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# Acidification of Surface Waters in Eastern Canada and its Relationship to Aquatic Biota 

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#### Abstract

Kelso, J. R. M., C. K. Minns; J. E. Gray, and M. L. Jones. 1986. Acidification of surface waters in eastem Canada and its relationship to aquatic biota. Can. Spec. Publ. Fish. Aquat. Sci. No. 87: 42 p.

Data collected by the Department of Fisheries and Oceans in lakes and rivers of eastern Canada subjected to atmospheric deposition, essentially $>20 \mathrm{~kg} \mathrm{SO}_{4}^{2-} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$, indicated that the trend of fewer species of fish, phytoplankton, zooplankton, and benthos below pH 6 persists. Not only are there fewer species below pH 6 , but also the abunclance of at least fish (as reflected by catch per unit effort) declines with clecreasing pH. It is also evident that physical limits of the aquatic habitat exerts a strong influence upon diversity at all community levels. This intrinsic effect from the habitat is then further influenced by pH and alkalinity. Fish body burdens of trace metals ( $\mathrm{Hg}, \mathrm{Al}, \mathrm{Mn}, \mathrm{Fe}$ ) appear weakly related to lake $\mathrm{pH} /$ alkalinity conditions. All provinces had fish from remote lakes with body burdens of Hg in excess of human health guidelines. In all provinces except New Brunswick, $27-47 \%$ of lakes had fish exceeding these public healh guiclelines. All indicators of lake sensitivity suggest that freshwaters, and consequently the fishery resource, of Nova Scotia are by far the most sensitive ( $>1200 \mathrm{~km}^{2}$ of lake surface area already acidic; alkalinity $<0 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}$, approximately pH 5.3 and less). Overall, we estimate there are 700000 lakes in eastern Canada receiving deposition considerably above background; that $4243 \mathrm{~km}^{2}$ ( $>14$ 000 lakes) are currently acidic; and that more than 150000 lakes have a $\mathrm{pH}<6.0$, a level identified as a threshold of effect.


## Résumé

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. $87: 42$ p.

Des données recueillies par le ministère des Pêche et des Océans clans des lacs et des rivières de l'est du Canada, sujets à des dépôts atmosphéricques de plus cle 20 kg SO espèces de poisson, de phytoplancton, de zooplancton et de benthos au-dessous de pH 6 persiste. Non seulement il y a moins d'espèces sous un pH de 6 , mais l'abondance, de poissons du moins (d'après les prises par unité d'effort), décline au fur et à mesure que baisse le pH. Il est aussi évident que les limites de l'habitat aquatique ont une nette incidence sur lá diversité à tous les nivcaux de la communauté. Cet effet intrinsè cque de l'habitat est fonction du pHet de l'alcalinité. La charge corporelle des poissons en métaux à l'état de trace ( $\mathrm{Hg}, \mathrm{Al}, \mathrm{Mn}, \mathrm{Fe}$ ) semble peu liée à l'acidité et à l'alcalinité du lac. Dans toutes les provinces, il y avait des poissons venus de lacs éloignés et contaminés par des quantités de Hg dépassant les limites permises pour la santé des humains. Dans toutes les provinces, sauf le Nouveau-Brunswick, 27-47\% des lacs contenaient des poissons contaminés au-delà des limites acceptables pour la santé humaine. Tous les indicateurs de la sensibilité des lacs montrent que les caux douces, et par conséquent les ressources de la pêche, de la Nouvelle-Écosse sont de loin les plus touchées ( $>1200$ $\mathrm{km}^{2}$ de lacs déjà acides; alcalinité $<0 \mu$ éq $\cdot \mathrm{L}^{-1}$, pH de 5,3 environ ou moins). Au total, nous estimons que 700000 lacs dans l'est du Canada reçoivent des dépôts considérablement supérieurs aux concentrations de fond, que $4243 \mathrm{~km}^{2}$ de lacs ( $>14000$ ) sont actuellement acides et que 150000 lacs ont un $\mathrm{pH} 6,0$, niveau consictéré comme le seuil de contamination.

## Introduction

Concern about acid precipitation and its ecological effects in Canada was initially focused in areas associated with mining and smelting industries, particularly in the Sudbury, Ontario area where sulfur dioxide and heavy metal deposition setiously depleted fish stocks, damaged forests, and reduced zooplankton and phytoplankton diversity (Gorham and Gordon 1960; Beamish and Harvey 1972; Conroy et al. 1974). A much more ominous environmental problem that has or would threaten biota throughout sensitive areas in eastern Canada was indicated later by local instances of declining fish populations in Nova Scotia (Watt et al. 1983), reduced buffering capacity and elevated metal concentrations in southern Ontario lakes (Dillon et al. 1978; Scheider et al. 1979; Dillon et al. 1980), and acidic spring and storm runoff events (Jeffries et al. 1979). Unlike Scandinavia (Wright et al. 1976; Wright and Snekvik 1978; Braekke 1976), impacts associated with the long-range transport of atmospheric contaminants and the chemical and biotic status of aquatic systems in sensitive Canadian regions was poorly understood. A national perspective was needed.

In 1979, the Department of Fisheries and Oceans (DFO) began a survey of heachwater lakes in eastern Canada to determine the status of freshwater fisheries and their habitat in relation to atmospheric deposition. It was also intended that these data could serve as a baseline against which future change could be measured. Further, these data serve as input parameters to developed models (DFO 1982; Minns et al. 1986) and as a basis to validate at least some of the model assumptions. Finally, although there have been syntheses of the regional status of fisheries and/ or habitats in Scandinavia (Wright and Snekvik 1978; Almer et al. 1974), most North American studies have failed to reflect regional differences that must exist because of clifferences in atmospheric deposition and sensitivity. The primary purposes of this study are to examine these regional differences in lake status and fisheries and to evaluate factors influencing these conditions. A complete set of tabular clata is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont. K1A 0S2.

## Methods

## Selection of Sampling Sites

Sensitive, undisturbed headwater lakes were initially chosen (1979-1981). In 1982, lakes of higher lake order, greater lake and watershed areas, wider range in deposition, and differing bedrock-soil sensitivity were included. The following criteria for lake selection applied:

- lakes were not dystrophic or bog systems (in some provinces "brown water lakes" could not be avoided);
- lakes had no waterflow regulation;
- lakes were not perturbed from logging, forest fires, or cottage clevelopment;
- there was no immediate point source of atmospheric contamination.

Access to lakes was usually by float-equipped aircraft or helicopter; therefore, access for fishermen was naturally restricted. The final lake selection using these criteria was the responsibility of the four DFO regions involved in the study. Roughly 100-200 lakes were selected in each province. Rivers sampled either currently or historically produced Atlantic salmon (Salmo salar). All rivers were sampled near their mouth but above any tidal influence.

## Sample Collection Procedures

Standard sampling techniques were used at a station at or near the center of each lake. Data collection procedures included at least the following:

- an aerial and shoreline photograph;
- an assessment of the dominant vegetation, exposed bedrock, shoreline, aquatic vegetation;
- depth soundings to determine maximum depth;
- an integrated tube sample of water (MOE 1979) from a maximum depth of 5 m or 1 m from the bottom if depth $<5 \mathrm{~m}$. If a thermocline existed at $<5 \mathrm{~m}$, a sample was taken to the bottom of the metalimnion.
The 1.5 -L water sample was subdivided into acid-washed, distilled-water-rinsed linear polyethylene Nalgene bottles of 250 mL for alkalinity, conductivity and field pH determinations. Five hundred mL was stabilized with 1 mL concentrated nitric acid for trace metal analyses and 250 mL was retained for major ion analyses. For each lake, 500 mL of whole water was preserved with Lugol's solution for phytoplankton identification and enumeration. All water samples were stored in a refrigerated cooler at $4^{\circ} \mathrm{C}$ or kept cool until field and laboratory analyses were completed. Phytoplankton were identified and counted using the Utermohl inverted microscope technique (Vollenweider 1969).

A zooplankton tow was carried out on selected lakes using a plankton net with a $20.5-\mathrm{cm}$ diameter opening, mesh size of $64 \mu \mathrm{~m}$ and overall length of 1.2 m . The net was lowered just above bottom and hauled vertically to the
surface. Samples were preserved with formalin (may have been buffered and/or sucrose added) or Lugol's iodine solution.

Five replicate benthic samples [one sample in Quebec (Menard 1982)] were collected in the vicinity of the water sampling station for a selected set of lakes using a Birge - Ekman dredge. Samples were washed through a 0.5 mm screen and benthic invertebrates preserved with $75 \%$ ethanol or $9 \%$ formalin (may have been buffered and/or had sucrose added). Organisms were stained appropriately and hand picked over a white background.

Multifilament experimental gill nets of six or seven panels of mesh sizes $3.8,5.1,6.4,7.6,8.9,10.2$, and 12.7 cm were bottom set (Aug., Sept., and Oct.) with one end set as close as possible to shore and perpendicular to the shoreline with the offshore end anchored. In Newfoundland, gill nets were set both on the surface and at the bottom (Scruton 1983). Nets varied in length from 46 m in Quebec, to 63.7 m in Nova Scotia, New Brunswick, and Ontario to 107.1 m in Newfoundland and Labrador. Nets were set overnight; however, if less than 10 fish were collected, the net was reset for another night. Occasionally, due to inclement weather, nets may have remained set for several days. Catch data were adjusted to a standard length of net ( 100 m ) set for 24 h . Fish were removed from the net, weighed, measured, and scales and/or otoliths removed. Sex and maturity were determined. Retained fish were individually wrapped and frozen.

Fish were selected for contaminant analysis based on how representative that species was in the region. A range in fish size, where possible, was analyzed. Whole fish were homogenized by being passed thrice through a grinder following removal of gonads and stomach contents. In Newfounclland, a tissue sample was taken from the dorsal musculature (Scruton 1983).

## Analytical Methods

Analytical procedures (carried out by laboratories indicated in Appendix A) and their precision are summarized in Table 1. Interlaboratory comparisons were arranged during mid-1982 for organizations participating in LRTAP studies. The selection of samples for intercomparison of laboratories, clistribution of samples, and analysis of results was carried out by the Quality Assurance and Methods Section, Analytical Methods Division, National Water Research Insitute, Burlington, Ontario. Participants in the intercomparison studies were provided appraisal

Table 1. Analytical methods for water and fish analysis for data used in analysis only.

| $\underline{\text { Parameter }}$ | Analytical procedures | Regional range of detection limits |
| :---: | :---: | :---: |
| Water |  |  |
| pH | Combination glass and reference electrode pH meter | 0.01-0.1 pH units |
| Alkalinity | Potentiometric gran titration ${ }^{\text {a }}$ | $\begin{aligned} & 0.06-0.1 \mathrm{mg} \cdot \mathrm{~L}^{-1} \\ & \mathrm{CaCO}_{3} \end{aligned}$ |
| Calcium | Atomic absorption ${ }^{\text {b }}$ | $0.001-0.2 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Magnesium | Atomic absorption | $0.01-0.05 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Sodium | Flame photometry | $0.01-0.2 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Chloride | Colormetric mercuric thiocyanate | $0.1-0.5 \mathrm{mg} \cdot \mathrm{l}^{-1}$ |
| Sulfate | Colormetric methylthymol blue | $0.1-0.5 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Potassium | Flame photometry | $0.01-0.02 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Iron | Atomic absorption | $0.001-0.02 \mathrm{mg} \cdot \mathrm{l} .^{-1}$ |
| Nickel | Atomic absorption | $0.001 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Copper | Atomic absorption | $0.001-0.0015 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Zinc | Atomic absorption | $0.001-0.002 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Lead | Atomic absorption | $0.001 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Aluminum | Atomic absorption <br> (Graphite furnace solvent extraction) | 0.001-0.01 mg $\cdot \mathrm{L}^{-1}$ |
| Manganese | Atomic absorption | $0.001-0.01 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Carbon | Carbon analyser | $1 \mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Color | Color comparator | - |
| Fish |  |  |
| Mercury | Cold vapor atomic absorption | 0.01-0.02 ppm |
| Lead | Graphite furnace or flame atomic absorption | $1.0-10.0 \mathrm{ppb}$ |
| Nickel | Flame atomic absorption | $1.0-10.0 \mathrm{ppb}$ |
| Zinc | Flame atomic absorption | $1.0-10.0 \mathrm{ppb}$ |
| Cadmium | Graphite furnace or flame atomic absorption | 0.1 ppb |
| Copper | Flame atomic absorption | 1.0 ppb |

${ }^{\text {a Stumm }}$ and Morgan (1970).
${ }^{\text {b }}$ Environment Canada (1979).
reports on their performance. Regions were to ensure that contractors participated either directly in the intercomparison studies or through the local Federal and/or Provincial laboratories. Reports (e.g. Aspila and Todd 1984) of these intercomparison studies are available (using codes to protect the identity of individual laboratories).

Because individual laboratories were notified of the findings, it is assumed that corrective action was taken or data adjusted accordingly. In spite of this national quality assurance program and additional self-imposed intralaboratory quality control measures, we recognize that there may still be problems in data comparability.

## Statistical Methods

All of the analyses reported herein were performed on an Amdahl V8 mainframe located at the University of Alberta. With the exception of some data formatting using customized FORTRAN programs, a statistical analysis software package, Michigan Interactive Data Analysis System (MIDAS), was used exclusively (Fox and Guire 1976).

## Water Chemistry and Lake Morphometry

## General Lake Characteristics

A total of 814 lakes were sampled (Table 2) throughout six provinces of eastern Canada. We compared the morphometries of sampled lakes (Table 2) with measurements made on all lakes within 4-30 whole watersheds selected from each region (Fig. 1); lake area, drainage area, and order were taken from topographic maps for whole watersheds. Only in Ontario could the survey sample be considered representative and then only for headwater lakes. In other provinces, the bias is toward larger lakes. However; the bias that exists in the data probably only applies to morphometric characters. The water chemistry appears to represent conditions in each region (Kelso and Minns 1982).

Significant differences were found in the distributions of morphometric variables (lake and watershed areas and maximum depth) among regions (Table 3). This result was expected as the lake selection criteria varied somewhat between regions resulting in fewer sampled headwater lakes in Labrador ( $41.5 \%$ ), Quebec ( $76.9 \%$ ), and Nova Scotia (85.5\%) than in New Brunswick (88.2\%), Newfoundland (97.2\%), and Ontario (100\%).

## Charge Balance

In addition to the interregional analytical quality assurance program, a further check on the water chemistry determinations was made by a comparison of the sum of anions and the sum of cations before and after marine salt corrections (Table 4). Sea salt corrections were performed as in Thompson and Hutton (1982). The sums of the major cation $\left(\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{H}^{+}\right)$and anion $\left(\mathrm{SO}_{4}^{2-}, \mathrm{Cl}^{-}, \mathrm{HCO}_{3}^{-}\right)$concentrations for each region were calculated and compared in a regression analysis. Deviation was computed by $\mathrm{D}=\frac{\sum \text { cations }-\Sigma \text { anions }}{\left(\sum \text { cations }+\Sigma \text { anions }\right) / 2} \times 100$. For a perfect charge balance, the regressions should have a slope of one and an intercept of zero. The linear correlation between anions and cations was highly significant for all regions both before and after sea salt corrections. There were 135 ( $16.5 \%$ of total sampled) lakes that had an ion balance with a deviation of greater than $15 \%$ (a value used for comparative purposes only, M. E. Thompson, National Water Research Institute, Burlington, Ontario). In most cases, a highly significant relation, with a slope near 1, existed between measured and computed conductivity (Table 5), suggesting that the major ions measured were adequate and accurate. In Ontario, the discrepancy likely resulted from lack of $\mathrm{K}^{+}$measurements.

Inclusion of a correction for organic anions (Oliver et al. 1983), did not significantly alter the slope (near 1) or the correlation coefficient ( $r^{2}=0.98$ ) but did result in a negative intercept $(-39)$ for data both corrected and uncorrected for sea salt.

## Does the watershed to lake area ratio affect alkalinity of lakes in eastern Canada?

The ratio of watershed area to lake area is one of the factors which influences a lake's suseptibility to potential acidification (DFO 1982; Eilers et al. 1983; U.S. Fish and Wildlife Service 1982). The alkalinity of a lake should be related to a function of its watershed size and area in a region where deposition of acid is relatively uniform and where soils and bedrock are also reasonably homogeneous. The prediction was tested by regressing alkalinity against the WA:LA ratio, first for all lakes and then for lakes divided into deposition categories (Table 6). These deposition categories were derived from the U.S. Canada Memorandum of Intent on Transboundary Air Pollution (1983) deposition maps. Regressions were not significant, suggesting that either lake sensitivity or deposition (or both) is highly variable within regions.

Table 2. Data summary (mean, range, standard deviation of mean) for lakes sampled in eastern Canada.

|  | Ont. |  |  | Que. |  |  | N.S. |  |  | N.B. |  |  | Nfld |  |  | Lab. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Mean | Range | sD | Mean | Range | S1 | Mean | Range | sp | Mean | Range | sD | Mean | Range | sD | Mean | Range | so |
| No. of lakes | 179 |  |  | 251 |  |  | 76 |  |  | 69 |  |  | 109 |  |  | 130 |  |  |
| Lake area (ha) | 8.4 | 0.2-110 | 14.5 | 147 | 12-1784 | 166 | 93 | 3-600 | 102 | 101 | 3-1980 | 245 | 133 | 21-1 177 | 162 | 165 | 5-1217 | 189 |
| Max. depth (m) | 2.2 | 0.5-36.0 | 5.3 | 17.5 | 1.0-90.0 | 15.6 | 3.3 | 1.0-9.0 | 1.5 | 4.5 | 1.1-12.3 | 2.8 | 11.6 | 2.0-29.0 | 7.7 | 8.4 | 0.3-70.0 | 11.7 |
| Watershed area (ha) | 39 | 1-485 | 73 | 2534 | 78-53192 | 5590 | 578 | 15-4200 | 622 | 592 | 29-4740 | 771 | 837 | 98-5110 | 849 | 1792 | 23-14691 | 2432 |
| Elevation (m) | 1249 | 700-1800 | 217 | 403 | 30-920 | 140 | 159 | 15-430 | 90 | 184 | 30-578 | 111 | 248 | 24-709 | 142 | 447 | 101-689 | 111 |
| pH | 6.34 | $4.30-7.70$ | 0.63 | 6.54 | 4.71-8.38 | 0.65 | 5.36 | 4.23-7.67 | 0.79 | 6.36 | 4.51-8.63 | 0.84 | 6.12 | 4.84-7.96 | 0.65 | 6.36 | 4.84-7.76 | 0.41 |
| Alkalinity ( $\mu \mathrm{eq} \cdot \mathrm{L}^{-1}$ ) | 151 | $-36.0-881.0$ | 179.3 | 124.6 | 0.0-1 607.0 | 217.4 | 10.3 | -81.9-370.0 | 60.8 | 78.3 | -21.9-1 076.0 | 142.3 | 112.4 | 0.0-1740.0 | 261.4 | 67.0 | $2.0-800.0$ | 84.9 |
| Conductivity ( $\mu \mathrm{S} \cdot \mathrm{cm}^{-1}$ ) | 28.1 | 8.7-103.0 | 12.8 | 25.6 | 5.0-185.0 | 25.5 | - | - | - | - | - | - | 28.9 | 11.4-199.0 | 29.6 | 12.7 | 5.7-80.7 | 8.4 |
| Total organic carbon ( $\mathrm{mg} \cdot \mathrm{L}^{-1}$ ) | - | - | - | 6.1 | 1.0-15.0 | 2.3 | 6.8 | 1.6-19 | 3.6 | 5.4 | 1.3-15.0 | 2.5 | - | - | - | - | - | - |
| Dissolvedorganic carbon ( $\mathrm{mg} \cdot \mathrm{L}^{-1}$ ) | - | - | - | 3.3 | 1.0-16.0 | 3.2 | - | - | - | - | - | - | 0.62 | 0.27-1.99 | 0.32 | 4.8 | 0.8-14.0 | 2.3 |
| Color | - - | - | - | - | - | - | - | - | - | - | - | - | 48 | 5-225 | 41 | 33 | 5-175 | 28 |
| Camg-L-1 | 218.0 | 74.8-698.6 | 137.0 | 134.6 | 15.9-1437.1 | 175.9 | 44.8 | 7.9-364.2 | 50.9 | 107.7 | 14.4-1047.9 | 129.7 | 102.5 | 13.0-1400.0 | 202.1 | 60.6 | 19.5-480.0 | 54.3 |
| $\mathrm{Mg} \mathrm{mg} \cdot \mathrm{L}^{-1}$ | 75.7 | 24.6-345.4 | 47.2 | 51.3 | $6.2-516.5$ | 61.7 | 38.0 | 18.1-93.7 | 16.1 | 32.7 | 16.4-111.8 | 13.9 | 50.2 | 12.0-410.0 | 75.1 | 32.2 | 7.5-416.7 | 40.0 |
| Na mg-L ${ }^{-1}$ | 34.7 | 8.7-165.3 | 14.5 | 25.5 | 8.2-54.8 | 8.3 | 123.2 | 62.6-264.9 | 43.2 | 58.6 | 10.8-130.5 | 18.1 | 82.3 | 33.0-278.0 | 46.2 | 22.1 | 4.4-69.6 | 10.2 |
| $\mathrm{Kmg} \cdot \mathrm{L}^{-1}$ | - | - | - | 7.2 | 0.7-20.4 | 4.2 | 6.7 | 2.5-19.6 | 2.7 | 7.3 | 1.0-14.3 | 2.4 | 3.3 | 1.0-17.0 | 2.4 | 3.1 | 0.5-14.9 | 2.1 |
| $\mathrm{Cl} \mathrm{mg} \cdot \mathrm{L}^{-1}$ | 19.1 | 5.6-67.7 | 11.6 | 12.6 | 2.8-36.6 | 5.5 | 130.1 | 59.2-304.6 | 52.8 | 43.0 | 8.4-132.5 | 23.5 | 87.8 | 25.0-394.0 | 58.4 | 9.4 | 1.4-45.1 | 8.1 |
| $\mathrm{SO}_{4} \mathrm{mg} \cdot \mathrm{L}^{-1}$ | 143.9 | 45.8-308.2 | 53.7 | 77.9 | 20.8-229.1 | 39.6 | 78.9 | 56.2-106.2 | 12.6 | 83.3 | 45.8-135.3 | 16.6 | 46.8 | 14.0-127.0 | 19.6 | 28.2 | 4.2-91.7 | 12.5 |
| A $\mu \mathrm{Mg} \cdot \mathrm{L}^{-1}$ | 69.5 | 3.6-625.0 | 81.7 | 90.4 | 7.2-299.5 | 56.8 | 119.4 | 9.9-379.5 | 70.5 | 43.1 | 9.9-189.8 | 37.8 | 114.0 | 23.3-429.9 | 80.4 | 64.0 | 8.9-35.43 | 44.0 |
| $\mathrm{Pb} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | 5.03 | 0.00-62.16 | 10.09 | 0.92 | 0.0-41.58 | 5.65 | - | - | - | - | - | - | - | - | - | - | - | - |
| $\mathrm{Mn} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | - | - | - | 10.8 | 0.0-41.2 | 8.3 | 22.9 | 8.2-79.6 | 18.4 | 18.3 | 8.2-68.7 | 13.7 | 12.9 | 2.7-52.2 | 10.6 | - | - | - |
| $\mathrm{Cd} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | - | - | - | 0.35 | 0.06-1.79 | 0.27 | - | - | - | - | - | - | 1.04 | 1.01-2.47 | 0.17 | - | - | - |
| Fe $\mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | - | - | - | 112.9 | $6.7-1608.5$ | 143.4 | 162.4 | 20.1-589.8 | 125.0 | 76.1 | 20.1-440.1 | 74.9 | 164.6 | 2.2-1 197.4 | 222.8 | - | - | - |
| $\mathrm{Cu} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | 4.48 | 0.98-21.98 | 3.07 | 1.92 | 0.98-13.98 | 2.15 | - | - | - | - | - | - | 2.06 | 1.96-3.27 | 0.32 | - | - | - |
| $\mathrm{Zn} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | 13.47 | 0.98-97.0 | 12.13 | 7.36 | 1.99-30.99 | 3.75 | - | - | - | - | - | - | 2.04 | 2.02--2.42 | 0.93 | - | - | - |
| Ni $\mu \mathrm{g} \cdot \mathrm{L}^{-1}$ | 2.56 | 1.0-26.98 | 3.40 | 2.11 | 0.99-9.98 | 1.51 | - | - | - | - | - | - | trace | - | - | - | - | - |



Figure 1. Relation of lake size in the survey sample to an unbiased sample of lakes. N represents the number of lakes surveyed (righthand side) and number of lakes in the unbiased sample.

Table 3. Kruskal-Wallis nomparametric analysis of variance on selected variables (stratified by region).

| Variable | Region | $n$ | Average rank | Median | $n<$ Median | $n>$ Median | $n=$ Median | $P^{*}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Lake area | N.S. | 76 | 419 | 65 ha | 43 | 32 | 1 | $<0.0001$ |
|  | N.B. | 69 | 383 |  | 40 | 29 | 0 |  |
|  | Nfld. | 109 | 491 |  | 38 | 68 | 3 |  |
|  | Lab. | 130 | 527 |  | 33 | 96 | 1 |  |
|  | Que. | 251 | 525 |  | 75 | 174 | 2 |  |
|  | Ont. | 179 | 109 |  | 176 | 3 | 0 |  |
| Watershed area | N.S. | 76 | 389 | 446 ha | 46 | 30 | 0 | $<0.0001$ |
|  | N.B. | 69 | 379 |  | 44 | 25 | 0 |  |
|  | Nfld. | 109 | 469 |  | 39 | 70 | 0 |  |
|  | Lab. | 130 | 543 |  | 32 | 98 | 0 |  |
|  | Que. | 251 | 542 |  | 68 | 180 | 3 |  |
|  | Ont. | 179 | 101 |  | 177 | 2 | 0 |  |
| Maximum depth | N.S. | 76 | 154 | 7 m | 74 | 1 | 1 | $<0.0001$ |
|  | N.B. | 69 | 214 |  | 58 | 10 | 1 |  |
|  | Nfld. | 10 | 431 |  | 2 | 8 | 0 |  |
|  | Lab. | 130 | 273 |  | 75 | 51 | 4 |  |
|  | Que. | 251 | 481 |  | 61 | 182 | 8 |  |
|  | Ont. | 179 | 385 |  | 72 | 95 | 12 |  |
| Lake area: watershed area ratio | N.S. | 76 | 395 | 6.4 | 42 | 34 | 0 | $<0.0001$ |
|  | N.B. | 69 | 441 |  | 27 | 42 | 0 |  |
|  | Nfld. | 109 | 416 |  | 55 | 54 | 0 |  |
|  | Lab. | 130 | 490 |  | 48 | 82 | 0 |  |
|  | Que. | 251 | 483 |  | 92 | 159 | 0 |  |
|  | Ont. | 179 | 228 |  | 143 | 36 | 0 |  |

aDesignates the probability of the distributions all having been sampled from the same underlying distribution.

Table 4. Summary of charge balance relationship (sum of cations versus sum of anions) before and after sea salt correction.

|  | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. | Overall |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $r^{2}$ before correction | 0.83 | 0.99 | 0.99 | 0.99 | 0.99 | 0.98 | 0.97 |
| Slope | 0.96 | 0.98 | 0.97 | 0.97 | 1.00 | 1.02 | 0.98 |
| Intercept | 31.6 | 8.6 | 3.3 | 9.6 | -8.84 | 5.95 | 4.50 |
| $r^{2}$ after correction | 0.83 | 0.99 | 0.96 | 0.98 | 0.99 | 0.98 | 0.96 |
| Slope | 0.96 | 0.98 | 0.97 | 0.97 | 1.01 | 1.03 | 1.01 |
| Intercept | 29.4 | 8.2 | -1.6 | 7.4 | -9.9 | 6.2 | 7.83 |
| \% lakes with deviation > 15\% before correction | 20.4 | 15.9 | 1.3 | 10.3 | 13.9 | 27.7 |  |

Table 5. Summary of measured versus computed conductivity analyses.

| Region | No. of lakes | No. of lakes with deviation $>15 \%$ | Proportion with cleviation > $15 \%$ |  |  | Regression |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Color $>50$ |  | Color<50 | Slope | Intercept | $r$ |
| Ont. | 179 | 95 | - | . 53 | - | 0.543 | 11.25 | 0.74 |
| Que. | 245 | 182 | 0.82 |  | 0.73 | 0.899 | 6.25 | 0.83 |
| N.S. | - | Conductivity | Not measured |  |  | - | - | - |
| N.B. | - | Conductivity | Not measured |  |  | - | - | - |
| Nfld. | 108 | 77 | 0.71 |  | 0.71 | 1.000 | 4.04 | . 99 |
| Lab. | 130 | 81 | 0.65 |  | 0.61 | 0.888 | 2.90 | . 98 |

Table 6. Regional division of the database on presumed wet deposition levels (U.S. Canada Memorandum of Intent on Transboundary Air Pollution 1983).

| Region description | Presumed deposition levels ( $\mathrm{mmolSO} \mathrm{A}_{4} \cdot \mathrm{~m}^{-2}$ ) |
| :---: | :---: |
| 1. New Brunswick and western Nova Scotia | $>30$ |
| 2. Rest of Nova Scotia | 20-30 |
| 3. Newfoundland island except northern peninsula | 20-30 |
| 4. Northern Newfoundland, southern and eastern Labrador, far western Quebec | 10-20 |
| 5. Northern, western, and central Labrador | $<10$ |
| 6. Quebec west of $62^{\circ}$ longitude, north of $50^{\circ}$ latitude; west of $71^{\circ}$ longitude, north of $49^{\circ}$ latitude; west of $76^{\circ}$ longitude, north of $48^{\circ}$ latitude | 10-20 |
| 7. Quebec: $70-74^{\circ}$ longitude, $48-49^{\circ}$ latitude; $74-77^{\circ}$ longitude, $47-48^{\circ}$ latitude; Ontario: Parry Sound, Temagami regions | 20-30 |
| 8. Quebec: $72-74^{\circ}$ longitude, $47-48^{\circ}$ latitude; south of $47^{\circ}$ latitude | $>30$ |
| 9. Rest of Ontario | 10-20 |

## Is there evidence that lakes have been chemically affected by the deposition of acid?

The calcite saturation index (CSI) is a measure of how vulnerable a lake is to acidification: $\mathrm{CSI}=-\log \left(\mathrm{Ca}^{2+}\right)$ $-\log \left(\mathrm{HCO}_{3}^{-}\right)-\mathrm{pH}+2.0$ (adapted from Thompson and Hutton 1982). CSI values of $<1$ and $1-3$ represent waters that have no or limited potential for acidification. Values of 3 and more represent waters that are susceptible to acidification. The U.S. Canada Memorandum of Intent on Transboundary Air Pollution (1983), however, suggests that a quantitative relationship between acidification potential and CSI units has not been developed. The CSI was highly correlated (Fig. 2) with alkalinity (overall $r^{2}=0.94$ ) as expected. The majority ( $77 \%$ ) of the lakes surveyed in eastern Canada were classed (CSI $>3$, Table 7) as sensitive to acidification (Haines and Akielaszek 1983). The distribution of the CSI in surveyed lakes suggested that lakes in Nova Scotia (95\%), Labrador (92\%), and Newfoundland ( $87 \%$ ) had less buffering capacity than lakes in Quebec ( $73 \%$ ), New Brunswick ( $72 \%$ ), and Ontario (62\%) (Table 7).


Figure 2. Relation between Calcite Saturation Inclex and alkalinity for each region of eastern Canada. Numbers represent more than one lake.

Table 7. Percentage of lakes in each calcite saturation index class for eastern provinces.

| Class | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| $<1$ | 3.0 | 6.2 | - | 1.7 | 4.6 | 0.8 |
| $1-3$ | 35.2 | 21.2 | 5.0 | 26.7 | 8.3 | 6.9 |
| $>3$ | 61.8 | 72.6 | 95.0 | 71.7 | 87.0 | 92.3 |

Considerable variation was found in the distribution of pH within each province. Mean pH of the sampled lakes (Fig. 3a, b) varied from $4.9(n=76)$ in Nova Scotia, $5.6(n=68)$ in New Brunswick, $5.7(n=109)$ in Newfoundland, $5.8(n=179)$ in Ontario to $6.1(n=251)$ in Quebec and $6.1(n=130)$ in Labrador. The pH for all sampled lakes ranged from a minimum of 4.2 , mean of 5.6 , to a maximum of $9.9(n=813)$.

Variations in lake $\mathrm{SO}_{4}^{2-}$ concentrations throughout the regions were evident (Fig. 4a, b). Higher mean concentrations in Quebec ( $76.9 \mu \mathrm{eq} \cdot \mathrm{L}^{-1} \pm \mathrm{sD} 39.7$ ), Ontario ( $141.9 \pm 53.1$ ), Nova Scotia ( $65.5 \pm 10.6$ ), and New Brunswick ( $78.9 \pm 16.2$ ) than in Newfoundland ( $37.7 \pm 16.2$ ) and Labrador ( $27.2 \pm 12.3$ ) may be related to deposition.

Regional $\mathrm{pH}, \mathrm{SO}_{4}^{2-}$ and cation concentration histograms (Fig. 5) were grouped by deposition level categories (Table 6). A trend in the Atlantic provinces for lower levels of sulphate, cations, and pH's in lakes under comparable deposition levels relative to the western provinces is apparent (Fig. 3, 4, and 5). Regional variations in soils and bedrock may account for some of the differences. Higher sulphate and lower pH's are generally found in areas with higher deposition.



Legend
Dotted lines bound regions included in histogram
Number at top right of each histogram is total number of lakes
$M=$ mean


Figure 3a, b. Regional histograms of pII (in 0.5 pII unit classes) for all provinces in eastern Canada


Legend
Dotted lines bound regions included in histogram
Number at top right of each histogram is total number of lakes
$M=$ mean


Figure 4a, b. Regional concentrations of $\mathrm{SO}_{4}^{2-}$ (in 50 and $20 \mathrm{mg} \cdot \mathrm{I}^{-1}$ classes in a and b respectively) for all provinces in eastern Canada.


Figure 5. Regional variations in $\mathrm{pH}, \mathrm{SO}_{4}^{2-}$ (classes as in Fig .3 and 4) and the total cations (in $50 \mathrm{mg} \cdot \mathrm{L}^{-1}$ classes) in relation to soils potential for reducing acidity and atmospheric deposition of sulphate.

## Do lakes at higher elevations have higher $\mathrm{SO}_{4}^{2-}$ levels?

The hypothesis that higher elevation lakes experience greater total deposition of acids than lakes at lower elevations in the same area and thus exhibit higher sulphate concentrations was tested (Table 8). Four morphometric variables (watershed area, lake area, maximum depth, and WA:LA ratio) were included in this analysis together with elevation. Nonmarine $\mathrm{SO}_{4}^{2-}$ was the dependent variable.

When all lakes from all deposition levels were combined, the regression (independent variables were elevation and lake size) was significant $(P<0.001)$ but $r^{2}=0.26$ was low. Dividing the lakes into deposition groups resulted in significant regressions with elevation in Nova Scotia, Newfoundland, Ontario, and Quebec. However, when elevation was included in the multiple regression, its slope was negative. A positive relationship between lake sulphate and elevation is to be expected when dry deposition rates increase at higher elevations. The variables, watershed and lake area, were marginally significant in Newfoundland (Scruton 1983) suggesting that a geological source of $\mathrm{SO}_{4}^{2-}$ bearing minerals such as pyrite and gypsum may be present. Significant regressions between

Table 8. Results of multiple linear regression using variables 1-5 as independent variables to determine the lake effect upon sulphate.

| Deposition group | Deposition level | $n$ | Probability of slope $=0$ | $r^{2}$ | Variables considered | Variables included ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| All lakes | - | 714 | $<0.0001$ | 0.257 | 1-5 | 1,3 |
| New Brunswick and western Nova Scotia | $>30$ | 72 | No significant regression |  | 1-5 | - |
| Rest of Nova Scotia | 20-30 | 73 | 0.0011 | 0.256 | 1-5 | 1 |
| Newfoundland except N. peninsula | 20-30 | 85 | $<0.0001$ | 0.264 | 1-3, 5 | 2,5 |
| N. Nfld., S. and E. Lab., far western Que. | 10-20 | 69 | 0.0333 | 0.066 | 1-5 | 5 |
| North, west, and central Lab. | $<10$ | 75 | No significant regression |  | 1-5 | - |
| Part of Quebec | 10-20 | 141 | 0.0009 | 0.114 | 1-5 | 1, 2, 4 |
| Part of Que. and Parry Sound and Temagami regions in Ont. | 20-30 | 71 | $<0.0001$ | 0.520 | 1-5 | 1, 3 |
| Part of Quebec | $>30$ | 66 | 0.0001 | 0.220 | 1-5 | 1 |
| Rest of Ontario | 10-20 | 139 | No significant | ession | 1-5 | 2 |

avariable legend: $1=$ elevation, $2=$ watershed area, $3=$ lake area, $4=$ maximum depth, $5=$ watershed area: lake area ratio.
$\mathrm{SO}_{4}^{2-}$, elevation, and lake area in part of Quebec and the Parry Sound, Temagami area of Ontario ( $r^{2}=0.52$ ) also suggest geological sources.

Thompson and Hutton (1985) indicated that high sulphate yields for a Quebec lake may have been due to its elevation; however, this data set uses only wet deposition information and does not permit adequate testing of factors, other than elevation, affecting the hypothesis. Nevertheless, it appears that although elevation influences lake $\mathrm{SO}_{4}^{2-}$ levels, other factors are strongly involved, making simple generalizations impossible.

## Is there a relation between lake $\mathrm{SO}_{4}^{2-}$ levels and atmospheric deposition?

To relate lake $\mathrm{SO}_{4}^{2-}$ levels to sulphate deposition, we corrected lake sulphate concentrations for regional differences in runoff (Thompson and Hutton 1982). This provides an estimate of the expected deposition to a lake assuming no watershed retention of $\mathrm{SO}_{4}^{2-}$ nor any "background" lake $\mathrm{SO}_{4}^{2-}$ level. These corrected lake $\mathrm{SO}_{4}^{2-}$ measurements were compared by regressing these values on presumed deposition levels. A significant ( $P<0.05$ ) overall $(n=806)$ relationship $\left(r^{2}=0.43\right)$ with a positive slope (1.62) exists indicating an influence of deposition on lake $\mathrm{SO}_{4}^{2-}$ concentrations.

Thompson and Hutton (1985) also showed that when using both wet and dry deposition data with lake $\mathrm{SO}_{4}^{2-}$ concentrations, there is good agreement between lake sulphate yields and deposition. Their study also showed that, as in Fig. 5, atmospheric deposition is a significant source of $\mathrm{SO}_{4}^{2-}$.

## Does the observed pH -alkalinity relation conform to the theoretical model?

The $\mathrm{H}^{+}$driving most chemical weathering reactions is supplied from both external (largely atmospheric in origin) and internal (biological and chemical processes within the system) sources. The major ions in atmospheric deposition that contribute significantly to the acidification of aquatic ecosystems are $\mathrm{H}^{+}$and $\mathrm{NH}_{4}^{+}$ (Dillon et al. 1984). Bicarbonate, a dominant ion for most aquatic systems, plays an important role in assimilating acidic deposition.

Consequently, to examine the relation between pH and alkalinity we compared the actual pH measurements to the theoretical pH bicarbonate relationship (the difference we call the residual) assuming equilibrium with atmospheric $\mathrm{CO}_{2}$. Methods for calculations of the expected values are given in Appendix B .

From comparing the estimated pH to the measured pH for the lake (Fig. 6), it is obvious that, at low pH's, estimated pH is slightly less than measured. The converse is true at high pH . A multiple linear regression of the residuals (difference between estimated and measured pH ) against dissolved organic carbon and total aluminum indicated that neither variable significantly ( $P<0.05$ ) influenced the residuals. These small differences in pH may result from either systematic measuring errors at high and low pH 's or in assumptions of the model (see Appendix B).

## Do the chemistries of lakes in eastern Canada conform to the Henriksen model?

As lakes are subjected to acidic precipitation, cations are mobilized and bicarbonate replaced with sulphate. Henriksen $(1979,1980,1982)$ proposed that the process of acidification is analogous to titrating a bicarbonate


Figure 6. Relation between estimated pH (see text) and measured pII for all lakes. Numbers represent more than one lake.


Figure 7. Regional plots of $\mathrm{Ca}^{2+}$ plus $\mathrm{Mg}^{2+}$ against $\mathrm{SO}_{4}^{2-}$ in Henriksen (1980) nomograph form.

Table 9. Percentage of lakes in Henriksen's classes.

|  | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| Bicarbonate | 71.2 | 71.3 | 18.9 | 58.5 | 67.7 | 99.2 |
| Transition | 21.6 | 27.3 | 33.8 | 26.2 | 28.3 | 0.8 |
| Acidified | 1.6 | 1.4 | 47.3 | 15.4 | 4.0 | - |
| Number of |  |  |  |  |  |  |
| $\quad$ lakes | 125 | 216 | 74 | 65 | 99 | 127 |

solution with a strong acid. The sum of nonmarine Ca and Mg is plotted against nonmarine sulphate with the nomograph then divided into three sections, corresponding to segments of the titration curve:

- the first stage of titration - "bicarbonate lakes" characterized by low sulphate content, significant acid neutralizing capacity, and pH's generally above 5.3;
- the second stage - "transitional lakes" characterized by intermediate sulphate content, a significant loss of bicarbonate buffering, pH's near 5.0, and episodic biotic crises;
- the final stage - "acid lakes" which have no bicarbonate neutralizing capacity, high sulphate and metal levels, pH's generally below 4.7, and severe impacts on biota.
Although the majority ( $69.3 \%$ ) of the lakes in eastern Canada would be classed as bicarbonate dominated by this model (Fig. 7), substantial differences are apparent between regions (Table 9). Only 19\% of the lakes surveyed in Nova Scotia, but 99\% of Labrador's lakes had bicarbonate buffering systems, with generally high pH's, in this model. Out of the total database, 163 , or $23.1 \%$ of the lakes, fell into the transitional stage. Approximately 54 ( $7.6 \%$ ) lakes were classed as acidified with significant regional differences. Sixty-five percent ( $n=35$ ) of Nova Scotia's lakes, $15 \%(n=10)$ of New Brunswick's lakes compared to an average of $3 \%$ of the lakes sampled in Ontario, Quebec, and Newfoundland fell into the acidified section of the nomogram. From Fig. 7, the acid and transitional lakes fell into the expected position on the nomogram. However, many ( $29 \%$ ) of the bicarbonate lakes appeared to have an excess of $\mathrm{SO}_{4}^{2-}$ relative to the levels predicted by the Henriksen model.


Figure 8. Relation between alkalinity $\left(\mathrm{HCO}_{3}{ }^{-}\right)$and $\mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2}+$ for all provinces in eastern Canada.


Figure 9. Comparison of $\mathrm{SO}_{4}^{2-}$ with the sum of $\mathrm{Ca}^{2+}$ plus $\mathrm{Mg}^{2+}$ less $\mathrm{HCO}_{3}-$ for all provinces in eastern Canada.
An examination of alkalinity vs. Ca plus Mg (Fig. 8), particularly in the bicarbonate lakes, shows an alkalinity deficit that is greater than one would expect. If lakes are in transition from bicarbonate-dominated to sulphatedominated (caused by acidic precipitation) the deficit of alkalinity relative to $\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}$ should increase. Where strong acids from precipitation dominate watershed weathering, a base cation is released into solution without any bicarbonate alkalinity being formed. The greatest deficits appear in Nova Scotia, New Brunswick, Quebec, and Ontario.
A comparison of sulphate to the sum of Ca plus Mg minus bicarbonate was made for all regions (Fig. 9). Sulphate levels appeared to be much higher than expected in all provinces, except Ontario. A balance between $\mathrm{SO}_{4}^{2-}$ and $\left(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}-\mathrm{HCO}_{3}^{-}\right.$) is expected if lakes are being impacted by strong acids (if other ions (e.g. $\mathrm{Na}^{+}, \mathrm{K}^{+}$) arc not significant, simply due to the principle of charge balance). Haines and Akielaszek (1983) found that the cations, $\mathrm{Na}^{+}, \mathrm{K}^{+}$and $\mathrm{H}^{+}$were associated with sulphate. A regression of the residuals from the $45^{\circ}$ line of [ $\mathrm{SO}_{4}^{2-}-\left(\mathrm{Ca}^{2-1}\right.$ $\left.\left.+\mathrm{Mg}^{2+}\right)\right]$ against $\mathrm{Na}^{+}+\mathrm{K}^{+}$suggests that these additional cations do account for some of the excessive sulphate levels. The relationship is improved ( $r^{2}$ range $0.12-0.57, P<0.05$ ) by addition of the other cations in all provinces except Newfoundland.

High levels of dissolved organic carbon have been known to confound sulphate determinations (Kerekes and Pollock 1983); however, an examination of the relation between color and the residuals from the $45^{\circ}$ line was not significant for any regions ( $r^{2}<0.04$ ). Thus, although the Henriksen model can be used to classify the status of lakes, many lakes appear to have high $\mathrm{SO}_{4}^{2-}$ levels not strictly as a function of organic acid interference in the analytical methodology.

## Is deposition or location (geology) most important in determining metal concentrations in lakes?

Lakes in Norway, Sweden, and Ontartio have higher concentrations of $\mathrm{Zn}, \mathrm{Pb}, \mathrm{Cu}, \mathrm{Cd}$, and Ni than do unacidified lakes from nearby areas (Beamish 1976; Wright and Gjessing 1976; Beamish and Van Loon 1977). Concentrations of Al and Mn also increase in surface waters known to be impacted by acidic inputs (Almer et al. 1978; Cronan and Schofield 1979; Driscoll et al. 1980).

Elevated levels of Al may have serious effects on fish and other aquatic biota; however, the complexation of Al with organic ligands seems to ameliorate its toxicity (Driscoll et al. 1980). The measurement of total Al in the lakes should be treated with some caution as the potential to overestimate Al-induced toxicity exists.

Table 10. Summary of multiple linear regressions of individual metals with pH and color.

*Not included in regression (ie. did not explain a significant amount of the variance in the dependent variable).
N/A - parameter not measured.
Total Al concentrations (Table 2) ranged from a minimum $3.6 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ to $625 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ (mean $83.6 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{SD}$ 68.5) for all lakes $(n=810$ ). Aluminum concentrations were significantly related to pH when all data were combined $\left[\log (\mathrm{Al})=2.3513-0.2422(\mathrm{pH}), r^{2}=0.23, n=808\right]$. Aluminum values for lakes in Ontario (mean $69.5 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{SD} 81.7$ ), Quebec (mean $90.4 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{sD} 56.8$ ), and New Brunswick (mean $43.1 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{sD}$ 37.8) were related to pH . (Table 10). Aluminum levels in Nova Scotia (mean $119.4 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm$ sD 70.5 ), Newfoundland (mean $114.0 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{sD} 80.4$ ), and Labrador (mean $64.0 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1} \pm \mathrm{sD} 44.0$ ) were related to organic acids (color). These correlations (Table 10) suggest that much of the available Al is organically complexed and less toxic to fish. This correlation also supports other evidence that highly colored waters in the maritime provinces confound simple analysis of acidification chemistry.

An analysis of covariance (Table 11) indicated substantial differences in the adjusted means but not the slopes of the regression of Al vs. pH among regions, suggesting that regional differences may be attributable to geological supply of the metal. The range of Al values in Canadian lakes is between the nonacidified lakes in Norway (Wright et al. 1976) and Sweden (Dickson 1975), and acidified lakes in Norway (Henriksen and Wright 1977; Wright et al. 1976; Wright and Snekvik 1978) and Sweden (Dickson 1975, 1980)).

Because all regions had Al concentrations spanning a considerable range, we also classified lakes by whether they met or exceeded the water quality criteria of $100 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ (IJC 1984) designed to protect aquatic life:

| Al concentration | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\$ 100$ | 145 | 142 | 35 | 64 | 63 | 105 |
| $\geqslant 100$ | 33 | 102 | 41 | 4 | 44 | 25 |

Although each province had lakes with Al levels exceeding available water quality criteria, the greatest proportion of noncomplying lakes were in Quebec, Nova Scotia, and Newfoundland.

Manganese is another good indicator of watershed acidification as it is readily removed from soil by acid runoff (Schieder et al. 1979). The mean concentration of Mn for all lakes ( $n=502$ ) was $140 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$. Nova Scotia and New Brunswick lakes had the highest concentrations. However, there is little difference among all regions' mean concentrations (Table 2). Manganese was significantly related to pH in New Brunswick and Quebec and with color in Newfoundland (Table 10). A significant difference among regions in the adjusted means (Table 11), of the regression of Mn vs. pH suggests that regional differences probably in the geological availability of Mn may account for some of the differences.

Iron concentrations were strongly associated, statistically, with lake color, particularly in Nova Scotia and Newfoundland (Table 10). These provinces had sampled, by necessity, a higher number of "brown water" lakes than the other regions. Little difference was found in the $\mathrm{pH}-\mathrm{Fe}$ relationship among regions. The limited difference among regions' mean concentrations (Table 11) may be due to regional differences in geology and/or supply, but more likely is a product of the disparity in the number of "brown water" lakes among regions.
Mean concentrations of $\mathrm{Cd}, \mathrm{Cu}, \mathrm{Zn}$, and Ni (Table 2) were below levels known to be toxic to fish (Spry et al. 1981). However, high copper concentrations were in the range known to cause behavioral or growth effects for some species (Spry et al. 1981) were often found, particularly in Ontario.

| Metala ${ }^{\text {( }} \mu \mathrm{g} \cdot \mathrm{L}^{-1}$ ) | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe |  |  |  |  |  |  |
| $\leqslant 300$ | No | 233 | 65 | 66 | 95 | No |
| >300 | Data | 18 | 11 | 2 | 13 | Data |
| Cu |  |  |  |  |  |  |
| $<5$ | 103 | 112 | No | No | 18 | No |
| $>5$ | 71 | 6 | Data | Data | 0 | Datȧ |
| Zn |  |  |  |  |  |  |
| <30 | 170 | 250 | No | No | 18 | No |
| $>30$ | 9 | 1 | Data | Data | 0 | Data |
| Ni |  |  |  |  |  |  |
| <25 | 127 | 138 | No | No | 18 | No |
| $>25$ | 1 | 0 | Data | Data | 0 | Data |

The ranges in concentrations of all of these metals reflect positions between nonacidified and acidified lakes (Haines 1981). Copper and Ni was related to pH in Ontario and Quebec but the $r^{2}$ values were low (Table 10).
A stepwise discriminant analysis (Table 12) evaluated the effectiveness of discriminant functions, derived from metal concentrations, to classify lakes according to regional or deposition level groupings. A higher proportion of lakes were correctly classified according to metal distributions in deposition rather than regional groupings. However, the improvement is not sufficient to allow one to conclude that deposition rates are significantly more important than regional groupings in determining differences among lakes in metals concentrations.

Table 11. Results of covariance analysis for aluminum, manganese, and iron versus pH , stratified by region.

| Metal | $n$ | $F$ - test probabilitics (degrees of freedom) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | $\begin{gathered} \text { Overall } \\ \text { slope }=0 \end{gathered}$ | All slopes equal | Adjusted means equal |
| Al | 809 | $<0.0001$ (1802) | 0.0003 (5802) | $<0.0001(5802)$ |
| Mn | 501 | $<0.0001(1496)$ | $0.0315(3493)$ | $<0.0001(3496)$ |
| Fe | 502 | $<0.0001$ (1497) | 0.1396(3494) | 0.0087 (3497) |

Table 12. Stepwise discriminant analyses of regional metal distributions.

| Classification criterion | Variables considered | Variables included | Portion lakes correctly classified ${ }^{4}$ | Probability of correct classification of chance alone |
| :---: | :---: | :---: | :---: | :---: |
| Regional | Al | Al | 0.18 | 0.17 |
|  | $\mathrm{Al}, \mathrm{Mn}, \mathrm{Fe}$ | $\mathrm{Al}, \mathrm{Mn}$ | 0.41 | 0.25 |
| Deposition | Al | Al | 0.32 | 0.25 |
| class | $\mathrm{Al}, \mathrm{Mn}, \mathrm{Fe}$ | $\mathrm{Al}, \mathrm{Mn}$ | 0.50 | 0.33 |

## What are the factors attributing to the differences among lakes?

A substantial portion of the lakes in eastern Canada were found to be very low in acid neutralizing capacity and therefore vulnerable to acidification. Factor analysis (Table 13) of all the water chemistry data indicated that $\mathrm{Ca}^{2+}$, $\mathrm{Mg}^{2+}$ and alkalinity are the dominant factors in characterizing the overall variability in chemistry among lakes. Clearly, parameters associated with chemical weathering processes were the dominant factor characterizing the variability among the lakes sampled in eastern Canada.

Table 13. Significant loading factors from principle component analysis for 579 lakes.

|  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
| 1 | 2 | Factor |  |  |
| Alkalinity | Elevation | 3 | 4 |  |
| $\mathrm{HCO}_{3}$ | Na | K | Secchi |  |
| Ca | Cl | $\mathrm{SO}_{4}$ | Color |  |
| Mg |  | $\mathrm{XSSO}_{4}$ | Al |  |
| XSCa |  |  |  |  |
| XSMg |  |  |  |  |
| $\mathrm{XS}=$ Sea salt corrected values. |  |  |  |  |

## Fisheries

In Canada, community and population changes in the fishery have been used as indicators of anthropogenic impacts in the Sudbury, Ontario, area (Beamish and Harvey 1972; Beamish 1976) and in southwestern Nova Scotia (Watt et al. 1983). Wide scale surveys in Norway have documented the loss of fish populations in relation to pH in hundreds of lakes (Wright and Snekvik 1978; Overrein et al. 1980). Surveys in the Adirondack Mountains of New York have shown changes in fisheries over time (Schofield 1976; Pfeiffer and Festa 1980). Increases in concentrations of some metals may exacerbate the effect of acidification on fish. Mortality of stocked rainbow trout (Salmo gairdneri) in cages in acidified lakes near Sudbury, Ontario, was attributed to Cu or Cu and Zn in combination with low pH (Yan et al. 1979). Cronan and Schofield (1979) and Schofield and Trojnar (1980) reported that mortality of brook trout (Salvelinus fontinalis) in New York was caused by Al and pH in combination. Numerous laboratory studies have examined metal and pH toxicity in fish (Spry et al. 1981); however, the significance of metal toxicity to fish in the field is still largely unknown.

The fisheries component of this study was designed to assess whether the distribution, growth, abundance, and metal body burdens of fish had any relation to chemical and physical lake characteristics, in particular, whether fish communities in eastern Canada may be responding or showing symptoms of being impacted by acidifying environments.

Table 14. Proportional frequency of occurrence of main fish species within each region.

|  | Ont. | N.S. | N.B. | Nfld. | Lab. | Que. ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Brook trout | 0.21 | 0.36 | $0.56{ }^{\text {b }}$ | $0.69{ }^{\text {b }}$ | $0.42^{\text {b }}$ | $0.66{ }^{\text {b }}$ |
| White sucker | 0.29b | 0.47 | 0.52 |  | 0.28 | 0.26 |
| Brown bullhead | 0.01 | 0.37 | 0.28 |  |  | 0.03 |
| Northern pike | 0.10 |  |  |  | 0.22 | 0.21 |
| Yeilow perch | 0.08 | $0.64{ }^{\text {b }}$ | 0.23 |  |  | 0.05 |
| White perch |  | 0.13 | 0.10 |  |  |  |
| Walleye |  |  |  |  |  | 0.11 |
| Longnose sucker |  |  |  |  | 0.18 | 0.11 |
| Northern hog sucker | 0.04 |  |  |  |  |  |
| Lake trout | 0.01 |  |  |  | 0.22 | 0.08 |
| Lake chub | 0.10 | 0.03 | 0.09 |  |  |  |
| Lake whitefish |  |  |  |  | 0.13 |  |
| Atlantic salmon (landlocked) (anadromous) |  |  | 0.03 | $\begin{aligned} & 0.28 \\ & 0.11 \end{aligned}$ | 0.03 |  |
| Total number of species caught | 13 | 10 | 13 | 5 | 10 | 11 |

[^0]Table 15. Number of species caught per lake and number of lakes fished with no catch (headwater and non-heaclwater lakes).

|  | Ont. | Que. | N.S. | N.B. | Nfld. | Lab. |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| No. lakes fished <br> \% total no. lakes fished <br> that were headwaters | 72 | 91 | 76 | 69 | 108 | 94 |
| No. lakes fished <br> with no catch | 100.0 | 78 | 85.5 | 88.4 | 98.1 | 52.1 |
| \% lakes fished <br> with no catch |  |  |  |  |  |  |
| \% lakes fished with no catch <br> that were headwaters | 29 | 70.3 | 7.7 | 9 | 8 | 27 |

## Species Representation

A single gillnet set over a period of $1-2 \mathrm{~d}$ can be used to determine the presence of fish species with only limited reliability even for larger, vulnerable species. A greater sampling effort using a variety of sampling gear would be required to increase reliability. The mean number of hours fished ranged from 18.5 h in Nova Scotia, 21.9 h in Quebec, 26.3 h in New Brunswick to 41.2 h in Ontario, 47.8 h in Newfoundland, and 54.4 h in Labrador (mean $35.0 \pm$ sD 13.5 h for all regions combined).

Thirty-nine species [ $21.5 \%$ of the total freshwater fish fauna in Canada (Scott and Crossman 1973)] were caught in the 510 lakes fished throughout eastern Canada. Brook trout was the only species that occurred in all regions and was the dominant species in New Brunswick, Newfoundland, Labrador, and Quebec (Table 14). White sucker (Catostomus commersoni) and yellow perch (Perca flavescens) were the dominant species in Ontario and Nova Scotia, respectively. Other species commonly caught were brown bullhead (Ictalurus nebulosus), lake chub (Couesius plumbeus), lake trout (Salvelinus namaycusb), and landlocked Atlantic salmon or ouananiche (Salmo salar).

There was little difference (except for Newfoundland) in the total number of species caught among the regions (mean $10.3 \pm \mathrm{sD} 2.7$ species per region) (Table 14). Not all species known or suspected to occur in cach region, however, were caught. Considerable variation among regions was apparent. Quebec and Ontario caught an average of $10.2 \%$ of the species known to occur in their regions. Nova Scotia, New Brunswick, and Newfoundland caught $27.2 \%$ (combined mean) and Labrador reported $48.0 \%$ of the species clocumented in Scott and Crossman (1973).

## What factors influence the diversity of fish species and their abundance in eastern Canada?

It has been demonstrated that community complexity and lake size are related; larger (non-headwater) lakes contain more species (Minns 1981). Arctic char (Salvelinus alpinus) and walleye (Sizostedion vitreum vitreum) were caught only in non-headwater lakes in Quebec's survey. All other species were caught in both non-headwater and headwater lakes. In Ontario and Newfoundland where almost all lakes sampled were headwaters, fewer species per lake were caught than in the other regions (Table 15); these areas also had a higher proportion of lakes with no fish. The smallest lakes were in Ontario. The largest sampled lakes were in Quebec; however, the number of fishless lakes and species per lake there are comparable to Nova Scotia and New Brunswick. Mean lake areas in these regions were among the smallest in the survey.

Species assemblages varied among regions and show differences in geographic distribution. The fish communities found in Nova Scotia and New Brunswick lakes were dominated by brook trout, yellow perch, and white perch (Morone americana), white sucker and brown bullhead (Table 14). This compares to other fisheries surveys completed by Peterson and Martin-Robichaud (1982) and reflects the dominant community in these regions. This contrasts with brook trout, white sucker, northern pike (Esox lucius), walleye, and yellow perch in Ontario and Quebec (Table 14). These results are similar to Minns (1981) who suggested that smaller lakes containing brook trout only are the most common community in Ontario. The species associations in Quebec and Labrador may be expected due to the larger lakes sampled (Johnson et al. 1977) and the known zoogeographic distribution of species (Scott and Crossman 1973). In Newfoundland, number of species and their dominance in communities were similar to survey results from the Avalon Peninsula completed by Whelan and Wiseman (1975, 1977).

## Does pH influence the diversity and abundance of fishes in eastern Canadian lakes?

A change in the number and kind of species is expected as a lake acidifies (Haines 1981; Harvey 1982; Schofield 1982; Kelso and Gunn 1984). Differences in the number of species caught at varying pH ranges were evident (Fig. 10) in our data. Combining all regional data, the greatest decrease in the number of species occurred below pH 6.0. An examination of the same data for each region suggests that small sample sizes in certain pH classes resulted in minor inconsistencies (Table 16) within some regions.

If lake size were to confound the trend of fewer fish species at lower pH 's, then one would expect a relation to exist between lake size and pH . We first examined the lake sizes bounded by the pH classes of Fig. 10:

| pH class <br> from Fig. 10 | Mean lake size <br> ha | Range <br> ha | SlD <br> of Mean |  |
| :---: | :---: | :---: | :---: | :---: |
| $4.00-4.49$ | 12 | 66 | $3-150$ | 55 |
| $4.50-4.99$ | 36 | 74 | $1-600$ | 107 |
| $5.00-5.49$ | 64 | 104 | $0.3-941$ | 145 |
| $5.50-5.99$ | 121 | 98 | $0.5-1177$ | 142 |
| $6.00-6.49$ | 254 | 120 | $0.3-1784$ | 163 |
| $6.50-6.99$ | 211 | 110 | $0.2-1217$ | 160 |

Clearly, with the range and broad standard deviations of mean lake sizes, each pH class covers a wide range in lake sizes. Further, there was no significant statistical relation ( $r^{2}=0.01, F=0.8, n=811$ ) between lake size and pH. Consequently, although an effect of lake size upon fish diversity may exist, in this data set the major influence upon number of species is pH (Fig. 10).
The generalized response of fish communities to eutrophication (Colby et al. 1972; Leach et al. 1977) and acidification (Kelso and Gunn 1984) suggest that the occurrence and persistence of salmonids, percids, centrarchids, and cyprinids should be predictable. Yellow perch, brown bullhead, pumpkinseed (Lepomis gibbosus), and golden shiner (Notemigonus crysoleucas) commonly caught in Nova Scotia (mean pH 4.9) and New Brunswick (mean pH 5.6 ) are known to be more tolerant of low pH than lake trout, northern pike, and walleye caught in one or more of the regions with higher mean pH's (Quebec, Labrador, and Ontario) (Rahel and Magnuson 1983; Haines 1981; Harvey 1982; Beamish 1976). However; it is difficult to determine from the data whether these species and community differences are based solely on acid sensitivity.

Regression analysis of catch per unit effort (CUE) with lake pH (Table 17) was conducted on lakes where fishing effort fell in the range of 18 to 36 h . A significant association existed between the total number of fish caught per 24 $h$ in headwaters and pH in Nova Scotia, Newfoundland, and Ontario. In Newfoundland, a stronger relation existed ( $n=14, r^{2}=0.37$ ) between fish weight and pH . When all regions were $\operatorname{combined}(n=176$ ), the abundance- pH regression was significant for CUE at the $5 \%$ level but explained only $2 \%$ of the variance in CUE Similar results ( $n=70, P=0.09, r^{2}=0.04$ ) were obtained for the aggregated analysis of CUE (weight of fish). No significant relation existed between lakes (headwater and non-headwater) with a $\mathrm{pH}<5.4$ and CUE as number ( $n=69$ ) of fish caught.

## What factors generally influence fish species diversity and abundance in lakes of eastern Canada?

The principles of island biogeography have been applied to species diversity data by Browne (1981) who showed that lake size alone exerts a considerable influence on diversity. We have shown (Fig. 10, Tables 16 and 17) that pH influences both catch (abundance) and the diversity of fish communities.

To investigate further the lake's influence on species diversity and catch per unit effort (CUE), we carried out a stepwise multiple regression analysis (Table 18). The greatest effect upon diversity resulted from the influence of lake size followed by lake depth. As lake depth increased, diversity decreased. Lake size also had the greatest influence upon CUE followed by lake depth, pH , and alkalinity. These data emphasize that any treatment of atmospheric deposition effects must include the intrinsic variability imposed naturally by the limits of habitat.

## Does $\mathbf{p H}$ affect fish growth (reflected by condition factor) in eastern Canadian lakes?

To examine the effect of pH on fish growth, a regression analysis of pH on condition factor was conducted (Table 19). Condition factor $(K)$ is defined as $K=$ weight/length $^{3}$ (Lagler et al. 1962).

Fish condition has been a good indicator of acid stress in yellow perch (Perca flavescens) from acid lakes in the La Cloche Mountains, Ontario, and in white sucker populations in the Muskoka-Haliburton area of Ontario (Harvey 1982). However, our results generally did not support the hypothesis that there is a consistent relationship between condition factor and pH for a given species. Inconsistent results were obtained for the sign of the slope constant for the same species in different regions and in the same region in different years. In Nova Scotia where the mean pH of sampled lakes was 4.9 , the condition factor for brook trout was only slightly higher $\left(0.15 \times 10^{-4}\right)$ than for Ontario brook trout $\left(0.14 \times 10^{-4}\right)$ caught in lakes with higher pH's (mean 6.1). A substantial proportion


Figure 10. Relation between numbers of fish species and the lake pII for all lakes in eastern Canada.

Table 16. Mean number of fish species by pil category and region (number in brackets is the number of lakes fished) for headwater lakes only.

| pH | N.S. | N.B. | Nfld. | Lab. | Que. 1981 | Ont. 1982 | Ont. | All regions |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $4.0-4.49$ | $1.2(11)$ | $-(0)$ | $-(0)$ | $-(0)$ | $-(0)$ | $-(0)$ | $-(0)$ | $1.2(11)$ |
| $4.5-4.99$ | $1.1(14)$ | $1.4(5)$ | $0.4(5)$ | $-(0)$ | $1.0(3)$ | $-(0)$ | $0.8(4)$ | $1.0(31)$ |
| $5.0-5.49$ | $2.6(18)$ | $1.2(5)$ | $0.5(13)$ | $1.0(1)$ | $1.8(4)$ | $1.0(3)$ | $0.4(8)$ | $1.9(52)$ |
| $5.5-5.99$ | $3.8(6)$ | $1.7(10)$ | $1.0(31)$ | $1.6(12)$ | $1.4(8)$ | $3.4(5)$ | $0.8(16)$ | $1.5(88)$ |
| $6.0-6.5$ | $2.9(14)$ | $2.6(5)$ | $1.4(28)$ | $1.5(23)$ | $1.9(8)$ | $2.4(9)$ | $1.2(15)$ | $1.8(102)$ |
| $6.5+$ | $2.0(2)$ | $3.0(36)$ | $1.3(28)$ | $2.9(13)$ | $-(0)$ | $2.5(16)$ | $1.1(29)$ | $2.1(124)$ |

Table 17. Regression of catch per efforta on pH for headwater lakes.

|  | Number of lakes <br> with fish | Slope | Intercept | $r^{2}$ | $P$ (slope $=0)$ |
| :--- | :---: | ---: | ---: | :---: | :---: |
| Region | 34 | 31.393 | -136.64 | $0.363^{\text {b }}$ | 0.0002 |
| N.S. | 34 | 8.098 | -25.00 | 0.040 | 0.260 |
| N.B. | 41 | 5.575 | -25.90 | $0.224^{\mathrm{b}}$ | 0.002 |
| Nfld. | 16 | 0.973 | 5.96 | 0.001 | 0.916 |
| Lab. | 22 | 15.513 | -64.20 | 0.11 | 0.130 |
| Que. | 40 | 4.592 | -22.87 | $0.232^{\mathrm{b}}$ | 0.002 |
| Ont. |  |  |  |  |  |

${ }^{\text {a }}$ Catch per effort $=$ catch $/ 24$ hours: for effort in the range of $18-36$ hours. Catch is total number of fish caught for all species.
${ }^{\text {b }}$ Significant at $5 \%$ level.
Table 18. Results of stepwise multiple regression of four morphometric and chemical variables on fish species diversity and catch per unit of effort (CUE).

| $n$ | Variables: included | Variables ${ }^{\text {a }}$ not included | $r^{2}$ |
| :---: | :---: | :---: | :---: |
| $\log _{10}$ no. fish species +1 | 1,2 | 3, 4 | $0.15{ }^{\text {b }}$ |
| $\log _{10}$ CUE +1 | 1,2,3,4 |  | $0.38{ }^{\text {b }}$ |
| aVariable legend: |  |  |  |
| $1 \log$ area $=\log _{10}$ lake area |  |  |  |
| 2 log depth $=\log _{10}$ maximum depth |  |  |  |
| $3 \log \mathrm{pH}=\log _{10}(\mathrm{pH})$ |  |  |  |
| $4 \log$ alkalinity $=\log _{10}\left(\right.$ alkalinity $\left.+100 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}\right)$. |  |  |  |
| ${ }^{1}$ Indicates significance at $P<0.01$. |  |  |  |

Table 19. Significant analyses (probability $(P)$ shown in right hand column) of the effect of pH on fish growth as represented by condition factor ( $w / L^{3}$ ).

|  | $n$ | Slope | Intercept | $r^{2}$ | $P($ slope $=0)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Brook trout |  |  |  |  |  |
| N.S. | 14 | $1.615 \times 10^{-6}$ | $4.444 \times 10^{-6}$ | 0.209 | 0.101 |
| Que. 1982 | 927 | $-1.847 \times 10^{-6}$ | $1.277 \times 10^{-6}$ | 0.040 | 0.000 |
| Ont. | 53 | $2.372 \times 10^{-6}$ | $-1.325 \times 10^{-6}$ | 0.149 | 0.004 |
| White sucker |  |  |  |  |  |
| N.B. | 38 | $-1.761 \times 10^{-6}$ | $2.385 \times 10^{-6}$ | 0.089 | 0.068 |
| Lab. | 621 | $1.365 \times 10^{-6}$ | $5.426 \times 10^{-6}$ | 0.860 | 0.000 |
| Que. 1982 | 490 | $1.403 \times 10^{-6}$ | $9.227 \times 10^{-7}$ | 0.046 | 0.000 |
| Que. 1981 | 88 | $-1.077 \times 10^{-6}$ | $1.652 \times 10^{-5}$ | 0.097 | 0.003 |
| Ont. | 146 | $5.054 \times 10^{-7}$ | $9.050 \times 10^{-6}$ | 0.026 | 0.053 |
| Yellow perch |  |  |  |  |  |
| Que. 1982 | 19 | $-4.034 \times 10^{-6}$ | $3.913 \times 10^{-5}$ | 0.228 | 0.039 |
| Lake trout |  |  |  |  |  |
| Que. 1982 | 7 | $1.403 \times 10^{-7}$ | $9.227 \times 10^{-7}$ | 0.046 | 0.000 |
| Walleye |  |  |  |  |  |
| Que. 1982 | 178 | $5.981 \times 10^{-7}$ | $4.798 \times 10^{-6}$ | 0.022 | 0.047 |

Table 20. Discrimination of fish species absence-presence by region.

| Species (by area) | 1 | 2 | Discriminant variables: |  |  |  |  |  | $n$ | Absence: presence | Discriminant classification |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | Percent classified successfully ( $P_{o}$ ) |  | Percent expected by chance ( $P_{c}$ ) | Kappa ${ }^{\text {b }}$ | $Z^{\text {c }}$ |
|  |  |  | 3 | 4 | 5 | 6 | 7 | 8 |  |  |  |  |  |
| Brook trout |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Nova Scotia |  | 0 d |  | 0 | 0 | X |  | 0 | 76 | 49:27 | 0.62 | 0.55 | 0.16 | $1.27^{*}$ |
| New Brunswick | 0 | 0 | 0 | 0 | X | 0 |  | 0 | 52 | 26:26 | 0.62 | 0.50 | 0.23 | $1.66{ }^{*}$ |
| Newfoundland | 0 |  | 0 | 0 | X | 0 | 0 | 0 | 107 | 32:75 | 0.60 | 0.52 | 0.17 | 1.68 |
| Labrador | 0 | 0 | X | 0 | 0 | 0 | 0 | 0 | 95 | 41:54 | 0.60 | 0.49 | 0.21 | 2.05 |
| Quebec - 1982 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | X | 53 | 34: 19 | 0.79 | 0.52 | 0.56 | 3.91** |
| Quebec - 1981 | 0 | 0 | 0 | X | 0 | 0 | 0 | 0 | 32 | 24: 8 | 0.75 | 0.47 | 0.53 | 3.17** |
| Ontario | X | 0 | 0 |  | 0 | 0 | 0 |  | 70 | 55:14 | 0.84 | 0.74 | 0.40 | 1.76 |
| All regions | 0 | X | X |  | 0 | 0 |  | X | 214 | 118:96 | 0.63 | 0.51 | 0.25 | 3.58** |
| Common white sucker |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Nova Scotia |  | X |  | X | X | 0 |  | 0 | 76 | 40:36 | 0.74 | 0.50 | 0.47 | 4.11** |
| New Brunswick | 0 | 0 | 0 | 0 | X | 0 |  | 0 | 52 | 19:53 | 0.77 | 0.53 | 0.51 | 3.51 ** |
| Labrador | 0 | 0 | 0 | X | 0 | X | 0 | 0 | 95 | 51: 44 | 0.65 | 0.49 | 0.32 | 3.12** |
| Quebec - 1982 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 53 | 40: 13 |  | - nf |  |  |
| Quebec - 1981 | 0 | 0 | 0 | 0 |  | 0 | 0 | 0 | 32 | 24: 8 |  | nf |  |  |
| Ontario | 0 | 0 | 0 |  | 0 | 0 | 0 |  | 70 | 50: 20 |  | - nf |  |  |
| Yellow perch |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Nova Scotia |  | 0 | 0 | 0 | 0 | X |  | 0 | 76 | 27: 49 | 0.64 | 0.55 | 0.22 | 1.73 |
| New Brunswick | 0 | 0 | 0 | 0 | X | 0 |  | X | 52 | 37: 15 | 0.73 | 0.49 | 0.47 | 3.45** |
| Quebec - 1982 | 0 | 0 | X | 0 | 0 | 0 | 0 | 0 | 53 | 40:13 | 0.72 | 0.56 | 0.35 | 2.27 |
| Ontario | 0 | 0 | 0 |  | 0 | 0 | 0 |  | 70 | 64: 6 |  | nf |  |  |
| Walleye |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Quebec - 1982 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 53 | 40: 13 |  | nf |  |  |
| Arctic char |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Labrador | 0 | X | 0 | 0 | 0 | 0 | 0 | 0 | 95 | 87: 8 | 0.78 | 0.75 | 0.12 | 0.66 |
| Lake trout |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Labrador | 0 | 0 | X | 0 | X | 0 | 0 | 0 | 95 | 67:28 | 0.80 | 0.51 | 0.59 | 5.64** |
| Quebec - 1982 | 0 | 0 | 0 | 0 | X | 0 | 0 | 0 | 53 | 49: 4 | 0.79 | 0.72 | 0.27 | 1.23 |
| Ontario | 0 | X | 0 |  | 0 | 0 | 0 |  | 70 | 69: 1 | 0.93 | 0.90 | 0.27 | 0.74 |
| Atlantic salmon |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| L - Newfoundland | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 107 | 77:30 |  | nf |  |  |
| L - Labrador | 0 | 0 | 0 | 0 | X | X | 0 | 0 | 95 | 91: 4 | 0.85 | 0.80 | 0.25 | 1.20 |
| A - Newfoundland | 0 |  | 0 | 0 | 0 | 0 | 0 | 0 | 107 | 96: 11 |  | nf |  |  |
|  | 1 | 4 | 4 | 3 | 8 | 4 | 0 | 3 |  |  |  |  |  |  |

[^1]Table 21. Fish body burdens ( $\mu \mathrm{g} \cdot \mathrm{g}^{-1}$ ) of metals; based on whole fish, except in Newfoundland.

| Metals |  | Ont. | Que. 1981 | Lab. | Nfld. | N.B. | N.S. | Total no. of samples | All regions combined |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Hg | Range | 0.01-0.99 | 0.05-1.64 | 0.02-1.86 | 0.02-1.30 | 0.01-.711 | 0.01-3.2 | 2782 | 0.01-3.2 |
|  | Mean | 0.17 | 0.29 | 0.22 | 0.22 | 0.205 | 0.38 |  |  |
| Pb | Range | 0.008-14.1 | 0.008-1.82 | - | - | 0.008-4.98 | 0.008-1.25 | 709 | 0.008-14.1 |
|  | Mean | 2.12 | 0.19 |  |  | 0.48 | 0.18 |  | 0.24 |
| Al | Range | - | - | 0.4-8.1 | 0-4.6 | - | - | 1798 | 0-8.1 |
|  | Mean |  |  | 0.97 | 0.59 |  |  |  | 0.78 |
| Mn | Range | - | 0.08-11.15 | - | 0.02-3.24 | - | - | 1085 | 0.08-11.15 |
|  | Mean |  | 1.68 |  | 0.22 |  |  |  | 0.53 |
| Se | Range | - | - | - | 0.008-1.48 | - | - | 882 | 0.008-1.48 |
|  | Mean |  |  |  | 0.57 |  |  |  | 0.57 |
| Ni | Range | 0.07-12.01 | 0.01-0.54 | - | 0.15-5.19 | - | - | 681 | 0.01-12.01 |
|  | Mean | 1.1 | 0.23 |  | 0.41 |  |  |  | 0.69 |
| Zn | Range | 20.5-212.0 | 2.8-78.0 | - | 0.65-25.0 | 60.0-169.0 | 20.3-152.0 | 1634 | $0.65-212.0$ |
|  | Mean | 54.6 | 11.83 |  | 7.54 | 90.3 | 90.4 |  | 27.5 |
| As | Range | - | - | - | 0.0007-0.36 | - | - | 671 | 0.0007-0.36 |
|  | Mean |  |  |  | 0.02 |  |  |  | 0.02 |
| Cd | Range | - | 0.009-0.16 | - | 0.011-0.10 | 0.008-0.82 | 0.009-0.56 | 461 | 0.008-0.82 |
|  | Mean |  | 0.03 |  | 0.05 | 0.13 | 0.16 |  | 0.09 |

of the variance in condition factor for white sucker in Labrador was associated with the regression on pH ( $r^{2}=0.86$ ).

## Can the presence of certain species be predicted in lakes?

Stepwise discriminant analysis was performed to determine whether the presence or absence of a species could be predicted, based on 8 lake morphometric and chemical variables (Table 20). With a larger database, selected with less bias towards the presence or absence of particular fish species, the dependence of fish absence-presence on lake morphometry and acidic state, could be used to estimate communities in lakes, then to predict changes in fish distribution on a regional basis following a change in atmospheric deposition. Where significant discriminant functions were obtained, the variables included, in order of precedence, pH , alkalinity, maximum depth, elevation, Secchi depth, color, and lake area. Using the chance-corrected classification statistic (kappa) of Titus et al. (1984), under half ( 8 of 19) of the discriminant functions predicted better than chance expectation. The best case was for lake trout in Labrador: In the three cases where functions were obtained for common white sucker, the classifications were significantly better than chance. While the overall function for brook trout did better, only two of six regional functions did so.

Buffering related factors ( pH and alkalinity) were important contributors to the discriminant functions for most species in Nova Scotia, New Brunswick, and Labrador. Of these regions, two had the lowest mean pH's in the data set. Overall, brook trout occurrence was dependent on morphometry (maximum depth and elevation) and color. Occurrence of lake trout was dependent on pH , Secchi depth, and maximum depth. Minns (1981) found, in Ontario, that discriminant functions for fish assemblages made up from brook trout, lake trout, northern pike, smallmouth bass, and walleye were strongly dependent on lake area, maximum depth, and elevation. In that case, pH and conductivity were not important.
Thus, the discriminant functions (Table 20) were good for predicting the presence/absence of certain fish species (lake trout and Atlantic salmon), but poor for other common species. Development of a capability to predict species presence by using lake chemical/physical/morphometric variables obviously requires an even broader survey database and perhaps a process-oriented approach.

## What factors influence the body burdens of trace metals in fish of lakes in eastern Canada?

Fish from acidifying lakes may contain elevated concentrations of Hg and other metals. High Hg levels in fish from Sweden (Jernelov et al. 1975), Ontario (Scheider et al. 1979; Kelso and Gunn 1984), and Minnesota (Glass and Loucks 1980) were associated with lower pH or alkalinity. Increased concentrations of Hg in fish from Adirondack lakes with low alkalinity were reported by Armstrong and Sloan (1980). Lead concentrations in the blood of rainbow trout increased as water pH was reduced in a laboratory study by Hodson et al. (1978). Aluminum, Mn, and Zn , which have consistently exhibited increased concentrations in water with low pH (Beamish and Van Loon 1977; Gjessing et al. 1976; Wright et al. 1980), are known to have serious effects on fish (Baker and Schofield 1980;

Spry et al. 1981). Elevated body burdens of these latter trace metals in fish from acidified lakes has not been documented.

Mercury was the only metal analyzed in all six regions (Table 21). Mercury concentrations in freshwater fish ranged from 0.01 to $3.2 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ with a mean of $0.25 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ for all regions combined. Each region's mean concentration and the overall mean level are similar to levels reported for dressed fish samples from Lake Ontario and Lake Erie (Uthe and Bligh 1971), some Lake Superior offshore fish (Armstrong and Lutz 1977b), pike muscle concentrations from rural Sweden (Johnels et al. 1967), and North Atlantic fin fish (Windom et al. 1973). The average levels are all below the minimum standard of $0.5 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ in fish tissue intended for human consumption (National Health and Welfare). However, each region had fish with Hg levels in tissues above human health guidelines:

| Region | Total no. samples | Total no. <br> lakes sampled | No. $>0.5 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ | \% | $\begin{aligned} & \text { No. lakes } \\ & \text { with fish } \\ & >0.5 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1} \end{aligned}$ | \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| N.S. | 121 | 51 | 31 | 25.6 | 18 | 35 |
| N.B. | 91 | 48 | 1 | 1.1 | 1 | 2 |
| Nfld. | 863 | 74 | 76 | 8.8 | 24 | 32 |
| Lab. | 1199 | 88 | 135 | 11.3 | 40 | 45 |
| Que. | 244 | 32 | 29 | 11.9 | 15 | 47 |
| Ont. | 264 | 37 | 11 | 4.2 | 10 | 27 |

Each region had fish with high levels that are roughly comparable to those in areas where Hg contamination from chloralkali plants was suspected or known to have occurred (Johnels et al. 1967; Fimreite et al. 1971; May and McKinney 1981; Fimreite and Reynolds 1973; Armstrong and Lutz 1977a). The highest levels were observed in Nova Scotia where sampled lakes had the lowest overall mean pH's in the survey. New Brunswick had the fewest ( $2 \%$ ) number of lakes with fish exceeding human health guidelines. In the remaining five regions, 27 to $47 \%$ of lakes had fish with Hg body burdens $>0.5 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$.

To determine the factors influencing Hg body burdens of fish, we carried out a stepwise multiple regression analysis of Hg body burden against fish length, fish weight, lake size, lake depth, lake elevation, pH, calcium, and alkalinity by region. The only consistent factor having a significant ( $P<0.05$ ) influence on Hg body burden was fish length. In Ontario and Labrador Hg concentrations decreased with increasing Ca ${ }^{+}$, and in Nova Scotial and New Brunswick the converse was found. Because the majority of lakes are headwaters, there is no upstream Hg source.

Lead was analyzed in fish from four regions. Concentrations ranged from 0.009 to $14.1 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ with an overall mean of $0.24 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$. All Quebec, New Brunswick, and Nova Scotia values were below the standard of $10 \mu \mathrm{gPb} \cdot \mathrm{g}^{-1}$ in fish for human consumption. These concentrations were similar to levels reported in fish fillets from Wisconsin (Konrad et al. 1974), in dressed fish from nonindustrialized and heavily industrialized freshwater areas in Ontario (Uthe and Bligh 1971), and to nearshore (MOE 1976) and offshore (Armstrong and Lutz 1977b) Lake Superior fisheries. High levels in all regions were similar to those reported by May and McKinney (1981) from areas in the United States known to have point industrial sources of Pb . Significant geological sources may be a factor in Ontario.

Aluminum levels in fish from Newfoundland and Labrador ranged from undetectable to $8.1 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ with an overall mean of $0.78 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$. It is not known whether these levels represent background concentrations.

Mean Mn concentrations in Quebec and Newfoundland are similar to those reported in freshwater fish by Uthe and Bligh (1971). Selenium levels in fish from Newfoundland are similar to concentrations found in a national survey in the United States (May and McKinney 1981) and to levels in Lake Superior offshore fish (Armstrong and Lutz 1977b). Arsenic in Newfoundland fish were also close to background levels found in Great Lakes fish by Uthe and Bligh (1971) and Lucas et al. (1970).

Cadmium concentrations in fish from Quebec and Newfoundland are similar to levels found in areas that were not heavily contaminated (Lucas et al. 1970; Uthe and Bligh 1971; Lovett et al. 1972; Windom et al. 1973; Kelso and Frank 1974; Giesy and Wiener 1977). However, mean Cd concentrations in New Brunswick and Nova Scotia were more than double the levels in either Newfoundland or Quebec (Table 21). The highest concentrations were in the ranges reported by May and McKinney (1981) for fish sampled in industrialized areas, near zinc-smelting operations and near major ore deposits.

Nickel body burdens varied a great deal between regions (Table 21). Mean concentrations of $0.23 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ in Quebec and $0.41 \mu \mathrm{~g} \cdot \mathrm{~g}^{-1}$ in Newfoundland compare with some levels in nearshore fisheries in Lake Superior (MOE 1976) but exceed levels reported by Uthe and Bligh (1971) in other Canadian freshwater fish. A significant geological source of Ni may be associated with elevated levels in Ontario.

The largest ranges in metal concentrations are found in Zn body burdens within and among the regions (Table 21). Quebec and Newfoundland body burdens were similar to levels in Lake Superior and Lake Huron nearshore and offshore fish (Armstrong and Lutz 1977a, b; MOE 1976), in other Canadian freshwater fish (Uthe and Bligh 1971) and in Wisconsin fisheries (Konrad et al. 1974). Zinc levels in New Brunswick, Nova Scotia, and Ontario fish were generally higher than levels reported above (background?) and were in agreement with body burdens in fish

Table 22. Results of canonical analysis relating trace metal body burdens (criteria) to state variables. The metals marked (*) are influenced by indicated $\left({ }^{+}\right)$variables. Eigenvalue ( $\left.R^{2} / \mathrm{Cp}\right)$ represents the portion of variance in metal burdens which is predicted by the predictor variables.

|  | Ont. | Que. | N.S. | N.13. | NIfd. | lab. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spectes | Brook trout | Brook trout | Brook trout | Brook trout | Brook trout | Brook trout |
| Metal ("criteria") | $\mathrm{lg}^{*}, \mathrm{~Pb}, \mathrm{Ni}, \mathrm{Za}$ | $\mathrm{Hg}^{*}, \mathrm{~Pb}, \mathrm{Mn}, \mathrm{Zn}$ | $\mathrm{Pb}^{*}$, Se, $\mathrm{Cd}, 7 \mathrm{Zn}{ }^{\text { }}$ | $\mathrm{Pb}, \mathrm{Se}^{*}, \mathrm{Cd}, \mathrm{Zn}$ | $\mathrm{Hg}^{*}, \mathrm{Al}, \mathrm{Mn}, \mathrm{Sc}^{*}, \mathrm{Zn}, \mathrm{As}$ | $1 g^{*}, \mathrm{Al}$ |
| Predictor variables | Ao ${ }^{\text {il }}, \mathrm{Aw}^{\text {b }}$, max. depth, $\mathrm{pH}^{+}$, alk. ${ }^{+}$, cond., fish length, fish wt., lipid | Ao, Aw, max. depth, elevation, Secchi, pil, alk., cond., color, fish length ${ }^{+}$, fish wt. ${ }^{+}$ | Max. depth, Secchi ${ }^{+}$, $\mathrm{pHI}^{+}$, alk. ${ }^{+}, \mathrm{TOC}^{+\mathrm{c}}$, fish length, fish wt. | Ao, max. depth, Aw, elevation ${ }^{+}$, Secchi, $\mathrm{pH}^{+}, \mathrm{alk}^{+}, \mathrm{TOC}$, fish length, fish wt. | $\mathrm{AO}^{+}, \mathrm{An}^{+}$, elevation, Secchi, $\mathrm{pH}^{+}$, alk. ${ }^{+}$, cond., color, fish rength ${ }^{+}$, fish wt. ${ }^{+}$, lipid | Ao, Aw, max. depth, elevation, Secchi ${ }^{\ddagger}$, pH, alk, cond., color, fish length, fish wt.* |
| Eigenvalue | 0.49 | 0.46 | 0.73 | 0.44 | 0.22 | 0.24 |
| Species | White sucker |  | White sucker | White sucker | Atantic salmon | White sucker |
| Metal ("criteria") | $\mathrm{Hg}, \mathrm{Pb}, \mathrm{Ni}, \mathrm{Zn}^{+}$ |  | $\mathrm{Pb}, \mathrm{Se}, \mathrm{Cd}, 7 \mathrm{n}^{\text {- }}$ | $\mathrm{Pb}, \mathrm{Sc}^{*}, \mathrm{Cd}, 7 \mathrm{n}{ }^{*}$ | $\mathrm{Hg}^{*}, \mathrm{Al}, \mathrm{Mn}, \mathrm{Sc}, \mathrm{Zn}, \mathrm{As}{ }^{*}$ | $1 \mathrm{Hg}^{\circ} \mathrm{Al}$ |
| Predictor variables | $\mathrm{Ao}^{+}, \mathrm{Aw}^{+}$, max. depth, pil, alk., cond., fish length, fish wt., lipid |  | Max depth, elevation ${ }^{+}$, Secchi, pH, ttk., TOC, fish lengh ${ }^{+}$, fish wt. ${ }^{+}$ | Ao, max. depth, Aw, elevation, Secchi ${ }^{+}$, pH, alk, TOC, fish length ${ }^{+}$, fish wt. ${ }^{\text {. }}$ | Ao, Aw, clevation, Secchi, pII, alk., cond., color, fish length ${ }^{+}$, fish wt. ${ }^{+}$ | Ao, Av, max. depth, elevation, Secchi, $\mathrm{pH}^{-1}$, alk. ${ }^{+}$, cond. ${ }^{+}$ color ${ }^{+}$, fish length, fish wt. |
| Eigenvalue | 0.41 |  | 0.75 | 0.63 | 0.36 | 0.41 |
| Species |  |  | Yellow perch | Yellow perch |  | Lake trout |
| Metal ("criteria") |  |  | $\mathrm{Pb}^{*}, \mathrm{Sc}, \mathrm{Cd}, \mathrm{Zn}$ | $\mathrm{Pb}, \mathrm{Se}, \mathrm{Cd}, \mathrm{Zn}$ |  | $1 \mathrm{Ig}^{*}, \mathrm{Al}$ |
| Predictor variables |  |  | Max. depth, elevation, Secchi, $\mathrm{pH}^{+}$, alk ${ }^{+}$, TOC, fish lengh ${ }^{+}$, fish wh. ${ }^{+}$ | Ao, max. depth, Aw, elevation, Secchi, pli, alk., TOC, fish length, fish wt. |  | Ao, Av, max deprth, clevaion, Secchi ${ }^{\text {t }}$, pH , alk, cond., color, fish lengun ${ }^{+}$, fish wt. ${ }^{+}$ |
| Eigenvalue |  |  | 0.62 | 0.69 |  | 0,46 |

"no $=$ lake area.
${ }^{\text {has }} \mathrm{w}=$ watershed area.
$\cdot \mathrm{TOC}=$ Total organic carbon.
from areas with known contamination (Giesy and Wiener 1977; Murphy et al. 1978; Vinikour et al. 1980). Most regional concentrations were above levels found in North Atlantic inshore and offshore fisheries (Windom et al. 1973).

Canonical correlation analysis was used to determine whether trace metals ( $\mathrm{Pb}, \mathrm{Se}, \mathrm{Cd}, \mathrm{As}, \mathrm{Hg}, \mathrm{Mn}, \mathrm{Al}, \mathrm{Ni}, \mathrm{Zn}$ ) in fish were related to lake morphometry (lake area, watershed area, elevation, maximum depth), chemistry (Secchi, pH , alkalinity, conductivity, color) and/or fish weight, length, or lipid content. In canonical correlation analysis, successive canonical equations are developed for both criteria variables (metal body burden) and predictor variables to maximize their canonical correlate. The square of the canonical correlate ( $R^{2} / c p$ ) is the cigenvalue that represents the proportion of the variance in one canonical variate accounted for by the other.

The highest eigenvalues (Table 22) and thus the strongest correlations among the variates were found in Nova Scotia.

Overall, a variety of factors influence trace metal body burdens of fish including fish size, total organic carbon, lake color, and Secchi depth. However, in Ontario, Nova Scotia, New Brunswick, and Labrador a variety of metals $\mathrm{Hg}, \mathrm{Pb}, \mathrm{Zn}, \mathrm{Se}$, and Al - were found to increase in fish with low pH and/or alkalinity.

## Plankton and Benthos

Acidification of lakes in regions impacted by acidic deposition can result in substantial changes to communities of planktonic and benthic organisms (Almer et al. 1974; Sprules 1975; Braekke 1976; Kwiatkowski and Roff 1976; Wright et al. 1977; Raddum 1980; Conway and Hendrey 1982; Malley et al. 1982; Vaughan et al. 1982). Changes in the occurrence, abundance, seasonal succession of species, and in the diversity of the community have been indicators of lake acidification.

The plankton and benthos component of this study was designed to examine whether lake chemistry and morphometry may control patterns of plankton species composition and benthic abundance and biomass.

Table 23. Mean number of phytoplankton species per lake in pH ranges, all regions combined.

| $\begin{gathered} \mathrm{pH} \\ \text { range } \end{gathered}$ | No. of lakes | All groups combined | Chrysophytes | Bacillarophytes | Chlorophytes | Cryptophytes | Dinophytes | Cyanophytes |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| <4.5 | 1 | 8.0 | 2.0 | 1.0 | 2.0 | 1.0 | 1.0 | 1.0 |
| 4.5-4.99 | 12 | 25.4 | 8.1 | 6.5 | 5.7 | 1.5 | 0.9 | 0.6 |
| 5.0-5.49 | 36 | 24.3 | 9.2 | 4.1 | 5.8 | 1.9 | 1.2 | 1.1 |
| 5.5-5.99 | 81 | 27.8 | 8.6 | 4.1 | 7.5 | 2.0 | 2.8 | 2.5 |
| 6.0-6.49 | 98 | 28.1 | 8.5 | 3.8 | 7.7 | 2.0 | 0.7 | 2.9 |
| $\geq 6.5$ | 123 | 28.8 | 8.2 | 3.9 | 7.7 | 2.0 | 1.0 | 3.1 |

Table 24. Regression analysis between number of taxa (1) and weight (2) and lake size (3), pH (4), and alkalinity (5) for benthos and plankton.

| Region | Group | $n$ | Dependent variable | Independent variable | Included | $r^{2}$ | $P($ slope $=0)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| N.S. | Benthos | 48 | 1 | 3 | NA | 0.058 | 0.0989 |
|  |  | 48 | 2 | 3 | NA | 0.016 | 0.3953 |
| Nfld. | Benthos | 83 | 1 | 3 | NA | 0.024 | 0.1646 |
|  |  | 83 | 2 | 3 | NA | 0.007 | 0.4619 |
|  |  | 82 | 1 | 3, 4, 5 | 4 | 0.148 | 0.0004 |
|  |  | 82 | 2 | 3, 4, 5 | 4 | 0.080 | 0.0101 |
|  | Zooplankton | 107 | 1 | 3 | NA | 0.014 | 0.2235 |
|  |  | 106 | 1 | 3, 4, 5 | 4, 5 | 0.152 | 0.0002 |
|  | Phytoplankton | 77 | 1 | 3 | NA | 0.053 | 0.0440 |
|  |  | 76 | 1 | 3, 4, 5 | 3 | 0.053 | 0.0440 |
| Que. | Benthos | 33 | 1 | 3 | NA | 0.006 | 0.6707 |
|  |  | 33 | 2 | 3 | NA | 0.036 | 0.2889 |
|  | Zooplankton | 36 | 1 | 3 | NA | 0.019 | 0.4208 |
|  |  | 26 | 1 | 3, 4, 5 | 5 | 0.168 | 0.0377 |
|  | Phytoplankton | 175 | 1 | 3 | NA | 0.003 | 0.4824 |
| Ont. | Benthos | 36 | 1 | 3 | NA | 0.000 | 0.9525 |
|  |  | 36 | 2 | 3 | NA | 0.013 | 0.5099 |
|  | Zooplankton | 132 | 1 | 3 | NA | 0.161 | 0.0000 |
|  |  | 128 | 1 | 3,4,5 | 3, 4 | 0.198 | 0.0000 |
|  | Phytoplankton | 100 | 1 | 3 | NA | 0.001 | 0.7900 |
|  |  | 98 | 1 | 3,4,5 | 4 | 0.122 | 0.0004 |

Variable legend (all data $\log _{10}$ transformed)

1. number of taxa
2. ash free dry weight
3. lake area
4. pH
5. alkalinity

NA - denotes simple regressions with only one independent variable. Selection procedure of stepwise multiple regression for inclusion of variables in the 'best fit' model thus does not take place.

## What lake factors influence the community composition and diversity of phytoplankton?

Phytoplankton data from a total of 351 lakes were available from Ontario, Quebec, and Newfoundland. Since all data were collected between the end of August and mid-November, the seasonal effect upon community structure was assumed to be minimal. When all regional data were combined, crysophytes (yellow-green algae) and chlorophytes (green algae) were the dominant groups at all pH ranges followed by Bacillarophytes (diatoms), cryptophytes (cryptomonads), cyanophytes (blue-green algae), and dinophytes (dinoflagellates). In Quebec, bacillarophytes and chlorophytes were the dominant groups. This community composition is typical for nonacidic oligotrophic lakes in Eastern Canada (Schindler and Holmgren 1971) and elsewhere in North America (Hendrey 1982). Our results do not agree with Almer et al. (1978), Yan and Stokes (1978), and Hendrey (1982) who reported that Dinophycaeae and Chrysophyceae tend to dominate at lower pH's. Since we sampled fewer low pH lakes, our sample may not be representative of the community at all pH 's.

Overall, the mean numbers of species of chlorophytes and cyanophytes were consistently lower at low pH (Table 23). A decrease in Cyanophyteae in each region (Ontario, Quebec, Newfoundland) at lower pH was also

Table 25. Variables used in discriminant analyses.

|  | Region |  |  |  | All regions |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Nfld. | N.S. | Que. | Ont. |  |
| Biota sampled | (B, Z, P ${ }^{\text {a }}$ | (B) | ( $3,7, P$ ) | ( $\mathrm{B}, \mathrm{Z}, \mathrm{P}$ ) |  |
| Variables sampled: |  |  |  |  |  |
| Latitude | $x$ | $x$ | $x$ | $x$ | $\times$ |
| Longitude | $x$ | $x$ | $x$ | $\times$ | $\times$ |
| Lake area | $\times$ |  | $\times$ | $x$ |  |
| Maximum depth |  | $x$ |  | $x$ |  |
| Drainage area | $\times$ |  | $x$ | $x$ |  |
| Elevation | $x$ |  | $\chi$ |  |  |
| Distance to sea | $x$ |  |  |  |  |
| Secchi depth |  | $\times$ | $\times$ |  |  |
| Lab pHI | $\times$ | $x$ | $\times$ | $x$ | $x$ |
| Lab alkalinity | $\times$ | $\times$ |  | $x$ |  |
| Conductivity | $\times$ |  | X | $\times$ |  |
| TDS | $\times$ |  |  |  |  |
| Color | $x$ | $x$ | $\times$ |  |  |
| $\mathrm{HCO}_{3}^{-}$ |  | $\times$ |  | $\times$ |  |
| $\mathrm{Ca}^{2+}$ | $\times$ | $x$ | $x$ | $x$ | $x$ |
| $\mathrm{Mg}^{2+}$ | $\times$ | $\times$ | $x$ | $x$ | $x$ |
| $\mathrm{Na}+$ | $x$ | $x$ | $x$ |  |  |
| $\mathrm{K}^{+}$ | $x$ | $\times$ | $\times$ |  |  |
| Cl- | $x$ | $x$ | $\times$ | $x$ | $\times$ |
| $\mathrm{SO}_{4}^{2-}$ | $x$ | $\times$ | $\times$ | $x$ | $\times$ |
| $\mathrm{PO}_{3}^{-}-\mathrm{P}$ | $x$ |  |  |  |  |
| $\mathrm{NO}_{3}^{-}-\mathrm{N}$ | $\times$ |  |  |  |  |
| Pb |  |  |  | $x$ |  |
| Al | $x$ | $x$ | $x$ | $x$ | $\times$ |
| Mn | $x$ | $\times$ | $x$ |  |  |
| Cd | $x$ |  |  |  |  |
| Fe | $\times$ | $x$ | $\times$ |  |  |
| Cu |  |  | $x$ | $\times$ |  |
| Zn |  |  | $\times$ | $x$ |  |
| Ni |  |  | $\times$ |  |  |

$a B=$ benthos $; Z=$ zooplankton $; P=$ phytoplankton.
noted. There was little variation in the number of species in the other major groups at different pH ranges (Table 23). When all plankton data were combined, the greatest change in species numbers occurred in the pH interval 5 to 6 (Table 23). This agrees with other data from Norway, Sweden, and Ontario as reported by Conway and Hendrey (1982).

Regression analyses between the number of phytoplankton taxa, lake size, pH , and alkalinity (Table 24) generally indicate rather weak relationships. In most cases lake size was the significant contributor to diversity. In Ontario, there was an effect from pH .

Lakes in each region were divided into clusters (dendrograms produced by Jaccard index ${ }^{1}$ were inspected for greatest distances between recently formed clusters) based on their planktonic community structure. Discriminant analysis was then used to determine whether the lake clusters were characterized by distinctive combinations of chemical and morphometric/geographic characteristics (Table 25).

The discriminant functions explained over $95 \%$ of the overall variance among lakes in Ontario and Newfoundland but only $59 \%$ of the variance in Quebec lakes (Table 26). No single variable dominated the discriminant functions overall or regionally. In Ontario and Quebec, latitude, longitude, chloride, $\mathrm{SO}_{4}^{2-}$, and color were important in at least one of the functions. Alkalinity and Mg in Ontario were important in all three functions but were not predominant. In Quebec, color was important in all four functions. Elevation, distance from sea, latitude, color, $\mathrm{pH}, \mathrm{Al}$, and Fe were significant in at least one discriminant function in Newfoundland. Sodium was relatively important in all four functions as well.

$$
\begin{aligned}
{ }^{{ }^{J_{i}}, j=A /(A+B+C)} \text { where } J_{i} j & =\text { Jaccard index for lakes } i, j \\
A & =\text { number of species present in both lakes } \\
B & =\text { number of species present in lake } i \text {, but not in } j \\
C & =\text { number of species present in lake } j, \text { but not in } i
\end{aligned}
$$

Table 26. Summary of discriminant analyses on benthos and plankton data. Biota abbreviations are $\mathrm{B}=$ benthos, $\mathrm{Z}=$ zooplankton, $\mathrm{P}=$ phytoplankton. The analysis was performed twice for Ontario zooplankton, once with five lake clusters and once with ten (ie. $Z_{5}$ and $Z_{10}$ ). With $n$ clusters, $100 \%$ of the variance in the discriminant space can be explained by ( $n-1$ ) discriminant functions.

| Features of discriminant analysis | Ontario |  |  |  | Quebec |  |  | Newfoundland |  |  | Noval Scotial |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | B | $\mathrm{Z}_{5}$ | $\mathrm{Z}_{10}$ | p | $B$ | Z | P | 13 | Z | P | 13 |
| No. lakes | 36 | 128 | 128 | 98 | 31 | 33 | 165 | 79 | 101 | 74 | 48 |
| No. clusters | 5 | 5 | 10 | 7 | 7 | 1 | 5 | 5 | 5 | 5 | 6 |
| No. DF (90\% V) ${ }^{\text {a }}$ | 3 | 2 | 4 | 3 | 3 | 2 | 4 | 3 | 4 | 4 | 4 |
| $\mathrm{W}^{2}$ | 0.937 | 0.743 | 0.919 | 0.949 | 1.000 | 0.979 | 0.589 | 0.809 | 0.823 | 0.961 | 0.826 |

:No. DF ( $90 \% \mathrm{~V}$ ) indicates how many discriminant functions are required to explain $90 \%$ of this variance.
$\mathrm{b}^{2}=1-\frac{n}{(n-k)\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right) \ldots\left(1+\lambda_{r}\right)+1}$
where, $n=$ number of lakes
$k=$ number of clusters
$\lambda_{j}=$ eigenvalue for the ith discriminant function
$r=$ number of discriminant functions.
$W^{2}$ is the fraction of the discriminant space variance which is relevant to discriminating between clusters. In computing W2, we only used the number of discriminant functions listed in line three.

Table 27. Mean number of zooplankton species per lake in pH ranges for all regions combined.

| pH <br> range | No. of <br> lakes | All species <br> combined | Cladorcera | Cyclopoida | Calanoida |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $<4.5$ | 1 | 24 | 7.0 | 5.0 | 4.0 |
| $4.5-4.99$ | 12 | 11.96 | 3.07 | 1.36 | 1.83 |
| $5.0-5.49$ | 27 | 13.96 | 3.39 | 2.1 | 1.92 |
| $5.5-5.99$ | 56 | 16.48 | 3.57 | 2.52 |  |
| $6.0-6.49$ | 73 | 15.64 | 3.56 | 2.49 | 2.48 |
| $>6.5$ | 103 | 16.84 | 4.26 | 2.46 |  |

## What lake factors influence the community composition and diversity of zooplankton?

Zooplankton data from 272 lakes in Ontario, Quebec, and Newfoundland were available. Cladocera was the dominant group at high and low pH ranges followed by Calanoida and Cyclopoida regionally and overall (Table 27).

Although sample sizes were smaller at low pH ranges, a general trend of fewer species at lower pH is apparent in the major groups and for all species combined (Table 27). Consistently fewer numbers of species were observed for Cladocera in Ontario, Cyclopoida in Quebec, and for all species combined in Newfoundland. The number of species begins to decrease as the pH falls below 6.0 and below pH 5.5 , the rate of loss is much more rapid (Table 27). A lower diversity of zooplankton species at lower pH ranges agrees with other cases in Canada (Sprules 1975; Kwiatkowski and Roff 1976), United States, and Norway (Leivestad et al. 1976; Raddum et al. 1980).

An examination of trends in the occurrence and abundance of Epischura lacustris, Daphnia sicilis, and Mysis relicta, taxa known to be acid sensitive (Carter 1971; Almer et al. 1974; Sprules 1975; Raddum et al. 1980; Nero and Schindler 1983) yielded ambiguous results. Often, a species would be more abundant in a lower pH category, than in a higher range in one region, and would not have been found at all in the other regions, making comparison impossible. Small sample sizes, geographically limited distributions, and sampling biases confound an examination of particular species. Of note, however, was $D$. sicilis in Ontario which was present only in lakes above pH 6.0. This species was the first to disappear from Lake 223 which was artificially acidified (Malley et al. 1982).

Regression analysis (Table 24) revealed significant associations between the number of taxa and pH in Newfoundland, Quebec, and Ontario, and between the number of taxa and alkalinity in Newfoundland. Although the low $r^{2}$ values indicate that these are not strong relationships, results are more consistent than those seen for phytoplankton.

Cluster and discriminant analyses (method as described for phytoplankton) explained over $80 \%$ of the variance among lakes in Ontario, Quebec, and Newfoundland (Table 26). No single or set of variables dominated any discriminant function overall or regionally. Acidity, alkalinity, $\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{HCO}_{3}^{-}$, and $\mathrm{Cu}^{2+}$ were significant in Ontario and Newfoundland. $\mathrm{Cl}^{-}$was important in these regions and in Quebec as well. These variables suggest

Table 28. Mean number of benthic species per lake in pH ranges for all regions combined.

| pH range | No. species | No. lakes |
| :--- | :---: | :---: |
| $<4.5$ | 3.6 | 7 |
| $4.5-4.99$ | 4.4 | 21 |
| $5.0-5.49$ | 5.2 | 30 |
| $5.5-5.99$ | 6.7 | 44 |
| $6.0-6.49$ | 7.1 | 49 |
| $\geq 6.5$ | 6.9 | 47 |

that geographic characteristics for these regions and lake factors influenced by acid deposition in Ontario and Newfoundland both play a role in determining community structure.

## What factors influence community composition and abundance of benthos?

Benthos data were available from 198 lakes in Ontario, Quebec, Newfoundland, and Nova Scotia. Benthic invertebrates were identified to different taxonomic levels in different regions; thus, for analysis we aggregated data to the highest taxon employed to report a particular group of animals.

A general trend of fewer groups with lower pH was found when all regional data was combined ('Table 28). The same trend was seen in Newfoundland benthos. An examination of molluscs, oligochaetes, and Gammarus lacustris, taxa known to be acid sensitive (Raddum 1980; Braekke 1976; Wright et al. 1977; Singer 1982) yielded conflicting results due to small sample sizes and limited geographic distributions. A general trend of fewer numbers of molluscs with low pH in Quebec was noted. The mean density declined by $91 \%$ below pH 5.5.

Significant regressions between ash-free dry weight and pH , and between number of taxa and alkalinity, were found for benthos from Newfoundland only (Table 24). The lack of significant regressions in the other regions, and the low significant $r^{2}$ values, suggest that plankton communities may show a greater sensitivity to acidification than do benthic communities.

Cluster and discriminant analyses (methods as described for phytoplankton) explained over $80 \%$ of the variance among lakes in Ontario, Quebec, Newfoundland, and Nova Scotia (Table 26). No single or set of variables consistently dominated one or more discriminant function regionally or overall. Latitude, longitude, lake area, elevation, and maximum depth appear as significant in one or more regions. Calcium, Mg , and Mn were important in Quebec. Alkalinity, color, Na , and Fe appear to be significant for Nova Scotia benthos. Chloride, $\mathrm{Al}, \mathrm{Cu}$, and Zn are significant in one or more functions for Ontario benthos. Newfoundland benthic communities were influenced by alkalinity, conductivity, Ca , and Al .

## Rivers

River water chemistry was available from 91 major rivers from Nova Scotia, Newfoundland, and Quebec. Most of these rivers are or were, significant salmon producers (Watt et al. 1983; Brouard et al. 1983; Scruton 1984). Significant declines in some populations and the unknown impacts of acidic precipitation on river chemistry and fisheries in general resulted in regional surveys.

In addition to the analytical safeguards discussed earlier, a further check on the water chemistry determinations was made by a comparison of the sum of anions and the sum of cations before and after marine salt corrections (Table 29). The linear correlation between anion $\left(\mathrm{SO}_{4}^{2-}, \mathrm{Cl}^{-}, \mathrm{HCO}_{3}^{-}\right)$and cation ( $\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{H}^{+}$) concentrations for each region were significant before and after sea salt corrections except in Quebec (Table 29). Although there were 231 ( $31.3 \%$ of the total sampled) samples that had an ion balance with a deviation of greater than $15 \%$ before correction, the overall high $r^{2}$ values suggest no major analytical errors.

Table 29. Summary of charge balance for river chemistry before and after sea salt corrections.

|  | Nova Scotia | Newfoundland | Quebec |
| :--- | :---: | :---: | :---: |
| $r^{2}$ before correction | 0.87 | 0.83 | 0.89 |
| $r^{2}$ after correction | 0.71 | 0.57 | $0.02^{\mathrm{a}}$ |
| $\%$ samples with deviation | 17.7 | 25.0 | 57.5 |
| $15 \%$ before correction |  |  |  |

${ }^{\text {a }}$ Low $r^{2}$ value is a result of anomalies in Mistassini River chloride concentrations.

Table 30. Regressions of pH versus log discharge for five Nova Scotia rivers.

| River | $n$ | Slope | Intercept | $r^{2}$ | $P($ slope $=0)$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Liscomb | 25 | -0.248 | 5.23 | $0.486^{a}$ | 0.0001 |
| Medway | 29 | -0.342 | 5.91 | $0.370^{a}$ | 0.0005 |
| LaHave | 26 | -0.379 | 6.38 | $0.475^{a}$ | 0.0001 |
| Tusket | 19 | -0.249 | 5.11 | 0.186 | 0.0655 |
| Seaway 1 | 17 | -0.201 | 4.71 | 0.135 | 0.1471 |

aSignificant $\mathrm{P}<.05$.

Table 31. $\mathrm{pH}, \mathrm{SO}_{4}^{2-}$, and cation concentrations in rivers.

| Region | Number of rivers | Month of peak discharge | Chemistry during month of peak discharge mean (range) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | pH | $\mathrm{SO}_{4}^{2-}$ | Cations |
| Nova Scotia | 24 | April | $\begin{gathered} 4.9 \\ (4.4-6.6) \end{gathered}$ | $\begin{gathered} 68.32 \\ (55.19-186.52) \end{gathered}$ | $\begin{gathered} 91.02 \\ (60.93-318.43) \end{gathered}$ |
| Quebec | 23 | May | $\begin{gathered} 5.5 \\ (5.0-6.6) \end{gathered}$ | $\begin{gathered} 52.87 \\ (37.18-66.09) \end{gathered}$ | $\begin{gathered} 118.21 \\ (59.55-205.79) \end{gathered}$ |
| Newfoundland | 44 | May | $\begin{gathered} 6.2 \\ (5.4-7.7) \end{gathered}$ | $\begin{gathered} 39.43 \\ (7.3-118.10) \\ \hline \end{gathered}$ | $\begin{gathered} 126.09 \\ (33.76-571.01) \\ \hline \end{gathered}$ |

## Does discharge influence pH of rivers?

It has been shown that a good relationship exists between the concentration of various chemicals and river discharge in some systems (Johnson et al. 1969; Watt et al. 1983). Chemicals which are normally derived from precipitation, such as hydrogen ion in acidic precipitation, tend to be positively correlated to discharge. Higher discharge rates imply a greater direct contribution of precipitation to total runoff relative to groundwater sources. Thus the runoff is less "diluted" by goundwater, which presumably has a higher pH . Also, high precipitation rates normally result in lower average contact time between the runoff and soils in the watershed, thereby reducing the opportunity for cation exchange, consequently, the removal of acidity from the runoff.

This hypothesis was tested for five Nova Scotia rivers; significant regressions between pH and log discharge were found for three rivers (Table 30).

Considerable variation was also found in the distribution of $\mathrm{pH}, \mathrm{SO}_{4}^{2-}$, and cation concentrations among regions during peak discharge times of the year (Fig. 11). Nova Scotia rivers had the lowest pH and cation concentrations and the highest sulphate concentrations when compared with other regional data (Table 31). Quebec rivers had lower pH and cation concentrations than in Newfoundland.

## Estimating the Resource at Risk

The water chemistry conditions reported here do not appear to be any different from the conditions found in each region by Kelso and Minns (1982) who treated data collected historically. In our data set, the key indicators of lake status - pH and alkalinity - are not significantly correlated with lake size and so the sampled conditions were assumed to be representative of the total resource.

By combining the sample data and whole watershed data on the numbers and area of lakes, the extent of the resources at risk in eastern Canada can be estimated. As was done in the U.S. Canada Memorandum of Intent on Transboundary Air Pollution (1983), we have assumed on the basis of deposition that the area at risk is east of the Ontario-Manitoba border and south of latitude $52^{\circ}$. Most of that area receives greater than 20 kg $\mathrm{SO}_{4}^{2-} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ (Barrie and Hales 1984).

By assuming that freshwaters are distributed in proportion to the land masses above and below latitude $52^{\circ}$, we estimated that the area of freshwater resources receiving elevated deposition is $161980 \mathrm{~km}^{2}$ (Table 32), of which $56 \%$ is in Quebec. Assuming the whole watersheds we examined are representative for each region, we estimate that there are more than 700000 lakes in eastern Canada receiving deposition above background.


Table 32. Freshwater resources in eastern Canada.


Table 33. Freshwater resources in eastern Canada by alkalinity class and province, $\mathrm{km}^{2}$.

| Alkalinity class $\mu \mathrm{eq} \cdot \mathrm{L}^{-1}$ | Ontario | Quebec | Newfoundland/ Labrador | N.B. | N.S. | Total |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| -100 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| - -50 | 0.0 | 0.0 | 0.0 | 0.0 | 103.6 | 103.6 |
| - 0 | 2946.0 | 0.0 | 0.0 | 78.0 | 1115.2 | 4139.2 |
| 50 | 15296.3 | 47009.9 | 5924.1 | 565.0 | 1258.6 | 70054.0 |
| 100 | 10084.2 | 18352.0 | 3355.5 | 429.2 | 103.6 | 32324.4 |
| 150 | 10764.1 | 5785.8 | 601.2 | 96.9 | 0.0 | 17247.9 |
| 200 | 5835.2 | 5424.2 | 317.0 | 117.0 | 0.0 | 11693.5 |
| 300 | 2606.0 | 4701.0 | 185.8 | 18.8 | 34.5 | 7546.2 |
| 400 | 3909.1 | 1446.5 | 87.4 | 0.0 | 34.5 | 5477.5 |
| 400 | 5212.1 | 7593.9 | 459.1 | 39.0 | 0.0 | 13304.1 |

Table 34. Summary of lake sensitivity indices for surveyed lakes and extension to all lakes south of latitude $52^{\circ}$ in eastern Canada.

| Province | Sensitivity index |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CSI}>3$ |  | [Alk] $<50 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}$ |  | $\mathrm{pH}<6$ |  | "Acidified"a |  |
|  | \% ${ }^{\text {b }}$ | No ${ }^{\text {c }}$ | \% | No. | \% | No. | \% | No. |
| Ontario | 61.8 | 78040 | 32.2 | 40662 | 22.9 | 28918 | 1.6 | 2020 |
| Quebec | 72.6 | 320712 | 52.0 | 229711 | 16.3 | 72006 | 1.4 | 6185 |
| Newfoundland/ |  |  |  |  |  |  |  |  |
| Labrador | 89.9 | 124701 | 54.2 | 75181 | 29.9 | 41475 | 1.8 | 2497 |
| New Brunswick | 71.7 | 2578 | 47.8 | 1718 | 35.3 | 1269 | 15.4 | 554 |
| Nova Scotia | 95.0 | 6256 | 93.3 | 6144 | 73.7 | 4853 | 47.3 | 3115 |
| Total |  | 532287 |  | 353417 |  | 148521 |  | 14371 |

${ }^{2}$ after Henriksen (1980).
bercentage of survey sample.
cAfter Table 31.

When the survey alkalinity data from each province were sorted into classes and combined with the whole watershed data, we found that $4243 \mathrm{~km}^{2}$ (Table 33) of the freshwaters in eastern Canada currently have an alkalinity of zero or less (equivalent to a pH of approximately 5.3 or less). More than two-thirds of this area is in Ontario.

By classifying the survey data according to identified criteria - alkalinity $<50 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}, \mathrm{pH}<6$ or acidified $\mathrm{pH}<4.7$ (Henriksen 1980), we can estimate the number of lakes falling in any of these categories. More than 350000 lakes are estimated to have an alkalinity $<50 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}$ (Table 34). There are nearly 150000 lakes with a $\mathrm{pH}<6$, a condition that we have shown is a threshold for lower species diversity. Finally, we estimate that there are more than 14000 acidified lakes.

These numbers, albeit estimated from a small sample of 814 lakes out of 716922 , do serve to indicate the magnitude of the freshwater resource at risk in eastern Canada.

## Executive Summary

Canadian freshwaters east of the Ontario-Manitoba border and south of latitude $52^{\circ}$ are assumed to be at risk from acidic deposition. Most of the area south of $52^{\circ}$, containing $161890 \mathrm{~km}^{2}$ of freshwater ( $56 \%$ of which is in Quebec) receives $>20 \mathrm{~kg} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ of $\mathrm{SO}_{4}^{2-}$. Overall, we estimate there are more than 700000 lakes in eastern Canada receiving deposition considerably above background, and that $4243 \mathrm{~km}^{2}$ of freshwater in eastern Canada is currently acidic. More than two-thirds of this lake surface area is in Ontario.

Fresh waters and fishery resources of Nova Scotia are by far the most sensitive to the effects of the long range transport of atmospheric pollutants (LRTAP): of more than $1200 \mathrm{~km}^{2}$ of acidic lakes in Nova Scotia, $104 \mathrm{~km}^{2}$ have an alkalinity $<-50 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}$ (Table 33).

Overall, the estimated numbers of lakes, based on a range of indices (Table 34), illustrate the magnitude of the resources at risk or already affected. Nearly 150000 lakes have a pH less than 6 and more than 14000 are classified by Henriksen's (1980) criterion as acidified. More than 350000 lakes have alkalinities $<50 \mu \mathrm{eq} \cdot \mathrm{L}^{-1}$.

Throughout eastern Canada, the trend of fewer species of fish, phytoplankton, zooplankton, and benthos below pH 6 persists. This biological response necessitates broadening the area of concern to include systems with pH levels up to and including pH 6. It is also apparent that not only are there fewer species in lower pH lakes, but also that the abundance of fish decreases with decreasing pH in most regions. This empirical relation suggests that not only are lakes with low pH supporting a community with diminished species richness but also that production of fish may be lower in acid systems. It also became evident that the physical limits of the aquatic habitat exert a strong influence upon community diversity of all the biotic components we examined; this intrinsic effect from the habitat is further influenced by pH and alkalinity.

In the biological community, the least response is seen in the benthos. However, this is expected as members of the benthic community tend to receive the benefits of buffering from their substrate.

There is limited evidence in the literature that metal body burdens increase in fish with decreasing pH and alkalinity. The best relation between metal concentrations ( $\mathrm{Al}, \mathrm{Mn}, \mathrm{Fe}$ ) and lake $\mathrm{pH} /$ alkalinity was found in Nova Scotia and New Brunswick. All regions had high levels of one or more metals in fish that were similar to levels reported from areas of known contamination. All provinces had some fish with Hg burdens in excess of human health guidelines, even though their lakes were remote and pristine. In all provinces except New Brunswick, $27-47 \%$ of lakes had fish exceeding the public health guidelines for Hg .

The range in Al levels (provincial mean values range from $43-119 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ ) of lakes in eastern Canada are midway between the nonacidified and acidified lakes in Scandinavia. Overall, Al is statistically related to lake pH but there are regional differences in availability of the metal with Nova Scotia having generally higher values. Manganese was related to pH in New Brunswick which, along with Nova Scotia, had the highest mean concentrations in eastern Canada. Copper and Ni were also statistically related to lake pH in Ontario and Quebec where levels spanned the greatest range. In fact some Cu concentrations exceed levels known to cause behavioral and growth effects. Because trace metals are implicated in the effects observed during lake acidification, those regions of Canada with greater availability of metals conceivably can suffer a greater impact from atmospheric deposition.

Differences among lakes of eastern Canada are largely attributable to variations in their major ion status particularly alkalinity, Ca , and Mg . Further the data suggest that regional differences (probably imposed by geological differences) may be masking variations in chemical conditions known to be influenced by atmospheric deposition.

It is clear that a considerable portion of the eastern Canadian freshwater resource is at risk and that a significant portion of freshwaters are underproductive from a fisheries point of view. Both the history and future of the resources are, however, poorly understood.

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## Appendix $A$

## Laboratories Involved in the Analysis of Fish and Water Samples

| Ontario: |  |  |
| :---: | :---: | :---: |
|  | Fish | — Great Lakes Fisheries Research Branch, D.E.O., Sault Ste. Marie. <br> - National Water Quality Lab., Environment Canada, Burlington. |
|  | Water | - Great Lakes Fisheries Research Branch, D.F.O., Sault Ste. Marie. <br> - Great Lakes Forestry Research Centre, Environment Canada, Sault Ste. Marie. <br> - National Water Quality Lab., Environment Canada, Burlington. |
| Quebec: |  |  |
|  | Fish | - Capitaine Bernier Lab., D.F.O., Longueuil. |
|  | Water | - Institut national de la recherche scientifique, Université du Québec. <br> - Le Groupe Dryade, Conseillers en environnement. |
| Labrador: |  |  |
|  | Fish | - Barringer Magenta Ltd., Toronto. |
|  | Water | -Environmental Chemistry Lab., Victoria General Hospital, Halifax N.S. <br> - Dobrocky Seatech Ltd., St. John's, Nfld. |
| Newfoundland |  |  |
|  | Fish | - Dobrocky Seatech Ltd., B.C. |
|  | Water | - Environmental Chemistry Lab., Halifax. <br> — Dobrocky Seatech Ltd., St. John's, Nfld. |
| Nova Scotia and New Brunswick: |  |  |
|  | Water | - Washburn and Gillis Assoc. Ltd., Fredericton, N.1B. <br> - K.F. Laboratories, Fredericton, N.B. |

## Appendix B

## Calculation of $\mathbf{p H}$ from Alkalinity and DOC

We used a table of tiration curves (Table B1) to compute the steady state pH values from each lake's predicted alkalinities and dissolved organic carbon (DOC), assuming saturation of atmospheric $\mathrm{CO}_{2}$. These titration curves were computed by iteratively solving the equation (U.S. Fish and Wildlife Service A82):

Alk. $=\left[\mathrm{HCO}_{3}^{-}\right]+2\left[\mathrm{CO}_{3}=\right]+\left[\mathrm{OH}^{-}\right]+\left[\mathrm{RCOO}^{-}\right]-\left[\mathrm{H}^{+}\right]$
where:
Alk. $=$ total alkalinity ( $\mathrm{eq} \cdot \mathrm{L}^{-1}$, as are all concentrations)

$$
\begin{aligned}
& {\left[\mathrm{HCO}_{3}^{-}\right] }=\frac{K_{H} K_{1}-\mathrm{PCO}_{2}}{\left[\mathrm{H}^{+}\right]} \\
&=10^{-1.5} \\
& K_{H}=10^{-6.3} \\
& K_{1}=3.5 \\
& \mathrm{PCO}_{2}=\frac{K_{2}\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}^{+}\right]} \\
& {\left[\mathrm{CO}_{3}=\right] } \\
&=10^{-10.3} \\
& K_{2}=\frac{K_{W}}{\left[\mathrm{H}^{+}\right]} \\
& {\left[\mathrm{OH}^{-}\right] }=10^{-14} \\
& K_{W}=\frac{K_{A}\left[D_{t}\right]}{\left(\left[\mathrm{H}^{+}\right]+K_{A}\right)} \\
& {\left[\mathrm{RCOO}^{-}\right] } \text {concentration of organic base } \\
&=10^{-4.41} \\
& K_{A}=\mathrm{DOC} \text { in acid/base equivalents; and } \\
& {\left[D_{t}\right] }=\left(2.62 \times 10^{-6}\right) \times \text { DOC }\left(\mathrm{mg} \cdot \mathrm{~L}^{-1}\right)+\left(7.63 \times 10^{-6}\right)
\end{aligned}
$$

(a regression equation from Driscoll, C. T., in Andrews et al. 1980).
Both Newton's method and the Regula Falsi method were used to iteratively solve the equation.
Different investigators have made different assumptions concerning the solubility of carbon dioxide in water $\left(\mathrm{PCO}_{2}\right)$. We therefore computed titration curves consistent with aqueous $\mathrm{CO}_{2}$ concentrations of $1.0,2.25$, or 10 times atmospheric $\mathrm{CO}_{2}$.

Table B1. Assumed relationship between pH , alkalinity, and DOC with aqueous and atmospheric $\mathrm{CO}_{2}$ in equilibrium. Similar tables are available for alternative $\mathrm{CO}_{2}$ assumptions.

|  | DOC ( $\mathrm{mg} \cdot \mathrm{L}^{-3}$ ) |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | 0 | 2 | 4 | 6 |
|  | 8 | 10 | 12 | 14 |
| Alkalinity$\left(\mu \mathrm{eq} \cdot \mathrm{~L}^{-1}\right)$ |  |  |  |  |
| 400 | 7.889 | 7.883 | 7.877 | 7.871 |
|  | 7.865 | 7.859 | 7.853 | 7.847 |
| 340 | 7.817 | 7.811 | 7.804 | 7.797 |
|  | 7.789 | 7.782 | 7.775 | 7.767 |
| 280 | 7.731 | 7.723 | 7.715 | 7.706 |
|  | 7.697 | 7.688 | 7.679 | 7.669 |
| 220 | 7.624 | 7.613 | 7.602 | 7.591 |
|  | 7.579 | 7.567 | 7.555 | 7.542 |
| 160 | 7.48 | 7.466 | 7.45 | 7.434 |
|  | 7.417 | 7.399 | 7.381 | 7.362 |
| 100 | 7.264 | 7.24 | 7.213 | 7.185 |
|  | 7.155 | 7.122 | 7.087 | 7.049 |
| 90 | 7.215 | 7.186 | 7.156 | 7.123 |
|  | 7.088 | 7.05 | 7.007 | 6.961 |
| 80 | 7.159 | 7.126 | 7.091 | 7.053 |
|  | 7.011 | 6.965 | 6.914 | 6.855 |
| 70 | 7.094 | 7.057 | 7.015 | 6.969 |
|  | 6.918 | 6.88 | 6.794 | 6.715 |
| 60 | 7.019 | 6.973 | 6.923 | 6.866 |
|  | 6.8 | 6.722 | 6.629 | 6.512 |
| 50 | 6.927 | 6.871 | 6.806 | 6.729 |
|  | 6.637 | 6.522 | 6.369 | 6.154 |
| 40 | 6.811 | 6.736 | 6.645 | 6.532 |
|  | 6.382 | 6.168 | 5.859 | 5.536 |
| 30 | 6.652 | 6.542 | 6.394 | 6.183 |
|  | 5.866 | 5.519 | 5.276 | 5.116 |
| 20 | 6.407 | 6.198 | 5.874 | 5.499 |
|  | 5.24 | 5.075 | 4.961 | 4.875 |
| 10 | 5.896 | 5.475 | 5.198 | 5.029 |
|  | 4.915 | 4.829 | 4.762 | 4.706 |
| $-20$ | 4.605 | 4.558 | 4.518 | 4.484 |
|  | 4.454 | 4.427 | 4.403 | 4.381 |
| -40 | 4.359 | 4.337 | 4.317 | 4.299 |
|  | 4.281 | 4.266 | 4.251 | 4.237 |
| $-60$ | 4.201 | 4.188 | 4.175 | 4.164 |
|  | 4.153 | 4.143 | 4.133 | 4.124 |
| -80 | 4.083 | 4.075 | 4.067 | 4.059 |
|  | 4.051 | 4.044 | 4.037 | 4.031 |
| -100 | 3.99 | 3.984 | 3.979 | 3.973 |
|  | 3.968 | 3.962 | 3.957 | 3.952 |



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[^0]:    ${ }^{\text {a }}$ Data only from the 1981 survey.
    ${ }^{\mathrm{b}}$ Species occurring most frequently in a region.

[^1]:    a - lake area, 2 - maximum depth, 3 - elevation, 4 - Secchi depth, 5 - pH, 6 - alkalinity, 7 - conductivity, 8 - color: ${ }^{1}$ 'After Titus et al. (1984).
    ${ }^{\text {c** }} P=0.001$ significance ${ }^{*} P=0.01$.
    ${ }^{4} 0$ - for discriminant analysis, X - major variable in discriminant function.
    ${ }^{4} \mathrm{~L}$ - landlocked, A - anadromous
    nf - no discriminant function.

