A Survey of Selected Lakes in Labrador, with an Assessment of Lake Status and Sensitivity in Relation to Acid Precipitation

D.A. Scruton

Fisheries Research Branch
Department of Fisheries and Oceans
P.O. Box 5667
St. John's, Newfoundland A1C 5X1

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A SURVEY OF SELECTED LAKES IN LABRADOR, WITH AN ASSESSMENT OF LAKE STATUS AND SENSITIVITY IN RELATION TO ACID PRECIPITATION

by

D. A. Scruton

Fisheries Research Branch Department of Fisheries and Oceans P.O. Box 5667 St. John's, Newfoundland AlC 5X1

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CONTENTS	Page
Abstract/Resumé	iv/v
Introduction	1 1 2 4
Materials and Methods Selection of Lakes for Study Lake Morphometry Water Sample Collection Field Analysis of Water Samples Laboratory Analysis of Water Samples Plankton Sample Collection Fish Collection and Sample Analysis Fish Tissue Analyses	4 4 5 5 6 6 7 7 8
Results and Discussion  General Lake Characteristics Lake Water Chemistry  Lithological Determinants  Ions of Marine Origin  Anthropogenic Inputs  Lake pH  Alkalinity  Conductivity  Lake Status  Ratio of Bicarbonate to Sulphate  Cation - Alkalinity Relationships  pH - Calcium Relationship  Henriksen's Nomograph  Aluminum in Lake Water  Fish Resources  Contaminant Body Burden of Fish	9 9 12 12 14 15 17 18 20 21 22 23 24 26 28 34
Conclusions	36
Acknowledgements	37
References	37
Appendix 1: Matrix of Correlation Coefficients (Log vs Log Regression) of 45 Parameters Measured in Headwater Lakes Survey	98

### **ABSTRACT**

Scruton, D. A. 1984. A survey of selected lakes in Labrador, with an assessment of lake status and sensitivity in relation to acid precipitation. Can. Tech. Rep. Fish. Aquat. Sci. 1296: v + 115 p.

One hundred and thirty (130) lakes in Labrador, ranging in size from 5.0 to 1217.5 ha, were surveyed from August 16 to October 20, 1982 as part of the Department of Fisheries and Oceans' National Inventory Survey (NIS). Ninety-five (95) lakes were sampled for morphometry, water chemistry, zoo- and nanno-plankton, and fish. Thirty-five (35) lakes were surveyed for water chemistry only. Chemistry was variable between lakes with lithology being the major controlling feature. Input of marine aerosols, input of organic matter from the watershed, and atmosphere deposition of anthropogenic pollutants were minor features. Lake pH ranged from 4.80 to 7.84 (mean of 6.40) with three lakes of pH less than 5.50. Ninety-seven lakes had alkalinities of less than 200  $\mu$ eq L<sup>-1</sup> indicating moderate to high sensitivity to potential acidification. Excess sulphate values varied from 3.7 to 90.2  $\mu$ eq L<sup>-1</sup> (mean of 27.2). Total aluminum in lake water ranged from 10 to 394  $\mu$ g L<sup>-1</sup> (mean of 71). Use of models developed by Henriksen and others did not indicate strong evidence of anthropogenic acidification in Labrador lakes, despite the high sensitivity of study systems. Ten fish species were netted from study lakes including brook trout, lake trout, arctic char, Atlantic salmon, lake whitefish, round whitefish, northern pike, white sucker, longnose sucker, and burbot. Aluminum and mercury levels were determined in tissue from 1191 fish. Long lived and/or piscivorous fish demonstrated the highest levels of mercury while there was strong evidence of bioaccumulation of mercury in several species.

## RÉSUMÉ

Scruton, D. A. 1984. A survey of selected lakes in Labrador, with an assessment of lake status and sensitivity in relation to acid precipitation. Can. Tech. Rep. Fish. Aquat. Sci. 1296: v + 115 p.

Du 16 août au 20 octobre 1982, dans le cadre du Levé national d'inventaire (LNI) du ministère des Pêches et des Océans, on a étudié 130 lacs du Labrador dont la superficie variait de 5,0 à 1 217,5 ha. La morphométrie, la chimie de l'eau, le nanoplancton, le zooplancton et les poissons ont été étudiés dans 95 lacs tandis que seulement la chimie de l'eau a été examinée dans les 35 autres. Les caractères chimiques variaient entre les lacs, mais la lithologie était le principal facteur déterminant. L'apport d'aérosols marins, l'arrivée de substances organiques provenant du bassin versant et le dépôt atmosphérique de matières polluantes anthropogènes représentaient des facteurs mineurs. Les valeurs du pH lacustre variaient de 4,8 à 7,84 (moyenne: 6,4) et, dans trois lacs, le pH était inférieur à 5,5. Dans 97 lacs, l'alcalinité était inférieure à 200  $\mu$ eq L $^{-1}$ , ce qui porte à croire à une sensibilité à l'acidification potentielle allant de modérée à élevée. Les valeurs du sulfate excédentaire variaient de 3,7 à 90,2  $\mu$ eq L<sup>-1</sup> (moyenne: 27,2) tandis que l'aluminium total allait de 10 à 394  $\mu$ g L<sup>-1</sup> (moyenne: 71). L'utilisation de modèles mis au point par Henricksen et d'autres n'a pas donné de preuves solides d'acidification anthropogène dans les lacs du Labrador, malgré la sensibilité élevée des systèmes étudiés. Dix espèces de poisson ont été capturés dans les lacs expérimentaux, soit l'omble de fontaine, le touladi, l'omble chevalier, le saumon de l'Atlantique, le grand corégone, le ménomini rond, le grand brochet, le meunier noir, le meunier rouge et la lotte. Les taux d'aluminium et de mercure ont été quantifiés dans les tissus de 1 191 poissons. Les poissons piscivores ou longévifs possédaient les plus hauts taux de mercure et plusieurs espèces donnaient des signes probants d'une bioaccumulation de mercure.



#### INTRODUCTION

### BACKGROUND INFORMATION

Labrador constitutes the mainland portion of the Province of Newfoundland and Labrador and has a total land area of approximately 288,000 km $^2$ . Most of the region lies north of 52° N latitude and south of 60° N latitude. The eastern boundary is 55°30' W longitude and 67°30' W longitude on the western margin. Labrador's underlying structure is a tilted plateau elevated in the southwest and sloping to the coastal lowlands in the southeast. The plateau attains a maximum elevation of 750 m in the southeast near the Quebec-Labrador border, descending to about 300 m in the east. North of Nain, the Kaumajet, Kiglapait and Torngat Mountains rise from the coastal margins to elevations exceeding 1500 m. Two other distinct upland areas include the Benedict and Mealy Mountains, northeast and south of Lake Melville, respectively. The Lakes Plateau, an extensive area in the interior of Labrador, generally has an elevation of 400 to 600 m.

Labrador has an abundance of water mostly in the form of lakes, streams, rivers, and bogs, the basins of which drain into the Labrador Strait in the Atlantic Ocean or through Quebec into the Gulf of St. Lawrence. In western and southern Labrador large complexes of sphagnum bog and open water occur. These drain into lake systems which form the headwaters of the Churchill River and other major river systems, including the Eagle River. It has been estimated there are 12,000 km² of bog in Labrador south of  $56^{\circ}30N$  latitude (Shawinigan 1968). Hare (1950) has measured an area of 15,200 km² near Menihek Lake and calculated the surface water area to be 18% of the total land area. Additionally, hydroelectric development at Churchill Falls has resulted in creation of massive hydroelectric reservoirs of some  $6650 \text{ km}^2$ .

The geologic character of the region is similar to much of Northern Ontario and Quebec in that the easternmost portion of the Canadian Shield, a massive core of Precambrain rocks, dominates all of Labrador (Sutton 1972). Rock types are largely igneous and metamorphic overlain by irregular patches of sedimentary and volcanic rocks (Fig. 1). Igneous rocks are dominated by granites and related rocks which are widely distributed and anorthosites and related rocks (gabbros, peirodites, etc.) which are more coherent but less widely distributed (Sutton 1972). The overlying sedimentary and volcanic rocks tend to have a patchy distribution. Major sedimentary domains include the Labrador Trough and a large area near Seal Lake, dominated by sandstones, shales and basalts of marine origin. Small patches of limestones occur in the extreme south of Labrador (McKillop 1982).

The surface morphology of Labrador can be attributed to uplifting, warping and faulting during the Pliocene epoch with subsequent modification of this uplifted surface by glaciation during the Pliestocene. Pleistocene glaciation has produced two broad geomorphological domains in Labrador. These domains include firstly the source areas, which are found in the highlands and to the north and are characterised by marked topographic relief and bare rocky slopes with little loose surface material. Secondly, the sink areas, which include the lowlands of Central and Southern Labrador, are generally topographically subdued areas with isolated hills of more resistant rock protruding through the

glacial deposits. The retreating ice sheet deposited ground moraine unevenly resulting in the formation of many shallow lakes and bogs between ridges of glacial till (McKillop 1982). A regular but immature drainage pattern has established itself on the post-glacial surface, although in many lowland areas a coherent drainage pattern is undiscernable.

Much of Labrador is primarily a rockland with very limited soil development. Organic soils are common in lowlands and poorly drained marine deposits. Hills, mountains, and other topographical high points tend to have minimal to no soil cover. The Lakes Plateau region is particularly characterized by poorly drained acid soils. The vegetation of the region lies within the Boreal Forest and Tundra classifications of Rowe (1977). The Tundra region (Northern Labrador, Harp Lake Plateau, Mealy Mountains) is dominated by lichen mosses and low-lying shrub species, while the Boreal Forest Region is characterized by limited tree growth dominated by white spruce, black spruce, and balsam fir. Sphagnum bog development is extensive in many areas of Labrador with poorly developed drainage patterns (Lopouknine et al. 1975).

The climate of the region is dominated by geographical location (latitude), altitude (topography) and coastal influences. Labrador lies in an area exposed to prevailing westerly winds originating over Hudson Bay with some seasonal alteration of flows. Westerly flows dominate western and southern Labrador while northerly flows are very common in north coastal Labrador. Winters are long and harsh with snow prevalent from November to June in many areas. As a result most of Labrador has a mean annual temperature of less than 0°C (MacPherson and MacPherson 1981).

Mean annual precipitation ranges from 500 mm in the north to 1200 mm in southeastern Labrador (Fig. 2). Precipitation is greatest over the southern upland areas and there is a general north to south gradient in precipitation. Much of the precipitation falls as snow with a range of 500 cm of snow in the southeast to 200 cm in the far north. Snow cover lasts from 180 days in the Strait of Belle Isle area to over 240 days in far northern Labrador (MacPherson and MacPherson 1981).

Generally, lakes in Labrador are completely frozen over by November 1 and rivers some two weeks later. Rivers become ice-free by July 1 while lakes usually lose their ice cover several weeks later. Consequently, the ice free period of Labrador freshwaters is extremely short, between four and five months. Duthie and Ostrofsky (1974) found that lakes in western Labrador were ice free from late July to late October, with larger lakes freezing up some three to four weeks later.

### A LABRADOR PERSPECTIVE ON ACID DEPOSITION

An evaluation of acid deposition in Labrador is difficult owing to the sparsity of precipitation monitors in northern parts of Eastern Canada. Precipitation monitoring in Labrador is confined to one CANSAP (Canadian Network for Sampling Precipitation) station located at Goose Bay, in operation since May 1977 (Fig. 3). An additional CANSAP station is located in

Nitchequon, Quebec, 250 km west of the Quebec-Labrador border, and this monitor can provide some insight into deposition levels in western Labrador.

In 1980 the mean annual (volume-weighted) precipitation pH recorded at Goose Bay was 4.92 and at Nitchequon, Quebec it was 4.97 (CANSAP Data Summary 1981). In the first two years of operation (May 1977-June 1979), the mean volume-weighted rainfall pH at Goose Bay was 4.75, ranging from 4.20 to 5.50 (MacPherson and MacPherson, 1981). Subsequent modelling efforts by the Atmospheric Environment Service of Environment Canada indicate that most of southern Labrador, south of 54° North latitude is receiving rainfall less than pH 5.00, while more northerly areas are likely receiving rainfall in excess of pH 5.00. The most northerly CANSAP station in eastern Canada, at Fort Chimo, Quebec (N58°06' latitude), recorded a rainfall pH of 5.36 in 1980.

Deposition of sulphate (kg/ha/yr), the dominant ion of concern in the acid precipitation phenomenon, is the widely accepted standard for interregional comparisons. Sulphate deposition in eastern Canada ranges from 10 to 40 kg/ha/yr and in insular Newfoundland from 10 to 20 kg/ha/yr or greater (Harvey et al. 1981). Sulphate deposition in Labrador is considered to be in the order of 10 kg/ha/yr or less (Fig. 3). Thompson and Hutton (1982) have determined the annual excess sulphate "load" for Labrador to be in the order of 20 meg/ $m^2$ /yr (9.6 kg/ha/yr).

Present deposition levels are unlikely to remain constant and the forecast is for increased levels of emissions which will translate to increased acidic deposition unless action is taken to reduce emissions at source. Forecast emissions are for a 7.6% growth in  $\mathrm{SO}_2$  emissions and a 26% growth in  $\mathrm{NO}_{\mathrm{X}}$  emissions to the year 2000 in North America (Rivers and Riegel, 1983). Labrador, however, is extremely remote from concentrations of emission sources and prevailing winds originate largely from non-industrial regions (over Hudson Bay and northern regions). There is no evidence to raise concern about significant increases in deposition in Labrador over the immediate future.

A sensitivity map of Labrador (Fig. 4) based on available geological information (as produced by The Newfoundland Department of Mines and Energy) is a first order evaluation of potential susceptibility to acidification. It is readily apparent that most of Labrador is moderately to highly sensitive to potential acidification with the only extensive area low to moderate in sensitivity restricted to the Labrador Trough. Extensive distribution of granites, gneisses and associated igneous rock types poor in carbonates characterize the moderate to highly sensitive regions. Large areas of gabbros and anorthosites are considered to be of moderate sensitivity.

Soils are assumed to be derived from the underlying bedrock but in Labrador glaciation has modified this relationship by distributing the overburden (Schilts 1981). Hills and uplands tend to be limited in soil cover while glacial deposits are concentrated in near-coastal areas and river valleys. Labrador soils tend to be thin in must areas, very stoney and high in organic content, all characteristics of acid sensitive soil types. Sphagnum bogs cover vast expanses of land area and contribute a natural organic acidity to surface waters. However, drainage systems are more well established in

Labrador than they are in insular Newfoundland and organic deposits are less abundant and not as widespread (Lopouknine et al 1975)

#### DEPARTMENTAL PROGRAM AND OBJECTIVES

The Department of Fisheries and Oceans (DFO) has undertaken a departmental program on acid precipitation whose ultimate goal is to protect freshwater and anadromous fisheries resources threatened by acid precipitation and related pollutants and to ensure the long-term maintenance of social and economic benefits associated with this resource. Initially it was important to determine the scope of the acidification phenomenon in potentially impacted regions and develop a national perspective on the problem. In 1981, DFO initiated a National Inventory Survey (or N.I.S.) to obtain a comprehensive data base for a number of lakes in sensitive terrain to evaluate the regional implications of acid deposition. This inventory program to date has been undertaken in the provinces of Ontario, Quebec, Nova Scotia, New Brunswick, and in insular Newfoundland (1981) and Labrador (1982). The program emphasizes common study elements, the utilization of common sampling techniques, and quality control to permit a regional evaluation of the acidification problem.

The primary objective of this inventory program was to establish a data base that would permit an inter- and intra-regional evaluation of the susceptability and status of lakes and resident biota in relation to acid deposition. A second objective was to contribute to an understanding of the processes governing susceptablity to provide a basis for prediction of the potential future impacts for projected levels of deposition. Thirdly, this inventory was to provide a comprehensive and well-defined data base that would lend itself to future monitoring programs. Emphasis has also been placed on determining the contaminant body burden of selected trace metals in fish as a result of atmospheric deposition or possibly as influenced (mobilized) by acidification.

### MATERIALS AND METHODS

## SELECTION OF LAKES FOR STUDY

A representative sample of study lakes was selected for survey subject to certain selection criteria. Lakes were located in remote, relatively pristine areas distant from local population centres and point sources of pollution. Lakes selected were generally small, headwater lakes at high altitude within their respective watersheds (first, second, and third order lakes with 15% representation of higher order lakes). Lake selection was somewhat different in Labrador than in the similar survey of insular Newfoundland lakes (Scruton 1983). It was recognized that the sample needed to be more representative of existing lake distributions as opposed to sampling only highly sensitive headwater lakes (K. Minns, pers. comm.). As a consequence first order lakes represented 43% of the sample in Labrador as opposed to 90% in insular Newfoundland.

A total of 130 lakes were successfully sampled from August 16 to October 20, 1982. Ninety-five (95) lakes were designated for detailed study including water chemistry, bathymetry, and sampling of biota (fish and plankton). An additional 35 lakes were sampled for water chemistry only at the completion of the study (October 18 and 19). All study lakes were located in remote areas, inaccesssable by road. Field personnel and sampling equipment were transported to study lakes by float equipped deHavilland Beaver aircraft (110 lakes) and Bell Jet Ranger 206B helicopter (20 lakes).

Lakes were generally distributed throughout Labrador south of 56° latitude (Fig. 5) with a slight bias to sample more lakes in sensitive terrain and in areas of suspected higher deposition (southern Labrador). The thirty-five lakes sampled for water chemistry only were surveyed using Goose Bay as an operations center. This is apparent in the abundance of study lakes within a 250 km radius of Goose Bay. The regional distribution of study lakes is as follows: Northern Region - 2, Central Region - 44, Eastern Region - 12, Southern Region - 43, and Western Region - 29.

Lakes were selected in seven out of nine major geological zones delineated for Labrador. Ninety-four lakes (72%) were located in geotypes highly sensitive to potential acidification (gneisses and granites), 18 lakes (14%) in the high to intermediately sensitive geotypes (volcanics, anorthosites, etc.), and 10 lakes (8%) in zones of intermediate sensitivity (conglomerates, sandstones, basic volcanics). There are no extensive areas with bedrock of low sensitivity in Labrador. Eight (8) lakes were not classified due to the occurrence of two or more geotypes representing different sensitivities within their watersheds.

## LAKE MORPHOMETRY

Initially each lake was depth sounded to identify the point of maximum depth and to permit subsequent calculation of lake volume. Lakes were sounded using a Raytheon DE-719B depth sounder with transducer mounted on the wing support of the float plane. A longitudinal sounding transect was made along the long axis of the lake, followed by one or more transects across the width. Maximum depth was read directly from the chart traces in order to establish the water quality sampling station. Lake volume was later calculated according to Welch (1948).

Surface area, watershed area, lake elevation and distance from the coast (nearest salt water) were determined for all lakes. Lake surface and watershed (drainage) area were measured on 1:50,000 topographic maps with a compensating polar planimeter. Lake elevation was estimated from topographic maps. Distance from the coast was determined on a 1:1,000,000 scale map of Labrador.

## WATER SAMPLE COLLECTION

A water quality sampling station was established in the vicinity of maximum lake depth. A vertical temperature and dissolved oxygen profile was

obtained using a Yellow Springs Instrument (YSI) model 51B oxygen meter. Temperature and oxygen readings were recorded at one-meter intervals, with an accuracy and reproducibility  $\pm$  0.7°C and  $\pm$  0.2 mgL<sup>-1</sup>, respectively. Attached to the base of the probe assembly was a 30.5 cm diameter Secchi disc. Secchi depths were determined upon lowering and retrieving the probe during the temperature/oxygen profiling.

A water sample was obtained from each lake for detailed analysis. In lakes where depths exceeded 3 m, a depth integrated water sample was obtained using a tube sampler in accordance with procedures outlined in the Ontario Ministry of Natural Resources Manual (1980). In shallow lakes (< 3 m) a surface dip was used to collect the sample. A surface dip was also used to collect the sample for aluminum analysis. The water sample was then subdivided into various prelabelled containers as required for field and laboratory analysis (see Scruton 1983).

#### FIELD ANALYSIS OF WATER SAMPLES

Water samples were routinely analyzed for pH, dissolved CO  $_2$ , dissolved oxygen, alkalinity and conductivity at the field laboratory. Alkalinity determinations were made by Gran titration within 24 hours of collection as described by the Ontario Ministry of Natural Resources (1980). Alkalinity was later calculated from the data set obtained by titration according to a modified computer routine. Samples for free carbon dioxide determination were kept cool and dark, and were analyzed within 12 hours of collection. Free CO  $_2$  was determined by potentiometric titration using method 407B as described by the American Public Health Association et al. (1975). A number of dissolved oxygen samples were analyzed to provide calibration of results obtained from the oxygen meter. Determination of dissolved oxygen content was carried out using the Winkler titration method described in Strickland and Parsons (1972). Specific conductance or conductivity was measured using a Fisher model 152 conductivity meter. Samples were measured at ambient temperature and corrected to 25°C.

## LABORATORY ANALYSIS OF WATER SAMPLES

Water samples were shipped in insulated coolers from the mobile lab by air to the selected analytical laboratory. Water samples from 130 lakes were analyzed for 16 separate parameters and several other parameters were calculated. A list of the analytical procedures used to determine all water sample parameters and the limit of detection is provided in Table 1. Analytical methods followed those outlined in Environment Canada (1979) and in the American Public Health Association et al. (1975).

Sulphate was determined by the methyl-thymol blue procedure. In highly coloured waters, a preliminary hydrogen peroxide UV oxidation step can be incorporated to reduce potential interference. The laboratory provided data for both methods.

Excess or non-marine concentrations of sulphate, calcium, magnesium, sodium and potassium were calculated using the equations of (Watt et al. 1979). The sum of anions (SO<sub>4</sub>, C1, HCO<sub>3</sub>, NO<sub>3</sub>), cations (Ca, Mg, Na, K, H), percent difference, and sum of constituents (as mgL<sup>-1</sup>) were calculated as a check on analytic quality. An EPA standard reference sample and three blind batches of lake water samples were also analyzed by participating labs to permit an interlab comparison of data.

#### PLANKTON SAMPLE COLLECTION

A zooplankton tow was carried out at each lake using a Wisconsin type plankton net with a 20.5 cm diameter opening, mesh size of 64  $\mu$ , and overall net length of 1.2 m. A vertical tow was made at the water quality station established at each lake from a depth of 1 m above the maximum depth of the sampling station. In lakes 2 m or less a horizontal tow of approximately 1 m was made. The mesh and cod-end buckets were thoroughly rinsed and samples were preserved with 25 ml buffered formalin in 500 ml glass jars.

A surface water sample was collected in a 500 ml glass jar from each lake for nannoplankton analysis. The sample was fixed immediately with Lugol's iodine solution and stored for subsequent analysis.

### FISH COLLECTION AND SAMPLE ANALYSIS

Multifilament surface and bottom gillnets, 107.1 m long and 1.8 m deep consisting of seven 15.3 m panels of mesh sizes 3.8, 5.1, 6.4, 7.6, 8.9, 10.2 and 12.7 cm (stretched measure), were set at each lake. In lakes with a small surface area (sampled by helicopter), only one gillnet was set. Each net was attached to shore (with smallest mesh inshore), set perpendicular to the lake shoreline, and the offshore end was anchored and marked with a float for retrieval. Selection of the optimum placement of the net(s) was determined during the reconnaissance pass made by the aircraft prior to landing.

Nets were recovered the following day and fishing effort normally varied from 18 to 30 h. On occasion, due to weather grounding of the aircraft, nets were left fishing in excess of two days (and on one occasion up to 5 days). Nets were routinely retrieved from the offshore end (largest mesh). Fish were removed from the net and retained for subsequent analysis.

Analysis of fish samples was performed at the field laboratory within 24 hours of collection. Each fish was identified to species according to Scott and Crossman (1973). Fork lengths were measured on a standard measuring board and wet weights were determined on an Ohaus model 710 triple-beam balance. Individuals in excess of 3000 g were weighed using an Ohaus spring scale. Sex and maturity were determined from a visual examination of the gonads. Salmonid sexual maturity was based solely on gonadal development and not on body size or coloration. Samples were taken to permit subsequent aging of specimens. Scale ageing was carried out on all fish species except lake trout (Salvelinus namaycush), Arctic char (Salvelinus alpinus) and burbot (Lota Tota), where otoliths were used to determine ages. Back-calculation of lengths at earlier

ages were determined to the nearest mm using the method described by (Nickerson et al. 1980).

Tissue samples were taken from approximately 1200 fish for mercury and aluminum analyses. From each lake a stratified sample (by length) of up to 15 specimens of the dominant species (by number) were retained. Sections of dorso-lateral musculature were removed from the type species of each lake as well as from 66 top carnivores (primarily northern pike and lake trout). These fillets, from the left side of the fish, were then placed in individual plastic bags, labelled and frozen. Individual fish specimens were cleaned, with bones, head, and tail removed, but skin left intact. Specimens were packed into insulated coolers and shipped frozen to the selected analytical laboratory.

### FISH TISSUE ANALYSES

A tissue sample from each specimen was prepared by blending a 50 g portion of tissue using Osterizer blenders (model 861-61) equipped with stainless steel blades and 237 mL plastic cups. A 1:1 dilution of the tissue was prepared by adding 50 mL of distilled, demineralized water. The resulting homogeneous paste was stored in 110 mL plastic specimen jars and subsampled for analysis. Blanks used during the analytical program were obtained by blending 50 mL distilled, demineralized water.

Mercury determination required digestion of a 4 g aliquot of the homogenate (with HNO $_3$  and H $_2$ SO $_4$ ) in a heating block until a clear solution was obtained. A KMnO $_4$  solution was then added followed by 10 mL of K $_2$ S $_2$ O $_8$ . The mixture was digested for four hours at 70°C. The digestate was then removed and made up to 50 mL with distilled, demineralized water. Up to 25 mL of this digestate was analyzed using a Spectro Products Model HG-2 mercury analyzer employing cold-vapour atomic absorption. The limit of detection for this technique is 0.00001  $\mu$ moles of total mercury per g of original wet weight of tissue.

Aluminum determination required refluxing a 10 g aliquot of the homogenate (with HNO $_3$  and HC1O $_4$ ) in a stand bath until a clear colourless digestate was obtained. This was allowed to evaporate to incipient dryness and the residue was redissolved in HNO $_3$  and made up to a final volume of 10 mL. The solution was analyzed on a Varian Model AA-5 atomic absorption spectrophotometer using a nitrous oxide-acetylene flame and a wavelength of 309.3 nm. The limit of detection is 0.015  $\mu moles$  per g of tissue.

Analytical procedures for mercury were verified using National Bureau of Standards certified reference materials (bovine liver, oyster tissue and albacore tuna). Since none of these tissue standards had certified values for aluminum, the laboratory prepared a calibration standard at the onset of the program. A pool solution of 500 mL was first checked against in-house Inductively Coupled Plasma standards, then used consistently throughout the analysis. Values were compared with concentrations presented in Gladney (1980).

Tissue samples were run in batches of approximately 65 specimens. Within each batch, five reference standards were analyzed and blanks (or replicates) followed every tenth sample measured. For replicate metal determinations, the following conditions were obtained for the mean:

- i) If a mean value for the replicate sample had previously been established, the systmatic error of the mean was less than 50% and the coefficient of variation was less than twice the previously established value; or,
- ii) If the sample had not been analyzed, the coefficient of variation (CV) could not exceed either 15%, or the limit described below, whichever was the greater:

 $CV < (X_0/X)^{0.3} \times 100$  [Equation 1]

where: CV = coefficient if variation

 $X_0$  = detection limit of element

X = mean level of element in replicate sample

### RESULTS AND DISCUSSION

### GENERAL LAKE CHARACTERISTICS

Study lakes ranged in size from 5.0 to 1217.5 ha (mean of 165.0 ha) and the distribution of lakes by surface area is presented in Fig. 6. Thirteen lakes (10%) were less than 10 ha, 45 lakes (35%) from 10 to 100 ha, 66 lakes (51%) from 100 to 500 ha, 4 lakes (3%) from 500 to 1000 ha, and 2 lakes (1%) were in excess of 1000 ha. Lake surface area was highly correlated with drainage area (r = 0.83), maximum depth (r = 0.49), lake volume (r = 0.74) and lake order (r = 0.42). These variables are expected to be interrelated in regions of similar topography (Hutchinson 1957), such as the wide ranging Labrador Plateau.

The distribution of lakes by order is as follows: first order -55 lakes (43%), second order - 33 lakes (25%), third order - 18 lakes (14%), fourth order - 11 lakes (8%), and fifth or higher order - 13 lakes (10%). Lake order was correlated with lake surface area (r = 0.42), drainage area (r = 0.51), drainage area to surface area ratio (r = 0.38) and with maximum lake depth (r = 0.34). Headwater lakes (first order) are characteristically smaller, with a small drainage area, low DA:LA ratio, and are usually shallow. These are characteristics that are acknowledged to contribute to the high sensitivity of headwater systems (Harvey et al. 1981). Lake order and elevation were not correlated owing to the uniform elevation of lakes of all orders in the upland regions of Labrador.

Lake elevations ranged from 101 to 689 m (mean of 448 m) with 4 lakes (3%) from 100 to 200 m, 8 lakes (7%) from 200 to 300 m, 25 lakes (19%) from 300 to 400 m, 46 lakes (35%) from 400 to 500 m, 43 lakes (33%) from 500 to 600 m, and 4 lakes (3%) in excess of 600 m (Fig. 7). Lake elevations generally reflect the moderate relief of Labrador south of  $56^{\circ}$ N latitude. High elevation lakes (> 500 m) were largely restricted to the Mealy and Benedict Mountains, and on the plateau region of western Labrador near the Quebec border. The abundance of lakes between 300 and 600 m (86%) reflect the extensive distribution of the Labrador Lakes Plateau and also that few lakes were located on near coastal plains or in the major river valleys.

Lake distances from the sea coast ranged from 24 to 487 km (mean of 171 km). Ninety (90) lakes (69%) were located in excess of 100 km from salt water. The distance of lakes from the coast is in sharp contrast with a comparable set of 109 lakes in insular Newfoundland, where no lakes were greater than 88 km from salt water (Scruton 1983). This serves to highlight an essential difference between the two study regions, and the resulting data sets. The marine environment is considered to have less influence on the climate and freshwater chemistry of continental Labrador than it has in insular Newfoundland (MacPherson and MacPherson 1981).

Lake watershed area to lake area ratios (WA:LA) ranged from 2.7 to 49.3 (mean of 12.9). Seventy-nine lakes (61%) had a WA:LA ratio of less than 10:1 (Fig. 8). Labrador lakes had a higher mean WA:LA ratio (12.9 vs 8.4) and a higher representation of lakes with a ratio of greater than 10:1 (39% vs 25%) than did study lakes in Newfoundland, owing to the greater representation of higher order lakes in the Labrador study. Lakes with a ratio of 5:1 or less were also more common in the Labrador sample as small lakes less than 10 ha were sampled, while that lake size was not selected for study in insular Newfoundland. The ratio is a convenient index of interaction between acidifying (depositional) and buffering agents, as lakes with low WA:LA ratios and high runoff are particularly susceptable to potential acidification (Harvey et al. 1981).

Maximum lake depths ranged from 1 to 70 m (mean of 11.4 m). Thirty-six lakes (28%) had maximum depths of less than 3 m while 52 lakes (40%) had maximum depths exceeding 10 m. Many of the smaller lakes on the plateau are shallow and occupy ice sourced basins or have been created by low ridges of glacial origin. Duthie and Ostrofsky (1974) found that 9 of 10 large lakes in western Labrador had a maximum depths of 10 m or less. Mean lake depth ranged from 1.4 to 25.1 m. Thirty-one lakes (24%) also had mean depths in excess of 10 m.

Surface water temperatures varied from 1.3°C (Lake #488, October 11) to 16.7°C (Lake #360, August 17). Duthie and Ostrofsky (1974) found that the maximum surface temperature in lakes in western Labrador were reached by mid-August and did not exceed 16 to 17°C. Lakes showed no evidence of thermal stratification, with the exception of Lake #361 (65 ha, 30.2 m maximum depth) which demonstrated a clear thermal gradient and true thermocline. Wind induced circulation and the short open-water period experienced by Labrador lakes likely inhibit lake stratification. Structural geology and glaciation have resulted in the longitudinal axis of most lakes lying in a general west to east

(or northwest to southeast) direction. The longitudinal axis of lakes is in the same direction as prevailing winds, therefore facilitating circulation. Duthie and Ostrofsky (1974) and Rawson (1959) have also demonstrated the lack of strongly developed thermal stratification in northern lakes and attributed it to continuous wind circulation, low solar energy input and the short ice-free season.

Dissolved oxygen (D.O.) ranged from 8.0 to 13.4 mg  $L^{-1}$  with no evidence of an oxygen deficiency (D.O. < 5.0 mg  $L^{-1}$ ) in any lake. There was also no evidence of an oxygen gradient with temperature or depth in the lakes. Duthie and Ostrofsky (1974) found that 10 lakes investigated in western Labrador were saturated with oxygen at all depths throughout the ice-free period and this was attributed to their low productivity and unstratified nature. In some instances they observed a slight oxygen depletion near the bottom of several lakes (72-77% saturation) in the spring immediately after eight months of ice cover.

Secchi depths ranged from 0.5 to 16.5 m (mean of 3.6 m) and in 13 lakes (14%), the disc was visible at the bottom of the lake. In the remaining lakes secchi depths also ranged from 0.5 to 16.5 m with a mean of 3.8 m. Secchi depth was negatively correlated with water color (r = -0.81), organic carbon (r = -0.81), TDS (r = -0.61) and turbidity (r = -0.58), factors that determine the absorption of light within a water column. (Regression analysis did not differentiate the 13 lakes with Secchi disc still visible on the lake bottom.) Duthie and Ostrofsky (1974) found secchi disc transparencies in 10 western Labrador lakes to be between 3.5 and 8.25 m, and the depth of the euphotic zone (as determined by Secchi visibility) was largely a function of water color. Secchi depth was also positively correlated to maximum depth (r = 0.78) and surface area (r = 0.31), illustrating the interaction between morphometric, physical, and chemical properties in determining water clarity.

Turbidity ranged from 0.3 to 5.5 JTU (mean of 0.8 JTU) and turbidity exceeded 1.0 JTU in 33 lakes (26%). Turbidity in 10 lakes in western Labrador was found to rarely exceed 6.0 JTU. except during the spring thaw when levels reached 15 JTU or more (Duthie and Ostrofsky 1974). Turbidity in aquatic ecosystems can be highly variable and high turbidities are linked to periods of high runoff in the hydrological cycle (Gower 1980). Kerekes (1978) suggested that high turbidity in small exposed ponds in insular Newfoundland is related to wind driven circulation and resuspension of particulate matter from lake sediments. Turbidity and maximum lake depth were negatively correlated (r = -0.41) suggesting a similar mechanism controlling turbidity in Labrador lakes.

Lake water color ranged from 5 to 175 TCU (mean of 33.5 TCU). Color is a good indicator of dissolved organic content in lake water (Hutchinson 1957) and was highly correlated to dissolved organic carbon (r=0.90) in Labrador lakes. Lakes were divided into three color classifications to assist in the evaluation of weak organic acids in relation to water chemistry (Fig. 9). Fifty-four (54) lakes (42%) were classified as clear water (0-15 TCU), 45 (35%) as brown water (16-50 TCU) and 31 (23%) as highly coloured (<50 TCU). Clearwater lakes were considerably more prevalent in Labrador than in insular Newfoundland (42% vs 16%) supporting the suggestion that the organic deposits may not be as widespread in Labrador as in insular Newfoundland (Lopouknine et al. 1975).

Water colour was also correlated to a number of lake morphometric parameters. Color and the WA:LA ratio were positively correlated (r=0.32) suggesting that as the proportion of drainage area increases the likelihood of organic deposits within the watershed increases. Color was inversely correlated to maximum and mean lake depth, r=-0.61 and -0.47, respectively. Kerekes (1978) reported that clearwater lakes in Gros Morne National Park in insular Newfoundland were generally the headwater, high altitude lakes, with a low relative basin size (WA:LA ratio), suggesting a relationship between drainage order and the occurrence of organic deposits. Small lakes (< 10 ha) in Labrador demonstrated a higher color (mean of 51 vs 33.5 TCU) than the remainder of the lakes and color was inversely correlated to lake surface area (r=-0.23). The relative uniformity of basin slopes for lakes on the Labrador Plateau contributes to the poor correlation between lake order, size, and water colour.

### LAKE WATER CHEMISTRY

The relative proportion of major ions in the study lakes varies considerably and reflects four principle determinants; chemical weathering of the underlying bedrock and associated overburden, input of particulate or dissolved organic matter from the watershed, atmospheric inputs of ions of marine origin, and possibly the atmospheric input of anthropogenic pollutants. The contribution of each factor is determined by the relative intensity of each and can be largely considered a dynamic interaction of acids and bases. Atmospheric inputs of seawater salts is considered to supply most of the chloride and a proportion of sodium to surface waters (Faust and Aly 1981). Carbonic acid weathering of the lithological components is considered to supply most of the calcium, magnesium, potassium, and bicarbonate ions (Hem 1970). Sulphate and nitrate in fresh water can be largely of both biological and atmospheric origin (Harvey et al. 1981).

The sum of constituents (or salinity) of the study lakes ranged from 2.2 to 42.6 mgL<sup>-1</sup> (mean of 6.1 mgL<sup>-1</sup>). This mean is low by global standards and is considerably lower than those reported for lakes in the Experimental Lakes Area on the Canadian Shield (12.5 mg L<sup>-1</sup>) and places Labrador's fresh waters among the softest in the world (Armstrong and Schindler 1971). The world average is 112 mg L<sup>-1</sup> (Livingstone 1963), almost 20 times that of Labrador freshwater lakes. Lakes underlain by acid volcanics, granites, gneisses and anorthosites had particularly low mean salinities of 2.3, 4.6, 5.3 and 5.3 mg L<sup>-1</sup>, respectively. Lakes in insular Newfoundland were also very dilute (mean salinity of 12.8 mg L<sup>-1</sup>) with marine ions contributing an average 29% of this total, on an equivalent basis (Scruton 1983).

# <u>Lithological Determinants</u>

The relationship between water chemistry and surficial geology is most apparent when examining relative ionic composition of lakes within each geological type (Fig. 10). Calcium was the dominant cation in all lakes with the order of cationic dominance, Ca > Mg > Na > K (with the exception of one lake underlain by acid volcanics with an order of Ca > Na > Mg > K). The major

cations, calcium and magnesium, were highly correlated (r = 0.82) with the Ca:Mg ratio ranging from 1.3 (lakes underlain by siltstone) to 3.2 (lakes underlain by conglomerate/sandstone). In the igneous geotypes, highly sensitive to acid precipitation, the Ca:Mg ratio was largely 2:1. Calcium and magnesium are commonly found in association and calcium is routinely the dominant ion (Faust and Aly 1981). Comparatively, lakes in insular Newfoundland, with considerable input of marine aerosols, were often sodium dominated, or alternatively sodium was the second most important cation, routinely found in greater concentration than magnesium (Scruton 1983; Kerekes 1978; Kerekes and Hartwell 1980). Most other lakes on the Canadian Shield are calcium dominated and demonstrate a similar order of cationic dominance to Labrador lakes (Armstrong and Shindler 1971; Bobée et al. 1982; Duthie and Ostrofsky 1974). Lakes in the James Bay region of Quebec demonstrated ionic dominance in the order of Ca > Na > Mg > K and in some cases sodium was dominant to calcium (Magnin 1977). This demonstrates that dilute shield lakes in close proximity to, and downwind of, a marine environment do exhibit the influence of marine deposition.

Bicarbonate was the dominant anion in lakes from all geotypes with the order of anionic dominance  $HCO_3 > SO_4^{-2} > Cl$ . A similar order of ionic dominance is reported for remote Shield lakes (Duthie and Ostrofsky 1974; Armstrong and Shindler 1971; Magnin 1977) while a recent survey of acid sensitive shield lakes in the southern reaches of Quebec demonstrated a sulphate dominance over bicarbonate (Bobée et al. 1982). Comparatively, acid-sensitive lakes in insular Newfoundland were dominated by chloride ion, again highlighting the marine influence on freshwater chemistry on the island. Bicarbonate was highly correlated with both calcium and magnesium (r = 0.89 and 0.81, respectively) as expected stoichiometrically when the primary source for these ions is from geochemical weathering. Mean bicarbonate concentrations were generally quite low and lakes with values of 200  $\mu$ eq L<sup>-1</sup> and greater were associated with the siltstone geotype only.

The spatial distribution of the dominant ions; calcium, magnesium, and alkalinity (bicarbonate) is in good agreement with the occurrence of geological types (Fig. 1). Distribution maps for calcium and magnesium (Fig. 11 and 12) demonstrate that highest values are associated with the Labrador Trough region in western Labrador (dolomites, limestone, other sedimentary rocks) and an area northeast of Seal Lake (conglomerates, basalts and stromatolytic limestones). Highest magnesium levels are found in southwestern Labrador and are associated with gabbros and diorites, both minerals high in magnesium content. Highest alkalinity values are also associated with the Labrador Trough and carbonate bearing sedimentary minerals (Fig. 13). Lowest values for all three parameters are associated with the igneous rock types, particularly gneisses, granites, shists, and anorthorsites, all low in readily available calcium or magnesium carbonates. Duthie and Ostrofsky (1974), in 10 western Labrador lakes, found that lowest values for conductivity, pH and alkalinity were associated with lakes underlain by granite, while highest values were associated with lakes underlain by gabbros and sedimentary rocks. Sedimentary rocks weather more readily than the highly resistant igneous rocks subsequently contributing a higher concentration of dissolved constituents to surface waters (Stumm and Morgan 1981).

## Ions of Marine Origin

The atmospheric entrainment and deposition of ions of marine origin, deposited as aerosols or in precipitation, can be considerable in maritime environments (Ogden 1982). The relative contribution of marine salts is determined by the distance of a water body from the sea, the pattern of prevailing winds, precipitation, and topography (Wright et al. 1975). Marine aerosols rapidly fall out as dry deposition or are readily washed out in precipitation, resulting in a sharp coastal gradient (Wright et al. 1977).

The two dominant ions associated with marine deposition are sodium and chloride. Chloride ion demonstrated good correlation with distance from the coast (r = -0.50) and the distribution map (Fig. 14) demonstrates a clear coastal gradient. Most elevated levels of chloride are evident in lakes along the eastern coast of Labrador, and lakes with levels of 5.0  $\mu$ eq L<sup>-1</sup> or greater are largely within 25 km of salt water. Studies in Nova Scotia indicate that 80% of the deposition of marine aerosols can be within 20 km of the coast (Ogden 1982). Sodium, on the other hand, does not demonstrate a clear coastal gradient (Fig. 15) and was not significantly (p > 0.05) correlated with distance from the coast, although levels in excess of 20  $\mu$ eq L<sup>-1</sup> are associated with lakes with the higher chloride values. The sodium:chloride ratio in Labrador lakes is 2.35:1 (on an equivalent basis), considerably greater than 0.86:1 ratio in salt water (Stumm and Morgan 1981). Sodium and chloride were also significantly correlated (r = 0.46, p > 0.01), but not as highly correlated as expected if both ions are predominantly of salt water origin. There is therefore strong evidence of considerable geochemical weathering and input of sodium to Labrador lakes.

Chloride ion in remote regions is considered to be entirely contributed by marine aerosols while significant amounts of sodium can also be of atmospheric origin. Other major cations including calcium, magnesium and potassium are also contributed by marine aerosols although terrestrial sources usually predominate. Sulphate can be largely deposited from the atmosphere, originating from both marine and anthropogenic sources. To extract the influence of sea salts, and to later permit an evaluation of acidification, the non-marine or "excess" concentrations of the above ions were determined. The marine contribution was calculated on the basis of the ratio of calcium, magnesium, sodium, potassium and sulphate ions to chloride in salt water. From the measured levels of chloride in each lake, the marine contribution of each ion was then determined. The marine component was subtracted from the measured ion concentration in each lake to determine "excess" or non-marine values (Watt et al. 1979).

The relative contribution of ions of marine origin to lakes in Labrador and in insular Newfoundland is presented in Table 3. In insular Newfoundland about 29% (on the average) of major ionic constituents are of marine origin while in Labrador the proportion is only 3%. In insular Newfoundland marine ions can account for 38 to 57% of the total ionic constituents in lakes underlain by the igneous geotypes resistant to geochemical weathering (Scruton 1983). Mean chloride and sodium values for Labrador lakes (9.4 and 22.1  $\mu$ eq L<sup>-1</sup>, respectively) are considerably less than those reported for insular Newfoundland lakes (87.8 and 82.3  $\mu$ eq L<sup>-1</sup>, respectively). The fact

that the prevailing westerly winds track over several hundred kilometers of northern Quebec before reaching Labrador explains the relatively minor influence the marine environment has on freshwater chemistry in Labrador.

# Anthropogenic Inputs

Four principal ions of concern in relation to atmospheric deposition of anthropogenic pollutants include hydrogen (H<sup>+</sup>), nitrate (NO $_3^{-2}$ ), ammonium (NH $_4^+$  and sulphate (SO $_4^{-2}$ ) (Harvey et al. 1981). The relationship between the input of ammonium and nitrate ions and concentrations in surface waters has been difficult to assess because of the variety of mediating biological and chemical processes in the natural environment. In addition, much of the deposition information for these ions is uncertain. Nitrogen compounds are more readily washed out of the atmosphere than are sulphates and hence are deposited closer to emission sources (Whelpdale 1979). Sulphate, however, is a conservative element in natural systems, and hydrological pathways tend to dominate biological processes. Ogden (1982) has demonstrated that continental precipitation is dominated by ammonium sulphate ((NH $_4$ ) 2SO $_4$ ) while precipitation in maritime areas tends to be sulphuric acid (H $_2$ SO $_4$ ) dominated.

To evaluate exclusively the anthropogenic input of sulphate in spatial terms, values for "excess" or non-marine concentrations were mapped (Fig. 15). The long range transport of sulphate is associated with smaller particles and gaseous forms (SO<sub>2</sub>) which settle out more slowly and are transported farther inland than is sulphate entrained from marine aerosols and therefore should not demonstrate any coastal gradient (Wright et al. 1977). There appears to be a general southwest to northeast gradient in sulphate levels in lake water which is consistent with proximity to emissions sources, meterological patterns, and precipitation gradient. Higher values, relative to surrounding areas, are also associated with the Mealy and Benedict Mountains, demonstrating an apparent relationship between elevation and atmospheric deposition of sulphate. The Water Quality Branch of Environment Canada found highest sulphate levels (greater than 50  $\mu$ eq L<sup>-1</sup>) in southern Labrador and the Benedict Mountains perhaps also in association with topography (T. Clair, pers. comm.). Bobée et al. (1982) found a southwest to northeast gradient in lake sulphate in Quebec, relating the spatial variation to a gradient in atmospheric deposition.

Unfortunately there is insufficient depositional information for northern regions in Canada, including Labrador, to permit a comparison between precipitation inputs of sulphate and concentrations in lake water. Regions that have an established and well distributed precipitation monitoring network and that tend to be geologically homologous have demonstrated good correlations between anthropogenic inputs of sulphate and levels in freshwaters (Almer et al. 1978; Gjessing et al. 1976). In addition, Thompson and Hutton (1982) have calculated atmospheric deposition of sulphate from existing lake data and have demonstrated reasonable correspondence with measured wet deposition for regions in Eastern Canada. Sulphate levels in Labrador lakes are largely 50  $\mu eq~L^{-1}$  or less with the exception of several lakes in west central Labrador (Fig. 16). It is probable that in those lakes there is sulphate of geological origin possibly from pyroxene deposits in the area as suggested on the Geological Map

of Labrador (Newfoundland Department of Mines and Energy, no date). Detailed minerology of the area would be required to confirm geological inputs to individual lakes. Sulphate anomalies in lakes in insular Newfoundland were associated with pyrite and gypsum deposits (Scruton 1983).

Values for "excess" sulphate in Labrador lakes ranged from 3.7 to 90.2  $\mu$  eq L<sup>-1</sup> with a mean of 27.2  $\mu$  eq L<sup>-1</sup> (Fig. 17). A high proportion of the lakes (94%) had values less than 50  $\mu$  eq L<sup>-1</sup>. Excess sulphate values for Labrador lakes were compared with others in eastern North America (Fig. 18). It is apparent that sulphate levels in these study lakes are considerably less than those in areas experiencing acidification damage, specifically southern and central Ontario and Quebec, where sulphate levels in freshwaters range from 100 to over 300  $\mu$  eq L<sup>-1</sup>. The range of values in Labrador is similar to other regions of Atlantic Canada, and similar to those previously reported for Labrador (8.7 to 82.9  $\mu eq$  L<sup>-1</sup>) (T. Clair, pers. comm.). Duthie and Ostrofsky (1974) reported sulphate levels in 10 lakes in western Labrador range from 54.1 to 68.7  $\mu$ eq L<sup>-1</sup>. Studies in Quebec determined that most lakes north of 50°N latitude have sulphate concentrations of 50 μeg L-1 or less (Bobée et al. 1982). Thompson and Hutton (1982) determined the sulphate loading in Labrador to be in the order of  $9.6~kg~ha^{-1}~yr^{-1}$ , the lowest of any region in eastern Canada downwind of emission sources, and similar to non-impacted regions such as the Experimental Lakes Area (5.8 kg ha<sup>-1</sup> yr<sup>-1</sup>) and Quetico (9.1 kg ha<sup>-1</sup>  $yr^{-1}$ ) in Western Ontario.

Although excess sulphate is assumed to be totally of anthropogenic origin, there are other potential sources for the ion in fresh waters, including the aforementioned geological inputs. Work on Shield Lakes in Ontario (Harvey et al. 1981) and in Sweden (Almer et al. 1974) has suggested that there may be natural background levels of sulphate of biological origin in lake water, perhaps as much as 20-60  $\mu$  eq L $^{-1}$ . If this is so then much of the sulphate in Labrador lakes could be considered of natural origin. Work in the Kejimikujik calibrated watershed in Nova Scotia has indicated that organic deposits act as sulphur reservoirs and under certain conditions, sulphur is reduced to sulphate and transported to lake waters (Kerekes et al. 1982). Input from terrestrial organics can largely be a seasonal phenomenon (Harvey et al. 1981), which further complicates the scenario.

An additional important consideration is that the automated colorimetric method for sulphate determination has been demonstrated to overestimate the ion in highly colored waters, particularly in waters with color values in excess of 50 T.C.U. (Henriksen 1980; Kerekes et al. 1982). Water samples in this study were given a UV pre-treatment to minimize colorimetric interference, but ion chromatography is now recognized as the preferred analytical method for sulphate determination in fresh waters with considerable organic input. Excess sulphate and colour were highly correlated (r = 0.61) suggesting either colourimetric interference in measurement or possibly sulphate input from terrestrial organics. Environment Canada is actively researching colorimetric interference in the automated method for sulphate determination, with the aim of minimizing interference or possibly correcting historical data in colored waters for this problem (M. Thompson, T. Clair, pers. comm.).

## Lake pH

Lake pH was determined during routine analysis in the analytical laboratory and prior to  $\rm CO_2$  measurement in the field laboratory. Field and lab measured pH were found to be highly correlated (r = 0.92) with no trend to the variability between measurements. Stumm and Morgan (1981) have reported on the instability of pH between collection and analysis, which can influence the interpretation of the results. Field measured values were taken to be most representative of ambient conditions, owing to the importance of aqueous carbon dioxide in natural systems, and were used in all subsequent evaluation of pH.

Lake pH ranged from 4.80 to 7.84 (mean of 6.40). One lake had a pH of less than 5.00, 2 lakes (2%) with pH from 5.01 to 5.50, 18 lakes (14%) from pH 5.51 to 6.00, while 106 lakes (82%) had pH values from 6.00 to 7.00 (Fig. 19). Median summer pH values for 10 lakes in western Labrador were found to vary from 6.0 to 6.5 (Duthie and Ostrofsky 1974) while an acid sensitivity survey of Labrador lakes by the Water Quality Branch of Environment Canada found pH values in 96 lakes to vary from 5.0 to 7.9 with a mean of 6.4 (T. Clair, pers. comm.). Comparatively, a similar set of study lakes in insular Newfoundland had 26% of the sample with pH less than 6.00 and 9% with pH less than 5.50 (Scruton 1983)

pH levels in Labrador lakes may be influenced by the acidity of precipitation but appear to be dominated by lithological determinants. Spatial distribution of pH values (Fig. 20) illustrates that lowest pH values (6.00 and less) are located north of Lake Melville and in south-central Labrador while highest pH values (7.00 and greater) are found in Western Labrador, particularly in association with the Labrador Trough. Extensive areas of gneisses, granites, shists, and acid volcanics are associated with the distribution of lakes with pH less than 6.00, while the highest pH values are associated with low to intermediate sensitivity geotypes (siltstones, quartzites). Agreement between bedrock geology and lake pH is relatively good, although distribution of glacial deposits appear to have obscured the relationship in some regions (the southeastern corner of Labrador for instance).

Lakes in sensitive terrain receiving high levels of acid deposition have been demonstrated to exhibit a bimodal distribution of pH (Almer et al. 1974; Schofield 1976; Wright and Gjessing 1976; Bobée et al. 1982). This bimodal distribution is consistent with titration of a bicarbonate buffering system and reflects division into two general lake types; lakes with pH greater than 6.50 with an intact buffering system and lakes with pH less than 5.50 which have experienced serious depletion of limited buffering capacity. Lakes in the intermediate range (pH 5.5 to 6.0) are in transition from adequately buffered to acidified, and as this portion of the titration curve is steep, the period of transition is short. A bimodal pH distribution is considered to reflect a sensitive area that has been impacted by atmospheric deposition of acids.

The pH of Labrador lakes did not demonstrate a bimodal distribution, and the majority of the lakes (109 or 84%) had pH values in excess of 6.00.

Atmospheric loading does not appeared to have titrated available bicarbonate buffer, despite the extreme sensitivity of most of the study lakes.

Organic acids (humics and fulvics) are contributing to the natural acidification of freshwaters but because of the complexity of the organic fraction, it has been difficult to characterize this contribution in terms of physical and chemical properties (Henriksen and Seip 1980, Bangay and Riordan 1983). Organic acids do demonstrate acidic properties and are considered to contribute significantly to acidity in highly colored, dilute waters, particularly organic compounds with low pKa's (Bangay and Riordan 1983). in Norway (Henriksen and Seip 1980) has estimated the organic acid concentration to be 5  $\mu$ eq per mg of carbon, while Schnitzer (1978) found the acid concentration of a theoretical fulvic acid to be 20 µeg per mg of carbon. Recent work in Nova Scotia has suggested that organic anions (COOH-) can be quantified from dissolved organic carbon (COOH- as  $\mu$ eg L-1 = 10±1 DOC as mg  $L^{-1}$ ) (Oliver et al. 1983) and that organic anions should be included in the ion balance (J. Kerekes, pers. comm.). More research is required to test the validity of these considerations. This variability suggests that component organics differs between regions, therefore influencing the relative acidity of the organic fraction. Organic anions can also assume a role as a weak buffer in the pH range less than 5.00, (at a maximum of pH 4.5) in bicarbonate-poor systems.

In organic-rich dilute waters as in Labrador and insular Newfoundland, weak acids contribute hydrogen (H<sup>+</sup>) ions to fresh water and, as pH is an intensity function based on hydrogen ion concentration, will result in a decline in alkalinity and pH. The three study lakes in Labrador with a pH less than 5.50 were highly colored (100 to 175 T.C.U.) with dissolved organic carbon concentrations from 8.6 to 14.0 mg L<sup>-1</sup>. For the entire data set, lake pH was inversely correlated to lake color (r = -0.35) and to dissolved organic carbon (r = -0.30), so it appears that organics are contributing to freshwater acidity across the data set.

## Alkalinity

Alkalinity was determined at the field laboratory by potentiometric titration and subsequent Gran Plots (Total Inflection Point Alkalinities) and also in the analytical laboratory by the routine two-end-point titrimetric method. Values as determined by both methods were highly correlated (r = 0.94), with field alkalinities generally lower than lab measured values. Field (TIP) alkalinities were considered to be a more reliable and accurate measure (Stumm and Morgan 1981), particularly in dilute waters, and were used to calculate bicarbonate ion and in all subsequent assessments of buffering status and acidification. The two end point method is considered to overestimate "true" alkalinity in waters sensitive to acidification (Jefferies and Zimmerman 1980). In low alkalinity waters, the presence of organics can also lead to a significant underestimation of alkalinity when the two-end-point acidimetric method is used (Driscoll 1980).

Alkalinity values ranged from -17.4 to 831.0  $\mu eq~L^{-1}$  CaCO $_3$  (mean of 72.3) reflecting a relatively wide range of sensitivity to potential acidification. Applying the Ontario Ministry of the Environment's (1981) standards for

classification of lake sensitivity, 41 (32%) lakes are classified as extremely sensitive (0-40  $\mu eq~L^{-1}$ ), 84 lakes (65%) as of moderate sensitivity (40-200  $\mu eq~L^{-1}$ ), 4 lakes (3%) as of low sensitivity (200-500  $\mu eq~L^{-1}$ ), and one (1) lake is considered insensitive to potential acidification (> 500  $\mu eq~L^{-1}$ ) (Fig. 21). In addition, one lake with a negative alkalinity is classified as acidified. One hundred and twenty-six of the study lakes (97%) fell below the accepted 200  $\mu eq^{-1}$  standard for susceptability to potential acidification. The Water Quality Branch of Environment Canada found alkalinity (as measured by the two-end-point method) in 96 Labrador lakes to vary from 4.0 to 2160  $\mu eq~L^{-1}$  (mean of 97.3) with 91% under 200  $\mu eq~L^{-1}$  (T. Clair, pers. comm.). By comparison 92% of selected study lakes in insular Newfoundland fell below the 200  $\mu eq~L^{-1}$  standard (Scruton 1983). The distribution of alkalinity values confirms the extreme sensitivity of Labrador lakes, and indeed most lakes on the Canadian Shield, to potential acidification.

Alkalinity of fresh waters is due primarily to the carbonate-bicarbonate-carbonic acid system, and all study lakes (maximum pH of 7.41) are expected to have bicarbonate dominated buffer systems (Stumm and Morgan 1981). However, in dilute waters or acidifying waters (experiencing exhaustion of bicarbonate) other minor components of the buffering regime can assume importance. Weber and Stumm (1963) and Kramer (1976) state that waters with pH in the range of 4.0 to 6.0 may contain a number of additional buffer systems including anions of weak acids (silicic, phosphoric, hydrofloric, humic, fulvic), ammonia, metal oxides (aluminum, iron and others), or silica oxides. Aluminum and organic anions may act as the most significant of potential buffers in bicarbonate poor waters (Henriksen and Seip 1980, Driscoll 1980). The buffer intensity of these two components is at a maximum between pH 4.0 and 5.0, the end point of bicarbonate titration (Bisogni and Driscoll 1979).

Lee and Brossett (1978), Glover and Webb (1979), Henriksen and Seip (1980), Wiltshire and Machell (1981) and others have reported on the availability of potential buffers in bicarbonate poor waters, focusing on organic anions. The behaviour of organics can vary considerably between regions, perhaps as a consequence of analytical methodologies or due to differences in the components of the dissolved organic fraction. It is difficult to characterize or quantify any acid-base response on the basis of quantity of dissolved organic carbon (DOC) although the concentration of organic anions can be estimated with a knowledge of pH and DOC (Oliver et al. 1983).

Kramer (1976), Cronan and Shofield (1979), Johnson (1979) and others have reported on the role of aluminum in buffering acid inputs in terrestrial and aquatic regimes. In regions receiving high acid loadings hydrogen ion consumption in the soil fraction is accompanied by the rapid dissolution of aluminum in an ion exchange reaction. This aluminum acidity stage is a rapid process that can persist to become involved in the slower second stage of geochemical weathering. Henriksen (1982a) suggests that in calcium poor regions the second stage of buffering may not take place to any significant extent resulting in acid, aluminum rich waters. This serves to explain in part the episodic nature of aluminum availability particularly during periods of high runoff. The buffering potential of aluminum is related to its concentration and the speciation of the metal, but generally the metal and its complexes are believed to be operative as a buffer only in the pH range 4.5-5.0

(Johannessen 1980) while its solubility is at a maximum at pH 6.0 (Stumm and Morgan 1981). Henriksen (1980) found that lakes with a pH of 4.6 to 4.8 had a higher pH than predicted from theoretical bicarbonate titration curves and suggested that additional buffering be ascribed to aluminum. Organic complexing of aluminum will also diminish the buffering potential of the ion. The buffering potential of aluminum is also related to its speciation and only total aluminum was measured in this study.

No attempt has been made to determine the component anionic species, other than bicarbonate, contributing to alkalinity in the study lakes. Considering the number of colored lakes in the sample, the question of buffering potential of organic anions is important. An analysis of Gran plots (after Lee and Brossett 1978) indicated that there is no apparent contribution of organic anions in the buffering regime over the pH range 5.0 to 3.5. Both highly colored and clear water lakes, low in bicarbonate, demonstrated similar titration curves and inflection points. Further, humics have been shown to have very low buffering capacity even when present in high concentrations (Wilson 1979).

# Conductivity

Specific conductance or conductivity provides a measure of the total concentration of charged ions in a water sample and is a reliable indicator of sensitivity to acidification. Conductivity values for Labrador lakes ranged from 5.7 to 80.7  $\mu$  S cm<sup>-1</sup> (mean of 12.7) emphasizing the extremely dilute nature of Shield Lakes in Labrador. A total of 54 lakes (42%) had conductivities of less than 10  $\mu$  S cm<sup>-1</sup>, while 65 (50%) had values from 10 to 20  $\mu$  Scm $^{-1}$  , and 6 lakes (5%) had values of between 20 and 30  $\mu$  S cm $^{-1}$ (Fig. 22). The Water Quality Branch of Environment Canada found conductivities in 96 Labrador lakes to vary from 1 to 208  $\mu$  S cm<sup>-1</sup> (T. Clair, pers. comm.) while Duthie and Ostrofsky (1974) report condictivities of 10.2 to 32.0  $\mu$  S cm<sup>-1</sup> for lakes in western Labrador. Bobée et al. (1982) found that lakes on the Shield in Quebec north of 40°N latitude routinely had condictivities less than 20  $\mu$  S cm  $^{-1}$  . Environment Canada (1981) and Clair et al. (1981) has considered lakes with a specific conductance less than 30  $\mu$  S cm<sup>-1</sup> to be critically sensitive to acid precipitation, and this would include 125 lakes or 96% of the sample. Comparatively, 86% of the lakes in insular Newfoundland had conductivities of 30  $\mu$  S cm<sup>-1</sup> or less (Scruton 1983).

Conductivity is strongly related to certain ionic species and less closely to others, depending on the specific conductivities of each ion. Conductivity in the lakes was found to be highly correlated with the following: calcium (r=0.95), magnesium (r=0.87), bicarbonate (r=0.86), sodium (r=0.61) sulphate (r=0.51), the sum of cations (r=0.98), the sum of anions (r=0.98) and the sum of constituents (r=0.99).

Conductivity is commonly related to the lithology of drainage basins in a heterogeneous sample of lakes, specifically to the solubility of minerals in the watershed. In a region with strong marine influence, and dilute waters, ions of marine origin (chloride and sodium) can obscure the influences of geochemistry. This situation was readily apparent in insular Newfoundland

(Scruton 1983) but is only evident in lakes occupying the immediate coastline of southeastern Labrador. Conductivities in Labrador lakes were found to be similar to those for other continental lakes on the Canadian Shield with similar lithology (Armstrong and Schindler 1971; Magnin 1977). Labrador lakes underlain by granites, gneisses and anorthosites had particularly low mean conductivities of 10.3, 11.2, and 11.4  $\mu$  S cm $^{-1}$ , respectively.

#### LAKE STATUS

To evaluate lake water chemistry and potential damage from acidification, it is important to consider that the hydrological and chemical components of aquatic systems are dynamic and can experience wide fluctuations over time. This is particularly true of systems of intermediate acidity (pH 5.5-6.0) that are considered sensitive to potential acidification (Overrein et al. 1980). Seasonal changes in water chemistry are strongly related to hydrological dynamics and can often be greater than year to year alterations (Harvey et al. 1981). Temporal fluctuations are controlled by a variety of physical, chemical and biological factors but seasonal variation in many water quality parameters is most strongly related to surface runoff or discharge (Hem 1970; Hutchinson 1957; Gower 1980).

The hydrological data for guaged rivers in Labrador in 1982 (Environment Canada, Water Survey of Canada 1982) were examined for seasonal trends. Examination of seven (7) unregulated systems indicates that August and September were months of low discharge relative to July and October. Discharge increased in October and was extremely high in July. Lowest discharge for the year was recorded over the winter months of February to April. Highest values of pH, alkalinity and other variables associated with acidification are usually associated with periods of low runoff (Gjessing et al. 1976). As the first six weeks of the study period corresponded to the period of lowest runoff during the open water (ice free) season, we are in a sense evaluating a "best case" scenario in relation to sensitivity to or damage from acidification.

## Ratio of Bicarbonate to Sulphate

Anthropogenic inputs of acid are partially or wholly neutralized within the hydrological or terrestrial regime associated with each water body (Harvey et al. 1981). In lakes whose watersheds have a limited ability to regenerate buffers receiving continuous high atmospheric loadings of acids, the available reservoir of buffers will become depleted, soil and runoff acidity will increase, resulting in a pH decline in receiving waters. Freshwaters that are affected by atmospheric inputs have characteristically lost much of their bicarbonate buffering ability, and sulphate (in the absence of significant inputs of chloride) has become the dominant anion (Oden 1976).

Oden (1976) suggested the comparison of bicarbonate and excess sulphate concentrations be used as a preliminary indicator of acidification. A plot of lake pH versus the ratio of bicarbonate to excess sulphate (Fig. 23) suggests that bicarbonate is the dominant anion in most of the study lakes, and indeed bicarbonate was the dominant ion in lakes in all geological types (on

the average). Sulphate is dominant to bicarbonate in 18 lakes (14%), all with pH of 6.30 and less. Comparatively, in insular Newfoundland 48 lakes (44%) were demonstrating a sulphate dominance (Scruton 1983). This plot would indicate intact buffering systems in the majority of Labrador lakes. In Quebec, a high proportion of lakes in southern regions on the Canadian Shield have demonstrated a sulphate dominance over bicarbonate (84% of the sample) (Bobée et al. 1982). Langois et al. (1983) have reported that 70% of lakes surveyed in Quebec south of 52°N latitude had a bicarbonate/sulphate ratio of less than 1.0, while 40% had a ratio of less than 0.25, including many lakes just south of the Quebec-Labrador border.

## Cation - Alkalinity Relationships

As regions are subjected to acidic inputs of anthropogenic origin, cations are mobilized within watersheds, primarily through soil acidification and cation exchange, and sulphate replaces bicarbonate resulting in the alteration of the normal balance between major cations (calcium and magnesium) and bicarbonate (Harvey et al. 1981). Henriksen (1979) states that since the alkalinity of fresh waters is primarily dependent upon the availability and weathering of carbonates, then non-marine calcium and magnesium should be proportional to bicarbonate ion in unaffected regions subject to natural carbonic acid weathering only. A departure from this stoichiometric relationship indicates bicarbonate consumption in response to mineral acid loading. Henriksen (1979) and others (Almer et al. 1974; Harvey et al. 1981) have substantiated this relationship for affected and unaffected regions in Norway, Sweden, and North America.

The equivalence between major cations and bicarbonate alkalinity, as expected for non-impacted regions, is evident in the study lakes, and most of the lakes fell near or below the 1:1 line (Fig. 24). A sample of 20 lakes studied in Quebec (north of Schefferville and west of the Labrador border) did not show any alkalinity deficiency relative to the major cations (Bobée et al. Previous evidence had suggested that Labrador could be considered a non-impacted area (Harvey et al. 1981) but there appears to be a small deficiency in bicarbonate alkalinity relative to major cations, in the order of 25  $\mu eq~L^{-1}$  or less, on the average. The distance below the equivalence line has been suggested as a measure of the degree of acidification, and this has largely been substantiated in a comparison of lakes unaffected by acid deposition to those undergoing moderate to high acid loadings (Harvey et al. 1981). A comparison of the cation-alkalinity relationships between regions in eastern Canada (NIS data for Quebec, Ontario, New Brunswick, Nova Scotia, as provided by J. Cooley, pers. comm.) and insular Newfoundland (Scruton 1983) indicated that lakes in Labrador appear to be demonstrating the smallest depletion of buffering status (distance below the equivalence line) of all regional data sets, and it is probable that this reflects lower atmospheric loadings. The extreme sensitivity of many lakes in Labrador is evident and a further decline in alkalinity in the order of 50  $\mu$  eq L<sup>-1</sup> would push many lakes with non-marine calcium and magnesium concentrations of less than 75  $\mu$  eq L<sup>-1</sup> towards acidification (0 or negative alkalinities).

Researchers have postulated that calcium and magnesium levels in fresh waters may be elevated due to increased rates of weathering by strong mineral acids (Almer et al. 1974). If the input of acid is proportional to excess sulphate, a relationship should be evident between excess sulphate and the sum of calcium and magnesium minus bicarbonate, on an equivalent basis. Several researchers have reported an increase in cation export in watersheds receiving high acid loadings which supports this hypothesis (Overrein et al. 1980; Harvey et al. 1981). A plot of this stoichiometric relationship for Labrador lakes indicates that, for the most part, lakes were widely scattered about the equivalence line (Fig. 25). Study lakes in Labrador did not demonstrate good agreement with this relationship, while lakes in high deposition areas have demonstrated reasonable correspondence (Harvey et al. 1981). This suggests that loadings may not be high enough for mineral acid weathering of cations to be significant in Labrador, as was also suggested by lake data in insular Newfoundland (Scruton 1983).

## pH - Calcium Relationship

Henriksen (1979) has developed a first order means of identifying acidification based on the relationship between pH and non-marine calcium. His model is based on the premise that pre-acidification alkalinity and pH can be estimated from current calcium levels; that is the process of acidification reduces alkalinity without altering calcium levels. Henriksen determined that the ratio of calcium to magnesium was constant for his study lakes, and therefore calcium alone can be used to represent cations and the associated equivalence of alkalinity. The calcium/magnesium ratio in lakes in sensitive geotypes in Labrador has been demonstrated to approximate 2:1, and would therefore meet the criteria to use calcium in the model.

Henriksen drew an empirical curve to separate acidified and non-acidified lakes in Norway. Lakes above the line were receiving strongly acid precipitation (< pH 4.6) and were demonstrating evidence of acidification, while lakes below the line were receiving rainfall of pH 4.6 or greater and were showing little or no signs of acidification. Henriksen's relationship has proved valid for lakes in Norway, Sweden, the United States, and Canada (Henriksen 1979, Harvey et al. 1981) and consequently this model is presented as a first order approach in the identification of acidified or acidifying water bodies. Bobée et al. (1982) however found that this relationship wasn't applicable to highly mineralized waters in the Gaspé region of Quebec, probably due to the association of bicarbonate with other cations. The term "acidification" is considered by Henriksen to be synonomous with loss of alkalinity, therefore enabling the model to identify lakes with apparently safe levels of pH that may have experienced a significant loss of buffering capacity.

The relationship between pH and calcium for study lakes in Labrador is plotted against Henriksen's empirical curve in Fig. 26 (Henriksen's Indicator Diagram). A total of six (6) lakes fell in the "acidified" part of the diagram while the remaining 129 lakes fell in the "non-acidified" region. The six lakes in the acidified portion were geographically dispersed, and were characterized by high color values (75-175) and high levels of dissolved

organic carbon (8.3-14.0 mg L<sup>-1</sup>). Excess sulphate levels for the six lakes were also higher than the mean for all lakes, ranging from 38 to 62  $\mu$  eg L<sup>-1</sup>. Considering the depositional criteria Henriksen used to establish his empirical curve (i.e. precipitation pH of 4.6 or below) and the "apparent" atmospheric loadings in Labrador, it would be expected that lakes would fall near or below the curve. The high color and DOC in the six lakes (#369, 371, 403, 474, 481, 486) suggest that organic acids are reducing alkalinity and pH in these lakes. The empirical relationships used by Henriksen in developing this model would not apply to lakes receiving unusual input of strong acids of natural origin (such as organics, oxidation of mineral sulphur, or reduction of hydrogen sulphide).

The role that organic acids appear to be playing in the pH balance of these lakes is important. Studies in Nova Scotia (Wiltshire and Machell 1981; Underwood and Josselyn 1980) and in Scandinavia (Henriksen and Seip 1980; Glover and Webb 1979) have suggested that weak organic acids do contribute hydrogen ions to fresh waters and lower the pH in dilute highly colored waters. As mentioned previously, lake pH was correlated to dissolved organic carbon. As a result, the pH - calcium relationship will demonstrate the effects of acidification by both strong mineral acids and weaker organic acids (Fig. 23). Attempts to characterize or quantify organic contribution to acidification have been highly variable, due in part to methodological and regional differences, and do not lend themselves to universal applicability (Henriksen and Seip 1980; Wiltshire and Machell 1981).

To further emphasize the important role dissolved organic constituents are playing in the acid-base control of the study lakes, pH was regressed against colour (a correlate to dissolved organic carbon concentration, r = 0.90) for lakes grouped by calcium concentrations (Fig. 27). It is apparent there are highly significant correlations between pH and colour for lakes with similar calcium levels, with corresponding relationships do not exist between lake pH and non-marine sulphate. These relationships suggest that organics are heavily implicated in alkalinity depletion and pH control of Labrador's freshwater lakes, perhaps moreso than mineral acids of anthropogenic origin. This plot is similar to one presented by Seip and Tollan (1978) to demonstrated a linkage between non-marine sulphate and freshwater pH in Scandinavian lakes and rivers.

# Henriksen's Nomograph

Henriksen (1980) has developed a more refined model or nomograph to evaluate the stages of acidification, considering the process to be continuous and dynamic. This empirically derived model has been useful to evaluate water chemsitry on a regional scale. The underlying premis of the model is that the process of acidification is analogous to the titration of a bicarbonate buffering system (of geochemical origin) with strong mineral acids (of atmospheric origin), more specifically with dilute sulphuric acid. This model is also based on equivalency between the major cations (calcium and magnesium) or calcium alone to bicarbonate in non-acidified waters, and the use of present cationic concentrations to predict original alkalinity.

The sum of non-marine calcium and magnesium is plotted against non-marine sulphate with the ordinate representing geological determinants and the abcissa representing anthropogenic inputs of acid. Using empirically derived relationships, the nomograph is divided into three sections, corresponding to segments in the titration of a bicarbonate buffered system. The first stage (Bicarbonate Lakes) is characterized by small decreases in alkalinity but maintenance of the bicarbonate buffering system. The second stage (Transition Lakes) is characterized by the loss of the bicarbonate buffering regime, severe fluctuations in pH, and episodic effects on biota. The final stage (Acidified Lakes) is characterized by chronically low pH's, elevated levels of trace metals, and severe perturbation of resident biota. It is generally accepted that once lakes have reached this final stage, the process is irreversible, or can only be reversed over a long period of unstressed chemical weathering (Overrein et al. 1980).

A plot of the study lakes in Labrador on Henriksen's Nomograph is contained in Fig. 28. All but one lake fell within the "Bicarbonate" region (1 lake is in "Transition") and no lakes were evident in the "Acidified" region. This supports the evidence of other relationships, that is the majority of Labrador lakes, while higly dilute and sensitive to acidification, have intact bicarbonate buffering systems and are showing little evidence of alteration of chemical status from atmospheric deposition of acids. Comparatively, in insular Newfoundland ten (10) lakes (9%) were in the transition zone, and seven (7) of these lakes demonstrated chemical alteration in relation to sulphate levels in lake waters (Scruton 1983).

Henriksen's nomograph can be used in a predictive capacity, using the precipitation pH scale on the abcissa. This precipitation scale has only general applicability (owing to regional differences in the ratio of wet to dry deposition, relative sulphuric or nitric acid component in precipitation, total amount of precipitation, evapotranspiration rates, etc.) but it does permit an examination of a scenario of increased deposition. To examine the implictions of increasing deposition a dotted line was drawn in at pH 4.5, which is presently the lowest annual pH rainfall being received in insular Newfoundland. Under this scenario all lakes with a sum of excess calcium and magnesium of less than 65  $\mu eq~L^{-1}$  would move into transition or become acidified, implicating 56 of the study lakes (44%). A further decline in precipitation pH would have severe effects on the dilute and sensitive freshwater lakes in Labrador.

There are some limitations in applying and interpreting Henriksen's models. Firstly, one must assume that data examined represent steady state conditions. A basic premise of both models is that cations and alkalinity are proportional under conditions of natural carbonic acid weathering, and these remain conservative under conditions of mineral acid deposition, therefore enabling one to predict pre-acidification alkalinity and subsequent depletion. Researchers have demonstrated that calcium and magnesium export is increased under conditions of strong mineral acid deposition, therefore Henriksen's models would overestimate pre-acidification alkalinity and hence the amount of acidification (Bangay and Riordan 1983). Henriksen (1982b) has examined this problem using historical data and data from lakes with similar geologies but experiencing a gradient in acid deposition. His evaluation did not clearly indicate increased cationic concentrations in areas receiving high acid inputs,

although he did propose a "cation increase factor" for incorporation into his empirically derived nomograph. This question is currently under study and more time series information is required to fully resolve the issue.

A particular concern in aquatic studies in insular Newfoundland and Labrador is that weak acids, particularly organics, may disturb the cation/alkalinity/pH relationship making it difficult to isolate the roles of mineral and organic acids in lake acidification. Henriksen (1980) points out that lakes with high concentrations of organic acids do not meet several of the implicit assumptions used to develop his models. While organic anions can act in a buffering capacity in the lower pH ranges, they likely serve to heighten the sensitivity of dilute, colored lakes to chemical alteration from atmosphric deposition. A discussion of the role that organics play in the other major deleterious feature of acidification, that is the availability and toxicity of aluminum, is to follow.

The applicability of Henriksen' nomograph to North American locales is an important consideration. Relationships between cations and lake sulphate may vary between regions due to essential differences in geochemistry. Further, the empirical relationships between lake sulphate and atmospheric sulphate must be established for each geographical region. Therefore, for accurate predictions, it would be appropriate to develop regression relationships and predator nomographs that are region-specific (Bangay and Riordan 1983).

### ALUMINUM IN LAKE WATER

A major concern in lake acidification is the increased leaching of toxic metals, or increased availability of toxic species of metals, and the associated implications for resident fish and other biota (Baker 1982). Elevated levels of trace metals including aluminum, manganese, zinc, cadmium, lead, copper and nickel have been documented in Europe and North America (Glass et al. 1981; Haines 1981; and Harvey et al. 1981). Metals such as zinc and lead in lakes in southern Norway (Henriksen and Wright 1978) and nickel and copper in lakes near Sudbury, Ontario (Beamish 1976) are linked to direct atmospheric deposition (wet and dry). The principal sources for aqueous aluminum and manganese, on the other hand, is the dissolution and leaching of the metal from surrounding soils or lake sediments (Harvey et al. 1981; Johnson et al. 1981). These two metals demonstrate an increasing solubility with declining pH (over the range pH 5.0 to 7.0), so as soil acidity is increased through atmospheric deposition, aluminum and manganese are released and transported to lakes and streams (Cronan and Schofield 1979).

Aluminum was found in detectable quantities across the data set. Values for total aluminum ranged from 10 to 394  $\mu g$  L $^{-1}$  (mean of 71). The majority of the values were less than 200  $\mu g$  L $^{-1}$  (99%) with the one value of 394  $\mu g$  associated with a very highly colored lake (175 TCU).

Aluminum was significantly correlated with lake pH (r=-0.38), water color (r=0.61), and dissolved organic carbon (r=0.55) (Fig. 29). Clearwater lakes were associated with low values of aluminum ( $100~\mu g~L^{-1}$  and less) and may represent "background" levels for the metal. Organic anions

appear to be playing a role in the dissolution and mobilization of aluminum. Johnson (1979) has reported that the presence of organic ligands can enhance aluminum solubility by forming organic-aluminum complexes and facilitate transport through the soil profile into receiving waters. Study lakes demonstrating aluminum values in excess of 120  $\mu g$  were the highly colored systems (colour values from 75 to 175). Dickson (1978) for lakes in Sweden and Wiltshire and Machell (1981) for lakes in Nova Scotia and New Brunswick have reported similar relationships between organic carbon, color and total aluminum values.

Generally total aluminum values for Labrador lakes were considerably lower than those reported for lakes and streams in acidified regions of North America and Scandanavia (Overrein et al. 1980; Harvey et al. 1981; and Haines 1981) and were somewhat lower than those reported for insular Newfoundland lakes (ranging from 0 to 430  $\mu g$  L<sup>-1</sup>, mean of 112) (Scruton 1983). Lakes along the west coast of Sweden had aluminum values of 200 to 650  $\mu g$  L<sup>-1</sup> (Almer et al. 1978) while lakes in high deposition areas in southern Norway demonstrated values between 40 and 600  $\mu$ g L<sup>-1</sup> (Wright et al. 197%). Lakes with pH < 5.0 in Finland had aluminum levels of 180 to 470 µg L<sup>-1</sup> (Anonymous 1982). In North America, lakes in the Adirondack Mountains of New York had aluminum levels of from 4 to 850 μg L-1 (Driscoll 1980: Baker and Schofield 1980). Some acid lakes in Ontario had values ranging from 80 to 700  $\mu g$  L $^{-1}$  (Spry et al. 1981) and near Sudbury aluminum ranged from 150 to 1150 mgL $^{-1}$  (Scheider et al. 1979). In a Quebec study 74% of the lakes had total aluminum values in excess of 50  $\mu$ g L<sup>-1</sup>, 27% in excess of 150  $\mu$ q L<sup>-1</sup> and 6% in excess of 250  $\mu$ g L<sup>-1</sup> (Bobée et al. 1982). Lakes of intermediate pH (5.4 to 6.0) in Norway and Ontario had aluminum values of from 50 to 90  $\mu$ g L<sup>-1</sup> (Harvey et al. 1981) or from 80 to 100  $\mu$ g L<sup>-1</sup> in Finland (Anonymous 1982). These values are similar to levels in Labrador lakes and in many of insular Newfoundland's clearwater lakes. Scheider et al. (1979) have suggested background levels of aluminum in Shield lakes of from 2 to 10  $\mu$ g L<sup>-1</sup>.

Levels of aluminum alone, or in relation to pH toxicity, may be the primary mechanism limiting the survival of fish and other biota (Haines 1981). Similarly, pH tolerance can be affected by the availability of toxic forms of aqueous aluminum. In laboratory studies brook trout have demonstrated toxic response to aluminum concentrations above 200  $\mu g$  L<sup>-1</sup> over the pH range 4.4 to 5.9, while sublethal effects were demonstrated at aluminum concentrations of 100-300  $\mu$ g L<sup>-1</sup> (Cronan and Schofield 1979). Aluminum speciation and toxicity is primarily governed by pH and the availability of potential ligands (flouride and organic complexes), with the hydroxyl or inorganic forms most toxic and the organically complexed forms relatively non-toxic (Driscoll et al. 1980). They further report that aluminum-organic complexes were the dominant monomeric form available in the surface waters of the Adirondack region and this component increased linearly with organic carbon content. Aluminum values in our study, and indeed most values reported in the literature, are for total aluminum and not for the component species of the metal. However, as aluminum values in Labrador lakes were correlated with dissolved organic carbon and color, it is probable that much of the available aluminum is organically complexed and non-Stumm and Morgan (1981) have indicated there is a strong tendency for humics and fulvics to form complexes with metal ions, and these complexes can be the dominant species of available metals. Organics can therefore increase total metal solubility but may also decrease the concentration of biologically

available species (Reuter and Purdue 1977). Environment Canada is currently developing a cost effective methodology for determination of free ionic (labile) aluminum which may facilitate toxicological interpretation of survey data in the future (T. Clair, pers. comm.).

The dissolution and transport of metals to surface waters in response to mineral acidification can also be largely an episodic phenomenon (Harvey et al. 1981). High aluminum levels have been found to be associated with pH depression in surface waters during periods of high runoff (Gjessing et al. 1976; Jeffries et al. 1979). The episodic nature of aluminum availability was not investigated in this study.

#### FISH RESOURCES

It is initially important to outline several constraints in interpretation of the results of the gillnet survey of study lakes in Labrador, or that apply to synoptic surveys of this type in general. Firstly, it is difficult to reliably determine presence/absence of fish or a particular species in lakes from a single gillnet set over a period of one or two days. The presence of fish is much easier to demonstrate than absence, and a much greater sampling effort, using a variety of sampling methods, is required to reliably determine if a lake is "fishless." Different species also have different catchabilities dependent upon activity, foraging behaviour, distribution, etc. The survey period (August 17 to October 18) overlapped with the spawning period of resident salmonids and as brook trout are predominantly stream spawners (Scott and Crossman 1973), it is possible fish may have moved into streams for spawning. Lake spawners (e.g. lake trout and whitefish) may have been in prespawning concentrations in an unsampled portion of the study lakes. Of a total of six lakes in which no fish were captured, five were sampled in the first two weeks of the survey (before September 2) while one was sampled on October 21. There were no strong indications of seasonal influences on fish capture, as there were in a similar survey of insular Newfoundland lakes (Scruton 1983).

In relation to any assessment of abundance, in this case catch per unit of effort (CPUE), similar considerations apply. In addition to fish availability in relation to spawning activities, there is also a progressive decline in water temperatures over the study period. Reduced water temperatures and spawning activities may result in a decline in foraging activity for some species. As gillnetting is a passive sampling technique, reduced activity would make fish less susceptable to capture. For these two reasons it is difficult to compare fish abundance between lakes sampled over the two month period of survey. The minimum mesh size employed in the survey was 3.8 cm (stretched measure) which did not permit sampling of the younger age classes (0<sup>+</sup>, 1<sup>+</sup>, and to a lesser extent 2<sup>+</sup>) of resident fish or forage species (e.g. cyprinids). For this reason, and because of the small sample size obtained from many lakes, it is of little value to assess age class structure and possible recruitment failure (missing age classes) as early indicators of potential acidification damage (as suggested by Overrein et al. 1980 and Harvey et al 1981). Certainly the assessment of lake status does not indicate an

acidification threat to resident biota however, owing to the extremely dilute nature of many study lakes, episodic problems are possible.

A total of 2470 fish were netted from 89 of 95 lakes sampled (94%). Six salmonid species were captured, as well as two catastomids, one esocid and one gadid. The distribution of species in order of dominance (numerically) is as follows: white sucker (Catostomus commersoni), 765 (31%); brook trout (Salvelinus fontinalis), 526 (21%); longnose sucker (Catostomus catostomus), 328 (13%); lake trout (Salvelinus namayacush), 309 (13%); lake whitefish (Coregonus clupeaformis), 222 (9%); northern pike (Esox lucius), 165 (7%); round whitefish (Prosopium cylindraceum), 70 (3%); arctic char (Salvelinus alpinus), 46 (2%); Atlantic salmon (Salmo salar), 27 (1%); and burbot (Lota lota), 3 (< 1%).

Other reported freshwater inhabitants of Labrador that were not captured during this survey include American smelt (Osmerus mordax), lake chub (Couesius plumbeus), American eel (Anguilla rostrata), longnose dace (Rhinichthys cataractae), mottled sculpin (Cottus bairdi), slimy sculpin (Cottus cognatus), threespine stickleback (Gasterosteus aculeatus), ninespine stickleback (Pungitius pungitius), pearl dace (Semotilus margarita), and Atlantic sturgeon (Acipenser oxyrhynchus). Smelt and sturgeon are anadromous in Labrador and infrequent permanent residents of freshwaters (Scott and Crossman 1973) while the remaining species were either too small to be susceptible to gillnet capture (dace, chub, sculpins, sticklebacks) or are impossible to capture by gillnet (eels).

Brook trout were the most generally distributed of all species throughout Labrador being netted from four of the five geographical regions (being absent from the Northern Region) and from 51 of 87 lakes (59%) in which fish were captured (Fig. 30a). Trout were not taken from the four lakes sampled north of 55°30'N latitude. The species is known to occur in more northerly locations, including northern Labrador and the Ungava region of Quebec (Scott and Crossman 1973). Brook trout was the dominant salmonid in the Central, Eastern and Southern Regions both in terms of numbers caught and lakes with fish present. In nineteen (19) of the lakes brook trout was the only species captured. The species was particularly dominant in lakes in the Southern Region comprising 76% of the total salmonid catch (by numbers). By contrast, brook trout were netted from only eight of 28 lakes (29%) in the Western Region and, with the exception of two brook trout only lakes, were a relatively minor component of the fish communities in that region. Kelso and Minns (1982) suggest brook trout are the species most threatened by continuing acidification of freshwaters owing to the association of the species with the most sensitive habitats.

Lake trout were the second most abundant salmonid captured during the survey being taken from 28 lakes (32%) and from four of the five geographical regions (being absent from the Eastern Region) (Fig. 30a). Lake trout comprised 82% and 37% of the salmonid catch in the Northern and Western Regions, respectively. The natural range of lake trout distribution in North America follows closely the limits of Pleistocene glaciation (Lindsay 1964). Study results suggest the species is largely confined to the Western and Northern regions and is largely absent from lakes in central, Eastern and

Southern areas (Fig. 27). Lake trout are one of the more sensitive salmonids to potential damage from acidification (Spry et al. 1981) but they also tend to occupy larger, deep, high order lakes (i.e. the less sensitive habitats). Lindsay (1964) states that lake trout, in the southern part of their range, occur in the deeper cool lakes, while in the more northerly part of their range where thermal limitations are not as prevalent, they can also occur in shallower lakes and rivers.

Arctic char were found to have a limited distribution (Fig. 30a) being netted from only seven (7) lakes, but the species was was represented in lakes from four of the five geographical regions (being absent from the Eastern Region). Although one fish was captured in the Western Region (Lake #521) char were not taken in lakes west of 63°30'W longitude. Analyses of age/growth relationships would indicate that char in two lakes (#358 and #363, 142 and 109 m above sea level, respectively) were anadromous while in all other lakes resident fish would appear to represent relict landlocked populations. Char apparently had both southerly and northerly refugia from Wisconsin glaciation but have not rejoined their range since, as evidenced by the number of isolated populations (Lindsay 1974). Lake trout and arctic char were found to be largely mutually exclusive (they cohabited only one lake) and this may be partly explained by their post glacial distribution. Char were generally found alone (three lakes) or in association with brook trout (three lakes).

Atlantic salmon were netted from a total of only four (4) study lakes, all in the Eastern Region and east of 60°W longitude (Fig. 30a). Examination of age, growth, and scale characteristics suggest that the one salmon taken from lake #401 was anadromous while the salmon taken from the other three lakes were landlocked (ouananiche). Study results would indicate that ouananiche are a minor component of the salmonid community in Labrador and have a restricted distribution. By comparison, ouananiche are a dominant salmonid in lakes in insular Newfoundland, second only to the ubiquitous brook trout, where fish communities are less complex (Scruton 1983). Atlantic salmon were found alone (one lake) or in association with brook trout (three lakes).

Lake whitefish were the most abundant and widely distributed of the two coregonid species occurring in Labrador, being taken from sixteen (16) lakes and comprising 9% of the total catch (by numbers). Lake whitefish distribution was largely confined to the western half of Labrador, as none were captured east of 63°W longitude (Fig. 30a). Lake whitefish were always found in association with other fish species and generally as part of complex fish communities.

Round whitefish were netted from eleven (11) lakes and comprised 3% of the total catch (by numbers). Round whitefish generally demonstrated a similar distribution to lake whitefish, being restricted to western Labrador, but were not always found in association with the other coregonid (lake and round whitefish cohabited five lakes) (Fig. 30b). Round whitefish were always found in association with lake trout.

White sucker were the most abundant species captured during the survey comprising 31% of the total catch (by numbers) and were netted from 35 lakes in four of the geographical regions (being absent from the Northern Region). The

species is widely distributed in the southern half of Labrador but were absent from all lakes north of 50°30'N latitude (Fig. 30b).

Longnose sucker were the third most abundant species captured during the survey comprising 13% of the total catch (by number) and were taken from 22 lakes in four of the geographical regions (being absent from the Northern Region). The species is widely distributed throughout western and eastern Labrador (they were largely absent from lakes in the central portion) and were found in more northerly lakes than were white sucker (Fig. 30b).

Northern pike were netted from 28 lakes in three regions and represented 7% of the total catch (by numbers). The species was largely absent from lakes in eastern and northern Labrador (Fig. 30a). Northern pike were the only species taken from four (4) lakes but were found in lakes of different community complexities.

Burbot were the least abundant species captured during the survey with a total of three individuals taken from two lakes (Fig. 30a).

The fish communities or species assembleges across the survey lakes generally reflect the distribution and ranges of the resident fish species in northeastern North America. A total of 10 species were captured during the survey and three species (arctic char, Atlantic salmon and brook trout) demonstrated both anadromous and landlocked populations. Considering all species (and including fishless lakes), there were a total of forty-one different fish communities identified from the study lakes (Table 3). In order of increasing diversity there were 6 lakes (6%) with no fish captured, 30 lakes (32%) with 1 species, 25 (26%) with 2 species, 15 (16%) with 3 species, 8 (8%) with 4 species, 6 (6%) with 5 species, and 3 lakes (3%) with a community consisting of 6 species. By comparsion, only three species representing 8 different fish communities were evident in a survey of lakes in insular Newfoundland (Scruton 1983). One lake in insular Newfoundland demonstrated a fish community of three species (all others were two or less) while communities of three species or more were evident in 32 lakes (34%) in Labrador. This serves to emphasize the geographic differences in fish species diversity and assembleges and in particular the isolating role salt water has played in limiting the distribution of freshwater fish to an insular region.

The diversity of fish communities demonstrated somewhat of a geographical trend. While fishless lakes and lakes with one species tended to be randomly distributed, the more complex fish communities (4, 5, 6 species) were confined to western Labrador, in the Lakes Plateau region. This is consistent with the distribution pattens of individual species as lake and round whitefish, lake trout, and northern pike are absent or have limited distribution in eastern Labrador (Scott and Crossman 1973). The more northerly lakes, on the other hand, were characterized by simple (one or two species) fish communities.

Lakes in which brook trout only were captured are the dominant fish community in Labrador, being found in 20 lakes (21%) while brook trout and sucker (white and/or longnose) combinations were found in 9 lakes (10%). The more complex fish communities (4, 5, and 6 species) were found in 17 lakes (18%) and represented various combinations of northern pike, brook trout, lake

trout, lake and round whitefish, and longnose and white sucker. Species communities representing burbot, ouananiche, and Arctic char were the least abundant owing to the small number of lakes containing these species.

Lakes in which brook trout only were captured were also the dominant community in insular Newfoundland (Scruton 1983) as well as in a regional evaluation of Ontario lakes (Minns 1981). This is not too surprising as the lake selection criteria (small lakes located in headwaters) resulted in a sample biased to preferred trout habitats. This is apparent in Western Labrador where multispecies communities dominated but lakes which contained brook trout only were also evident. Brook trout is apparently the only species that has been able to successfully colonize some of these headwaters systems.

A summary of length, weight, and age data and size and maturity data for each species and by region is summarized in Tables 4 and 5, respectively.

Estimates of catch per unit of effort (CPUE), that is, the catch per 24 hours of one standard gillnet gang, by weight and by numbers, were calculated for all lakes in which fish were captured. Estimates of CPUE, by numbers, ranged from 0.35 to 82.04 fish per day for all species combined and from 0.00 to 60.59 fish per day for salmonids only. Estimates of CPUE, by weight, varied from 0.06 to 49.69 kg per day for all species and from 0.00 to 17.91 kg per day for salmonids only. Maximum numbers did not regularly coincide with maximum weight, reflecting a dominance of a particular species and/or size class at a given lake. Peak numbers were obtained from two mesh sizes (5.1 and 7.6 cm) while maximum weights were obtained in the 7.6 cm panel. Effort ranged from 0.79 to 6.07 days per net per lake and from 0.79 to 16.14 net days per lake. Effort for most lakes ranged between 0.80 and 2.00 net days.

Estimates of catch per unit effort by numbers and weight (for all species and for salmonids only) were then regressed against parameters representing geography (region), bedrock geology, chemical status (pH), lake morphometry (surface area and mean depth), and productivity indices (morphoedaphic index or MEI). No parameters were highly significant in determining the variance in CPUE (P > 0.05). The CPUE by weight, for salmonids only, was weakly correlated with lake pH (r = 0.19, P = 0.011).

Potential fish production is governed by morphometric and chemical parameters and can be expressed by the MEI, or morphoedaphic index, as described by Ryder (1965) and Ryder et al. (1974). The morphoedaphic index (metric) of 75 Labrador lakes ranged from 0.21 to 22.86 with a mean of 4.57. (Only 75 lakes were depth sounded to obtain an estimate of mean depth). The range of MEIs for the study lakes, by region, is as follows: Northern Region; 0.96-1.43 (mean of 1.20, N = 2); Central Region, 0.21-7.20 (mean of 2.19 (n = 17); Eastern Region, 1.35-22.5 (mean of 9.78, n = 6); Southern Region, 1.31-22.86 (mean of 7.00, n = 21); and the Western Region, 0.25-8.29 (mean of 3.36, n = 29). Ryder (1965) considers an MEI of 6.56 as distinguishing between oligotrophic (< 6.56) and eutrophic (> 6.56) lakes. Sixteen of the lakes (21%) had indices exceeding this value. The relatively high MEI in these lakes was primarily a consequence of their shallow depth (average mean depth of 2.3 m for the 16 lakes) and not due to chemical or productivity parameters. These lakes cannot be considered eutrophic in a limnological sense (Hutchinson 1957). The

potential yield for the 75 lakes ranged from 0.32 to 3.35 kg  $ha^{-1}$   $yr^{-1}$  (mean of 1.50).

In regions experiencing acidification damage to fish stocks, a relationship has been demonstrated between the presence/absence of one or more fish species with lake or river pH (Overrein et al. 1980; Harvey et al. 1981; MOI 1983). Kelso et al. (1980) reported an increase in fishless lakes with declining pH in lakes near Sault Ste. Marie, Ontario. In Insular Newfoundland a similar increase in the incidence of "apparently" fishless lakes was evident in relation to declining pH, although the relationship was not necessarily linked to a cause-effect reltionship between atmospheric deposition and lake chemistry (Scruton 1983).

In Labrador, fish were not sampled from 6 of the 95 lakes surveyed. These apparently "fishless" lakes represented pH of 5.66 to 6.80, surface area from 7.5 to 146.0 ha, and were confined to two geographical regions (Central and Southern). Three of these six lakes received only half the sampling effort that most lakes received (one net night vs. two net nights). There was no relationship between the incidence of apparently "fishless" lakes and lake pH. Fish presence/absence was assessed in relation to organic content (DOC and water color) and no relationship was apparent. Naturally acid, dystrophic lakes are considered to have limited potential for fish production, but a number of small, highly colored ponds in Labrador were found to have good numbers of brook trout and/or suckers. Dystrophic lakes (low pH, highly colored, dilute) are not considered to contribute significantly to fish production in Ontario (Minns 1981) but in insular Newfoundland dystrophic lakes are recognized as important fish producers, owing to the abundance of that lake type (W. Bruce, pers. comm.).

An important consideration in interpreting fish presence/absence is that lakes high up in their respective drainage systems may not have been susceptable to recolonization after glaciation due to the high gradient or intermittent nature of outlet streams. In addition, in northern regions, winter kill in shallow exposed lakes is a consideration. Pope (1973), and Langois et al. (1983) have reported that the absence of fish in some Quebec headwater lakes, particuarly along the North Shore of the St. Lawrence River, may be primarily due to the inaccessability of the headwaters of some river systems. All six "fishless" lakes in Labrador were small, first order lakes, suggesting that biogeographic factors (size, depth, availability of spawing habitat, access) may be more important than chemical factors in the apparent lack of fish in these lakes.

Harvey et al. (1979) have suggested that observations on lowest pH in relation to fish occurrence may be used as a functional definition of the pH tolerance of the species. The pH range of the lakes in which each species was captured, including the critical pH range for reproduction and recruitment (as obtained from the literature) is presented in Fig. 31. While the discontinuous distribution of several species and the low number of lakes with pH less than 6.0 (21 lakes) make it difficult to interpret interspecific differences in acid tolerance, several tendencies reported in the literature were evident in the survey. Brook trout were captured in lakes representing the full range of pH and the species has been reported to be relatively acid tolerant with respect

to other salmonids (Daye and Garside 1975). Brook trout were also well represented in low pH, dystropic lakes on the island at Newfoundland (Scruton 1983). Lake trout are considered to be relatively acid sensitive (Harvery 1980) and were not found in lakes below pH 6.13. White sucker have also been reported to be relatively acid tolerant (Harvey 1980) and the species was captured from lakes with pH ranging from 4.80 to 7.84. Lake white fish, however, were found in lakes with pH from 6.13 to 7.84 which is not consistent with acid sensitivity as reported in the literature (Beamish 1976, Harvey 1980). Post-glacial distribution has restricted the species largely to Western Labrador, which coincides with the occurrence of the more mineralized (higher pH) lakes of the Labrador Trough. It is apparent in some instances, that zoogeographical influences overwhelm the interpretation of species presence/absence in relation to physical-chemical parameters.

There was also a slight trend to increasing diversity with increasing lake pH, between pH 5.5 and 8.0 (Fig. 32). While this trend may be primarily governed by species distributions and productivity considerations it is consistent with trends to decreased diveristy in low pH lakes as reported for most levels of aquatic biota (Harvey et al. 1979; Haines 1981). Species richness (diversity) of the study lakes, however, is not absolute as the low amount of sampling effort, selective nature of the sampling gear, seasonal aspects of fish distribution, etc. may have prevented in all fish species present in any one lake from having been sampled.

## CONTAMINANT BODY BURDEN OF FISH

Tissue samples from 1191 fish, representing nine species were analyzed for mercury and aluminum. A summary of mercury and aluminum levels in fish tissue by species and by lake is contained in Table 6. The percent of the sample with mercury values in excess of the National Health and Welfare Standard of 0.5 ppm for fish intended for human consumption is also included.

There is considerable evidence linking lake pH to mercury in fish (Brouzes et al. 1977; Jernelov et al. 1976). Fish from acidified lakes may contain elevated mercury and other metals and this is commonly related to a reduction in pH and alkalinity (Haines 1981) and can further be extrapolated to the influence of acidification on fish population parameters (Brouzes et al. 1977). The mechanisms for the increased availability of mercury are likely related to increased mobilization from the watershed and sediments and increased methylation of inorganic mercury in low pH water; in particular over the range 5.0 to 7.0 (Spry et al. 1981). Methylation of mercury is at a maximum around a pH of 5.0. Tomlinson et al. (1980) believe that lower pH leads to higher mercury in fish due to increased retention of mercury in the water column under acid conditions and the concentration of metals in fish tissue due to declining biomass and growth rates in response to pH decline. Loss of younger year classes may result in predatory fish feeding on larger individuals with higher mercury content. Other factors that also determine the mercury burden in fish includes mercury availability in soils and sediments, Take trophic state (food chains), organic content of water, Take flushing rates, and watershed area to lake area ratio (Jernelov et al. 1976).

Levels of mercury in the nine freshwater species sampled ranged from 0.02 to 1.55 ppm (Table 6). Six of the nine species demonstrated mercury levels in excess of 0.5 ppm. Mean mercury levels for fish species, from this study are compared with those of the Fisheries and Oceans Mercury Survey of freshwater and anadromous fish conducted in 1977 and 1978 (Bruce and Spencer 1979) in Table 7. Levels compare favorably between the two surveys with the piscivorous species (lake trout, northern pike, arctic char) demonstrating the highest mean values and anadromous fish demonstrating relatively low levels. Species that feed largely on invertebrates (brook trout, whitefishes, suckers) demonstrated relatively low mercury levels, generally less than 0.5 ppm. Lake trout sampled in the our survey had a lower mean mercury concentration than those sampled in the 1977-78 study (0.43 vs 1.00 ppm, respectively). Lakes sampled in the headwater lakes survey were relatively small, with a small watershed to lake area ratio, in comparison to the larger lakes (with large drainage areas) and reservoirs sampled by Bruce and Spencer (1979). These larger lakes would be considered to have greater potential for mercury availability owing to leaching from larger drainage systems and through flooding of mineral soils.

Higher concentrations of mercury were associated with the larger, older fish. Methylmercury is considered to accumulate in aquatic organisms according to trophic level with highest concentrations found in the larger and older carnivorous fish. Jernelov et al. (1976) suggests that in non-predatory species, 10% of mercury in tissue is uptaken through the food chain and 90% through gill and skin transport, while in piscivorous fish the two mechanisms may be of equal importance.

For individual lakes with a sample size of 10 or more fish of one species, levels of mercury in fish tissue was regressed against body size (length and weight) and age. Correlation coefficients for significant regressions (p < 0.05) are contained in Table 8. It is apparent that there are strong relationships between body size and mercury burden for eight of the nine species. By species, the proportion of lakes demonstrating significant body size/mercury burden relationships is as follows: lake trout (8 of 8, 100%), round whitefish (1 of 1, 100%), Atlantic salmon (1 of 1, 100%), northern pike (3 of 4, 75%), white sucker (11 of 15, 73%), brook trout (8 of 13, 62%), lake whitefish (3 of 6, 50%), longnose sucker (2 of 6, 33%), and arctic char (0 of 1, 0%). Age was also correlated to mercury body burden in the eight species, but not in as many populations as was body size. There is strong evidence of bioaccumulation of mercury in a number of fish populations. Bruce and Spencer (1979) reported that mercury levels in tissue was commonly positively correlated with the length, weight, and age of the fish.

Owing to the strong evidence of bioaccumulation of mercury in fish tissue, the range in size and age of individuals, the narrow range in lake pH (82% of the sample between pH 6.0 and 7.0), and the variety of factors influencing mercury availability in the aquatic environment, mercury and aluminum burdens were not assessed in relation to lake pH. In the survey of insular Newfoundland lakes there was some evidence for pH control of mercury uptake in fish when individuals of similar size were compared across the data set (Scruton 1983). Brook trout and ouananiche from all insular Newfoundland lakes were grouped into length classes (25 or 50 mm increments), to isolate the bioaccumulation effect, and then mercury burden was regressed against lake pH.

In four length classes for brook trout and ouananiche (each), lake pH was significant (p > 0.01) in determining the variance in mercury in fish tissue.

Levels of aluminum in the nine freshwater species sampled ranged from 0.40 to 8.10 ppm and is summarized in Table 6. For lakes with a sample of 10 fish or more of one species, levels of aluminum in fish tissue were regressed against body size (length and weight) and age. Significant regressions (p > 0.05) were apparent only in the two sucker species in a total of three lakes. No significant relationships were obtained for the salmonids or coregonids or for the species occupying the higher trophic levels. There is little evidence of bioaccumulation of aluminum in fish tissue in the Labrador study.

## CONCLUSIONS

There is no evidence from this survey of Labrador lakes that an acidification problem exists in the region at present. The lakes are among the most sensitive in eastern North America, on the basis of terrestrial and chemical sensitivity, but show little deterioration in chemical status in relation to the anthropogenic deposition of acids. Lakes in Labrador are not as affected as those in other regions of eastern Canada, which is consistent with apparent rates of deposition and proximity to emissions sources, and suggest that Labrador could be considered an unaffected region.

Lakes were highly colored relative to those included in other regional data sets, making it difficult to isolate the roles of natural organic acidity and mineral acidity of anthropogenic origin in the acid-base control of lakes. Organic acidity is contributing to pH and alkalinity decline and would appear to play a role in mobilization of aluminum. Organics are also likely chelating the metal, thereby influencing its biological potential for toxicity. Levels of aluminum in lake water were less than those documented for affected global regions, but measurement of total aluminum did not permit evaluation of the levels of potentially toxic species.

There is no evidence of affected fish populations in relation to the chemical status of lakes. Levels of mercury and aluminum in fish tissue were considered, for the most part, to represent "background" levels. Long-lived piscivorous species demonstrated higher mean mercury levels than those of lower trophic order and several individuals demonstrated fish mercury levels in excess of the accepted Canadian standard of 0.5 ppm. There was strong evidence of bioaccumulation of mercury in several fish populations.

A further evaluation of the influence of acidification in Labrador awaits a finer resolution of the depositional scenario. Rainfall acidity, at present, is above levels whereby sensitive regions in the world have documented acidification damage. Forecasts for increased rates of deposition in the future are highly tenuous. The location of Labrador relative to emissions sources and meteorlogical patterns in the north does not suggest any immediate threat to Labrador's freshwaters. However, the extreme sensitivity of the region's lakes is apparent, and it is important that monitoring be initiated

and continued in order to detect any deterioration in chemical status with time, or any potential episodic problems.

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Table 1. Water quality parameters, methods of laboratory determination, and detection limits.

Parameter	Analytical Procedure	Required Vol. (ml)	Limit of Detection (mgL <sup>-1</sup> )
Conductivity	Hach Conductivity Meter Model 2511	20	0.5 (μS cm <sup>-1</sup> )
Color	Visual Comparison using Platinum Color Plasma	10	5 (TCU)
рН	Combination Glass & Reference Electrode Radiometer Model 26 pH Meter	8	0.01 (pḤ units)
TDS	Evaporation of filtrate	100	0.01
Turbidity	Nephelometric Method - Hach 2424 Turbidmeter	10	**
Sodium	Atomic Absorption on Perkin Elmer AA	2	0.1
Potassium	Atomic Absorption on Perkin Elmer AA	2	0.02
Calcium	Atomic Absorption (ICP) on Jarrel Ash AA	2	0.01
Magnesium	Atomic Absorption (ICP) on Jarrel Ash AA	2	0.02
Hardness	Calculated from calcium and magnesium	-	0.02
Alkalinity	Auto Analyzer II Colormetric Bromophenol Blue	8	0.1
Bicarbonate	Calculated from field alkalinity	-	0.01

<sup>. . .</sup> Cont'd.

Table 1. (Cont'd.)

Parameter	Analytical Procedure	Required Vol. (ml)	Limit of Detection (mgL <sup>-1</sup> )
Sulphate	<ul> <li>a) Auto Analyzer II</li> <li>Colormetric</li> <li>Methylthymol Blue</li> <li>b) Hydrogen-peroxide uv</li> <li>pre-treatment</li> </ul>	8	0.3
Chloride	Auto Analyzer II Colormetric Mercuric Thiocyanate	8	0.1
Phosphate total as P	Auto Analyzer II Colormetric U.V. Digestion & Molybate Ascorbic Acid	8	0.001
Nitrogen total as N	Auto Analyzer II Colormetric U.V. Digestion & Diazotization	8	0.02
Aluminum	Atomic Absorption - (ICP) on Jarrel Ash AA	50	0.010 ( $\mu g L^{-1}$ )
Dissolved Organic Carbon (DOC)	Oxidation to CO <sub>2</sub> and Colorimetric determination	50	0.1

Table 2. A comparison of the contribution of ions of marine origin to freshwater chemistry in lakes from insular Newfoundland (Scruton 1983) and Labrador (this study).

	Insular	Newfoundland $(n = 109)$	La	abrador (n = 135)
Ion	Mean value	Marine contribution	Mean value	Marine contributio
Chloride	87.8	100%	9.4	100%
Sodium	82.3	60%	22.1	35%
otassium	3.3	55%	3.2	5%
Sulphate	46.8	26%	28.2	3%
1agnesium –	50.2	12%	32.2	6%
Calcium	102.5	< 1%	60.6	< 1%

Table 3. Fish communities or assembleges from the study lakes. (BT-brook trout, LT-lake trout, AC- arctic char, AS- Atlantic salmon or ouananiche, LW- lake whitefish, RW- round whitefish, WS- white sucker, LS- longnose sucker, NP- northern pike, B-burbot).

Assemblege			ļ	Lake i	#		
BT				367,			
				408,			45/,
LT	467 <b>,</b> 502	4/3,	402,	485,	501,	514	
AC		359,	521				
NP		474,		516			
AS	407	,	· ,	• •			
BT/LT	358						
BT/AC	363,	484					
BT/WS		459,	465,	466			
BT/AS	404,						
BT/NP	475,						
BT/LS	406,						
LT/RW LT/AC	301, 302	217					
LT/WS	503						
NP/LW		506,	509				
NP/WS		468					
4S/LS	488						
WS/B	469						
BT/LT/LS	357,	362					
BT/AS/LS	401						
BT/WS/LS		456,	472				
BT/WS/NP	453,	463					
BT/WS/B _T/LS/LW	486 360						
_T/WS/NP	373 <b>,</b>	513					
_T/RW/WS	518	313					
_T/RW/LS	527						
AC/NP/WS	462						
BT/WS/NP/LS	458						
BT/WS/LS/LT	523						
LT/LW/WS/LS	511	-0-					
LT/LW/WS/NP	522 <b>,</b>						
_T/LW/RW/NP BT/WS/LW/NP/LS	515, 504	320					
BT/WS/LW/NP/LT	517						
LT/LS/WS/LW/NP	526 <b>,</b>	529					
_T/LS/WS/LW/RW	505,	528					
BT/LT/WS/LS/RW/LW	508,	519					
BT/LT/WS/LS/RW/NP	524						

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Table 4. Summary of length, weight, and age data for all fish captured by region and species.

				L	ength (m	m)	We	eight (gm	n)	Min.  7 5 8 2 5 7 6 6 3 8 2 2 3 6 4 2 3 3 8	years)
Region	Species	No. of lakes	Sample size	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
NORTHERN	Lake trout	2	68	230	620	442	133	2763	1010	7	32
(n=2)	Arctic char	1	9	210	450	317	102	1098	421		11
	Round whitefish	1	6	305	350	329	347	511	397	8	11
CENTRAL	Brook trout	14	168	155	460	265	37	7551	260	2	6
(n=24)	White sucker	3	69	204	492	316	120	1036	449	5	13
	Lake whitefish	1	45	285	495	444	233	1664	1251	7	15
	Arctic char	4	34	220	550	424	89	1492	831	6	22
	Lake trout	4	42	340	790	504	467	4845	1477	6	29
	Longnose sucker	3	8	185	285	228	94	314	169		10
	Northern pike	3	8	302	755	571	185	1949	1317	8	14
EASTERN	Longnose sucker	3	184	190	460	278	75	2180	319	2	14
(n=9)	Brook trout	8	62	160	470	275	53	2460	295	2	6
	Atlantic salmon	4	27	140	490	339	36	2104	559	3	10
	White sucker	1	17	285	385	359	345	898	731	6	9
SOUTHERN	White sucker	15	350	173	480	342	99	1870	556	4	12
(n=31)	Brook trout	22	202	150	570	263	62	3050	273		7
	Northern pike	11	61	390	1335	650	396	6804	1637	3	17
	Longnose sucker	5	52	200	455	328	102	869	463		12
	Lake whitefish	1	4	321	535	443	410	2342	1343		12 7
	Burbot	2	3	381	470	437	324	687	553	5	7
	Arctic char	2	2	218	405	312	108	750	429	7	8
	Lake trout	1	2	604	630	617	2456	2721	2589	21	26

Table 4. (Cont'd.)

				Le	ength (mm	1)	We	eight (gm	1)	_Age (y	/ears)
Region	Species	No. of lakes	Sample size	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
WESTERN (n=29)	Lake trout White sucker Lake whitefish Northern pike Brook trout Longnose sucker Round whitefish Arctic char	25 16 15 14 8 11 10	197 188 173 96 94 84 64	227 202 158 414 210 209 225	824 525 533 880 420 615 372	502 380 339 661 283 423 299 260	128 113 72 488 99 106 122	7484 2365 2140 5670 1108 3289 550	1546 908 573 2220 276 1150 306 181	4 4 7 2 6 4	34 18 15 21 6 16 9
TOTALS (n=95)	White sucker Brook trout	35 52	765 526	173 150	525 570	351 269	99 37	2365 3050	656 272	4 2	18 7
	Longnose sucker	22	328	185	615	322	75	3289	551	2	16
	Lake trout	32	309	227	824	490	128	7484	1425	4	35
	Lake whitefish	16	222	158	533	362	72	2342	732	4	15
	Northern pike	28	165	302	1353	653	396	6804	1960	3	21
	Round whitefish	11	70	225	372	302	122	550	314	4	- 11
	Arctic char	8	46	210	550	395	89	1492	719	5	22
	Atlantic salmon	4	27	140	490	339	36	2104	559	3	10
	Burbot	2	3	381	470	437	324	687	553	5	7

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Table 5. Sex and maturity data for fish captured during the study, by region and species (Note: Sex was not determined for all samples).

					Male	<u>s</u>		Fema1	es	Male:Female ratio  1.33 2.00 5.00  1.22 1.13 1.33 0.61 0.69 0.61 1.00  1.56 2.13 1.08 1.00  0.82 1.43 1.10 0.68 0.33
Region	Species	No. of lakes	No. of fish	No.	%	% Mature	No.	%	% Mature	
NORTHERN	Lake trout	2	68	39	57	61.5	29	43	55.2	1.33
n=2)	Arctic char	1	9	6	67	16.7	3	33	33.3	
	Round whitefish	1	6	5	83	100	1	17	100	5.00
CENTRAL	Brook trout	14	168	92	55	50.0	76	45	35.5	1.22
(n=24)	White sucker	3	68	36	53	38.9	32	47	53.1	1.13
	Lake whitefish	1	44	25	57	100	19	43	100	
	Arctic char	4	43	13	38	38.5	21	62	53.3	0.61
	Lake trout	4	42	17	41	17.6	25	59	96.0	0.69
	Longnose sucker	3	8	3	38	100	5	62	100	0.61
	Northern pike	3	8	4	50	100	4	50	25	1.00
ASTERN	Longnose sucker	3	184	37	61	62.5	24	39	70.8	1.56
n=9)	Brook trout	8	62	42	68	40.5	20	32	75.0	2.13
	Atlantic salmon	4	27	13	52	30.8	12	48	0	1.08
	White sucker	1	17	8	50	85.7	8	50	100	1.00
OUTHERN	White sucker	15	327	143	44	69.4	175	56	73.7	0.82
n=31)	Brook trout	22	202	119	59	41.3	83	41	62.5	1.43
	Northern pike	11	61	32	52	93.7	29	48	89.6	1.10
	Longnose sucker	5	52	21	40	72.7	31	60	54.8	0.68
	Lake whitefish	1	4	1	25	100	3	.75	100	0.33
	Burbot	2	3	1	33	100	2	67	50	0.50
	Arctic char	2	2 2	2	100	100	0	0	0	-
	Lake trout	1	2	0	0	0	2	100	100	-

. . . Cont'd.

Table 5. (Cont'd.)

,			` .		Ma1	es		Fema	iles	Male:Female ratio  0.68 1.41 0.51 0.80 1.73 0.76 0.73 - 1.01 1.46 0.91 0.79 0.63 0.92 0.85
Region	Species	No. of lakes	No. of fish	No.	%	% Mature	No.	%	% Mature	
WESTERN	Lake trout	25	197	76	40	69.7	112	60	70.0	
(n=29)	White sucker	16	187	104	58	56.7	74	42	74.3	
	Lake whitefish Northern pike	15 14	173 96	52 35	34 44	65.5 90.9	101 44	66 56	74.0 97.5	
	Brook trout	8	94	. 57	63	36.2	33	37	63.8	
	Longnose sucker	18	84	34	43	75.0	45	57	88.8	
	Round whitefish	10	84	24	42	96.0	33	58	91.4	
	Arctic char	1	1	1	100	100	0	-	***	
TOTALS	White sucker	35	765	291	50	61.5	289	50	72.7	1.01
(n=95)	Brook trout	52	526	310	59	42.6	212	41	54.2	1.46
	Longnose sucker	22	328	95	47	70.5	105	53	74.3	0.91
	Lake trout	32	309	132	44	60.6	168	56	71.4	0.79
	Lake whitefish	16	222	78	39	76.9	123	61	87.0	0.63
	Northern pike	28	165	71	48	91.5	77	52	90.9	0.92
	Round whitefish	11	70	29	46	96.6	34	54	91.2	0.85
	Arctic char	8	46	22	48	40.9	24	52	50.0	0.92
	Atlantic salmon	4	27	13	52	30.8	12	48	0	1.08
	Burbot	2	3	1	33	100	2	67	50.0	0.50

Table 6. Mercury and aluminum levels (ppm) in fish tissue, by species and lake number.

			ľ	Mercury			Aluminum	
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Specie	es: La	ake trout						
302 357 360 362 373 487 502 503 505 507 512 513 515 518 591 520 533 524 525 526 528 529	50 5 6 10 5 2 8 10 1 3 10 5 3 36 8 1 13 7 2 2 10 3	0.06 0.15 0.20 0.20 0.43 0.59 0.28 0.13 0.63 0.24 0.20 1.03 0.03 0.30 0.15 0.26 0.91 0.62 0.37 0.77	0.68 0.56 0.99 0.91 1.55 0.74 1.21 0.44 0.76 0.87 0.36 1.18 1.37 1.14 1.44 0.51 1.05 0.81 0.86 1.05	0.20 0.29 0.51 0.40 0.78 0.67 0.59 0.33 0.54 0.69 0.49 0.30 1.12 0.24 0.62 1.27 0.48 0.43 0.98 0.71 0.60 0.86	4 20 33 20 80 100 63 0 100 100 20 0 100 3 63 100 33 29 100 100 100	0.81 0.40 0.81 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40 0.40	3.64 0.81 2.43 2.83 0.81 0.81 1.21 0.81 1.21 0.81 0.81 0.81 0.81 0.40 0.40 4.04 0.40	1.46 0.49 1.08 1.30 0.73 0.60 0.97 0.81 0.73 0.49 0.81 1.17 0.46 0.40 0.40 0.40 0.40
TOTALS	200	0.03	1.55	0.43	27	0.40	4.04	0.75

<sup>. . .</sup> Cont'd.

Table 6. (Cont'd.)

			Mer	cury			Aluminum	
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Specie	es: Bi	rook trout	_					
357 358 361	3 2 1	0.08 0.22	0.10 0.67	0.09 0.44 0.02	0 50 0	0.40	0.80 2.83	0.54 2.43
363 364 366 367 369	10 7 10 50 3	0.07 0.05 0.05 0.02 0.07	0.23 0.25 0.64 0.09 0.08	0.12 0.10 0.25 0.05 0.08	0 0 30 0	0.40 0.81 0.40 0.40 0.81	1.62 1.21 3.64 2.43 1.21	0.97 0.94 1.09 0.73 0.94
370 372 375 376 401	10 1 1 1 3	0.06	0.67	0.14 0.09 0.17 0.12 0.26	10 0 0 0 0 33	0.40	0.40	0.81 0.81 1.21 0.40
403 408 409 410	10 3 3 6	0.04 0.09 0.12 0.07	0.09 0.18 1.14 0.49	0.13 0.64 0.29	0 67 0	0.40 0.81 0.81 1.21	1.62 0.81 1.21 1.21	0.69 0.81 0.94 1.21
451 455 457 466	8 10 8 3 3	0.14 0.04 0.09 0.05	0.20 0.08 0.14 0.06	0.16 0.07 0.11 0.06	0 0 0	0.40 0.40 0.40 0.40	0.81 1.21 0.81 0.81	0.50 0.73 0.52 0.54
467 473 476 477 482	1 10 10 1	0.07 0.05 0.04	0.09 0.12 0.12	0.08 0.08 0.08 0.06 0.18	0 0 0 0	0.81 0.40	3.24 2.43 1.21	2.70 1.21 1.21 0.68 0.81
484 485 486 487	10 10 2 1	0.06 0.06 0.09	0.13 0.12 0.16	0.17 0.08 0.13	0 0	0.40 0.40 0.40	1.62 0.81 1.21	1.01 0.65 0.81 0.40
501 508 514	28 10 10	0.04 0.04 0.05	0.14 0.19 0.43	0.09 0.09 0.17	0 0 0	0.40 0.40 0.40	1.62 1.21 1.62	0.71 0.89 0.81
Total (33)	249	0.02	1.14	0.21	3	0.40	3.64	0.82

. . . Cont'd.

Table 6. (Cont'd.)

			Me	rcury			Aluminum	Mean 0.40 0.81 0.61
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Species	: A	tlantic sa	lmon					
401 404 409	1 10 1	0.11	0.44	0.32 0.30 0.30	0 0 0			
TOTALS (3)	12	0.11	0.44	0.30	0	0.40	0.81	•
Species	<u>:</u> : A	rctic char						
355 358 462 521	10 5 1 1	0.21 0.05	0.76 0.22	0.56 0.10 0.07 0.25	70 0 0 0	0.40	1.62 2.43	0.77 1.70 0.40 0.40
TOTALS (4)	17	0.05	0.76	0.41	41	0.40	2.43	1.00

<sup>. . .</sup> Cont'd.

Table 6. (Cont'd.)

			Me	rcury	<i>0</i>		Aluminum	
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Specie	<u>s</u> : N	orthern pil	ke					
373	3	0.45	1.55	0.98	67	0.81	2.43	1.35
377		0.45	0.87	0.66	50	0.81	0.81	0.81
378	3	0.12	0.32	0.22	0	0.40	0.81	0.68
462	2 3 3	0.63	0.69	0.66	100	0.40	1.21	0.81
468	1			0.99	0			0.49
474	7	0.10	0.25	0.16	0	0.40	1.21	0.69
475	10	0.18	1.11	0.44	20	0.40	0.81	0.57
480	2	0.48	1.07	0.77	50	0.81	1.62	1.21
481	10	0.08	0.33	0.20	0	0.40	1.21	0.89
487	4	0.64	1.07	0.88	100	0.40	1.21	0.71
506	15	0.17	0.89	0.47	40	0.40	1.21	0.81
509	6	1.07	1.86	1.39	100	0.40	1.22	0.74
513	3	0.43	0.48	0.46	0	0.81	1.21	0.94
515	5	0.45	1.15	0.66	60	0.00	1.21	0.49
516	5 2 3	0.33	0.58	0.45	50	0.40	1.21	0.69
517	3	0.36	0.53	0.47	67	0.40	0.81	0.68
520	13	0.48	0.99	0.72	85	0.40	1.21	0.54
524	1			0.47	0			0.81
525	5	0.52	1.29	0.76	100	0.40	1.21	0.81
526	5	0.23	0.42	0.36	0	0.40	4.86	2.19
528	2	0.28	0.71	0.49	50	1.22	2.44	1.82
529	6	0.32	0.67	0.51	50	0.40	0.40	0.40
TOTALS (22)	111	0.08	1.39	0.56	37	0.40	4.86	0.81

<sup>. . .</sup> Cont'd.

Table 6. (Cont'd.)

		Mercury			<u> </u>			
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Species	: Lá	ake Whitef	ish					
301 360 480 505 507 509 511 515 517 519 522 525 529	10 44 4 9 5 10 7 10 4 2 10 1	0.19 0.10 0.18 0.05 0.22 0.04 0.18 0.09 0.08 0.07 0.08	0.74 0.39 0.27 0.38 0.29 0.34 0.45 0.19 0.21 0.09 0.15	0.41 0.22 0.22 0.24 0.24 0.21 0.26 0.14 0.12 0.08 0.12 0.18 0.18	30 0 0 0 0 0 0 0	0.81 0.40 0.81 0.81 0.40 0.40 0.40 0.40 0.40	2.43 2.43 2.02 1.21 1.21 3.24 0.81 1.21 0.40 0.81 0.81	1.37 1.08 1.21 0.90 0.81 1.54 0.46 0.69 0.40 0.61 0.49 0.81 0.98
TOTALS (13)	123	0.05	0.74	0.22	2	0.40	3.24	0.97
Species	: R	ound white	fish					
507 518 524	2 14 3	0.10 0.11 0.19	0.22 0.23 0.34	0.16 0.18 0.26	0 0 0	2.02 0.40 0.40	2.02 3.64 0.81	2.02 1.88 0.54
*TOTALS (3)	19	0.10	0.34		0	0.40	3.64	1.68

<sup>. . .</sup> Cont'd.

Table 6. (Cont'd.)

			Mei	Aluminum				
Lake	N	Minimum	Maximum	Mean	% sample greater than 0.5 ppm	Minimum	Maximum	Mean
Species: White sucker								
373 374 378 402	2 10 3 10	0.11 0.05 0.12 0.07	0.21 0.38 0.20 0.11	0.16 0.12 0.15 0.09	0 0 0	0.81 0.40 0.81 0.40	0.81 1.62 1.21 0.81	0.81 0.97 0.94 0.61
453 456 458 459	10 50 10	0.06 0.02 0.05 0.10	0.53 0.15 0.42 0.27	0.19 0.07 0.13 0.18	10 0 0 0	0.81 0.40 0.81 0.40	1.62 1.21 1.62 3.64	1.13 0.66 1.13 1.62
462 463 465	6 10 50	0.06 0.05 0.06	0.19 0.57 0.15	0.09 0.15 0.10	0 0 0	0.40 0.40 0.40	1.62 1.21 1.62	0.81 0.77 0.70
466 468 469 472	4 10 10 10	0.06 0.12 0.08 0.11	0.09 0.25 0.39 0.33	0.07 0.19 0.16 0.23	0 0 0 0	0.40 0.40 0.40 0.81	0.81 0.81 4.05 2.43	0.51 0.73 1.30 1.21
478 486 487 504	5 8 2 34	0.15 0.09 0.03 0.02	0.21 0.44 0.13 0.21	0.18 0.17 0.08 0.06	. 0 0 0 0	0.81 0.81 0.40 0.40	1.62 2.02 0.81 2.43	0.97 1.11 0.61 1.08
511 513 517	3 2 3	0.04 0.07 0.07	0.05 0.09 0.28	0.04 0.08 0.15	0 0	0.40 0.81 0.81	0.81 1.21 1.62	0.54 1.01 1.08
525 526 528 *529	9 10 50 23	0.05 0.05 0.08 0.05	0.22 0.18 0.44 0.32	0.08 0.08 0.21 0.12	0 0 0 0	0.40 0.40 1.21 0.40	2.43 8.10 4.05 1.62	0.99 2.23 2.27 0.90
TOTALS	354	0.02	0.53	0.13	< 1	0.40	8.10	1.12

<sup>. . .</sup> Cont'd.

Table 6. (Cont'd.)

			Mei	Aluminum				
Lake N		Minimum Maximum Mean		% sample greater than 0.5 ppm	Minimum	Maximum	Mean	
Specie	<u>s</u> : Lo	ongnose su	cker					
357	2	0.08	0.32	0.20	0	0.81	0.81	0.81
401	39	0.05	0.20	0.10	0	0.40	1.21	0.68
406	10	0.06	0.14	0.10	. 0	0.40	1.21	0.69
488	10	0.05	0.12	0.07	0	0.40	1.62	0.85
504	16	0.06	0.49	0.14	0	0.40	1.62	0.94
505	1			0.09	0			1.21
527	10	0.08	0.44	0.21	0	1.21	4.05	2.27
529	16	0.09	0.25	0.18	0	0.40	2.83	0.99
Totals (8)	104	0.05	0.49	0.13	0	0.40	4.05	0.95

Table 7. Comparison of mean mercury levels in fish tissue from this survey with fish sampled during the DFO mercury survey of 1977-78.

Species	Labrador Headwater Lakes (this study)		Labrador Sites (Bruce and Spencer 1979)		Smallwood Reservoir Sites (Bruce and Spencer 1979)	
	n	- Нg	n	<del>-</del> Нд	n	- Нд
Lake trout	200	0.43	682	1.01	318	1.10
Brook trout	249	0.21	504	0.23	69	0.41
Arctic char (anad.) (landlocked)	17	0.41	377 107	0.04 0.35		
Atlantic salmon (anad.)	1	0.32	58	0.08		
Ouananiche	11	0.30	71	0.35	7	0.79
Northern pike	111	0.56	735	0.87	207	0.91
Lake whitefish	123 ·	0.22	2052	0.33	766	0.34
Round whitefish	19	0.19	77	0.14		
White sucker	354	0.13	420	0.16	54	0.35
Longnose sucker	104	0.13	826	0.35	153	0.38

Table 8. Correlation coefficients for significant regressions (p > 0.05) of mercury burden vs. length, weight, and age for species with a sample size of 10 fish or greater per lake.

Species	Lake #	N	Length	Weight	Age
Atlantic salmon	404	10	0.88	0.80	0.90
Brook trout	366 367 370 476 477 484 501 514	10 50 10 10 10 10 28 10	0.82 0.62 0.87 0.91 0.66 0.69 0.62 0.80	0.86 0.56 0.92 0.94 0.78 0.72 0.57	0.76 - 0.86 - - 0.70
Lake trout	301 302 362 503 512 518 519 523	10 50 10 10 10 36 (8)	0.87 0.75 0.83 0.77 0.94 0.81 0.81	0.81 0.85 0.76 0.64 0.95 0.91 0.77	0.93 0.67 0.81 - 0.93 0.86 0.87 0.96
Lake whitefish	360 509 511	44 10 (7)	0.46 0.64 0.86	0.53 0.66 0.73	- 0.79
Round whitefish	518	14	0.78	0.74	-
Northern pike	475 506 520	10 15 13	0.86 0.84 0.68	0.74 0.86	- 0.93 -
Longnose sucker	401 504	39 15	0.77 0.63	0.79 0.55	0.51
White sucker	374 453 456 463 465 469 472 504	10 10 50 10 50 10 10 10 35	- 0.89 0.59 0.85 0.59 0.83 0.64 0.83	0.80 0.56 0.89 0.63 0.84	0.87 - 0.53 0.86 0.38 0.70 - 0.66

. . . Cont'd.

Table 8. (Cont'd.)

Species	Lake #	N	Length	Weight	Age
	525 528 529	(9) 50 23	0.77 0.50 0.77	0.92 0.51 0.73	0.74 0.28 0.56
For all lakes combin	ned:				
Atlantic salmon		12	-	-	0.59
Arctic char		19	0.81	0.79	0.80
Brook trout		249	0.40	0.17	0.40
Lake trout		216	0.79	0.73	0.35
Lake whitefish		113	0.31	0.29	-
Round whitefish		19		-	-
Northern pike		112	0.40	0.55	0.61
Longnose sucker		98	0.60	0.63	0.50
White sucker		361	0.19	0.13	-

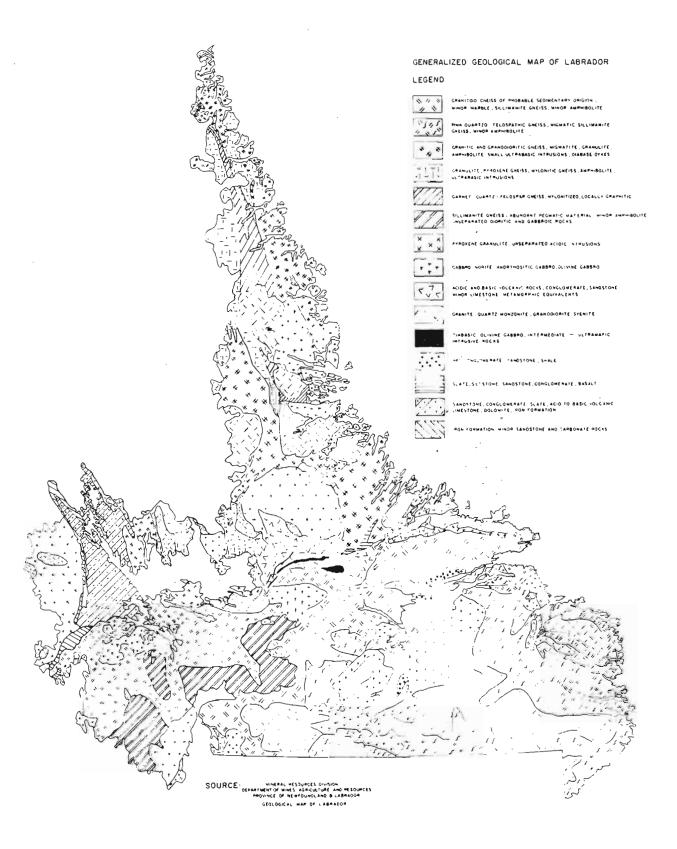


Fig. 1. Bedrock geology of Labrador.

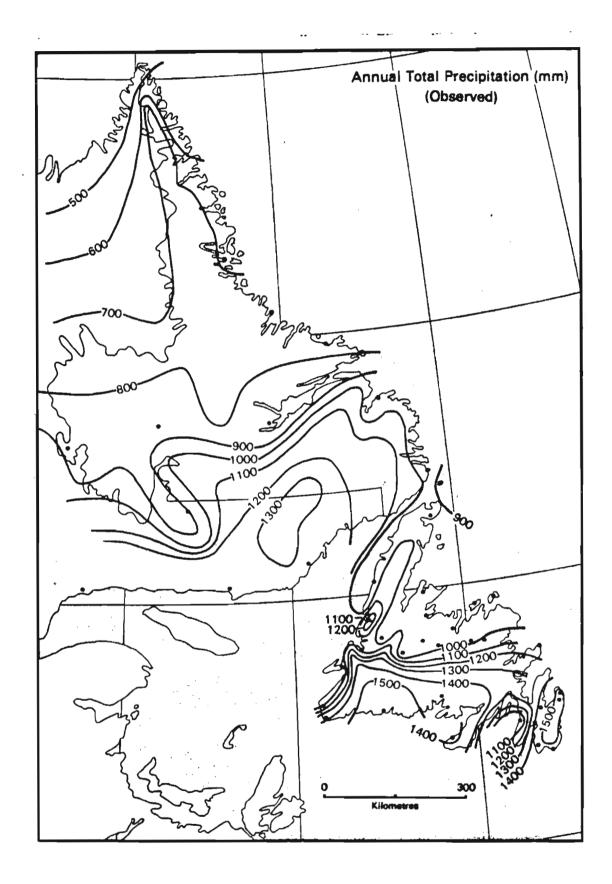


Fig. 2. Mean annual total precipitation (mm) for Newfoundland and Labrador (from MacPherson and MacPherson 1981).

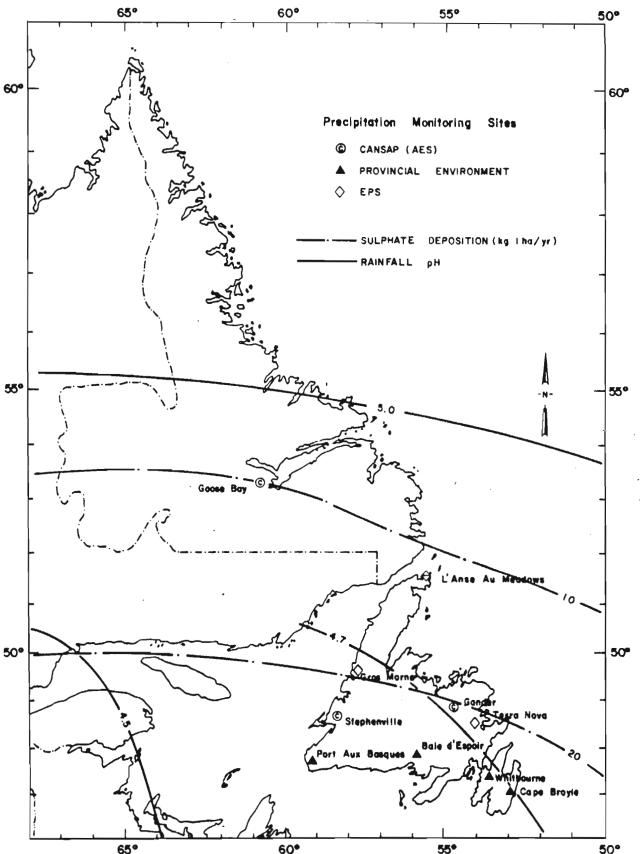


Fig. 3. Present deposition scenario in Newfoundland and Labrador, as rainfall pH and sulphate deposition (kg  $ha^{-1}$   $yr^{-1}$ ), including the location of existing precipitation monitors.

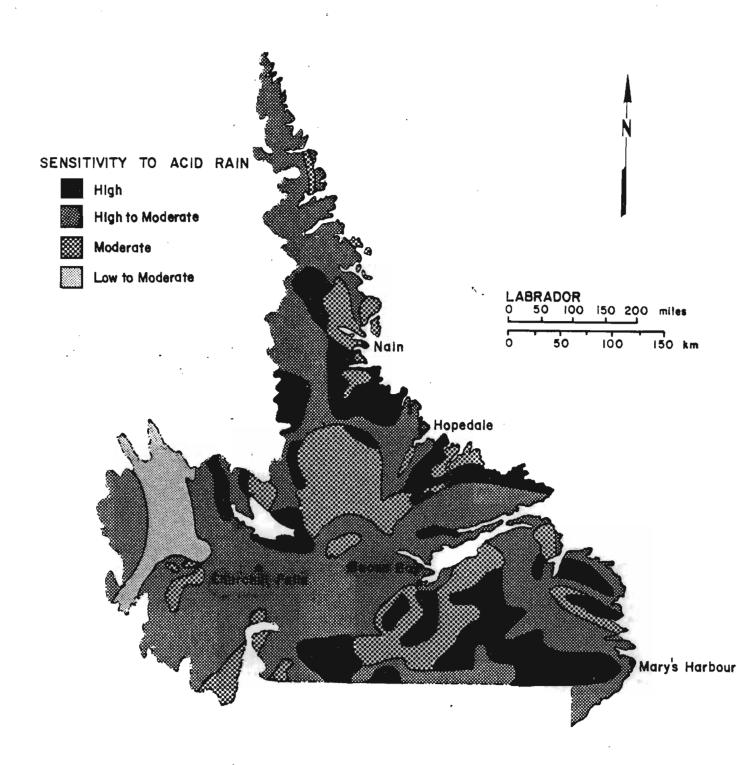


Fig. 4. Sensitivity of Labrador to acid deposition on the basis of bedrock geology (as produced by the Newfoundland Department of Mines and Energy).

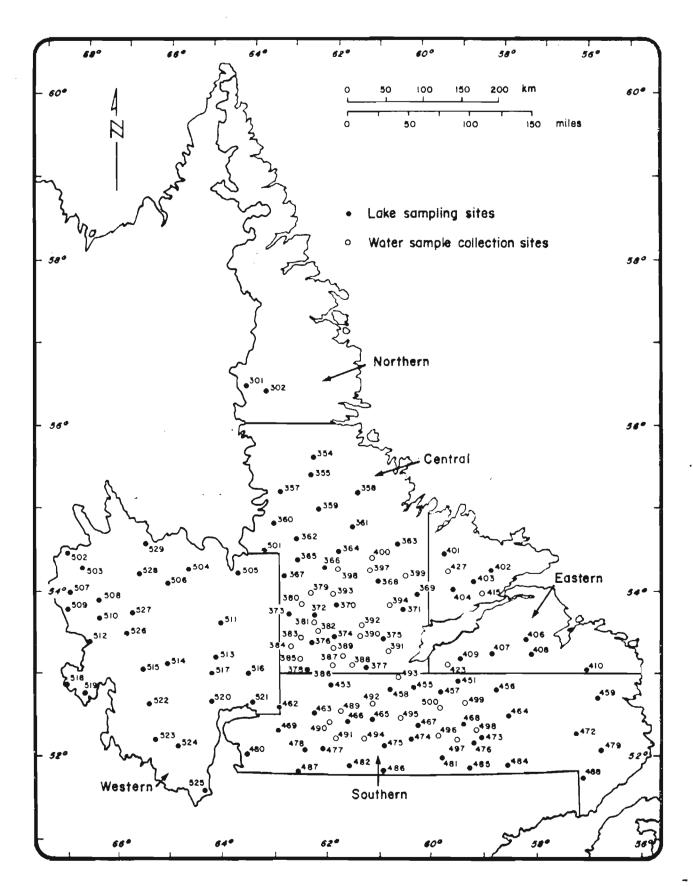


Fig. 5. Distribution of study lakes and geographical regions.

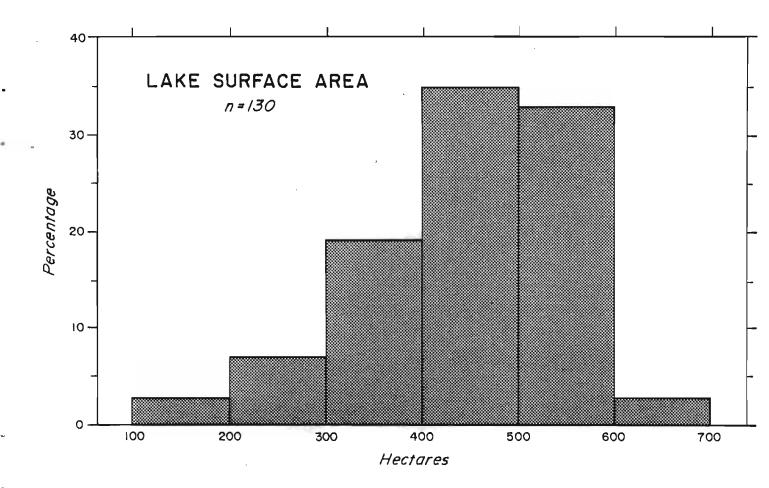


Fig. 6. Distribution of lakes by surface area (ha).



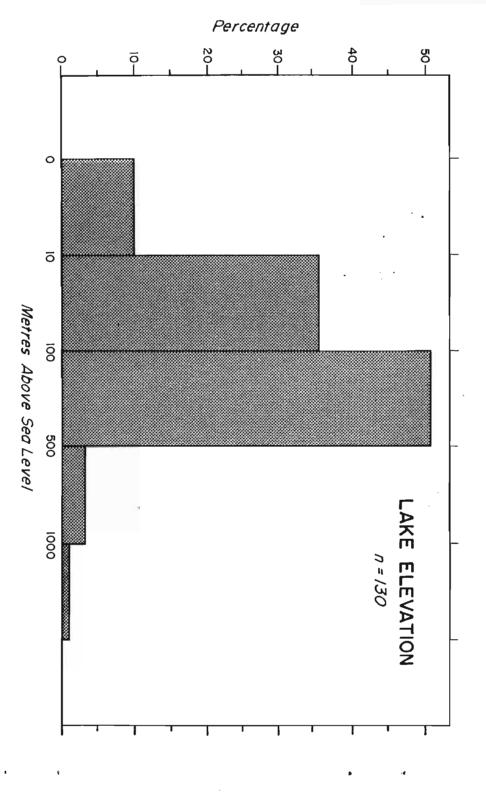


Fig. 7. Distribution of lakes by elevation

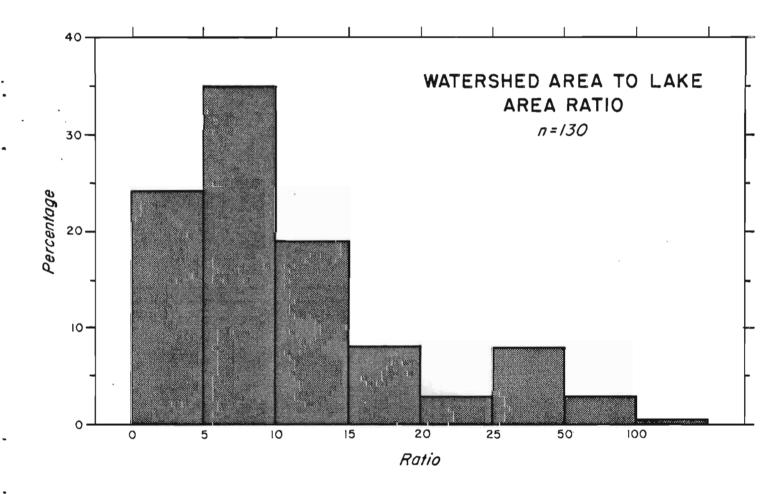


Fig. 8. Distribution of lake watershed area to lake surface area ratios (WA:LA).

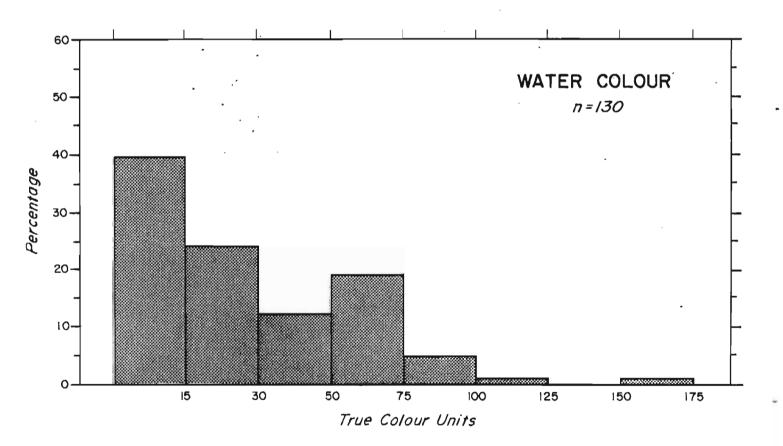


Fig. 9. Distribution of lakes by water color.

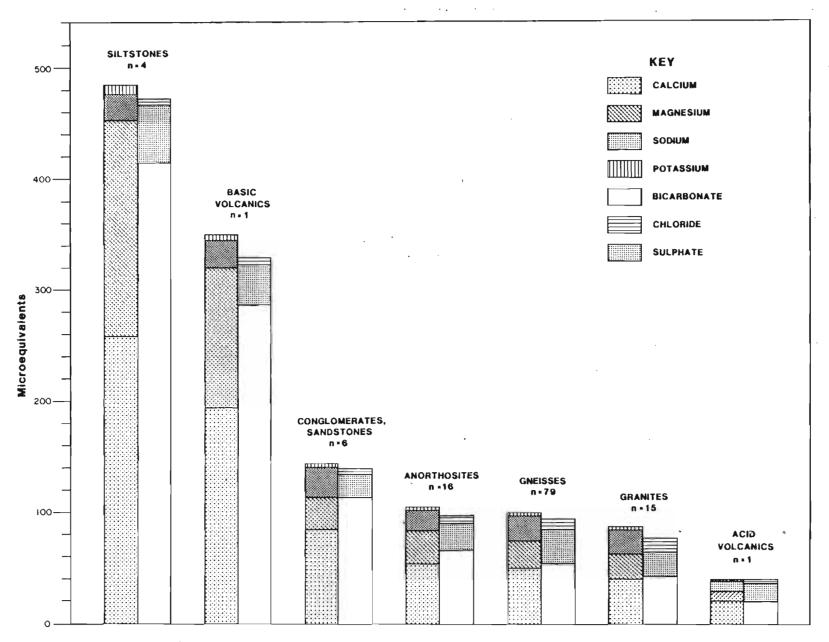


Fig. 10. Mean ionic composition of Labrador lakes within each geological type.

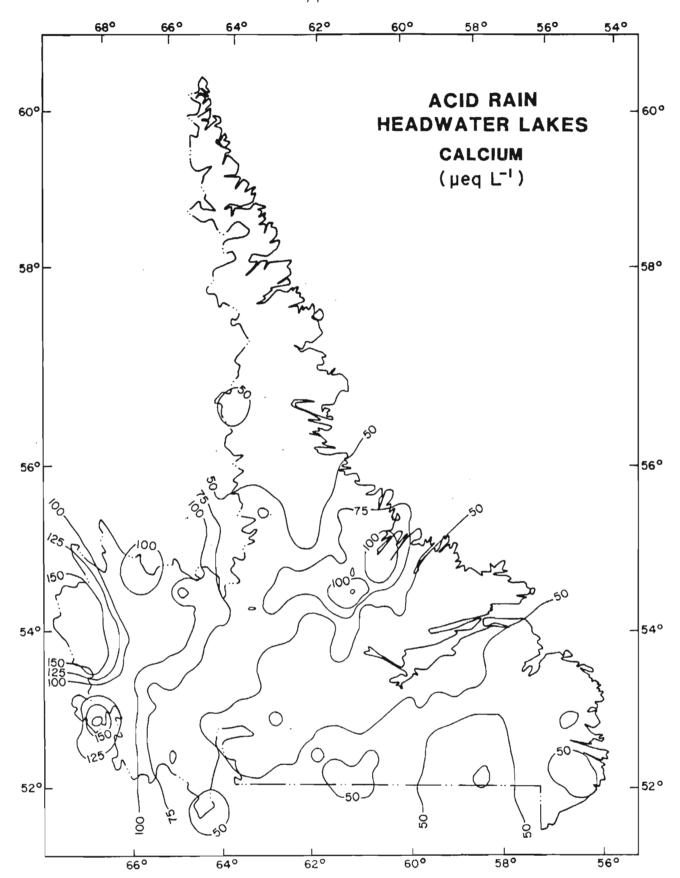


Fig. 11. Spatial distribution of calcium ( $\mu eq L^{-1}$ ).

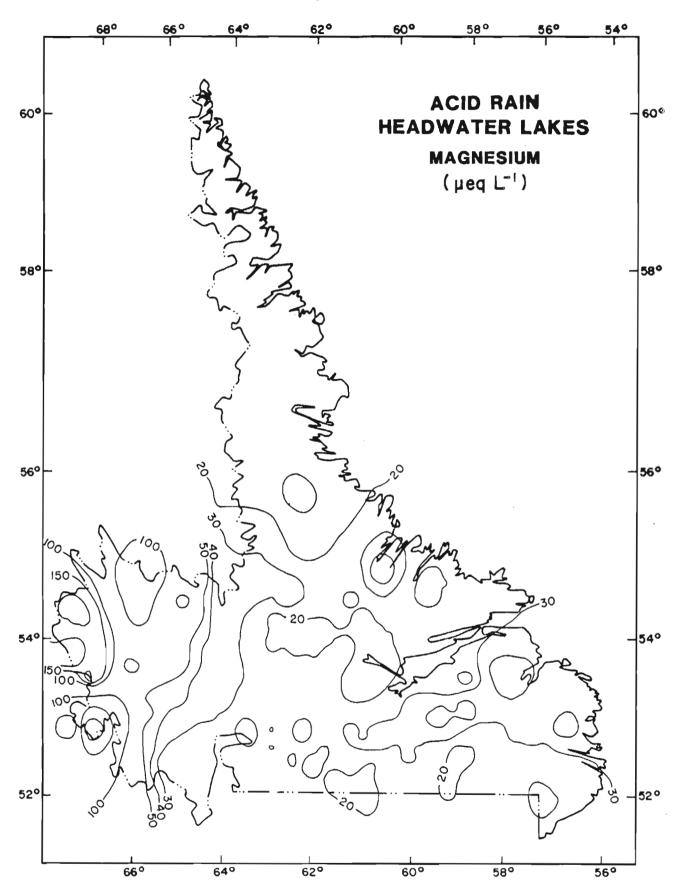


Fig. 12. Spatial distribution of magnesium ( $\mu eq\ L^{-1}$ ).

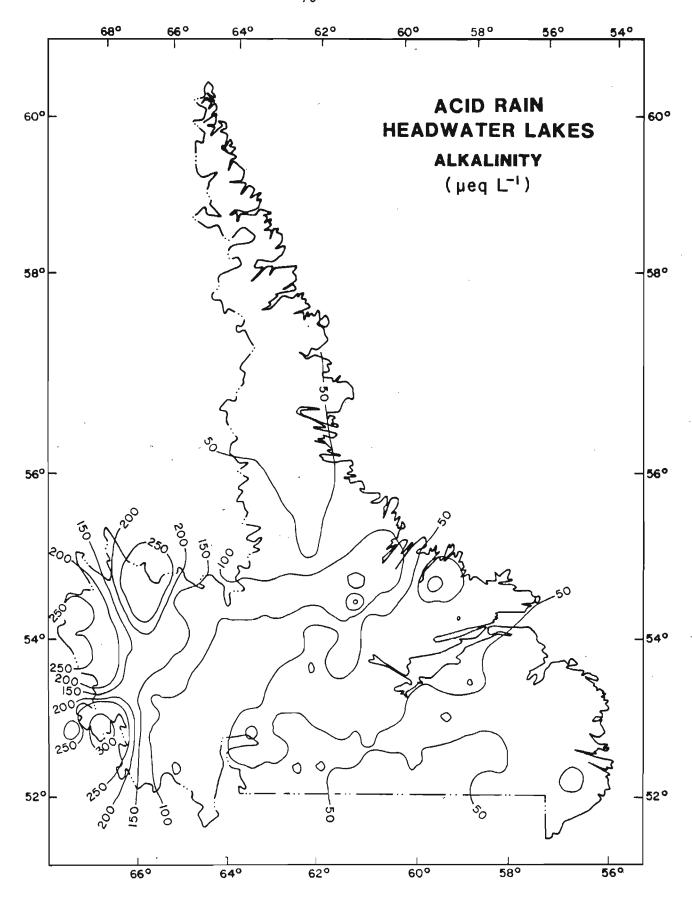


Fig. 13. Spatial distribution of alkalinity determined in the field (  $\mu eq~L^{-1}$  CaCO  $_3$  ).

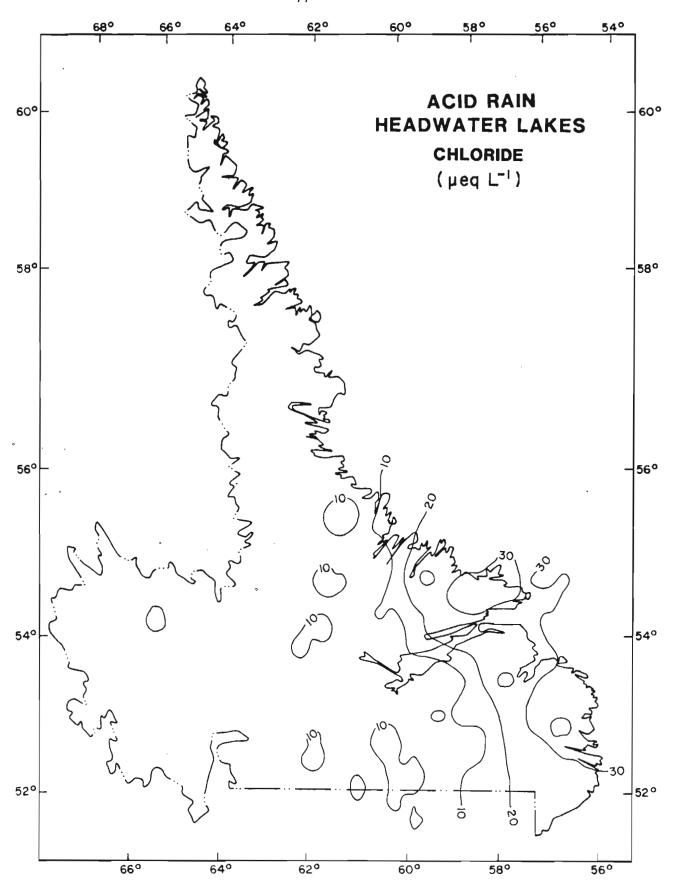


Fig. 14. Spatial distribution of chloride ( $\mu eq\ L^{-1}$ )

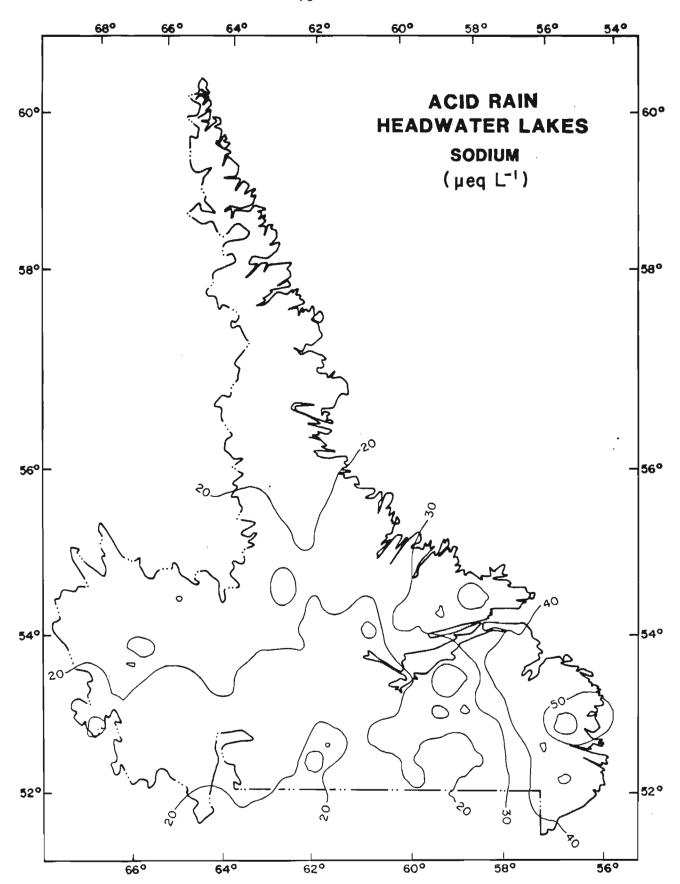


Fig. 15. Spatial distribution of sodium ( $\mu eq L^{-1}$ )

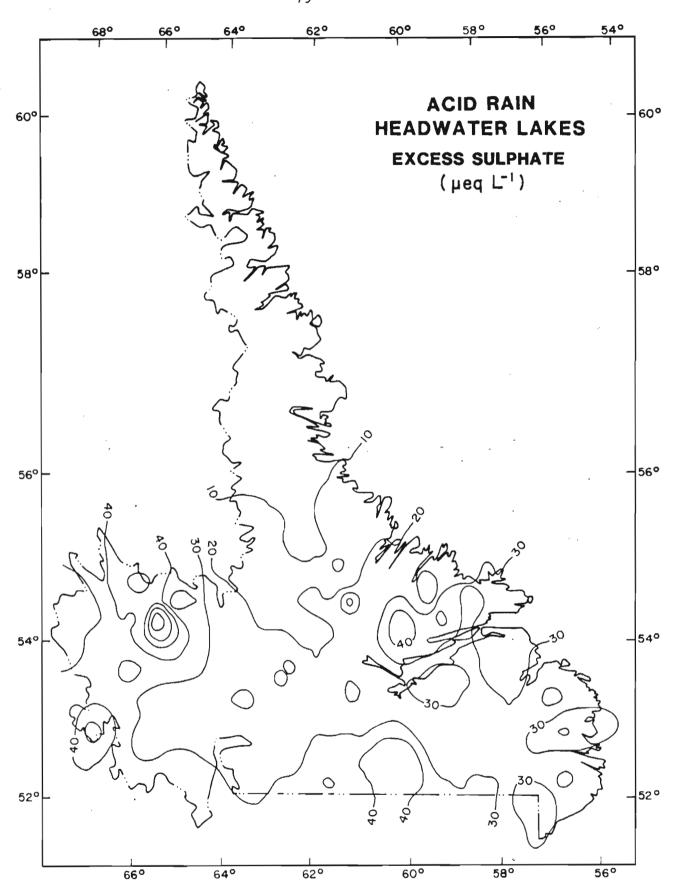


Fig. 16. Spatial distribution of "excess" sulphate ( $\mu eq L^{-1}$ )

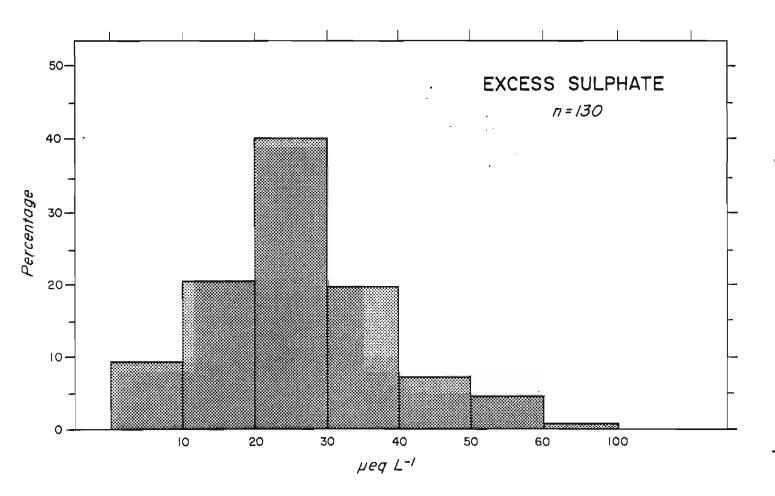
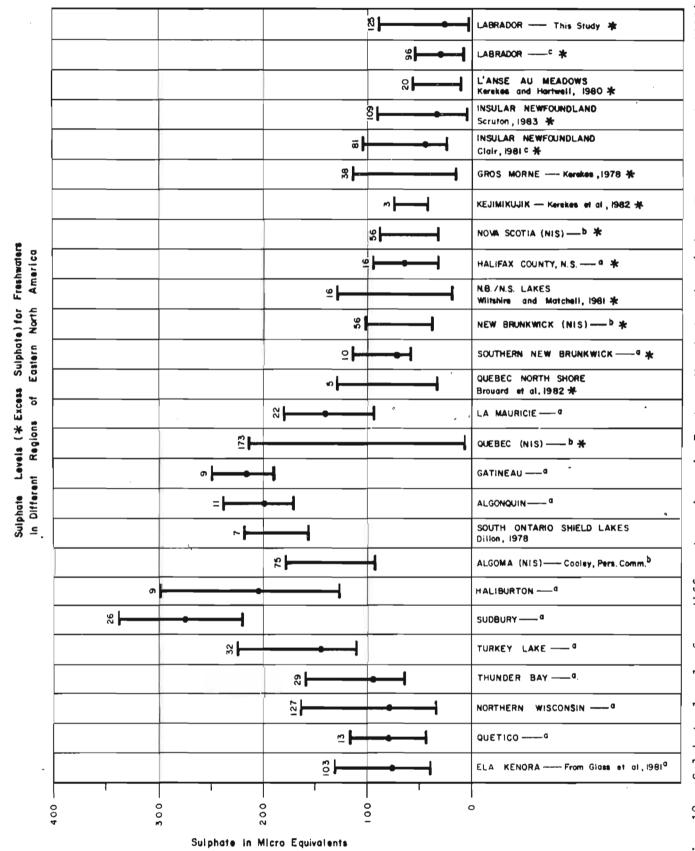


Fig. 17. Distribution of lakes by "excess" sulphate values ( $\mu eq~L^{-1}$ )



Eastern North America (after Thompson and Hutton 1982) ij different regions from Sulphate levels 18.

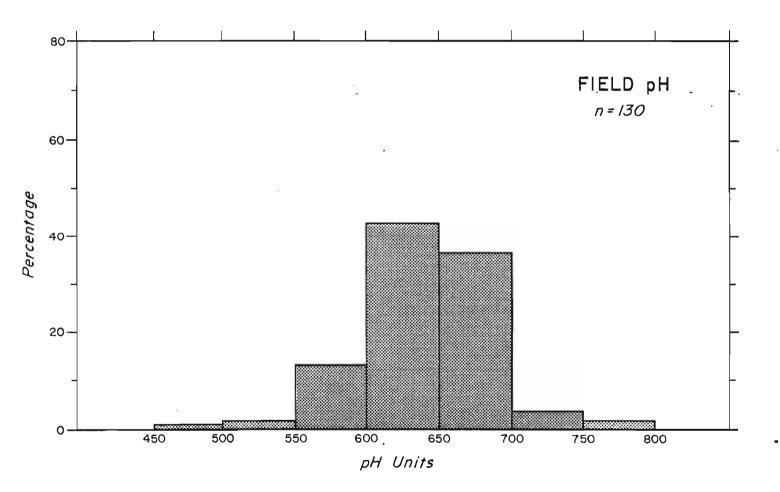


Fig. 19. Distribution of lakes by field pH.

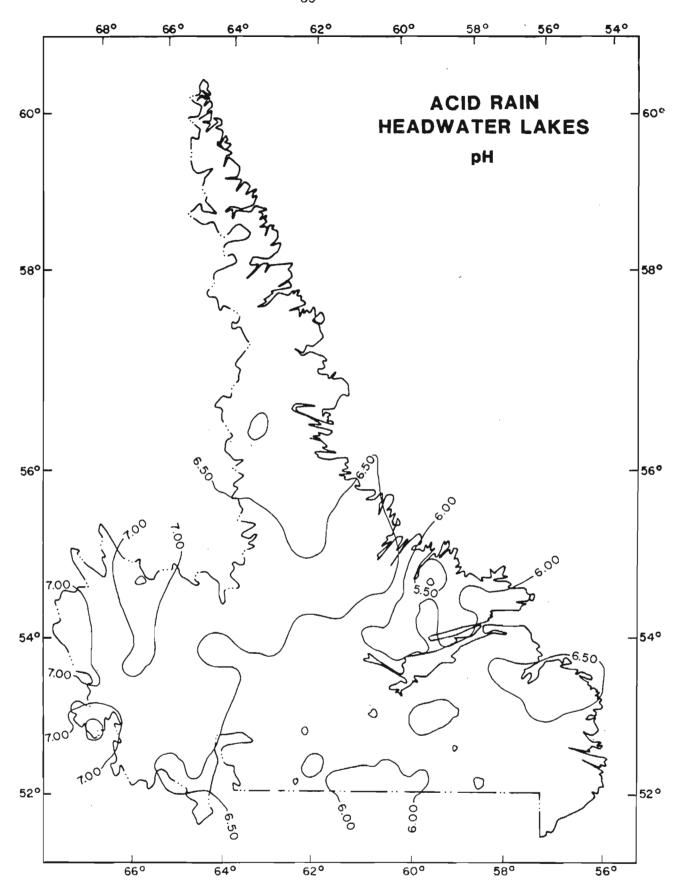


Fig. 20. Spatial distribution of pH values.

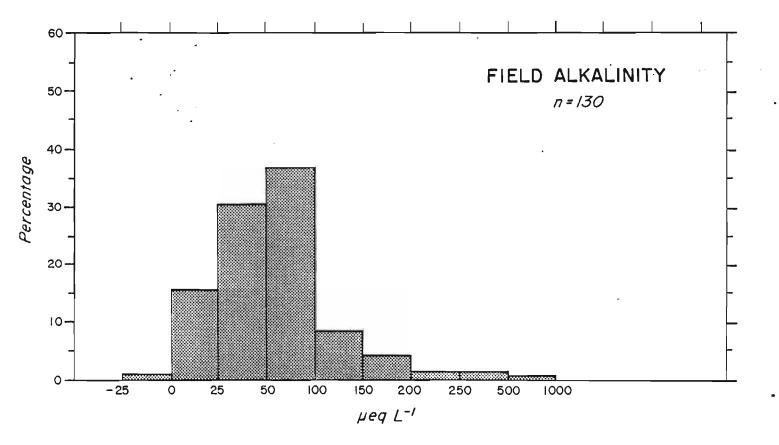


Fig. 21. Distribution of lakes by field alkalinity ( $\mu eq~L^{-1}~CaCo_3$ )

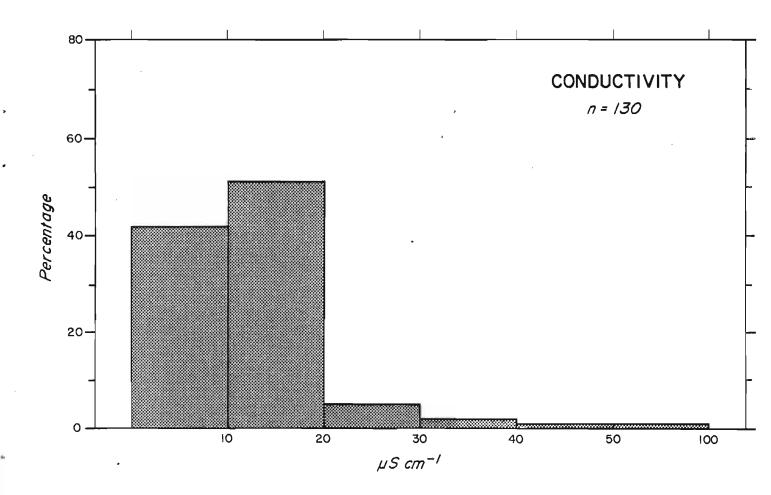


Fig. 22. Distribution of lakes by conductivity ( $\mu$  S cm<sup>-1</sup>).

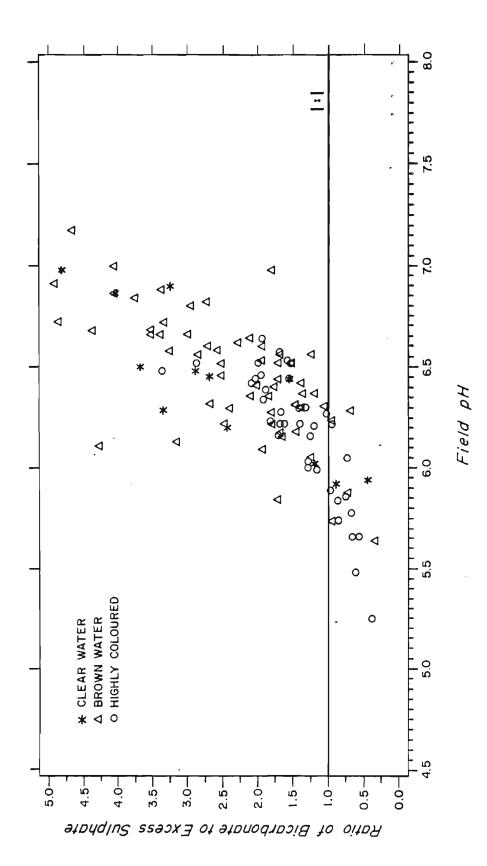


Fig. 23. A plot of lake pH versus the ratio of bicarbonate to "excess" sulphate.

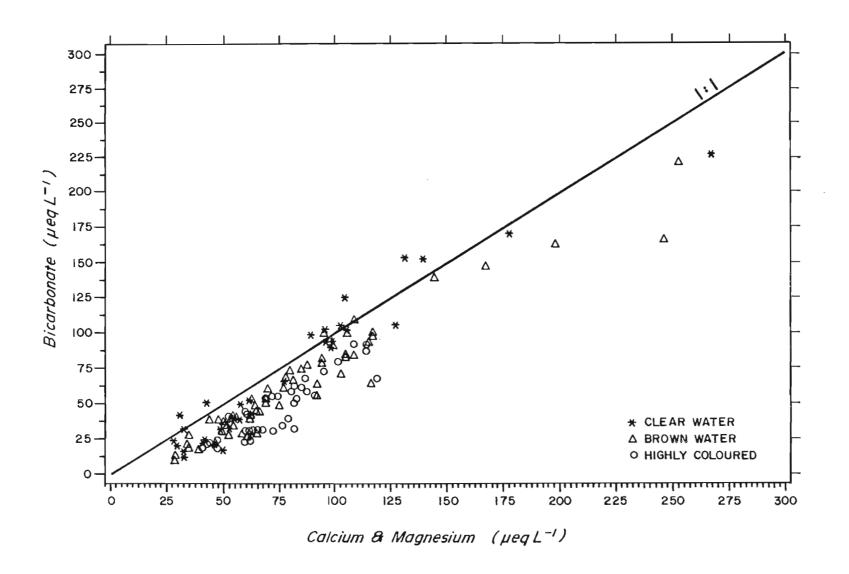


Fig. 24. A plot of the sum of "excess" calcium and magnesium (Ca+2 and Mg+2)versus bicarbonate (HCO $^{3}$ -).

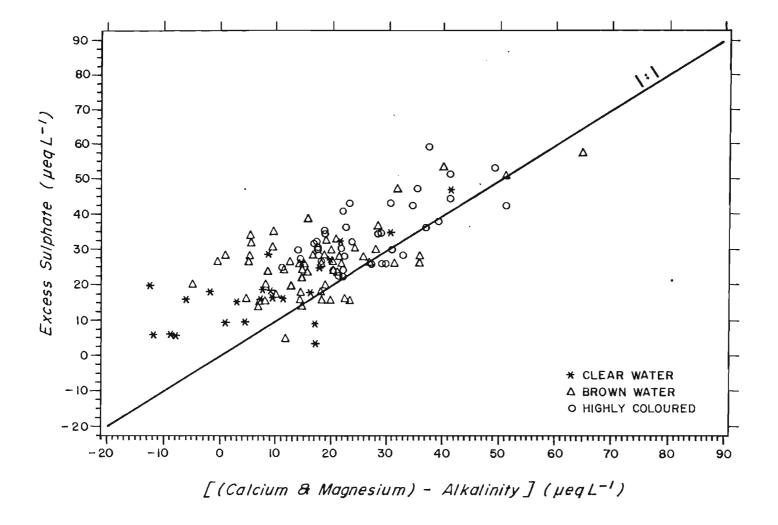


Fig. 25. A plot of the sum of "excess" calcium and magnesium minus nd  ${\rm Mg^{+2}}$ ) versus bicarbonate (HCO  $_3^-$ ). bicarbonate [(Ca $^{+2}$  + Mg $^{+2}$ ) - HCO $_3$ ] versus "excess" sulphate (SO $_4^{-2}$ ).

# **HENRIKSEN INDICATOR DIAGRAM**

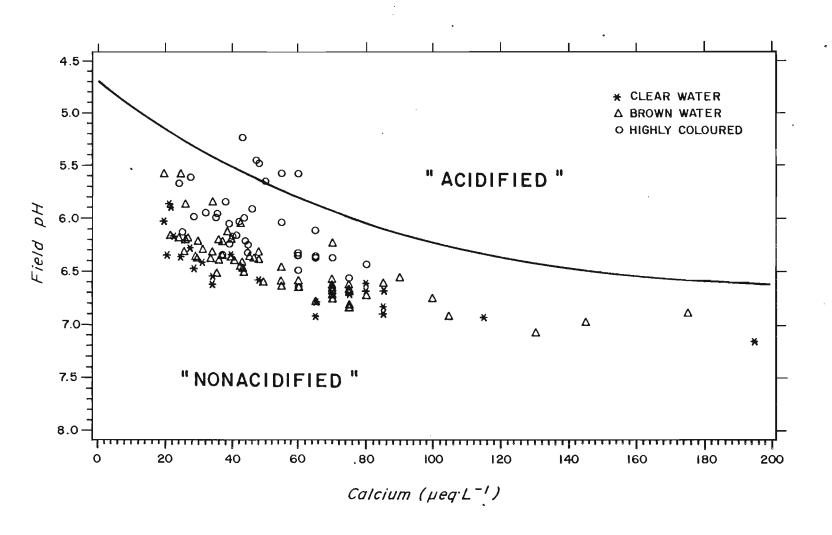


Fig. 26. A plot of Labrador study lakes on Henriksen's Indicator Diagram (Lake pH versus "excess" calcium).

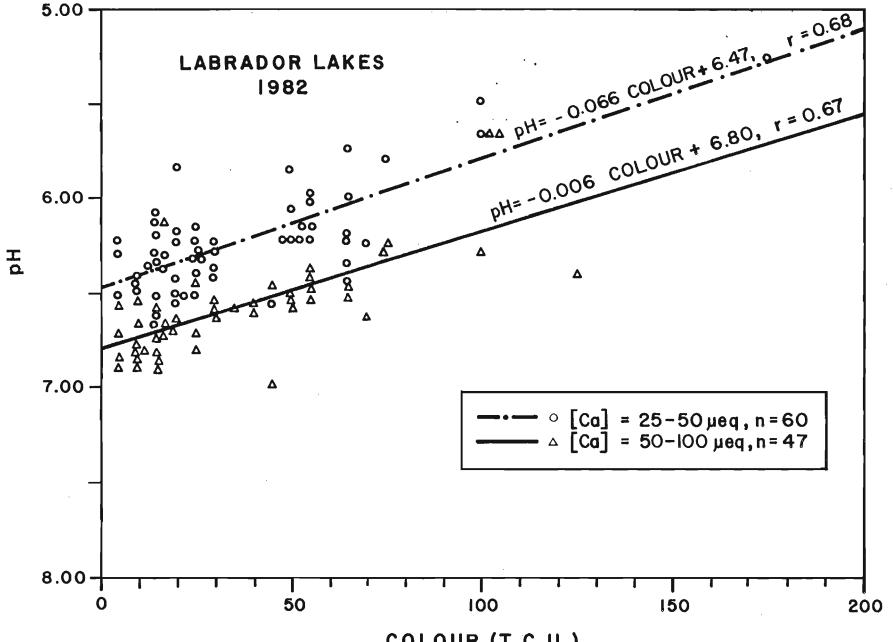


Fig. 27. A plot of pH vs colour for lakes grouped by calcium conentration.

# HENRIKSEN'S NOMOGRAPH

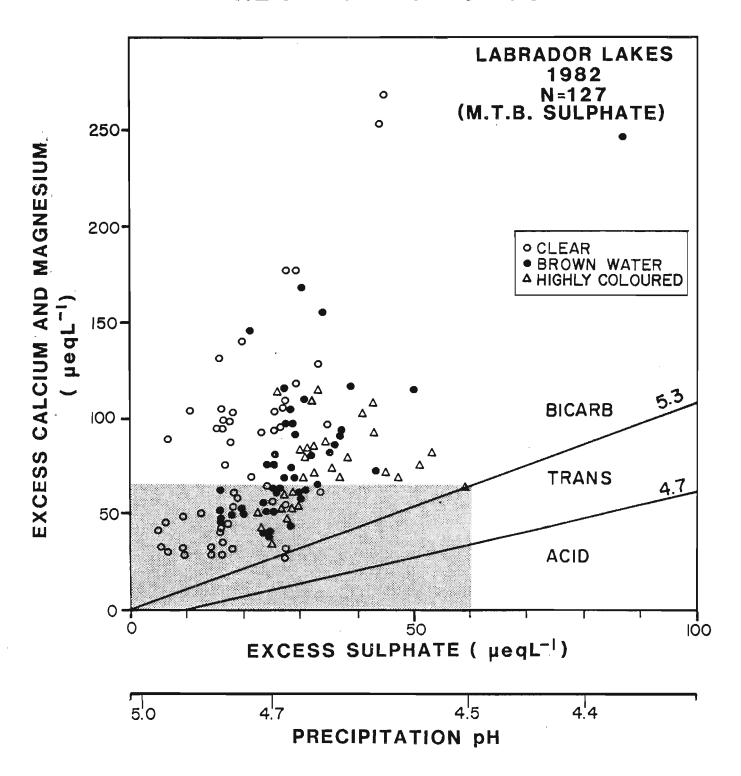


Fig. 28. A plot of Labrador study lakes on Henriksen's Nomograph ("excess" calcium and magnesium versus "excess" sulphate, or precipitation pH).

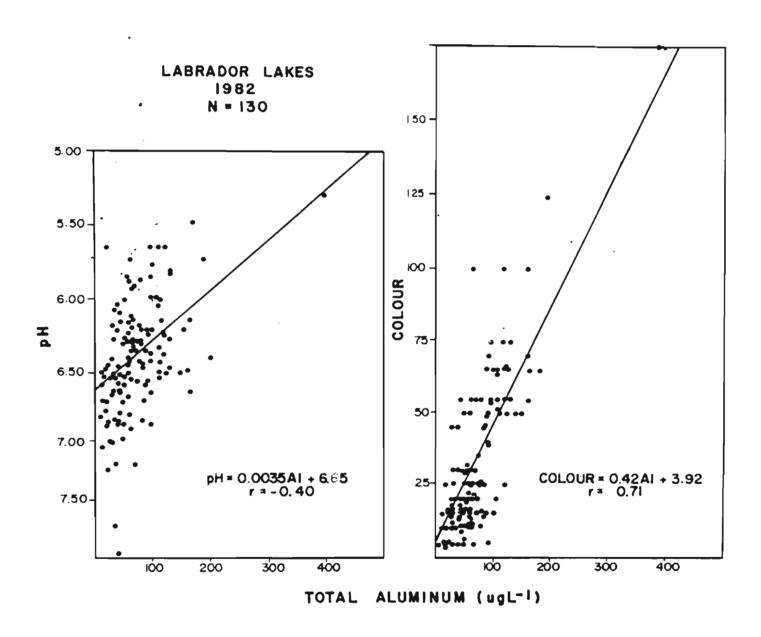


Fig. 29. pH and colour vs total aluminum for Labrador lakes.

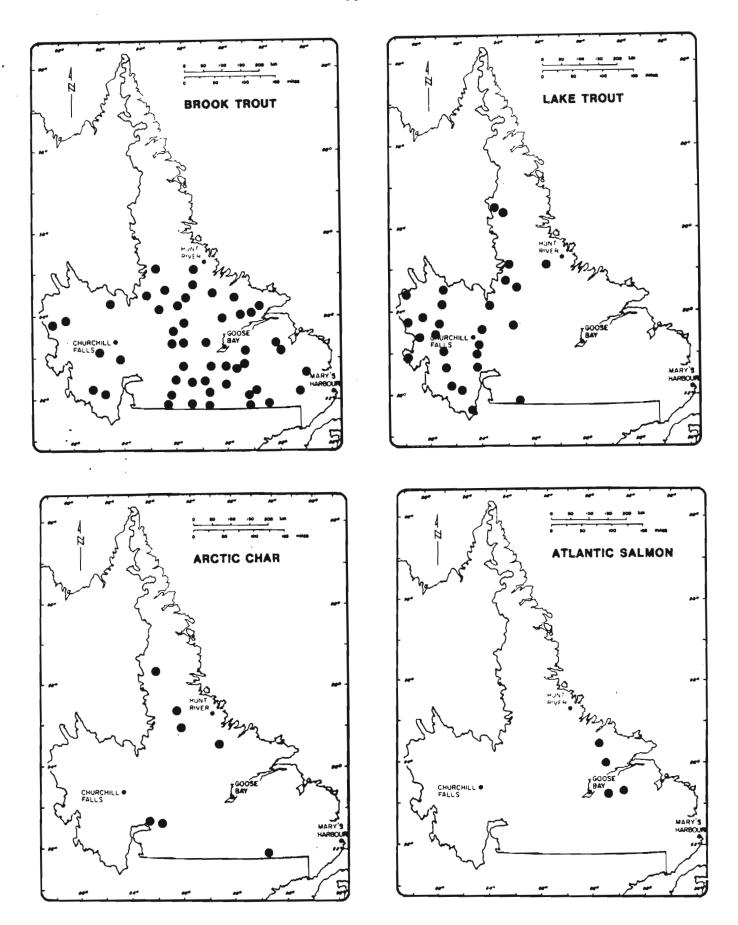


Fig. 30a. The distribution of fish species in the study lakes.

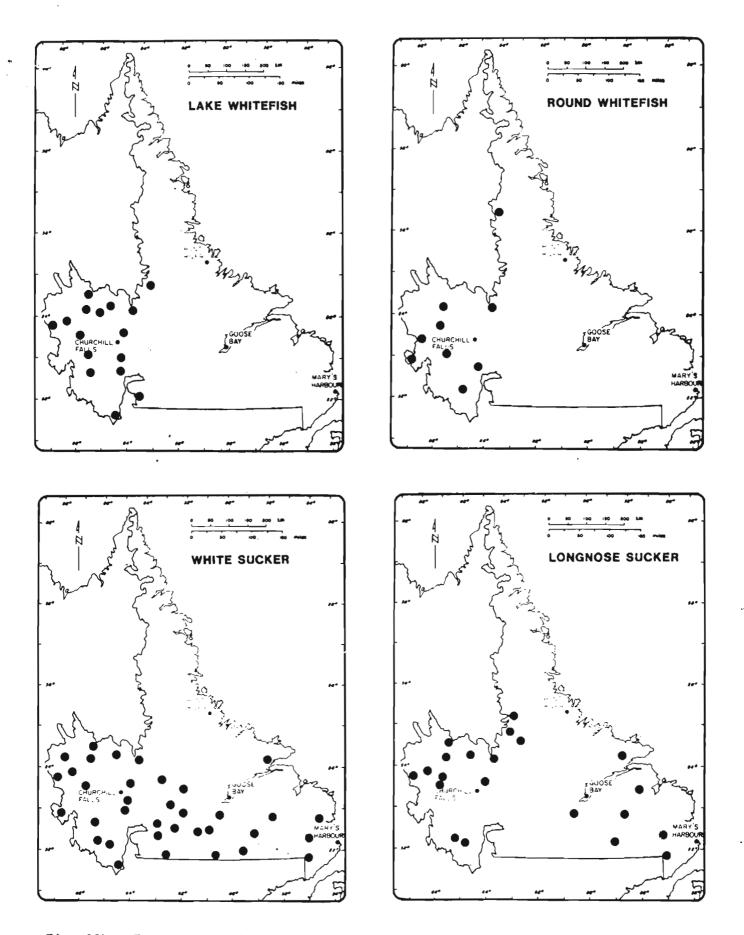


Fig. 30b. The distribution of fish species in the study lakes.

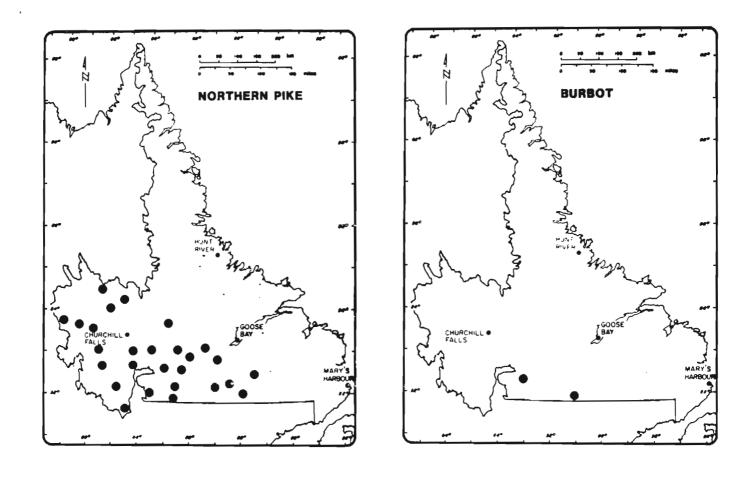
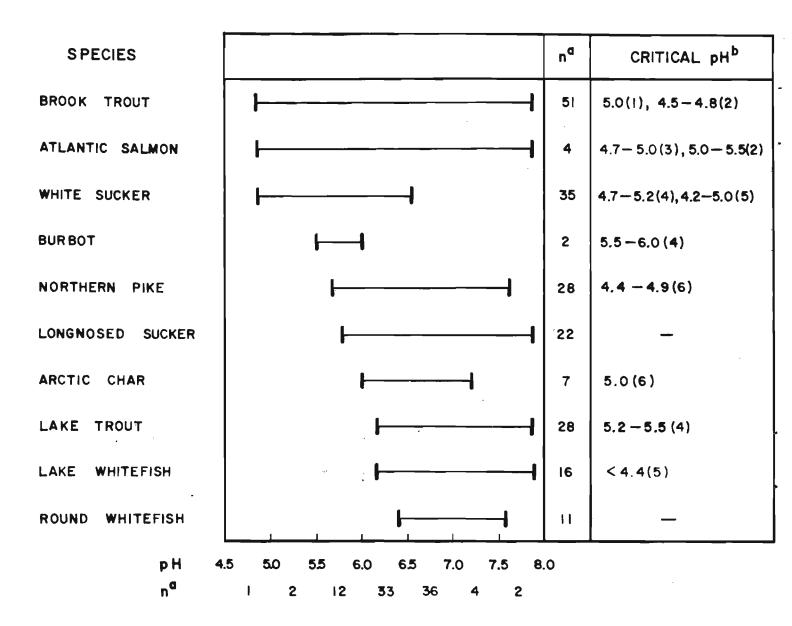


Fig. 30c. The distribution of fish species in the study lakes.



### References

- 1. Schofield 1976
- 2. Grande et al. 1978
- 3. Watt et al. 1983
- 4. Beamish 1976
- 5. Harvey 1980
- 6. Almer et al. 1974

Fig. 31. Occurrence of fish species from the study lakes in relation to pH, including critical pH levels of reproduction and recruitment (from the literature).

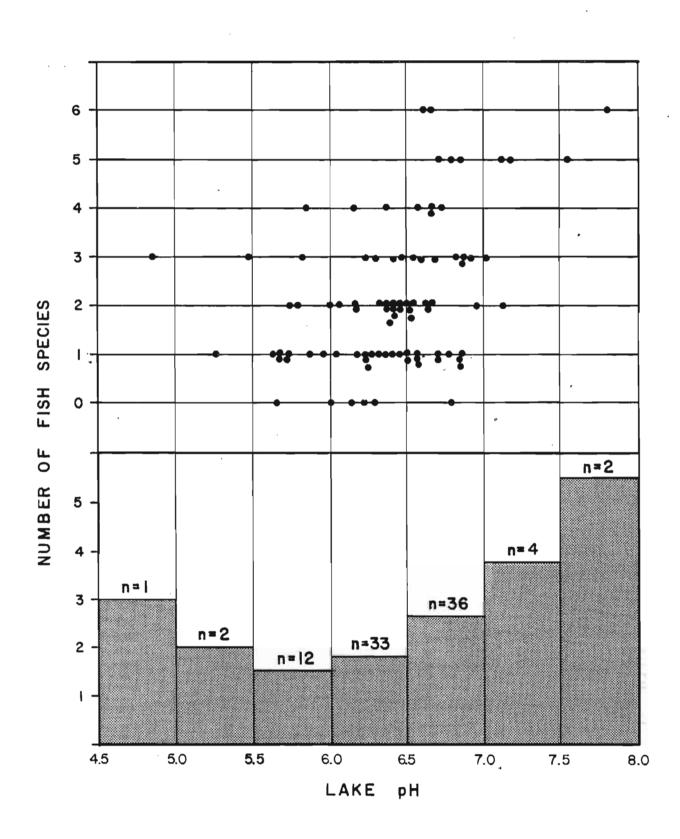


Fig. 32. Fish species diversity in relation to lake pH.

CORRELATION COFFEIGLENTS	/ PRAR >	IRI HNDER	HU-BHU=U	/ NIMBER (	NE CHSERVATIONS

APPENDIX 1: MATRIX OF CORRELATION COEFFICIENTS (LOG VS LOG REGRESSION) OF 45 PARAMETERS MEASURED IN

HEADWATER LAKES SURVEY

	FLD_PH	LAB_PH	SURFACE	MEAN_D	MAX_D	VOLUME	ELEVAT	DIST	DRAIN	RATIO	C02	DISC
FLD_PH	1.00000 0.0000 130	0.92186 0.0001 130	0.18816 0.0320 130	-0.03481 0.7669 75	0.22099 0.0314 95	-0.02323 0.8431 75	0.05535 0.5317 130	0.31576 0.0003 130	0.21683 0.0132 130	0.07410 0.4021 130	-0.21588 0.0136 130	0.30949 0.0023 95
LAB_PH	0.92186 0.0001 130	1.00000 0.0000 130	0.27439 0.0016 130	0.11105 0.3429 75	0.35293 0.0005 95	0.02034 0.8625 75	0.00654 0.9411 130	0.32403 0.0002 130	0.29625 0.0006 130	0.06460 0.4653 130	-0.10838 0.2197 130	0.41791 0.0001 95
SURFACE LAKE SURFACE AREA	0.18816 0.0320 130	0.27439 0.0016 130	1.00000 0.0000 130	0.13300 0.2553 75	0.49251 0.0001 95	0.73801 0.0001 75	-0.10804 0.2211 130	0.16947 0.0539 130		-0.19436 0.0267 130	-0.03859 0.6629 130	0.30568 0.0026 95
MEAN_D	-0.03481 0.7669 75	0.11105 0.3429 75	0.13300 0.2553 75	1.00000 0.0000 75	0.93223 0.0001 75	0.55663 0.0001 75	0.16244 0.1638 75	0.17089 0.1427 75	0.02604 0.8245 75	0.01550 0.8950 75	0.19981 0.0857 75	0.64496 0.0001 75
MAX D MAXTMUM DEPTH	0.22099 0.0314 95	0.35293 0.0005 95	0.49251 0.0001 95	0.93223 0.0001 75	1.00000 0.0000 95	0.50298 0.0001 75	0•19561 0•0575 95	0.27779 0.0064 95	0.39274 0.0001 95	-0.06612 0.5244 95	-0.04857 0.6402 95	0.78407 0.0001 95
VOLUME TO THE POWER OF 10	-0.02323 0.8431 75	0.02034 0.8625 75	0.73801 0.0001 75	0.55663 0.0001 75	0.50298 0.0001 75	1.00000 0.0000 75		-0.07507 0.5221 75	0.46618 0.0001 75	-0.05545 0.6366 75	-0.10681 0.3617 75	0.27730 0.0160 75
ELEVAT	0.05535 0.5317 130	0.00654 0.9411 130	-0.10804 0.2211 130	0.16244 0.1638 75	0.1956! 0.0575 95	-0.09770 0.4044 75	1.00000 0.0000 130		-0.16321 0.0635 130	-0.06360 0.4722 130	-0.09950 0.2600 130	0.12484 0.2280 95
DIST DISTANCE FROM COAST	0.31576 0.0003 130	0.32403 0.0002 130	0.16947 0.0539 130	0.17089 0.1427 75	0.27779 0.0064 95	-0.07507 0.5221 75	0.62954 0.0001 130	1.00000 0.0000 130	0.09998 0.2577 130	-0.05800 0.5121 130	0.16799 0.0561 130	0.15531 0.1329 95
DRAIN DRAINAGE AREA	0.21683 0.0132 130	0.29625 0.0006 130	0.82544 0.0001 130	0.02604 0.8245 75	0.39274 0.0001 95	0.46618 0.0001 75	-0.16321 0.0635 130	0.09998 0.2577 130	1.00000 0.0000 130	0.34915 0.0001 130	0.00717 0.9355 130	0.16601 0.1079 95
RATIO DRAINAGE/LAKE AREA	0.07410 0.4021 130	0.06460 0.4653 130	-0.19436 0.0267 130	0.01550 0.8950 75	-0.06612 0.5244 95	-0.05545 0.6366 75	-0.06360 0.4722 130	-0.05800 0.5121 130	0.34915 0.0001 130	1.00000 0.0000 130	0.08688 0.3257 130	-0.20882 0.0423 95

## APPENDIX 1 (Cont'd.).

### CORRELATION COEFFICIENTS / PROB > IRI UNDER HO:RHO=0 / NUMBER OF OBSERVATIONS

	FLD_PH	LAB_PH	SURFACE	MEAN_D	MAX_D	VOLUME	ELEVAT	DIST	DRAIN	RATIO	C02	DISC
CO2 ·	-0.21588 0.0136 130	-0.10838 0.2197 130	-0.03859 0.6629 130	0.19981 0.0857 75	-0.04857 0.6402 95	-0.10681 0.3617 75	-0.09950 0.2600 130	0.16799 0.0561 130	0.00717 0.9355 130	0.08688 0.3257 130	1.00000 0.0000 130	-0.09097 0.3806 95
DISC SECCHI DISC READING	0.30949 0.0023 95	0.41791 0.0001 95	0.30568 0.0026 95	0.64496 0.0001 75	0.78407 0.0001 95	0.27730 0.0160 75	0.12484 0.2280 95	0.15531 0.1329 95	0.16601 0.1079 95	-0.20882 0.0423 95	-0.09097 0.3806 95	1.00000 0.0000 95
FLD_ALK	0.85234 0.0001 129	0.77583 0.0001 129	0.08111 0.3608 129	-0.14568 0.2156 74		-0.04756 0.6874 74	-0.09785 0.2700 129	0.20860 0.0177 129	0.18034 0.0408 129	0.16522 0.0613 129	-0.11043 0.2128 129	0.13336 0.2001 94
LAB_ALK	0.92012 0.0001 130	0.88543 0.0001 130	0.13267 0.1324 130	-0.09807 0.4026 75		-0.10089 0.3891 75	-0.02645 0.7652 130	0.29473 0.0007 130	0.22219 0.0111 130	0.15153 0.0853 130	-0.06677 0.4504 130	0.15578 0.1317 95
CONDUCTIVITY	0.65973 0.0001 130	0.58146 0.0001 130	0.05440 0.5387 130	-0.14880 0.2026 75		-0.05155 0.6605 75	-0.21453 0.0142 130	0.11828 0.1802 130	0.16571 0.0595 130	0.17732 0.0436 130	-0.05474 0.5362 130	-0.04278 0.6806 95
TDS	0.04331 0.6246 130	-0.05704 0.5192 130	-0.22148 0.0113 130	-0.38931 0.0006 75		-0.04386 0.7087 75	-0.26858 0.0020 130	-0.17786 0.0429 130	-0.09486 0.2830 130	0.21338 0.0148 130	-0.01412 0.8733 130	-0.61450 0.0001 95
HARD TOTAL HARDNESS	0.72750 0.0001 130	0.63410 0.0001 130	0.03081 0.7278 130	-0.14823 0.2044 75	-0.04719 0.6497 95	-0.06306 0.5910 , 75		0.23294 0.0077 130	0.14318 0.1041 130	0.18383 0.0363 130	-0.05975 0.4995 130	-0.04478 0.6665 95
BICAR BICARBONATE	0.84191 0.0001 130	0.77176 0.0001 130	0.07420 0.4015 130	-0.15312 0.1897 75	0.05610 0.5892 95	-0.07537 0.5204 75	-0.08592 0.3311 130	0.22124 0.0114 130	0.17186 0.0506 130	0.16323 0.0635 130	-0.09528 0.2809 130	0.11755 0.2566 95
CA ,	0.71647 0.0001 130	0.65200 0.0001 130	0.06427 0.4676 130	-0.12781 0.2745 75	-0.01951 0.8511 95	-0.04507 0.7010 75		0.17401 0.0477 130	0.16652 0.0583 130	0.16292 0.0640 130	-0.05579 0.5284 130	0.9079
MG	0.69470 0.0001 130	0.59286 0.0001 130	0.00906 0.9185 130	-0.16987 0.1451 75	0.3629 95	-0.06481 0.5807 75	-0.02596 0.7694 130	0.26409 0.0024 130	0.09769 0.2689 130	0.15495 0.0784 130	-0.07206 0.4152 130	-0.11442 0.2696 95

APPENDIX 1 (Cont'd.).

### CORRELATION COEFFICIENTS / PROB > IRI UNDER HO:RHO=0 / NUMBER OF OBSERVATIONS

	FLD_PH	LAB_PH	SURFACE	MEAN_D	MAX_D	VOLUME	ELEVAT	DIST	DRAIN	RATIO	CO2	DISC
NA	0.31084 0.0003 130	0.28226 0.0011 130	-0.03968 0.6540 130				-0.41487 0.0001 130	-0.23688 0.0067 130	0.17626 0.0449 130	0.36013 0.0001 130	0.10656 0.2276 130	-0.19928 0.0529 95
κ .	0.27255 0.0017 130	0.21869 0.0124 130	0.14753 0.0939 130		0.4208		0.0329		0.15363 0.0810 130		0.03666 0.6788 130	-0.12946 0.2112 95
CL	-0.26383 0.0024 130	-0.22628 0.0096 130				-0.06481 0.5807 75	0.0001					-0.34975 0.0005 95
SO4	0.08908 0.3135 130	-0.03211 0.7169 130				0.5041	-0.07395 0.4030 130		0.00802 0.9279 130		0.17045 0.0525 130	-0.57318 0.0001 95
EX_SO4	0.10860 0.2187 130	-0.01661 0.8512 130				0.4867	0.6455			0.18802 0.0322 130		-0.56863 0.0001 95
P0 <b>4</b>	0.04095 0.6436 130	0.04739 0.5924 130	0.12564 0.1543 130						0.08544 0.3338 130	-0.06953 0.4319 130		0.04808 0.6436 95
NO3	-0.28686 0.0009 130	-0.25598 0.0033 130	0.5753	0.0564	0.23568 0.0215 95	0.0407	0.1399		0.01776 0.8411 130	-0.06299 0.4765 130	0.1225	0.26574 0.0092 95
CATION SUM OF CATIONS	0.71731 0.0001 130	0.63891 0.0001 130	0.03862 0.6626 130	-0.17863 0.1252 75			0.0363		0.16212 0.0653 130	0.20336 0.0203 130	-0.04255 0.6307 130	-0.06489 0.5321 95
ANION SUM OF ANIONS	0.69979 0.0001 130	0.63573 0.0001 130						0.18623 0.0339 130				-0.05071 0.6255 95
CONST SUM OF CONSTITUENTS	0.64817 0.0001 130	0.57374 0.0001 130	0.04941 0.5767 130		0.4317	0.5470			0.17979 0.0407 130	0.21471 0.0142 130	0.8038	-0.10272 0.3219 95

	FLD_PH	LAB PH	SURFACE	MEAN_D	MAX_D	VOLUME	ELEVAT	DIST	DRAIN	RATIO	CO2	DISC
TURBID TURBIDITY	-0.43234 0.0001 130	-0.45990 0.0001 130	-0.02759 0.7554 130	-0.33240 0.0036 75	-0.41143 0.0001 95	-0.07634 0.5151 75	-0.17277 0.0493 130	-0.22902 0.0088 130	0.04958 0.5754 130	0.11480 0.1934 130	0.24149 0.0056 130	-0.57645 0.0001 95
COLOR	-0.35081 0.0001 130	-0.41362 0.0001 130	-0.22842 0.0090 130		-0.61269 0.0001 95	-0.22882 0.0483 75	-0.22093 0.0115 130	-0.13605 0.1227 130	-0.04111 0.6424 130	0.32096 0.0002 130	0.27053 0.0019 130	-0.81474 0.0001 95
AL	-0.37985 0.0001 130	-0.36710 0.0001 130	-0.20599 0.0187 130	-0.09040 0.4405 75	-0.24570 0.0164 95		-0.20397 0.0199 130	-0.10174 0.2494 130	-0.08183 0.3547 130	0.21945 0.0121 130	0.17192 0.0505 130	-0.43084 0.0001 95
EX_NA	0.59713 0.0001 130	0.55716 0.0001 130	0.00405 0.9635 130	-0.16011 0.1700 75	-0.00868 0.9334 95		-0.18013 0.0403 130		0.11567 0.1900 130	0.20774 0.0177 130	0.06245 0.4802 130	0.02411 0.8166 95
EX_K	0.32577 0.0002 130	0.26457 0.0024 130	0.16630 0.0586 130	-0.17494 0.1333 75	-0.05942 0.5673 95	-0.10847 0.3543 75	0.22063 0.0117 130	0.0001	0.14768 0.0936 130	0.00719 0.9353 130	0.04261 0.6302 130	-0.10200 0.3253 95
EX_CA	0.71982 0.0001 130	0.65503 0.0001 130	0.06388 0.4703 130	-0.12541 0.2837 75	-0.01732 0.8677 95	-0.04434 0.7056 75	-0.16761 0.0566 130		0.16430 0.0618 130	0.16024 0.0686 130	-0.05676 0.5212 130	-0.00952 0.9271 95
EX_MG	0.72101 0.0001 130	0.61699 0.0001 130	0.00410 0.9630 130		-0.08709 0.4014 95	-0.06184 0.5982 75	0.02866 0.7462 130	0.0003	0.07437 0.4004 130	0.12784 0.1472 130	-0.06772 0.4440 130	-0.10595 0.3068 95
DOC	-0.29673 0.0006 130	-0.40750 0.0001 130	-0.27198 0.0017 130	-0.50686 0.0001 75	-0.64890 0.0001 95	-0.19764 0.0892 75	-0.14801 0.0928 130	-0.09416 0.2866 130	-0.13413 0.1282 130	0.23009 0.0084 130	0.18244 0.0377 130	-0.81044 0.0001 95
HOUR_F	0.24368 0.0179 94	0.26867 0.0088 94	0.40735 0.0001 94	-0.04880 0.6776 75	0.21050 0.0417 94	-0.08818 0.4519 .75	0.09506 0.3621 94	0.20781 0.0444 94	0.27242 0.0079 94	-0.17085 0.0997 94	0.04079 0.6963 94	0.26245 0.0106 94
DEP_ZOO	0.14845 0.1511 95	0.28177 0.0057 95	0.34274 0.0007 95	0.83790 0.0001 75	0.90930 0.0001 95	0.36436 0.0013 75	0.15806 0.1261 95	0•21761 0•0341 95	0.28543 0.0051 95	0.00503 0.9614 95		0.78868 0.0001 95

	FLD_ALK	LAB_ALK	COND	TDS	HARD	BICAR	CA	MG	NA	К	CL	S04
DIST DISTANCE FROM COAST	0.20860 0.0177 129	0.29473 0.0007 130	0.11828 0.1802 130	-0.17786 0.0429 130	0.23294 0.0077 130	0.22124 0.0114 130	0.17401 0.0477 130	0.26409 0.0024 130	-0.23688 0.0067 130	0.40029 0.0001 130	-0.50336 0.0001 130	0.18860 0.0316 130
DRAIN DRAINAGE AREA	0.18034 0.0408 129	0.22219 0.0111 130	0.16571 0.0595 130	-0.09486 0.2830 130	0.14318 0.1041 130	0.17186 0.0506 130	0.16652 0.0583 130	0.09769 0.2689 130	0.17626 0.0449 130	0.15363 0.0810 130	0.16608 0.0590 130	0.00802 0.9279 130
RATIO DRAINAGE/LAKE AREA	0.16522 0.0613 129	0.15153 0.0853 130	0.17732 0.0436 130	0.21338 0.0148 130	0.18383 0.0363 130	0.16323 0.0635 130	0.16292 0.0640 130	0.15495 0.0784 130	0.36013 0.0001 130	0.04460 0.6144 130	0.28862 0.0009 130	0.20257 0.0208 130
C02	-0.11043 0.2128 129	-0.06677 0.4504 130	-0.05474 0.5362 130	-0.01412 0.8733 130	-0.05975 0.4995 130	-0.09528 0.2809 130	-0.05579 0.5284 130	-0.07206 0.4152 130	0.10656 0.2276 130	0.03666 0.6788 130	0.08379 0.3433 130	0.17045 0.0525 130
DISC SECCHI DISC READING	0.13336 0.2001 94	0.15578 0.1317 95	-0.04278 0.6806 95	-0.61450 0.0001 95	-0.04478 0.6665 95	0.11755 0.2566 95	-0.01202 0.9079 95	-0.11442 0.2696 95	-0.19928 0.0529 95	-0.12946 0.2112 95	-0.34975 0.0005 95	-0.57318 0.0001 95
FLD_ALK	1.00000 0.0000 129	0.93583 0.0001 129	0.88920 0.0001 129	0.33823 0.0001 129	0.88321 0.0001 129	1.00000 0.0001 129	0.89790 0.0001 129	0.81246 0.0001 129	0.48661 0.0001 129	0.35347 0.0001 129	-0.06762 0.4464 129	0.28254 0.0012 129
LAB_ALK	0.93583 0.0001 129	1.00000 0.0000 130	0.77967 0.0001 130	0.22499 0.0101 130	0.84157 0.0001 130	0.91080 0.0001 130	0.84120 0.0001 130	0.80209 0.0001 130	0.42120 0.0001 130	0.30728 0.0004 130	-0.14434 0.1013 130	0.24237 0.0055 130
COND CONDUCTIVITY	0.88920 0.0001 129	0.77967 0.0001 130	1.00000 0.0000 130	0.51233 0.0001 130	0.94006 0.0001 130	0.86388 0.0001 130	0.95921 0.0001 130	0.86830 0.0001 130	0.60876 0.0001 130	0.43418 0.0001 130	0.15840 0.0719 130	0.50824 0.0001 130
TDS .	0.33823 0.0001 129	0.22499 0.0101 130	0.51233 0.0001 130	1.00000 0.0000 130	0.49919 0.0001 130	0.32505 0.0002 130	0.46642 0.0001 130	0.51812 0.0001 130	0.41113 0.0001 130	0.18375 0.0364 130	0.36364 0.0001 130	0.64659 0.0001 130
HARD TOTAL HARDNESS	0.88321 0.0001 129	0.84157 0.0001 130	0.94006 0.0001 130	0.49919 0.0001 130	1.00000 0.0000 130	0.87996 0.0001 130	0.94068 0.0001 130	0.91731 0.0001 130	0.51578 0.0001 130	0.41860 0.0001 130	0.02723 0.7585 130	0.49526 0.0001 130

CORRELATION COEFFICIENTS / PROB > IRI UNDER HO:RHO=0 / NUMBER OF OBSERVATIONS

	FLD_ALK	LAB_ALK	COND	TDS	HARD	BICAR	CA	MG	NA	K	CL	S04
BICAR BICARBONATE	1.00000 0.0001 129	0.91080 0.0001 130	0.86388 0.0001 130	0.32505 0.0002 130	0.87996 0.0001 130	1.00000 0.0000 130	0.89262 0.0001 130	0.81324 0.0001 130	0.46900 0.0001 130	0.33835 0.0001 130	-0.09194 0.2982 130	0.28961 0.0008 130
CA	0.89790	0.84120	0.95921	0.46642	0.94068	0.89262	1.00000	0.81550	0.51206	0.40604	0.05773	0.46929
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.5142	0.0001
	129	130	130	130	130	130	130	130	130	130	130	130
MG	0.81246	0.80209	0.86830	0.51812	0.91731	0.81324	0.81550	1.00000	0.46189	0.39707	-0.00804	0.55314
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.9276	0.0001
	129	130	130	130	130	130	130	130	130	130	130	130
NA	0.48661	0.42120	0.60876	0.41113	0.51578	0.46900	0.51206	0.46189	1.00000	0.14613	0.46302	0.29748
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0971	0.0001	0.0006
	129	130	130	130	130	130	130	130	130	130	130	130
Κ	0.35347	0.30728	0.43418	0.18375	0.41860	0.33835	0.40604	0.39707	0.14613	1.00000	-0.10043	0.40137
	0.0001	0.0004	0.0001	0.0364	0.0001	0.0001	0.0001	0.0001	0.0971	0.0000	0.2556	0.0001
	129	130	130	130	130	130	130	130	130	130	130	130
CL	-0.06762	-0.14434	0.15840	0.36364	0.02723	-0.09194	0.05773	-0.00804	0.46302	-0.10043	1.00000	0.24365
	0.4464	0.1013	0.0719	0.0001	0.7585	0.2982	0.5142	0.9276	0.0001	0.2556	0.0000	0.0052
	129	130	130	130	130	130	130	130	130	130	130	130
SO4	0.28254	0.24237	0.50824	0.64659	0.49526	0.28961	0.46929	0.55314	0.29748	0.40137	0.24365	1.00000
	0.0012	0.0055	0.0001	0.0001	0.0001	0.0008	0.0001	0.0001	0.0006	0.0001	0.0052	0.0000
	129	130	130	130	130	130	130	130	130	130	130	130
EX_SO4	0.28675	0.25704	0.49545	0.63865	0.49592	0.29717	0.46727	0.55857	0.26338	0.40636	0.18149	0.99714
	0.0010	0.0032	0.0001	0.0001	0.0001	0.0006	0.0001	0.0001	0.0025	0.0001	0.0388	0.0001
	129	130	130	130	130	130	130	130	130	130	130	130
P04	0.02422	0.02214	-0.00492	-0.04346	-0.00312	0.02591	0.01628	-0.05309	0.02557	-0.02728	0.00586	-0.08161
	0.7853	0.8026	0.9557	0.6234	0.9719	0.7698	0.8541	0.5486	0.7727	0.7580	0.9472	0.3560
	129	130	130	130	130	130	130	130	130	130	130	130
NO3	-0.06328 0.4762 129	-0.31128 0.0003 130	0.00918 0.9174 130	-0.01792 0.8396 130		-0.14106 0.1094 130	-0.04835 0.5849 130	-0.16658 0.0582 130	0.00223 0.9799 130	-0.06361 0.4721 130	0.04316 0.6258 130	-0.16381 0.0626 130

	FLD_ALK	LAB_ALK	COND	TDS	HARD	BICAR	CA	MG	NA	Κ	CL	SO4
CATION SUM OF CATIONS	0.89553 0.0001 129	0.84321 0.0001 130	0.98342 0.0001 130	0.51626 0.0001 130	0.95930 0.0001 130	0.88908 0.0001 130	0.96333 0.0001 130	0.90421 0.0001 130	0.64167 0.0001 130	0.43213 0.0001 130	0.11650 0.1868 130	0.51212 0.0001 130
ANION SUM OF ANIONS	0.88924 0.0001 129	0.83495 0.0001 130	0.97942 0.0001 130	0.49435 0.0001 130	0.94784 0.0001 130	0.87812 0.0001 130	0.95484 0.0001 130	0.0001	0.58891 0.0001 130	0.43381 0.0001 130	0.14640 0.0965 130	0.53161 0.0001 130
CONST SUM OF CONSTITUENTS	0.86886 0.0001 129	0.78778 0.0001 130	0.98746 0.0001 130	0.54125 0.0001 130	0.0001	0.85110 0.0001 130	0.95382 0.0001 130	0.88576 0.0001 130	0.62342 0.0001 130	0.45894 0.0001 130	0.17555 0.0457 130	0.57900 0.0001 130
TURBID TURBIDITY	-0.20855 0.0177 129	-0.25074 0.0040 130	-0.04848 0.5839 130	0.31274 0.0003 130	-0.07339 0.4067 130	-0.20317 0.0204 130	-0.10564 0.2316 130	-0.03346 0.7055 130	0.07184 0.4166 130	0.02534 0.7748 130	0.39760 0.0001 130	0.35303 0.0001 130
COLOR	-0.15432 0.0808 129	-0.16302 0.0638 130	0.02991 0.7355 130	0.60586 0.0001 130	0.06462 0.4651 130	0.1119		0.2054	0.21097 0.0160 130	0.09352 0.2899 130	0.44462 0.0001 130	0.63209 0.0001 130
AL	-0.26453 0.0025 129	-0.24941 0.0042 130	-0.12769 0.1477 130	0.36687 0.0001 130	-0.14356 0.1032 130			-0.11944 0.1759 130	0.01131 0.8984 130	-0.13122 0.1367 130	0.26221 0.0026 130	0.35485 0.0001 130
EX_NA	0.58354 0.0001 129	0.64978 0.0001 130	0.53172 0.0001 130	0.21250 0.0152 130	0.0001	0.59349 0.0001 130	0.53961 0.0001 130	0.50708 0.0001 130	0.70041 0.0001 130	0.18685 0.0333 130	-0.11704 0.1848 130	0.18468 0.0354 130
EX_K	0.38955 0.0001 129	0.34615 0.0001 130	0.44610 0.0001 130	0.17125 0.0514 130	0.44319 0.0001 130	0.37559 0.0001 130	0.42852 0.0001 130	0.42525 0.0001 130	0.13099 0.1374 130	0.97710 0.0001 130	-0.16437 0.0617 130	0.38445 0.0001 130
EX_CA	0.89889 0.0001 129	0.84352 0.0001 130	0.95720 0.0001 130	0.46407 0.0001 130	0.94080 0.0001 130	0.89397 0.0001 130	0.99992 0.0001 130	0.81586 0.0001 130	0.50666 0.0001 130	0.40637 0.0001 130	0.04744 0.5919 130	0.46765 0.0001 130
EX_MG	0.81097 0.0001 129	0.82075 0.0001 130	0.82550 0.0001 130	0.49640 0.0001 130	0.89886 0.0001 130	0.81465 0.0001 130	0.79596 0.0001 130	0.98770 0.0001 130	0.40145 0.0001 130	0.39303 0.0001 130	-0.12049 0.1721 130	0.53234 0.0001 130

APPENDIX 1 (Cont'd.).

	FLD_ALK	LAB_ALK	COND	TDS	HARD	BICAR	CA	MG	NA	κ	CL	S04
DOC	-0.08141	-0.12488	0.12520	0.68062	0.16636	-0.07807	0.07188	0.24336	0.24339	0.13982	0.40532	0.72027
	0.3591	0.1569	0.1558	0.0001	0.0585	0.3773	0.4164	0.0053	0.0053	0.1126	0.0001	0.0001
	129	130	130	130	130	130	130	130	130	130	130	130
HOUR_F	0•21040 0•0429 93	0.14874 0.1525 94	0.12684 0.2231 94	-0.19290 0.0625 94	0.10883 0.2964 94	0.18248 0.0783 94	0.10283 0.3240 94		0.05041 0.6294 94	0.28771 0.0049 94	-0.17413 0.0933 94	-0.17912 0.0841 94
DEP_ZOO	0.02415	0.06180	-0.06278	-0.46222	-0.06232	0.00510	-0.03906	-0.09933	-0.19112	-0.08571	-0.26064	-0.34321
	0.8173	0.5519	0.5456	0.0001	0.5486	0.9609	0.7071	0.3382	0.0636	0.4089	0.0107	0.0007
	94	95	95	95	95	95	95	95	95	95	95	95
ORDER	0.07453	0.11424	0.00682	-0.14861	-0.00453	0.06435	0.02350	-0.01727	0.08790	0.01917	-0.02686	-0.14540
	0.4012	0.1956	0.9386	0.0915	0.9592	0.4670	0.7908	0.8454	0.3200	0.8287	0.7617	0.0988
	129	130	130	130	130	130	130	130	130	130	130	130
GEOL WT WEIGHTED GEOLOGY	-0.45343 0.0001 119	-0.44830 0.0001 120	-0.33788 0.0002 120	0.08257 0.3699 120		0.0001	-0.43246 0.0001 120	-0.25862 0.0043 120		-0.00371 0.9679 120	0.27592 0.0023 120	0.09102 0.3228 120
	EX_S04	P04	NO3	CATION	ANION	CONST	TURBID	COLOR	AL	EX_NA	EX_K	EX_CA
FLD_PH	0.10860	0.04095	-0.28686	0.71731	0.69979	0.64817	-0.43234	-0.35081	-0.37985	0.59713	0.32577	0.71982
	0.2187	0.6436	0.0009	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001
	130	130	130	130	130	130	130	130	130	130	130	130
LAB_PH	-0.01661	0.04739	-0.25598	0.63891	0.63573	0.57374	-0.45990	-0.41362	-0.36710	0.55716	0.26457	0.65503
	0.8512	0.5924	0.0033	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0024	0.0001
	130	130	130	130	130	130	130	130	130	130	130	130
SURFACE LAKE SURFACE AREA	-0.10731 0.2243 130	0.12564 0.1543 130	0.04959 0.5753 130	0.03862 0.6626 130	0.07265 0.4114 130	0.04941 0.5767 130	-0.02759 0.7554 130	-0.22842 0.0090 130	-0.20599 0.0187 130	0.00405 0.9635 130	0.16630 0.0586 130	0.06388 0.4703 130
MEAN_D	-0.24251	-0.13584	0.22129	-0.17863	-0.16612	-0.18020	-0.33240	-0.46932	-0.09040	-0.16011	-0.17494	-0.12541
	0.0361	0.2452	0.0564	0.1252	0.1543	0.1219	0.0036	0.0001	0.4405	0.1700	0.1333	0.2837
	75	75	75	75	75	75	75	75	75	75	75	75

	EX_SO4	P04	NO3	CATION	ANION	CONST	TURBID	COLOR	AL	EX_NA	EX_K	EX_CA
MAX D MAXTMUM DEPTH	-0.36008 0.0003 95	-0.04892 0.6378 95	0.23568 0.0215 95	-0.06751 0.5156 95		-0.08162 0.4317 95	-0.41143 0.0001 95	-0.61269 0.0001 95	-0.24570 0.0164 95	-0.00868 0.9334 95	-0.05942 0.5673 95	-0.01732 0.8677 95
VOLUME TO THE POWER OF 10	-0.08155 0.4867 75	-0.12770 0.2749 75	0.23694 0.0407 75	-0.08680 0.4590 75				-0.22882 0.0483 75		-0.21614 0.0625 75	-0.10847 0.3543 75	-0.04434 0.7056 75
ELEVAT	-0.04073 0.6455 130	-0.09322 0.2915 130	-0.13018 0.1399 130	-0.18380 0.0363 130			-0.17277 0.0493 130	-0.22093 0.0115 130	-0.20397 0.0199 130	-0.18013 0.0403 130	0.22063 0.0117 130	-0.16761 0.0566 130
DIST DISTANCE FROM COAST	0.21907 0.0123 130	-0.09363 0.2894 130	-0.18500 0.0351 130	0.14938 0.0898 130	0.18623 0.0339 130	0.15684 0.0748 130	-0.22902 0.0088 130	-0.13605 0.1227 130	-0.10174 0.2494 130	0.05916 0.5037 130	0.45540 0.0001 130	0.17974 0.0407 130
DRAIN DRAINAGE AREA	-0.00853 0.9233 130	0.08544 0.3338 130	0.01776 0.8411 130	0.16212 0.0653 130	0.20232 0.0210 130	0.0407	0.04958 0.5754 130	-0.04111 0.6424 130	-0.08183 0.3547 130	0.11567 0.1900 130	0.14768 0.0936 130	0.16430 0.0618 130
RATIO DRAINAGE/LAKE AREA	0.18802 0.0322 130	-0.06953 0.4319 130	-0.06299 0.4765 130	0.20336 0.0203 130	0.21157 0.0157 130	0.21471 0.0142 130	0.11480 0.1934 130	0.32096 0.0002 130	0.21945 0.0121 130	0.20774 0.0177 130	0.00719 0.9353 130	0.16024 0.0686 130
CO2	0.16712 0.0574 130	0.03915 0.6583 130	-0.13614 0.1225 130	-0.04255 0.6307 130	-0.03610 0.6834 130		0.24149 0.0056 130	0.27053 0.0019 130	0.17192 0.0505 130	0.06245 0.4802 130	0.04261 0.6302 130	-0.05676, 0.5212 130
DISC SECCHI DISC READING	-0.56863 0.0001 95	0.04808 0.6436 95	0.26574 0.0092 95	-0.06489 0.5321 95	-0.05071 0.6255 95	-0.10272 0.3219 95	-0.57645 0.0001 95	-0.81474 0.0001 95	-0.43084 0.0001 95	0.02411 0.8166 95	-0.10200 0.3253 95	-0.00952 0.9271 95
FLD_ALK	0.28675 0.0010 129	0.02422 0.7853 129	-0.06328 0.4762 129	0.89553 0.0001 129	0.88924 0.0001 129	0.86886 0.0001 129	-0.20855 0.0177 129	-0.15432 0.0808 129	-0.26453 0.0025 129	0.58354 0.0001 129	0.38955 0.0001 129	0.89889 0.0001 129
LAB_ALK	0.25704 0.0032 130	0.02214 0.8026 130	-0.31128 0.0003 130	0.84321 0.0001 130	0.83495 0.0001 130	0.78778 0.0001 130	-0.25074 0.0040 130	-0.16302 0.0638 130	-0.24941 0.0042 130	0.64978 0.0001 130	0.34615 0.0001 130	0.84352 0.0001 130

APPENDIX 1 (Cont'd.).

CORRELATION COEFFICIENTS	/ PROB	> 181	UNDER HO:RHO=0	/ NUMBER	OF	OBSER VATIONS

	EX_S04	P04	103	CATION	ANION	CONST	TURBID	COLOR	AL	EX_NA	EX_K	EX_CA
COND CONDUCTIVITY	0.49545 0.0001 130	-0.00492 0.9557 130	0.00918 0.9174 130	0.98342 0.0001 130	0.97942 0.0001 130	0.98746 0.0001 130	-0.04848 0.5839 130	0.7355	-0.12769 0.1477 130	0.53172 0.0001 130	0.44610 0.0001 130	0.95720 0.0001 130
TDS	0.63865 0.0001 130	-0.04346 0.6234 130	-0.01792 0.8396 130	0.51626 0.0001 130	0.49435 0.0001 130	0.54125 0.0001 130	0.31274 0.0003 130	0.0001	0.36687 0.0001 130	0.21250 0.0152 130	0.17125 0.0514 130	0.46407 0.0001 130
HARD TOTAL HARDNESS	0.49592 0.0001 130	-0.00312 0.9719 130	-0.08593 0.3310 130	0.95930 0.0001 130	0.94784 0.0001 130	0.94349 0.0001 130	-0.07339 0.4067 130		-0.14356 0.1032 130	0.55210 0.0001 130	0.44319 0.0001 130	0.94080 0.0001 130
BICAR BICARBONATE .	0.29717 0.0006 130	0.02591 0.7698 130	-0.14106 0.1094 130	0.88908 0.0001 130	0.87812 0.0001 130	0.85110 0.0001 130	0.0204			0.59349 0.0001 130	0.37559 0.0001 130	0.89397 0.0001 130
CA	0.46727 0.0001 130	0.01628 0.8541 130	-0.04835 0.5849 130	0.96333 0.0001 130	0.95484 0.0001 130	0.95382 0.0001 130	-0.10564 0.2316 130		-0.14730 0.0945 130	0.53961 0.0001 130	0.42852 0.0001 130	0.99992 0.0001 130
MG	0.55857 0.0001 130	-0.05309 0.5486 130	-0.16658 0.0582 130	0.90421 0.0001 130	0.89538 0.0001 130	0.88576 0.0001 130	-0.03346 0.7055 130		-0.11944 0.1759 130	0.50708 0.0001 130	0.42525 0.0001 130	0.81586 0.0001 130
NA	0.26338 0.0025 130	0.02557 0.7727 130	0.00223 0.9799 130	0.64167 0.0001 130	0.58891 0.0001 130	0.62342 0.0001 130	0.07184 0.4166 130	0.0160		0.70041 0.0001 130	0.13099 0.1374 130	0.50666 0.0001 130
К	0.40636 0.0001 130	-0.02728 0.7580 130	-0.06361 0.4721 130	0.43213 0.0001 130	0.43381 0.0001 130	0.45894 0.0001 130	0.02534 0.7748 130	0.09352 0.2899 130	-0.13122 0.1367 130	0.18685 0.0333 130	0.97710 0.0001 130	0.40637 0.0001 130
CL	0.18149 0.0388 130	0.00586 0.9472 130	0.04316 0.6258 130	0.11650 0.1868 130	0.14640 0.0965 130	0.17555 0.0457 130	0.39760 0.0001 130	0.0001	0.26221 0.0026 130	-0.11704 0.1848 130	-0.16437 0.0617 130	0.04744 0.5919 130
SO4	0.99714 0.0001 130	-0.08161 0.3560 130	-0.16381 0.0626 130	0.51212 0.0001 130	0.53161 0.0001 130	0.57900 0.0001 130	0.35303 0.0001 130	0.63209 0.0001 130	0.35485 0.0001 130	0.18468 0.0354 130	0.38445 0.0001 130	0.46765 0.0001 130

	EX_SO4	P04	поз	CATION	ANION	CONST	TURBID	COLOR	ΑL	EX_NA	EX_K	EX_CA
EX_SO4	1.00000	-0.08020	-0.18143	0.50520	0.52181	0.56715	0.33446	0.61756	0.34394	0.19520	0.39307	0.46645
	0.0000	0.3644	0.0388	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0260	0.0001	0.0001
	130	130	130	130	130	130	130	130	130	130	130	130
P04	-0.08020	1.00000	-0.03739	-0.00491	-0.01115	-0.01425	0.01657	-0.05098	-0.01064	0.03898	-0.03570	0.01681
	0.3644	0.0000	0.6728	0.9558	0.8998	0.8722	0.8516	0.5646	0.9044	0.6597	0.6868	0.8495
	130	130	130	130	130	130	130	130	130	130	130	130
N03	-0.18143	-0.03739	1.00000	-0.07610	-0.03598	-0.00955	-0.09488	-0.23785	-0.01868	-0.21130	-0.08633	-0.05037
	0.0388	0.6728	0.0000	0.3895	0.6845	0.9141	0.2829	0.0064	0.8330	0.0158	0.3287	0.5692
	130	130	130	130	130	130	130	130	130	130	130	130
CATION SUM OF CATIONS	0.50520 0.0001 130	-0.00491 0.9558 130	-0.07610 0.3895 130	1.00000 0.0000 130	0.98221 0.0001 130	0.98606 0.0001 130	-0.06458 0.4654 130	0.05149 0.5607 130	-0.13680 0.1207 130	0.61097 0.0001 130	0.45048 0.0001 130	0.96211 0.0001 130
ANION SUM OF ANIONS	0.52181 0.0001 130	-0.01115 0.8998 130	-0.03598 0.6845 130	0.98221 0.0001 130	1.00000 0.0000 130	0.99345 0.0001 130	-0.04859 0.5830 130	0.04220 0.6336 130	-0.10664 0.2272 130	0.53251 0.0001 130	0.44251 0.0001 130	0.95306 0.0001 130
CONST SUM OF CONSTITUENTS	0.56715 0.0001 130	-0.01425 0.8722 130	-0.00955 0.9141 130	0.98606 0.0001 130	0.99345 0.0001 130	1.00000 0.0000 130	-0.01355 0.8784 130	0.2888	-0.08069 0.3615 130	0.53781 0.0001 130	0.46628 0.0001 130	0.95175 0.0001 130
TURBID TURBIDITY	0.33446 0.0001 130	0.01657 0.8516 130	-0.09488 0.2829 130	-0.06458 0.4654 130	-0.04859 0.5830 130	-0.01355 0.8784 130	1.00000 0.0000 130	0.60115 0.0001 130	0.33315 0.0001 130	-0.20326 0.0204 130	-0.02457 0.7814 130	-0.11024 0.2118 130
COLOR	0.61756	-0.05098	-0.23785	0.05149	0.04220	0.09374	0.60115	1.00000	0.61184	-0.00774	0.05487	-0.00913
	0.0001	0.5646	0.0064	0.5607	0.6336	0.2888	0.0001	0.0000	0.0001	0.9304	0.5352	0.9179
	130	130	130	130	130	130	130	130	130	130	130	130
AL	0.34394	-0.01064	-0.01868	-0.13680	-0.10664	-0.08069	0.33315	0.61184	1.00000	-0.16315	-0.16365	-0.14994
	0.0001	0.9044	0.8330	0.1207	0.2272	0.3615	0.0001	0.0001	0.0000	0.0636	0.0628	0.0886
	130	130	130	130	130	130	130	130	130	130	130	130
EX_NA	0.19520	0.03898	-0.21130	0.61097	0.53251	0.53781	-0.20326	-0.00774	-0.16315	1.00000	0.22406	0.54138
	0.0260	0.6597	0.0158	0.0001	0.0001	0.0001	0.0204	0.9304	0.0636	0.0000	0.0104	0.0001
	130	130	130	130	130	130	130	130	130	130	130	130

APPENDIX 1 (Cont'd.).

	EX_SO4	P04	NO3	CATION	ANION	CONST	TURBID	COLOR	AL	EX_NA	EX_K	EX_CA
EX_K	0.39307 0.0001 130	-0.03570 0.6868 130	-0.08633 0.3287 130	0.45048 0.0001 130	0.44251 0.0001 130	0.46628 0.0001 130	-0.02457 0.7814 130	0.05487 0.5352 130	-0.16365 0.0628 130	0.22406 0.0104 130	1.00000 0.0000 130	0.42987 0.0001 130
EX_CA	0.46645 0.0001 130	0.01681 0.8495 130	-0.05037 0.5692 130	0.96211 0.0001 130	0.95306 0.0001 130	0.95175 0.0001 130	-0.11024 0.2118 130			0.54138 0.0001 130	0.42987 0.0001 130	1.00000 0.0000 130
EX_MG	0.54761 0.0001 130	-0.04585 0.6044 130	-0.20815 0.0175 130	0.87357 0.0001 130	0.85711 0.0001 130	0.0001	-0.07180 0.4169 130	0.3220	-0.13559 0.1240 130	0.52453 0.0001 130	0.43126 0.0001 130	0.79806 0.0001 130
DOC	0.70944 0.0001 130	-0.09386 0.2882 130	-0.16871 0.0550 130	0.14940 0.0898 130	0.13315 0.1310 1,30		0.55820 0.0001 130	0.0001	0.54703 0.0001 130	0.02478 0.7796 130	0.10821 0.2204 130	0.06891 0.4360 130
HOUR_F	-0.17801 0.0861 94	0.17454 0.0925 94	0.01264 0.9038 94	0.12171 0.2426 94	0.10705 0.3044 94	0.09913 0.3418 94		-0.28269 0.0058 94	-0.28761 0.0049 94	0.15698 0.1308 94	0.30427 0.0029 94	0.10372 0.3198 94
DEP_ZOO	-0.33998 0.0007 95	-0.00094 0.9928 95	0.26436 0.0096 95	-0.08190 0.4301 95	-0.06290 0.5448 95		-0.38339 0.0001 95	-0.51813 0.0001 95	-0.17365 0.0924 95	-0.03387 0.7446 95	-0.06489 0.5322 95	-0.03711 0.7210 95
ORDER	-0.14676 0.0957 130	0.08710 0.3244 130	0.06388 0.4702 130	0.01892 0.8308 130	0.04013 0.6503 130	0.01844 0.8351 130	-0.08160 0.3560 130		0.01125 0.8989 130	0.16150 0.0664 130	0.03123 0.7243 130	0.02421 0.7846 130
GEOL WT WEIGHTED GEOLOGY	0.07430 0.4199 120	0.05927 0.5202 120	-0.14079 0.1251 120	-0.36855 0.0001 120	-0.37477 0.0001 120	-0.34209 0.0001 120	0.29014 0.0013 120		0.22747 0.0125 120	-0.28851 0.0014 120	-0.01710 0.8529 120	
	EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT						
FLD_PH	0.72101 0.0001 130	-0.29673 0.0006 130	0.24368 0.0179 94	0.14845 0.1511 95	0.11101 0.2086 130	-0.45219 0.0001 120						

	EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT
LAB_PH	0.61699 0.0001 130	-0.40750 0.0001 130	0.26867 0.0088 94	0.28177 0.0057 95	0.17332 0.0486 130	-0.41417 0.0001 120
SURFACE LAKE SURFACE AREA	0.00410 0.9630 130	-0.27198 0.0017 130	0.40735 0.0001 94	0.34274 0.0007 95	0.41948 0.0001 130	0.02169 0.8141 120
MEAN_D	-0.15669 0.1794 75	-0.50686 0.0001 75	-0.04880 0.6776 75	0.83790 0.0001 75	0.13680 0.2419 75	-0.00300 0.9799 73
MAX D MAXTMUM DEPTH	-0.08709 0.4014 95	-0.64890 0.0001 95	0.21050 0.0417 94	0.90930 0.0001 95	0.33538 0.0009 95	-0.12025 0.2536 92
VOLUME TO THE POWER OF 10	-0.06184 0.5982 75	-0.19764 0.0892 75	-0.08818 0.4519 75	0.36436 0.0013 75	0.15171 0.1938 75	0.14440 0.2229 73
ELEVAT	0.02866 0.7462 130	-0.14801 0.0928 130	0.09506 0.3621 94	0.15806 0.1261 95	-0.03273 0.7116 130	-0.10776 0.2414 120
DIST DISTANCE FROM COAST	0.0003	0.2866	0.0444	0.21761 0.0341 95	0.1965	0.2266
	130	130	94	95	130	120
RATIO DRAINAGE/LAKE AREA	130	130	94	90	150	120
CO2	-0.06772 0.4440 130	0.18244 0.0377 130	0.04079 0.6963 94	-0.02082 0.8413 95	0.11843 0.1796 130	0.10541 0.2519 120

APPENDIX 1 (Cont'd.).

CORRELATION COEFFICIENTS	/ PROR >	TRI	INDER HOURHOOD	/ NUMBER	OF	ORSERVATIONS

	EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT
DISC SECCHI DISC READING	0.3068 95	0.0001 95	0.0106 94	0.0001 95	0•0731 95	0.0872 92
FLD_ALK						
LAB_ALK	150	150	- '		130	, ,,,,
COND CONDUCTIVITY	0.82550 0.0001 130	0.12520 0.1558 130	0.12684 0.2231 94	-0.06278 0.5456 95	0.00682 0.9386 130	-0.33788 0.0002 120
TDS	130	130	94	95	130	120
HARD TOTAL HARDNESS	0.89886 0.0001 130	0.16636 0.0585 130	0•10883 0•2964 94	-0.06232 0.5486 95	-0.00453 0.9592 130	-0.39947 0.0001 120
BICAR BICARBONATE	0.81465 0.0001 130	-0.07807 0.3773 130	0.18248 0.0783 94	0.00510 0.9609 95	0.06435 0.4670 130	-0.45847 0.0001 120
CA	0.79596 0.0001 130	0.07188 0.4164 130		-0.03906 0.7071 95		0.0001
MG	0.98770 0.0001 130	0.24336 0.0053 130	0.2707	-0.09933 0.3382 95	0.8454	0.0043
NA	0.40145	0.24339 0.0053 130	0.6294		0.3200	

CORRELATION COEFFICIENTS / PROB > IRI UNDER HO:RHO=O / NUMBER OF OBSERVATIONS

		EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT
К		0.39303 0.0001 130		0.0049	0.4089	0.01917 0.8287 130	
CL		-0.12049 0.1721 130	0.40532 0.0001 130	-0.17413 0.0933 94	-0.26064 0.0107 95	-0.02686 0.7617 130	0.27592 0.0023 120
SO4		0.53234 0.0001 130	0.72027 0.0001 130	0.0841	0.0007	-0.14540 0.0988 130	0.3228
EX_SO4		0.54761 0.0001 130	0.70944 0.0001 130	-0.17801 0.0861 94	-0.33998 0.0007 95	-0.14676 0.0957 130	0.07430 0.4199 120
P04		0.6044 130	0.2882 130	0.0925 94	0•9928 95	0.08710 0.3244 130	0.5202 120
NO3		-0.20815 0.0175 130	-0.16871 0.0550 130	0.01264 0.9038 94	0.26436 0.0096 95	0.06388 0.4702 130	-0.14079 0.1251 120
CATION SUM OF	CATIONS	0.87357 0.0001 130	0.0898	0.2426	0.4301	0.01892 0.8308 130	
ANION SUM OF	ANIONS	0.85711 0.0001 130	0.13315 0.1310 130	0.3044	0.5448	0.04013 0.6503 130	0.0001
CONST SUM OF	CONSTITUENTS	0.84416 0.0001 130	0.19168 0.0289 130		0.3577	0.01844 0.8351 130	0.0001
TURBID TURBIDI	TY	-0.07180 0.4169 130	0.0001	0.0406	-0.38339 0.0001 95	-0.08160 0.3560 130	0.29014 0.0013 120

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	EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT
COLOR	0.3220	0.0001	0.0058	0.0001	0.2271	
AL	-0.13559 0.1240 130	0.54703 0.0001 130	-0.28761 0.0049 94	-0.17365 0.0924 95	0.01125 0.8989 130	0.22747 0.0125 120
	0.52453 0.0001 130	130	94	95	130	120
ex <u>k</u>	0.43126 0.0001 130	0.10821 0.2204 130	0.30427 0.0029 94	-0.06489 0.5322 95	0.03123 0.7243 130	-0.01710 0.8529 120
EX_CA .	0.79806 0.0001 130	0.4360	0.3198	0.7210	0.02421 0.7846 130	0.0001
EX_MG	1,00000 0,0000 130	0.0129		0.3596	-0.00541 0.9513 130	-0.28344 0.0017 120
DOC	0.21754 0.0129 130	0.0000	0.0071	0.0001	-0.22368 0.0105 130	0.0027
	0.11377 0.2749 94	94	94	94	94	91
DEP_ZOO	-0.09505 0.3596 95	-0.56074 0.0001 95	0.16570 0.1105 94	1.00000 0.0000 95	0.31776 0.0017 95	-0.03667 0.7286 92
ORDER	-0.00541 0.9513 130	0.0105	0.1206	0.0017	1.00000 0.0000 130	0.89/4

114

	EX_MG	DOC	HOUR_F	DEP_ZOO	ORDER	GEOL_WT
GEOL WT WEIGHTED GEOLOGY				-0.03667 0.7286 92		1.00000 0.0000 120