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**CHEMICAL TRENDS IN COASTAL
RIVERS OF EASTERN CANADA**

by

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EXECUTIVE SUMMARY

Since the early 1970s, excess sulfate yields of rivers in Nova Scotia and Newfoundland have decreased considerably, and the pHs of those rivers not dominated by organic acids have risen accordingly. Rates of wet deposition of excess sulfate in these areas have been monitored over a shorter time period, but from 1981 to 1983, have decreased dramatically at Kejimikujik National Park, Nova Scotia.

RÉSUMÉ ADMINISTRATIF

Depuis le début des années 70, le rendement du sulfate en excès dans les rivières de la Nouvelle-Écosse et de Terre-Neuve a diminué considérablement et le pH des rivières qui ne sont pas dominées par les acides organiques a augmenté proportionnellement. Les taux de formation de dépôts humides de sulfate en excès dans ces régions ont été surveillés pendant une plus courte période, mais de 1981 à 1983, ils ont diminué de façon spectaculaire au Parc national Kéjimkujik de la Nouvelle-Écosse.

ABSTRACT

The detection of chemical trends in coastal rivers of Nova Scotia and Newfoundland is hampered by changes over time in analytical methods, especially when the new method does not measure the same thing or things that the earlier method did. Nevertheless, it appears from the data that the maximum deposition rates of excess sulfate must have occurred in the early 1970s. From 1977 to 1983, several CANSAP (Canadian Network for sampling precipitation) stations operated in southern Nova Scotia, making it possible to compare measured rates of atmospheric wet deposition of excess sulfate with nearby river yields of excess sulfate, sulfate ions being analyzed by ion chromatography. Such comparisons generally agree quite well. The data show a considerable decrease in excess sulfate deposition rates in southern Nova Scotia since 1977.

RÉSUMÉ

On a du mal à détecter les tendances chimiques dans les rivières côtières de la Nouvelle-Écosse et de Terre-Neuve, car les méthodes d'analyse ont changé au fil des ans et les nouvelles méthodes ne mesurent pas la ou les mêmes choses que les anciennes. Cependant, selon les données, il semble que les plus hauts taux de formation de dépôts de sulfate en excès aient été enregistrés au début des années 70. De 1977 à 1983, plusieurs stations CANSAP (Réseau canadien d'échantillonnage des précipitations) ont été exploitées dans le sud de la Nouvelle-Écosse et ont ainsi permis de comparer les taux de formation des dépôts humides atmosphériques de sulfate en excès mesurés aux productions de sulfate en excès des rivières avoisinantes, les ions de sulfate étant analysés par chromatographie d'échange d'ions. En général, ces comparaisons concordent plutôt bien. Les données indiquent une diminution considérable des taux de formation de dépôts de sulfate en excès dans le sud de la Nouvelle-Écosse depuis 1977.

INTRODUCTION

The best long-term records of chemical data for rivers in Canada exist for rivers in Nova Scotia and Newfoundland. Monitoring, at monthly intervals, of some of the rivers commenced in 1965, but, for the present report, comparisons are made between the status of the rivers in the period 1971 - May, 1973 and in the period 1982 - 1984. The river water samples are analyzed in the Moncton, New Brunswick laboratory of Environment Canada's Water Quality Branch, Atlantic Region. The data are stored in NAQUADAT, Canada's national water quality storage system (Demayo, 1970). Discharge data for the rivers are available from annual reports of Environment Canada's Water Survey of Canada, Atlantic Provinces.

The detection of trends from these data is difficult because many of the rivers are very flashy (i.e. monthly samples may not be adequate to characterize the annual status of the river) and changes in analytical methods over the years have affected analytical results. The colorimetric method for chloride ion, used until mid-1978, was biased high by color in the water samples, and many of these river waters are tea-colored due to the presence of humic and fulvic acids. These coastal rivers receive considerable amounts of seasalt, however, and it is necessary to correct the data for seasalt (in the case of sulfate, to separate the marine component from the terrestrial or anthropogenic one). The other quantitatively important major ions

of seasalt, however, are also important products of freshwater chemical weathering (e.g. Na^+ , Mg^{++}), so chloride ions are the preferred indicators of seasalt. Chloride values that are too high will cause over corrections for seasalt, but, because marine sulfate is only 14% of marine chloride in weight units, the correction error is small. Moreover, the samples highest in seasalt are generally lowest in color.

The problems with sulfate analysis, using the autoanalyzer method that takes the pH to 11 or 12 in the presence of excess Ba^{++} and uses methyl thymol blue (MTB) as the colorimetric indicator, have been reported by Kerekes et al. (1984). The MTB method has been used in the Moncton laboratory starting in June, 1973. Since late in 1981, sulfate has also been analyzed by ion chromatography (IC). Cheam et al. (1985) evaluated the several methods for sulfate, and concluded that:

1. IC sulfate is sulfate, all the (ionized) sulfate, and nothing but sulfate.
2. MTB sulfate is sulfate plus some organic anion.
3. Thorin sulfate (the method used from 1965 to May 1973) if carefully done yields results similar to IC sulfate.

The Thorin sulfate method involves a titration carried out at low pH (pH 3.8 to 4.0). It is thought that the high pH reached in the MTB method makes the organic matter more reactive, and causes the interference (T. Pollock, Moncton Laboratory, personal communication, 1982).

The Mersey River, Nova Scotia, runs through Kejimikujik National Park (Keji), and since 1980 has been sampled frequently at two stations. The upper station, below Mill Falls (MERSEY MF) drains 295 km² and lies above Keji Lake. The lower station, at George Lake (MERSEY GL) drains 723 km² and lies below Keji Lake. From 1977 to 1982 a CANSAP station operated at Shelburne, Nova Scotia, about 70 km south of Keji Park, and since 1980, one has operated at Keji (Barrie and Sirois, 1982). These data make it possible to compare the annual rates of wet deposition of excess sulfate with the annual Mersey River yields of excess sulfate.

RESULTS

Tables 1 and 2 show excess sulfate yields of rivers in Nova Scotia and Newfoundland, respectively, for the two periods, 1971 - 1973 (May) and 1982 - 1984. Excess sulfate yields are calculated as mean discharge-weighted seasalt-corrected sulfate times mean runoff for the sampling period. The reliability of the results of this method of calculation increases with the number of samples available. That is why the data are grouped over several years - to increase the number of samples. As yet, however, only a small number of samples from some rivers have been analyzed by IC. The data indicate a marked decrease in excess sulfate yields in 1982 - 1984 compared to 1971 - 1973.

If the excess sulfate yields have decreased, then logically the mean pHs should have increased. Table 3 shows the median pHs of the rivers in 1971 - 1973 and 1982 - 1984. The rivers are listed in order of mean discharge-weighted, seasalt-corrected sums of cations ($\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^+ + \text{K}^+$) (1982 - 1984), which in Nova Scotia range from 57 to 160 $\mu\text{eq L}^{-1}$, and in Newfoundland ranges from 62 to 300 $\mu\text{eq L}^{-1}$ for seven rivers, Harrys River being a hard water river at 1170 $\mu\text{eq L}^{-1}$. The soft water rivers of Nova Scotia show little or no change in pH between the two periods; their pHs are buffered to a large extent by organic acids. The soft water rivers in Newfoundland, on the other hand, all show higher pHs in the more recent period.

The annual wet deposition rates of excess sulfate at Shelburne and at Keji were calculated from data in the CANSAP data file (to 1982), from the CANSAP Data Summary for 1983 (1984), and from records of monthly precipitation (Met. Records) published by Environment Canada's Atmospheric Environment Service (1977 - 1984). In general the data on precipitation amounts in the CANSAP data file agree with the Met. Records, but there are some discrepancies - missing data in the CANSAP file, and slightly different precipitation amounts, carried to fewer significant figures than in the Met. Records. Table 4 shows some details of the calculations. Ideally, there should be 12 samples per year, and the CANSAP data on total precipitation should agree with the Met. Records, but, as can be seen, the agreement is not always perfect. The calculated wet deposition is

the product of the volume-weighted excess sulfate (converted to $\mu\text{eq L}^{-1}$) and total precipitation from the Met. Record. The units are $\text{meq m}^{-2} \text{ yr}^{-1}$. The reliability of the result is indicated by the number of samples and the degree of agreement between the two records of total precipitation. The uncertainties for some years, when there are fewer than 12 samples, are very large. The data indicate, nevertheless, a more or less steady decrease in wet deposition rates from 1979 to 1983.

Table 5 shows calculated excess sulfate yield of MERSEY GL and MERSEY MF, and the number of samples used for the calculations. Curiously, the excess sulfate yields of the river, while of the same order of magnitude as the wet deposition rates, are nearly constant over the three year period for which data are available.

DISCUSSION

Although the median pHs of all the rivers are somewhat higher in 1982 - 1984 than in 1971 - 1973, the pHs have not risen as much as might be expected, given the reductions in excess sulfate yields, in the soft water rivers in Nova Scotia. That is because the pHs of these rivers are buffered to some extent by naturally occurring organic acids. The headwater regions of these rivers contain large areas of wetlands and bogs, and the river waters are tea colored due to the presence of undegraded humic and fulvic acids. Oliver et al.

(1983) provide a method for calculating the organic anion A^- , from pH and DOC. Moreover, the difference between sulfate measured by the MTB and IC methods gives a measure of what may be called soluble reactive A^- , or SRA^- . Data on DOC and MTB and IC sulfates are being accumulated as part of the LRTAP monitoring program, and after a few more years it may be possible to ascertain whether the natural processes of acidification are increasing in rate or are at a steady state.

Sulfate may be retained and used in the bogs during the growth season, and released later after decay of plant material, and such processes may explain why the excess sulfate yield of the Mercey River are more or less constant, while the wet deposition rates of excess sulfate have decreased sharply at Keji 1981 - 1983.

Whether the low deposition rate for 1983 was a one year phenomenon, or the start of a downward trend, will not be known until several more years of monitoring data are accumulated.

SUMMARY AND CONCLUSION

1. Sulfate yields as measured by ion chromatography are lower in 1982 - 1984 than sulfate yields measured by the Thorin method in 1971 - 1973.
2. The median pHs of the river are higher in the latter period.
3. In Nova Scotia, the pHs of the softer water rivers are buffered to some extent by organic anions.

4. Wet deposition of excess sulfate at Kejimikujik National Park decreased sharply from 1981 to 1983.
5. More data, which will be obtained by the LRTAP monitoring program, will show whether anthropogenic and/or natural acidification trends will dominate these rivers in the future.

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TABLE I Excess sulfate yields of rivers in Nova Scotia, 1971 - 1973 (May), and 1982 - 1984.

River	n	Excess Sulfate Yield 1971 - 1973 meq m ⁻² yr ⁻¹	n	Excess Sulfate Yield 1982 - 1984 meq m ⁻² yr ⁻¹
Meteghan	27	104.0	22	40.5
Kelley	26	81.3	22	38.2
Wallace	22	86.3	14	45.7
Tusket	29	74.3	20	43.5
Roseway	20	74.5	20	32.8
Mersey GL	28	63.0	99	31.9
Mersey MF	13	60.4	405	33.8
Medway	26	64.4	21	34.8
La Have	25	79.0	28	44.1
Liscomb	25	78.2	20	47.5
St. Marys	29	76.4	11	41.3
Clam Harbour	27	94.3	16	71.0

TABLE II Excess sulfate yields of rivers in Newfoundland, 1971 - 1973 (May), and 1982 - 1984.

River	n	Excess Sulfate Yield 1971 - 1973 meq m ⁻² yr ⁻¹	n	Excess Sulfate Yield 1982 - 1984 meq m ⁻² yr ⁻¹
Harrys	28	85.0	12	57.9
Exploits	30	41.6	16	38.5
Torrent	22	99.6	9	54.7
Pipers Hole	29	36.7	18	15.3
Indian Brook	21	32.0	18	10.2
Isle aux Morts	27	101.0	10	52.8
Garnish	19	63.7	11	30.3
Rocky	29	63.7	22	18.2

TABLE III Median pHs of rivers in Nova Scotia and Newfoundland, 1971 - 1973 (May), and 1982 - 1984.

River	n	Median pH 1971 - 1973	n	Median pH 1982 - 1984
Roseway	20	4.4	27	4.5
Tusket	29	4.6	27	4.7
Mersey MF	12	4.85	417	4.9
Mersey GL	29	4.80	105	5.0
Liscomb	26	4.8	28	5.05
Medway	26	5.0	33	5.6
Meteghan	24	5.5	29	5.8
La Have	24	5.8	35	6.0
Kelley	27	5.65	30	6.0
St. Marys	29	5.9	27	6.1
Clam Harbour	28	6.3	27	6.4
Wallace	22	6.5	32	6.7
Isle aux Moris	27	5.5	14	6.1
Garnish	20	6.1	16	6.3
Rocky	30	6.1	32	6.4
Pipers Hole	29	6.2	28	6.3
Exploits	31	6.3	28	6.4
Indian Brook	22	6.6	29	6.7
Torrent	23	6.9	14	7.0
Harrys	28	7.7	26	7.8

TABLE IV Data used to calculate annual rates of wet deposition of excess sulfate at Shelburne and at Kejimikujik National Park, Nova Scotia.

Year	n	Total Precipitation CANSAP Record m yr ⁻¹	Total Precipitation MET. Record m yr ⁻¹	Volume-Weighted Excess Sulfate mg L ⁻¹	Calculated Wet Deposition meq m ⁻² yr ⁻¹
Shelburne, Nova Scotia					
1977	9	1.115	1.529	2.368	75.4
1978	11	1.025	1.010	2.056	43.3
1979	9	1.220	1.668	2.792	97.0
1980	11	1.181	1.317	1.651	45.3
1981	12	1.527	1.539	1.129	36.2
1982	12	1.294	1.304	1.430	38.8
Kejimikujik National Park					
1980	11	1.045	1.129	1.484	34.9
1981	12	1.573	1.579	1.182	38.9
1982	12	1.278	1.172	1.220	29.8
1983	12	1.340	1.275	0.769	20.4

TABLE V Excess sulfate yields of the Mersey River at George Lake and below Mills Falls, 1982, 1983 and 1984, and n, the number of samples used for the calculations

Year	n	George Lake meq m ⁻² yr ⁻¹	n	Mill Falls meq m ⁻² yr ⁻¹
1982	59	29.5	138	34.8
1983	28	33.2	127	33.3
1984	12	34.0	141	34.5