

**LONG RANGE TRANSPORT OF ATMOSPHERIC POLLUTANTS  
EASTERN CANADA DATABASE CHARACTERISTICS**

**by**

**A.S. Fraser, J.L. Jones and D.S. Jeffries**

**Rivers Research Branch  
National Water Research Institute  
Canada Centre for Inland Water  
Burlington, Ontario, Canada L7R 4A6**

**March 1990  
NWRI Contribution #90-61**

## ABSTRACT

As a requirement for the determination and evaluation of aquatic effects due to the long range transport of atmospheric pollutants, all available aquatic data necessary for this determination was brought together. Screening and editing protocols were developed and applied to all data on a record by record, parameter by parameter basis. Statistical summaries were evaluated and all data sets were corrected for marine influence where necessary. Ion balance techniques were used to assess sample integrity. The final database consists of 324 tertiary watersheds containing 8,505 stations with 20,629 lake sample records. The region of eastern Canada was divided into 22 aggregates to minimize the spatial variance associated with regions of diverse geological composition and a graded  $\text{SO}_4^{2-}$  deposition field.

## RÉSUMÉ

Comme prérequis pour la détermination et l'évaluation des effets aquatiques causés par le transport à grande distance des polluants atmosphériques, toutes les données aquatiques disponibles nécessaires à cette fin ont été assemblées. Les protocoles de dépistage et de traitement des données ont été élaborés et appliqués à toutes les données, enregistrement par enregistrement et paramètre par paramètre. Des résumés statistiques ont été évalués et tous les ensembles de données ont été corrigés pour tenir compte de l'influence marine au besoin. Des techniques de bilan ionique ont été utilisées pour évaluer la valeur des échantillons. La base de données finale porte sur 324 bassins versants tertiaires comptant 8 505 stations et 20 629 enregistrements d'échantillons de lacs. La région de l'Est du Canada a été divisée en 22 ensembles pour minimiser la variance spatiale associée à des régions de composition géologique diverse et à un champ de dépôts triés de  $\text{SO}_4^{2-}$ .

## MANAGEMENT PERSPECTIVE

Aquatic chemistry databases representing all available sampled lakes east of the Manitoba/Ontario boarder in the region predominantly south of latitude 52 degrees N. were compiled for the preparation of the detailed assessment of aquatic effects of acid precipitation in Canada. Additional information for the western provinces of Canada were received for evaluation and inclusion. All data sets were subjected to rigorous examination for quality assurance including summary statistical evaluations on a parameter by parameter, record by record basis. Several ion balance techniques and parameter ratios were assessed to estimate data acceptance. For the region of eastern Canada after all editing and selection criteria had been applied, 324 tertiary watersheds containing 8,505 stations with 20,629 sample records formed the primary aquatic lake chemistry database. Of the samples that were sufficiently complete for ion balance calculation, 94% passed the testing criteria of the control chart technique after all editing had been completed.

Much of the region under study is classed as being under marine influence. All data located within aggregates so classed were subjected to a sea-salt correction function.

Due to the geographical extent of this study which includes regions of diverse geological and soil characteristics overlaid with a graded

atmospheric sulphate deposition field, the study area was divided, based principally upon a specific conductance criteria into 22 aggregates. This process minimized the spatial variance component within the respective aggregates. Parameter summaries are presented for each aggregate for the primary parameters Ca, Mg, CB\* (sum of base cations),  $\text{SO}_4^{2-}$ , ANC (acid neutralization capacity, and DOC (dissolved organic carbon).

The databases constructed for this project became the primary aquatic lake chemistry data source for the detailed aquatic effects assessment report to the RMCC. Similarly, many of the modelling activities that contributed to the RMCC report made use of these data sets for calibration, verification and application of various scenarios.

## PERSPECTIVE DE GESTION

Des bases de données de chimie aquatique représentant tous les lacs échantillonnés disponibles situés à l'Est de la frontière Ontario-Manitoba, dans une région dont la plus grande partie est au sud du 52<sup>e</sup> parallèle, ont été compilées pour la préparation d'une évaluation détaillée des effets aquatiques des précipitations acides au Canada. Des informations supplémentaires provenant des provinces de l'Ouest du Canada ont été reçues afin d'être évaluées et intégrées. Tous les ensembles de données ont été soumis à un contrôle rigoureux d'assurance de la qualité, y compris des évaluations statistiques sommaires paramètre par paramètre et enregistrement par enregistrement. Plusieurs techniques d'équilibre ionique et de rapport des paramètres ont été évaluées afin d'estimer l'acceptabilité des données. Pour la région de l'Est du Canada, après tout le travail de traitement des données et l'application de tous les critères de sélection, on a retenu 324 bassins versants tertiaires comptant 8 505 stations et 20 629 enregistrements d'échantillons pour former la base de données primaire sur la chimie aquatique lacustre. Quatre-vingt-quatorze pourcent des échantillons qui étaient suffisamment complets pour des calculs de bilan ionique étaient conformes aux critères d'essai selon la technique du diagramme de contrôle, après le traitement des données.

On classe une bonne partie de la région à l'étude dans la catégorie "influence marine". Toutes les données situées à l'intérieur des ensembles ainsi classés ont été soumises à une fonction de correction pour le sel marin.

A cause de l'étendue géographique de cette étude qui comprend des régions de caractéristiques géologiques et pédologiques diverses sur lesquelles est situé un champ de dépôts triés de sulfate atmosphérique, la zone de l'étude a été divisée en 22 ensembles, d'après des critères de conductance spécifiques. Ce procédé a permis de minimiser l'élément variance spatiale dans chacun des ensembles. Pour chaque ensemble, on présente des résumés des principaux paramètres : Ca, Mg, CB\* (somme des cations basiques),  $\text{SO}_4^{-2}$ , CNA (capacité de neutralisation de l'acide et COD (carbone organique dissous)).

Les bases de données élaborées dans le cadre de ce projet sont devenues les principales sources de données sur la chimie aquatique lacustre qui ont été utilisés pour le rapport détaillé sur l'évaluation des effets aquatiques, qui a été présenté au CCRS. De même, bon nombre des activités de modélisation qui ont été utilisées pour le rapport présenté au CCRS utilisaient ces ensembles de données pour l'étalonnage, la vérification et l'application de divers scénarios.

### ACKNOWLEDGEMENTS

The authors wish to thank the many individuals that contributed to this report. Particularly, Dr. R.L. Thomas who's guiding principles and advice in the aquatic effects assessment were a driving force in the work. We thank Dr. D.C.L. Lam for his continuing support and advice and J. Haemerli, G. Howell, P. Dillon, B. Neary and J. Dupont for their constructive comments and assistance during the course of the work. We also wish to express our gratitude to all the members of the informal working group on aquatic effects for their contributions. The authors also acknowledge the many, perhaps hundreds of personnel who were responsible for the collection, analysis and preparation of the millions of data points included in the databases that were interrogated during the course of this work.



## LONG RANGE TRANSPORT OF ATMOSPHERIC POLLUTANTS

### EASTERN CANADA DATABASE CHARACTERISTICS

#### INTRODUCTION

As the requirements for an overall assessment of the aquatic effects caused by the long range transport of atmospheric pollutants became clear, a grouping of interested science personnel who were actively working on acid precipitation research in the aquatic field was drawn together. The group consisted of Federal and Provincial scientists with both national and regional affiliations. Activities of the group were co-ordinated in the Rivers Research Branch, National Water Research Institute of Environment Canada located at Burlington Ontario. A listing of personnel included in the group is provided in Appendix A.

The principal aim of our work was to collate and evaluate all available data on aquatic effects in Canada and present a series of reports on our findings and conclusions. This report on data sets and their status is the first in a series that we hope will be a complete national perspective of the condition of Canada's lakes relative to acid precipitation. The reports include recommendations based upon these findings that may form part of a concerted effort to alleviate the problems of acid stressed lakes in Canada.

## DATABASES

The database for the overall aquatic effects assessment was divided into three primary areas, aquatic, terrestrial and atmospheric. Each of these data areas have distinctive characteristics that required specialized handling and analysis protocols. Regional divisions of Canada were maintained on a Provincial basis to enable ease of data manipulation. Of specific concern, due to large scale LRTAP related effects and availability of data, the region east of the Manitoba / Ontario boarder received a priori consideration and attention.

### AQUATIC DATABASE

The aquatic database for this assessment provides the detailed information required for aquatic resources at risk determination and the calibration and verification of modelling activities. The majority of the data obtained were retrieved from the NAQUADAT archive system maintained by Environment Canada. Supplementary data analyzed and collated by the Province of Nova Scotia plus provincial data for New Brunswick, Newfoundland, and Labrador were received via Environment Canada, Atlantic Region. Supplementary data for the Province of Quebec, were provided directly from Environment Quebec and individual researchers. Data for the Province of Ontario were received from the Dorset Research Station of the Ontario Ministry of the Environment.

Table 1 shows the summary of data holdings by Province for the years 1980 through 1988. It should be noted that the data base described here is the final result after all editing and application of a detailed data

---

Table 1: Final Aquatic Chemistry Database Holdings by Province

---

<u>PROVINCE</u>	<u>WATERSHEDS</u>	<u>STATIONS</u>	<u>SAMPLES</u>
NOVA SCOTIA	30	441	2036
NEW BRUNSWICK	18	193	571
PEI	2	4	17
NEWFOUNDLAND	29	205	535
LABRADOR	20	164	164
QUEBEC	80	2133	11941
ONTARIO	145	5365	5365
	==	==	==
EASTERN CANADA	324	8505	20629

---

protocol has been completed. The original raw data set was approximately 40% larger by the number of records than the final database actually used in the study.

Original data retrievals, work up and editing were in place for both rivers and lakes. However, the decision was made early in the project

to concentrate our efforts primarily upon lakes, as the overall characteristics of lakes reflect conditions in their respective basins more clearly than rivers. All water quality data assessed for the study therefore, were lake samples analyzed by various laboratories following standard documented procedures noted in the NAQUADAT analysis protocols (Water Quality Branch, 1988).

For most of the variables under study several analytical methods were in use by various laboratories during the study period. To assess comparability of analytical methodology all data sets were subjected to statistical assessment on a parameter by parameter basis. Where no significant differences were found between related analytical techniques, data sets were merged by parameter while assigning a method identification tag to the values on a sample by sample basis. Three parameters showed significant differences in analytical results and as such were maintained in discrete form within the database (Table 2).

---

Table 2: Parameters maintained as discrete values with the database

---

<u>NAME</u>	<u>DESIGNATION</u>	
pH	Lab	Field
Sulphate	MTB	IC
Alkalinity	Std.	Gran

---

When more than one analytical method was included for a sample a selection rule was applied to choose which value would be put in the final database. The following rules were applied for data selection. Laboratory pH was selected preferentially over field pH although the effect of air equilibrium for CO<sub>2</sub> partial pressure was not accounted for; GRAN alkalinity was selected over fixed endpoint titration and fixed endpoint data were allowed only for samples where pH > 6; Sulphate measured by ion chromatography (IC) was selected preferentially over Methyl Thymol Blue (MTB) colorimetric method; Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> determined by colorimetric methods were not used in highly coloured waters ( DOC > 4 and/or Colour > 30 ). Organic anion concentrations (A<sup>-</sup>) were calculated from the Dissolved Organic Carbon (DOC) content following a revision of Oliver's method (Oliver et al, 1983).

$$A^- = R * DOC * \frac{K}{K + H} \quad (1)$$

Where:

$$pK = 0.96 + 0.90(pH) - 0.039(pH)^2 \quad (2)$$

$$K = 10^{-pK + 3} \quad (3)$$

$$H = 10^{-pH + 3} \quad (4)$$

$$R = 5.0 \text{ ueq/mg}$$

#### Calculation of A<sup>-</sup> using revised Oliver's method

Numerous organizations and agencies contributed to the database holdings with no single sampling design strategy or program protocol being

followed. Sampling sites and parameters were for the greater part selected to meet the objectives of various individual studies. Therefore, the data are not representative of the greater lake population as was the case for the US Eastern Lake Survey (Landers et al, 1987) or the Finnish lake survey (Kortelainen et al, 1989). The case for the Canadian database finds only the Dupont (in review) data set representing the Outaouais and Mauricie regions to be a statistically designed sampling strategy representative of the lake population (10 - 2000 Ha. size fraction). These data are a sub-set of the overall Eastern Canada database.

The size distribution of the sampled lakes in eastern Canada with an estimated inventory of 774,662 lakes is composed of an extremely large number of very small lakes that are under-represented in both this database and the statistically designed surveys described above. Different components of the database emphasized sampling of different lake sizes. For example, lakes sampled by the National Inventory Survey (Kelso et al., 1986) are biased towards smaller headwater lakes (50 - 100% depending on Province), as are lakes sampled by Environment Canada in the Maritime provinces. The large Ontario component of the database is moderately biased towards important, larger, and accessible sport fisheries lakes. In remote locations (Labrador and other northerly locations), sampling is often accomplished by float plane and thus the lakes must be large enough to permit this type of access. Overall, the

database is not considered to be strongly biased towards a specific size class of lakes, and when combined with a large amount of data, confidence is increased in transferring conclusions based upon the sample population to the overall lake population.

The statistics presented in this report are given as sample estimates and the implications of this in terms of a greater population are noted where appropriate. Statistical extrapolation of sample information to the greater population will be discussed in another report in this series.

An assessment of the fresh water resources of Canada indicates that eastern Canada contains the majority of the water resource when considering both surface area and the number of water bodies (Table 3). The Province of Quebec holds approximately 64% of the water bodies of Canada and as such its vulnerability to the effects of acidic deposition is of major concern.

A large proportion (>80%) of the sampled lakes in the study area were sampled to obtain an integrated composite (ie. tube sample, combination of samples from various depths, etc.). This kind of sampling provides conservative information on lake water quality since it minimizes the large variations that can occur when samples are collected at the lake's surface (eg. due to snowmelt effects, high primary production, etc.).

The remaining samples were primarily one metre depth samples. There was no indication that the mixing of sample acquisition types introduced a data bias or significantly increased the sampling variance.

Table 3. Estimated fresh water resources and wetlands for Canadian Provinces and Territories.

	Freshwater Area (km <sup>2</sup> ) *	Number of Waterbodies **	Wetlands Area (Mha)
Newfoundland/Labrador	5,690/28,340	138,711/---	6792
Nova Scotia	2,650	6,600	177
New Brunswick	1,350	3,600	544
Quebec	183,890	899,700	12151
Ontario***	86,625	193,100	29241
Manitoba	101,590	57,200	22470
Saskatchewan	81,630	94,000	9687
Alberta	16,800	-----	13740
British Columbia	18,070	22,000	3120
Yukon	4,480	-----	1510
Northwest Territories	133,300	-----	27794
Canada	755,180	-----	127230

\* areas from Canadian World Almanac (1989)

\*\* numbers where estimated from Kelso et al (1986) for eastern Canada and Swain (1987) and WNLTC (1987) for western Canada; more accurate estimates for the region south of 52°N latitude and east of 90°W longitude are given in Figure 1.

\*\*\* freshwater area for Ontario excludes the Great Lakes

Laboratories contributing data to the LRTAP monitoring program were subject to a laboratory QA / QC program that was designed to assist contributors in providing the best possible results. All contributing



laboratories participated in both intra-lab and inter-lab quality assurance studies. Further details of the QA / QC program are available (Aspila, 1989).

Water quality sampling stations for eastern Canada were identified and selected based principally upon factors of data availability, period of record and regional representativeness. The long term data requirements for the regional scale LRTAP investigations required the accumulation of all available data from many sources. These data were collected by individuals many times for purposes other than the study of acidic aquatic effects. Thus, in some instances vital parameters may have been missing in a sample suite. Original station retrievals identified all stations that contained suitable data for the study. The restriction of the period of record to that of 1980 - 1988 and the elimination of stations of questionable location and/or suspect reported data, reduced the effective sampling sites to 8,505 in eastern Canada. The distribution of stations is dominated by locations south of latitude 52 degrees north for most of the study area, with less representation further to the north (Figure 1). Preferentially, a sampling program should be statistically designed taking into account spatial and temporal variances. This study did not have this luxury and most sampling took place in reasonably conservative areas. Similarly, lake size distributions favoured larger lakes avoiding any sampling of small lakes (< 1 Ha).

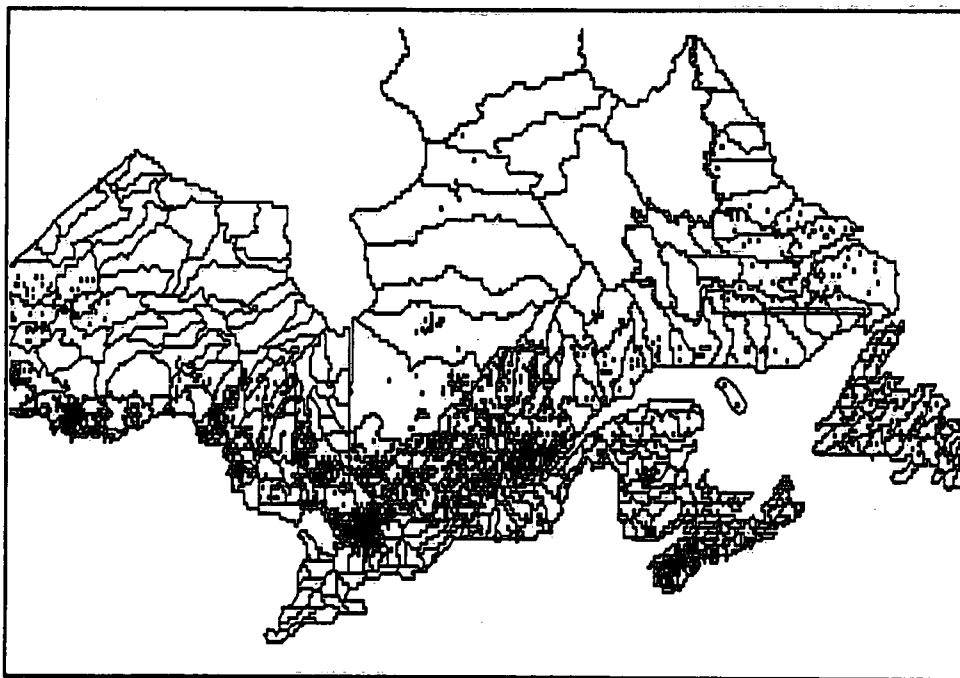


Figure 1: Eastern Canada Acid Precipitation Monitoring Stations.

Required parameters for the aquatic effects resources at risk study were selected as a sub-set of the NAQUADAT archive files. Originally, a suite of 27 parameters were retrieved for all stations selected (Table 4). Of the full aquatic suite available a selection of 15 primary parameters (\*) were identified.

Chemical analyses were performed at large federal or provincial government water quality laboratories using standard methods (Environment Canada, 1979). In constructing the working set of parameters several procedures were invoked as previously described. In all cases where parameter selection were made a code was added to the parameter value in the database to indicate specifically which analysis

technique had been used.

---

Table 4: Water Quality Parameters used in the study

---

<u>PARAMETER</u>	<u>UNITS</u>	<u>DESCRIPTION</u>
* Na	mg/L	Sodium, Dissolved
* K	mg/L	Potassium, Dissolved
* Ca	mg/L	Calcium, Dissolved
* Mg	mg/L	Magnesium, Dissolved
* SO <sub>4</sub>	mg/L	Sulphate, Dissolved
* IC-SO <sub>4</sub>	mg/L	IC-Sulphate, Dissolved
* Cl	mg/L	Chloride, Dissolved
* Alkalinity	mg/L	Alkalinity (CaCO <sub>3</sub> )
* Gran Alk.	mg/L	Gran Alkalinity (CaCO <sub>3</sub> )
* pH	(pH)	Field pH
* pH Lab	(pH)	Laboratory pH
* Colour	(Colour)	Colour, Apparent
* Colour	(Colour)	Colour, True
* SpCon	(usie/cm)	Specific Conductance
Al-D	mg/L	Aluminum, Dissolved
Al-E	mg/L	Aluminum, Extractable
Fe-D	mg/L	Iron, Dissolved
Fe-E	mg/L	Iron, Extractable
Fe-OE	mg/L	Iron, Organic Extractable
Hg-E	mg/L	Mercury, Extractable
Mn-D	mg/L	Manganese, Dissolved
Mn-E	mg/L	Manganese, Extractable
Pb-D	mg/L	Lead, Dissolved
Pb-E	mg/L	Lead, Extractable
NO <sub>3</sub> + NO <sub>2</sub>	mg/L	Nitrate + Nitrite - N
NH <sub>4</sub>	mg/L	Ammonia, Dissolved - N
* DOC	mg/L	Dissolved Organic Carbon

---

In some cases the critical parameter ANC was missing from a sample analysis. Acid Neutralization Capacity (ANC) when taken in accord with the pH approximates the bicarbonate concentration and can account for deficits in alkalinity. Rather than accepting a missing data point or

accepting a logged value of zero (occasionally a laboratory would log a zero value as detection limit) the cations and anions for the sample were evaluated to determine if sufficient parameters were present to estimate the missing alkalinity by ion balance. Under these circumstances ANC would be estimated and a flag added to the value to identify it as an estimated value. The ANC estimation factor was not widely required in the data evaluation, finding use principally on data from Quebec in less than 10% of the incidents. Correction factors therefore, do not strongly bias or otherwise influence the overall data set.

#### DATA VALIDATION

The onerous task of examining and validating such a large and diverse data set was handled by stages.

- 1) Preparation of summary statistics including the following:  
mean, median, standard deviation, standard error, skewness,  
kurtosis, variance, maximum, minimum.
- 2) Identification of spurious errors and outliers by  
identifying problems with analytical and sampling  
procedures.

3) Removal of suspect data either by entire station or by individual parameter. All missing data or removed parameter values were set to -99.9 as a flag in the data sets.

4) Application of ion balance techniques described below.

There were many data points that were suspect for individual and sometimes unique reasons. On several occasions data work up and evaluation detected major inconsistencies in the data records for specific stations. When identified, such stations were investigated on a direct basis to determine their exact location and the nature of the sampling that took place. The chief cause of major data discrepancies was the inclusion of industrial sampling sites or sites with major anthropogenic influence (eg. road salting), in the files of otherwise ambient water quality data stations. Such stations were deleted from the database. When possible, consultation with the scientist responsible for the station data was sought to identify specific causes. A record of all such station deletions was maintained. Similarly, major deviations in analytical results on a parameter by parameter basis were evaluated and if necessary deletions made. Consultation with the appropriate project scientists regarding suspect data was made where possible to document significant problems. The editing procedures were not used to sanitize the database and thereby remove all unusual points that were not readily explainable. The intent of the editing component was to verify that the

data were internally consistent and that it met the criteria for balanced ion chemistry when there were sufficient parameters present.

#### ION BALANCE

Three procedures were used to check upon the overall ion balance.

- 1) Control chart analysis for anion - cation balances (APHA, 1985).

This procedure required a complete suite of cations and anions to operate. Approximately 8,000 out of 20,500 passed the initial criteria for the test to be run. Of these 8,000 samples 94% passed the testing criteria within one normalized deviation for natural waters.

- 2) A 10% cation : anion ratio deviation filter was applied to the database.

- 3) A 20% cation : anion ratio deviation filter was applied to the database.

The data quality for the samples in which all ions required for a full

balance were present indicated that the overall data is acceptable for further analysis. When considering individual parameters the restrictive criteria of complete ion presence would eliminate large amounts of data unnecessarily and we chose to evaluate individual parameters on the basis of distributions to determine acceptance. In the case of the Ontario database very small amounts of chloride data were in the data set received from the Province. Ion balances of these data were made neglecting the contribution of chloride. The principal Ontario investigator indicated that chloride plays a negligible contribution to ion chemistry in the lakes under study (Neary et al, 1990; Dillon, Pers. Comm).

It should be noted that charge balances were assessed excluding any compensation for the contribution of the organic anion ( $A^-$ ). Results of the ion balance calculations by aggregate are shown in Table 5. Of the approximately 8000 samples sufficiently complete for calculation, 91% fell within  $\pm 10\%$  of charge balance, therefore giving greater confidence to the data from the remainder where calculation was not possible. As  $A^-$  was not included in the charge balance, the high rating of balance, within  $\pm 10\%$  (ie. generally small differences between columns 3 and 4 in Table 5) suggests that organic anions are not of major significance within the database except for a few cases.

Table 5: Quality of chemical data by tertiary watershed aggregate (AG) available for interpretation of the effects of acidic deposition on lakes in eastern Canada. The proportion of samples (%) having data records sufficiently complete to permit charge balance calculation is indicated (note that  $\text{A}^-$  is not included in balance) as is the proportion that balance within  $\pm 10\%$ .

AG	Sample n	Percent of n	
		All Ions*	Charge Balance* $\pm 10\%$
1	1830	74	72
2	270	98	95
3	477	75	60
4	46	91	87
5	49	22	22
6	223	99	99
7	96	100	99
8	158	91	91
9	11	100	82
10	468	43	43
11	54	48	31
12	3353	3	2
13	1526	32	30
14	3286	36	35
15	2238	36	34
16	689	36	33
17	2160	50	46
18	2	0	0
19	845	41	39
20	1474	44	29
21	625	55	39
22	749	16	13

\*most samples in the Ontario database do not contain  $\text{Cl}^-$  ; since marine influences in Ontario are negligible, "All Ions" and "Charge Balance" the requirement for  $\text{Cl}^-$  was removed for Ontario data.



Major elements of the data evaluation and editing procedures were performed using the database / graphics capabilities of the RAISON system (Swayne and Fraser, 1986; Fraser et al, 1987). As an example of the determination of ion balance, the results for aggregate #1 ( S Nova Scotia - New Brunswick ) are presented in Figure 2. Included in this plot is the estimate of the percentage of lakes by ANC class.

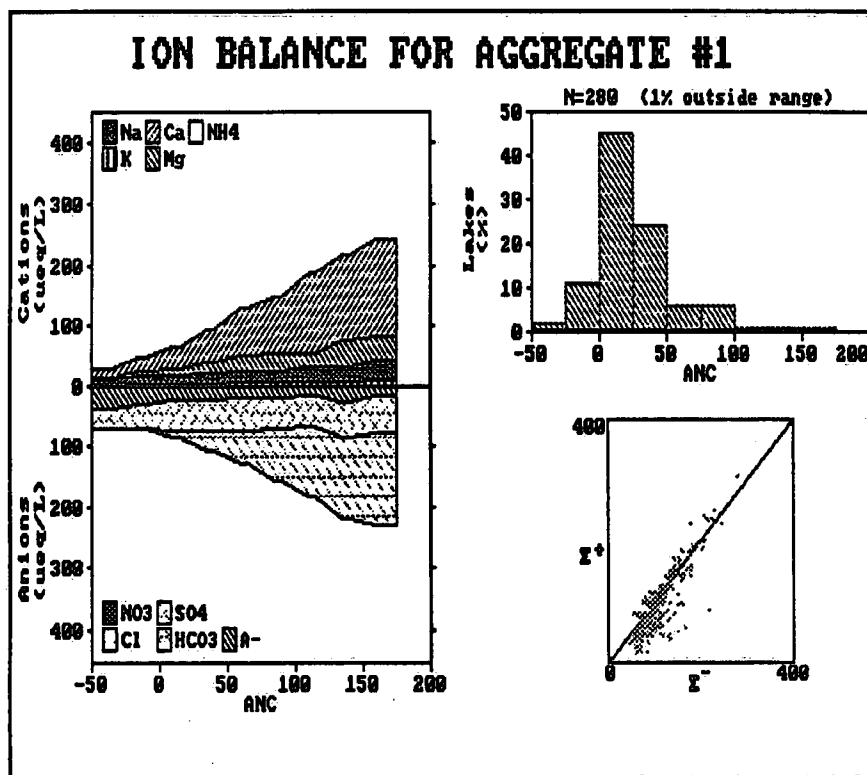


Figure 2: Ion balance plots for aggregate one showing parameter composition and scatter plots. A percentage of lakes by ANC category is also included.

The composition of lake waters in marine coastal regions is influenced by the deposition of marine salts. All lake data in the database for New

Brunswick, Nova Scotia, PEI, Newfoundland (insular and Labrador), and for all lakes from Quebec and Ontario that are located in a tertiary watershed abutting salt water were corrected for marine influence. The procedure for sea-salt correction was to apply the chloride to major ion ratio in sea water (Sverdrup, 1942) to all major ions in the designated watersheds. In the case of Ontario very few lakes contained data on chloride as previously noted. Those areas that required any correction for sea-salt were located well to the north and did not play a major part in the study.

#### REGIONAL SEGMENTATION

The base unit of geographical segmentation for the purpose of aggregating stations together was set at the tertiary watershed level as identified by the Water Survey of Canada (1977) hierarchical procedure for defining main divisions, subdivisions and sub-subdivisions for basin drainage areas of Canada. Such basin areas are referred to in this report as primary, secondary and tertiary watersheds respectively.

Due to the regional diversity of Eastern Canada with respect to terrestrial and aquatic characteristics, as discussed by Fraser (1986), tertiary watersheds were aggregated to larger geographical units for analysis and display of spatial trends and conditions. Reasonably

homogeneous areas with respect to terrain sensitivity, local effects, and sulphate deposition were obtained. The method of determining which watersheds should be aggregated to form regional scale units for analysis was the determination of a frequency distribution for specific conductivity where four classes were selected (<25, 25 - 49, 50 - 100, >100 uS/c). In addition to this, knowledge of regional and local influences were also taken into account. When this process was completed 22 tertiary watershed aggregates were formed for Eastern Canada (Figure 3, Table 6).

Certain aggregates grouped together tertiary watersheds that were located in differing geological regimes. This factor caused some aggregates to be split according to geological requirements (eg. AG 7 is split by the geomorphologically dissimilar AG 8; AG 15 is split by the differing geology of the Ottawa Valley; and AG 17 is split by AG 19 which contains the major smelter emission at Sudbury - Noranda). In Nova Scotia, New Brunswick, and Newfoundland ( an area having relatively low gradients in deposition), purely objective cluster analyses produced nearly identical data subgroups (Howell and El-Shaarawi, submitted).

Within the aggregates all aquatic chemistry parameters were considered to belong to the same statistical distribution. Analyses were carried

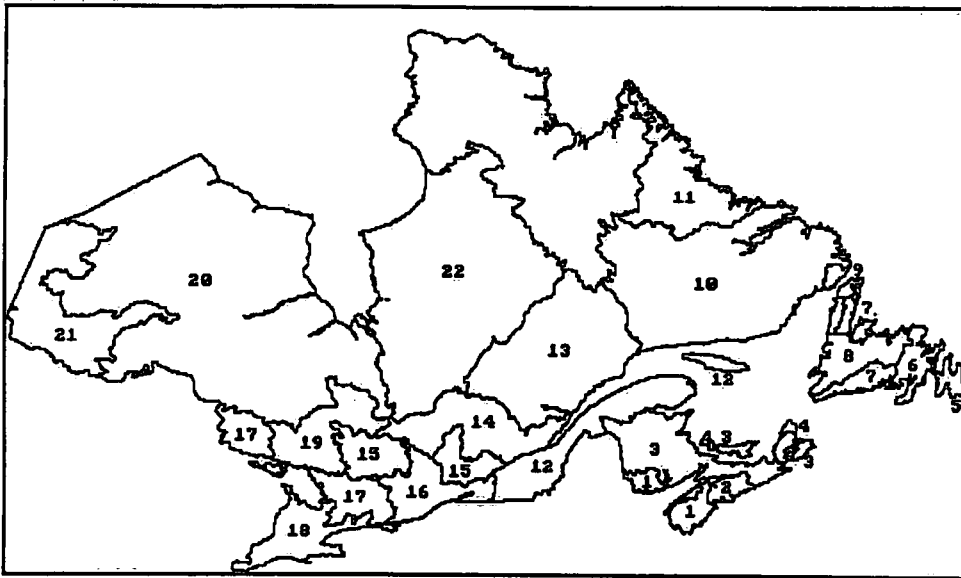


Figure 3: Eastern Canada aggregate partitions used in the aquatic effects assessment of data quality and interpretation activities.

out on distributions using percentile plots for evaluations. The selection of watershed aggregates as described above permitted medians to be calculated from the populations for each parameter of interest. Comparisons between aggregates displayed significant differences. Differences in distributions between aggregates principally reflect geographic factors including terrestrial sensitivity and the shape and concentration gradients of the atmospheric sulphate deposition field. Median aggregate values for specific conductance (uSie) and wet sulphate deposition (kg/ha/yr) are presented in Table 6. Median specific conductance values are below 100 uSie for all aggregates with the exception of southern Ontario where the geology and derived soils are

Table 6. Name of data aggregates and median conductivity (uSie) and median wet SO<sub>4</sub> deposition (kg/ha/yr) (sea-salt corrected) for sample lakes within each aggregate.

Aggregate Number	Aggregate Name	Specific Conductance (uSie)	Wet SO <sub>4</sub> <sup>2-</sup> Deposition (kg/ha/yr)	Comment*
1	S Nova Scotia-New Brunswick	28	14.5	
2	Mid-eastern Nova Scotia	45	13.7	li
3	N Nova Scotia-New Brunswick	36	13.8	
4	Cape Breton Highlands	26	12.9	col
5	Avalon	34	9.5	li
6	E Newfoundland	28	8.9	col
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	few
19	Sudbury-Noranda	39	19.4	li
20	N Ontario	89	14.9	
21	NW Ontario	33	8.3	col
22	N. Quebec	19	15.9	

\* li = local influences; col = many coloured lakes; few = few lakes

predominately calcareous in nature. Aggregate 12, which is located on the south side of the St. Lawrence River in Quebec also has a high

median specific conductance which can be related to calcium based geology and soils.

Summary information on median concentrations by aggregate for the primary parameters Ca, Mg, CB\* (sum of base cations),  $\text{SO}_4^{2-}$ , ANC, and DOC are presented in Table 7. The differences between aggregate values for these parameters is principally indicative of the differences in basin aggregate characteristics in conjunction with internal and external chemical stresses on the aquatic environment. Taken in conjunction with the data of Table 6 on specific conductance and sulphate deposition, statements can be made about the aggregation of watersheds and the aquatic chemistry observed in the lakes of these regions. Aggregates 1 through 10 primarily represent the eastern maritime region of Canada, where low conductivities indicate sensitive aquatic systems which experience moderately high levels of sulphate deposition particularly in the province of Nova Scotia. These findings are supported by corresponding low levels of ANC in the region. The south shore of the St. Lawrence river (Aggregate 12) has a median sulphate level of 114 ueq/L under a wet deposition of 26.9 Kg/Ha/Yr of sulphate. Despite this high level of deposition stress the ANC remains high (568 ueq/L ANC) due to relatively high proportions of limestones and dolomites in the aggregate region. Southern Quebec, north of the St. Lawrence river

Table 7. Median concentration for Ca, Mg, CB\*,  $\text{SO}_4^{2-}$ , ANC, DOC from sampled lakes within tertiary watershed aggregates in eastern Canada. Ion data are sea-salt corrected where appropriate. The sample size for the analysis is presented in parenthesis.

Ag	Ca ueq/L	Mg ueq/L	CB* ueq/L	$\text{SO}_4^{2-}$ ueq/L	ANC ueq/L	DOC mg/L
1	42 (363)	13 (363)	77 (363)	53 (363)	18 (363)	4.8 (280)
2	42 (82)	5 (82)	102 (82)	73 (82)	13 (82)	4.1 (59)
3	96 (158)	28 (158)	154 (158)	54 (158)	74 (157)	4.8 (90)
4	21 (33)	4 (33)	40 (33)	17 (33)	2 (33)	4.7 (33)
5	---	---	---	---	---	---
6	67 (76)	15 (76)	108 (76)	38 (76)	62 (76)	8.5 (60)
7	37 (36)	11 (36)	67 (36)	30 (36)	15 (36)	4.3 (17)
8	77 (70)	24 (70)	126 (70)	39 (70)	60 (70)	5.7 (30)
9	---	---	---	---	---	---
10	43 (213)	16 (213)	72 (210)	30 (212)	34 (211)	5.1 (103)
11	61 (52)	0 (52)	75 (52)	15 (52)	91 (52)	2.2 (10)
12	144 (129)	145 (94)	585 (94)	114 (91)	568 (131)	4.5 (65)
13	89 (430)	32 (434)	151 (428)	52 (434)	56 (440)	3.8 (57)
14	94 (736)	41 (627)	165 (626)	83 (734)	43 (743)	0.0 (36)
15	149 (701)	66 (629)	257 (594)	146 (708)	78 (753)	4.0 (358)
16	173 (177)	72 (121)	313 (121)	134 (168)	208 (237)	4.9 (30)
17	139 (1454)	57 (1318)	230 (1092)	150 (1383)	62 (2123)	4.2 (1025)
18	---	---	---	---	---	---
19	144 (479)	65 (467)	234 (360)	208 (484)	35 (704)	2.7 (296)
20	648 (817)	227 (817)	1024 (692)	90 (801)	641 (1423)	7.6 (592)
21	199 (404)	82 (403)	338 (385)	67 (371)	188 (624)	13.2 (36)
22	109 (91)	49 (90)	190 (90)	62 (90)	86 (100)	8.3 (28)

(aggregates 14,15) display high levels of wet sulphate deposition and aquatic concentration with corresponding low levels of ANC. The ANC levels are below expected levels relative to the base cation concentrations in these aggregates indicating system stress due to

excess sulphate concentrations. The highest median wet sulphate deposition value is found in southern Ontario (Aggregate 18). High values of specific conductivity ( > 300 uS/c) are indicative of relatively hard waters and therefor even with very high wet sulphate deposition values the aquatic chemistry is dominated by the calcareous geologic regime. The Sudbury region (Aggregate 19) also displays a high wet sulphate deposition value with corresponding elevated aquatic sulphate concentrations and depressed ANC values relative to that which would normally be expected for this region as indicated by the base cation concentrations.

Consideration of the lake distribution in western Canada for the parameters pH,  $\text{Ca}^{2+}$  and ANC shows that the resource is fairly well protected by buffering capacity as evidenced by the overall high ANC concentrations and pH values >6.0. Some areas of Saskatchewan and Manitoba exhibit sensitivity with low  $\text{Ca}^{2+}$  and ANC values (Table 8). A small percentage of lakes in Alberta and British Columbia present low pH values representing about 1% of the sampled lakes.

Lakes sampled in the Province of Alberta come from diverse areas with some lakes located on the Canadian shield in the northeast portion of the province. Some lakes were also sampled from the western part of the province where peatlands with coloured waters are located. The inclusion of data from such basin areas would provide an explanation for the



somewhat reduced pH, Ca<sup>2+</sup> and ANC values observed in Alberta relative the other western Provinces.

**Table 8**    Distribution of lake waters from Manitoba, Saskatchewan, Alberta, and British Columbia within concentration classes for pH, Ca<sup>2+</sup> and ANC.

		Percent of sampled lakes			
Parameter	Class	Manitoba	Saskatchewan	Alberta	British Columbia
pH	<5.0	0	0	1	0
	5.0-5.9	1	0	1	1
	6.0-6.9	22	31	15	23
	>7.0	78	69	83	77
Ca <sup>2+</sup>	<200 ueq/L	31	52	8	15
	200-400	24	12	9	17
	>400	45	36	83	66
ANC	<200 ueq/L	13	31	3	13
	200-400	33	13	5	18
	>400	55	56	92	69

### CONCLUSION

This report has emphasized the characteristics of the database used in the intensive evaluation of the aquatic effects due to acidic deposition in Canada. Data quality and the usability of the various data sets included in the studies were rigorously assessed using accepted

procedures. The subsequent assessments that made use of the final databases resulting from this work had available to them the best possible input for analysis and verification of results.

As this report forms a part of a series of interpretive reports on aquatic effects of lake acidification, no attempt was made to elaborate greatly upon the interpretation of results. Subsequent reports and publications detailing the acid precipitation effects in Canadian waters using these databases will address these subjects.

APPENDIX A

Mr. A.G. Bobba

Rivers Research Branch

National Water Research Institute

Canada Centre for Inland Waters

867 Lakeshore Rd.

Burlington, Ontario

L7R 4A6

Mr. T. Dafoe

Inland Waters Directorate

Place Vincent Massey

17<sup>th</sup> Floor

Hull, Quebec

K1A 0H3

Dr. P. Dillon

Dorset Research Centre

Bellwood Acres Rd.

Box 39

Dorset, Ontario

P0A 1E0

Dr. A. El-Shaarawi

Rivers Research Branch

National Water Research Inst.

Canada Centre for Inland Waters

867 Lakeshore Rd.

Burlington, Ontario

L7R 4A6

Mr. A.S. Fraser

Rivers Research Branch

National Water Research Institute

Canada Centre for Inland Waters

867 Lakeshore Rd.

Burlington, Ontario

L7R 4A6

M. J. Haemmerli

Inland Waters Directorate

1141 Route De L'Eglise

Box 10100

Sainte-Foy, Quebec

G1V 4H5

**M. R.G. Helie**

**Canadian Wildlife Service**

**Sustainable Development Branch**

**Environmental Applications Research**

**Place Vincent Massey**

**Hull, Quebec**

**K1A 0E7**

**Mr. G. Howell**

**Inland Waters Directorate**

**5<sup>th</sup> Floor**

**Queen's Square**

**Dartmouth Nova Scotia**

**B2Y 2N6**

**Dr. D.S. Jeffries**

**Rivers Research Branch**

**National Water Research Institute**

**Canada Centre for Inland Waters**

**867 Lakeshore Rd.**

**Burlington, Ontario**

**L7R 4A6**

**Dr. L. Johnston**

**Inland Waters Division**

**Nat. Hydrology Research Centre**

**11 Inovation Blvd.**

**Saskatoon, Saskatchewan**

**37N 3H5**

**Dr. D.C.L. Lam**

**Rivers Research Branch**

**National Water Research Institute**

**Canada Centre for Inland Waters**

**867 Lakeshore Rd.**

**Burlington, Ontario**

**L7R 4A6**

**Dr. C.K. Minns**

**GLLFAS**

**Canada Centre for Inland Waters**

**867 Lakeshore Rd.**

**Burlington, Ontario**

**L7R 4A6**

Mr. R. Stevens  
Water Quality Branch  
Conservation and Protection  
Place Vincent Massey  
Hull, Quebec  
K1A 0E7

Dr. P. Summers  
Atmospheric Environment Service  
4905 Dufferin St.  
Downsview, Ontario  
M3H 5T4

Dr. R.L. Thomas (Chairman)  
Rivers Research Branch  
National Water Research Inst.  
Canada Centre for Inland Waters  
867 Lakeshore Rd.  
Burlington, Ontario  
L7R 4A6

Dr. P. Whitfield  
Inland Waters Directorate  
Pacific and Yukon Region  
#502-1001 West Pender St.  
Vancouver B.C.  
V6E 2M9

Dr. H. Vaughan  
Rivers Research Branch  
National Water Research Institute  
Canada Centre for Inland Waters  
867 Lakeshore Rd.  
Burlington, Ontario  
L7R 4A6

## REFERENCES

- Aspila, K.A. 1989. A manual for effective interlaboratory quality assurance. NWRI #89-99. pp. 103.
- Canadian World Almanac, 1989.
- Dupont, J. 1988. Etat de l'acidite des lacs de la region hydrographique de l'Outaouais. Quebec Ministry of the Environment, No. PA-29, pp.110.
- Dupont, J. 1989. Etat de l'acidite des lacs de la region hydrographique de la Mauricie. Quebec Ministry of the Environment, No. PA-33/1, pp.119.
- Landers, D.J., J.M. Eilers, D.F. Brakke, W.S. Overton, P.E. Kellar, M.E. Silverstein, R.D. Schonbrod, R.E. Crowe, R.A. Linthurst, J.M. Omernik, S.A. Teague and E.P. Meier. 1987. Characteristics of lakes in the western United States. Vol. 1, Population descriptions and physio-chemical relationships. EPA 1600/3-86/054a, U.S.E.P.A., Washington, D.C., pp.476.
- Environment Canada. 1979. Analytical methods manual. Inland Wat. Dir., Water Qual. Branch, Ottawa.

- Fraser, A.S. 1986. Aquatic characterization for resources at risk in eastern Canada. Wat., Air & Soil Pol. 31: 1069-1078.
- Fraser A.S., D.A. Swayne, J. Storey and D.C.L.Lam. 1987. An expert system/intelligent interface for acid rain analysis. Proc. Soc. Compu. Simul., Montreal, Canada.
- Howell, G.D. and A.J. El-Shaarawi, (submitted). Atlantic region spatial overview. J. Environmetrics.
- Kelso, J.R.M., C.K. Minns, J.E. Gray, and M.L. Jones. 1986. Acidification of surface waters in eastern Canada and its relationship to aquatic biota. Can. Spec. Publ. Fish. Aquat. Sci., No. 87, 42.
- Kortelainen, P., J. Mannio, M. Forsius, J. Kamari and M. Verta. 1989. Finnish lake survey: the role of organic and anthropogenic acidity. Wat. Air, Soil Pollut. 46, p235.
- Neary, B.P., P.J. Dillon, J.R. Munroe and B.J. Clark. 1990. The acidification of Ontario lakes: an assessment of their sensitivity and current status with respect to biological damage. Ont. Min. Env., ISBN:0-7729-6550-1.

- Oliver, B.G., E.M. Thurman and R.L. Malcolm. 1983. The contribution of humic substances to the acidity of coloured natural waters. *Geochem. et Cosmochi. Acta*, 47: 2031-2055.
- Standard Methods. 1985. For the examination of water and wastewater. *Amer. Public Health Assoc. Washington D.C.* p. 32-33.
- Sverdrup, H.U. 1942. In: The Oceans. Prentice-Hall, p.166.
- Swain, L.G. 1987. Chemical sensitivity of B.C. lakes to acidic inputs. *British Columbia Ministry of Environment, Victoria, B.C.* pp.31.
- Swayne D.A. and A.S. Fraser. 1986. Development of an expert system/intelligent interface for acid rain analysis. *Micro. Compu. in Civil Eng.* 1, 181-185. Elsevier.
- Water Quality Branch. 1988. NAQUADAT, Directory of parameter codes. *Data Sys. Sec. Water Qual. Br., Env. Can., Ottawa.*
- Water Survey of Canada. 1977. Reference index hydrometric map supplement. *IWD, Env. Can., Ottawa.*



WNLTC. 1987. Sensitivity of western and northern Canada to acidic inputs, Western and Northern Canada LRTAP Tech Commit., Ottawa, Ontario. pp.23.

Wright, R.F. 1983. Predicting acidification of North American lakes. Norwegian Instit. for Water Res., Tech. Paper 4/1983/pp.165.2