

SULFATE IN LAKES OF EASTERN CANADA:
CALCULATED ATMOSPHERIC LOADS COMPARED WITH
MEASURED WET DEPOSITION.

by

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EXECUTIVE OVERVIEW

The chemistry of precipitation and of surface waters is determined by the contamination of the water through chemical reactions or physical absorption of materials with which the waters come into contact. The portion of the variation in chemical content that is due to natural causes such as chemical weathering of geological materials or of transport of seasalt and that due to anthropogenic atmospheric pollution is a primary concern of the Long Range Transport of Airborne Pollution (LRTAP) program.

This paper reports the results of the application of standard methods of factor analysis to a series of surface water and precipitation chemistry data. The analysis clearly identifies factors due to chemical weathering, seasalt, and LRTAP. The LRTAP factor, which appears as pH heavily loaded in one sense and sulfate and in some cases also nitrate and lead heavily loaded in the opposite sense, is generally more prominent in the precipitation data than in the surface water data. The LRTAP factor explains 15% of the variance in precipitation chemistry data for Sable Island, Nova Scotia, 19% at Shelburne, Nova Scotia, and 40% at Sept Iles, Quebec. In Ontario data, however, because of apparent higher levels of continental dust, the variance explained by the LRTAP factor decreases or the factor becomes obscure.

In surface water data, fortunately, the LRTAP factor does not appear as a strongly developed factor in ^wmay of the data sets. It explains 19% of the variance in the data for the Northeast Pond River, Newfoundland; it is overwhelmed by the loadings for colour, aluminum, and total organic carbon in the data for the Mersey River, Nova Scotia; it explains 9% of the variance in the

data for the Ste. Anne River, Quebec, 18% of the variance in the data for lakes in or near Laurentide Provincial Park, 15% of the variance in the data for lakes in the valley of the St. Maurice River, Quebec, and does not show clearly in the other surface water data sets.

The factor loadings lack quantitative significance because the results are so sensitive to the choice of variables to factor, and to the choice of the method of factoring and of rotation of the factor matrix. The relative importance of the LRTAP factor and of the variables contributing to this factor, however, are clearly demonstrated.

Résumé à l'intention des cadres

Les réactions chimiques et les mécanismes d'absorption des substances avec lesquelles l'eau entre en contact déterminent la composition chimique des précipitations et des eaux superficielles. Le programme sur le transport à distance des polluants atmosphériques (TADPA) s'intéresse particulièrement aux variations de la composition chimique attribuables à des causes naturelles, notamment à l'altération chimique de matériaux géologiques, au transport du sel marin, et à la pollution atmosphérique d'origine anthropique.

Le présent document expose les résultats de l'application de méthodes normalisées d'analyse de facteurs à une série de données sur la chimie des eaux superficielles et des précipitations. Ces analyses ont permis d'identifier clairement les facteurs dus à l'altération chimique, à l'action du sel marin et au TADPA. Le facteur TADPA, qui est parfois représenté en grande partie par le pH dans un sens et par les sulfates, et dans certains cas par les nitrates et le plomb dans le sens inverse, joue généralement un rôle plus important dans les données sur les précipitations que dans celles sur les eaux superficielles. Le facteur TADPA rend compte de 15 % de la variance observée dans les données sur les précipitations à l'Ile de Sable en Nouvelle-Écosse, de 19 % à Shelburne en Nouvelle-Écosse et de 40 % à Sept-Iles au Québec. Par contre, en Ontario, en raison de la présence d'une plus grande quantité de poussière continentale, la variance du facteur TADPA décroît, ou ce facteur devient obscur.

Heureusement, le facteur TADPA ne semble pas aussi important dans un grand nombre de séries de données sur les eaux superficielles. Il rend compte de 19 % de la variance des données sur le tronçon nord-est de la rivière Pond à Terre-Neuve; il est masqué par les charges élevées en couleur, en aluminium et en carbone organique total dans les données sur la rivière Mersey en Nouvelle-Ecosse; il rend compte de 9 % de la variance des données sur la rivière Ste-Anne au Québec, de 18 % de la variance des données sur les lacs se trouvant à proximité ou à l'intérieur du parc provincial des Laurentides, de 15 % de la variance des données sur les lacs de la vallée de la rivière St-Maurice au Québec et il n'apparaît pas clairement dans les autres séries de données obtenues sur les eaux superficielles.

Ces facteurs ne sont pas quantitativement significatifs, car les résultats sont étroitement liés au choix des variables et au choix du mode de détermination des facteurs et du mode de rotation de la matrice. L'importance relative du facteur TADPA et de ses variables a toutefois été clairement établie.

ABSTRACT

Chemical data on Canadian lakes have been assembled, corrected for seasalt if necessary, and their SO_4^{--} concentrations have been compared on an approximately west to east axis. Runoff values have been assigned to each group of lakes. The product of lake concentration times runoff is an estimate of atmospheric deposition. Atmospheric deposition of SO_4^{--} calculated from lake data is compared with measured wet deposition. The agreement is good for the westernmost and easternmost regions, but in southern Ontario and southeastern Quebec, the deposition calculated from lake data is significantly higher than measured wet deposition, and the differences may represent dry deposition.

RESUME

Les résultats de l'analyse de facteurs appliquée aux données obtenues sur la chimie des eaux de rivières, de lacs et de précipitations sont présentés. La chimie des eaux superficielles est principalement influencée par des facteurs tels que le sel marin (près des côtes), l'altération chimique et les précipitations acides. De la même façon, la chimie des précipitations dépend surtout de facteurs tels que le sel marin (près des côtes), les précipitations acides et la poussière continentale.

L'analyse permet de mettre en évidence des relations au sein d'une série de données et de mieux comprendre l'origine des variations dans le cas de problèmes environnementaux complexes. Toutefois, il ne faut pas attribuer une valeur quantitative précise aux facteurs, car les valeurs obtenues sont très sensibles au choix des variables et au choix du mode de détermination des facteurs et du mode de rotation de la matrice.

INTRODUCTION

In two unpublished reports (Thompson and Hutton 1981, 1982), data on the major ion chemistry of lakes in eastern Canada were assembled, and first a plot was made showing how the mean and range of SO_4^{--} concentration, or, near the coast, excess SO_4^{--} concentrations, varied when plotted on an approximately west-to-east axis, from ELA (Experimental Lakes Area, Kenora, Northwestern Ontario) to Labrador and the Island of Newfoundland. In the second report, a more direct comparison with measured wet deposition (Barrie and Sirois 1982) was attempted, by using regional or locally measured runoff to convert the lake SO_4^{--} concentrations into units more directly comparable with the wet deposition data. Atmospheric deposition amounts of SO_4^{--} are commonly expressed as $\text{kg ha}^{-1} \text{ yr}^{-1}$ or $\text{meq m}^{-2} \text{ yr}^{-1}$.

In order to present the lake data in the same units as the wet deposition data ($\text{meq m}^{-2} \text{ yr}^{-1}$), regional runoff values as shown on Map 24 of the Hydrological Atlas of Canada (1978) or locally calculated runoff from river discharge data (Environment Canada 1980, 1981, 1982; Quebec 1980) are used to convert the lake data:

$$\text{SO}_4^{--} (\mu\text{eq L}^{-1}) = \text{SO}_4^{--} (\text{meq m}^{-3}).$$

$$\text{runoff} = \text{m yr}^{-1} = \text{m}^3 \text{ m}^{-2} \text{ yr}^{-1}.$$

$$\text{SO}_4^{--} \text{ (meq m}^{-3}\text{) times runoff (m}^3 \text{ m}^{-2} \text{ yr}^{-1}\text{) =}$$
$$\text{SO}_4^{--} \text{ (meq m}^{-2} \text{ yr}^{-1}\text{).} \quad (1)$$

The result of (1), lake SO_4^{--} concentration times runoff, is then compared with measured wet deposition in the same units. It is recognized that there are other possible sources of SO_4^{--} to at least some of these lakes, such as S-bearing minerals in the watershed or municipal or industrial pollution. It is also recognized that all the SO_4^{--} supplied by atmospheric precipitation to the watershed of a given lake may not appear within a short time as dissolved SO_4^{--} in the lake water, but may suffer other fates, such as retention by biomass or soils of the watershed, and possibly reduction and precipitation and/or volatilization, either in the watershed or in the lake sediments. Nevertheless, as will be seen, the comparison of lake SO_4^{--} times runoff to atmospheric wet deposition yields useful information, and from the comparison it may be inferred that in general other sources of SO_4^{--} to these lakes are small in comparison to the atmospheric loading. Nor do sinks for SO_4^{--} appear to be important.

The lake data have been accumulated from several sources and because so many different laboratories generated the data, the data were subjected to a series of quality control tests, such as charge balance, calculated conductance, calculated CO_2 pressure, ratio of Ca^{++} to Mg^{++} , and calcite saturation index. For a complete list of the laboratories and data, see Thompson and Hutton (1982).

Sulfate Concentrations in Lakes

The year the lakes were sampled, the mean SO_4^{--} or excess SO_4^{--} concentrations in each data set, the uncertainty of the mean at the 95% confidence level, expressed as a percentage of the mean, the runoff value used, the product of the lake SO_4^{--} and the runoff, and 1980 measured wet deposition of SO_4^{--} ³ and dry deposition calculated from measurements of air concentration (Barrie, L.A., personal communication) are listed in Table I.

The locations of the lake sampling sites and the CANSAP (Canadian Network for Sampling Precipitation) and APN (Canadian Air and Precipitation Monitoring Network) sites are shown in Figure 1. Consideration of Figure 1 will explain some of the data listed in Table 1. Runoff is very low near the Ontario-Manitoba border, increases a little, closer to Lake Superior, is higher in the lees of Lake Superior and Georgian Bay, increases as a function of elevation in the Laurentian Highlands of Quebec, and is high in Atlantic Canada, due to marine influences.

Dry deposition is highest at Long Point, because of its exposed location on the north shore of Lake Erie, and is relatively high at Chalk River, Ontario because it is located in the continental pollution plume. Maniwaki, Quebec, is 125 km ENE of Chalk River, so

for purposes of comparison we have combined the CANSAP data at Maniwaki with the APN data for Chalk River in Figure 2. Figure 2 shows, on an approximately west to east axis, the product of lake SO_4^{--} times runoff, compared with 1980 wet and dry deposition of SO_4^{--} . The wet deposition at some lake sites is necessarily interpolated between CANSAP stations. The data are not all matched in time, e.g., Kenora, Thunder Bay, Sudbury, and Ste. Agathe lakes were sampled in 1973, 1977, 1976, and 1976, respectively, but the other lakes were all sampled in 1980 or early in 1981.

DISCUSSION

The comparison between lake SO_4^{--} times runoff and measured wet and dry deposition is remarkably good, considering all the sources of uncertainty.

A few of the sources of uncertainty for the lake calculations are:

1. Analytical problems in determining SO_4^{--} at low concentrations.
2. The possible terrestrial sources of SO_4^{--} .
3. The possible retention or transformation of SO_4^{--} in the watershed or in lake sediment.

4. The errors in applying runoff to lakes of unknown hydrology.
5. Variations in sampling dates and sampling frequencies.

For measured wet deposition, uncertainties arise from:

1. Analysis of SO_4^{--} , as above.
2. Undercatch, evaporation, etc.
3. Interpolation between stations.
4. Local influences.

For dry deposition, the same difficulties exist as for wet, with the additional problem of estimating deposition velocities.

In the future, it will be possible to eliminate some, if not all, of these uncertainties, but from the present data, it can be concluded that the principal source of SO_4^{--} to these lakes is atmospheric, and that retention in the watershed or other sinks for SO_4^{--} are quantitatively unimportant.

The very high product of lake SO_4^{--} times runoff obtained for Lac Laflamme may be explained by its location at 850 m on a south slope of the Laurentians. More recent data on SO_4^{--} in lakes of

Quebec may be used to help clarify topographic effects on atmospheric transport and deposition.

Early in 1982, 177 lakes in Quebec between latitude 70° and 77°W and longitude 45°30' and 48°30N were sampled. This area is generally described as the Laurentian Highlands of Quebec, but locally higher parts of the Highlands occur in the vicinity of Mont Tremblant and again, and higher, in the Laurentides Provincial Park, north of Quebec City. Runoff is consistently higher in these more elevated areas than in the surrounding relatively lower areas. Runoff data for 1981 and 1982 are not yet available, but total precipitation data for 1981 show below normal rainfall at Maniwaki but normal or above normal amounts of precipitation further south and further east. From consideration of runoff and precipitation patterns, a runoff value was assigned to each lake, and lake SO_4^{--} times runoff was plotted for each lake on a map of Quebec. Within each sub-area formed by the latitude and longitude lines, there are from 2 to 27 lakes. For each sub-area a mean lake SO_4 times runoff was calculated, outliers being discarded, and mean values so calculated are shown on Figure 3, together with some CANSAP/APN data for 1981/80. The agreement is generally good, and shows the effect of topography. The dip in the contour between 73° and 74°W and 46° and 47°N is likely due to the lakes being in a shadow area behind Mont Tremblant. The same dip is shown in a plot of lake concentrations of SO_4^{--} from some earlier surveys (Bobée et al. 1982).

The contours in Figure 3 are very approximate, because runoff was estimated very generally, but the general patterns of atmospheric deposition it suggests are entirely reasonable.

Topographic effects on the amounts of precipitation and associated SO_4^{--} deposition may be seen in Figure 4, a generalized topographic map of the Island of Newfoundland. Rivers in Newfoundland have been monitored with monthly samples in some cases from 1965 to 1981.

In Figure 4, for rivers with large data sets, long term mean excess SO_4^{--} times long term mean runoff is plotted on a generalized topographic map of the Island of Newfoundland. The plot shows the highest products of rivers SO_4^{--} times runoff in the southwest, next highest in peninsula regions, and lowest in inland or topographically sheltered regions. The plot also suggests that the polluted air masses that have been channeled down the St. Lawrence Valley are deflected mainly to the northeast by the Long Range Mountains. Along the northern part of the peninsula, however, bedrock consists of Ordovician limestones and other sedimentary rocks, and the possibility of some terrestrial sources of SO_4^{--} cannot be excluded.

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FIGURE CAPTIONS

Figure 1. Map of eastern Canada showing locations of CANSAP/APN stations (dots) and lake sampling sites (named).

Figure 2. Comparison of lake SO_4 times runoff with measured wet and dry deposition, with data shown on an approximately west to east axis.

Figure 3. Map of part of southern Quebec showing mean lake SO_4^{--} times runoff compared with measured wet and dry deposition.

Figure 4. Generalized topographic map of the Island of Newfoundland showing long term mean SO_4^{--} in rivers times long term mean runoff.

Table 1. Summary of Data used in preparing Figure 1.
 The lake or CANSAP or APN station locations, the year of the samples, the mean SO_4^{--} (or excess SO_4^{--}) for each set of lake data, the uncertainty on the mean at the 95% confidence level using student's T test, expressed as a percent of the mean, the runoff, the product of lake SO_4^{--} times runoff, wet deposition (CANSAP) and dry deposition (APN) in 1980.

	Yr	$\bar{x}\text{SO}_4^{--}$		Runoff ($\bar{x}\text{SO}_4$)(Runoff)		Deposition	
		meq m ⁻³	±%x	m yr ⁻¹	meq m ⁻² yr ⁻¹	WET meq m ⁻²	DRY yr ⁻¹
ELA	73	78	4	0.15	12	12	5
Quetico	81	77	14	0.25	19	23	
Thunder Bay	77	98	10	0.3	29	26	
Algoma	80	131	2	0.5	66	41	
Sudbury	76	258	5	0.4	103	76	
Long Point	80	-	-	--	--	72	72
Haliburton	81	203	19	0.5	101	77	
Algonquin	80	211	3	0.44	93	64	
Maniwaki-Chalk R.	80	-	-	--	--	63	24
Ste. Agathe	76	139	5	0.57	79	56	
Mauricie	80-81	151	3	0.6	91	70	
Laflamme	81	124	6	0.93	115	80	
New Brunswick	81	76	5	0.7	53	56	
Nova Scotia-Keji	80	45	6	0.93	42	35	7
Newfoundland	80	42	5	1.0	42	44	
Labrador	80	33	14	0.6	20	20	

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