

EVALUATION OF THE EFFECTS OF ACID PRECIPITATION IN EASTERN CANADA USING THE RAISON SYSTEM

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Abstract. Evaluations have been made of the key chemical factors in the aquatic effects upon surface waters due to acidic precipitation in eastern Canada. The region of Canada east of the Manitoba / Ontario border was divided into 22 aggregates and assessments of inorganic and organic ion chemistry appraised relative to sulphate deposition rates and distributions. Aquatic sensitivity is largely dominated by the concentration, distribution and magnitude of SO_4^{2-} (sulphate) deposition and by the prevalent geology and derived soils found in each aggregate. The RAISON system provided an adaptable and highly flexible platform to evaluate interactively, multiple data sets of divergent characteristics. Attributes usually associated with geographical information systems are significantly augmented by quantitative numerical and stochastic capabilities that were used extensively in this study.

1. Introduction

Expert systems are finding expanded uses in many applications including the industrial, military and business sectors. The field of environmental evaluation and research has long been involved in large scale data intensive investigations and simulation modelling for both forecasting and diagnostic studies. By using advances in the field of computation such as expert systems investigators can now handle interactively the typically large data sets with relative ease. The expert system, RAISON (Swayne and Fraser, 1986), which combines database, spreadsheet and GIS (geographical information systems) with environmental system modelling has been used to assess the aquatic effects of acidic precipitation in eastern Canada (RMCC, 1990a). Using the RAISON system facilitated the entire task by providing flexibility in data handling, analysis and display. This paper will describe only a part of the overall assessment, namely the quantitative evaluation of the relationships between atmospheric deposition and surface water chemistry.

The principal relationship governing aquatic chemistry effects due to deposition is a three way factor between (1) SO_4^{2-} deposition, (2) ionic composition of the receiving waters, and (3) geology and soil characteristics of the receiving watershed. Although nitrogen (NO_x) compounds are important, their significance in control scenarios is secondary to sulphate compounds, which dominate the chemistry of acidification processes in eastern Canada.

Evaluation of aquatic resources at risk requires accurate estimation of surface water chemistry. The regions of Canada most susceptible to the acidic deposition are those which have terrain characteristics with little ability to neutralize acids either organic or

mineral in nature (ie. having silicate bedrock and thin coarse-grained soils). Terrain of this type that receives elevated SO_4^{2-} deposition is located principally within the Precambrian geological formations known as the Canadian Shield east of the Manitoba-Ontario border and approximately south of 52° N latitude. This is the area of primary concern for aquatic effects in Canada.

2. System Characteristics

One of the distinctive features of the RAISON expert system is its capability for quantitative numerical analysis and evaluation in conjunction with GIS mapping functions (Swayne *et al.* 1989). The system is capable of database manipulations of data of differing type and format. These data can be accessed in database form or transferred to the spreadsheet sub-system where functional relationships can be applied. Within the spreadsheet module expert system rule sets can also be formulated and/or edited. Once activated, results of analyses whether from rule sets, functions or other forms of analysis, can be transferred directly to the map sub-system for display and further GIS type assessments.

Database design using a schema protocol allows user control over the appearance of the database user interface. In structuring the database, individual parameter fields are designated for type and length. The import/export facility is compatible with major commercial packages and can be tailored to allow alternate field mapping to the database on import. This facility allows databases consisting of differing formats and data types to be accessed. The ability to permit multiple formats proved essential for the integrated analyses that were required for the aquatic effects studies described here.

The flexibility of the RAISON system is enhanced by the inclusion of the macro language RPL (RAISON Programming Language). Use of RPL enables the construction of production routines that action and manipulate RAISON system commands in a batch mode, permitting routines developed manually on sub sets of a database to be implemented on the entire data set. The construction of rule sets and models making use of the expert systems capabilities of the RAISON system may be implemented in RPL or, if long execution times would be required, 'C' including the use of a callable RAISON function library (Swayne *et al.* 1990).

3. Analysis

Due to the diversity of the watershed characteristics of eastern Canada and the spatial gradients of the SO_4^{2-} deposition field, the region was divided into 22 subregions composed of aggregates of tertiary watersheds (Figure 1, Table I). The aggregates were specified by an objective consideration of water conductivity coupled with subjective knowledge of terrain geology and SO_4^{2-} deposition. Presented in Table I also are the median wet SO_4^{2-} deposition estimates for each aggregate. These data were determined by a polygon overlay within the RAISON system using Kriged deposition fields provided by the Atmospheric Environment Service, Canada (RMCC, 1990b). Deposition is highest in

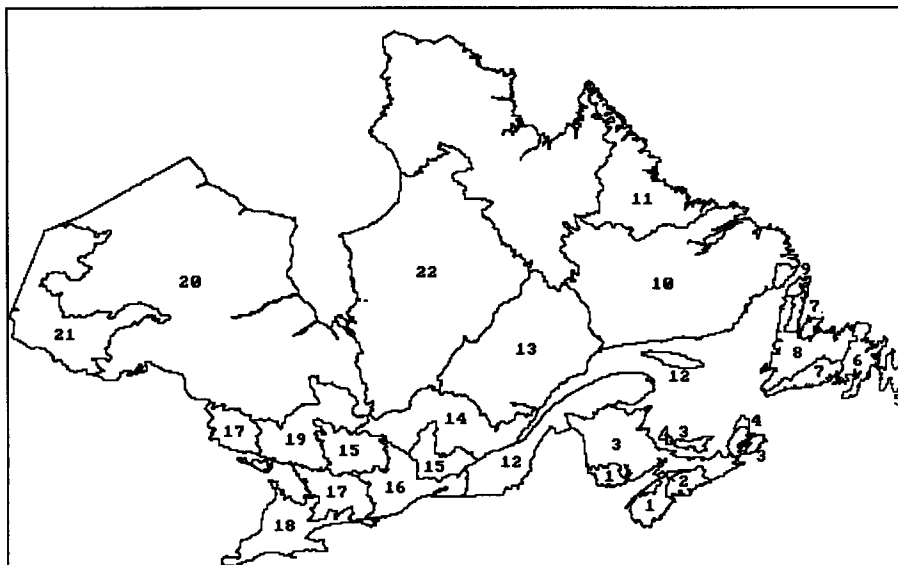


Fig. 1. Eastern Canada aggregate identification and locations.

southwestern Ontario and decreases to the north and east of the country. Total SO_4^{2-} deposition is composed of both wet and dry components. The wet component was computed as the mean of data for 1982–1986 (Table I). Dry SO_4^{2-} deposition was estimated to be approximately 15% of total for all aggregates (Barrie, 1989). Localized exceptions to this were in aggregates containing Sudbury, Ontario and Halifax, Nova Scotia.

All data were subjected to intensive QA/QC screening (Fraser *et al.* 1990). During the data screening process it was found that the contribution of the NO_3^- ion to the ion balance was quite small and hence this component was eliminated from the main ion balance determinations. Percentile analyses were carried out on all major ion parameters (H^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , and ANC^{2-} , Acid Neutralization Capacity). After the screening process, approximately 8500 lakes were distributed across the study area as shown in Figure 2.

3.1. BASE CATIONS

The sum of base cations is defined as: $\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ where the individual ion concentrations are corrected for sea salt contributions when necessary. Ca^{2+} and Mg^{2+} are the predominating base cations with Na^+ and K^+ representing only a small fraction, from 12–18% of the sum in the Ontario case (Neary and Dillon, 1990). For those aggregates in which sea salt corrections were applied, Na^+ and K^+ concentrations are negligible. The sum of base cations was assessed for each aggregate as an indicator of overall aquatic

TABLE I

Name of data aggregates and median conductivity (μS) and median wet SO_4^{2-} deposition ($\text{kg}/\text{ha}/\text{yr}$) for sample lakes within each aggregate.

Aggregate Number	Aggregate Name	Specific Conductance (μS)	Wet SO_4^{2-} Deposition ($\text{Kg}/\text{ha}/\text{yr}$)
1	S Nova Scotia-New Brunswick	28	14.5
2	Mid-eastern Nova Scotia	45	13.7
3	N Nova Scotia-New Brunswick	36	13.8
4	Cape Breton Highlands	26	12.9
5	Avalon	34	9.5
6	E Newfoundland	28	8.9
7	N&S Newfoundland	18	10.4
8	Central & W Newfoundland	24	10.1
9	Belle Isle	79	8.2
10	E Quebec - S Labrador	11	7.5
11	N Labrador	10	5.5
12	St. Lawrence S Shore	92	26.9
13	Saguenay	21	14.0
14	Laurentide	21	20.9
15	SW Quebec	32	22.9
16	Ottawa Valley	47	22.7
17	Central Ontario	32	24.7
18	S Ontario	315	>25.0
19	Sudbury-Noranda	39	19.4
20	N Ontario	89	14.9
21	NW Ontario	33	8.3
22	N Quebec	19	15.9

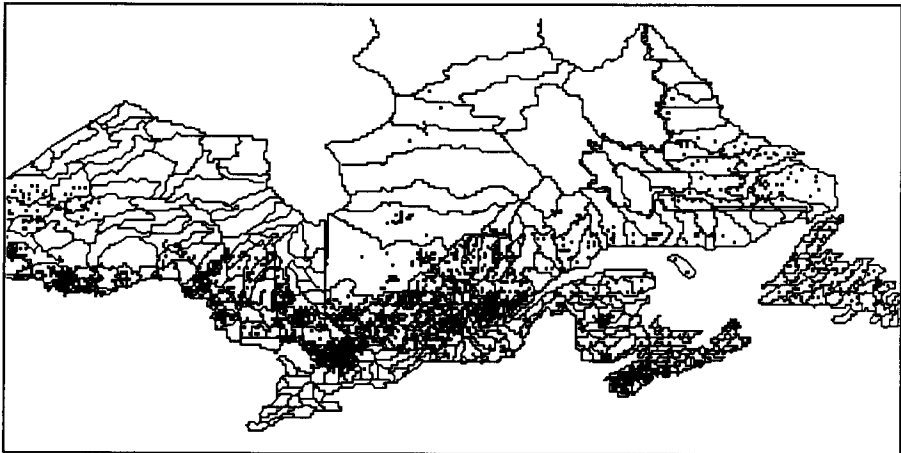


Fig. 2. Eastern Canada station locations after screening.

sensitivity to acidic precipitation. Aggregate box plots of the sum of base cations (Figure 3) display the 10th, 25th, 50th, 75th, and 90th percentile concentrations arranged geographically from west to east. They show a decreasing trend in base cations heading east from the Manitoba – Ontario border. In the box plot figures presented here the number located at the top of each bar is n , the number of samples included in the test. Of the 22 aggregates, northern Ontario (Aggregate 20) has an atypical frequency distribution showing high variance and a substantially higher median value (1036 $\mu\text{eq/L}$) than the remaining aggregates. The glacial tills that are present in aggregate 20 contain small amounts of easily weathered CaCO_3 derived from the region around Hudson's Bay (Shilts, 1981), thereby explaining the base cation distribution. Aggregate 12, which is located in the Eastern Townships of the Province of Quebec south of the St. Lawrence river stretching up and including the Gaspé region, has bedrock composed of limestone and dolomite. The cation distribution from this region also shows a high variance with a median value of 376 $\mu\text{eq/L}$. Regions of Canada that have low levels of base cations (eg. $< 200 \mu\text{eq/L}$) are considered to be sensitive to the effects of acidic precipitation. This includes much of Quebec and nearly all of the Atlantic Provinces.

Consideration of nitrogen compounds (NO_3^- and NH_4^+) and their relative importance to aquatic acidification processes has been made by Dillon and Malot (1990). It has been found that in the Canadian case N deposition and soluble nitrogen compounds have only a minor effect upon acidification in comparison to the strong influence of the S compounds. Base cation balances proceeded adequately without the inclusion of nitrogen compounds.

3.2. ACID NEUTRALIZATION CAPACITY

Acid Neutralization Capacity (ANC) is also an important parameter used to identify the level of sensitivity in lake chemistry. It shows predominantly low values for most

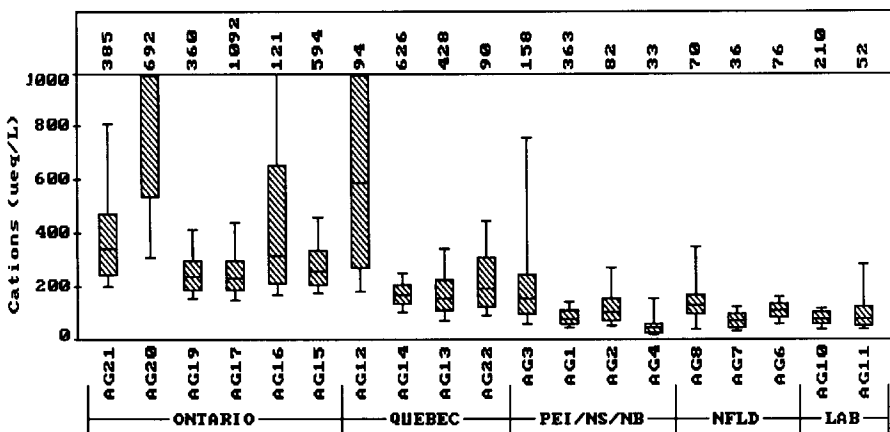


Fig. 3. Sum of cations for Eastern Canada aggregates.

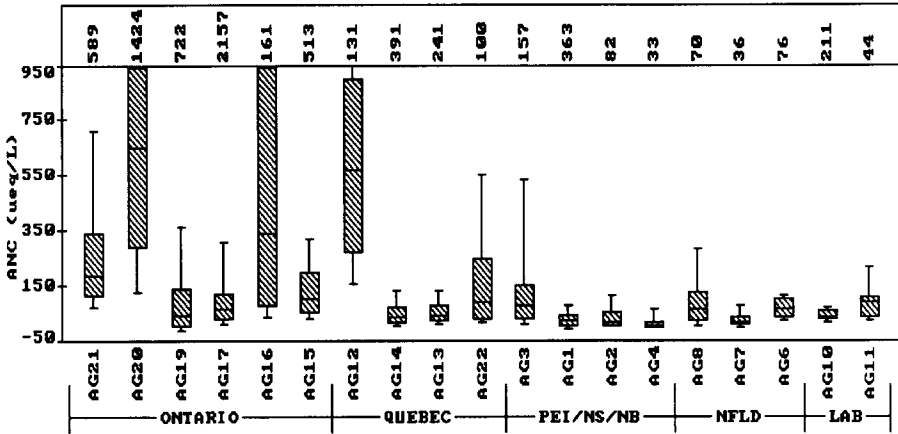


Fig. 4. Acid neutralization capacity for aggregates in Eastern Canada.

aggregates in Atlantic Canada, much like base cations (Figure 4). In fact, the spatial distribution of base cations and ANC are very similar (compare Figure 3 with Figure 4). Ratings of aquatic sensitivity have been determined for eastern North America based on ANC concentrations (Linthurst *et al.* 1986). Aquatic sensitivity ranges for ANC are used as shown in Table II.

Aggregates 12 (south of St. Lawrence River) and 20 (N Ontario) show median values in the range for low sensitivity. The variance is high, however, with approximately 30% of the distribution classed as sensitive or lower. Aggregate 16 (Ottawa Valley) also shows ANC variance primarily due to extremely variable geological sensitivity. The median value from the frequency distribution of 208 $\mu\text{eq/L}$ ANC indicates that overall the area is moderately sensitive to acidification with a high proportion of the lakes being acidic (43.9%) or very sensitive (9.7%). Median values for ANC in the aggregates are presented in Table III.

TABLE II
Aquatic sensitivity scale for acid neutralization capacity (ANC).

Range ($\mu\text{eq/L}$)	Rating
$\text{ANC} \leq 0$	acidic
$0 < \text{ANC} \leq 50$	very sensitive
$50 < \text{ANC} \leq 200$	sensitive
$\text{ANC} > 200$	not sensitive

TABLE III
Median ANC ($\mu\text{eq/L}$) by aggregate in Eastern Canada.

Aggregate	ANC ($\mu\text{eq/L}$)	Aggregate	ANC ($\mu\text{eq/L}$)
1	18.0	12	568.0
2	13.0	13	56.5
3	74.3	14	42.9
4	2.0	15	78.0
5	36.0	16	338.0
6	62.0	17	62.0
7	15.4	18	**
8	60.5	19	35.1
9	**	20	641.0
10	34.0	21	188.0
11	91.7	22	86.7

** Insufficient Data

3.3. SULPHATE

Determination of the source of SO_4^{2-} in the lakes of eastern Canada is a process of elimination. Geologically, the soils of eastern Canada do not significantly adsorb SO_4^{2-} , Rochelle *et al.* (1987) and there is very little evidence that natural occurrences of sulphur bearing minerals have a large effect on lake concentrations (Wright, 1983; Neary and Dillon, 1990). The only remaining factor to explain the aggregate distribution of lake SO_4^{2-} concentrations across eastern Canada is SO_4^{2-} deposition, which is highest in southern Ontario with decreasing gradients to the north and east with the exception of the local sources at Sudbury-Noranda. As can be seen in Figure 5, spatial variation in lake SO_4^{2-} distributions reflect closely the deposition pattern observed in eastern Canada.

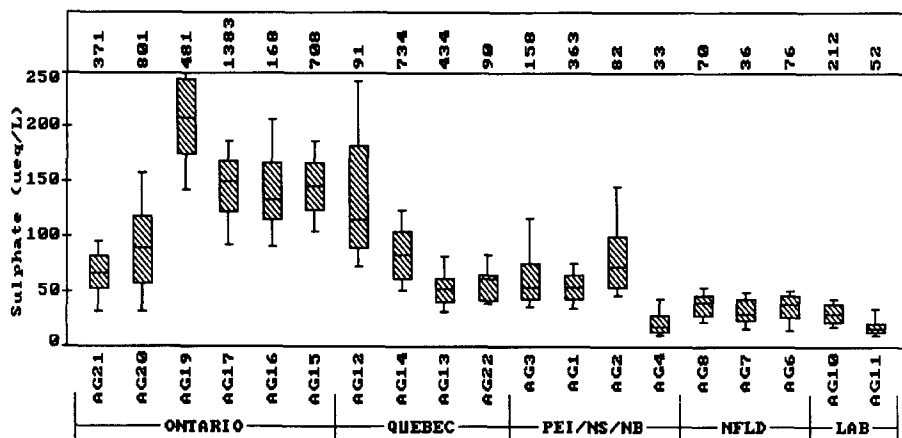


Fig. 5. Sulphate percentile plot by aggregate for Eastern Canada.

Localized influences in the Sudbury-Noranda region (aggregate 19; median value SO_4^{2-} 208.2 $\mu\text{eq/L}$) is clear from the overall distribution. Elevated SO_4^{2-} concentrations in aggregates between the Laurentide (14) and N Ontario (20) regions strongly relate to long-range transport and continental deposition fields. Median lake sulphate concentrations in Nova Scotia and New Brunswick (regions 1, 2 and 3), where sulphate depositions are lower, have values of approximately 54 $\mu\text{eq/L}$. Insular Newfoundland, at the far east of the deposition field, yields a median SO_4^{2-} value of 36 $\mu\text{eq/L}$.

When considered in conjunction with the distributions of ANC, these results indicate that the regions of Sudbury-Noranda (Aggregate 19), the Laurentian highlands (Aggregates 13, 14 and 15), Central Ontario (Aggregate 17) and the Atlantic region exhibit the most pronounced effects of aquatic acidification. Aggregate 19 (Sudbury) receives the highest rate of SO_4^{2-} deposition (wet + dry) in eastern Canada, and the highest median lake SO_4^{2-} concentration (200 $\mu\text{eq/L}$) was observed for the Sudbury region. In the highland region of southwestern Quebec (aggregate 15) a lower median value of 140 $\mu\text{eq/L}$ SO_4^{2-} was observed because local sources are of lesser importance here. To examine the overall influence of SO_4^{2-} deposition upon lakes in eastern Canada, total SO_4^{2-} deposition (wet + dry) was regressed against median lake SO_4^{2-} concentrations by aggregate. Dry deposition estimates were constant for all aggregates with the exception of the local effect areas of Sudbury (AG 19) and Halifax (AG 2) see RMCC (1990a). The relationship was significant ($p < 10^{-6}$) (where p is the probability function that the relationship is not significant) and strongly correlated ($R^2=0.92$) (Figure 6).

The sensitive shield lakes located in aggregates 15, 16 and 17 in central Ontario are grouped above the regression line. This indicates that relative to SO_4^{2-} , the lakes in these

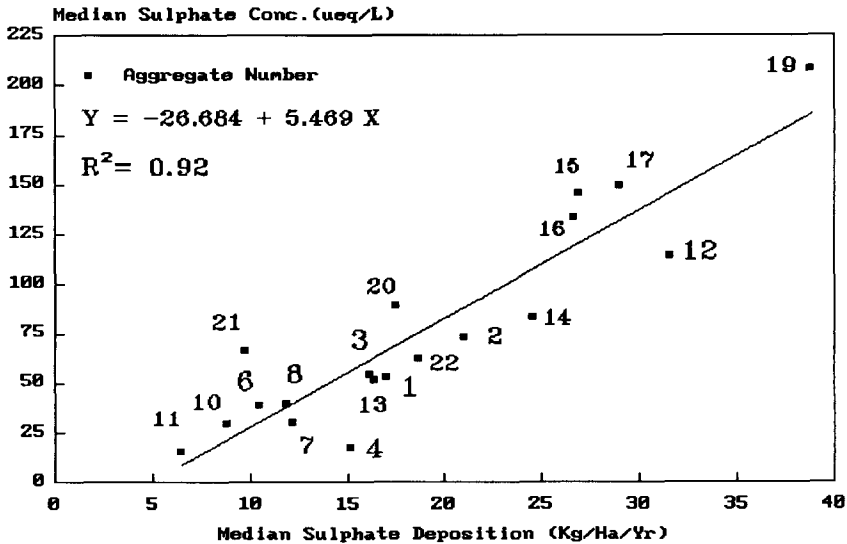


Fig. 6. Sulphate deposition vs sulphate in Lakes of Eastern Canada aggregates.

regions have little buffering capacity to moderate the effects of acidic deposition. Aggregate 12 (S St. Lawrence River) experiences high levels of SO_4^{2-} deposition moderated by good buffering capacity provided by the geology of the region. The relationship holds well also for soft water lakes (AG 6, 10, 11) located in Newfoundland and Labrador.

3.4. ORGANIC ACIDS

Naturally occurring organic acids may be a source of acidity and hence pH and ANC depression in natural waters. Their influence can be estimated from dissolved organic carbon (DOC) concentrations in surface waters by calculating the organic anion (A^-) concentration using the method of Oliver *et al.* (1983). In our analysis we used a charge density of $5 \mu\text{eq}/\text{mg C}$ rather than $10 \mu\text{eq}/\text{mg C}$ as specified by Oliver *et al.* (1983).

Aggregate boxplots of A^- show that much of eastern Canada has concentrations between 6 and $10 \mu\text{eq}/\text{L}$ (Figure 7). Notable exceptions to this are aggregates 6, 20 and 21, E Newfoundland, N Ontario and NW Ontario respectively. In these areas, median A^- values are greater than $20 \mu\text{eq}/\text{L}$. These results indicate the presence of systems producing greater amounts of organic acids. The importance of these A^- concentrations must be considered relative to the ionic composition of the waters. Using base cations (Figure 3) as a surrogate for the overall composition, it is apparent that A^- is of greater relative importance in eastern Quebec and the Atlantic Provinces.

3.5. A^- : ($\text{A}^- + \text{SO}_4^{2-}$) RATIO

Aquatic geochemical relationships inherent in acidification processes can be expressed in terms of ratios of the ionic components. Ratios have been extensively used in the assessment of surface water acidification processes (Jeffries, 1991; Schindler, 1988). Evaluation of A^- relative to SO_4^{2-} in lakes was determined for all aggregates (Figure 8). As

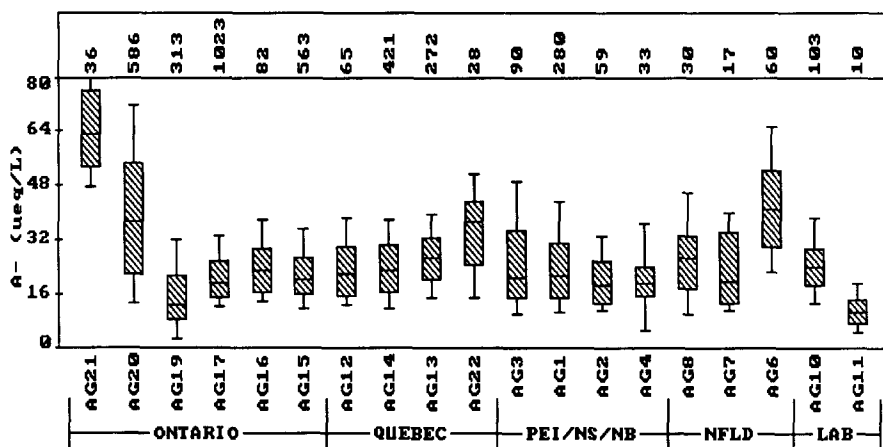


Fig. 7. Organic acids in Eastern Canada by aggregate.

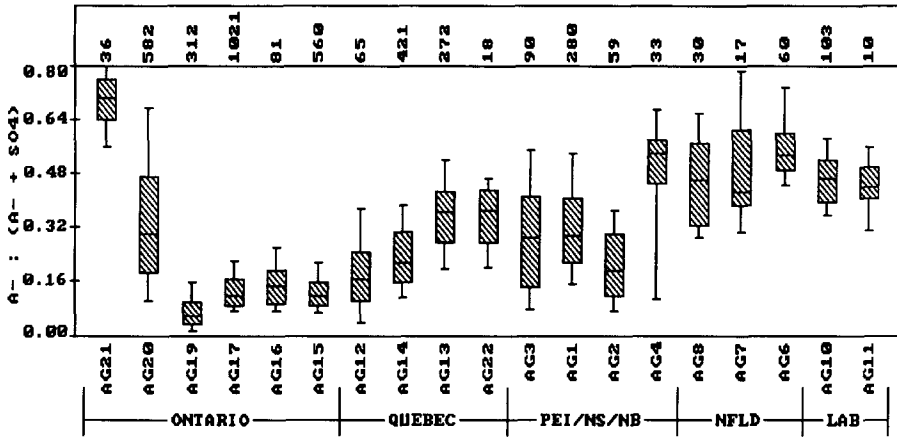


Fig. 8. Ratio of organic acids to sulphate + organic acids.

the ratio decreases from a value of 1, the relative importance of SO_4^{2-} increases. Once outside NW and N Ontario, the ratio increases from west to east. Such a change is due to the increases in lake SO_4^{2-} concentrations, not the concentration of A^- . Hence, SO_4^{2-} is relatively much more important (ratio < 0.2) in southern Ontario and southwestern Quebec, but A^- is increasingly more important to the east and northwest. However, there are few occasions when SO_4^{2-} and A^- are equally important (ratio = 1).

4. Conclusions

By use of the RAISON system, emphasizing the numerical and analytical capabilities within the system, a detailed assessment of the surface water chemistry for eastern Canada has been carried out. Lakes located on the Canadian Shield and in the Atlantic region where cation and ANC levels are generally lower, are more susceptible to the effects of acid precipitation. Although there is considerable variability, terrain considerations dominate the overall factors of buffering. In the presence of calcareous rocks such as limestones and dolomites, and their derived soils, as are found in southern Ontario and the south side of the St. Lawrence R. in Quebec, ANC levels are generally higher and hence the effect upon water courses is somewhat mitigated, permitting higher SO_4^{2-} loads to be buffered before damage may be identified.

In considering SO_4^{2-} in the surface waters of eastern Canada it is clear that atmospheric deposition is the dominant factor controlling aquatic concentrations. There is a strong spatial relationship between SO_4^{2-} deposition and surface water SO_4^{2-} concentrations.

Examination of possible alternate causes of lake acidification such as the presence of organic acids showed that in some areas such as Nova Scotia and parts of New Brunswick, the acid anion A^- was a significant contributing factor. However, overall, the predominating factor determining lake acidification was sulphate deposition.

The RAISON system has provided an extremely versatile, complete and flexible platform on which to evaluate problems involving interpretation of large scale databases. The ability to handle and manipulate multiple databases of differing data types within a single system proved invaluable in the work.

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