0.495	15.8	17.9	H	62.0	56.2	54.8
St. Marys	-0.572	52.7	52.4	N	105	97.9	96.0
Clam Harbour	-0.907	1.91	1.86	L	184	135	127
1977 - 1982							
Meteghan	-0.011	3.85	4.40	N	133	133	
Kelley	-0.562	1.68	2.20	H	107	93.3	89.0
Wallace	-0.795	8.24	10.1	H	216	179	157
Tusket	-0.256	32.8	36.6	H	87.5	81.5	68.0
Roseway	-0.206	13.9	16.6	H	78.4	71.6	
Mersey GL	0.170	20.8	19.7	H	68.4	71.7	
Mersey MF	0.028	8.64	8.07	N	89.6	90.6	
Medway	0.060	41.2	42.6	N	86.5	86.8	
La Have	-0.003	28.5	32.8	N	134	133	
Liscomb	-0.112	12.5	14.9	H	79.7	77.3	77.6
St. Marys	-0.426	37.0	45.3	H	116	106	104
Clam Harbour	-0.790	1.39	1.69	H	191	143	128

N = Nil, L = Low, H = High

TABLE 5. Analytical methods, showing by species, the NAQUADAT code, the date range over which it was used, and a brief indication of the analytical method

Species	Code	Date Range	Method
Ca ⁺⁺	20103L	Nov. 1970 - Jul. 1980	Atomic Absorption (AA)
	20110L	Aug. 1980	Automated AA
Mg ⁺⁺	12102L	Jan. - May 1971	AA
	12104L	Jun. 1971 - Jan. 1972	Colorimetric
	12102L	Feb. 1972 - Jul. 1980	AA
	12107L	Aug. 1980	Automated AA
Na ⁺	11102L	Jan. - Mar. 1971	AA
	11104L	Apr. 1971 - Dec. 75	Flame Photometry
	11103L	Jun. 1976	Flame Photometry on AA
K ⁺	19102L	Jan. - Mar. 1971	AA
	19104L	Apr. 1971 - Dec. 1975	Flame Emission Spectrophotometer
	19103L	Jun. 1976	Flame Photometry on AA
Cl ⁻	17203L	Jan. 1971 - Jul. 1978	Colorimetry on AA
	17205L	Sep. 1978	Specific Ion Electrode
So ₄ ⁻⁻	16303L	Jan. 1971 - May 1973	Titration with BaCl ₂ , Thorin indicator
	16304L	Jun. 1973 - continues	Methyl Thymol Blue on Auto Anal.
	16309L	Nov. 1981 - continues	Ion Chromatograph

TABLE 6. Mean pH, MTB sulfate yield, IC sulfate yield and the percent of the MTB sulfate yield represented by the difference between the MTB and IC sulfate yields

River	Mean pH	MTB Sulfate Yield	IC Sulfate Yield	MTB-IC Sulfate
				MTB Sulfate
Roseway	4.4	92.6	39.5	57
Tusket	4.6	78.4	44.4	43
Liscomb	4.8	112.2	45.6	59
Mersey Gl	5.0	60.9	38.8	36
Medway	5.4	49.8	31.3	37
Kelley	5.6	91.4	63.4	31
Meteghan	5.7	58.2	40.3	31
La Have	5.9	68.4	51.4	25
St. Marys	6.0	41.6	30.0	28
Clam Harbour	6.1	44.9	39.9	11
Wallace	6.5	78.0	70.5	10

TABLE 7. Runoff, discharge-weighted sum of cations, CDR, MTB SO_4^{--} yield, mean measured pH, and CDR model-predicted pH are shown for the period November 1981 to December 1983

	Runoff m yr^{-1}	DWSU+ $\mu\text{eq L}^{-1}$	CDR $\mu\text{eq m}^{-2}\text{yr}^{-1}$	MTB SO_4^{--} Yield $\mu\text{eq m}^{-2}\text{yr}^{-1}$	Mean pH	Model pH
Meteghan	0.724	137	99.0	58.2	5.7	5.9
Kelley	1.17	79.4	93.0	91.4	5.2	5.2
Wallace	1.23	150	186.0	78.0	6.3	6.3
Tusket	0.783	87.2	68.3	78.4	4.6	5.0
Roseway	1.00	61.2	61.5	92.6	4.5	4.5
Mersey GL	1.00	69.2	69.3	60.9	5.0	5.2
Medway	0.860	80.7	69.4	49.8	5.5	5.6
La Have	0.874	125	109.0	68.4	5.9	5.9
Liscomb	1.32	77.5	103.0	112.2	4.9	5.0
St. Marys	0.824	105	86.6	41.6	6.1	6.0
Clam Harbour	0.877	133	116.0	44.9	6.3	6.2

FIGURE CAPTIONS

- Figure 1 Schematic drawing showing the bias in the estimation of the mean SUM^+ in the case of an inverse or direct correlation of SUM^+ with flow (Q), if the mean flow of the sample dates is higher or lower than the mean annual flow.
- Figure 2 Mean Cl^- concentrations in 11 rivers in Nova Scotia, 1971-1974 and 1977-1982.
- Figure 3 Mean seasalt-corrected Na^+ in 1971-1974 and 1977-1982. Rivers are arranged in order of decreasing "mean" colour (1971-1974) from left to right.
- Figure 4 Mean Na^+/Cl^- in 1971-1974 and 1977-1982. Rivers are in the same sequence as for Figure 3.
- Figure 5 A plot of r , the correlation coefficient for the regression between SUM^+ and $\log Q$ versus the percent difference between DWSU^+ and AMSU^+ .
- Figure 6 A plot that compares the percent difference in DWSU^+ and in Na^+/Cl^- between the two periods 1971-1974 and 1977-1982.
- Figure 7 a plot that shows the excess sulfate yields (Thorin method) in 1971-1973 and (IC method) in 1981-1983.
- Figure 8 A plot that shows the geometric mean pH for the two periods 1971-1973 and 1981-1983.
- Figure 9 The CDR model plot showing data (November, 1981 - December 1983) on CDRs, mean pHs and MTB excess sulfate yields.

















