IMPACT ASSESSMENT
WORKING GROUP I

UNITED STATES – CANADA

MEMORANDUM OF INTENT
ON
TRANSBOUNDARY AIR POLLUTION

PHASE II INTERIM WORKING PAPER
OCTOBER 1981

DISCLAIMER

This is an Interim Report prepared by a U.S./Canada Work Group in accordance with the Memorandum of Intent on Transboundary Air Pollution concluded between Canada and the United States on August 5, 1980.

This is one of a set of four reports which represent an initial effort to draw together currently available information on transboundary air pollution, with particular emphasis on acid deposition, and to develop a consensus on the nature of the problem and the measures available to deal with it. While these reports contain some information and analyses that should be considered preliminary in nature, they accurately reflect the current state of knowledge on the issues considered. Any portion of these reports is subject to modification and refinement as peer review, further advances in scientific understanding, or the results of ongoing assessment studies become available.

A final complete report on transboundary air pollution impacts is expected in early 1982.

October 8, 1981

TO: Co-Chairmen
Canada/United States
Co-ordinating Committee

FROM: Co-Chairmen
Impact Assessment Work Group

In accordance with the approved work plan for the Impact Assessment Work Group, we are submitting our Phase II Working Paper.

This report completes our Phase II activities and provides a considerable improvement in the information base available to the Co-ordinating Committee in January 1981. As well, extensive peer review by internationally recognized authorities of the Phase II material has been undertaken. The results of this review have increased our confidence in the findings and conclusions of the Work Group.

The Work Group remains concerned that a structured opportunity to provide comments by a wider public in both Canada and the United States be undertaken. This action would undoubtedly improve the utility of our report as a basis for conducting negotiations on a Transboundary Air Pollution Agreement. This broader dialogue should be encouraged during Phase III.

In order to ensure that the Work Group is able to broaden the scope of its investigation beyond the serious problem of acid deposition, we wish to stress the need for the continued provision of resources. Without this support, the Work Group will be unable to enlist the involvement of other scientists knowledgeable in the field of transboundary impacts of air pollution.

We look forward to your comments and further direction.

Respectfully submitted,

Clare Harris

Clare I. Harris
United States Co-Chairman

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PREFACE

In August, 1980, the Governments of Canada and the United States signed a Memorandum of Intent concerning transboundary air pollution. This action was taken in response to concern for actual and potential damage resulting from the long-range transport of air pollutants between countries and in recognition of the already serious problem of acid rain.

Each country has demonstrated concern for the causing of damage to the other's environment by transboundary movement of its pollutants. This concern is rooted in international agreements, such as the 1909 Boundary Waters Treaty, the Great Lakes Water Quality Agreement, and the 1979 E.C.C. Convention on Long-Range Transboundary Air Pollution, all of which both Canada and the United States have signed.

The Memorandum noted that both countries have set a priority on developing a scientific understanding of long-range transport of air pollutants and resulting environmental effects, and on developing and implementing policies and technologies to combat such effects.

To achieve the first steps of this overall objective, the memorandum established a plan of action for the period October, 1980 to January, 1982, during which time five documents are to be prepared by the following work groups:

1. Impact assessment
2. Atmospheric modelling of pollutant movements
3A. Strategies development and implementation
3B. Emissions, cost and engineering assessment
4. Legal, institutional arrangements and drafting (preparation of the actual document to be signed).

General terms of reference that apply to all work groups were established, together with detailed terms dealing with each work group.

General Terms of Reference (as per MOI)

1. The Work Groups shall function under the general direction and policy guidance of a United States/Canada Coordinating Committee co-chaired by the Department of External Affairs and the Department of State.

2. The Work Groups shall provide reports assembling and analyzing information and identifying measures as outlined below, which will provide the basis of proposals for inclusion in a transboundary air pollution agreement. These reports shall be provided by January, 1982, and shall be based on available information.

3. Within one month of the establishment of the Work Groups, they shall submit to the United States/Canada Coordinating Committee a work plan to accomplish the specific tasks outlined below. Additionally, each Work Group shall submit an interim report by January 15, 1981.

4. During the course of negotiations, and under the general direction and policy of the Coordinating Committee, the Work Groups shall assist the Coordinating Committee as required.

5. Nothing in the foregoing shall preclude subsequent alterations of the tasks of the Work Groups or the establishment of additional Work Groups, as may be agreed upon by the Governments.

Specific Terms of Reference: Impact Assessment Work Group

The Group will provide information on the current, and projected impacts of air pollutants on sensitive receptor areas, and prepare proposals for the 'Research, Modelling and Monitoring' elements of an agreement.

In carrying out this work, the Group will:

1. identify and assess physical and biological consequences possibly related to transboundary air pollution;

2. determine the present status of physical and biological indicators, which characterize the ecological stability of each sensitive area identified;

3. review available data bases to establish historic adverse environmental impacts more accurately;

4. determine the current adverse environmental impact within identified sensitive areas—annual, seasonal, episodic;

5. determine the release of residues potentially related to transboundary air pollution, including possible episodic release from snowpack melt in sensitive areas;

6. assess the years remaining before significant ecological changes are sustained within identified sensitive areas;

7. propose reductions in the air pollutant deposition rates—annual, seasonal, episodic—which would be necessary to protect identified sensitive areas; and

8. prepare proposals for the 'Research, Modelling and Monitoring' elements of an agreement.

A time frame was established which called for a first draft of the impact assessment report by January, 1981, a second draft by May, 1981 (this report), and a final report by January, 1982.

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ACKNOWLEDGEMENTS

The Canada/United States Impact Assessment Work Group wishes to acknowledge the assistance of the numerous individuals and agencies involved in the various aspects of this study. The enthusiasm and dedication demonstrated during this second phase of the programme were fundamental to the successful completion of this interim report. These persons included A. Anders (University of Wisconsin), J. Barse (U.S. Department of Agriculture), D. Bjonback (Environment Canada), D. Cowell (Environment Canada), T. Crocker (University of Wyoming), L. Dochinger (U.S. Department of Agriculture), J. Donnan (Ministry of Environment), B. Forster (University of Guelph), N. Foster (Environment Canada), M. Griffith (Ministry of Environment), W. Hart (Environment Canada), W. Heck (North Carolina State University), B. Hosler (Environment Canada), J. Jacobsen (Boyce Thompson Institute), D. Johnson (Oak Ridge National Laboratory), M. Kelly (Oak Ridge National Laboratory), J. Kerekes (Environment Canada), O. Loucks (Institute of Ecology), A. Lucas (Environment Canada), C. Lucyk (Ministry of the Environment), W. McPhee (Purdue University), I. Morrison (Environment Canada), J. Nicholson (Environment Canada), R. Olson (Oak Ridge National Laboratory), R. Paolini (National Health and Welfare), D. Raynal (State University of New York), C. Rubec (Environment Canada), C. Schofield (Cornell University), S. Singh (Agriculture Canada), C. Russel (Resources for the Future), D. Shriner (Oak Ridge National Laboratory), J. Smith (Ministry of Environment) and M. Thompson (Environment Canada), N. Yan (Ministry of the Environment).

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SECTION I

SUMMARY

1.1 INTRODUCTION

Wet and dry deposition of acidic substances and other pollutants in long-range atmospheric transport are currently being observed in most of eastern North America. The Impact Assessment Work Group was charged with identifying and making an assessment of the physical and biological consequences related to these transboundary air pollutants.

During Phase II, the overall efforts of the Impact Assessment Work Group were dedicated to updating and reviewing the research results presented in the Phase I report for all sections of the working paper. While there are areas which have remained unchanged, most of the working paper has been rewritten to reflect the inclusion of new information.

The Work Group has stressed the following six areas in phase two:

(1) Identification of efforts to broaden our understanding concerning the dose/response relationship relating acidic deposition with specific reference to sulphate loadings in determining effects on aquatic ecosystems.

(2) Integration of information on soil characteristics and geology into an ecosystem approach to mapping areas sensitive to acid deposition for eastern North America.

(3) Consideration of the adverse effects due to corrosion processes on structures by both sulphur dioxide (SO_2) and sulphates (SO_4^{2-}).

(4) Broadening the discussion on health effects to ascertain impacts due to ozone acting either alone or in combination with sulphur compounds.

(5) Undertaking a review of the feasibility of determining the economic benefits of controlling transboundary air pollution.

(6) Completion of an initial external peer review of the phase two working paper - (see list of reviewers preceeding this section).

(7) Inclusion of an extensive review of additional research needs required to provide further understanding of the impacts associated with transboundary air pollution - (see listing of research needs at the conclusion of each Section of the report).

1.2 AQUATIC ECOSYSTEM IMPACTS

The potential impacts from the deposition of acid and associated ions (SO_4^{2-}, NO_3^- and others) on water quality, and on the aquatic ecosystem, appears to be more fully quantified and understood than for terrestrial ecosystems. A number of examples have occurred where dramatic changes in water quality are believed to be directly attributable to acidic deposition. The findings and conclusions of the work group with respect to these impacts are contained in the following statements:

- Nitric acid contributes to the acidity of precipitation, but is less important than sulphuric acid in acidification of surface waters, except during snowmelt in some areas. Sulphuric acid has been identified as the dominant compound contributing to the surface water acidification process. Studies of lakes in Eastern North America have provided strong evidence that it is atmospheric deposition that accounts for the elevated sulphate levels of surface waters.

- Trend analyses in acidification of streams and lakes date back 17 years in New Jersey and forty years in the Adirondacks and show a marked decline in pH values. The Adirondacks is one of the most sensitive lake districts in the eastern United States. A recent inventory has indicated that at least 180 former brook trout ponds will no longer support trout because of acidification.

- In Nova Scotia the pH measured in a number of salmon spawning rivers has shown a marked decline in the period 1954-55 to the present. Concurrently there has been a statistically significant decrease in angling success. Recent surveys have attributed this decrease in pH to an increase in sulphate loadings from anthropogenic sources.

- Many changes in aquatic life have been linked to acidification. In some instances a causal relationship with depressed pH has been established, but in the majority of cases, the observed changes in biota have simply been correlated with observed changes in pH. Results show that for most biological communities, acidification has been accompanied by decreases in species richness and changes in species dominance. Acidification results in changes in the makeup, size and metabolism of plankton communities. These alterations hold important implications for other organisms higher in the food chain.

- Short term depressed pH values and elevated metal concentrations have been observed during snowmelt periods in many streams.

- Evidence of stressed fish populations has been observed in lakes which experience short-term low pH and elevated metal concentrations. Adult fish kills have been observed in one study lake experiencing these conditions.

1.2.1 Target Sulphate Loadings and Dose/Response Relationships

- A number of different approaches have been examined to assist in the task of deriving relationships between acid loadings and system response. The work group has employed both empirical observations and modelling to estimate target sulphate loadings. The models are all under active development, and in the area of aquatic effects research they have advanced to the point where a preliminary application is possible, although it is important to stress that full validation remains to be achieved. There is, however, relative agreement between model outputs and the empirical observations.

- Atmospheric loadings of acid measured in terms of wet sulphate loadings in the range of 0-10 kg/ha/yr have been suggested as being protective for all surface waters. Wet sulphate loadings values of 11-20 kg/ha/yr have been suggested as being protective for the majority of surface waters. At this loading, some of the most sensitive waters, i.e., those with low alkalinity, may still experience some water quality damage, particularly during snowmelt and when additional acids (HNO_3) are present. Achieving levels suggested for moderately sensitive lakes may require a reduction in sulphate deposition of more than half.

1.3 TERRESTRIAL ECOSYSTEM IMPACTS

The assessment of terrestrial effects focuses on both impacts associated with acid deposition and oxidants. Field and laboratory studies have provided extensive documentation of the direct effects of O_3 on vegetation. It has been more difficult to determine adverse or beneficial effects of acid deposition on plant communities and direct effects have not been documented in the field. Several studies have, however, demonstrated the direct effects of acid deposition on soils.

Forested areas are generally associated with areas of lower pH soils with low nutrient status. Thus, any further loss of nutrients is considered significant, however small that loss may be. Forested regions have also traditionally received a much lower level of management than agricultural areas, in terms of such practices as liming and fertilization, thus increasing their susceptibility to acidic deposition. New harvesting technology, where more of the tree is removed from the site - reducing the availability of nutrients for recycling - may increase the problem.

The principal terrestrial effects associated with transboundary air pollution are as follows:

Acid Deposition

- Although simulated rainfall experiments have produced direct effects on plants exposed to higher than normal "H" concentrations, direct effects have not been documented in the field for vegetation exposed to ambient precipitation.

- Individual precipitation events which occur during critical growth stages of agricultural crops (i.e., during flowering or pollination) offer amplified potential for damage to agricultural crops.

- Direct effects of acid precipitation on soils have been shown to increase both SO_4^{-2} movement and increase the rate of nutrient cation denudation. Some soils, however, exhibit a substantial capacity to adsorb SO_4^{-2} and resistance to nutrient cation leaching, especially those soils rich in Fe and Al^{+++} sesquioxides.

- Much of the potential impact of atmospheric deposition stems from the input of H_2SO_4 to soils. Because of the N-limited status of many forests, most NO_3^- tends to be accumulated by plants during the growing season and tends not to contribute to cation leaching.

- Substantial transference of Al from soils into groundwater and then to streams and lakes, has been observed under field conditions in zones of very high acid deposition.

- For the first time, maps for eastern North America depicting areas sensitive to acid deposition have been prepared, integrating the factors of geology, soils depth and soil chemistry. Separate interpretations have been made for sensitivity to changes in forest cation nutrient status and for aquatic input sensitivity.

Ozone

- Field and laboratory studies with O_3 indicate that reductions in yield do occur for various tree species and such crops as beans, tobacco, potatoes, onions, radishes, grapes, and corn. Frequent exposures during the growing season to O_3 concentrations in excess of 0.1 ppm have produced yield losses of as much as 20 percent for susceptible species.

- Experiments with simulated acid precipitation and O_3 suggest greater plant growth reduction from the two together than would be expected from results of their individual effects.

1.4 HUMAN HEALTH AND VISIBILTY

Attention to health effects in this second phase of the MOI process has focused on health effects related to acid deposition and secondarily on health effects related to ozone. Available information gives little cause for concern over direct health effects from acid deposition. However, potential indirect effects associated with (1) contamination of edible fish by toxic materials, principally mercury; and (2) leaching and corrosion of watersheds and storage and distribution systems, leading to elevated levels of toxic elements, remain a concern.

With respect to ozone, concerns do exist with inhalation of high concentrations.

The principal conclusions in this area follow:

- Although some concern has been expressed over the effects of acid sulphates on mortality and/or morbidity, the available data appears insufficient to single out these species as the sole pollutant of concern in the sulphur-particle complex. Long range transport of fine particles should be viewed as a concern only where such transport contributes to violations of health-related particulate matter standards.
- Provided that present ambient air quality standards for ozone are maintained, no adverse human health effects should be evident. However, in areas subjected to repeated excursions above the ozone standards, adverse health effects cannot be ruled out.
- In areas subject to acid deposition, data on heavy metal migration into the food chain indicates an area of great concern. A correlation does exist between low pH in lakes and higher mercury concentrations in some species of fish, and further acidification may pose a threat to fish-eating birds and mammals.
- Acid deposition may liberate metals in some ground waters and drinking water supply systems. Evidence does exist where elevated metal concentrations in drinking water supplies have been found.

1.4.1 Visibility Effects

Effects of transboundary air pollution on visibility are related to air quality, not to acidic deposition. Acid precursors which can significantly affect visibility are sulphuric acid and various ammonium sulphate aerosols. Available data do not suggest that nitrates (predominantly in the vapour phase) play a significant role, but visible brown plumes from NO_2 have been reported at a distance of 100 km from isolated point sources.

From available information on background and incremental pollutant loadings and relative humidity, estimates of visibility impacts (reduction in visual range and contrast, discolouration from haze or plumes) can be made. Analysis of airport data indicate a substantial decline in regional summertime visibility, in eastern North America, between 1950 and 1974. This change may be associated with changes in the level and distribution patterns of sulphur oxide emissions.

Clean areas, such as those found in western North America, are the most sensitive to visibility degradation. Usually, good visibility is valued most highly in natural settings such as parks and wilderness areas. Any area, however, with normal viewing distances of a mile or more may be affected by episodic regional haze carrying acid precursor substances.

1.5 BUILDINGS AND STRUCTURES

Certain airborne chemicals can accelerate deterioration of non-living materials. There is considerable evidence that materials in urban areas of Europe and North America have suffered and are suffering from exposure to man-made pollutants. Such materials include statuary and structures of substantial cultural, historic and artistic value.

The principal airborne pollutant adversely affecting materials is SO_2. Other pollutants have been shown to have a lesser effect. These pollutants include ozone, particulate matter (PM), and sulphates. Sources of SO_2, and PM, are generally co-located with receptors and thus, material effects caused by these pollutants are primarily local in nature.

It is reasonable to assume that acid deposition due to long range transport and transformation of air pollutants contributes somewhat to material effects. Current understanding of material decay processes leads to the tentative conclusion that local sources of corrosive pollution overwhelm the effects resulting from long range transport of acid deposition.

The principal findings of the Work Group are:

- In assessing damage, exterior surfaces are the focus of interest, since the concentration of corrosive gases outside buildings is usually much higher than inside, and secondly, because outside surfaces are wetted.

- The dose/response related to corrosion damage on zinc and low-carbon steel is fairly well understood.

- Relationships between concentration of corrosive gases and damage are better understood than relationships between acidic precipitation and corrosion.

- Chemical corrosion processes include deterioration of calcareous building materials by the removal of calcium carbonate and the removal of protective oxide coverings on metals, particularly zinc and copper.

- Extended periods of dry deposition can lead to a high concentration of corrosive materials which can by activated during wetting or periods of high humidity.

- Physical deterioration occurs when chemical corrosion by-products or salts, enter porous building materials, with the subsequent internal rupturing of the material due to crystallization pressures. Surface flaking and efflorescence are common.

- Direct corrosive effects of ozone on paints, elastomers, and plastics are well known, and, where possible, corrective production procedures have resulted.

- At receptors which receive little rain, the infrequent precipitation may be beneficial, acting as a washing agent by removing deposited dry material.

1.6 ESTIMATING ECONOMIC BENEFITS OF CONTROL

Traditionally, the decision-making process has required an appreciation of the costs and benefits associated with following a prescribed set of actions. Basic to this process has been the transformation of the implications of these actions, i.e., converting changes in crop yield and fish catches into comparable units of measurement. Monetary units are widely accepted as providing comparable weighting units for individual variables. In order to provide the Canada/United States Coordinating Committee with guidance in this important area, the Work Group has undertaken a review of the methodologies available for assessing the economic benefits of controlling long range transport of air pollution.

- A number of methodologies have been reviewed but presently the basic conclusion of this effort is that application of available approaches for conducting a cost/benefit analysis must either omit real but intangible benefits or include a wide uncertainty range. This however does not preclude their application and the usefulness of their results.

- There are several techniques which can be applied to determine the primary economic benefits associated with a particular receptor category recognizing that option and legacy values are not captured. However, the lack of data on dose/response relationships limits the application of these techniques at this time. A range of assumptions can be used to overcome this.

- The value of the secondary benefits can be further estimated for specific economic sectors, and hence regions, to derive an estimate of the impacts in various geographical areas.

- It is evident that more economic research is required. Economic techniques have yet to be rigorously tested in some sectors, such as historical value, and are limited in their treatment of option and legacy values, and in dealing with the issue of property rights.

SECTION 2

INTRODUCTION

World attention was drawn to the problem of transboundary air pollutants and their deposition on surface waters in 1972, when Sweden and Norway reported the so-called "acid rain" phenomenon. From these Scandinavian studies, scientists in many other nations became increasingly aware that, because atmospheric dilution does not eliminate waste, there may be effects on "receiving" aquatic ecosystems, caused by the transport and deposition of pollutants. Since 1972, the acid deposition phenomenon has become recognized in North America, as detailed in many articles by both Canadian and U.S. scientists.

2.1 THE EXTENT OF RESOURCES EXPOSED TO ACID DEPOSITION AND POTENTIAL FOR LARGE-SCALE EFFECTS.

Acid deposition is currently being observed over most of eastern North America (Figure 2-1). The effects on watersheds and aquatic resources are most strongly expressed in the areas where elevated inputs of acid combine with low natural buffering of soils and water to reduce the pH of surface water, leading to impacts on aquatic ecosystems.

Over most of this area, acid rain, sulphate particulates, and oxidants occur together. In addition, there are local exposures occurring to sulphur dioxide, nitrogen oxides and fluorides, with biological uptake and subsequent cycling of these elements. Although acidic components of acid deposition remain the focus of this report due to their important impacts on aquatic/terrestrial ecosystems and on human health and man-made structures, the effects attributable to oxidants are also considered.

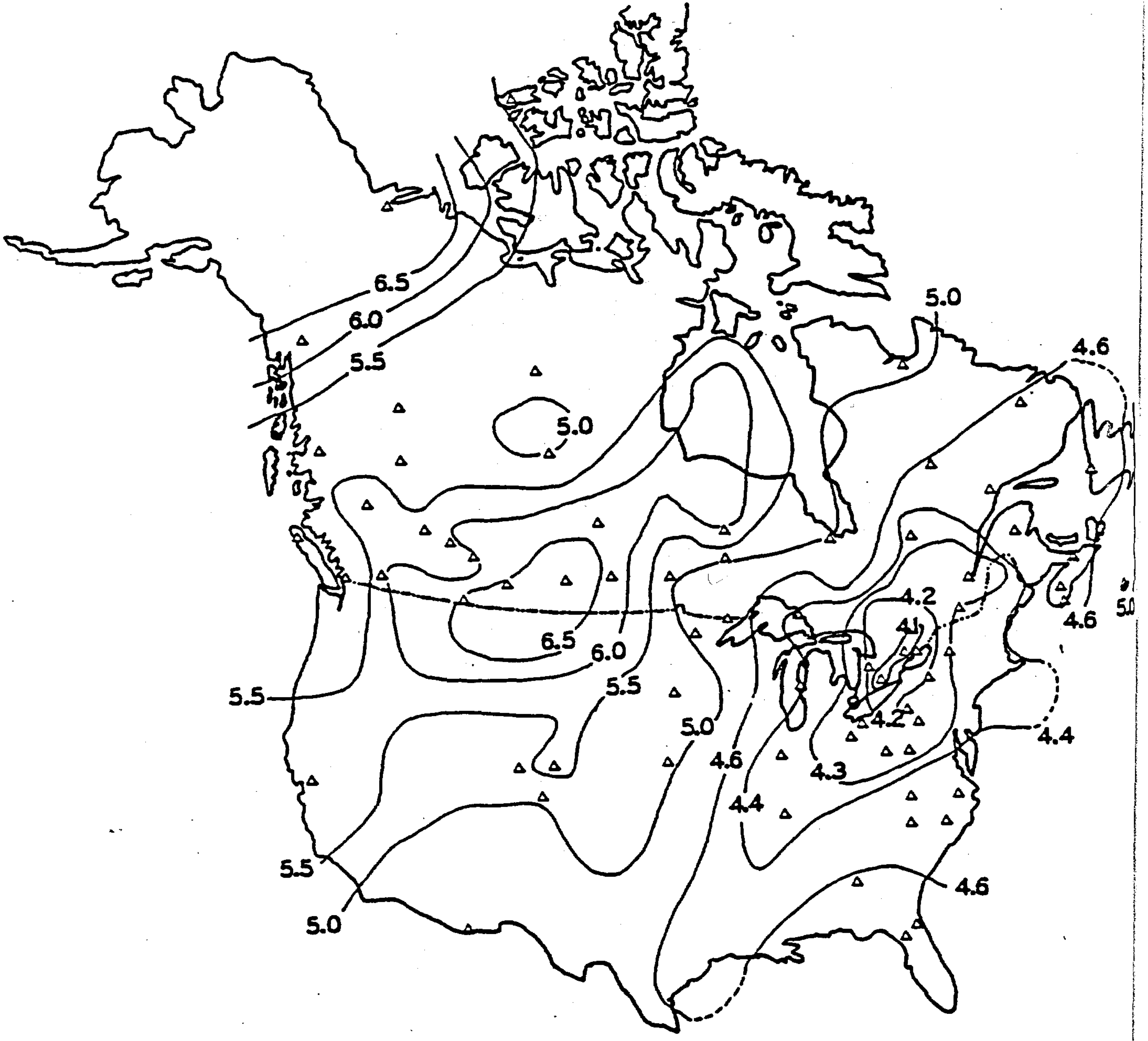


Figure 2-1 pH of precipitation in North America, volume weighted averages for the period April 1979 to March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass 1981).

Hydrogen ion concentration (acid, H^+) is a critical factor controlling the rate of most chemical reactions. Processes such as solubilization, corrosion, and mobilization of minerals and metals are accelerated by increasing the acid concentrations in soils and water. Soil weathering and nutrient balances are alerted by changes in the acidity of soilwater. Household water supplies from shallow wells, or acidic surface waters, in turn, can be modified by the further mobilization of metals from lead and copper pipes. Metal culverts at stream crossings are especially susceptible to corrosion from mild acidity.

The effect of acid rain on watersheds is quite different from one region to another, due to differences in climate, soils and geology. Generally speaking ecosystems seen as sensitive to acid deposition are characterized as having thin soils, low in exchangeable bases and cation exchange capacity, overlying granitic bedrock (non calcareous). Figure 2-2 provides a small scale overview of areas seen as sensitive based on bedrock geology. Efforts are now underway and preliminary results are presented in Sections 3 and 4 of larger scale mapping of sensitive areas. In the United States the four most susceptible regions are the Northeast, the Appalachian Mountains, the Minnesota-Wisconsin-Michigan highlands, and the western mountain areas of Colorado, Oregon, Washington, Idaho and California. In Canada, sensitive regions include parts of the Atlantic Provinces and the Precambrian shield areas of Ontario and Quebec. Other areas may be considered sensitive based on soil characteristics or other variables.

2.1.1 Methods of Measuring Effects

Lakes, rivers, and watersheds act as "collectors" of atmospheric pollution, so one research approach has been to study lakes and watersheds as large-scale "calibrated" collectors, since the surface environment experiences a total loading, an integration of all deposition processes. This approach has led to establishing "calibrated watersheds" as monitoring sites which are combinations of streams, lakes, and plant communities under intensive measurement. In these watersheds, hydrologic weirs are set up in streams entering and leaving small study lakes or settling pools. The flows of water and dissolved substances are measured upon entering and leaving the lake, and these data are combined with measures of atmospheric inputs and water loss by evaporation, to calculate "substance

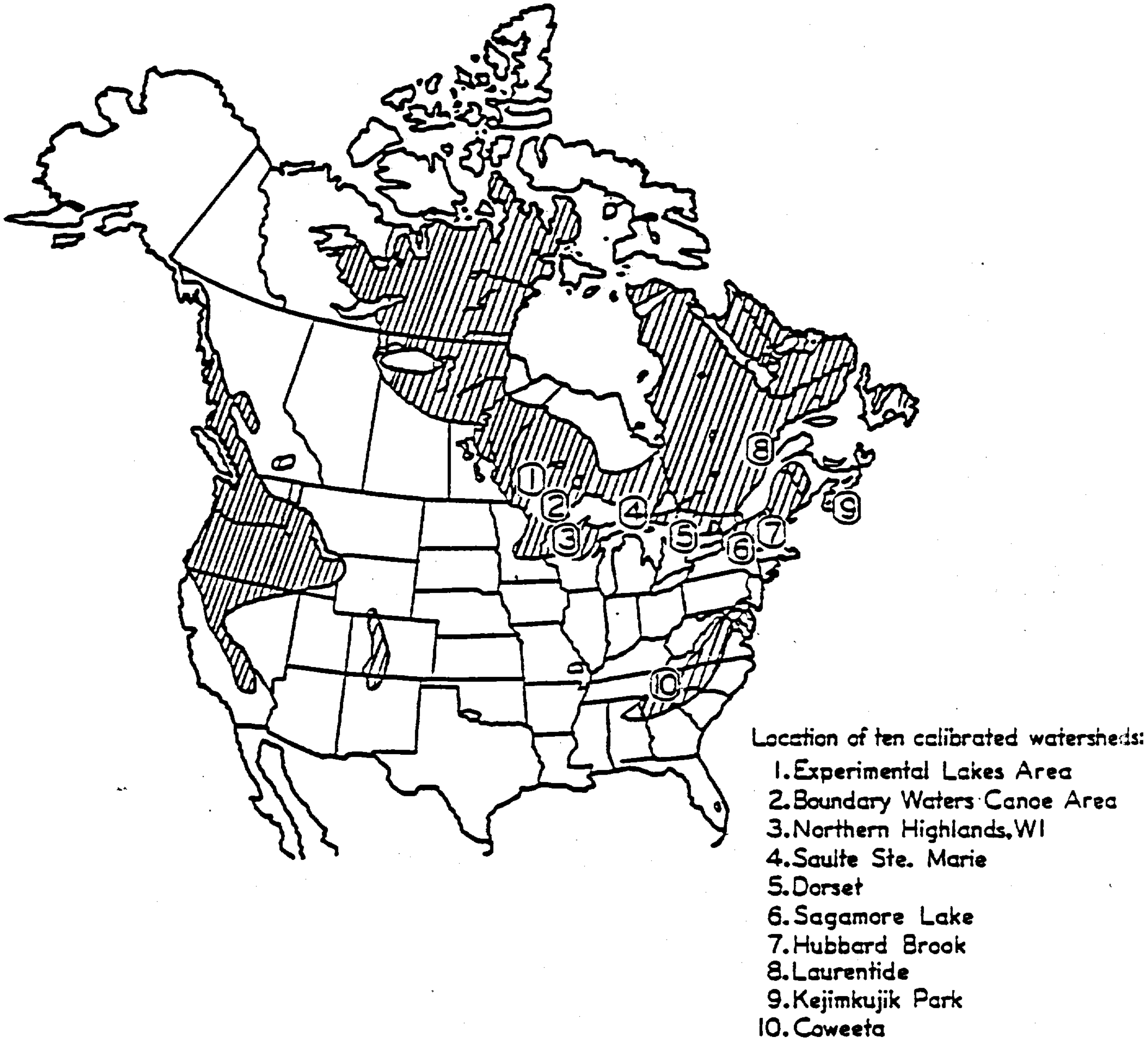


Figure 2-2 Regions of North America containing lakes that are sensitive to acidification by acid precipitation, based on bedrock geology, showing where calibrated watershed studies on sensitive areas are in progress. (Modified from Galloway and Cowling, 1978)

budgets". The difference between the inputs measured by the budgets and inputs measured from wet deposition monitoring can provide a preliminary estimate of dry and gaseous deposition.

Detailed sampling of biota within such a watershed, together with chemical data, allow an assessment of the chemical and biological effects that air pollution can have on the system. Calibrated watersheds have been established at a number of locations, such as Kenora, Sault Ste. Marie, and Dorset in Ontario; Laurentide Park, Quebec; Kejimkujik Park, Nova Scotia; Hubbard Brook, New Hampshire; Coweeta, North Carolina; and Sagamore Lake, New York (Figure 2-2).

2.1.2 Hydrologic Cycle

Although the hydrologic cycle seems to be well-known, questions do emerge as to the potential for high evaporation/precipitation ratios to concentrate sulphate, and the availability of water for many of the acid-forming reactions, as well as for the wet deposition and soil flux processes. For example, in low-humidity regions, or during drought periods, long-distance gaseous transport of SO_2 may provide a greater fraction of the deposition than in wet regions. Similarly, conditions of low rainfall and high evaporation, or seasonal droughts will alter the soil solution flux processes and associated reactions. In regions where annual precipitation is less than potential annual evaporation, movement of dissolved ions is upward (calcification). This movement of bases would tend to neutralize acid deposition falling onto soil surfaces. Indeed, in regions where potential evapotranspiration approaches total rainfall, flushing of H^+ or SO_4^{2-} becomes limited to short-season processes or those that occur only every few years.

Because of the evidence that in many poorly-buffered northern soils, the sulphate ion is a relatively conservative substance (Harvey et al. 1981), high rates of evaporation can leave the precipitation sulphate concentrated in the soil solution (and lake water) by a factor controlled by the evaporative losses. The equations for lake sulphate concentration developed by Henriksen (1980, see later sections) show this factor plus dry deposition to be 1.9 for central Norway. Regions of proportionately high evaporative losses have higher observed sulphate concentrations in lake water than are predicted by the Henriksen equations for a given atmospheric loading rate (G.E. Glass personal communication). These processes vary with precipitation and temperature patterns between regions and, in areas of strong topography, from one watershed to the next.

Thus, local processes governing the hydrologic balance need to be considered as a part of the surface water acidification process. Knowledge of the periodicity of atmospheric cycles, and of the geographic patterns of these transport processes and precipitation is essential to understanding what happens over long periods to sensitive aquatic systems, as well as when and where it will happen.

2.2 ATMOSPHERIC INPUT, TRANSPORT AND DEPOSITION OF POLLUTANTS

2.2.1 Emissions of Pollutants to the Atmosphere

Extensive research attributes most of the acid rain in eastern North America, and elsewhere, to the presence of sulphuric and nitric acids. These acids are formed by a complex series of chemical and physical processes during, and subsequent to, the burning of fossil fuels, ore smelting, and petroleum refining.

Vehicular transportation, construction, agriculture, municipal incineration and natural processes also contribute to the atmospheric burden. Other substances are also emitted to the atmosphere during these processes. Prevailing weather conditions in eastern North America foster the large-scale movement of pollutants within and between Canada and the United States, so that the movements of pollutants are regional issues.

Current emissions in the United States and Canada have been estimated by Work Group 3A (Table 2-1).

Increases in these emissions may be expected if consumption of fossil fuels increases. Emission rates for other constituents from the burning of coal are presented in Table 2-2. Estimates by Goldberg and Bertine (1971) and Klein et al. (1975) indicate that the amount of many trace constituents emitted to the atmosphere via the burning of coal in the U.S. approximates the quantity transported via rivers from continents to oceans. A recent U.S. National Academy of Sciences report (NAS 1978) further estimated that from 25 to 30 per cent of the present day atmospheric mercury burden is due to man-made emissions.

Much study is presently being devoted to the characterization of emissions from both natural and anthropogenic sources. Table 2-3 presents a comparison of these sources for several gases. It is evident that the natural sources of many gases far exceed the man-made sources on a global basis. However, because such natural gases are usually well distributed throughout the atmosphere, their concentration, known as the background concentration, is extremely low. Anthropogenic sources of many pollutants are centered near urban complexes and, therefore, their local pollutant concentrations are higher and may pose major threats to the urban environment. For

TABLE 2-1

CURRENT EMISSIONS IN THE U.S. AND CANADA (10^6 Tons)

	U.S.A. (1980 Estimated)		CANADA 1979*		TOTAL	
	NO_x	SO_x	NO_x	SO_x	NO_x	SO_x
Utilities	6.2	19.5	0.3	0.8	6.5	20.3
Industrial Boilers/ Process Heaters/ Residential/ Commercial	7.1	7.3	0.6	1.1	7.7	8.4
Non-Ferrous Smetlers	0.0	2.0	0.0	2.2	0.0	4.2
Transportation	9.0	.9	1.1	0.1	10.1	1.0
Other	-	-	0.2	1.1	0.2	1.1
TOTAL	22.3	29.7	2.2	5.3	24.5	35.0

* Inco, Sudbury at 1980 emission rate.

From: Canada/United States Work Group 3A Interim Report "Strategies Development & Implementation" Feb/81. Ottawa.

TABLE 2-2

AIR EMISSIONS FROM A TYPICAL 1000 MW COAL FIRED STEAM PLANT

Constituent	Mean concentration in coal[2]		Annual air emission (kg/yr)
Major			
Ash	11.4	(%)	2.5 x 10^6
Total carbon	70.3	(%)	10^{10} (as CO_2); 10^7 (as CO)
Total sulfur	3.3	(%)	65 x 10^6
Water	9.	(%)	450 x 10^6
Total nitrogen	1.3	(%)	10^6 (as NO_x)
Al	1.3	(%)	0.24 x 10^6
Ca	0.77	(%)	0.14 x 10^6
Cl	0.14	(%)	7 x 10^6 (mostly vapor)
Fe	0.9	(%)	0.31 x 10^6
K	0.16	(%)	0.062 x 10^6
Mg	0.05	(%)	0.014 x 10^6
Na	0.05	(%)	0.02 x 10^5
Si	2.49	(%)	0.54 x 10^6
Ti	0.07	(%)	0.034 x 10^6
Minor			
Organic C	-		5000.
Fluoranthane	-		35.
Benzo(ghl)perylene	-		14.
Benzo(a)pyrene	-		13.
Benzo(a)pyrene	-		7.
Pyrene	-		13.
Perylene	-		6.
Phenanthrene	-		3.
Corenene	-		0.6
Ag	0.1	(ppm)	31.
Au	0.001	(ppm)	0.3
As	14.	(ppm)	3,500.
B	102.	(ppm)	3,100.
Be	1.6	(ppm)	80.
Br	15.4	(ppm)	70,000. (mostly vapor)
Cd	2.5	(ppm)	680.
Co	9.6	(ppm)	540.
Cr	13.8	(ppm)	1,700.
Cu	15.2	(ppm)	915.
F	61.	(ppm)	15,000. (40% as vapor)
Ga	3.1	(ppm)	172.
Ga	6.6	(ppm)	1,600.
Hg	0.2	(ppm)	1,000.
Li	9.	(ppm)	365.
Mn	49.4	(ppm)	1,500.
Mo	7.5	(ppm)	940.
Ni	21.1	(ppm)	1,300.
P	71.1	(ppm)	2,700.
Pb	34.8	(ppm)	11,000.
Rb	40.	(ppm)	1,200.
Sb	1.3	(ppm)	360.
Se	2.1	(ppm)	335. (20% vapor)
Sn	4.8	(ppm)	1,200.
Sr	34.	(ppm)	1,100.
Ta	0.16	(ppm)	6.5
Te	50.	(ppm)	2,500.
Th	3.1	(ppm)	96.
Ti	680.	(ppm)	33,000.
U	5.	(ppm)	260.
V	32.7	(ppm)	3,400.
W	3.	(ppm)	90.
Zn	272.	(ppm)	37,000.
Zr	72.5	(ppm)	2,200.
Ra			0.1 (Ci)

---

[1] Plant has electrostatic precipitator efficiency of 99.5%, no scrubbers, and consumes 5 x 10^6 tons of coal per year.

[2] Western, midwest and eastern coal mean of 101 samples.

From: A.W. Andren personal communication, Bauer et al. 1982a & 1982b, EPRI 1980, Klein et al. 1975, NAS 1977, ORNL 1977.

TABLE 2-3

SUMMARY OF GLOBAL SOURCES, ANNUAL EMISSION, BACKGROUND CONCENTRATION, MAJOR SINKS, AND RESIDENCE TIME OF ATMOSPHERIC GASEOUS POLLUTANTS

Pollutant [1]	Major Source		Estimated Emission kg/yr			Major Identified Sinks	Residence Time[2]
	Anthropogenic	Natural	Anthropogenic	Natural	Concentration $\mu g\ m^{-3}$		Days
SO_2	Combustion of coal and oil (North America)[3]	Volcanoes	130×10^9 16×10^9	2×10^9 0.8×10^9	1-4	Scavenging: Chemical reactions; Soil and surface water adsorption; Dry deposition	1-5 (Average)
SO_2 (Aerosol)	Combustion	Sea Spray	-	-	0.5-5	Scavenging; Dry deposition	3-5
H_2S	Chemical processes; Sewage treatment	Volcanoes; Biological Decay	3×10^9	100×10^9	0.3	Oxidation to SO_2	1-3
N_2O	None	Biological decay	None	590×10^9	460-490	Photodissociation in stratophere; Surface water and soil adsorption	3,500
NO	Combustion	Bacterial action in soil; Photo-dissociation of N_2O and NO_2	53×10^9	768×10^9	0.3-2.5	Oxidation to NO_2	0.1-5
NO_2	Combustion	Bacterial action in soil; Oxidation to NO			.2-2.5	Photochemical reactions; Oxidation to nitrate;Scavenging	1-5
NH_3	Coal burning;Fertilizer; Waste treatment	Biological decay	4×10^9	170×10^9	4.0	Reaction with SO_2; Oxidation to nitrate scavenging	<7
CO	Auto exhaust and other combustion processes	Oxidation of methane; photo-dissociation of CO_2; Forest fires;Oceans	360×10^9	3000×10^9	100	Soil adsorption; Chemical oxidation	36
O_3	Electrical discharge; NO_x conversion processes	Tropospheric reactions and transport from stratosphere	(?)	(?)	20-60	Photochemical reactions; Absorption by land surfaces (Soil and Vegetation; Surface Water)	110
Non-reactive hydrocarbons	Auto exhaust; Combustion of oil	Biological processes in swamps	70×10^9	300×10^9	CH_4=1000 non-Ch_4<1	Biological action	700
Reactive hydrocarbons	Auto exhaust; Combusion of oil	Biological processes in forests	27×10^9	175×10^9	<1	Photochemical oxidation	-

From [1]Rasmussen et al. 1975,
[2]Robinson and Robbins 1970,
[2]Rodhe 1978,
[2]Söderlund and Svensson 1976,
[2]Spadding 1972,
[2]Stewart et al. 1978,
[2]Sze 1977,
[2]Liu 1978,
[2]Kellog et al. 1972,
[2]Junge 1972, 1974, 1977,
[2]Granat et al. 1976,
[3]Galloway and Whelpdale 1980.

example, Rasmussen and Kabel (1975) estimated that greater than 90 percent of the global anthropogenic SO_2 is emitted from the Northern Hemisphere. This spatial concentration of pollutant emission sources causes many atmospheric constituents to exceed their natural levels several fold.

2.2.2 Atmospheric Transport of Pollutants

The fate of a pollutant once emitted into the atmosphere depends on several factors, some meteorological and some a function of the pollutants themselves. It is important to have this information since most sensitive receptor areas are located at considerable distances from the pollutant sources regions.

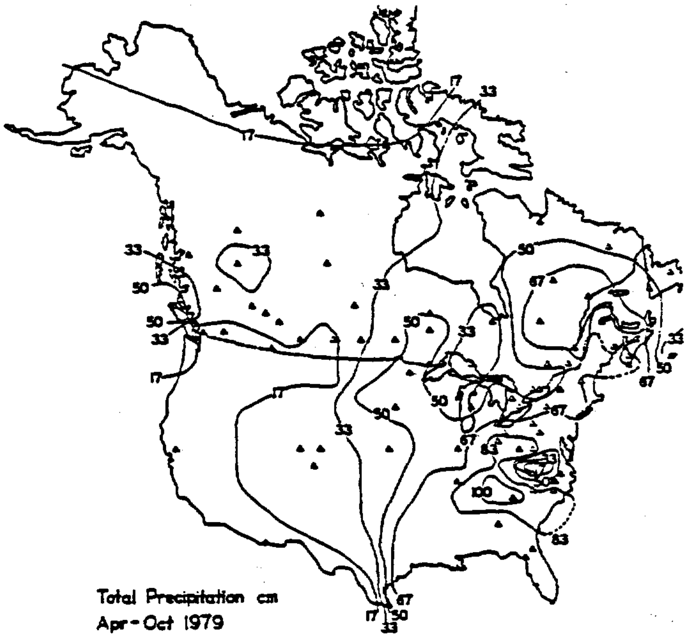
Several types of meteorological factors influence long distance transport. The prevailing wind regime over much of the eastern U.S. and Canada is one of westerly winds. This pattern is complicated by seasonal trends, in that there is a southerly component in the summer and a northerly component in the winter (Figure 2-3 a & b). "Long-range transport" is facilitated by tall stacks, high wind, and a stable lower atmosphere (i.e., where the temperature increases with altitude). Absence of precipitation also increases the distance of transport. Figure 2-4 shows isopleths of precipitation for the North American continent. The numbers on the contours represent the average number of centimeters of water falling on the land during two periods, warm and cool, over 12 months. The amount of precipitation in any particular locality usually varies from year to year, but over a long period its average is fairly constant. The precipitation patterns shown in Figure 2-4 partially govern the removal processes of pollutants from the atmosphere.

The properties of the pollutants also will determine their ultimate fate in the atmosphere. Junge (1977) has argued that atmospheric constituents may be put into three categories, each describing the fate of a set of compounds; (1) accumulative gases, (2) gases determined by chemical or physio-chemical equilibria with the earth's surface, and (3) gases and particulate matter (aerosols) determined by steady-state conditions of their cycles.

The third category comprises most trace gases and particulate matter and is the prime concern of this report. The atmospheric concentration of these constituents is determined by dynamic processes between sources and sinks. The average atmospheric residence time (T) of a constituent (sometimes also called turnover time) is defined as:

$$\frac{\text{Emission Rate}}{\text{Amount in Atmosphere}} = \frac{\text{Deposition Rate}}{\text{Amount in Atmosphere}} = T \text{ (at steady state)}$$

Figure 2-3, a&b Wind patterns for North America based on surface stream-lines for (a) January and (b) July (from Bryson and Hare 1974).



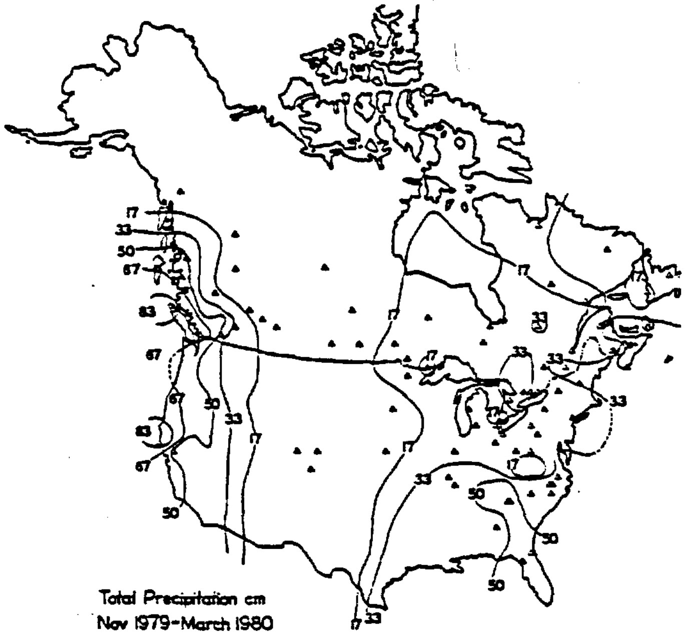


Figure 2-4 Seasonal precipitation for North America patterns, total precipitation as water depth (cm), shown for "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).

While pollutants generally are not at a steady state, T is valuable for predicting whether a constituent is accumulating in the atmosphere. Pollutants such as sulphur and nitrogen oxides, with residence times of just a few days, are particularly important on the regional scale, because these times are comparable to the times typically required for atmospheric transport across eastern North America. A large percentage of compounds with relatively short residence times (a few days) are deposited within tens to hundreds of kilometers from the point of emission. Compounds with longer residence times may travel thousands of kilometers. Galloway and Whelpdale (1970) estimate, for example, that some two-thirds of sulphur emissions in eastern North America are deposited there, the remainder being transported out over the Atlantic Ocean. Table 2-3 presents typical residence times for other selected parameters.

2.2.3 Atmospheric Removal Processes

Substances transported through the atmosphere are removed via wet and dry processes. There are presently a number of deposition models, both empirical and theoretical, which may be used in delineating pollutant deposition patterns. The suitability of these models depends on the time and space scales of the transport processes under consideration and the complexity of the chemicals of interest. The transport process models require knowledge of the chemical and physical characteristics of the airsheds involved, for example, reaction rates under ambient conditions; the concentration in the solid, vapour, and liquid states; size distributions, morphology, and sorptive characteristics of aerosols; and the vertical, aerial, and temporal variability of these parameters.

Particles and unreactive gases in air may be removed by rainout (in-cloud processes) and washout (below-cloud removal). The wet flux of these substances is a function of their concentration in precipitation and the amount of precipitation. The particle washout ratio has been completed by several authors for different chemicals (see, for example, Slinn et al. 1978). Slinn et al. (1978) have also summarized data on enhanced solubility coefficients for reactive gases. These gases include SO_2, where the dissolution, hydrolysis and oxidation to sulphuric acid are considered.

Accurate and direct measurements of dry deposition, both for aerosols and gases, are not possible at present (Hicks and Williams 1980). The mass transfer is especially difficult to estimate for trace chemicals because long sampling times are required (often greater than 24 hours) and meteorological conditions may change drastically during such a sampling interval. Dry flux estimates will undoubtedly change in the future as deposition measurement techniques and models improve. At the present time, it seems that the best experimental strategy is to collect accurate data for atmospheric constituents with the best possible time resolution, at an appropriate reference height, and with as much meteorological information as possible.

Several approaches are available for indirectly calculating mass transfer of aerosols to the earth's surface. The most popular approach has been to use the relation by Chamberlain (1966):

$$F = V_D C_Z \qquad (1)$$

where F = flux, V_D = deposition velocity, and C_Z = pollutant concentration at a certain reference height. Deposition velocity data, determined by wind tunnel experiments for several particle diameters, roughness lengths, and friction velocities, have been furnished by Sehmel and Sutter (1974), Cawse (1974) and Moller and Schuman (1970). The data, which have been summarized by Gatz (1974), represent time-averaged deposition velocities for a variety of meteorological conditions and thus do not necessarily give realistic values for aerosol depositions to water. Sievering (1980) has used the profile method for estimating fluxes across the air/water interface. Hicks and Williams (1980) have proposed a new spray capture model, indicating that very little (if any) transport is possible during calm conditions. Slinn (1980) has proposed a more sophisticated resistance model, where aerosol growth in the surface layer is included. Sehmel and Hodgson (1974) have presented a model based on dimensionless integral mass transfer resistances. Surface integral resistances were evaluated with deposition velocities of monodispersed aerosols determined in wind tunnel experiments.

Similar models are also available for gaseous deposition to various surfaces. Whelpdale (1980), Garland (1980), Gramat (1980) and Liss and Slater (1974) have devised models based on resistance of transfer to various surfaces, such as grass, snow, water, and forest canopies. These models usually include an aerodynamic, stagnant film, and stomatal (for vegetation) resistance. The same caveats are necessary on these models as are applied to dry particle deposition.

The relative importance of each process, i.e., dry vs. wet, has only recently been evaluated. Based on several modelling efforts, wet and dry deposition of sulphur compounds seem to be of equal importance in northern Europe and North America. Dry deposition seems to be of lesser importance in remote areas. Harvey et al. (1981) conclude that dry deposition is relatively more important in areas like the Ohio Valley, whereas the opposite is true in remote Canadian Shield lakes.

2.2.4 Alteration of Precipitation Quality

The seasonal quantity and quality of precipitation are important for determining the potential for acid rain impacts on the environment. Acid pollutants accumulating in the snowpack have a higher potential for causing deleterious effects on organisms and habitats in areas with higher snowfall, than in areas with lower amounts of snow accumulation. This is due to the rapid flushing of accumulated acid during snowmelt. Large storms, on the other hand, tend not to have as low a pH for the entire rainfall as do light rains. Thus, the distribution of precipitation during the year, the temporal behaviour of rainfall, and the location of pollution sources within rainfall pathways are linked to the potential for damage to the aquatic ecosystems. In addition, many areas in the east with the greatest annual precipitation have the least buffering capacity in soils and waterways.

Distilled water in equilibrium with atmospheric carbon dioxide has a pH value of about 5.6. Results of CANSAP + NADP monitoring presented in Figure 2-5 show large areas of North America which are receiving precipitation with a pH less than 5.6. This results in elevated deposition of acids to the surface as shown in Figure 2-6, in contrast to deposition which would occur if the precipitation had a pH of 5.6 (Figure 2-7).

All precipitation contains a wide variety of chemical constituents from sources such as sea spray, dust particles and the natural cycling of carbon, nitrogen and sulphur. The discharge of wastes to the atmosphere increases the amounts of compounds containing elements such as nitrogen, carbon and sulphur, and adds to the variety of compounds, such as PCBs and heavy metals, which are found in rainfall. The four ions usually of most importance to rainfall acidity are: hydrogen (H^+), ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}). Other ions, e.g., calcium, may be important under some conditions. Some of the nitrogen and sulphur-containing pollutants are oxidized to nitric and sulphuric acids, so that the acid content of precipitation is mainly a secondary result of the primary emissions.

Table 2-4 lists the concentrations of these four major ions in bulk precipitation and total bulk deposition for various sites in North America. Precipitation at pH 5.6 has a hydrogen ion content of about 2.5 µeq/l (microequivalents/litre). It is evident that the most westerly study area, the Experimental Lakes Area, has an acid concentration of about four times this value, while Dorset and Hubbard Brook are about 30 times this value. Sulphate is the dominant anion in terms of eq/l (equivalents/litre). In the wet precipitation at Kejimkujik National Park, Nova Scotia, the most easterly study area, the pH is about 4.6, while sulphate is the

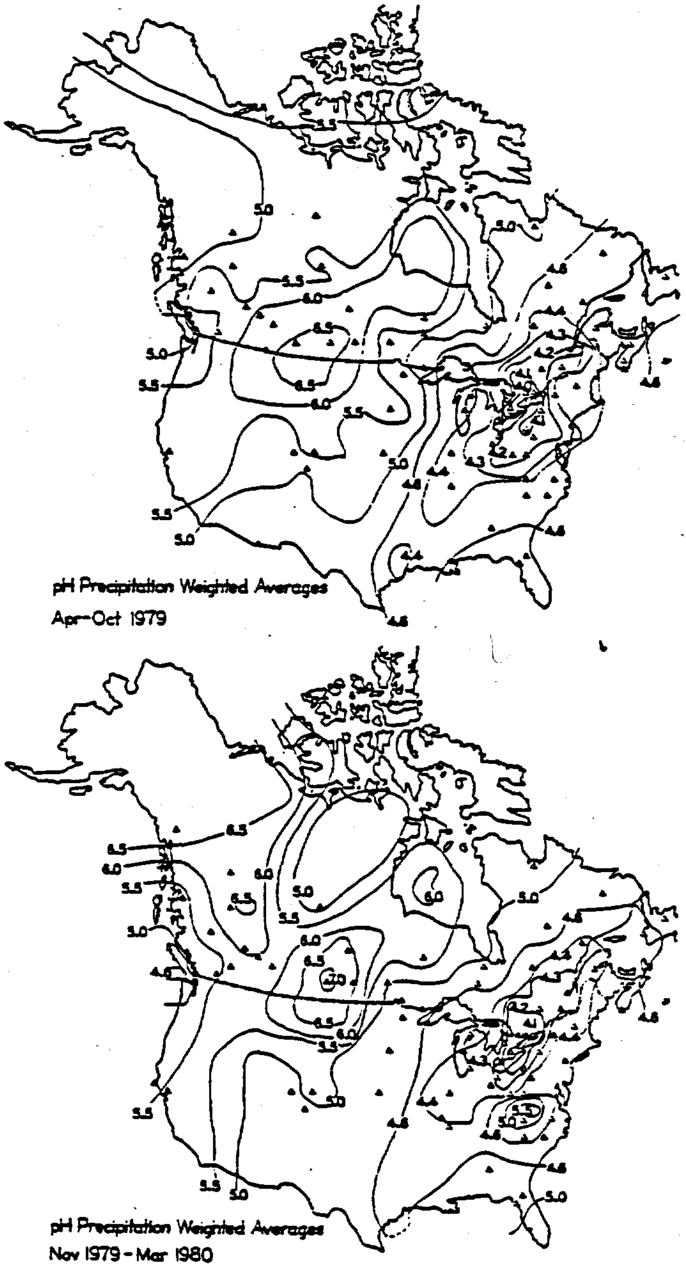
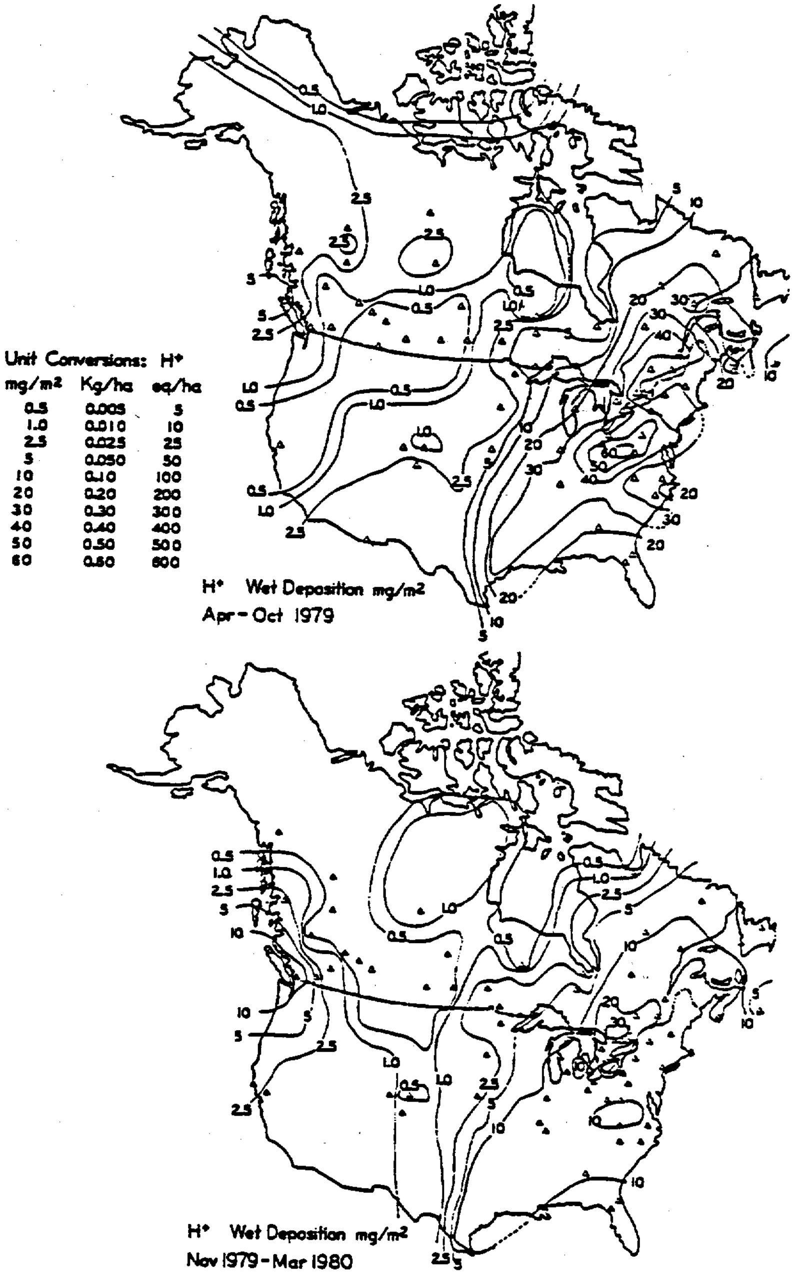


Figure 2-5. Seasonal pH of precipitation for North America, Volume Weighted Averages, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981)



Unit Conversions: H⁺

mg/m²	Kg/ha	eq/ha
0.5	0.005	5
1.0	0.010	10
2.5	0.025	25
5	0.050	50
10	0.10	100
20	0.20	200
30	0.30	300
40	0.40	400
50	0.50	500
60	0.60	600

Figure 2-6. Seasonal H⁺ Wet Deposition for North America, mg/m², "Summer" April – October 1979, and "Winter" November 1979 – March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981)

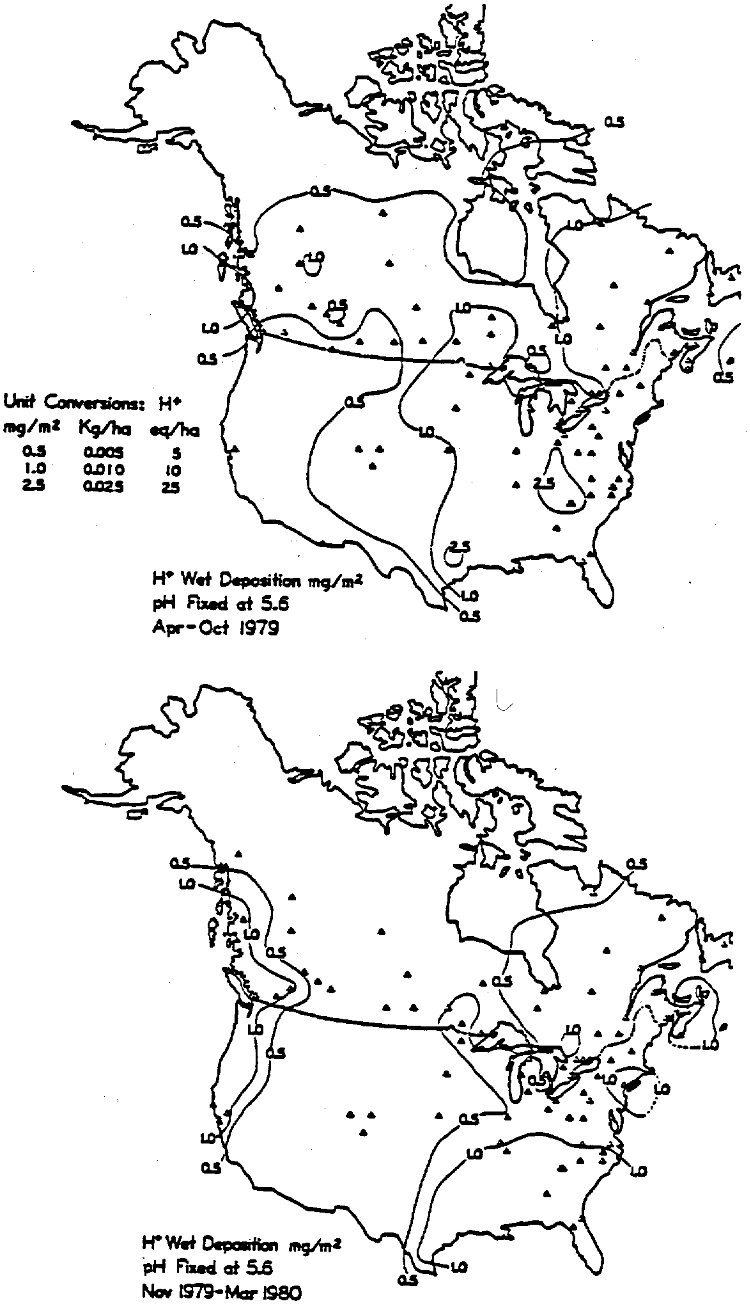


Figure 2-7. Calculated Seasonal H+ Wet Deposition mg/m^2, assuming background pH of 5.6, for "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).

TABLE 2-4

CONCENTRATIONS IN BULK DEPOSITION AND TOTAL BULK DEPOSITION OF FOUR IONS AT FOUR CALIBRATED WATERSHED STUDIES

CONCENTRATIONS IN BULK DEPOSITION μeq/l

	E.L.A.[1]	Dorset[2]	Hubbard Brook[3]	Kejimkujik* Park[4]	Sagamore Lake[5]
H+	11	70-90	72-74	24	-
NH_4^+-N	21	34-36	12.2	4.4	-
NO_3^--N	18.5	36-41	23.7	12.4	-
SO_4^{2-}	30	77-89	60.3	33(28.5)	-
Deposition in meq/m^2.yr from bulk deposition					
H^+	10	55-58	96	34	80-95
NH_4^+-N	-	22-28	16	6	20-26
NO_3^--N	-	25-34	30.6	17	37-50
SO_4^{2-}	20.7	62-64	79	46(40)	81-95

* Wet deposition only, ( ) indicating excess sulphate.

From: [1] Schindler et al. 1976

[2] Scheider et al. 1979

[3] Likens et al. 1977

[4] Kerekes 1980

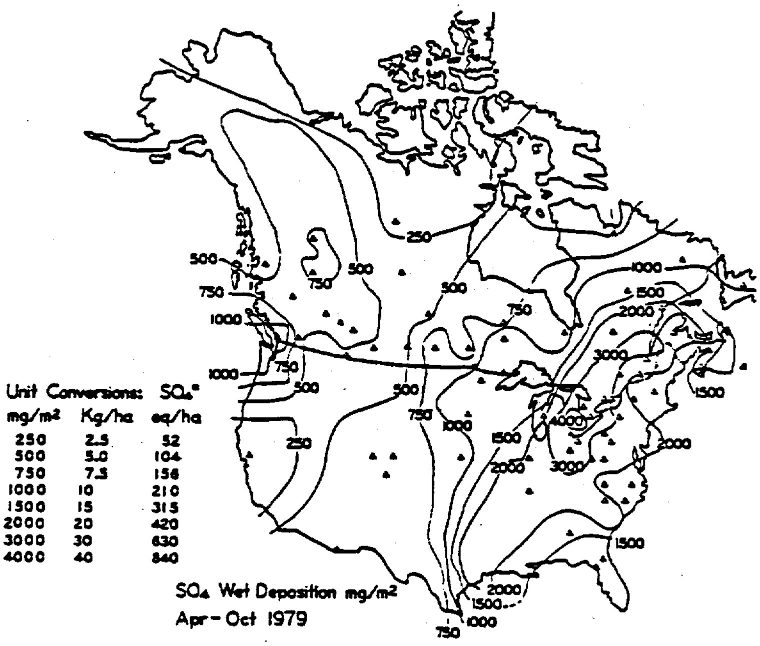
[5] Johannes and Altwicker 1980

NOTE: differences in values for areas, compared to the isoplot figures are due to year to year variations.

second highest anion, surpassed by chloride (41 μeq/l), which is a reflection of the strong maritime influence on the precipitation in Nova Scotia.

Figures 2-8 through 2-15 show the summer (April to October inclusive) and winter (November to March inclusive) wet deposition of sulphate, ammonium nitrate, chloride, calcium, magnesium, sodium, and potassium, respectively. The sulphate deposition is about 3 times greater in summer than in winter, particularly in the areas of greatest deposition in eastern North America. This is consistent with seasonal sulphur emissions (Work Group 2 report). Ammonium deposition also tends to be greater in the summer months, although some areas have similar winter and summer values. Nitrate deposition is similar to ammonium deposition, with a tendency toward higher values in the summer, although western areas have similar winter and summer values.

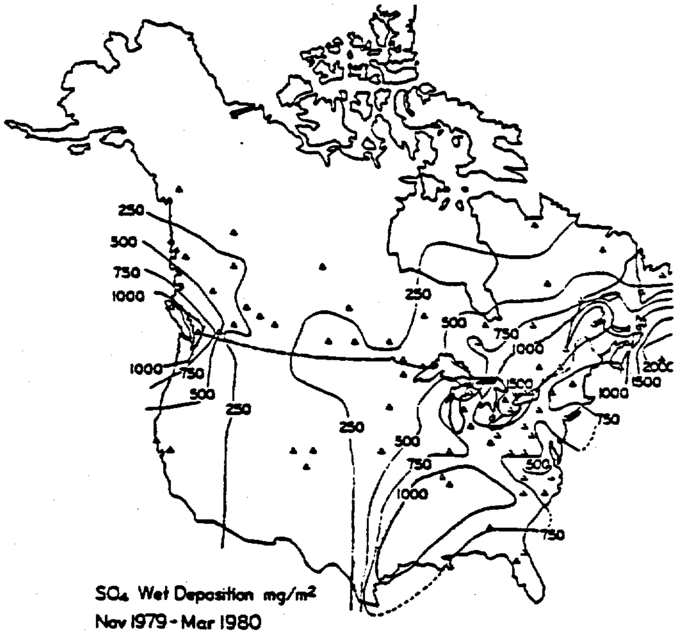
The alkali and alkaline earth metals (Figures 2-12 to 2-15) show major influences due to inputs from coastal and oceanic areas, especially in the mid-latitude regions of North America. However there are also significant regional sources for those metals, apparently from wind-blown dust in the arid and plains regions of central North America. These elevated levels of sodium, potassium, calcium and magnesium also coincide with the high pH values, Figure 6, indicating that the input of these alkaline substances acts to neutralize and, in many instances, to raise the pH of precipitation above that expected for background levels.



Unit Conversions: $SO_4^=$

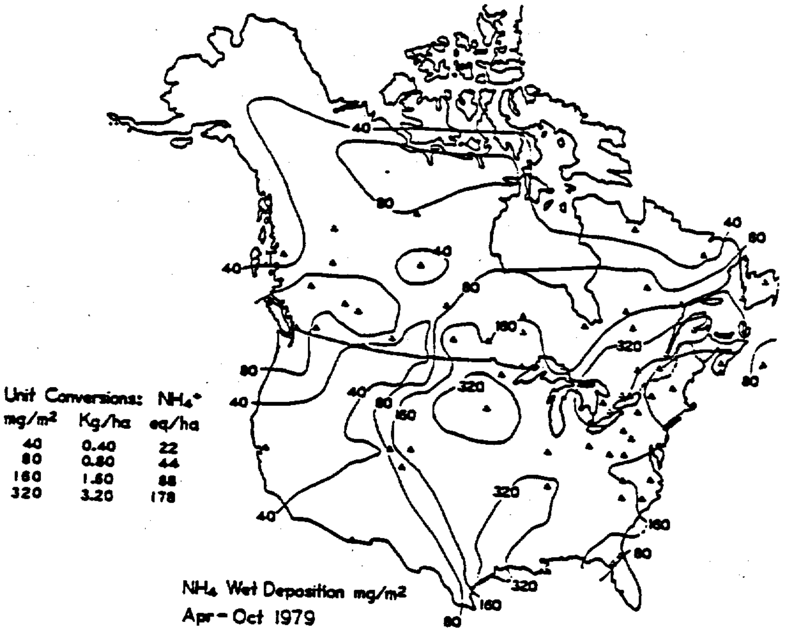
mg/m²	Kg/ha	eq/ha
250	2.5	52
500	5.0	104
750	7.5	156
1000	10	210
1500	15	315
2000	20	420
3000	30	630
4000	40	840

SO_4 Wet Deposition mg/m²
Apr-Oct 1979



SO_4 Wet Deposition mg/m²
Nov 1979-Mar 1980

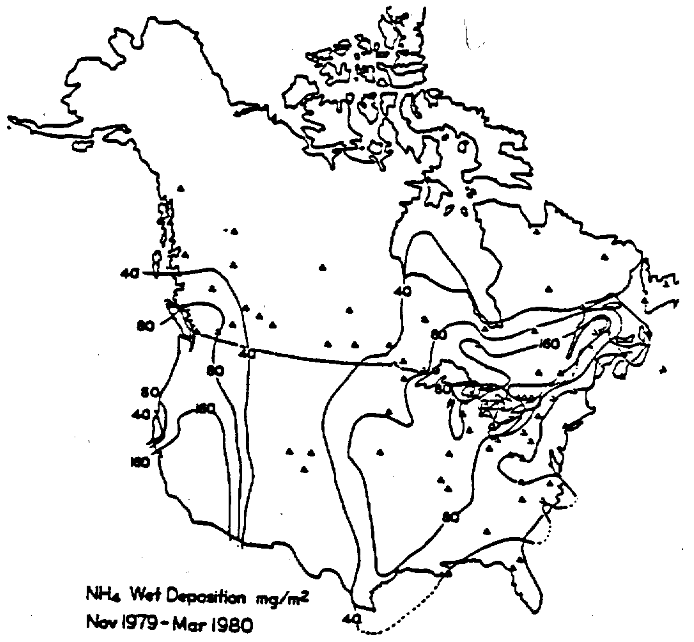
Figure 2-8. Seasonal SO_4^{2-} Wet Deposition, mg/m², for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



Unit Conversions: NH_4^+

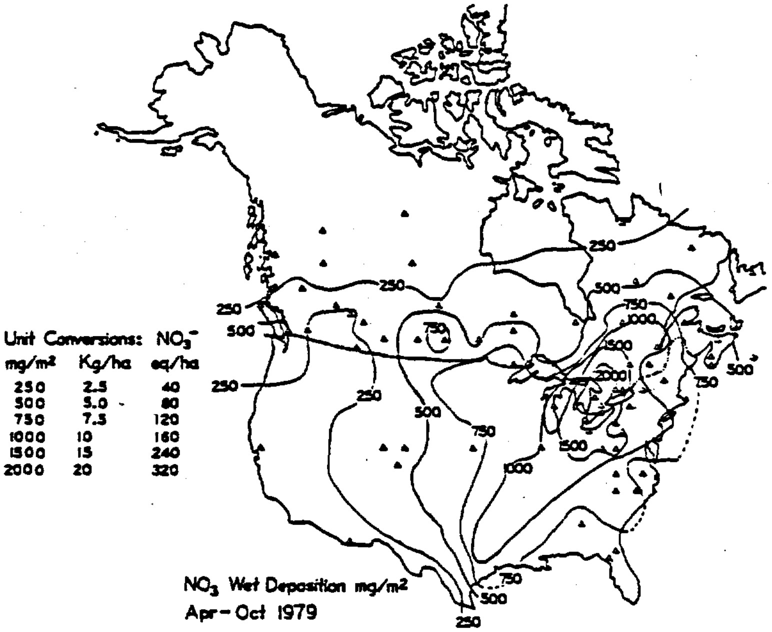
mg/m²	Kg/ha	eq/ha
40	0.40	22
80	0.80	44
160	1.60	88
320	3.20	178

NH_4 Wet Deposition mg/m²
Apr – Oct 1979

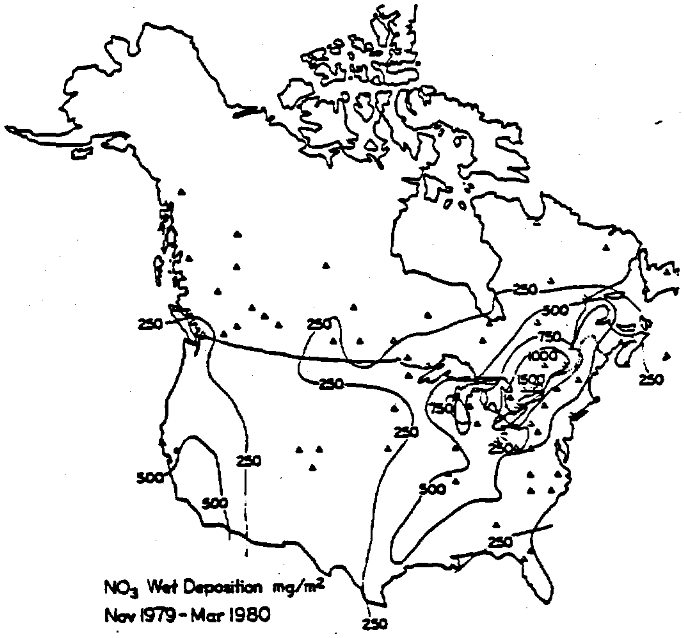


NH_4 Wet Deposition mg/m²
Nov 1979 - Mar 1980

Figure 2-9. Seasonal NH4+ Wet Deposition, mg/m², for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).

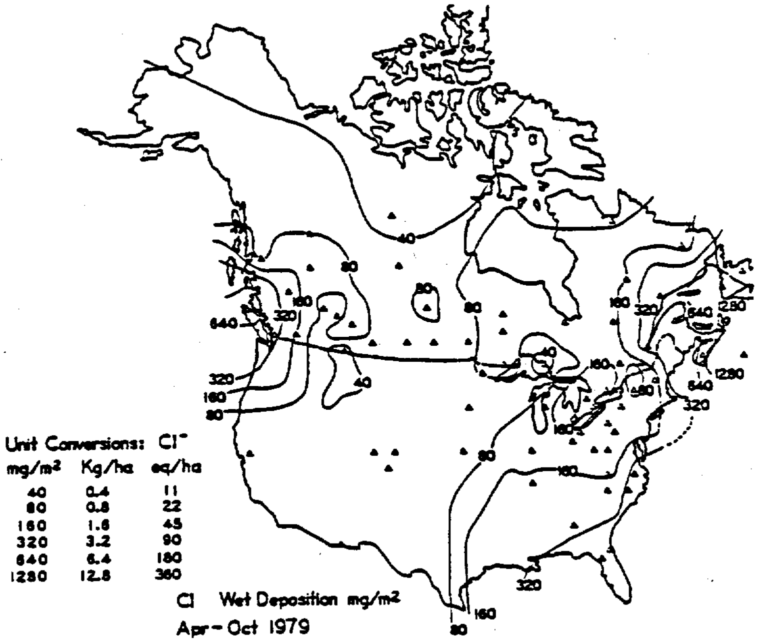


NO_3 Wet Deposition mg/m²
Apr – Oct 1979



NO_3 Wet Deposition mg/m²
Nov 1979 – Mar 1980

Figure 2-10. Seasonal NO_3^- - Wet Deposition, mg/m², for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



Unit Conversions: Cl⁻

mg/m²	Kg/ha	eq/ha
40	0.4	11
80	0.8	22
160	1.6	45
320	3.2	90
640	6.4	180
1280	12.8	360

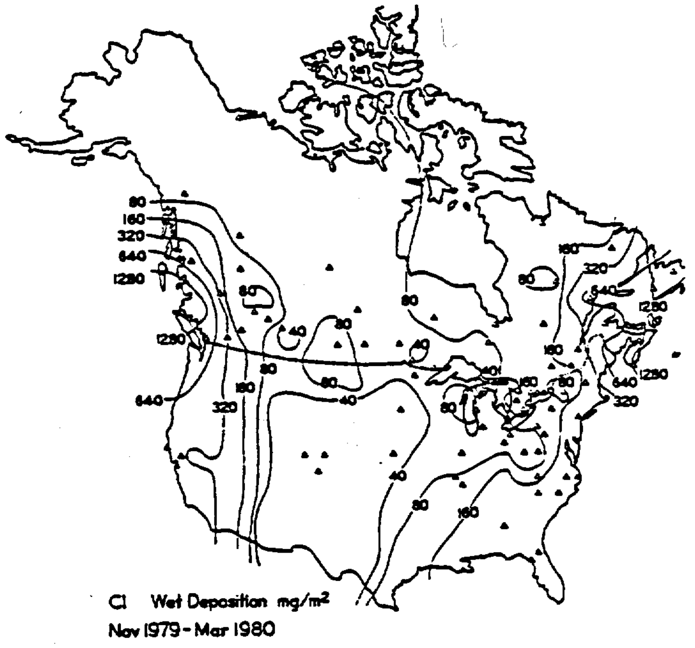
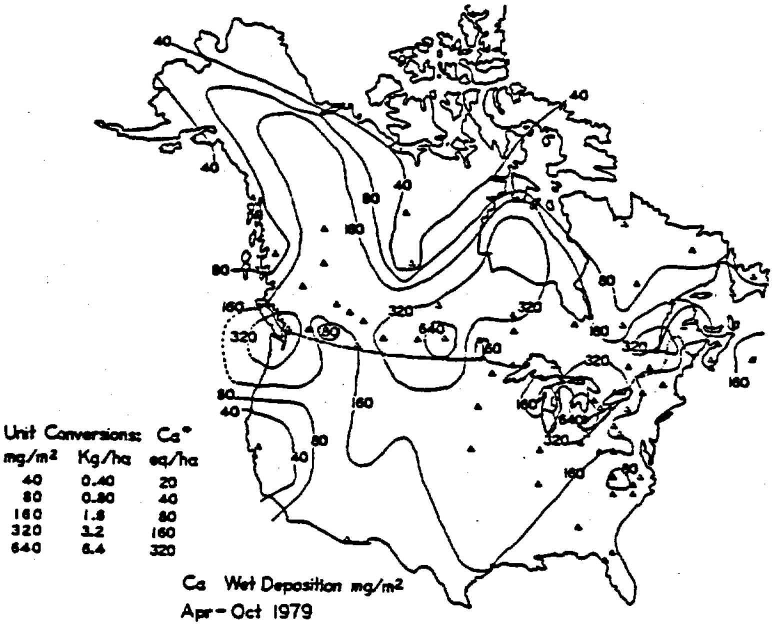


Figure 2-11. Seasonal Cl Wet Deposition, mg/m², for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



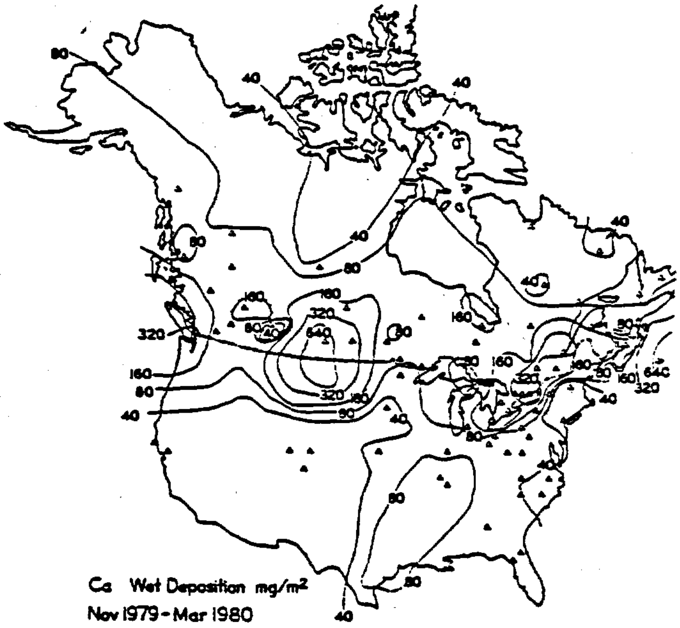
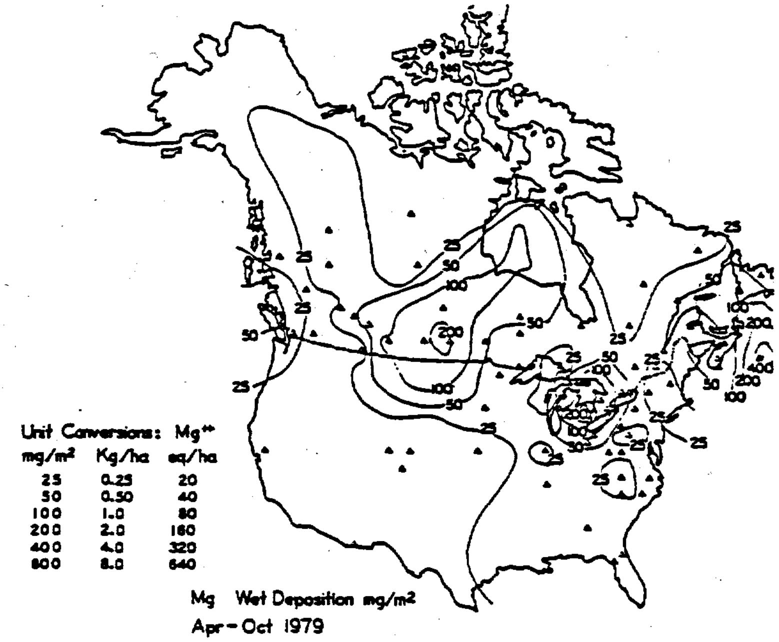


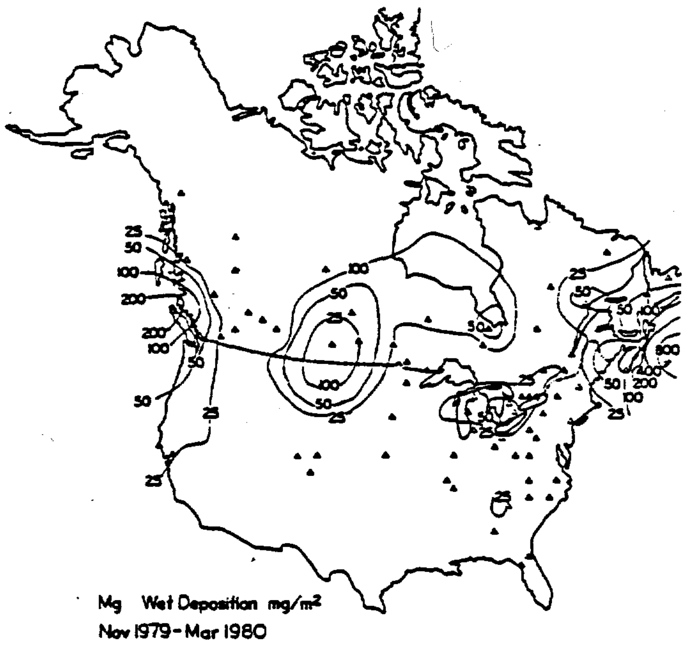
Figure 2-12. Seasonal Ca^{2+} Wet Deposition, mg/m^2, for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



Unit Conversions: Mg⁺⁺

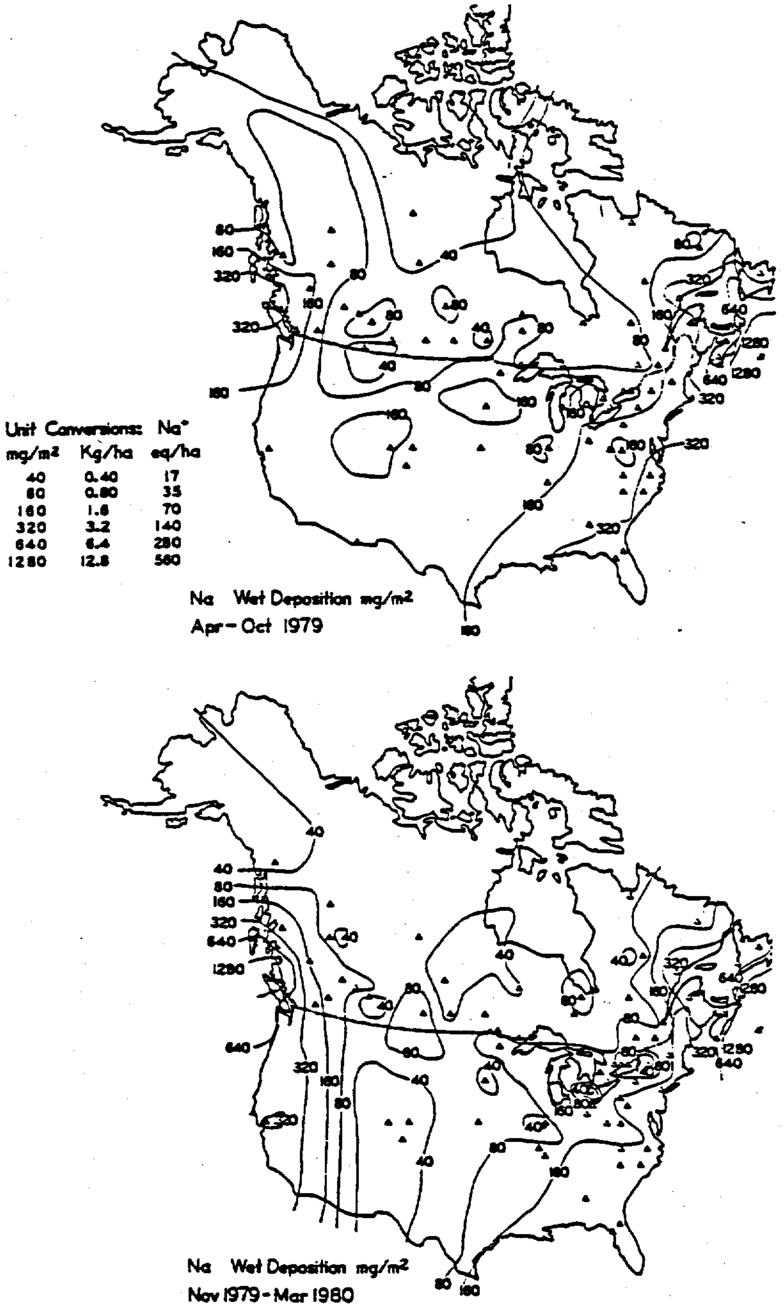
mg/m²	Kg/ha	eq/ha
25	0.25	20
50	0.50	40
100	1.0	80
200	2.0	160
400	4.0	320
800	8.0	640

Mg Wet Deposition mg/m2
Apr – Oct 1979



Mg Wet Deposition mg/m2
Nov 1979 – Mar 1980

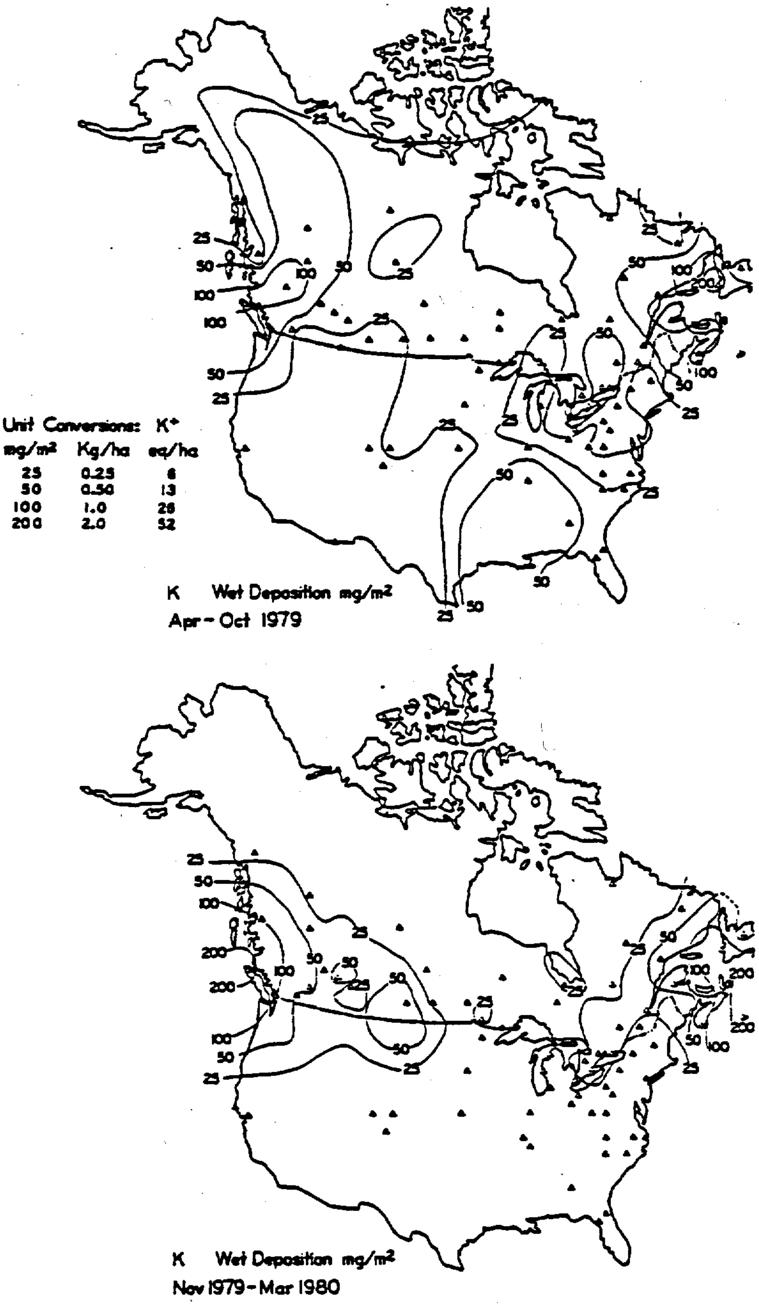
Figure 2-13. Seasonal Mg^{2+} Wet Deposition, mg/m^2, for North America, "Summer" April – October 1979 and "Winter" November 1979 – March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



Unit Conversions: Na+

mg/m2	Kg/ha	eq/ha
40	0.40	17
80	0.80	35
160	1.6	70
320	3.2	140
640	6.4	280
1280	12.8	560

Figure 2-14. Seasonal Na^+ Wet Deposition, mg/m^2, for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).



Unit Conversions: K+

mg/m2	Kg/ha	eq/ha
25	0.25	6
50	0.50	13
100	1.0	26
200	2.0	52

Figure 2-15. Seasonal K^+ Wet Deposition, mg/m^2, for North America, "Summer" April - October 1979 and "Winter" November 1979 - March 1980. Data reporting sites (Δ) are from the NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1981).

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SECTION 3

AQUATIC IMPACTS

3.1 INTRODUCTION

This assessment of Aquatic Impacts is structured to deal with three major questions about aquatic impacts of long-range pollutant transport and deposition in North America.

1. What is the nature and extent of the chemical alteration of the hydrologic cycle due to pollutant deposition?
2. What is the nature and extent of biotic alteration in aquatic ecosystems as a result of acid-induced chemical alteration?
3. What is the geographical distribution and acid loading tolerance, or threshold, for watersheds of varying sensitivity?

This section uses several approaches to these questions. First, emphasis is placed on identifying and substantiating all effects possibly related to transboundary movement of acidifying substances. This evaluation has required some consideration of the complexity of hydrologic systems, as well as of the complexity and the extent of aquatic resources which are at risk. Included are detailed documentations of impacted aquatic environments, both chemical and biotic components, and definition of the time trends for observed effects on these components.

Secondly, this section considers the significance of the episodic nature of atmospheric pollutant loading, and pollutant flushing processes, such as snowmelt, as well as the seasonal character of the receiving environments, such as periods of spawning. Thus, these sections relate pollutant loading levels to the observed extremes in chemical and biological effects.

Finally, this section focuses on the aquatic areas and populations which are sensitive to acidic deposition, believed to result from transboundary air pollution. It is, therefore, necessary to define an acid-loading tolerance, to list both aquatic resources at risk from higher loading levels, to show sensitive areas, and to discuss recovery possibilities for aquatic systems showing apparent damage.

3.2 ELEMENT FLUXES AND GEOCHEMICAL ALTERATIONS OF WATERSHEDS

For a complete understanding of aquatic impacts, it is necessary to examine the fate of ions deposited from the atmosphere, both directly on aquatic systems and by indirect means, through deposition on watersheds. Deposition occurring in the latter case results in the geochemical alteration of watersheds, which must be considered before a complete understanding of aquatic ecosystem impacts can be achieved.

3.2.1 The Hydrogen Ion

The hydrogen ion driving most chemical weathering reactions is supplied from both external and internal sources. The external source is the acid supplied by atmospheric deposition (meteorological input); the internal source stems from various biologic and chemical processes occurring within the soil zone. The average external net annual input of hydrogen ion equivalent, observed at the Hubbard Brook watershed over the 1963-74 decade, was 86.5 ± 3.3 meq/m^2.yr (milli-equivalents/square metre.year) (Likens et al. 1977). If this were the only source of H^+ ions at Hubbard Brook (and the ecosystem were in a steady state), one might expect this value for hydrogen fixation to be more or less balanced by the net rate at which ionic Ca, Mg, K, Na, and Al are leached from the system. In fact, there are more of these cations removed from the ecosystem each year than there are external hydrogen ions to replace them. The difference is statistically significant, and implies the action of internally generated H^+ and/or an underestimate of dry deposition and/or the influence of ammonium and nitrate ions on the charge balance. Internal sources of H^+ at Hubbard Brook are identified as: (1) nitrogen compounds, particularly NH_4^+ inputs; (2) reduced carbon oxidized in the soil zone; (3) organic acids, such as citric, tartaric, tannic, and oxalic acid, produced by biologic activity within the soil zone; and (4) small amounts of sulphide minerals in the bedrock, which are subject to oxidation, with concomitant production of sulphuric acid.

The amounts of hydrogen ion being deposited from acid precipitation, generally, are in the range of 50-100 meq/m^2.yr for the most heavily loaded areas, corresponding to 25 and 50 kg/ha.yr (kilograms/hectare.year) of calcium carbonate. Limestone soils can neutralize this amount of acid for an indefinite time, resulting in only a slight increase in total runoff of calcium and magnesium salts relative to amounts in the soil. However, in areas underlain by resistent rocks and with poor soils, such as much of the Precambrian Shield, the amount of salts and alkaline materials being leached are in the order of 10 to 100 meq/m^2.yr. Hydrogen ion loadings are of the same order of magnitude in these areas and thus influence normal weathering processes and modify the quality of surface runoff. For example, some of the acid results in leaching of such cations as aluminum, iron and manganese.

In most parts of the Precambrian Shield, hydrogen ions from rainfall are neutralized during most of the year. Retention or neutralization of hydrogen ions deposited in bulk deposition has been measured at 88, 94 and 98 per cent, on an annual basis, at Experimental Lakes Area, Hubbard Brook and Dorset respectively (Schindler et al. 1976, Likens et al. 1977, Scheider et al. 1979a.) Hydrogen ions deposited in snow tend to be stripped from snow crystals early in the spring snowmelt process, and much of the total annual H^+ export from the watershed occurs during a brief period in the spring. The large volume of water, coupled with less opportunity for partial infiltration and interaction with soil, results in "shock level" concentrations of acid to streams and surface waters of lakes (Schofield 1980). Hultberg (1976) reported on such pH depressions in lakes and rivers in Sweden and demonstrated that the water quality conditions were lethal to fish.

3.2.2 Nitrate and Ammonium Ions

The atmospheric deposition of nitrate ion tends to range from one-third to one-half of the rate of sulphate deposition in eastern North America, to about 60 per cent of acid fractions in rainfall in the western United States (Liljestrand and Morgan 1978). The significance of the nitrogen component of acid precipitation is difficult to interpret with any broad generality, since it has more complex response processes than those of sulphate.

The molecular forms of nitrogen deposited in acid rain can result in either acidification or neutralization of surface waters. Nitrogen, as nitrate ions (NO_3^-), can be incorporated directly by vegetation, and the resulting reactions release hydroxyl ions (OH^-) into the environment (Figure 3-1). The hydroxyl ions raise the pH of the soil and water, or neutralize the hydrogen ions of the nitric acid. Natural decomposition of nitrogenous plant materials releases hydrogen ions, but net accumulation of plant tissue dominates in most ecosystems; hence, net production of neutralizing capacity from nitrate addition is usually dominant. This is particularly significant where forest harvest, rather than decomposition, removes plant materials.

Ammonium salts are deposited with the sulphate particulates in both dry and wet precipitation. Ammonium is a source of hydrogen ions (Figure 3-1) when the nitrogen is utilized by plants. This release of hydrogen ions can be a significant source of acidification in poorly buffered soils and surface waters. Nitrogen is usually in short supply in terrestrial habitats, and is readily incorporated and retained by ecosystems (Reuss 1976). The uptake and retention of nitrate and ammonium by forested watersheds are summarized in Table 3-1.

As with acid sulphates, nitric acid (nitrates) and ammonium salts can be stored in the snowpack of northeastern North America and

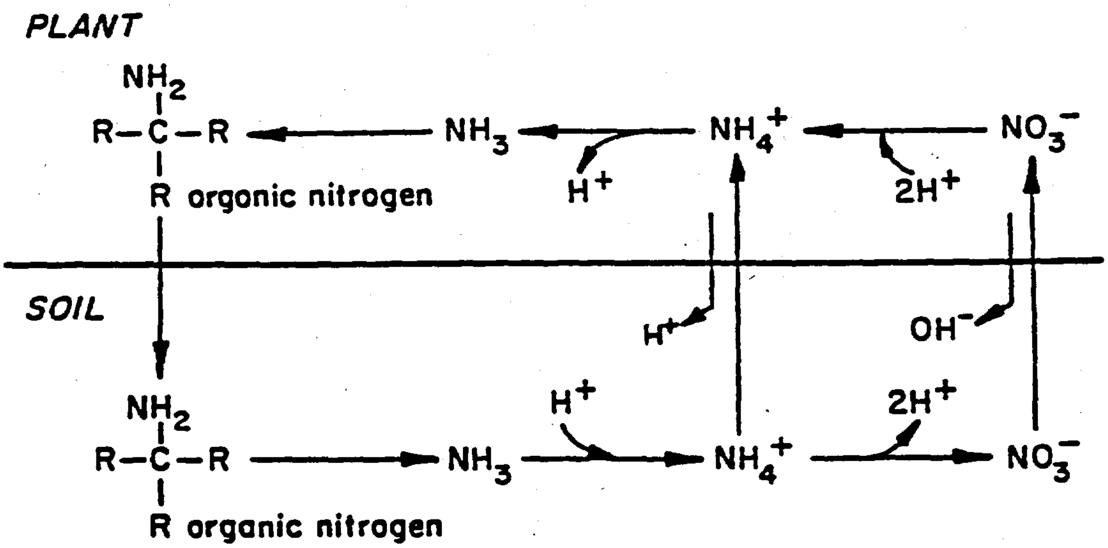


Figure 3-1 Simplified nitrogen cycle showing chemical changes caused by plant and soil processes (from Reuss 1976).

TABLE 3-1

THE UPTAKE OF NITRATE, AMMONIUM ION AND TOTAL NITROGEN BY FORESTED WATERSHEDS IN FIVE CALIBRATED WATERSHED STUDIES

	% Retention in the watershed on an annual basis						
Substance	E.L.A.[1]	Dorset[2]	Hubbard Brook[3]	Kejimkujik Park[4]	Sagamore Lake[5]	Woods Lake[5]	Panther Lake[5]
NO_3^-	-	75	15	99	43	70	15
NH_4^+	-	95	89	98	90	90	90
Total Nitrogen	81-90	-	-	-	-	-	-

From: 1 Schindler et al. 1976

2 Scheider et al. 1979a

3 Likens et al. 1977

4 Kerekes 1980

5 Galloway et al. 1980 (figures estimated from published bar graphs)

released as acid components to aquatic habitats during spring snowmelt. During the growing season, however, both terrestrial and aquatic vegetation take up nitrate, and may, therefore, be partially responsible for the observed decreases in acidity in aquatic ecosystems. The fact that nitrate tends to be in greater quantity in precipitation than ammonium ions, and that both are largely taken up by vegetation, result in a net production of alkalinity.

3.2.3 Sulphate

Sulphur, like nitrogen, is an essential plant nutrient, but it is usually in adequate supply for plant growth in soils, and is recycled through normal ecosystem cycling processes. Sulphate ions can be adsorbed by soils or reduced, mainly by bacterial action, which consumes acid and raises the pH of the soil-water environment. The reduced sulphide forms (S^{2-}) can be oxidized back to sulphate, resulting in the production of hydrogen ions. Sulphate, then, can react in ways analogous to nitrogen, and its influence on acidification can also be analogous. (Figure 3-2)

In spite of many possible reactions, much of the SO_4^{2-} deposited in acid precipitation is not retained in Precambrian Shield watersheds; thus, sulphate tends to be the anion balancing the transport of H^+ and other cations in surface water and shallow groundwater. The amount of SO_4^{2-} in runoff from the Shield areas is very close to the amount deposited. At the Experimental Lakes Area in Ontario, Schindler et al. (1976) found virtually 100 per cent of the atmospheric SO_4^{2-} input in the runoff. Likens et al. (1977) found 67 per cent of the total input in runoff at Hubbard Brook, New Hampshire, and Dillon et al. (1980) found 25 per cent more SO_4^{2-} in runoff from four watersheds than was measured in the bulk deposition. Kerekes (1980) reported that outputs of sulphate were about 80 per cent of the annual inputs for the Lower Mersey River system in Nova Scotia. At the Sagamore Lake Study area, Galloway et al. (1980) observed that sulphur inputs and outputs were in balance for two lake/watershed systems while a third watershed may have been accumulating some sulphur. In certain kinds of soils, such as are common in the southeastern U.S., sulphate may be retained in the soil by physical adsorption processes (D.W. Johnson, pers. comm.). This will have the very important effect of retarding the movement of cations, including H^+, from the soil to aquatic systems.

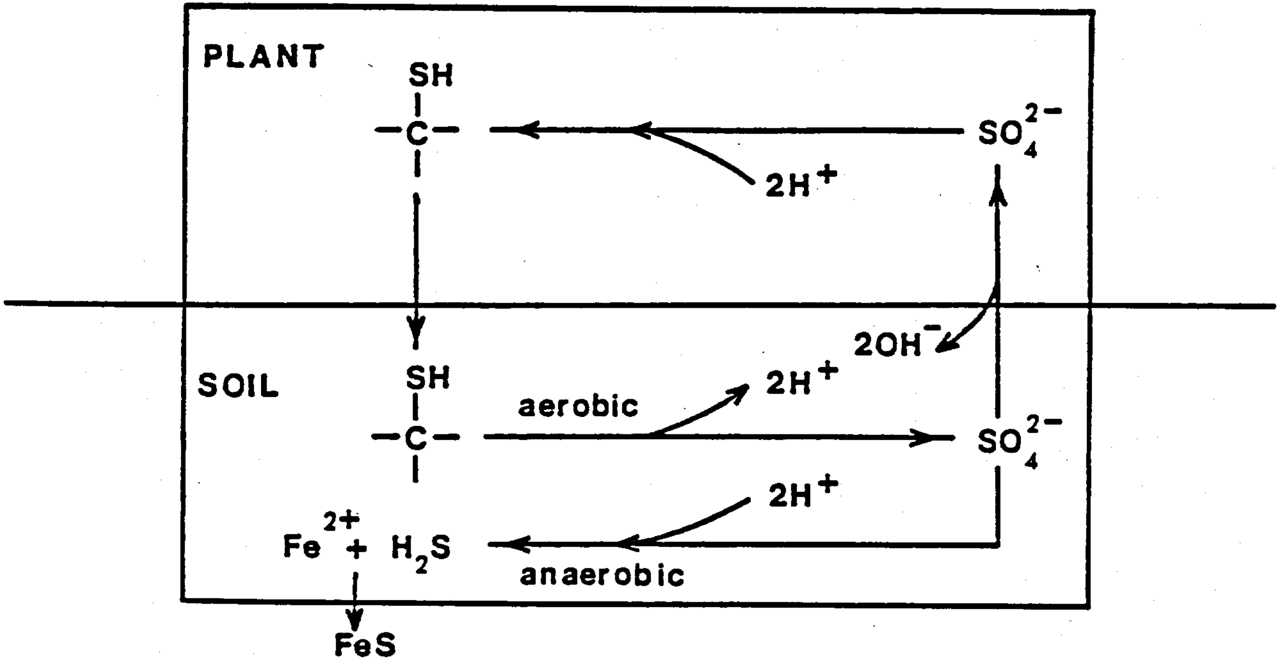


Figure 3-2 Simplified sulphur cycle showing chemical changes caused by plant and soil processes (modified from Reuss 1976).

3.2.4 Aluminum and Other Metals

One of the indirect effects of soil acidification is the mobilization of aluminum. The solubility of this metal is pH dependent, and increases with increasing acidity, as well as increasing alkalinity (Figure 3-3). Several reports have documented elevated aluminum concentrations in the surface waters of areas known to be impacted by acid inputs (Figure 3-4) (Wright and Gjessing 1976, Davis 1980, Cronan and Schofield 1979), and in effluent from lysimeters treated with acid solution (Dickson 1978, Abrahamsen et al. 1977). While aluminum ordinarily is leached from the upper soil horizon of podsol soils by carbonic acid, tannic and humic acids, and organic chelation, it is usually deposited in lower horizons. Under the influence of strong acids in precipitation, however, the aluminum may be mobilized in the upper (slightly acid) soil horizons and transported by saturated flow through the surface layers into lakes and streams (Cronan and Schofield 1979, Hall et al. 1980, Herrmann and Baron 1980). Elevated aluminum concentrations have been shown to occur during the spring melt of the snowpack, when large quantities of H^+ ions are released into the saturated surface layers (Seip et al. 1980, Driscoll 1980).

The mechanism supplying Al^{3+} to soil water, and therefore to shallow interflow water, is the decomposition of alumino-silicates and gibbsite. Norton (1976) and Reuss (1976) suggest the following model:

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_2 + H_2O$$
$$Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O$$
$$Al(OH)_2^+ + H^+ = Al(OH)^{2+} + H_2O$$
$$Al(OH)^{2+} + H^+ = Al^{3+} + H_2O$$

These reactions are likely to occur in watersheds where there are no carbonates to consume H^+, and the above reactions become the primary buffering mechanism (Johnson 1979, Kramer 1976). The pH at which this buffering occurs is around 4.5-5.0.

In aquatic systems, aluminum forms a variety of complexes with water and its constituents, including hydroxide, fluoride, silicate, organic matter, and sulphate (Everhart and Freeman 1973, Driscoll 1980, Baker and Schofield 1980). According to Johannessen (1980), these aluminum complexes act as a buffer in the pH range 4.5-5.0, but above and below these levels, buffering cannot be ascribed to aluminum complexes. Henriksen (1980) shows that lakes with pH 4.6-4.8 have a higher pH than expected from a theoretical "titration" curve based on bicarbonate buffering, and that the extra buffering can be explained by aluminum.

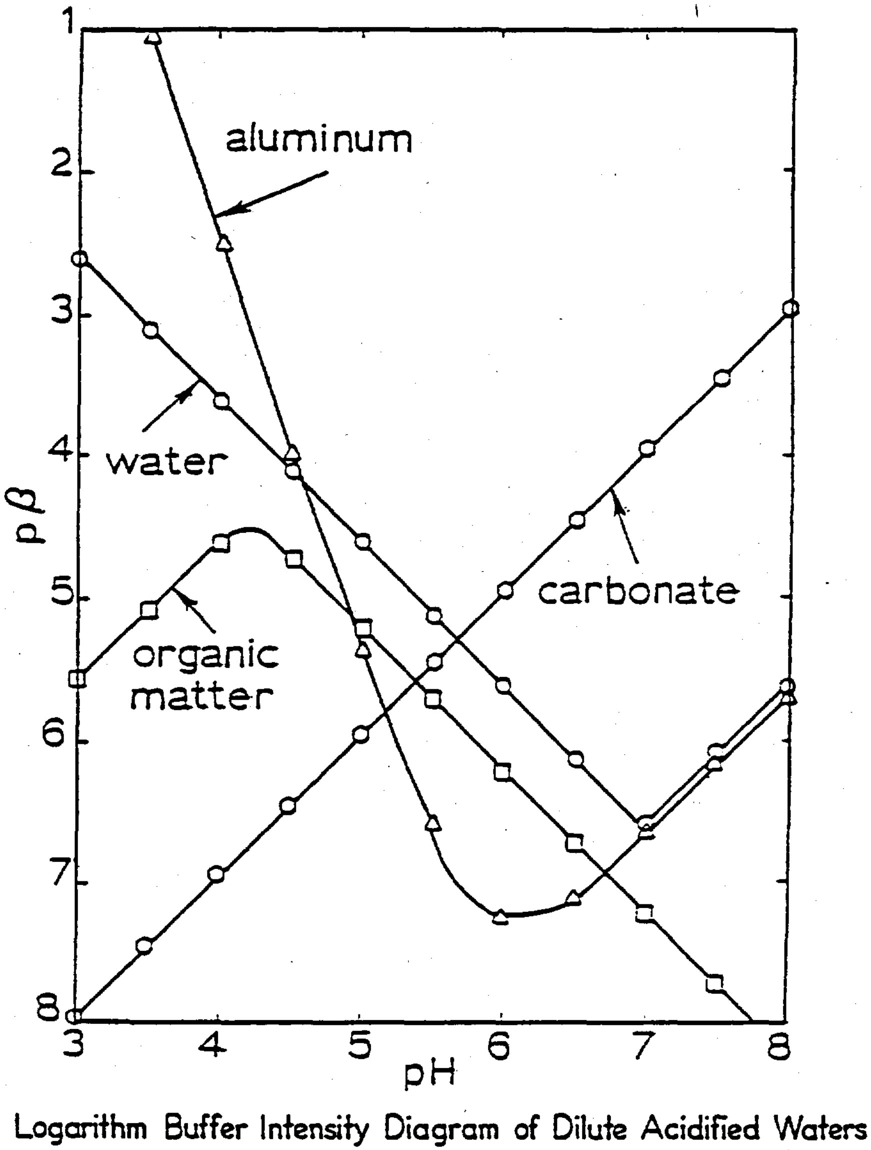


Figure 3-3 Logarithm buffer capacity diagram of dilute acidified waters (from Driscoll 1980).

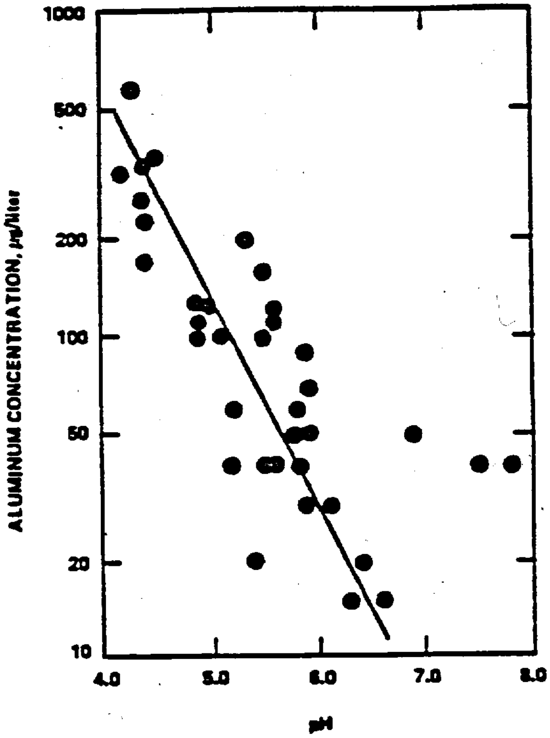


Figure 3-4 Relationship of observed stream concentrations of aluminum to the pH of surface water (Wright and Gjessing 1976).

In surface waters of the Adirondack Region of New York, Driscoll (1980) found aluminum-organic complexes as the predominant monomeric form (average = 44 per cent), which increased linearly with total organic carbon content. Aluminum-fluoride complexes were the most abundant inorganic form (average = 29 per cent of the total monomeric Al), with concentration increasing with decreasing pH, although their formation was generally limited by fluoride concentration.

A decrease in the pH of natural water columns has been shown to cause substantial increases in metal concentration due to their release from sediments. Schindler (1980) found substantial increases in lake water concentration of Al, Mn, Zn, and Fe, at pH 6 and 5, in acidified limnocoralls in the Experimental Lake Area. Zinc concentrations at pH 5 exceeded levels found to be toxic to fish. Also, radionuclides of Fe, Co, Mn, and Zn were found to be more soluble in acidified systems, where Hg and V radionuclides were less soluble. Elevated manganese, zinc and cadmium concentrations have been measured in acidified streams and lakes in Scandinavia (Wright and Gjessing 1976, Dickson, Almer et al. 1978).

Acid deposition is known to affect steel, copper, galvanized sheet and other metals, stone, paints, and plastics, both through dry and wet deposition. Exposure to atmospheric sulphur compounds can cause scaling and loss of surface cohesion in limestone and sandstone. Thus the effects for aquatic resources of acidic rainfall on construction materials, such as roofing, can be of importance to water quality. Similarly, materials such as are found in solid waste and mine tailing disposal sites may be influenced more by acidic rainfall and runoff than by relatively neutral rain. The magnitude of these effects is not known at this time.

3.3 THE EFFECT OF NATURAL ORGANIC ACIDS ON THE pH OF SOFT WATERS

3.3.1 Acidity Contribution

Certain lakes and streams can have low pH values as a result of natural processes. A major portion of the organics in natural waters are organic acids such as amino acids, produced by living organisms, and humic and fulvic acids, produced by the microbial degradation of plant and animal organic matter. The concentration of amino acids in water is usually in the low parts-per-billion range, and, since their acid dissociation constants are low, they do not contribute significantly to the acidity of the water. The concentration of humic and fulvic acids in water is usually much higher than that of the amino acids. Also, humics and fulvics have much higher acid dissociation constants, and can have a considerable influence on the pH of water. As an example, bogs or swamps containing high concentrations of humic material and low concentrations of major ions can have pH's between 3.8 and 4.2.

A dramatic example of the effect of humics on stream water acidity was recently reported by Ramberg (1981). A Swedish runoff brook, fed mainly by groundwater had an average pH of 4.9. When drainage ditches were dug so that the groundwater no longer flowed through the upper organic layer of the forest soil before reaching the brook, the pH of the stream increased to a mean value of 5.8.

3.3.2 Buffering Capacity

Humic materials have recently been shown to have low buffering capacity, even when present in high concentrations (Wilson 1979). The weak buffering capacity they do exhibit is between pH 4 and 5, the pH region in which the endpoint of alkalinity titrations occurs. In systems with low alkalinity, the presence of humics can lead to a significant overestimation of alkalinity when the usual acidimetric determination method is used (Wilson 1979). Whether or not humics interfere with the recently proposed "total fixed endpoint" alkalinity procedure is unknown (Jeffries and Zimmerman 1980). The relative contribution of organic matter to the buffer intensity, in relation to other buffering substances, is shown in Figure 3-3 (Driscoll 1980). However, these substances can influence the bioavailability of acid-leached cations such as Al, Mn, and Zn, by acting as chelators.

Work is currently in progress on determining the acid dissociation constants of diverse aquatic humics from across Canada. Also, methods are being developed to quantify the carboxylic acid groups in these materials, since common analytical techniques, such as colour, ultraviolet absorbance, fluorescence and total organic carbon, do not correlate well with each other, or with the acidic properties of the materials. The ultimate goal of this research is to define what portion of the H^+ ion in environmental samples is from the dissociation of weak acids, and what portion is from the strong acids in precipitation.

3.4 CATION AND ANION BUDGETS

Calibrated lakes and watersheds, that is, natural catchments for which the input and output rates of substances can be measured, are an established research tool in environmental studies. For example, the development of strategies for the management of eutrophication of lakes by phosphorus control was based largely on mass balance studies and models (Vollenweider 1975, Dillon and Rigler 1975, Oglesby 1977a, 1977b, Reckhow 1979).

Common reasons for the use of this approach include:

(a) the relative importance of the different inputs of a pollutant can be assessed and abatement planned accordingly;

(b) mass balances can be used with mathematical models to predict the chemical concentrations of the substance in the receiving body, either the stream draining the calibrated watershed, or the calibrated lake itself;

(c) the quantitative accounting of the flow of substances in the watershed or lake may provide information concerning the processes and mechanisms occurring there.

3.4.1 Element Budgets at Hubbard Brook, New Hampshire

Ionic balances of watersheds have been used as a means of quantifying the net basin reactions resulting from acid precipitation. Several studies have been underway since the early 1960's. The earliest study and the longest record (1963-present) is the work at Hubbard Brook, summarized by Likens et al. (1977).

The bulk ionic composition of precipitation at the Hubbard Brook ecosystem is essentially characterized by acids, such as H_2SO_4, NH_4^+ and HCl. In contrast, water leaving the system is characterized mainly by neutral salts, composed of Ca^{2+}, Mg^{2+} and Na^+ balanced in solution by SO_4^{2-} and, to a lesser extent, by chloride and bicarbonate species. The chemical and biological reactions of hydrogen ion, nitrate, ammonium, and sulphate are very important in driving displacement and weathering reactions, especially when considering the effects of acidic precipitation.

Observed trends and annual ion budgets for 11 years at Hubbard Brook demonstrate the influence of atmospheric inputs on surface water quality. Unusually high rates of H^+, NO_3^-, and SO_4^{2-} inputs were observed as early as 1964. The average annual weighted pH of precipitation from 1964-1965 through 1973-1974 ranged between 4.03 and 4.21. The lowest value recorded for a storm at Hubbard Brook was pH 3.0 and the highest was 5.95. During the period 1969-1974 (the latter being the last year of the 1977 summary), no weekly precipitation exceeded a pH of 5.0. Concentrations for SO_4^{2-} and NH_4^+ vary from year to year, but show no statistically significant time-trends for the period. In contrast, annual weighted NO_3^- concentrations were about 2.3-fold greater in 1974 than they were in 1955-1956 or in 1964-1965. The fluctuations in hydrogen ion deposition can be explained in large part by the fluctuation in total precipitation.

From 1964 to 1977 there has been a general downward trend in the sulphate contribution to the total anion equivalents (Figure 3-5). Since about 1970, the decline has been somewhat less, or even reversed. The proportion of nitrate to the total has more or less increased throughout the period. Two conclusions can be drawn:

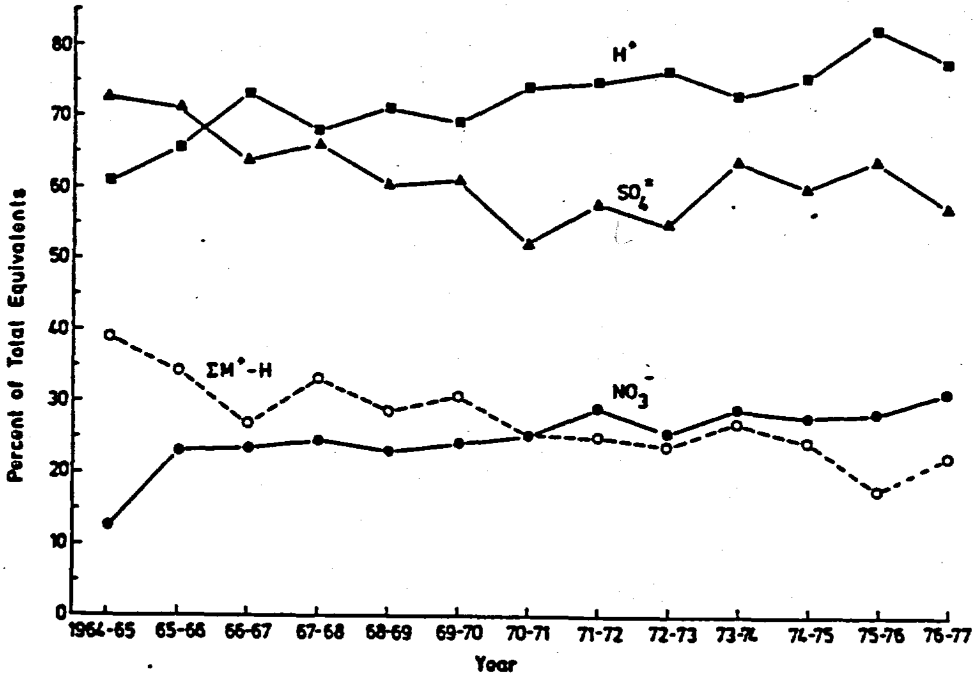


Figure 3-5 Percent of ionic composition of precipitation for the Hubbard Brook Experimental Forest during 1964 to 1977. ΣM^+ is sum of all cations. (Likens et al. 1980).

(1) There has been an increasing importance of nitric acid in precipitation at Hubbard Brook, as was reported earlier (Likens et al. 1976), and (2) the change has been somewhat less after about 1970 and is probably related to the lower increase in nitrate concentration in precipitation after 1970. The proportion of hydrogen ion to the total cations has increased throughout the period, but this is primarily a function of the decrease in total cation equivalents, of which hydrogen ion is the major component (Likens et al. 1980).

The Hubbard Brook study site is an isolated headwater catchment; thus, the influx of chemicals is limited to precipitation and dry deposition, and the outflow to drainage waters. Theoretically, differences between annual input and output for a given chemical indicate whether that constituent is being accumulated within the ecosystem, is being lost from the system, or is simply passing through the system. Likens et al. (1977), therefore, were able to estimate with reasonable accuracy the mean annual budgets for most of the major ions (Table 3-2). Over the long term, there is considerable variation, however, a net annual loss of calcium, magnesium, potassium, sodium, sulphate, aluminum, and dissolved silica has occurred, along with a net annual gain of ammonium, hydrogen ion, and phosphate, in these undisturbed, accreting watershed ecosystems.

Overall, during 1964-1974, there was an annual net loss of total dissolved inorganic substances from the experimental watersheds, amounting to 75.8 kg/ha.yr. The average net output of dissolved inorganic substances minus dissolved silica (1963-1974) was 37.4 kg/ha.yr. The smallest annual net loss of dissolved inorganic substances (27.8 kg/ha, or 7.0 kg/ha for total material, minus dissolved silica) occurred during 1964-1965, the driest year of the study. The largest net losses of dissolved inorganic substances occurred during the wettest year, 1973-1974 (139.7 kg/ha, or 986 cationic eq/ha).

Likens et al. (1977) also note the complexity of computation of the long-term cationic denudation rate in the Hubbard Brook ecosystem due to accumulations of living and dead biomass. The net accretion of biomass should be viewed as representing a long-term sink for some of the nutrients supplied from the weathering reactions. The total amount of cations sequestered by this means is 72.2 $meq/m^2.yr$. They conclude that: (a) cations stored within the biomass must be included in calculations of contemporary weathering; (b) the rate of storage is a consequence of the ecosystem's current state of forest succession, and so changes with time; and (c) that the existence of the forest, and its state of development, must be included in geological estimates of weathering.

TABLE 3-2

ANNUAL BUDGETS OF BULK PRECIPITATION INPUTS AND STREAM-WATER OUTPUTS OF DISSOLVED SUBSTANCES FOR UNDISTURBED WATERSHEDS OF THE HUBBARD BROOK EXPERIMENT FOREST (LIKENS et al. 1977)

Substance (kg/ha)	1963 to 1964	1964 to 1965	1965 to 1966	1966 to 1967	1967 to 1968	1968 to 1969	1969 to 1970	1970 to 1971	1971 to 1972	1972 to 1973	1973 to 1974	Total 1963-1974 kg/ha	Annua mean kg/h
CALCIUM													
Input	3.0	2.8	2.7	2.7	2.8	1.6	2.3	1.5	1.2	1.2	2.0	23.8	2.2
Output	12.8	6.3	11.5	12.3	14.2	13.8	16.7	13.9	12.4	15.6	21.7	151.2	13.7
Net	-9.8	-3.5	-8.8	-9.6	-11.4	-12.2	-14.4	-12.4	-11.2	-14.4	-19.7	-127.4	-11.5
MAGNESIUM													
Input	0.7	1.1	0.7	0.5	0.7	0.3	0.5	0.5	0.4	0.5	0.4	6.3	0.6
Output	2.5	1.8	2.9	3.1	3.7	3.3	3.5	3.1	2.8	3.3	4.6	34.6	3.1
Net	-1.8	-0.7	-2.2	-2.6	-3.0	-3.0	-3.0	-2.6	-2.4	-2.8	-4.2	-28.3	-2.5
ALUMINUM													
Input	*	*	*	*	*	*	*	*	*	*	*	*	*
Output	1.6°	1.2	1.7	1.9	2.1	2.2	2.2	1.8°	1.7°	2.3°	3.2°	21.9	2.0
Net	-1.6	-1.2	-1.7	-1.9	-2.1	-2.2	-2.2	-1.8	-1.7	-2.3	-3.2	-21.9	-2.0
AMMONIUM													
Input	2.6°	2.1	2.6	2.4	3.2	3.1	2.7	3.9	2.8	2.5	3.7	31.6	2.9
Output	0.27°	0.27	0.92	0.45	0.24	0.16	0.51	0.23	0.05	0.18	0.42	3.7	0.3
Net	2.3	1.8	1.7	2.0	3.0	2.9	2.2	3.7	2.8	2.3	3.3	27.9	2.6
HYDROGEN													
Input	0.85°	0.76	0.85	1.05	0.96	0.85	0.93	1.18	0.97	1.08	1.14	10.62	0.9
Output	0.08°	0.06°	0.05	0.07	0.06	0.09	0.09	0.14	0.13	0.16	0.20	1.13	0.1
Net	0.77	0.70	0.80	0.98	0.90	0.76	0.84	1.04	0.84	0.92	0.94	9.49	0.8
SULPHATE													
Input	33.7°	30.0	41.6	42.0	46.7	31.2	29.3	34.6	33.0	43.4	52.8	418.3	38.0
Output	42.7°	30.8	47.8	52.5	58.5	53.3	48.1	51.1	46.8	64.0	84.7	580.3	52.8
Net	-9.0	-0.8	-6.2	-10.5	-11.8	-22.1	-18.8	-16.5	-13.8	-20.6	-31.9	-162.0	-14.7
NITRATE													
Input	12.8**	6.7	17.4	19.9	22.3	15.3	14.9	21.6	21.4	26.3	30.9	209.5	19.0
Output	6.7**	5.6	6.5	6.6	12.7	12.2	29.6	24.9	18.7	19.2	34.8	177.5	16.1
Net	6.1	1.1	10.9	13.3	9.6	3.1	-14.7	-3.3	2.7	7.1	-3.9	32.0	2.9
BICARBONATE***													
Input	*	*	*	*	*	*	*	*	*	*	*	*	*
Output	6.2°	4.6°	6.2	9.4	9.6	7.0	6.0	7.1°	6.6°	9.0°	12.5°	84.2	7.7
Net	-6.2	-4.6	-6.2	-9.4	-9.6	-7.0	-6.0	-7.1	-6.6	-9.0	-12.5	-84.2	-7.7

* Not measured, but trace quantities.

° Calculated value based on weighted average concentration during years when chemical measurements were made on amount of precipitation or streamflow during the specific year.

** Calculated from weighted concentration for 1964-1966 times precipitation for 1963-1964. Based on annual concentration of 0.50 mg/l (Juang and Johnson, 1967).

*** Watershed 4 only.

If this appraisal of the biological system at Hubbard Brook is correct, the flux of cationic nutrients being diverted into biomass accretion (72.2 $meq/m^2.yr$) must be added to that actually removed from the system, in the form of dissolved load (126.7 $meq/m^2.yr$) and particulate organic matter (1.0 $meq/m^2.yr$). Therefore, their best estimation of cationic denudation (net loss from ecosystem plus long-term storage within the system) at Hubbard Brook is about 200 $meq/m^2.yr$.

These long-term estimates of cationic denudation at Hubbard Brook allow estimation of the relative importance of external and internal sources of H^+ ions. The external supply rate is 100 $meq/m^2.yr$ and, by difference, the internal source becomes 100 $meq/m^2.yr$. This suggests that under prevailing biological and chemical conditions (perhaps altered by changes in atmospheric precipitation), external and internal generation of H^+ ions play nearly equal roles in driving the weathering reactions.

3.4.2 Element Budgets in Canada

Input-output budgets (mass balances) for major ions are being measured at a number of locations in Canada described in Tables 3-3 and 3-4. In all cases, mass balance measurements have excluded possible contributions via subsurface flow, although the evidence available suggests that these contributions are negligible. Net exports of Ca^{2+}, Mg^{2+} and K^+ are shown in Table 3-4 for watersheds, along with input of H^+ by precipitation. Output of HCO_3^- and input-output data for SO_4^{2-}, NH_4^+ and NO_3^- are also included, where reported. Nicolson (1977) reported only output of major ions from 12 watersheds in the Experimental Lakes Area, northwestern Ontario; however, input by precipitation to the nearby Rawson Lake watershed (Schindler et al. 1976) was used to calculate a net export for these 12 watersheds.

Several general trendsuare evident in Table 3-4. All watersheds studied have a net output of the major cations ($Ca^{2+} + Mg^{2+} + Na^+ + K^+$). The net output of Ca^{2+} and Mg^{2+} dominates the budgets at all locations, particularly those in British Columbia where the watersheds have some calcareous till. The study sites in British Columbia receive a large amount of precipitation (260-450 cm/yr), a factor that also may increase the export of cations.

The H^+ input is 5-10 times lower, and the net output of cations from the ELA and Rawson Lake watersheds on the Canadian Shield in western Ontario is only 30-40 per cent of that from the more heavily acidified Harp Lake watersheds, which are also on the Shield, but in central Ontario. In all cases, there is a net accumulation of NH_4^+ and NO_3^- in the watersheds.

TABLE 3-3

DESCRIPTION OF WATERSHEDS IN CANADA UTILIZED FOR MASS BALANCE STUDIES

	Description of watershed				
Study location	A (km^2)	Annual ppt. (cm)	Forest, soil and bedrock geology	Study period	Reference
Carnation Creek, Vancouver Is.	10	300	Forest: hemlock, fir, cedar Soils: shallow, medium to coarse textured alluvial podzols; some areas of high organic content Bedrock: massive, metamorphic, primarily silicates of variable composition with some marble and igneous intrusions	2 yr.	Scrivener 1975
Jamieson Creek, Seymour Basin, Southwest B.C	2.99	450	Forest: fir, hemlock, cedar Soils: shallow, podzolic tills and colluvium (sometimes gleyed) Bedrock: massive, plutonic, horneblende-diorite	1 yr.	Zeman 1975
3 watersheds at Haney, Southwest B.C.	0.23-0.44	257	Forest: hemlock, cedar, fir Soils: generally deep,permeable podzolic tills and colluvium (sometimes gleyed) Bedrock: massive, plutonic, horneblende-diorite	2 yr.	Feller 1975, 1977
12 watersheds, Experimental Lakes Area, Western Ont.	0.35-12.5	est. 60-100	Forest: pine, spruce, birch, aspen Soils: shallow,podzolic basal tills; extensive bedrock exposure on hill crests; deep soils (10-15 m) in low areas	4 yr.	Nicolson 1977
Rawson Lake watershed,Experimental Lakes Area, Ont.	3.42	70-100	Bedrock: massive, plutonic, granodiorite	4 yr. published, 5 unpublished	Schindler *et al.* 1976

TABLE 3-3 (cont'd)

Rawson Lake watershed, Experimental Lakes Area, Ont.	3.42	70-100	Bedrock: massive, plutonic, granodiorite	4 yr. published, 5 unpublished	Schindler *et al.* 1976
Clear Lake watershed, Haliburton, Ont.	1.25	126	Forest: maple, beech, oak, birch, balsam, hemlock Soils: shallow, podzolic basal tills with bedrock exposure on steeper slopes Bedrock: jointed, intruded, metamorphic, granite gneiss	1 yr.	Schindler & Nighswander 1970
Harp Lake watershed, Haliburton-Muskoka, Ont.	3.70	82 (99 is long-term mean)	Forest: maple, beech, birch, balsam, and hemlock Soils: generally shallow podzolic tills with some deeper sand deposits Bedrock: jointed, intruded, metamorphic, horneblende-gneiss and amphibolite with small occurrence of diorite	4 yr. unpublished, ongoing	

TABLE 3-4

NET EXPORT OF MAJOR IONS FOR CALIBRATED WATERSHEDS IN CANADA (FROM NRC, 1981)

	Net export (meq m^{-2} yr^{-1})									
Watershed	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	ΣM	NH_4^+-N	NO_3^--N	HCO_3^-	SO_4^{2-}-S	Input of H^+ (meq m^{-2} yr^{-1})
Carnation Creek, Vancouver Is.	269	61.2	118.5	5.8	454.5	-7.7	-4.3	270.0	131.4	1-3
Jamieson Creek, B.C.	171.6	54.4	53.9	4.3	284	-0.2	-2.2	48.7	4.9	-
Twelve watersheds, ELA, Western Ontario	36.6[a] 17.7[b]	24.0 16.4	18.0 11.1	3.4 0.5	82.0 45.7	-0.9	-0.8	-	38.8	est. 7-10
Rawson Lake watershed, Western Ontario	11.2	12.1	9.0	0.4	32.7	Total N reported			0.9	~7-10
Four subwatersheds, of Harp Lake; Muskoka-Haliburton, Ontario	52.7	33.0	6.6	2.3	94.6	-30.2	-32.3	31.7	43.9	67

[a] Gross output.

[b] Estimated net output using input in precipitation from Rawson Lake watershed studies.

More sulphate is removed than is supplied at all watersheds, although at Rawson Lake and Jamieson Creek the SO_4^{2-} input and output are probably within experimental error of being balanced. However, the actual amount of SO_4^{2-} supplied may be underestimated due to canopy effects and possible gaseous deposition. The greatest net output of SO_4^{2-} was measured at Carnation Creek and Harp Lake, although at the latter there was a substantial input of SO_4^{2-} in precipitation (≃ 70 $meq/m^2.yr$) (Scheider et al. 1979a).

The mechanism for cation export is apparent in some cases. At Carnation Creek, the output of HCO_3^- is substantial, suggesting that carbonic acid is the principal weathering agent responsible for cation export. At Jamieson Creek, the output of cations greatly exceeds the output of HCO_3^- and supply of H^+, while at the Haney watershed, the opposite situation is observed. At the Experimental Lakes Area in northwestern Ontario (including the Rawson Lake studies), the release of cations probably is a result of carbonic acid weathering, although the loading of 7-10 $meq/H^+/m^2 \cdot yr$ in precipitation may account for 20 per cent of the net cation export. On the other hand, in southern Ontario, 50 per cent or more of the cation yield probably results from input of H^+ in strong acid form. Although the evidence is circumstantial, it appears likely that the increased H^+ input of southern Ontario has resulted in a two to three fold increase in net output of cations.

3.4.3 Regional Responses in Lake Chemistry

A decade of results in Scandinavia indicates that as lakes are subjected to acidic precipitation, cations are mobilized, and some of the bicarbonate ions are replaced by sulphate; thus, the normal relationship between the dominant cations, calcium and magnesium, and alkalinity appears to be altered. Although these lakes are not necessarily acidic, the alkalinity will be less than predicted, i.e., when calcium plus magnesium are summed.

The report by Harvey et al. (1981) gives a similar evaluation of lake data for North America. Their description is as follows:

> "Comparable data for lakes on the Canadian Shield are shown in Figure 3-6. Lakes that can be considered unaffected by acidic deposition include those in the Northwest Territories, probably Labrador and Newfoundland, and northern Manitoba and Saskatchewan. These lakes have close to a 1:1 relationship between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^-]$, as do several lakes in calcareous pockets in the Killarney area of Ontario. $[Ca^{2+} + Mg^{2+}]$ may be overestimated for several of the Newfoundland and Labrador lakes, because the concentrations are not corrected for sea salt contributions. Many of the other

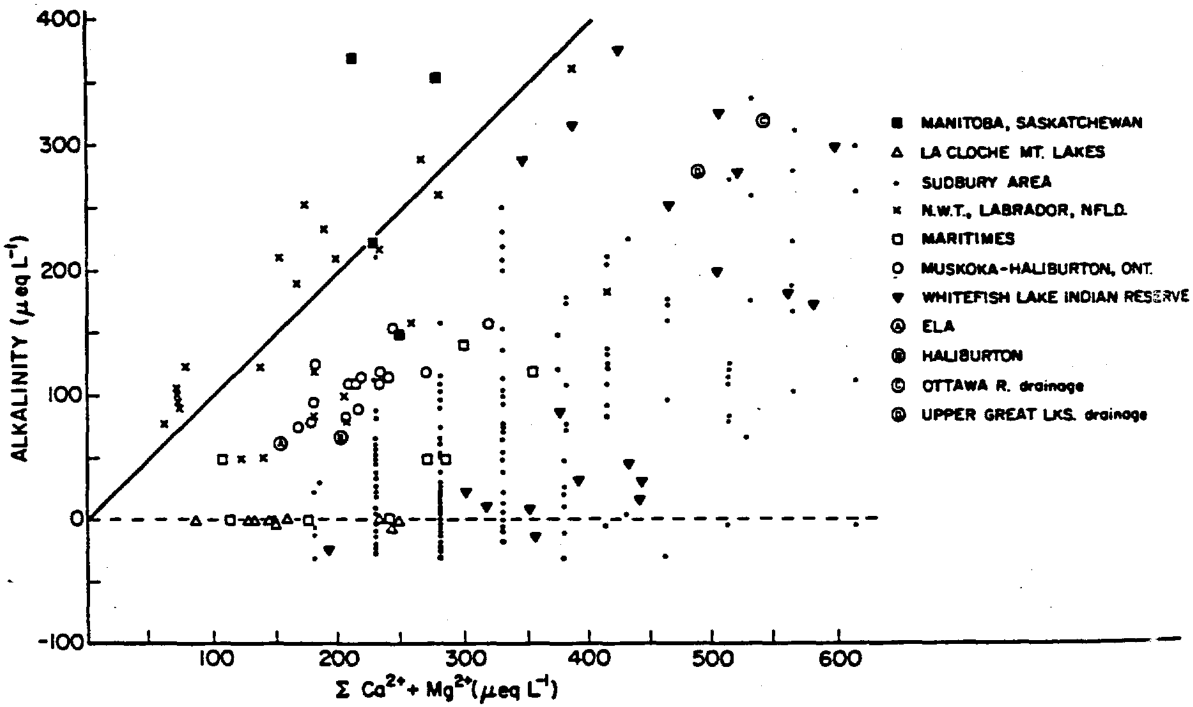


Figure 3-6 Summary of alkalinity data from several Canadian lake studies, including sites inside and outside of acidic deposition areas (Harvey et al. 1981).

lakes, however, have a HCO_3^- deficiency relative to Ca^{2+} plus Mg^{2+}; most of the Killarney lakes, including all the La Cloche Mountain lakes and many of the Whitefish Reservaton lakes, almost all of the lakes within a 100-km radius of Sudbury, Ontario, and all of the Muskoka-Haliburton lakes and Nova Scotia-New Brunswick lakes (although the latter data were also not corrected for sea salt contributions), have HCO_3^- deficiencies. The distance below the line in Figure 3-6 may be an indication of the extent of acidification; lakes found below zero alkalinity are considered to be acidified.

If the other major source of Ca^{2+} and Mg^{2+} in lake water is weathering by strong acids in precipitation, and if most of this acid is associated with sulphate, then there should be a good relationship between $[SO_4^{2-}]$ and $[Ca^{2+} + Mg^{2+} - HCO_3^-]$ on an equivalent basis. This relationship provides an estimate of the Ca^{2+} and Mg^{2+} not derived from carbonic acid weathering. Data for Canadian Shield lakes are shown in Figure 3-7; the agreement between $[SO_4^{2-}]$ and $[Ca^{2+} + Mg^{2+} - HCO_3^-]$ for most lakes is very good, although it can be argued that this may be expected, based on the principle of charge balance, and implies no cause-effect relationship. All of the lakes in Nova Scotia and New Brunswick have excess Ca^{2+} and Mg^{2+}, suggesting that Ca^{2+} and Mg^{2+} may be supplied in part by sea salt. The Whitefish Reservation lakes are outliers, but this may result from analytical error, as the total charge balance for the Whitefish Reservation data is not good, a problem that does not exist with the other data sets.

The fact that most lakes or groups of lakes have reasonably close correspondence between $[Ca^{2+} + Mg^{2+} - HCO_3^-]$ and $[SO_4^{2-}]$ supports the hypothesis that the Ca^{2+} and Mg^{2+} content of lakes is not derived from carbonic acid weathering, but is related to the input of sulphate. Because the other major strong acid anion, NO_3^-, is a nutrient in lakes and streams, (i.e., is non-conservative), it is not possible to incorporate it into a more complete relationship."

3.4.4 Effects of Forest Manipulation or Other Land Use Practices on Watershed Outputs

Land use practices within watersheds have been suggested as an influence on the budgets (Rosenquist et al. 1980, Likens et al. 1978, Henderson et al. 1980). Henderson et al. (1980) have summarized results from watersheds at Hubbard Brook, Fernow, and Coweeta which were experimentally manipulated through a series of forest cutting practices. The work was designed to estimate changes in streamflow

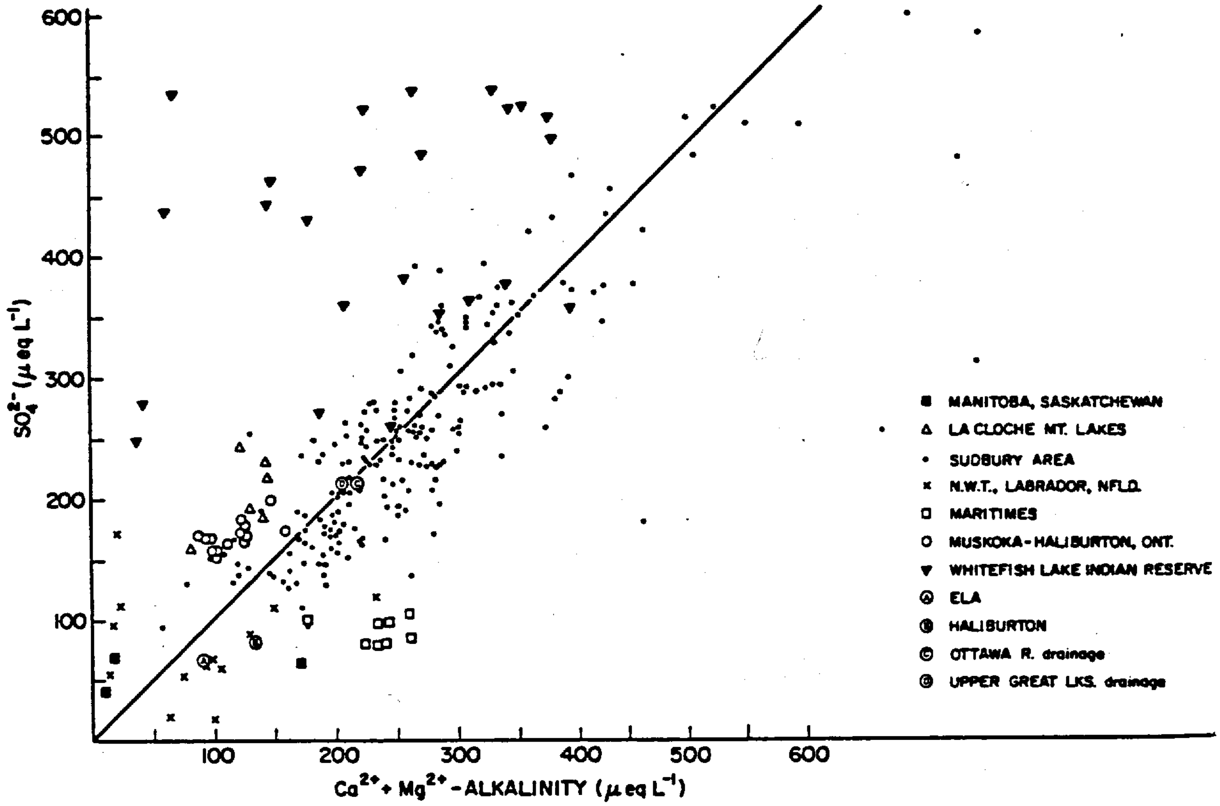


Figure 3-7 [Ca^{2+} + Mg^{2+} - alkalinity] vs [SO_4^{2-}] for lakes in Canada. The key to symbols is the same as in Fig. 3-6. Solid line represents theoretical relationship for [Ca^{2+} + Mg^{2+}] not derived from carbonic acid weathering reactions (see text for explanation and data sources).

of cations, particularly potential effects on H^+ concentrations. At Hubbard Brook, following felling of all vegetation and herbicide treatments for three successive years, an increase of 245.9 kg/ha of nitrogen discharges into stream flow was observed. Increased acidity from biomass decomposition amounted to 69.9×10^3 eq/ha of H^+ per hectare. This additional acidity is presumed to have been a major contributor to the loss of cations from the soil, shown in Table 3-5.

Strip cutting of one-third of the vegetation at a second Hubbard Brook watershed showed significantly less impact on soil leaching rates. Organic matter decomposition was about five per cent of that of the total vegetation removal (500 kg/ha versus 10,500 kg/ha). Subsequently, H^+ production was also less, as was resultant cation leaching.

Commercial clear-cutting at the Fernow watershed generated fewer H^+ equivalents. This result may have been due to removal of only "economic biomass", which reduced overall decomposition rates and resultant H^+ formation. The Coweeta clear-cut and cable logging experiments resulted in even less production of H^+ ions. When the Fernow watershed was fertilized with 260 kg/ha of urea, a ten fold stripping of calcium ions occurred, plus a six per cent fold increase in magnesium, a 50 per cent increase in potassium leaching, and a 3.6 fold increase in sodium ion denudation.

The high, medium and low cation release ratios from Table 3-8 were used to calculate leaching increase potentials for three precipitation acidity scenarios (Table 3-6). Additional H^+ inputs of 750, 3,990, and 14,250 eq/ha would be experienced for 150 cm of precipitation at pH 4.0, 3.5, and 3.0, respectively. At the more acidic pH values, aluminum leaching (and, therefore, buffering of effects on the other cations) would be expected to increase substantially.

The possibility of land use changes causing acidification of surface waters, rather than atmospheric inputs of acid, has been explored in great detail in two recent studies in Norway. Seip (1980) concluded that, while land use changes probably have contributed to the acidification process in some areas, "there is no reason to doubt that the increase in the deposition of acidifying components has played an important role in the acidification of freshwater."

Drablos et al. (1980) also reviewed land use changes in relation to lost fish populations in lakes and could find no relationship between the two. In fact, the greatest number of lakes from which fish populations have been lost occurred in areas of no farming

TABLE 3-5

SUMMARY OF TOTAL CATION RELEASE, HYDROGEN ION PRODUCTION, AND THE CATION RELEASE RATIO FOR THREE MANIPULATED-WATERSHED STUDIES

	H^+ produced (eq/ha)	Total cation release (eq/ha)	Cation release ratio (eq/eq/H^+)
Hubbard Brook			
Deforested	69,960	6,850	0.10
Strip-cut	8,400	390	0.05
Fernow			
Clear-cut	960	170	0.18
Fertilization	55,710	2,420	0.04
Coweeta			
Clear-cut and cable-logged	360	50	0.14

From: Henderson et al. 1980

TABLE 3-6

POTENTIAL INCREASE IN CATION LEACHING EXPECTED UNDER THREE PRECIPITATION ACIDITY REGIMES

pH	Additional H^+ (eq/ha)	Cation leaching potential (eq/ha)		
		Low	High	Median
4.0	750	30	135	75
3.5	3,990	160	720	400
3.0	14,250	570	2,565	1,425

From: Henderson et al. 1980.

activity. While it is well documented that land use changes affect the quality of runoff, including pH, the large scale acidification of lakes in Scandinavia is not due to land use changes.

3.5 AQUATIC ECOSYSTEMS SENSITIVE TO ACIDIC DEPOSITION

As the foregoing has indicated, accelerated changes in the natural evolution of soils may occur as a result of an increase in the rate of acidification and associated nutrient impoverishment. These changes hold important implications for aquatic sensitivity and/or long term, sustained forest/agricultural productivity (See Sections 4.4.1 and 4.4.2).

In assessing terrestrial and aquatic ecosystem linkages, special emphasis has been placed on those variables which act to modify surface runoff and groundwater flow in the watershed. Thus, attention is directed at the role played by the whole solum and bedrock (Table 3-7) in modifying surface runoff and groundwater flow. This approach assumes fairly simple basin-flow conditions, in which much of the aquatic input (soil drainage) interacts with the soil body, and/or the bedrock surface (Cowell et al. 1981). As defined, the criteria apply to regional evaluations more than to localized, site-specific evaluations. More critical limits and definitions will be applied as the scale of evaluation increases.

Soil chemistry, soil depth and bedrock type are factors common to assessing aquatic and forest sensitivity (Section 4). In Table 3-7 exchangeable bases and sulphate adsorption are shown as the ideal soil chemical parameters; that is, for judging the sensitivity of watersheds to changes from acidic inputs. In the absence of data on exchangeable bases, soil sensitivity can be assigned using a surrogate as shown. The three levels of sensitivity for exchangeable bases are taken from Wang and Coote (1980). These values incorporate a loading factor, which assumes a loss by leaching of 25 per cent of the exchangeable bases over 25 years under an acid loading impact of 60 kg/ha $CaCO3$ equivalent. Sulphate adsorption is not criticall defined as yet, but should be taken into account as a moderating influence for soils known to exhibit high $SO4^{2-}$ adsorption. These include the non-glaciated, deeply weathered Ultisols of the southern U.S. (See Section 4).

Limits for soil depth are more arbitrary but relate approximately to values reported in regional surveys (physiographic and soil surveys).

Sensitivity for bedrock types are taken directly from the Geological Survey of Canada assessment by Shilts et al. (1981). High, moderate

TABLE 3-7

AQUATIC INPUT SENSITIVITY

	SENSITIVITY		
TERRESTRIAL FACTORS	LOW	MODERATE	HIGH
Soil Chemistry			
i) Exchangeable Bases	>15 meq/100g	6 to 15 meq/100g	<6 meq/100g
Surrogate:			
Combinations of			
pH in water	clayey, >pH 5.0	clayey, pH 4.5 to 5.0	clayey, <pH 4.5
(or % Base Saturation)	loamy, >pH 5.5	loamy, pH 5.0 to 5.5	loamy, <pH 5.0
and one of (a) Family Particle Size	all calcareous soils	sandy, >pH 5.5	sandy, <pH 5.5
or (b) Texture	clay, silty clay, sandy clay (>35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam, loam (10 to 35% clay)	silt, sandy loam, loamy sand, sand (<10% clay)
or (c) Cation Exchange Capacity	>25 meq/100g	10 to 25 meq/100g	<10 meq/100g
ii) SO_4^{2-} Adsorption Capacity	high sulphate adsorption: low organic matter AND high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$	—	low sulphate adsorption: high organic matter AND/OR low Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$
Soil Depth	>1 m	25 cm - 100 cm	<25 cm
Soil Drainage	poor	imperfect to well	rapid
Landform Relief	level	rolling	steep
Vegetation	deciduous	mixed	coniferous
Vegetation Cover	continuous >60%	discontinous to sparse 20 to 60%	sparse to barren <20%
Underlying Material			
i) Parent Material	carbonate bearing	non-carbonate bearing	non-carbonate bearing
ii) Bedrock Material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with non-carbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, meta-equivalents	granite, granite gneiss, orthoquartzite, syenite

and low bedrock sensitivity correlates approximately with the types I + II, type III and type IV classes, respectively, of Hendrey et al. (1980) in their U.S. mapping.

Other factors considered necessary in assessing potential aquatic sensitivity are vegetation type and cover and soil drainage.

In terms of their influence on aquatic sensitivity, forest species appear to affect throughfall precipitation chemistry. There seems to be agreement that broadleaf deciduous species, and especially their leaf litter, provide more buffering of precipitation than coniferous species (Abrahamsen et al. 1977, Lee and Weber 1980). This is the basis for rating vegetation in Table 3-7, but it obviously ignores acid contribution from snowfall and, to some degree, dry deposition.

Soil drainage refers to the rate at which the soil/rock body is drained, which in turn is related to porosity and permeability. Poor drainage does not necessarily imply an impermeable soil, but rather, one that is drained slowly. An impermeable surface (soil or rock) results in rapid surface runoff, with little opportunity for chemical equilibration and, therefore, would be sensitive. Although rapidly drained soils are considered under high sensitivity, it should be noted that, under these conditions, there would also be less opportunity for drainage waters to leach significant concentrations of Al^{3+} into the aquatic system.

3.5.1 Aquatic Sensitivity Mapping for Eastern North America

Figures 3-8 and 3-9 are maps showing aquatic input sensitivity for eastern North America. They were interpreted using the Ecodistrict data base for Canada (Cowell et al. 1981) and the Geoecology data base for the United States (Olson et al. 1980). The evaluations have been made, using as many of the criteria suggested in Table 3-7 as possible. The information base varies considerably across eastern North America, in terms of type, scale and coverage, and thus it is presently impossible to incorporate all the criteria from this table for regional analyses. Nevertheless, basic information on soil chemistry, soil depth and bedrock geology are available which permit integration and evaluation of more than one parameter (Cowell et al. 1981, Kaplan et al. 1981).

Table 3-8 and Figure 3-10 show how the criteria have been integrated to make interpretations for aquatic input sensitivity for the United States and Canada respectively. The information base does not permit strictly comparable criteria or their surrogates within eastern Canada, or between Canada and United States. However, an attempt has been made to integrate factors in as comparable a fashion as the various data bases would allow.

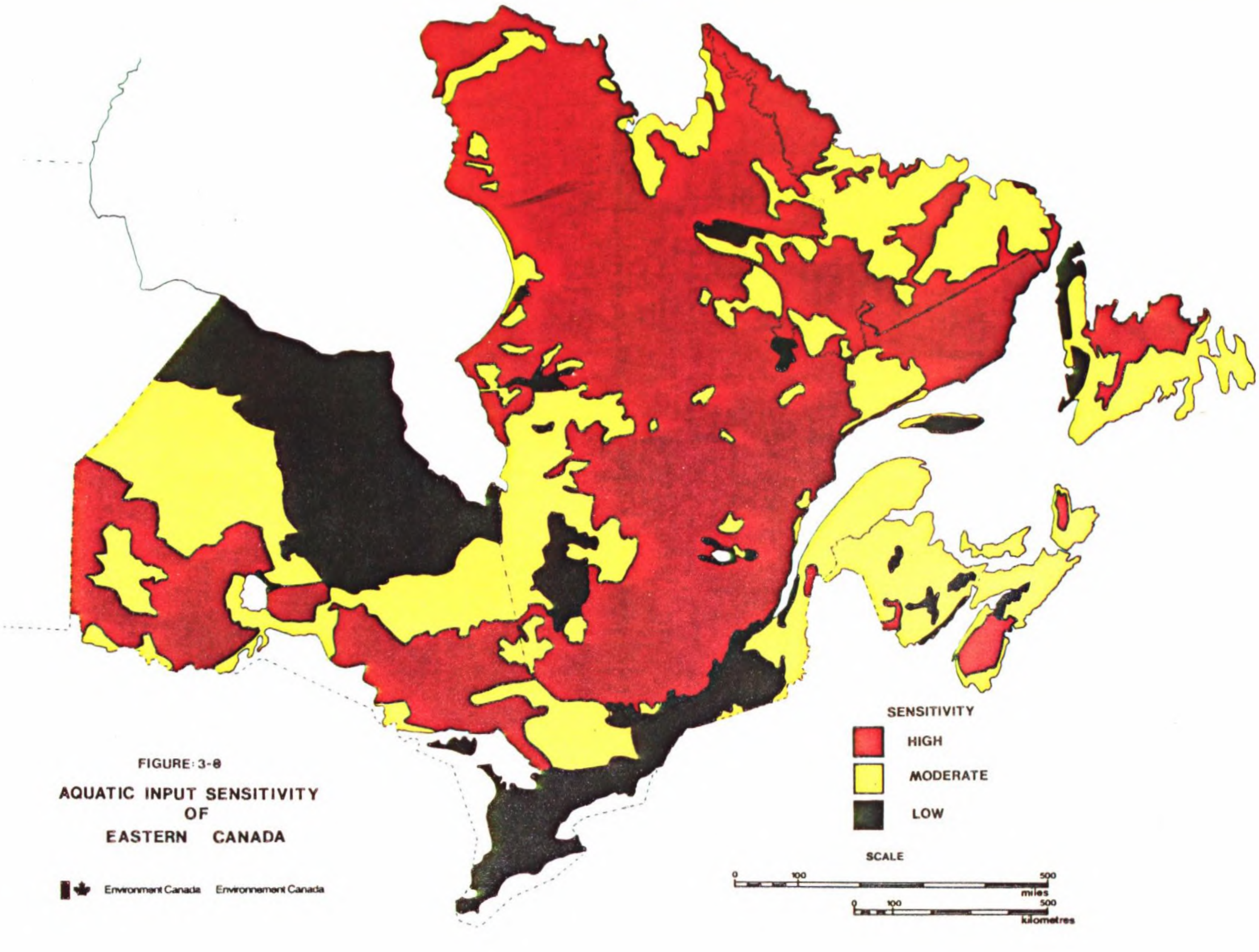


FIGURE: 3-8

AQUATIC INPUT SENSITIVITY
OF
EASTERN CANADA

Environment Canada Environnement Canada

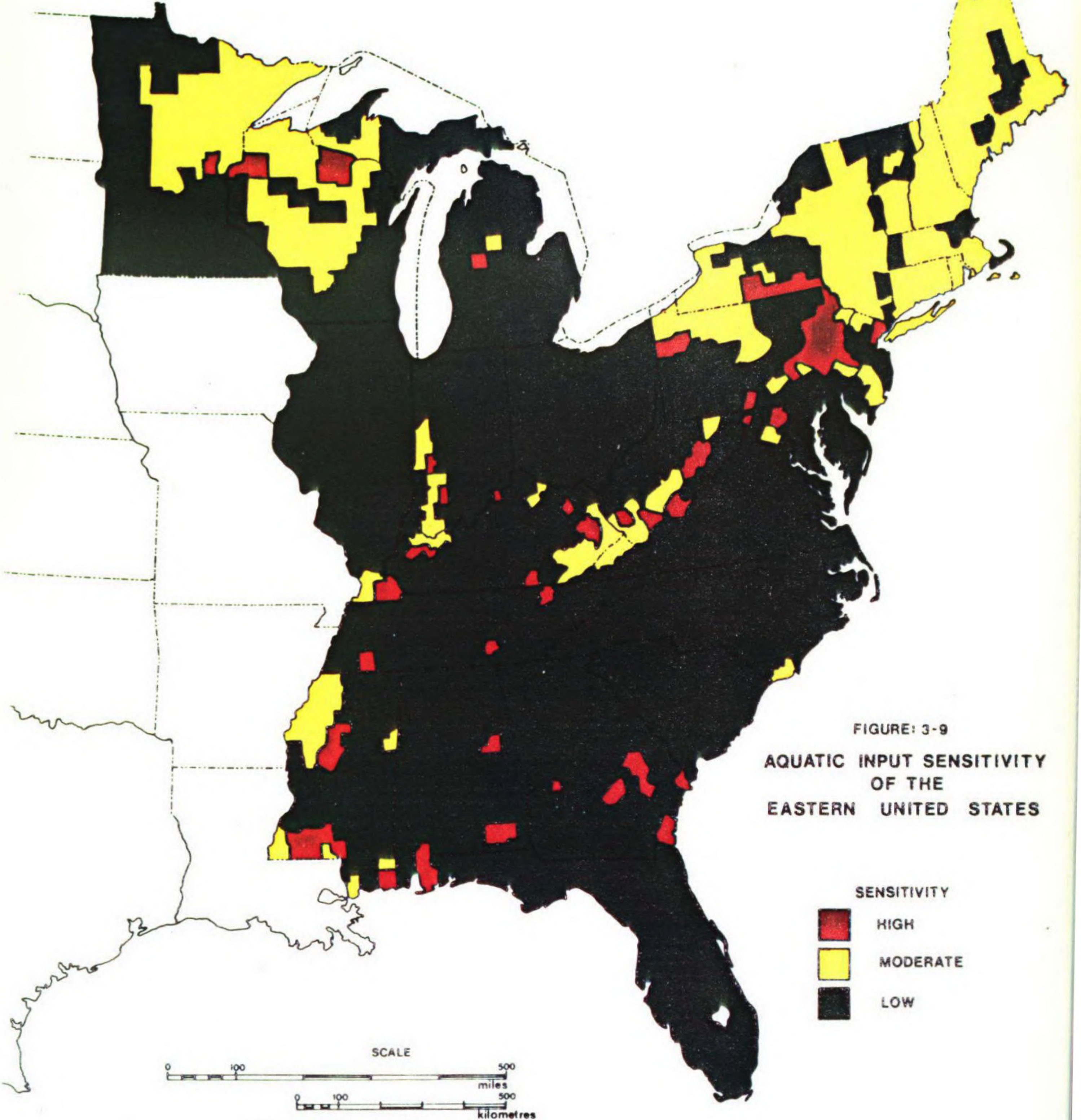


FIGURE: 3-9

AQUATIC INPUT SENSITIVITY
OF THE
EASTERN UNITED STATES

OAK RIDGE NATIONAL LABORATORY

TABLE 3-8 AQUATIC INPUT SENSITIVITY INTERPRETATIONS FROM THE GEOECOLOGY DATA BASE FOR THE EASTERN UNITED STATES.

Low Sensitivity:	(1)	areas of deep or shallow soils with exchangeable base content >15 meq/100 g
	(2)	areas underlain by low sensitive bedrock
	(3)	soils believed to have a high sulphate adsorption
Moderate Sensitivity:	(1)	areas of deep or shallow soils with exchangeable base content of 6-15 meq/100 g
	(2)	areas of shallow soils with <15 meq/100 g exchangeable base content but underlain by moderately sensitive bedrock
High Sensitivity:	(1)	deep soils with exchangeable base content <6 meq/100 g
	(2)	shallow soils with exchangeable base content >6 meq/100 g but underlain by highly sensitive bedrock

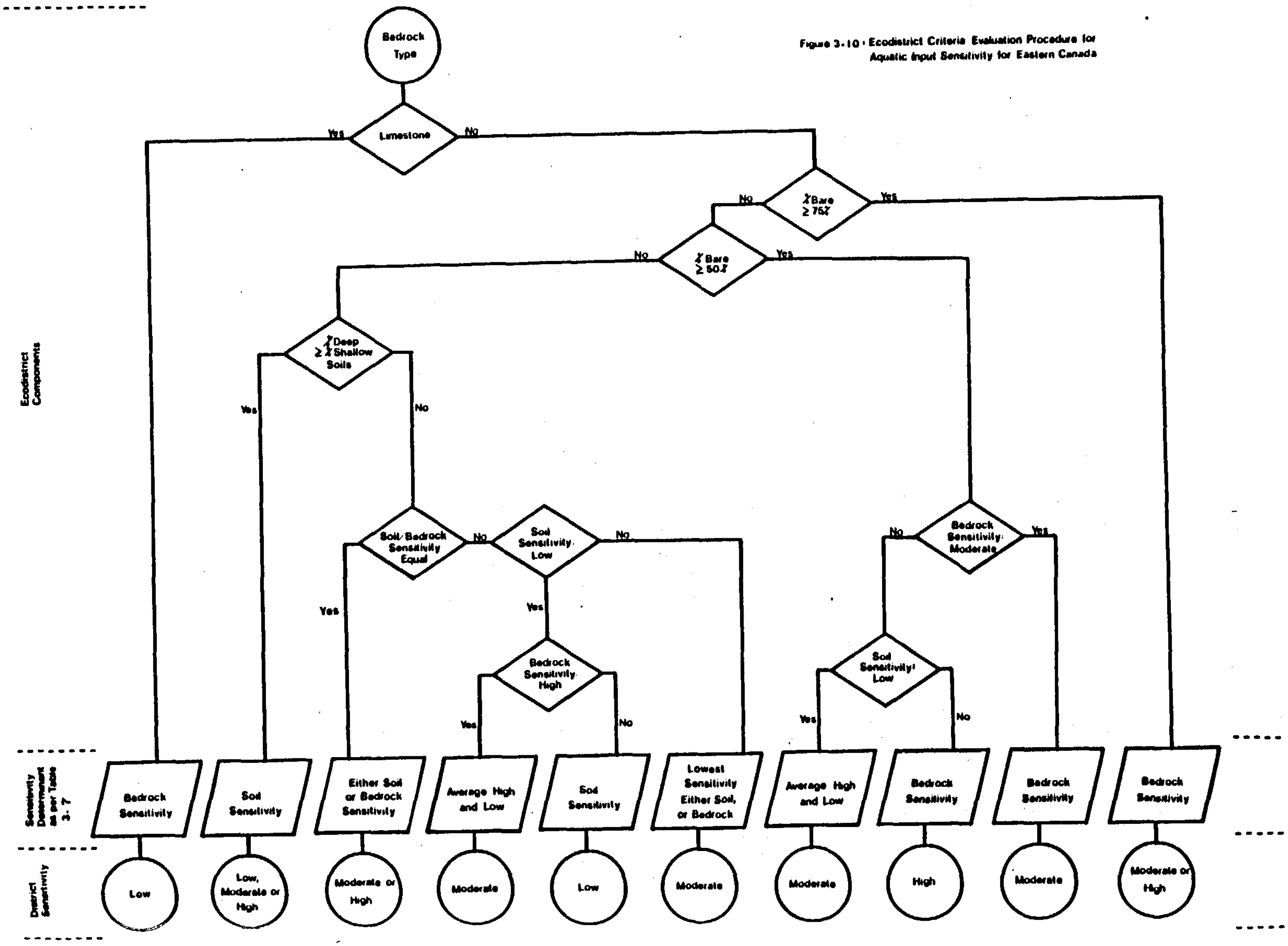


Figure 3-10: Ecodistrict Criteria Evaluation Procedure for Aquatic Input Sensitivity for Eastern Canada

Eastern Canada

The map of eastern Canada (Figure 3-8) was prepared using the Ecodistrict data base (Cowell et al. 1981). Ecodistricts are units of land characterized by a distinctive pattern of relief, geomorphology, vegetation, soils, water and land. These are interpreted using LANDSAT colour imagery, existing mapping, and ecological survey data. The Ecodistrict data base includes information on soil properties, bedrock geology, drainage, vegetation, and water bodies. At present it incorporates existing data, and thus the form of the data varies somewhat from region to region. However, the sensitivity criteria were integrated, using a common format to maintain a level of consistency and comparability (Cowell et al. 1981). Figure 3-10 shows the criteria evaluation procedures which denote high, moderate, and low sensitivity for aquatic input sensitivity.

Bedrock geology sensitivity was assigned according to Table 3-7, and relatively good geological mapping is available for all of eastern Canada. In Ontario, soil depth and soil petrography (estimated carbonate content) are well defined south of 50°N latitude for the Ontario Land Inventory (Cowell et al. 1981). Data for north of 50°N latitude was taken from Hills (1959) and other sources. Elsewhere texture, soil great group and parent material were used as surrogates for soil chemistry, and soil depth was taken from ecological land survey data, soil capability mapping and field knowledge. Ecodistricts dominated by peatland terrain were assigned a moderate soil sensitivity, because they have a high cation exchange capacity but are mostly low in base saturation. It is not known exactly how these soils are affected by acid precipitation.

Eastern United States

The map of the eastern United States (Figure 3-9) was produced at the Oak Ridge National Laboratory, using county-level data (Olson et al. 1981). Data on soils, land use and terrain characteristics was obtained from the Geoecology Data Base (Olson et al. 1980). Data on bedrock sensitivity was obtained from the Brookhaven National Laboratory ACID data base (Hendrey et al. 1980). Exchangeable base content, bedrock geology sensitivity, and land capability (surrogate for soil depth) were combined, in order to classify counties for aquatic input sensitivity (Table 3-8). In the present analysis, land capability has not proven to be a useful surrogate for soil depth in allowing for the identification of all areas of known sensitivity. Allowance for SO_4^{2-} adsorption was made on the United States map, as it is widely recognized that this plays a significant role in buffering the acidity in precipitation (Johnson 1980, Johnson et al. 1980), especially in the southern United States.

Olson et al. (1981) also produced maps of sensitivity, based on several of the soil factors listed in Table 3-7. Exchangeable bases were used in the final maps because these, along with $SO4^{2-}$ adsorption, are the preferred soil parameters to determine terrestrial sensitivities (Cowell et al. 1981). Table 3-9 shows average chemical properties for counties within each sensitivity level.

Chemical and physical soil characteristics employed in the analysis are average values, taken from published information representing the A horizons (upper 20-25cm) of each great soil group (Klopatek et al. 1980, Olson et al. 1981). Proportions of soil types within counties were estimated from the 1:7,500,000 scale soil map of the United States (USGS 1970). As in the case of eastern Canada, no allowance has been made in the interpretation for land management effects in agricultural areas. However, the majority of counties in the moderate and high categories have >30 per cent commercial forest (Table 3-9).

Counties with significant areas of shallow, steep or rocky soils were identified by using information collected as part of the 1967 Conservation Needs Inventory. Counties with more than 50 per cent Land Capability Classes 6, 7 or 8 with subclass limitation 's' were designated as having shallow soils. Land Capability Classes 6, 7 and 8 have limitations that make them unsuited for cultivation and restrict their use primarily to pasture or woodlands. Subclass 's' indicates soils with restrictions related to either shallow, steep or rocky conditions. Since this indirect indicator of soil depth has proven inadequate for accurately assessing soil depth, additional information on this parameter will be collected during the third phase of the WG I process.

Bedrock sensitivity was based on the occurrence of type 1 (low to no buffering capacity) and type 2 (medium to low buffering capacity) bedrock as defined and mapped by Norton (1980). These classes compare to high and moderate sensitivity, respectively, as shown in Table 3-7. Moderate bedrock sensitivity was assigned to counties having more than 50 per cent type 1 + 2 bedrock. Those counties having 50 per cent or more of type 1 bedrock were assigned high sensitivity. The remaining counties were assigned low bedrock sensitivity. These are in fact, combinations of type 3 + 4, but in the eastern United States are dominated by type 4 (infinite buffering capacity).

Sulphate adsorption was estimated on the basis of known characteristics of the great soil groups (Olson et al. 1981). Of particular interest for mapping purposes were soils that had a high sensitivity, based on exchangeable bases, but were known to adsorb $SO4^{2-}$. High $SO4^{2-}$ adsorption allows for greater buffering capacity, for water infiltrating the soil body, and has been accounted for in the

TABLE 3-9 AVERAGE SOIL SURFACE CHARACTERISTICS AND STANDARD DEVIATIONS OF COUNTIES CLASSIFIED AS TO THEIR POTENTIAL FOR CHANGES IN FOREST CATION NUTRIENT STATUS RELATED TO ACID RAIN. THE HIGH (SULPHATE) CLASS HAS HIGH SULPHATE ADSORPTION CAPACITY.

	Soil Sensitivity			
	Low	Moderate	High(sulphate)	High
Number of counties	265	462	625	306
Percentage of counties	16	28	38	18
Percentage of counties in commercial forest (>30%)	12	57	96	87
Exchangeable bases (meq/100g)	23 ± 6	9 ± 2	3 ± 1	4 ± 1
Cation exchange capacity (meq/100g)	31 ± 17	19 ± 7	9 ± 2	12 ± 3
Base saturation (%)	79 ± 15	52 ± 15	29 ± 7	39 ± 8
pH	6.0 ± .6	5.2 ± .5	4.9 ± .2	4.9 ± .3
Clay content (%)	24 ± 6	17 ± 5	10 ± 3	12 ± 5
Organic matter (%)	6 ± 2	6 ± 3	3 ± 1	4 ± 2

criteria (Table 3-8 and Figure 3-9). It should be noted that the capacity of the soil to adsorb SO_4^{2-} is not unlimited, and could be exceeded in areas of high anthropogenic acid loading.

Discussion

These maps are an approximation of sensitive areas based on a fairly strict definition of sensitivity applied using small-scale, polygon-format data. Polygons at this scale (Ecodistrict or County) are not as spatially accurate as individual overlays of bedrock geology or soil chemistry, but provide a convenient framework for integrating more than one coverage. Because criteria are selected on the basis of predominance of occurrence in a county or ecodistrict, the whole polygon is assigned a sensitivity based on dominant characteristics. Thus, depending on the size of individual polygons, real boundaries may be somewhat modified. This explains, in part, why sensitivity levels do not always corresond across the international boundary (or provincial and state borders in some cases). Generally, in these cases, one can expect to find a change near the border but the polygons (Ecodistrict or County) are not small enough to show its exact location.

The land capability data base, which was used as a surrogate for soil depth in the U.S. mapping, does not distinguish counties in the Blue Ridge or Adirondack Mountains which have sensitive bedrock and are suspected of having shallow soils (Figure 3-9). This is due either to the location of county boundaries which results in the majority of the county (>50 per cent) having deep soils, or to incomplete mapping for the Conservation Needs Inventory.

To improve the interpretations, the next step will be to use more accurate soil chemistry and depth data for the U.S. This could be accomplished with Soil Conservation Service county level soil survey data. The Canadian data base requires much improved soil chemistry information from non-agricultural areas. Once this has been achieved it will be necessary to carry out more spatially accurate computer mapping and analysis, in those areas of high or moderate sensitivity undergoing high atmospheric loadings of H_2SO_4. Only when this stage has been reached can the most significant comparisons be made; that is, between terrestrial/geographical characteristics and watershed chemistry.

3.6 ALTERATIONS OF SURFACE WATER QUALITY

Surface water chemistry provides an important integrative measure of the extent to which altered precipitation chemistry may be causing the biogeochemical changes described in the previous section. The available data can be viewed as relevant to three types of questions: the present status of aquatic systems; evidence as to time-trends in water quality measures; and the patterns of seasonal or episodic variation in water quality. Geographically, the data cover areas of North America east of Saskatchewan and largely focused along the U.S.-Canadian border. Sensitive areas are emphasized, whether or not they currently receive significant acidic deposition.

3.6.1 Present Status of Sensitive Aquatic Systems

Current data on pH, alkalinity, sulphate, and other chemical variables are available for a wide variety of climatic, geological and biological conditions in eastern North America. These data give an idea of the current status of aquatic systems, but do not necessarily indicate how or when that status was achieved, or whether it is currently changing. Some insight into these questions is given by comparisons of water quality data from areas with quite different rates of acidic deposition. The comparisons are valid, to the extent that geological conditions are comparable.

This approach is illustrated in Figure 3-11, where the mean and range of sulphate concentrations in lakes and streams from the ELA (Experimental Lakes Area, Kenora, Northwestern Ontario) to Labrador are plotted. The pattern of SO_4^{2-} concentrations in these surface waters bears a strong resemblance to the pattern of wet deposition of SO_4^{2-} shown in Figure 2-8, from low levels at ELA, Quetico, and Northern Wisconsin, rising in the neighbourhood of Lake Superior (Thunder Bay and Turkey Lake), reaching a maximum in the lakes near Sudbury, but decreasing only slightly in the lakes east of Sudbury as far as La Mauricie in Quebec. The concentrations in Atlantic Canada are lower, with the lowest of all seen in the Labrador lakes, the most remote from SO_2 source areas.

This cross-section of the excess sulphate in the surface waters, when considered in conjunction with the measured wet deposition of sulphate, provides strong evidence that the atmospheric deposition from long-range transport accounts for the elevated sulphate levels of the surface waters. Precise comparisons with the deposition values shown in Table 2-4 should not be expected as variations due to dry deposition and concentrations of sulphate by evapotranspiration, and year-to-year variations, influence the deposition measurements.

The data sources for Figure 3-11 are as follows:

ELA: Beamish et al. 1976.

Quetico: Quetico-Lac Mille Lakes Fisheries Assessment Unit Lakes, Quetico Provincial Park, January, 1981 (G. Beggs, Ontario Ministry of Natural Resources, personal communication).

Northern Wisconsin: Northern Wisconsin 1979 Fall Lake Survey (G. Glass, U.S. Environmental Protection Agency, Duluth, personal communication).

Turkey Lake: Lakes and streams in the Turkey Lake and Robertson Lake area, north of Sault Ste. Marie, Ontario, July, 1979 (Environment Canada, National Water Research Institute, F.C. Elder, personal communication).

Sudbury: Sudbury District Lake Trout Lakes. Two were sampled in October, 1979, twenty four in January 1980 (G. Beggs, Ontario Ministry of Natural Resources, personal communication).

Haliburton: Haliburton Highlands Fisheries Assessment Lakes, January, 1981 (G. Beggs, Ontario Ministry of Natural Resources, personal communication).

Algonquin: Algonquin Fisheries Assessment Lakes, Algonquin Provincial Park, means of midlake composite samples 1979 (G. Beggs, Ontario Ministry of Natural Resources, personal communication).

Gatineau: Gatineau Park, Quebec, near Ottawa, Ontario, NAQUADAT 1973.

La Mauricie: Parc National de la Mauricie, July, 1980 (Environment Canada, Quebec Region, R. Lemieux, personal communication).

New Brunswick: Peterson, 1980.

Halifax: Lakes and rivers near Halifax, Nova Scotia, April, 1980 (Environment Canada, Water Quality Branch, Atlantic Region, T. Clair, personal comunication).

Isle of Newfoundland: Newfoundland Headwater Lakes, November, 1980 (Environment Canada, Water Quality Branch, Atlantic Region, T. Clair, personal communication).

Labrador: Clair, 1981.

A number of other studies have documented the present status of surface water resources in Canada and the United States. They are summarized in the following sections:

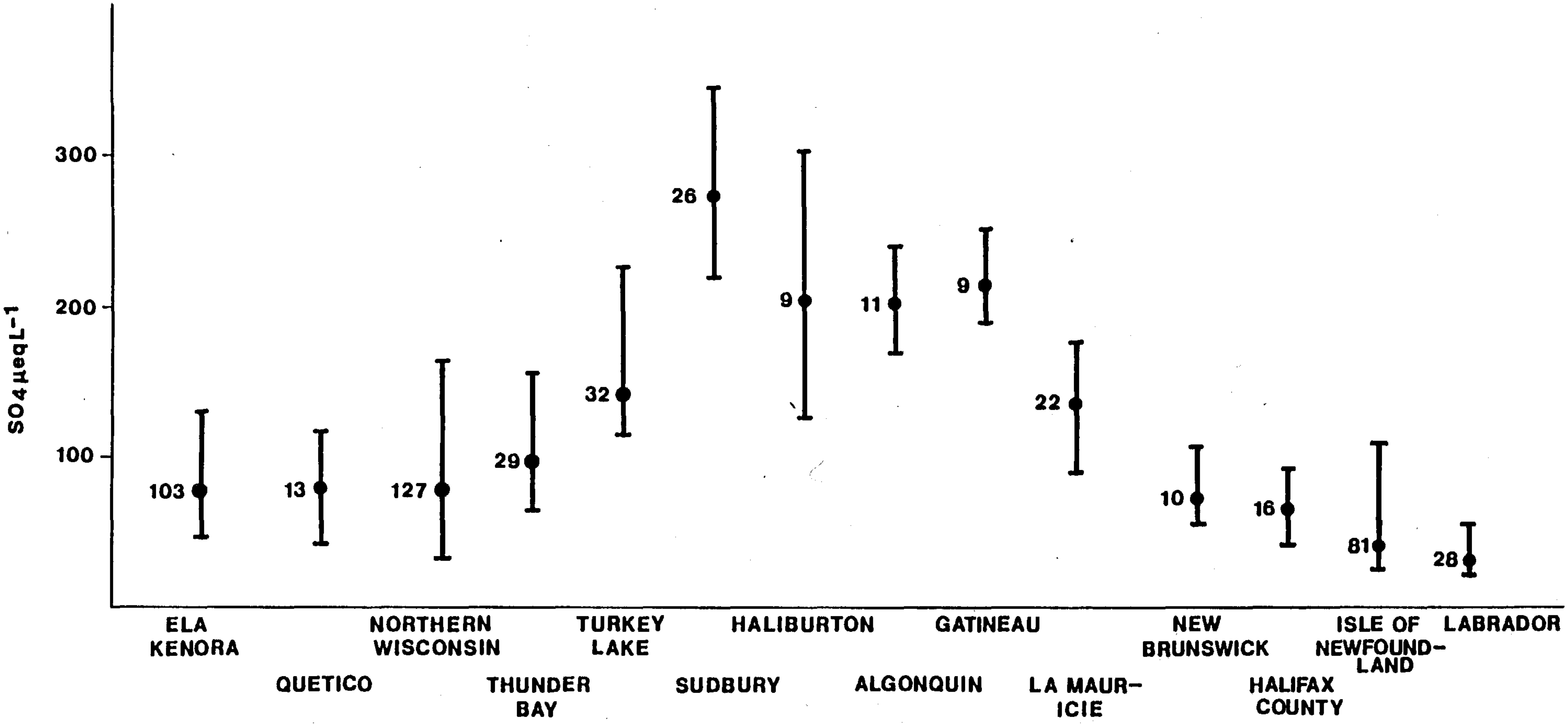
Saskatchewan

Total alkalinity, calcium, magnesium and pH of some 300 lakes in Saskatchewan's Shield and fringe Shield regions were analyzed to assess the sensitivity of these lakes to potential acid precipitation (Liow and Atton 1981). Concentrations of alkalinity in these lakes varied from 0.5 to 87 mg/l as $CaCO_3$. Forty-four per cent of the lakes surveyed had alkalinities of 10 mg/l or less, while 27 per cent had between 10 and 20 mg/l. These two groups of lakes are considered to be highly or moderately sensitive to acidification.

Measurements of pH, ranging from 5.56 to 8.2, indicate that, at present, Saskatchewan's Shield lakes are not very acidic; lakes with pH values between 6.5 and 7.5 accounted for nearly 80 per cent of all lakes investigated. Concentrations of calcium ranged from 0.33 to 31.60 mg/l. About 54 per cent of the lakes surveyed had calcium of 4 mg/l or less, while 25 per cent had between 4 and 8 mg/l. Concentrations of magnesium varied from 0 to 10.7 mg/l. Approximately 65 per cent of the lakes measured had magnesium concentrations of 2 mg/l or less, whereas 32 per cent had between 2 and 3 mg/l. Concentrations of calcium alone, or together with magnesium, were highly correlated to alkalinity.

A nomograph was constructed to depict the anticipated rate of acidification (to pH 5.5), given the mean depth and alkalinity of the lake, and an assumed sulphur deposition rate of 0.4 $g/m^2.yr$. The authors suggest that, in the event of acid rain, shallow and poorly buffered Shield lakes in northern Saskatchewan may be acidified in a matter of a few decades.

Figure 3-11 Mean and range of SO_4^{2-} or, near the coast, excess SO_4^{2-}, in lakes and streams of eastern Canada. Sampling dates range from 1973 to 1981. See text for data sources (from Thompson and Hutton, unpublished report, 1981).



Ontario

About 6 per cent of 1,527 lakes recently surveyed in Ontario were classified as acidified. These lakes were found to have an alkalinity equal to, or less than, 0 microequivalents per litre (μeq/l). An additional 12 per cent (187 lakes) were classified as extremely sensitive, and a further 32 per cent (482 lakes) were considered moderately sensitive (Table 3-10). Based on lake alkalinity data, it is reasonable to expect that up to 30 per cent of the lakes in the important tourist areas of Muskoka-Haliburton will be acidified by present acid loadings, although the time scale cannot yet be defined. Data for the Manitoulin and Sudbury Districts must be interpreted with some caution, since those areas were subjected to local problems related to smelting operations in Sudbury. Scheider et al. (1980) and Chan et al. (1980) indicate that long-range transport of acid to the area is substantial, but its influence relative to the historic local problems, with respect to acidifying lakes, cannot be determined.

Quebec

Vast areas of the Province of Quebec are composed of non-calcareous lithology, and glacial modifications have not provided calcareous tills to modify the local soil structures. Only in the marine sediments of the St. Lawrence Valley and calcareous lithology of the Gaspé region is significant buffering material found.

It is estimated that the Province contains greater than one million lakes, the vast majority of which have not been surveyed. Present surveys have been limited to the southern, more accessible areas and are therefore likely biased towards the more buffered waters. While it is not possible to assess the degree of this bias, examination of the buffering capacity of the surface waters of the surveyed area gives an indication of sensitivity of waters of Quebec to acidification.

Figure 3-12 is a distribution of Calcite Saturation Index (CSI, Kramer 1976) of 297 lakes surveyed between 1976 and 1980. The CSI incorporates both alkalinity and hydrogen ion concentration into a logarithmic index of sensitivity to acidification. Insensitive or calcium saturated waters have a negative CSI, while waters having positive values greater than 2.5 to 3 are considered sensitive, and values greater than 4, are highly sensitive. Figure 3-12 shows the distribution of CSI of surveyed lakes by hydrographic region of Quebec, with more detailed surveys of the Laurentide and La Mauricie Parks. It is evident that nearly all waters, other than the St. Lawrence Valley and the Gaspé Regions (Regions 01, 02 and 03), have CSI greater than 2.5 and are, as a result, sensitive to

TABLE 3-10

SUMMARY OF THE PERCENTAGE OF LAKES IN EACH ALKALINITY CLASS BY COUNTY OR DISTRICT AND FOR LAKE ONTARIO

County or District	Percentage of Total No. of Lakes in each Alkalinity Class					Total No. of Lakes
	Acidified (≤ 0 *ueq/l*)	Extreme Sensitivity (> 0 to 39.9 *ueq/l*)	Moderate Sensitivity (40 to 199 *ueq/l*)	Low Sensitivity (200 to 499 *ueq/l*)	Not Sensitive (≥ 500 *ueq/l*)	
Algoma Dist.	5	11	30	28	26	163
Bruce Co.					100	7
Cochrane Dist.		7		11	82	27
Durham Co.					100	1
Frontenac Co.				6	94	64
Grey Co.					100	3
Haliburton Co.		24	39	22	15	112
Hastings Co.			21	11	68	63
Huron Co.					100	1
Kenora Dist.			14	25	61	88
Lanark Co.					100	15
Leeds Co.					100	24
Lennox & Addington Co.			36	12	52	25
Manitoulin Dist.	52	29	3	3	13	31
Middlesex Co.					100	1
Muskoka Dist.	1	30	61	2	6	115
Nipissing Dist.		9	75	13	3	75
Northumberland Co.					100	1
Ontario Co.					100	5
Parry Sound Dist.	5	20	64	10	1	107
Peel Co.					100	1
Peterborough Co.		4	16	6	74	49
Prince Edward Co.					100	3
Rainy River Dist.		3	64	19	14	99
Renfrew Co.			8	32	60	50
Simcoe Co.					100	7
Stormont Co.					100	1
Sudbury Dist.	24	29	23	12	12	210
Thunder Bay Dist.	1	2	25	27	45	136
Timiskaming Dist.	13		7	27	53	30
Victoria Co.					100	11
York Co.					100	2
Province	6	12	31	16	35	
(No. of Lakes)	(87)	(187)	(482)	(241)	(530)	1,527

From Ontario Ministry of Environment

acidification. Surveys of the lakes of Laurentide and La Mauricie Parks appear to indicate a greater sensitivity than do the surrounding regions. This may be an actual indication of local differences in terrain geochemistry, but is believed to result from over-estimation of alkalinity in the older measurements. The actual sensitivity may, therefore, be even greater than indicated by the older surveys.

Atlantic Provinces

Except for northern New Brunswick and all of Prince Edward Island, most watersheds in this region provide little buffering capacity against acid precipitation. Much of the bedrock is granitic, overlain by thin podzol soils. Alkalinity values for 63 lakes located in eastern and southwestern Nova Scotia were all lower than 50 µeq/l with summer pH values at certain weirs decreasing to a minimum of 4.5 (Clair et al. 1981). Use of Henriksen's (1979) model on 16 Nova Scotia lakes suggests that acidification of 40 to 50 µeq/l has occurred over the past two decades, consistent with measured pH declines, (Thompson et al. 1980, Wiltshire and Machell 1981).

An earlier analysis of the same data base, but including only 215 lakes sampled between 1971 and 1977 (Legendre et al. 1980), has provided a summary of the lake status in terms of the sulphate/bicarbonate ratios. This ratio is an indication of the degree to which sulphate from atmospheric deposition has replaced bicarbonate resulting from weathering in the natural water. The summary shown in Table 3-11 has classified lakes into four values of the SO_4^{2-}/HCO_3^- ratio:

1. $R < 0.6$
2. $0.6 < R < 1.2$
3. $1.2 < R < 1.8$
4. $R > 1.8$

The lake summaries of Table 3-11 are shown by the same hydrographic regions as shown in Figure 3-12. It can be seen that Regions 01, 02, and 03 have the majority of lakes in category 1, i.e., HCO_3^- dominates the SO_4^{2-}/HCO_3^- ratio, while Regions 04, 05, 06 and 07 have large portions of the lakes where SO_4^{2-} equals or exceeds the HCO_3^-. In these cases much of the original HCO_3^- buffering has already been neutralized by the acidic sulphate deposition.

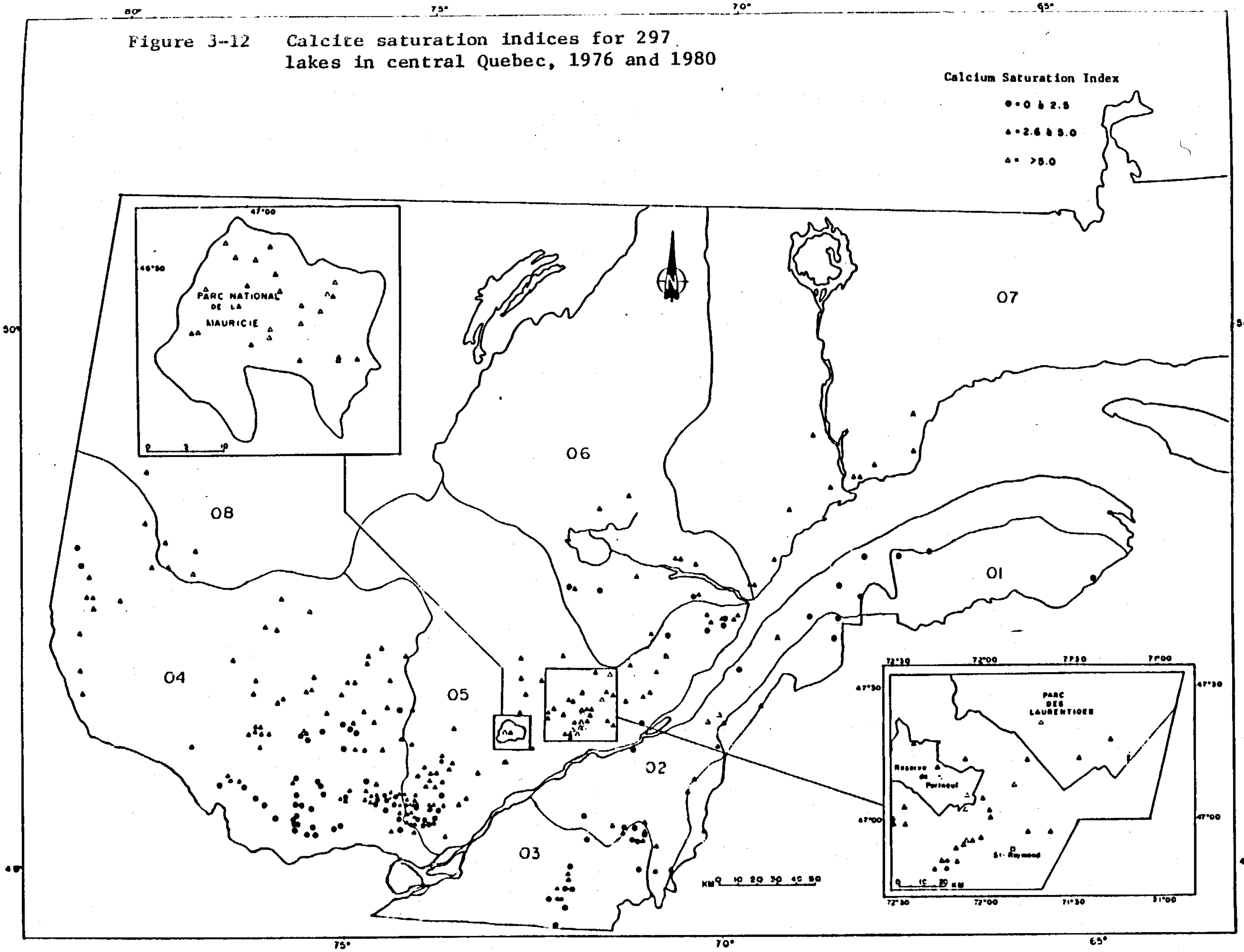
TABLE 3-11

SOME STATISTICS ON THE RATIO SO_4^{2-}/HCO_3^- FOR WATERS OF QUEBEC

	LAKES NORTH OF THE ST. LAWRENCE RIVER WEST → EAST HYDROGRAPHIC REGION							
Classes of Lakes	04		05		06		07	
	N	%	N	%	N	%	N	%
1	24	21.4	5	8.6	3	50.0	9	64.3
2	41	36.6	15	25.9	1	16.7	3	21.4
3	19	17.0	14	24.1	1	16.7	2	14.3
4	28	25.0	24	41.4	1	16.6	0	
TOTAL	112	100.0	58	100.0	6	100.0	14	100.0

	LAKES SOUTH OF THE ST. LAWRENCE RIVER WEST → EAST HYDROGRAPHIC REGION					
Classes of Lakes	03		02		01	
	N	%	N	%	N	%
1	21	95.4	13	76.5	5	100.0
2	1	4.6	3	17.6		
3	-	-	0			
4	-	-	1	5.9		
TOTAL	22	100.0	17	100.0	5	100.0

Figure 3-12 Calcite saturation indices for 297 lakes in central Quebec, 1976 and 1980



Labrador

As part of the Canadian Shield, Labrador is composed largely of granite and gneiss derived from sedimentary rock with basic rock intrusions found mostly in the centre of the region. It is covered by very thin topsoil and contains large numbers of sphagnum bogs. Major ion chemistry data have been gathered from 400 sites from 1978 to 1980, which shows alkalinity values rarely higher than 150 μeq/l except on anorthosite and gabbro intrusions (Clair 1981). Despite such high sensitivity, pH values are high with an average value near 6.4, suggesting that until now, acid precipitation has not changed the surface water quality of Labrador.

U.S. Surface Waters

The distribution of alkalinity in surface waters of various regions in the U.S. is summarized in Table 3-12. All of the lakes and streams are in defined sensitive regions with low soil cation exchange capacity, non-buffering bedrock types and low sulphate adsorption (see section 4.4). In general, the data show lowest alkalinity in eastern regions receiving the greatest acid deposition, with 38-81 per cent of lakes and streams being moderately sensitive to acidified (alkalinity from less than 0 to 200 μeq/l). Thirteen to 48 per cent of midwestern lakes and streams are in the same categories. In general, lakes appear to show lower alkalinity than streams for the same geology and deposition loading. In addition, Crisman and Brezonik (1980) report that nine out of eleven lakes sampled in northern Florida were acidified (alkalinity = 0).

Minnesota, Wisconsin and Michigan

Northern areas of Minnesota, Wisconsin, and Michigan are potentially susceptible to acid deposition (Galloway and Cowling 1978) because coarse-textured soils there are very low in calcium carbonate, and are underlain by acidic igneous and metamorphic bedrocks and poorly buffered sandstone. The region's rich resources and related industries, including recreation, forestry, farming, and mining, would be vulnerable to disruption if acid inputs reached levels presently being experienced in other areas of the United States.

Available estimates indicate that Minnesota has from 15,000 to 22,000 lakes, covering 10,000 square kilometers. Half the lakes in the BWCAW are susceptible to acidification, due to low buffering capacity associated with alkalinities below 200 μeq/l. Wisconsin has some 11,000 lakes more than 8 hectares in size, and 2,600 lakes have a pH at or below 6.0 with little or no alkalinity, (Glass 1980). Michigan has more than 10,000 lakes over 4 hectares in size,

TABLE 3-12. PERCENTAGE OF LAKES AND STREAMS IN VARIOUS SENSITIVITY CLASSES

Region	Percentage of Lakes and Streams Sampled					Total Number Lakes/Streams Sampled
	Acidified (≤ 0 μeq/ℓ)	Extreme Sensitivity (0-40 μeq/ℓ)	Moderate Sensitivity (40-200 μeq/ℓ)	Low Sensitivity (200-500 μeq/ℓ)	Not Sensitive (> 500 μeq/ℓ)	
Lakes						
Adirondack[a]	23	17	40	15	5	432
Northern Wisconsin[b]	3	20	19	32	26	276
Northern Minnesota[c]			48	35	17	85
Streams						
N.W. Pennsylvania[d]	11	11	39	28	11	18
E. Pennsylvania[d]		19	19	31	31	26
Connecticut[e]	4	4	48	44		23
Maine[e]		6	75	19		16
NC/VA[f]		5	59	33	3	38
Jackson Co.(Wis.)[g]		8	35	18	39	80
Oneida Co.(Wis.)[h]		2	11	33	54	195

[a] Pfeiffer and Festa (1980). (1979 data only.)
[b] Eilers *et al*. (1979).
[c] Glass and Loucks (1980).
[d] Arnold (1981).
[e] Haines (1981a, 1981b).
[f] Hendrey *et al*. (1980). (See text.)
[g] Klick and Threinen (1968).
[h] Andrews and Threinen (1966). (Includes only streams with watershed areas ≤ 3 mi^2.)

and susceptible to acidification. Of some 8,000 lakes and ponds in the western half of the upper peninsula of Michigan, more than 50 percent have an alkalinity in the range of 10 mg/l, indicating that they are potentially susceptible to acid inputs.

3.6.2 Time Trends in Surface Water Alterations

Questions of past and potential future changes in surface water acidification are best answered by detailed analysis of available long-term data. Such studies also give an indication of other anthropogenic effects, if accelerated acidification (over and above any natural acidification) is evident. Care must be taken in any historical studies, however, to account for differences between older methods of measurement and current methods. Precautions have been taken in the following analyses to correct for methodological differences, but these considerations must be remembered when making comparisons.

3.6.3 Time Trends in Nova Scotia, Newfoundland and New Brunswick

Data from the mid-1950s for six rivers in Nova Scotia and one river in Newfoundland are compared with data for 1973 in Table 3-13. The results show decreases in pH and concurrent increases in excess SO_4^{2-} loads. The SO_4^{2-} being carried by these rivers is believed to have only two sources: long-distance transport of air pollutants, and sea salt. Atmospheric deposition of sulphate ions at two monitoring stations in Newfoundland was compared with the sulphate ions carried by the local rivers. The result was a general correlation between sulphate ion load in the rivers and the amounts from precipitation. Also shown was a geographic pattern of decreasing sulphate loadings to the east and north, which was consistent with an assumption of long-distance transport of pollutants from urban centres.

Rivers in both Nova Scotia and Newfoundland show similar trends in pH and excess SO_4^{2-} loads over the period 1965 to 1980, as seen in Figure 3-13. Data for the Nova Scotia rivers since 1973 are sparse (four or fewer samples per year) so excess SO_4^{2-} loads cannot be calculated, but median pHs are shown. The lowest pHs and highest excess SO_4 loads were seen in 1973. The similarity in trends for rivers far apart in two different Provinces is good evidence that the changes are due to large scale atmospheric loading changes, that is, to long range transport of air pollutants. The figure also shows that, when excess SO_4^{2-} loads are reduced, the pH of the rivers recovers promptly. However, even the reduced loads since 1973 are too much for a very soft-water river such as the Medway. The margin between acceptable and excessive SO_4^{2-} loading is small for these and many similar rivers in Nova Scotia and Newfoundland.

Wiltshire and Machell (1981) have reported on a re-survey of 16 lakes in Nova Scotia and New Brunswick, which had historical data

TABLE 3-13

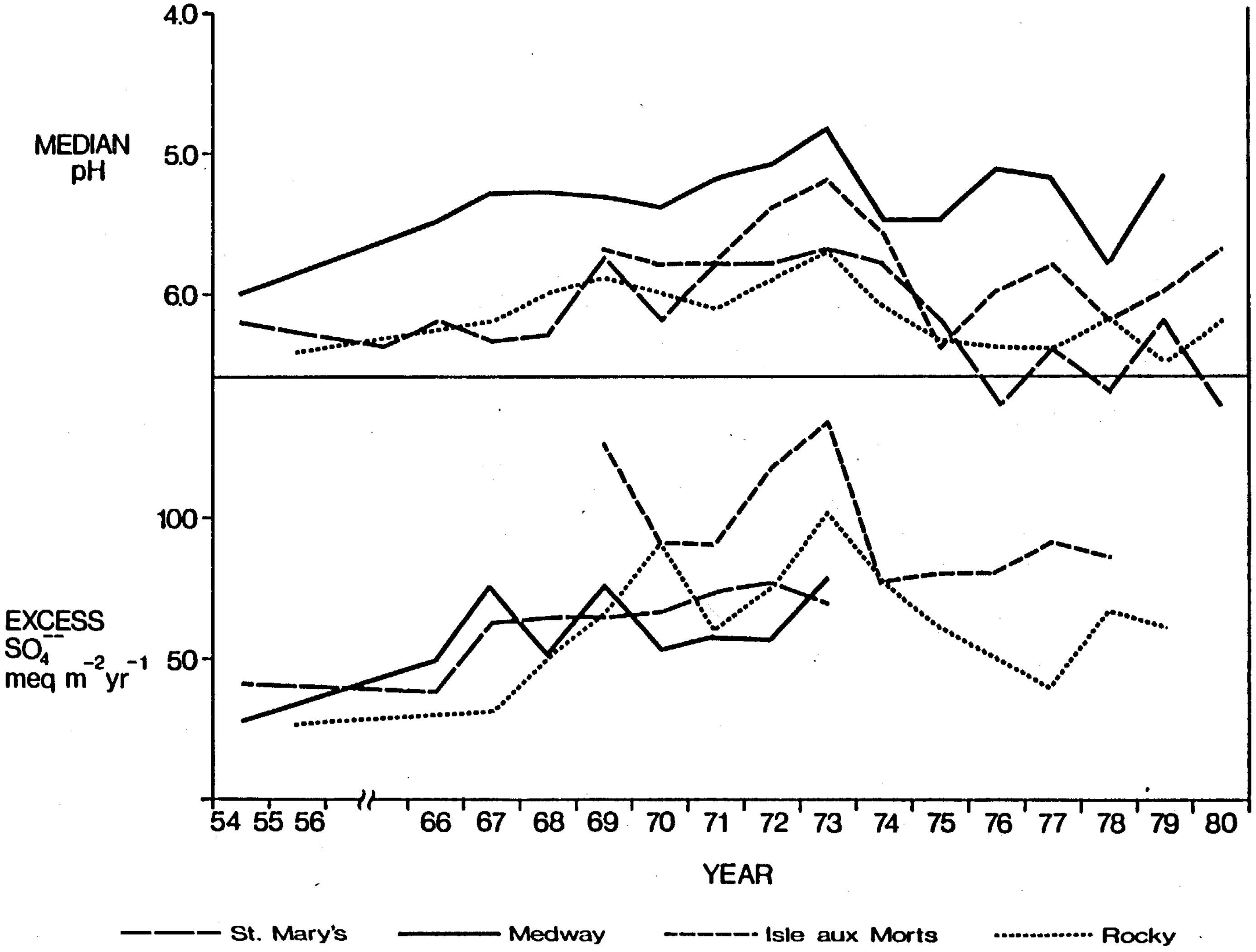
COMPARISON OF MEAN pH AND EXCESS SO_4^{2-} CONCENTRATIONS FROM THE MID 1950's to 1973, FOR SIX RIVERS IN NOVA SCOTIA AND ONE IN NEWFOUNDLAND

River	pH	Excess SO_4^{2-} meq m^{-2} yr^{-1}	Year
St. Mary's	6.20	42	1954-55
	5.16	60	1973
Roseway	4.66	30	1954-55
	4.28	128	1973
Tusket	5.16	51	1954-55
	4.38	101	1973
Mersey*	5.82	18	1954-55
	4.78	65	1973
Medway	5.67	29	1954-55
	4.88	78	1973
Le Have	5.94	34	1954-55
	5.20	80	1973
Rocky River, Newfoundland	6.15	27	1955-56
	5.3	101	1973

* Discharge date incomplete 1954-55

From: Thompson et al. 1980.

Figure 3-13 Annual changes in median pH and mean discharge-weighted excess SO_4^{2-} for the St. Mary's and Medway Rivers, Nova Scotia, and the Isle aux Morts and Rocky Rivers, Newfoundland.



going back to the 1930's in some cases. Eleven of the lakes are remote from local sources in Halifax and Saint John. Table 3-14, taken from their report, summarizes the data for 10 remote lakes with the most reliable historical information, and it is apparent that there has been a decline in pH in all cases, most notably since the 1950's. Herman and Gorham (1957) reported a mean pH of 5.7 for precipitation collected in the Kentville, Nova Scotia, area during the early 1950's, compared to values of about 4.6 in recent years. Wiltshire and Machell indicate that the surveys are being extended to year-round sampling to determine whether year-to-year variations have contributed to these apparent declines.

3.6.4 Historical Trends in New York State

Studies of lake chemistry in high-elevation lakes of the Adirondack region of New York have shown a marked decline in the pH of the lakes, compared with data of 40 years earlier (Figure 3-14). Of the 218 lakes measured in 1975 (Schofield 1976) approximately 50 per cent were significantly more acid in comparison to earlier observations. All surveyed lakes are very sensitive to acidification (less than 200 μeq/l alkalinity), and many are already acidified, as indicated by the low pH's (Figure 3-15).

A positive correlation between increased elevation and reduced pH of ponds and lakes appears to reflect the combined influence of heavier precipitation at higher elevations, the smaller surface acreage and watershed size which characterizes most headwater ponds, the prevalence of granitic bedrock and shallow soil deposits in the higher areas, and the direct impingement of acidic cloud water. The most recent (1975 to 1979) New York State Department of Environmental Conservation surveys (Pfeiffer and Festa 1980) indicate that 25 per cent of the lakes (comprising about 5 per cent by area of the sampled waters) were at a "critical" pH level, below 5.0. Overall, 7.9 per cent of the lakes in the Adirondacks were acidified from acid precipitation (228 lakes), totalling 3.9 per cent of the water acreages. From these studies, there is evidence suggesting that decreases in pH have occurred over a wide range of lake pH values. A set of 138 lakes in the Adirondacks is summarized in Figure 3-16.

The Hinckley Reservoir, a municipal water supply reservoir in New York state, built around 1910, receives the drainage of West Canada Creek in the southwestern Adirondack Mountains. Water quality records have been maintained since 1924. Results for total hardness and alkalinity over the period 1924 to 1975 indicate a significant long-term decline, which may have begun before 1920. Short-term upward and downward shifts in alkalinity and hardness occur over the period, apparently increasing in the early 1960's, due to drought conditions (C.L. Schofield, personal communication). The fact that alkalinity and hardness tend to increase and decrease together seems unusual, and suggests that, if the response is due to acid input, it is associated with complex geochemical alterations.

TABLE 3-14

APPARENT CHANGES IN SUMMER pH VALUES IN LAKES IN NOVA SCOTIA AND SOUTHERN NEW BRUNSWICK DURING THE PERIOD 1940-1979

	pH			pH		Calculated alkalinity change in µeq/l[d]	
	ca 1940[a]	1950's[b]	1979[c]	pre-1950's	post-1950's	pre-1950	post-1950
Boarsback (N.S.)	4.7	4.7	4.4	.0	-.3	0	-20
Jesse (N.S.)	6.5	6.5	5.8	.0	-.7	0	-14
Lily (N.S.)		6.5	5.8		-.7		-14
Kerr (N.B.)	6.8	6.6	6.0	-.2	-.6	-12	-16
Creasey (N.B.)	6.7	6.7	6.0	.0	-.7	0	-21
Tedford (N.S.)	6.3	6.6	6.3	+.3	-.3	5.5	-5.5
Sutherland (N.S.)		7.0	6.3		-.7		-41
Gibson (N.B.)	7.0	6.7	6.4	-.3	-.3	-25	-18
Black Brook (N.S.)		6.8	6.4		-.4		-20
Copper (N.S.)		7.3	7.0		-.3		-55

[a] Data from Smith (1937a, b, 1948, 1952, 1961).

[b] Data from Hayes and Anthony (1958).

[c] Wiltshire and Machell (1981).

[d] Liljestrand H.M., personal communication. PCO_2 assumed - $10^{-3.5}$ atm. with bicarbonate as major buffer. Negative alkalinity is a positive acidity.

From: Wiltshire and Machell 1981.

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post-1950

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-14

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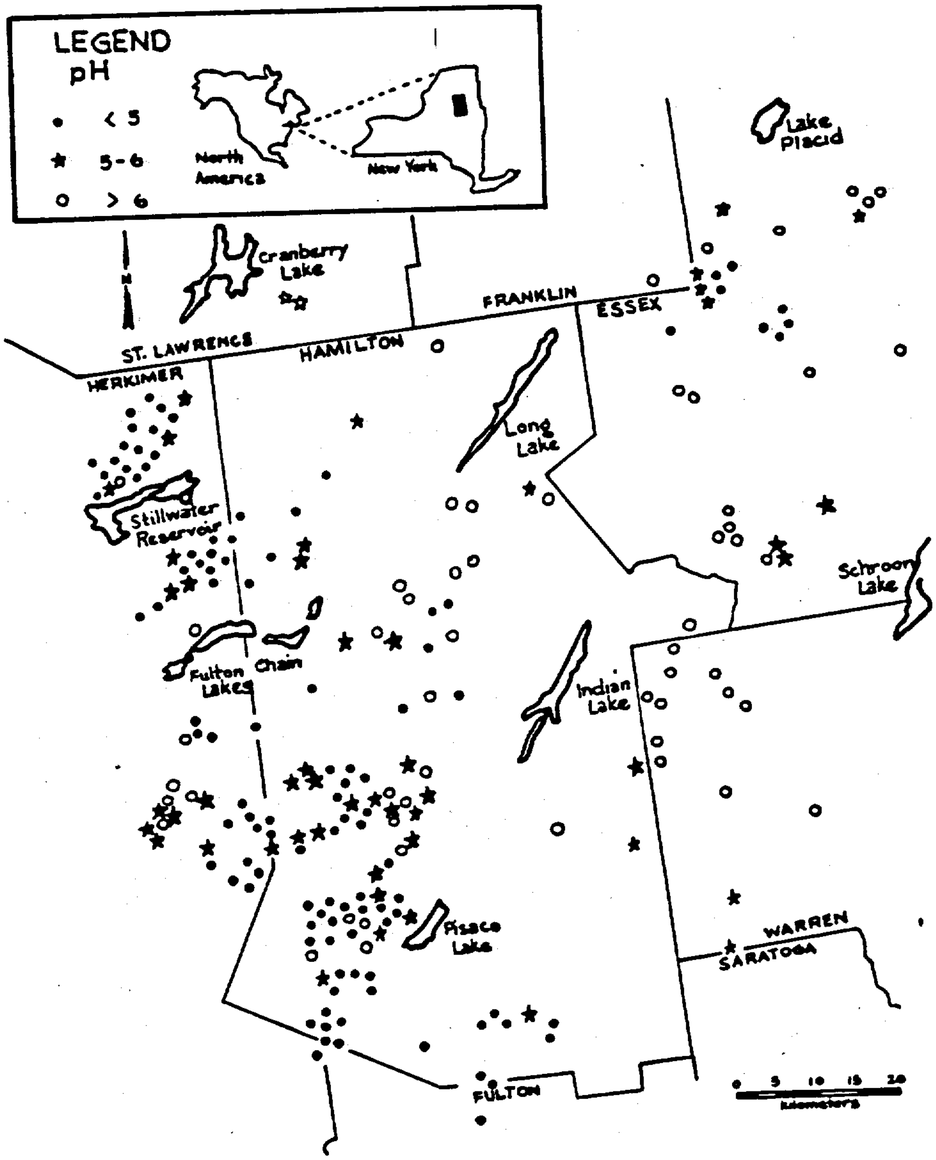


Figure 3-14 Geographic distribution of pH levels measured in Adirondack Lakes higher than 610 meters elevation, June 24-27, 1975 (Schofield 1976).

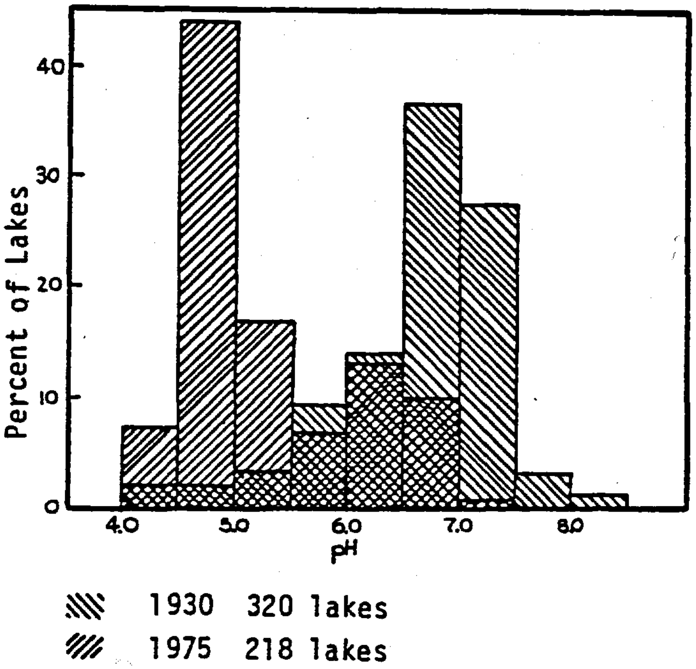


Figure 3-15 Comparison of lake pH, 1930 to 1975, for the Adirondack Mountains area of New York (Wright and Gjessing 1976).

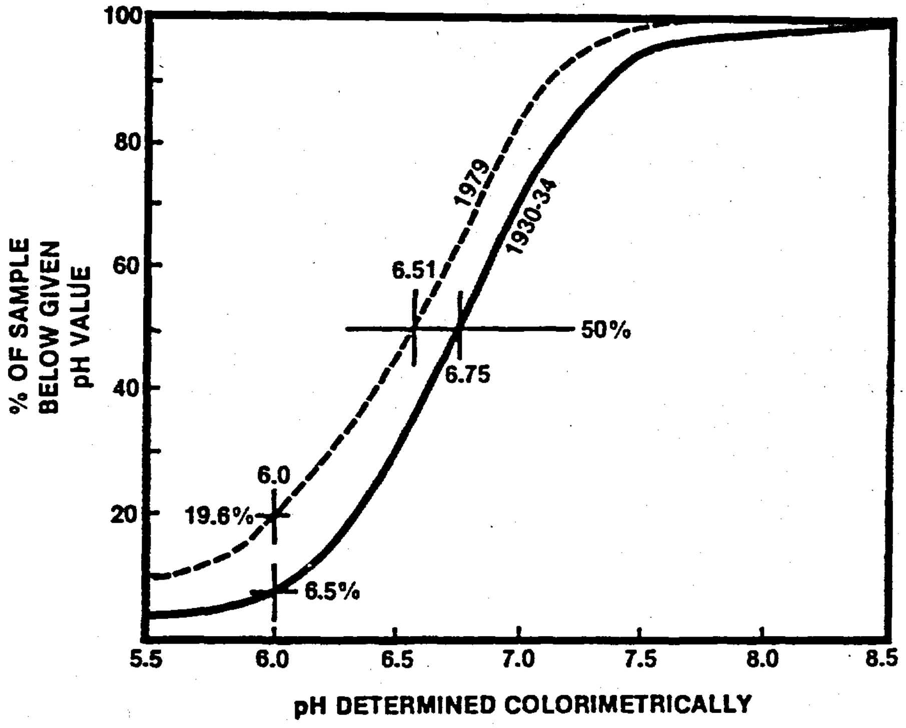


Figure 3-16 Cumulative comparison of historic and recent pH values for a set of 138 Adirondack Lakes, New York (Pfeiffer and Festa 1980).

3.6.5 pH Changes in Maine and New England

Summer pH measurements are available for 1,368 of the several thousand lakes in Maine, over the interval from the 1930's to the 1970s. The results show a decreased pH, on the average of from about 6.85 in 1937 to about 5.95 in 1974, an eight fold increase in H^+. Roughly three-fourths of the decrease occurred between 1950 and 1960, corresponding to the period in which the acidity of precipitation may have increased most rapidly (Haines 1981a).

A preliminary analysis of 300 headwater ponds and streams in the six New England states shows that alkalinity readings of less than 200 μeq/l cover most of the regions examined, with widespread readings below 20 μeq/l (Figure 3-17). For comparison, Thompson and Elder (1981) have considered lakes with alkalinity readings below 200 μeq/l as highly sensitive to acidification (Haines 1981b).

3.6.6 Time Trend in New Jersey

Johnson (1979) described a 17-year trend toward acidification of headwater streams in the New Jersey Pine Barrens which drain relatively undisturbed watersheds (Figure 3-18). The decline in pH is a statistically significant trend with time, and has amounted to approximately 0.4 units (pH) over the period - an estimated increase in H^+ concentration of about 50 μeq/l. In the sandy soils of this region, relatively little neutralization of acid input occurs by ion exchange or mineral weathering as precipitation moves through the soil. The low level of neutralization is evidenced by the low pH of shallow groundwater, averaging 4.3 for 78 samples in 1978 through 1979. One reason for the great variability in pH values is thought to be the timing and variable pH of individual storms (see following discussion of seasonal and episodic pH changes).

One possible cause is the acid content of precipitation over the last two decades, as described for other areas in the northeastern United States. Some precipitation pH data suggest a trend toward lower pH of precipitation in southern New Jersey (Johnson 1979). Precipitation samples, collected at several sites in the Mullica and Cedar Creek basins in 1970 through 1972, had an average pH of 4.4, and samples collected near Oyster Creek for 7 months in 1972 had an average pH of 4.25. From May, 1978 to April, 1979, the average pH of weekly precipitation samples at McDonalds Branch was 3.9. The SO_4^{2-} concentrations in McDonalds Branch and Oyster Creek are consistent with the hypothesis of an atmospheric source of acid, since SO_4^{2-} is the major anion balancing H^+ in the precipitation.

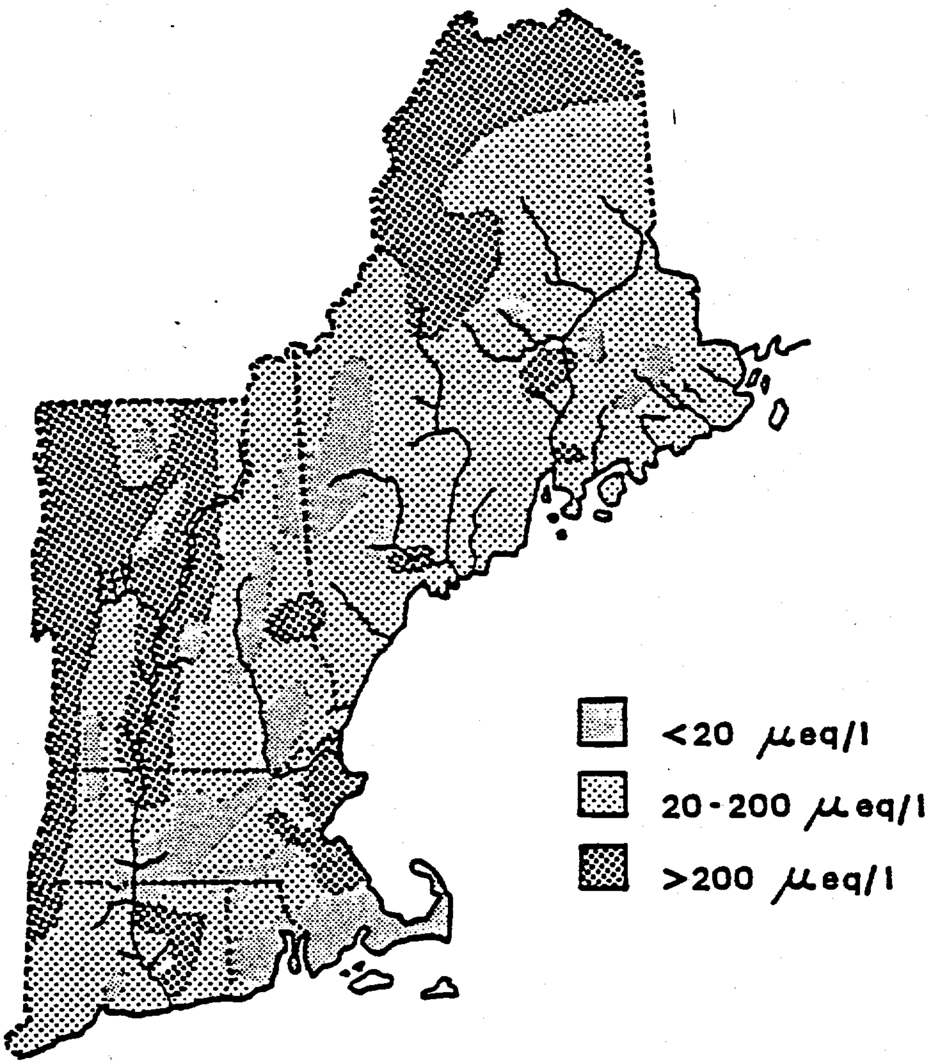


Figure 3-17 Surface water alkalinity of New England states (Haines 1981).

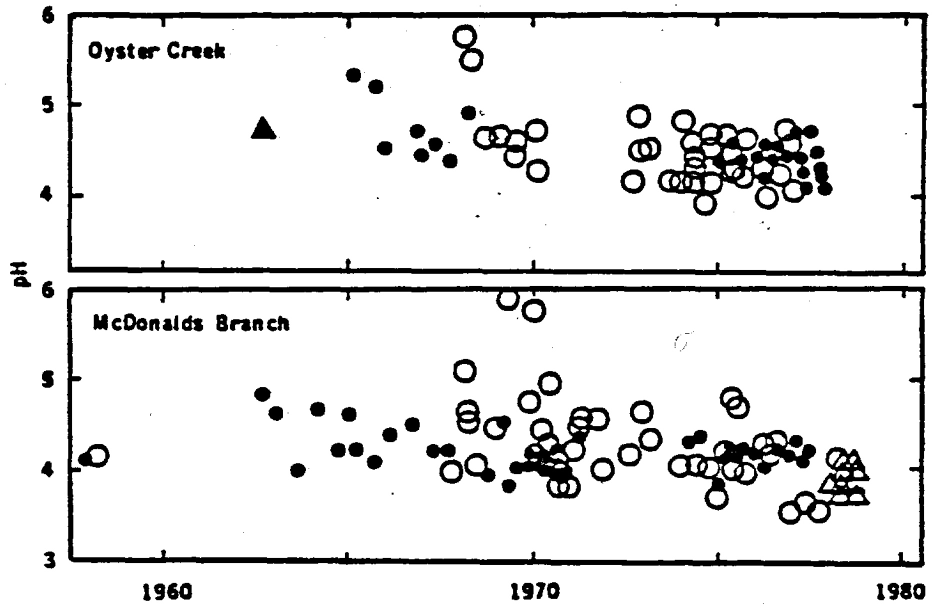


Figure 3-18 New Jersey stream pH, 1958-1979, Oyster Creek and McDonalds Branch. Closed circles represent samples in which anion and cation equivalents balanced, and calculated and measured specific conductances were equal. Open circles are samples for which the chemical analyses were incomplete, or for which discrepancies in anion and cation and conductivity balances could not be attributed to errors in pH. The closed triangle represents the average pH determined in a branch of Oyster Creek in a 1963 study. Open triangles are monthly means of pH data collected weekly from May 1978 to January 1979 during a University of Pennsylvania trace metal study (Johnson 1979).

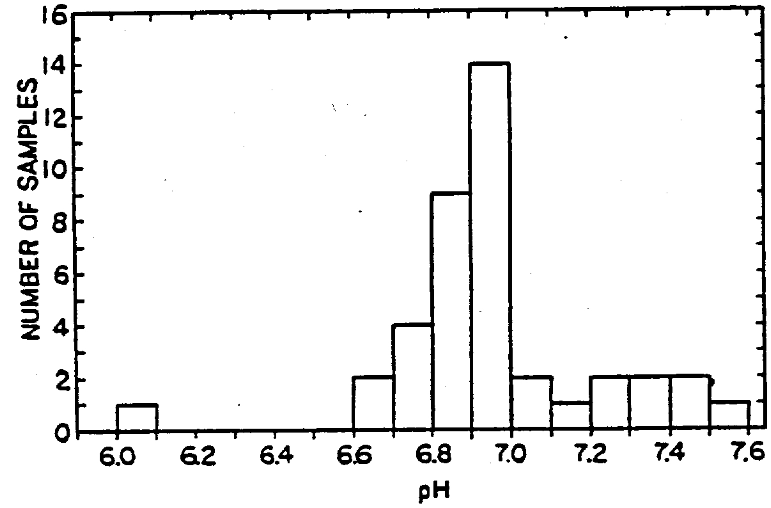
3.6.7 pH and Alkalinity Trends in North Carolina

Measurements of 38 streams in western North Carolina reported by Hendry et al. (1980), showed a decrease in pH and alkalinity in 80 per cent of the streams surveyed between 1960-63 and June and July, 1979. The distributions of apparent pH and alkalinity changed substantially over the 15 to 19 years between samples (Figures 3-19 and 3-20). Mean hydrogen ion concentrations changed from pH 6.77 in the early 1960's, to pH 6.51, in 1979 - an 82 per cent increase in hydrogen ion concentration. Mean alkalinity values have also declined significantly since the early 1960's, from 116 μeq/l (corrected for differences in methods), to 80 μeq/l in 1979, with 71 per cent of the 1979 values being lower than the earlier (corrected) values. Additional data are needed to confirm these observations, which represent the most sensitive streams in the area.

In the Great Smoky Mountains National Park, other symptoms have been observed in an independent study. Acid runoff at pH's as low as 4.3 in perennial mountain streams has produced elevated aluminum concentrations. Inhibiting effects upon population densities of benthic macroinvertebrates, and upon brook trout populations, have been connected to sulphuric acid loadings. Similarity of edaphic conditions in the park, and in the Adirondack Lake region of New York, was noted (Herrmann and Baron 1980).

3.6.8 Seasonal and Episodic pH Depression

One of the problems with survey data, both current and historical, is that the sample usually represents one or a few measurements at any one location, usually taken in the summer. This limited sampling period provides no record of pH and other chemical changes which take place, in relation to seasonal cycles or major weather events. If these changes coincide with sensitive periods in the life cycles of fish, e.g., spawning and hatching, significant mortality can occur. Individual pH values during the summer usually do not reflect these aspects of the dose/response relationship. In addition, occasional pH depressions may signal the beginning of lake or stream transition to acidified status (see later discussion). The following data describe recent results on episodic pH depressions; the extent to which these phenomena occurred in the past is not known, but comparisons can be made with "control" areas having low acid deposition.



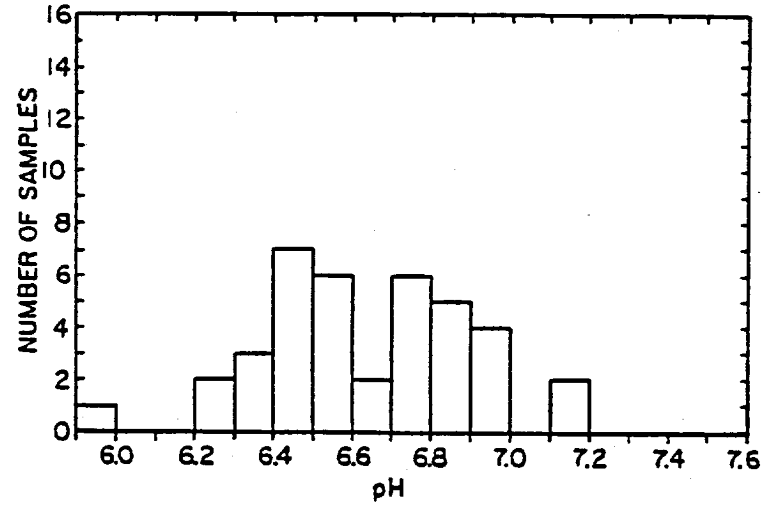


Figure 3-19 Distribution of pH of North Carolina streams June, July, August 1960-1963 (upper), compared with June, July 1979 (modified from Hendrey et al. 1980).

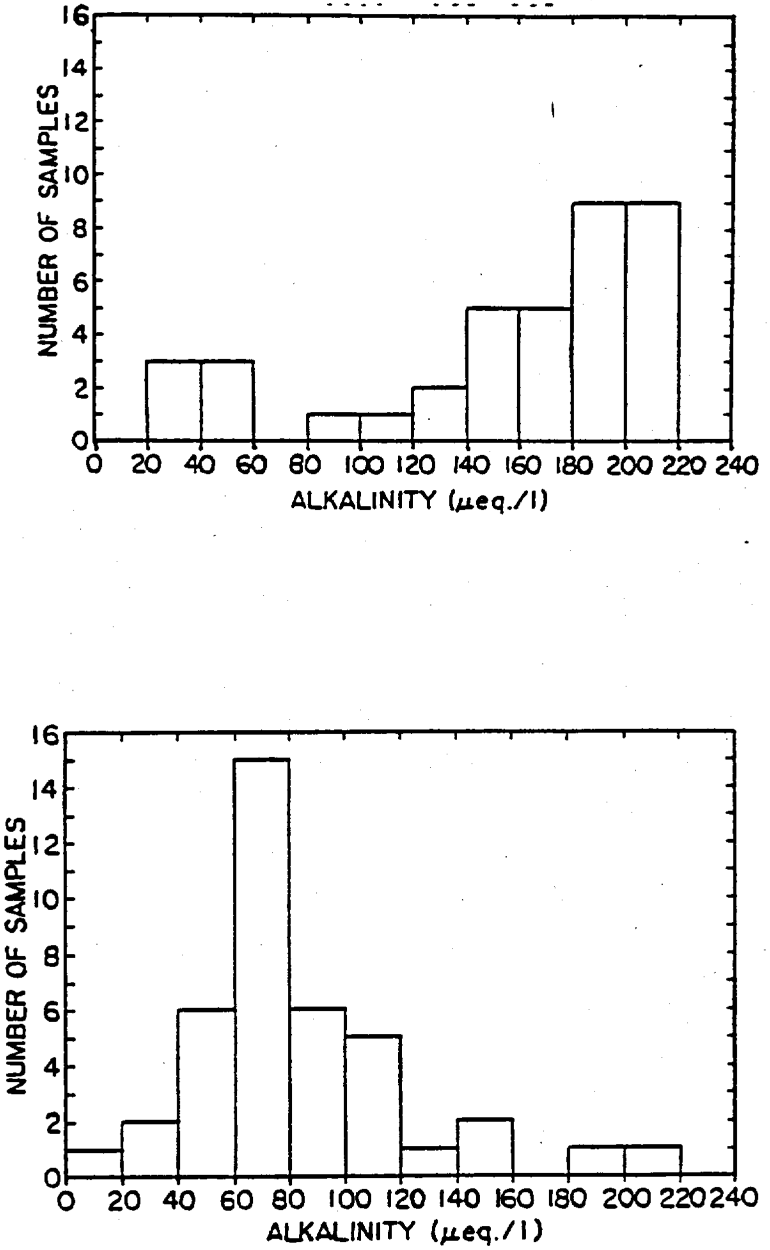


Figure 3-20 Distribution of alkalinity of North Carolina streams June, July, August 1960-1963 (upper), compared with June, July 1979 (modified from Hendrey et al. 1980).

3.6.9 Seasonal pH Depression in Northern Minnesota

The effects of acid deposition on the Boundary Waters Canoe Area Wilderness (BWCAW) of northern Minnesota were assessed during a synoptic study of lakes and streams, before and after the snow season, 1978-79. Studies of several lakes and streams, during the snowmelt period, revealed relatively large decreases in pH and alkalinity in the surface waters. pH depressions of as much as 1 unit were noted (Figure 3-21). Changes in water quality occurred, concurrent with the spring melt and the release of accumulated materials (SO_4^{2-}, NO_3^-, H^+). In addition, there were contributions of Ca^{2+} from watershed soils (Glass 1980).

3.6.10 pH Depression During Spring Runoff in Ontario

Detailed surface-water chemistry studies are being conducted in lakes near Dorset, Ontario, southwest of Algonquin Park. This area is within the Precambrian Shield. Jeffries et al. (1979) compared pH values of a series of small streams in the study area, before and during spring runoff (Table 3-15). The pH of the lake outflows demonstrates that the surface waters of the entire lakes were acidified during this period of time. The lowest pH values observed, 4.1 to 5.1, are within a range capable of causing damage to aquatic life, particularly fish. As much as 76.7 per cent of the measured yearly acid discharged from the streams in April. Figure 3-22 shows a typical hydrograph and pH response for one of the streams during the snowmelt period. Scheider et al. (1978) further showed that the pH of streams was depressed for periods of as little as a few hours during times of heavy runoff, during the summer months (Figure 3-23).

Heavy fall rains also cause depressed pH in runoff for days at a time. Scheider et al. (1978) observed as much as 25.8 per cent of the total annual hydrogen ion runoff, from small watersheds, in October. The biological implications of these periodic pH depressions are now being studied in detail.

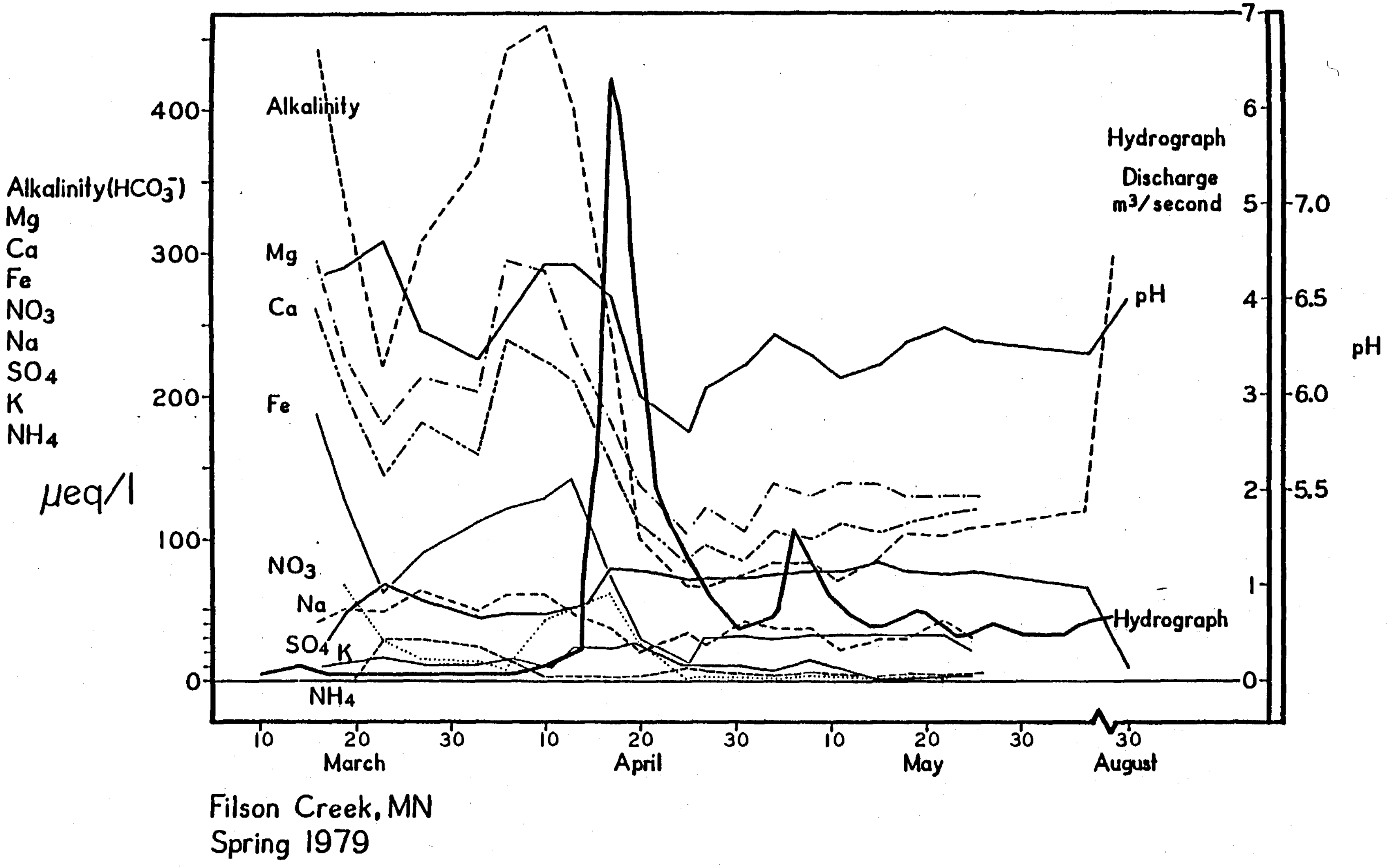


Figure 3-21 Snowmelt-runoff hydrograph and changing water quality for Filson Creek, Minnesota, Boundary Waters Canoe Area Wilderness region (Glass 1981).

TABLE 3-15

pH OF STREAMS IN MUSKOKA-HALIBURTON, ONTARIO, CANADA: STREAM pH IS GIVEN PRIOR TO SPRING RUNOFF (MID-MARCH 1978) AND AT MAXIMUM RUNOFF (MID-APRIL 1978)

		pH	
Watershed	Stream	Mid-March	Mid-April
Harp Lake	3	6.1	5.1
	3A	6.0	5.6
	5	5.9	4.8
	6	6.2	5.3
	6A	5.4	5.0
	Outflow	6.3	5.0
Dickie Lake	5	4.6	4.3
	6	4.6	4.4
	11	4.9	4.1
	Outflow	5.6	4.9
Chub Lake	1	5.8	5.1
	2	5.2	4.7
	Outflow	5.5	4.8
Red Chalk Lake	1	6.1	5.6
	2	4.5	4.3
	3	6.0	5.5
	4	6.2	5.5
	Outflow	6.1	5.9
Maple Lake	Maple Creek	6.2	5.8
Lake Simcoe	Black River (at Vankoughnet)	6.3	5.9
Lake of Bays	Oxtongue River	6.3	6.1

From: Jeffries et al. 1979.

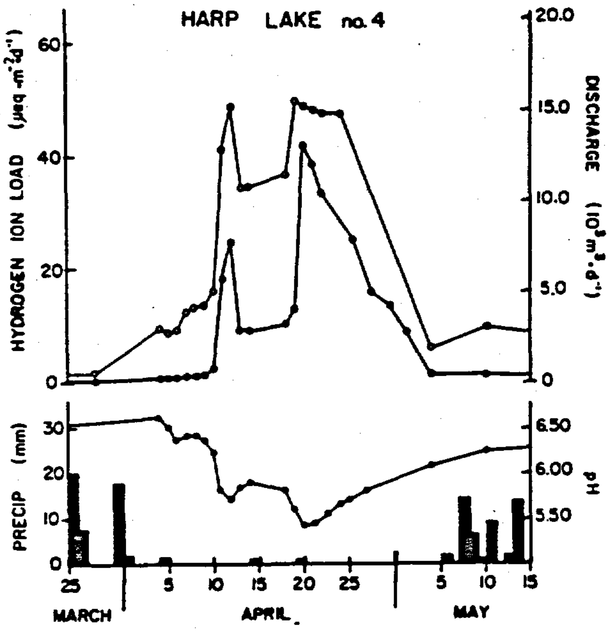


Figure 3-22 Discharge (upper line), hydrogen ion load per unit area (middle line), pH (lower line), and depth of precipitation for each day that a precipitation event occurred for Harp Lake no. 4. Daily H^+ load to the respective lakes can be calculated by multiplying by the watershed area: lake area (A_d/A_o); where A_d is the area of the subwatershed and A_o that of the lake; A_d/A_o is 1.85 for Harp Lake no. 4 (Jeffries et al. 1979).

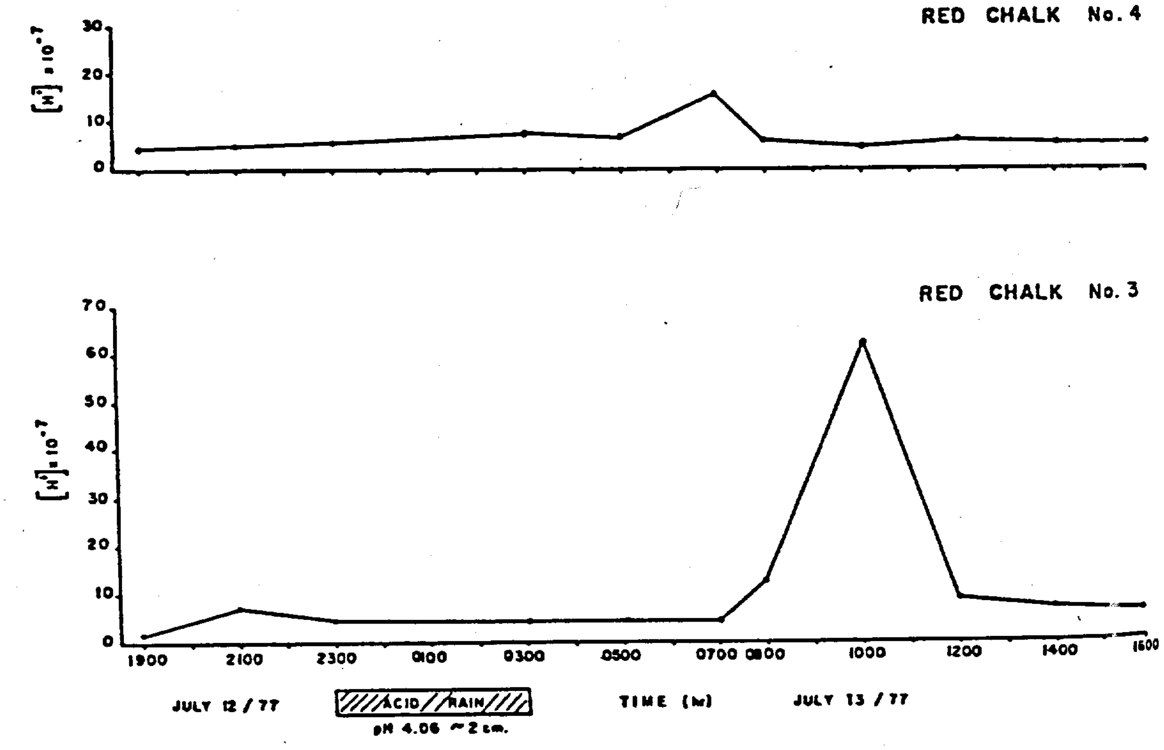


Figure 3-23 Hydrogen ion content of streams draining Red Chalk Lake watersheds No.3 and No.4 (Dorset, Ontario) showing effects of a 2 cm rainfall (pH 4.06) between 11:00 p.m. July 12, 1977 and 3:00 a.m. July 13, 1977 (Scheider et al. 1978).

3.6.11 pH During Flushing Events in West Virginia

Seasonally low pH, and a regular pattern of pH depression, have been documented for the Little Black Fork and Shavers Fork Rivers by the U.S. Forest Service in Monongahela National Forest (Dunshie 1979). The tributaries and the river are poorly buffered and subject to rapid changes in water quality, due to the influence of the poorly-buffered sandstone geology of the watershed. The lowest pH values in both streams (Little Black Fork is a control area, with no logging or coal mining) normally occur during the winter and early spring, apparently because of snowpack melting. The highest pH occurs during low stream flow periods in the summer and fall. Even though this is the period of highest deposition (see below), more extensive contact between soils and precipitation may lead to greater neutralization than during winter or spring.

Nearly 13 years of pH data have been collected at the Bowden Fish Hatchery river intake on the Shavers Fork River, showing a declining trend from a high in the summer to a low in the spring. This is important for aquatic organisms and has been measured in other lightly buffered streams. This pH trend occurs in streams and tributaries independent of watershed disturbance by mining.

The effect of rainfall on river pH is more apparent when individual events are examined. A graphic presentation, pairing daily river and precipitation events with pH during summer and winter periods, is shown in Figure 3-24. Daily precipitation accumulation and discharge are also shown. The data suggest that, during the growing season, a storm event, with a subsequent increase in discharge, lowers river pH below the natural non-storm daily variation. The magnitude of this downward shift is dependent upon rainfall characteristics (pH, amount, intensity, and area distribution) and antecedent soil moisture. Downward shifts in river pH, ranging from six to nine-tenths of a unit, occurred on July 11 and 26, and on August 15 and 25. On three of these days, at least 3.3 cm of rainfall fell within a 48-hour period; pH of the rainfall for these dates ranged from 3.7 to 4.2.

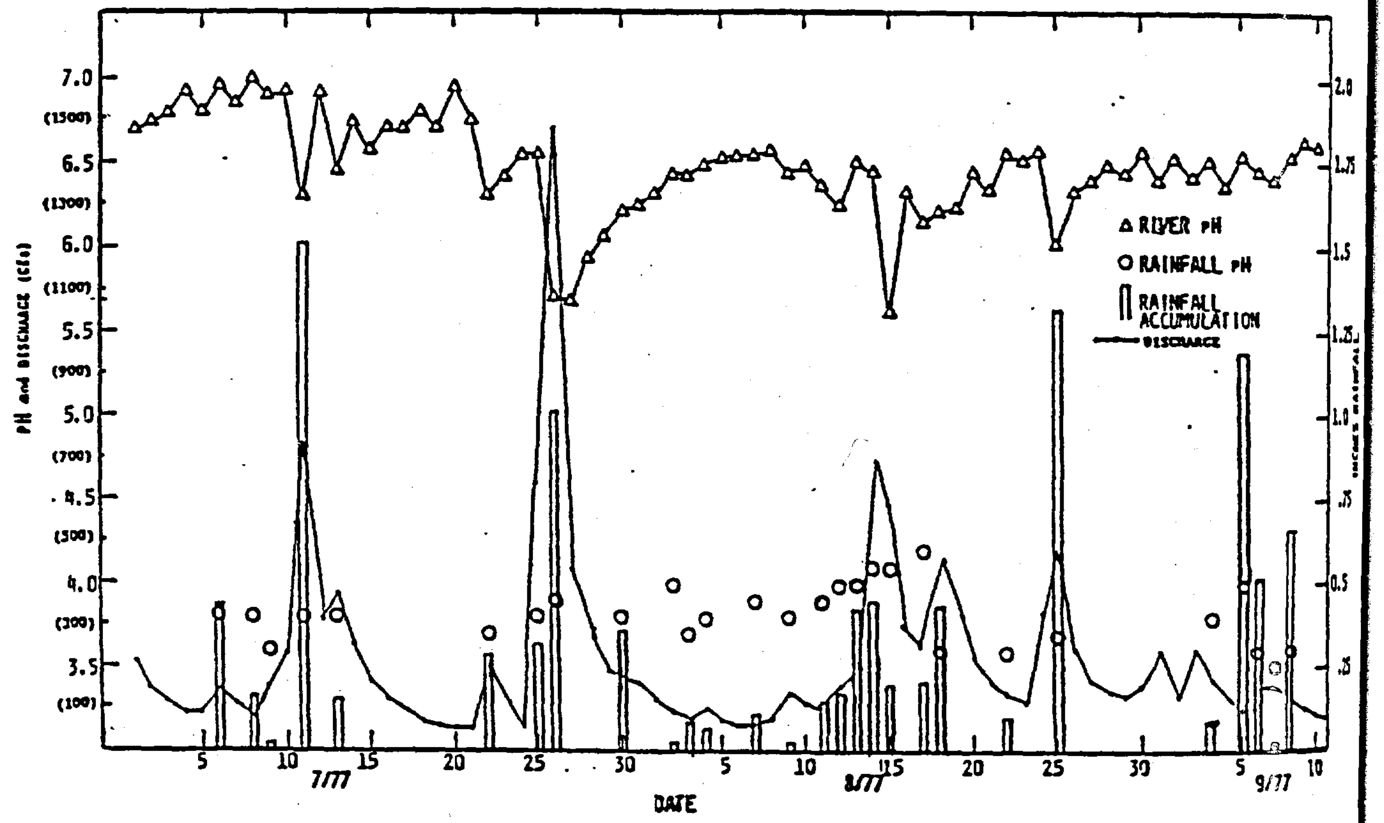


Figure 3-24 Mean daily pH for the Shavers Fork River at Bemis, West Virginia and precipitation event pH and accumulation at Arborvale, West Virginia (Dunshie 1979).

3.7 ALTERATION OF IMPACTED BIOTIC COMPONENTS

Many changes in biota have been linked to acidification. In some instances, a causal relationship with depressed pH has been established, but in the majority of cases, the observed changes in biota have simply been correlated with observed changes in pH and causality has not been established. For most biological communities, acidification has been accompanied by decreases in species richness and changes in species dominance. Acidification may be accompanied by species extinctions, or decreases in overall community standing stocks. Generalized summaries of aquatic organisms' response to low pH are given in Figures 3-25 and 3-26, and are presented here as a simplified overview of the complex interactions described below (Eilers and Berg 1981).

Definitive experiments are required to demonstrate whether such changes are directly attributable to increases in hydrogen ion concentration or whether they are attributable to secondary ecosystem interactions, such as elevation of trace metal levels or disruptions of normal food chains. In spite of incomplete understanding of the actual mechanisms underlying observed changes accompanying acidification, it is abundantly clear that acidification of surface waters destroys the health of aquatic ecosystems.

3.7.1 Effects on Algae

The free-floating (planktonic) and attached (benthic) algae are the major primary producers, in most aquatic ecosystems, and, directly or indirectly, provide most of the food for zooplankton and, ultimately, for fish.

Evidence gathered mainly from synoptic surveys in Scandinavia, Canada and the United States has demonstrated that the species diversity of benthic and planktonic algal communities is reduced in acidified lakes. Yan and Stokes (1976) observed only nine species of phytoplankton in a single sample from Lumsden Lake (pH 3.8), in the La Cloche Mountains in Ontario, but observed over 50 species in each of two nearby non-acidic lakes. Diversity indices for the La Cloche Mountain lakes decrease sharply as pH falls below 5.6 (Kwiatkowski and Roff 1976), while species numbers decrease most rapidly at a pH level of about 5.5 in Scandinavian lakes (Almer et al. 1978, Leivestad et al. 1976).

Some long-term functional adaptations to acidic environments may occur. Raddum et al. (1980) have suggested that such a mechanism explains the observation that a group of relatively recently acidified clearwater lakes in Norway have less diverse phytoplankton assemblages than naturally acidic, humic lakes. Additionally, the bioavailability and toxicity of trace metals may be lower in the

Fig. 3-25 Relative number of taxa of the major taxonomic groups as a function of pH

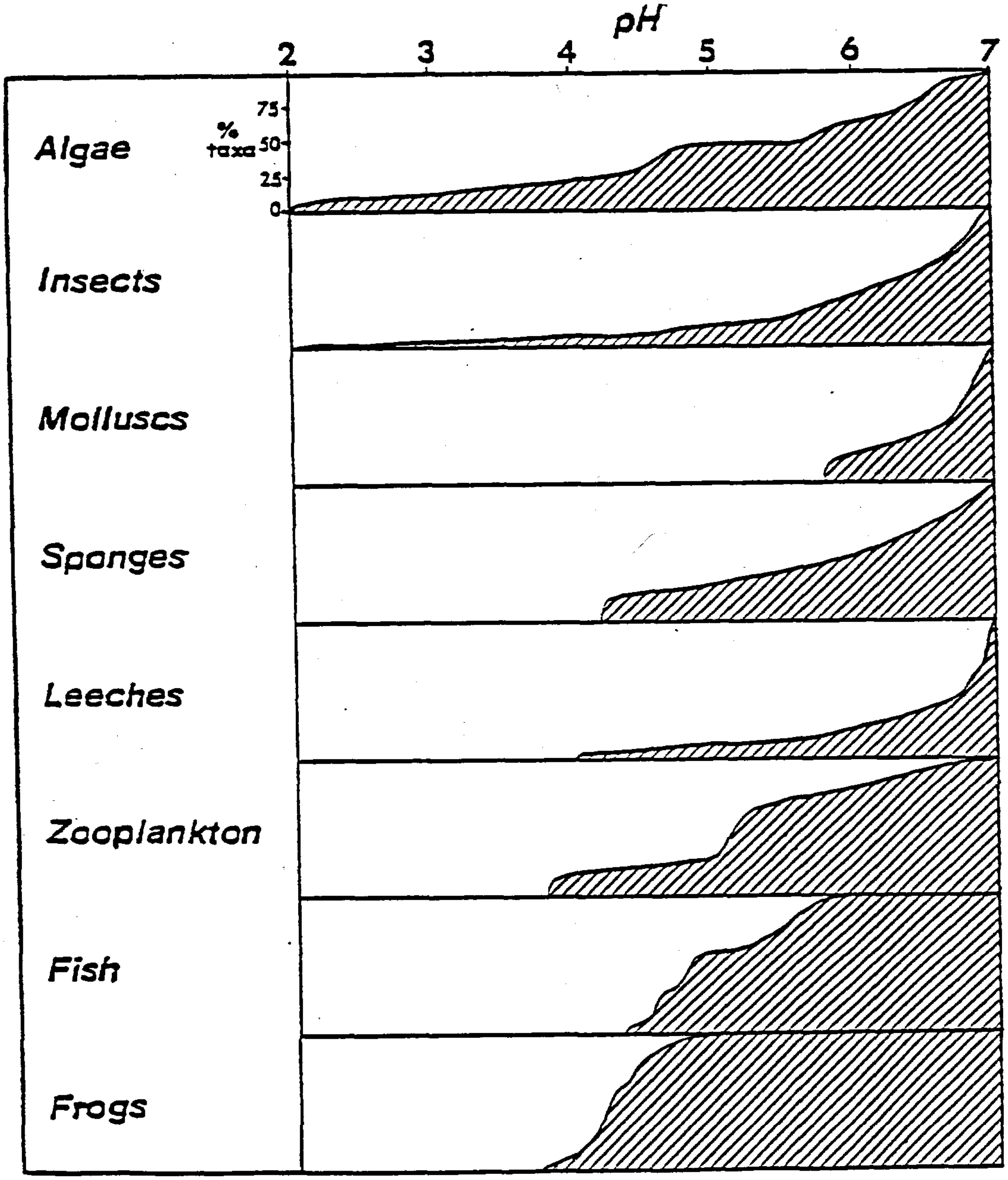
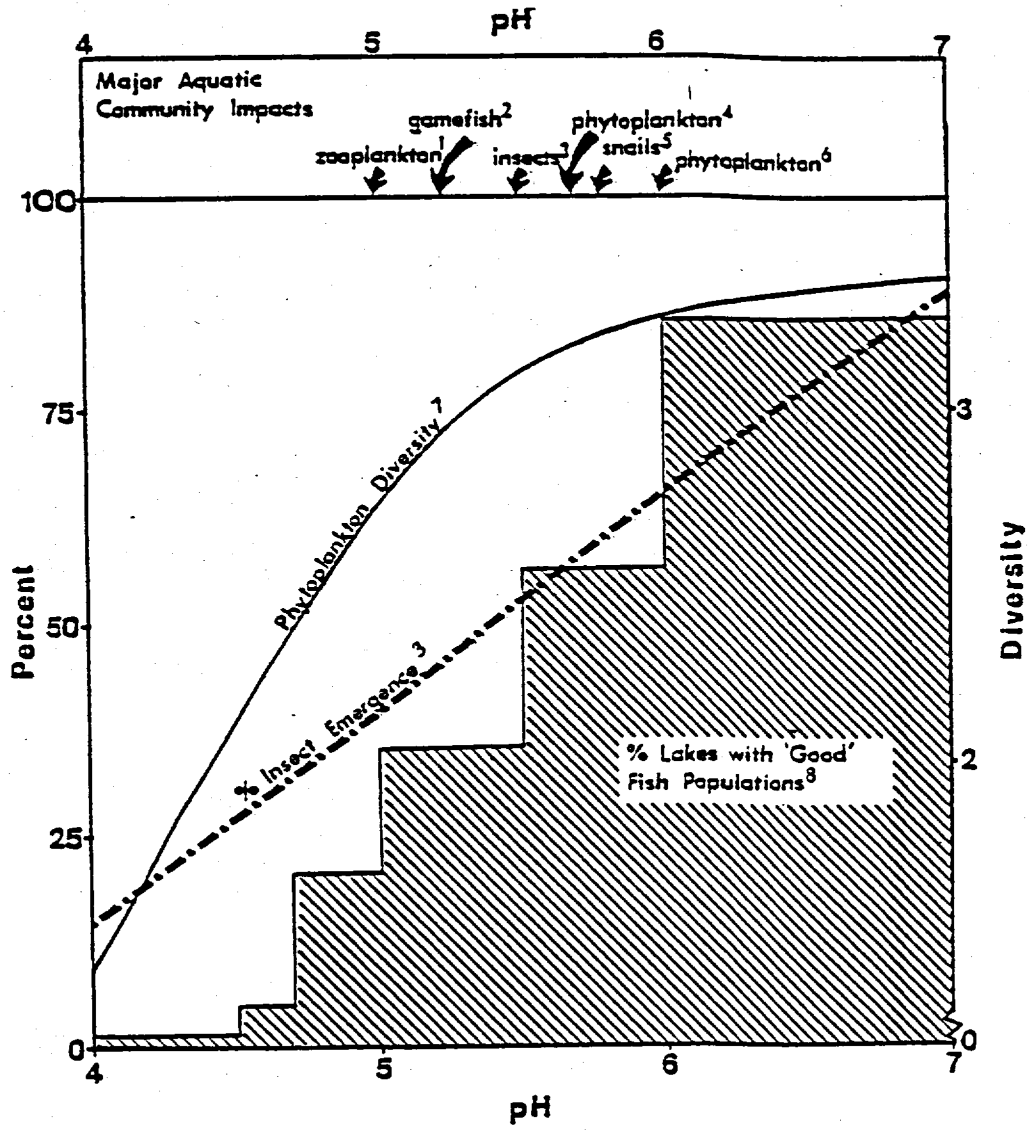


Fig 3-26 Generalized response of aquatic organisms to low pH



1	Sprules (1975) - Ontario	5	Okland (1969) - Scandinavia
2	Beamish (1976) - Ontario	6	Wright et al. (1976) - Norway
3	Bell (1971) - Laboratory TL_{50}	7	Kwiatkowski and Roff (1976) - Ontario
4	Yan and Stokes (1978) - Ontario	8	Snekvik (1974) - Norway

brownwater acidic lakes because of complexation of metals with humic materials.

Although species diversity of phytoplankton generally decreases with increasing acidity, biomass (Yan 1979) and productivity (Almer et al. 1978, Schindler 1980) are probably not reduced by acidification. Phosphorus, the nutrient that normally limits high phytoplankton productivity in soft-water lakes, may, however, be immobilized in acidic lakes because of interaction with aluminum and humic material (Almer et al. 1978).

Phytoplankton communities of non-acidic oligotrophic lakes in eastern Canada are typically dominated by chrysophytes (Schindler and Holmgren 1971), or by diatoms (Duthie and Ostrofsky 1974). In contrast, strongly acidic lakes are generally dominated by dinoflagellates. In Sweden, the Pyrrhophyta, especially the dinoflagellates, formed 85 per cent of the biomass in lakes of pH 4.6-5.5 (Dickson et al. 1975). Of 14 lakes in central Ontario, dinoflagellates formed between 30 and 70 per cent of the phytoplankton biomass in four acidic lakes (pH 4.2-4.8), but only 2-30 per cent of the biomass in ten lakes with pH levels of 5.8-6.8 (Yan 1979).

In certain poorly buffered lakes, some of the phytoplankton species may interfere with recreational use of the lakes. In five lakes in Ontario and New Hampshire with pH 5.5 to 6.2, for example, obnoxious odours developed during the summers of 1978, 1979, and 1980. The odours have been shown to be caused by the growth of the planktonic *Chrysochromulina breviturrita*. This species was first discovered in 1976, but it is now known to inhabit more than 40 lakes in Ontario, most of which are acidic (Nicholls et al. 1981). The "invasion", and associated odour production, by this organism is apparently a recent phenomenon. Although the relationship between lake acidification and the proliferation of this species has not been proven, data collected thus far show that the growth of this species, and the serious odour production, is restricted to acidic lakes.

Acidified lakes are characterized by increased growth of filamentous algae in the benthic algal communities and decreases in the importance of diatoms. In Sweden and in Ontario (Stokes 1981, Schindler 1980), unusually dense and extensive mats of algae, (mainly *Mougeotia* and *Zygonema*) proliferate in the littoral zone, either associated with macrophytes (Grahn et al. 1974, Hultberg and Grahn 1975, Hendrey et al. 1976) or on other surfaces. The accumulations of algae may reduce light availability to macrophytes, change microclimates for benthic macroinvertebrates, and reduce fish spawning and feeding habitats.

3.7.2 Effects on Aquatic Macrophytes

Information on the effects of acidification on the macrophyte communities of soft-water lakes is still incomplete. Scandinavian investigators have suggested that when lake pH is depressed, typical macrophyte dominants are replaced by very dense beds of Sphagnum (Grahn et al. 1974, Hultberg and Grahn 1975, Hendrey et al. 1976). The loss of some macrophyte species and the correlative increase in Sphagnum abundance may be indirectly related to depressed pH, through changes in inorganic carbon availability (Steemann-Nielsen 1944, 1946, Raven 1970).

Additionally, Sphagnum moss coverage of littoral zones creates a unique habitat, which is considered unsuitable for some species of benthic invertebrates, or for use as fish spawning and nursery ground (Hultberg and Grahn 1975). It may reduce the appeal of freshwater systems for certain recreational activities. In Scandinavia, the decline of macrophyte species and the concurrent Sphagnum invasion begins as pH falls to about 6.0, and proceeds rapidly when pH falls below 5.0. In Lake Colden in New York (pH 4.9), Sphagnum is abundant (Hendrey and Vertucci 1980), and in Beaverskin Lake in Kejimkujik National Park in Nova Scotia, a clear lake of pH 5.3, Kerekes (1981) has reported extensive Sphagnum growth. In Ontario lakes, some species of Sphagnum have been identified (Harvey et al. 1981), but accumulations as dense as those recorded in Scandinavia have not been observed. Through the release of hydrogen ions and polyuronic acids into their environment Sphagnum sp. certainly could acidify their immediate surroundings should they accumulate (Clymo 1963, Crum 1976).

3.7.3 Effects on Zooplankton

Four major groups of animals contribute to zooplankton communities: protozoans, rotifers, crustaceans and insects. They provide food for many species of fish, particularly for younger individuals, and thus are an essential component of the aquatic food chain, transferring energy and materials from the primary producers (algae) to consumers, including fish and man. Acidification apparently results in reduced zooplankton biomasses, as both the numbers and average size of community members are reduced (Yan and Strus 1981). Food availability to high trophic levels will, in consequence, be reduced.

Acidification of lakes is accompanied by changes in the occurrence, abundance and seasonal succession of species, and in the diversity of crustacean (and other) zooplankton components. It is often assumed that the direct cause of these changes is differences in tolerance among zooplankton species to increased H^+ concentration However, acidification also increases the transparency, thus affecting the light regime, of lakes; increases the concentration of chemical substances, including potential toxicants; and produces quantitative and qualitative changes in zooplankton predator and prey species (Harvey et al. 1981). Hence, the immediate causes for the changes in zooplankton communities that do occur, while linked to acidification, may be quite complex.

The most important components of zooplankton communities are usually the rotifers and crustaceans. Of these, the crustaceans usually form 90 per cent of the biomass (Pederson et al. 1976), while rotifers, because they have shorter generation times, may be responsible for 50 per cent of the zooplankton productivity (Makarawicz and Likens 1979). Studies from very acidic lakes such as acid-mine drainage lakes (Smith and Frey 1971), or the Smoking Hills Lakes of the Northwest Territories (Havas 1980), indicate that some species of rotifers can survive when all crustacean zooplankton have been eliminated by acidification (Smith and Frey 1971). Thus, rotifers may become more important contributors to the zooplankton community as lakes acidify. Available studies on the effects of acidification on rotifer populations are contradictory: both decreases (Roff and Kwiatkowski 1977) and increases (Yan and Miller 1981, Malley et al. 1981) in standing stocks have been observed in acidic lakes.

The diversity of zooplankton communities is usually drastically reduced by acidification (Sprules 1975b, Raddum et al. 1980). Whereas non-acidic lakes typically contain approximately ten species of planktonic crustacea in mid-summer collections, Sprules (1975b) observed that species richness of acidic lakes in the La Cloche Mountains in Ontario was drastically reduced. In several cases only a single species, Diaptomus minutus, remained.

Some predacious zooplankton, especially cyclopoid copepods (Raddum et al. 1980) and Epischura lacustris (Malley et al. 1981), are very sensitive to acidification and are often absent from acidic lakes. Densities of other predators, such as some species of Chaoborus (Eriksson et al. 1980) and Heterocope saliens (Raddum et al. 1980), apparently increase. The significance of these changes in predator populations to zooplankton community structure is not yet understood although it may be important (Eriksson et al. 1980).

3.7.4 Effects on Aquatic Macroinvertebrates

Numerous aquatic macroinvertebrates are known to be affected by the acidification of water. While in some cases, an entire phylum appears to be affected, in other situations, susceptibility is species-specific. Evidence indicates that molluscs, in general, are highly susceptible to pH change (Raddum 1980, Okland 1980, Wiederholm and Eriksson 1977), often being restricted to habitats with pH greater than 5.8 to 6.0. Similarly, oligochaetes have been found at lower densities in acid waters (Wiederholm and Eriksson 1977).

Sensitivity to low pH has been inferred from field investigations for certain Arachnida, Crustacea and Insecta. Arachnids were only briefly mentioned by Grahn and his co-workers (1974): acarina were absent in waters with pH values below 4.6. No crustaceans were found below pH 4.6 (Grahn et al. 1974). Gammarus lacustris was absent from waters with pH below 6.0 (Okland 1969), while the crayfish, Astacus astacus was rare in lakes where the summer pH value was less than 6.0 (Svardson 1974). Orders of Insecta exhibit a wide range of sensitivities to pH. While the number of species of Ephemeroptera and Plecoptera appears to be positively correlated with pH, larvae of Chironimidae, Hemiptera and Megaloptera are often abundant in acid lakes (Almer et al. 1978). Hutchinson et al. (1978) reported an extreme example of tolerance. They observed the larvae of red chironomids, Chironomus riparius, in waters of pH 2.2 in the Northwest Territories.

Although the field studies mentioned above provide evidence of the effects of acidification on certain species, in only two studies has the pH of a natural system been altered, and the impacts on invertebrates noted. The documented effects of decreased pH include, the disappearance of Mysis relicta in Lake 233, an experimentally acidified lake in the Experimental Lakes Area (Malley et al. 1981), elimination or reduction of Ephemeroptera populations in a stream in the Hubbard Brook Experimental Forest in New Hampshire (Fiance 1978, Hall et al. 1980), and decreased emergence of some species of Plecoptera, Trichoptera and Diptera in the same stream (Hall et al. 1980). Those species with acid-sensitive life stages (such as emergence in insects) which can coincide with snowmelt, or other events, such as flushing, may be especially sensitive to acid precipitation.

It is important to note, in considering the distribution of the above species in relation to waters of varying pH, that no causative relationship between hydrogen ion concentration and the observed changes has been determined as yet. Other factors vary with pH, including concentrations and availability of nutrients, bicarbonate, and various metals. From the results available, however, it appears that molluscs (perhaps because of their requirement for calcium) and moulting crustaceans (perhaps because of their large demand for calcium at the time of moult) are the macroinvertebrates most sensitive to low pH levels. It is still unclear why certain groups of aquatic insects are more sensitive than others.

3.7.5 Effects on Microorganisms

The decomposition of fixed carbon, both allochthonous and autochthonous organic matter, is, in large part, determined by microbial processes in the water column and in the surface layers of sediment. Several studies have demonstrated that rates of decomposition of organic matter are decreased in acidified waters. In a laboratory study, for example, Bick and Drews (1973) demonstrated that as pH was lowered, the number of bacteria and protozoans decreased, populations of fungi increased, and the rates of decomposition and nitrification were reduced. Traaen and Laake (1980) measured decomposition rates of homogenized birch litter and glucose/glutamate mixtures. When the pH was decreased from 7.0 to 3.5, litter decomposition dropped to 30 per cent of control levels, and a shift from bacterial to fungal dominance was observed. Traaen (1980) further observed that rates of weight loss of birch leaves and aspen sticks after one year in the laboratory or one to two years in field situations, were significantly lower at pH levels less than 5.0.

Reductions in numbers of heterotrophic bacteria have been observed previously in aquatic habitats acidified by acid mine drainage (Tuttle et al. 1968, 1969, Thompson and Wilson 1975, Guthrie et al. 1978). Caution must be exercised, however, in extrapolating results from acid mine drainage studies to situations where the source of protons is atmospheric. The pH is often much lower in acid mine drainage lakes, and the concentration of dissolved substances much higher than in atmospherically acidified lakes.

Jurkkovic and Robson (1981) are studying the effects on ammonifiers, denitrifiers, fungi and heterotrophic bacteria of a Sudbury area lake of reductions in pH to 4.1 in the laboratory. He observed no change in heterotroph levels, but noted a doubling in numbers of fungi, a twofold decrease in nitrogen cycle bacteria and a significant change in respiration rate. Densities of nitrogen cycle bacteria were also reduced in the lake.

Microbial transformations of sulphur and nitrogen species may influence lake alkalinity (Brewer and Goldman 1976). Schindler (1980) recently suggested that increases in $SO4^{2-}$ concentrations will stimulate sulphate-reducing bacteria in lakes that develop anoxic hypolimnia. The reduction of $SO4^{2-}$ generates base, i.e., it increases alkalinity. Stimulation of $SO4^{2-}$ reduction has been used with success to renovate acid mine drainage waters. However, sulphate-reducing bacteria require anoxic conditions, and are stimulated by large quantities of organic matter, i.e., they prefer conditions typical of eutrophic lakes. The hypolimnia of most acid susceptible lakes do not normally become anoxic, and could only be made anoxic by fertilization. Eutrophication is not a satisfactory trade-off for reducing acidity.

3.7.6 Effects on Amphibians

Because of the vulnerability of their habitat to pH depressions, amphibian populations will be one of the earliest forms of wildlife to be affected by the acidification of fresh waters. Many species of frogs, toads, and salamanders breed in temporary pools. The pH of these pools may be very low during the spring as they are formed by a mixture of snowmelt water and spring rains. Temporary pools used as breeding sites by Jefferson's (Ambystoma jeffersonianum) and yellow-spotted salamanders (A. maculatum) in New York were found to have hydrogen ion concentrations 1.5 pH units lower than nearby permanent ponds (Pough and Wilson 1977). Pough (1976) noted heavy embryonic mortalities and deformities in the yellow-spotted salamanders which breed in temporary meltwater ponds with pH less than 6.0. In central Ontario, Clark and Euler (1980) reported that the numbers of egg masses of yellow-spotted salamanders and male calling densities (an estimate of population size) of spring peepers (Hyla crucifer) were positively correlated with pH. This latter species often breeds in stream inflows and outflows or along the littoral zone of lakes, habitats also subjected to particularly heavy acid loads as a result of snow melt (Clark and Euler 1980). Strijbosch (1979) reported a negative correlation between pH and percentages of dead and moulded egg masses of frogs and toads in the Netherlands. The amphibian species of eastern Canada considered most susceptible to the effects of acid precipitation because of their breeding habitat are listed in Table 3-16.

The detrimental effects of acidity on adult amphibians have been shown in a number of field surveys. In England, Cooke and Frazer (1976) reported that no adult newts were caught from ponds of pH less than 3.8, while the natterjack toad (Bufo calamita) was not found below pH 5 (Beebee and Griffin, 1977) in England. The common toad (Bufo bufo) did not occur where pH was less than 4.2, and the smooth newt (Triturus vulgaris) occurred only rarely at pH values less than 6.0. Hagstrom (1977) observed that the common toad and common frog (Rana temporaria) disappeared when pH levels reached 4.0-4.5. In New Hampshire, when a section of Hubbard Brook was artificially acidified to mean pH 4.0, salamanders disappeared from the study area (Hall and Likens 1980).

Laboratory experiments have demonstrated that reductions in pH are both directly and indirectly responsible for mortalities and deformities found during amphibian embryonic development. Gosner and Black (1957) studied the sensitivity of 11 species of frogs and toads to conditions of depressed pH. They found that the embryos were more sensitive than larvae or adults. In the case of the cricket frog (Acris gryllus) and northern spring peeper, an exposure of embryos to water in the vicinity of pH 4.0 for a few hours resulted in greater than 85 per cent mortality. Beebee and Griffin

TABLE 3-16

SUSCEPTIBILITY OF BREEDING HABITAT TO pH DEPRESSION DUE TO ACID PRECIPITATION, FOR THOSE AMPHIBIANS IN CANADA WHOSE RANGE OVERLAPS THE IMPACTED AREA

Potential for acidification of egg-laying habitat	Habitat	Species
high	meltwater pools	*Ambystoma maculatum* - Yellow-spotted salamander
		Ambystoma laterale - Blue-spotted salamander
		Ambystoma tremblayi - Tremblays salamander
		Bufo americanus - American toad
		Pseudacris triseriata - Chorus frog
		Rana sylvatica - Wood frog
		Rana pipiens - Northern leopard frog
		Hyla crucifer - Northern spring peeper
		Hyla versicolor - Gray tree frog
moderate	permanent ponds	*Necturus maculosus* - Mudpuppy
		Notophthalmus viridescens - Red-spotted newt
		Bufo americanus - American toad
		Hyla versicolor - Gray tree frog
		Pseudacris triseriata - Chorus frog
		Rana catesbeiana - Bullfrog
		Rana clamitans - Green frog
		Rana pipiens - Northern leopard frog
		Rana septentrionalis - Mink frog
	streams	*Eurycea bislineata* - Northern two-lined salamander
		Necturus maculosus - Mudpuppy
	lakes	*Rana catesbeiana* - Bullfrog
low	bogs	*Hemidactylium scutatum* - Four-toed salamander
	logs and stumps	*Plethedon cinereus* - Red-backed salamander

From: Clark and Fischer 1981.

(1977) noted abnormalities in natterjack toad spawn exposed to low pH, and Noble (1979) observed delayed development and embryonic mortality at pH less than 4.75 in the leopard frog (Rana pipiens). In salamanders, the highest mortality of developing embryos occurs during neurulation, the late stages of gill development, and during hatching (Pough 1976; Pough and Wilson 1977).

Interspecific differences in embryonic tolerance to hydrogen ion concentration have been observed for the yellow-spotted salamander and Jefferson's salamander. Cook (1978) found no significant correlation between pond pH and percent embryonic mortality in either species, in six ponds with mean pH 5.6-5.3, whereas Pough (1976) found heavy embryonic mortalities and deformities in waters of pH less than 6.0. Egg transplant studies suggest that yellow-spotted salamander eggs from acidic ponds are more tolerant to acidity than eggs from neutral ponds (Nielsen et al. 1977). Anurans also exhibit variation in sensitivity. While Hagstrom reported the elimination of the common toad at pH 4.5-4.0, Cooke (cited in Beebee and Griffin 1977) found this species in waters of pH 4.2 and noted that tadpoles were able to tolerate this hydrogen ion level.

It is likely that other factors influenced by the acidity of the water may be causing detrimental effects upon amphibian development. Huckabee et al. (1975) suggest that the combined effects of low pH and increased concentrations of aluminum, manganese and zinc may be the cause of the high mortality of shovel-nosed salamander (Leurognathus marmoratus) larvae in Great Smoky Mountain National Park.

Because frogs, toads, and salamanders are important components of both aquatic and terrestrial ecosystems, reductions in the biomass of amphibians may have far reaching effects in both systems. Both salamanders and anurans are important contributors to the food web (DeBenedictis 1974, Burton and Likens 1975a, Cecil and Just 1979), and many birds and mammals depend heavily on these species for food. Orser and Shure (1972) reported that amphibians are among the top carnivores in temporary ponds and small streams, and are important predators of aquatic insects. In turn, they serve as a high protein food source for other wildlife (Burton and Likens 1975b).

Given the sensitivity of amphibians to depressed pH, it is inevitable that those species inhabiting temporary pools in acid-sensitive regions will suffer severe decreases in density, and may become locally extinct in parts of the Precambrian Shield. The ranges of some species of amphibians in eastern North America are restricted almost entirely to areas presently receiving high levels of acid precipitation (Table 3-16). However, elimination of these species may allow other species to expand, due to decreased competition.

3.7.7 Effects of Low pH on Fish

The purpose of this section is to review briefly how fish respond to increasingly acidic environments. For more comprehensive treatments of this subject, the reader is referred to reviews by Fromm (1980) and, especially, Spry et al. (1981). There is extensive literature available on laboratory studies (see Doudoroff and Katz 1950, and EIFAC 1969), designed to elucidate mechanisms of pH toxicity. These laboratory results are reviewed, as they are useful in explaining field observations and suggesting new directions for field studies.

Results from laboratory experiments demonstrate how overall water quality, (i.e., hardness, ionic strength) can affect pH toxicity. For example, as ionic strength and water hardness increase, the short-term sensitivity of fish to waters of pH 4 is decreased (reviewed in Spry et al. 1981). The ameliorative effects of high Ca^{2+} and ionic strength appear most beneficial to early larval stages at intermediate pH (≈5). This is consistent with field observations that, in more dilute water, fish communities disappear at higher pH (Leivestad and Muniz 1976) due to recruitment failure (Harvey 1979). In addition to hardness and ionic strength, survival of fish in water of low pH is influenced by the type of acid present (Packer and Dunson 1972 Swartz et al. 1978), temperature (Kwain 1975, Robinson et al. 1976), the level of dissolved carbon dioxide in the water (Neville 1979), and by the presence of metals (Swartz et al. 1978, Baker and Schofield 1980).

Field evidence suggests that the susceptibility to low pH appears to be species specific. From his studies of La Cloche Mountain lakes, Beamish (1976) estimated the pH at which reproduction ceased in 11 species (Table 3-17). Some species of fish have been reported to have a seasonal response to low pH (Lloyd and Jordan 1964, Falk and Dunson 1977). As well as interspecific differences in sensitivity, variability in the sensitivity of different strains of the same species has also been observed (Robinson et al. 1976, Swartz et al. 1978). However, it is probable that the acidification of lakes and rivers in North America is proceeding too rapidly to enable genetic selection for acid tolerant strains to occur naturally, on a wide scale (Schofield 1976).

Results of laboratory studies have demonstrated that some species of fish are particularly sensitive to low pH in certain reproductive stages (reviewed by Spry et al. 1981). Low pH can inhibit gonadal development (Ruby et al. 1977, 1978), reduce egg production (Mount 1973, Craig and Baksi 1977), affect egg and sperm viability (Menendez 1976, EIFAC 1969) and inhibit the spawning act (Menendez 1976, Craig and Baksi 1977). Embryonic development may be affected by low pH (Trojnar, 1977 Swartz et al. 1978) and low environmental pH can affect egg internal pH (Daye and Garside 1980a). Generally, fry appear less resistant to low pH than eggs (Spry et al. 1981).

TABLE 3-17

APPROXIMATE pH AT WHICH FISH IN THE LACLOCHE MOUNTAIN LAKES STOPPED REPRODUCTION

pH	Species	Family
6.0 to 5.5	Smallmouth bass *Micropterus dolomieui*	Centrarchidae
	Walleye *Stizostedion vitreum*	Percidae
	Burbot *Lota lota*	Gadidae
5.5 to 5.2	Lake Trout *Salvelinus namaycush*	Salmonidae
	Troutperch *Percopsis omiscomaycus*	Percopsidae
5.2 to 4.7	Brown bullhead *Ictalurus nebulosus*	Ictaluridae
	White sucker *Catostomus commersoni*	Catostomidae
	Rock bass *Ambloplites rupestris*	Centrarchidae
4.7 to 4.5	Lake herring *Coregonus artedii*	Salmonidae
	Yellow perch *Perca flavescens*	Percidae
	Lake chub *Couesius plumbeus*	Cyprinidae

From: Beamish 1976.

Consequently fry may be particularly vulnerable to low pH conditions associated with spring melt and storm events.

In the field, there have been several reports of fish kills apparently related to the acidification of rivers and lakes. In Scandinavia, for example, Jensen and Snekvik (1972) reported mass mortality of Atlantic salmon (*Salmo salar*), and Leivestad and Muniz (1976) reported a brown trout (*Salmo trutta*) kill. Both fish kills have been correlated with reduced water pH.

In North America, Harvey (1979) reported a kill of several species, primarily pumpkinseeds (*Lepomis gibbosus*) in Plastic Lake, Ontario, during spring snow melt. Surface water pH was 5.5, while the pH of the major inlet stream was 3.8. During the spring of 1981, some *in situ* bioassays were conducted in Plastic Lake (Harvey 1981). Rainbow trout, *Salmo gairdneri*, were placed in cages at four locations in Plastic Lake and at four locations in the control, Beech Lake. At each location, three non-metal cages of 35 fish were situated. No mortality occurred at any of the cage sites in the control (pH 6.09-7.34, alkalinity 132-390 μeq/l). In Plastic Lake, however, mortality ranged from 12 per cent at the lake outlet (pH 5.0-5.85) to 100 per cent at the inlet (pH 4.03-4.09). Although aluminum concentrations were not measured at the time of the 1979 fish kill and aluminum data for 1981 is not yet available, total aluminum concentrations in Plastic Lake during the 1979 and 1980 ice-free season varied between 9 and 30 μg/l in the lake, and between 240 and 490 μg/l in the major inlet.

One mechanism which appears to contribute to species extinction in acidified systems is the failure of recruitment of year-classes. In a study of 38 La Cloche Mountain lakes, Ryan and Harvey (1980) reported evidence of recruitment failure in the yellow perch (*Perca flavescens*) populations of the two lakes of lowest pH, Patten Lake (pH 4.1) and Terry Lake (pH 4.3). The age group composition of yellow perch in Patten Lake is illustrated in Figure 3-27. Ryan and Harvey (1980) also found evidence of reduced and missing year classes of young fish in five populations of rock bass (*Ambloplites rupestris*) in acid-stressed La Cloche lakes. The absence of older fish in populations in acid-stressed lakes has also been reported (Beamish et al. 1975, Ryan and Harvey 1980, Harvey 1980). This effect is illustrated by the changes in age composition of white suckers in George Lake, Ontario (Figure 3-28), in the time period from 1967 to 1979. Rosseland et al. (1980) also reported the absence of post-spawning-age perch and brown trout in three lakes within the Tovdal River System, Norway. The predominance of young fish occurred after a fish kill in 1975.

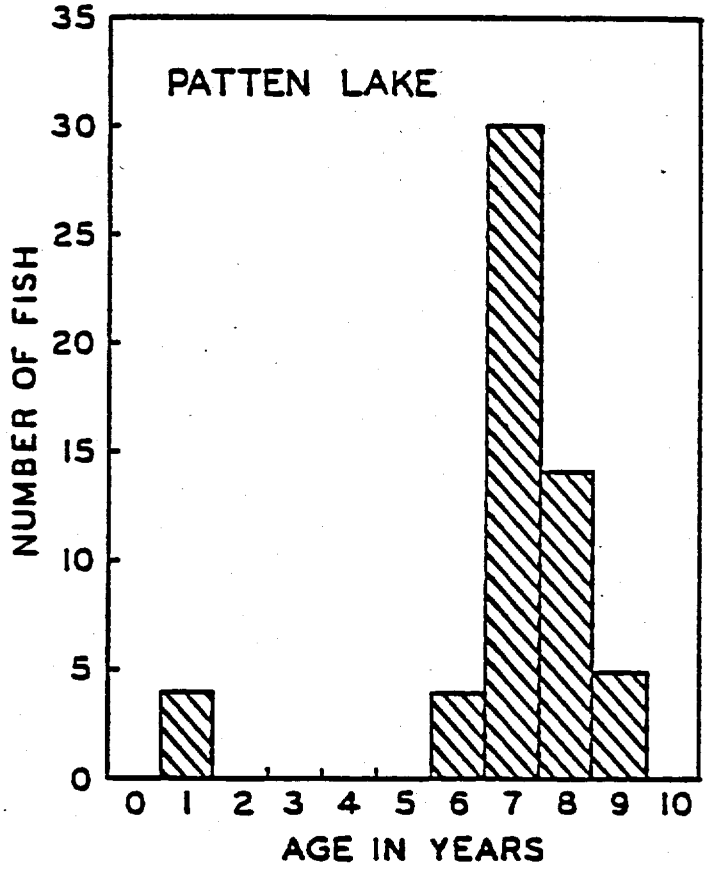


Figure 3-27 Age composition of yellow perch (<u>Perca flaviscens</u>) captured in Patten Lake, Ontario, pH 4.1 (Ryan and Harvey 1980).

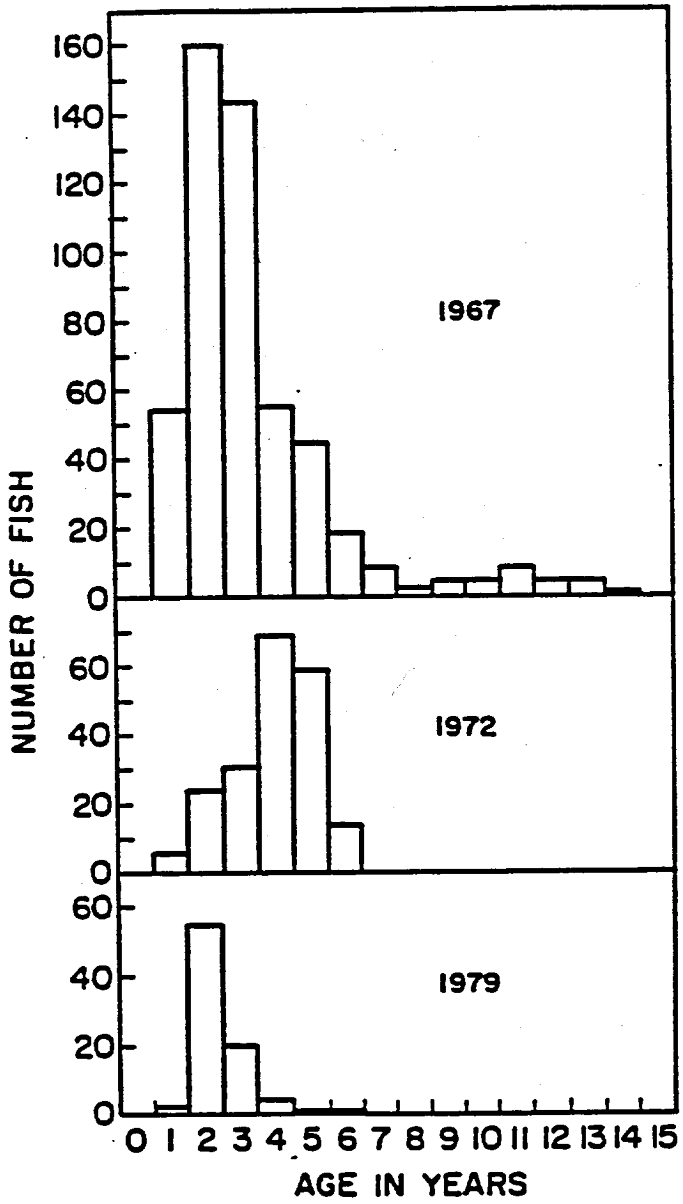


Figure 3-28 Changes in the age composition of the white sucker, *Catostomus commersoni*, in George Lake, Ontario.

3.7.8 Studies of Aluminum Effects on Fish

Concentrations of metals can be elevated in acid-stressed lakes (Beamish 1974a, Scheider et al. 1979b) because of increased atmospheric deposition, increased mobilization from the sediments and/or mobilization from the watershed. Probably the most important consequence of acidification is the mobilization of aluminum from the watershed to the aquatic environment (Scheider et al. 1979b, Cronan and Schofield 1979). Elevated levels of aluminum in waters affected by acidification have serious effects on fish within the pH range normally considered harmful to aquatic biota (Baker and Schofield 1980).

The chemistry of aqueous solutions of aluminum is complex. A simplified description of the relevant chemistry is contained in Spry et al. (1981). The solubility of aluminum is minimal at pH 5.5, increasing as pH increases or decreases. At pH greater than 5.5, soluble aluminum is mostly anionic; at pH less than 5.5 it exists increasingly as a cation. The solubility of aluminum is apparently regulated by some form of aluminum trihydroxide solid, $Al(OH)_2(S)$, which is minimally soluble at pH 5.6-6.0 (Driscoll 1980). Fewer hydroxyl ligands at lower pH allow the aluminum to become cationic, eventually becoming Al^{3+} at pH less than 5. Cationic aluminum is able to form complexes with a number of ligands, including soluble organics and fluoride, which can decrease its toxicity (Figure 3-29) (Baker and Schofield 1980, Driscoll et al. 1980).

Laboratory studies on the survival of brook trout (Salvelinus fontinalis) have shown reduction to less than 40 per cent after 14 days (Figure 3-29) at aluminum concentrations of 420 and 480 μg/l and pH levels of 5.2 and 4.4, respectively (Driscoll et al. 1980). Baker and Schofield (1980) found that the sensitivity of brook trout to elevated aluminum increased with age. They also found that the presence of aluminum actually mitigated the toxic effects of low pH to fish eggs. The survival of brook trout and white sucker embryos through the eyed stage at pH levels below 5 was significantly better in treatments with aluminum than without. After hatching, brook trout fry were more susceptible to aluminum at the extremes of the pH range tested (4.2 to 5.5) than at intermediate pH levels (Figure 3-30). The greater susceptibility of fry at these extreme pH's is due to a dual mechanism of aluminum toxicity. At low pH, aluminum (probably Al^{3+}) appears to cause osmoregulatory stress and loss of salts from blood plasma. At the higher pH, precipitation of $Al(OH)_3(s)$ damages the gills and leads to clogging by mucous (J.P. Baker, personal communication). Baker and Schofield (1980) also found that, at all stages, white suckers were substantially more sensitive to low pH levels and elevated aluminum concentrations than brook trout.

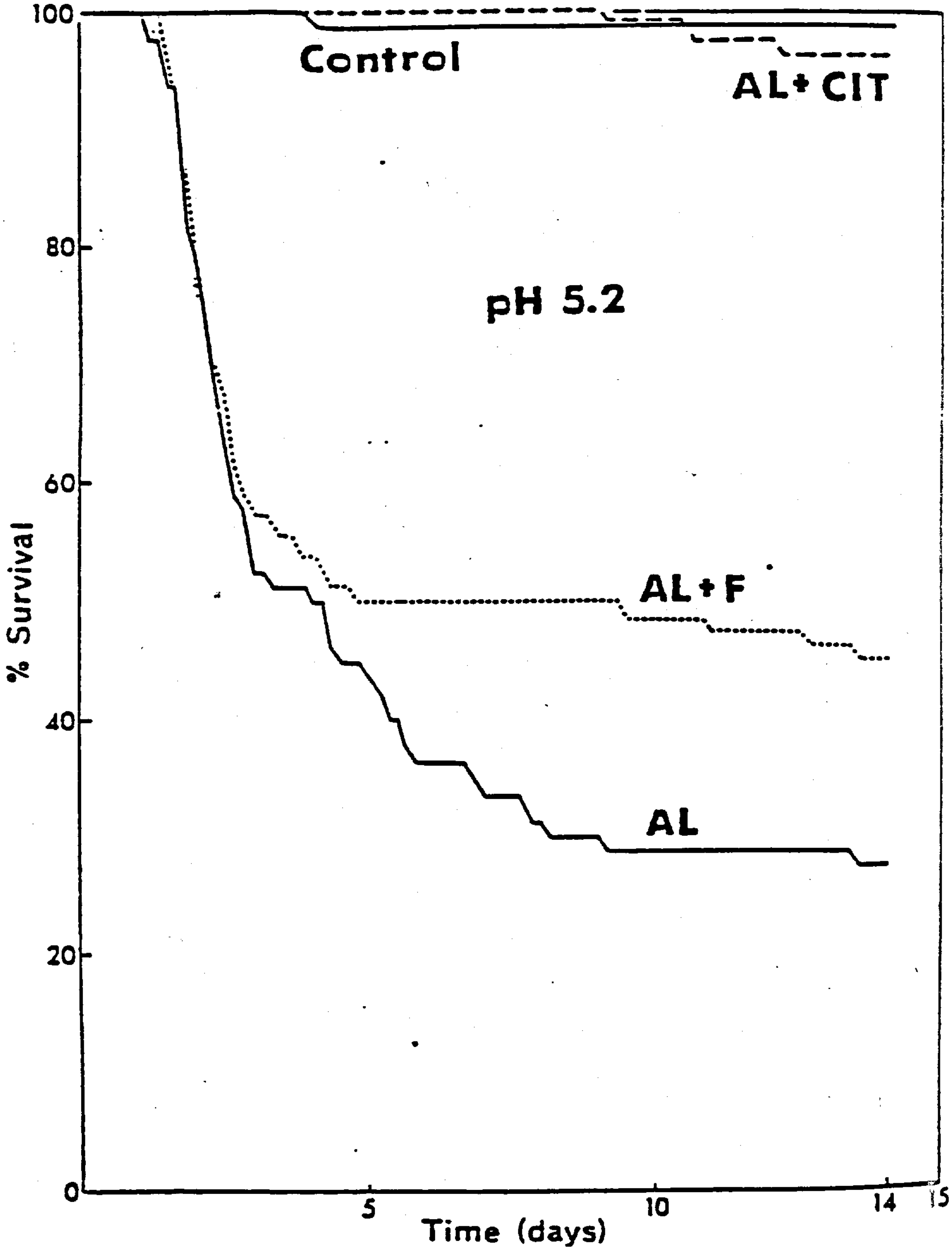


Figure 3-29 Percent survival of brook trout fry plotted as a function of time in treatment waters at pH level 5.2 with no aluminum (control) or with 0.5 mg Al added per liter with no additional complexing agents (Al) or with 0.5 mg fluoride/liter (Al + F) or with 30 mg citrate/liter (Al + CIT) (Baker and Schofield 1980).

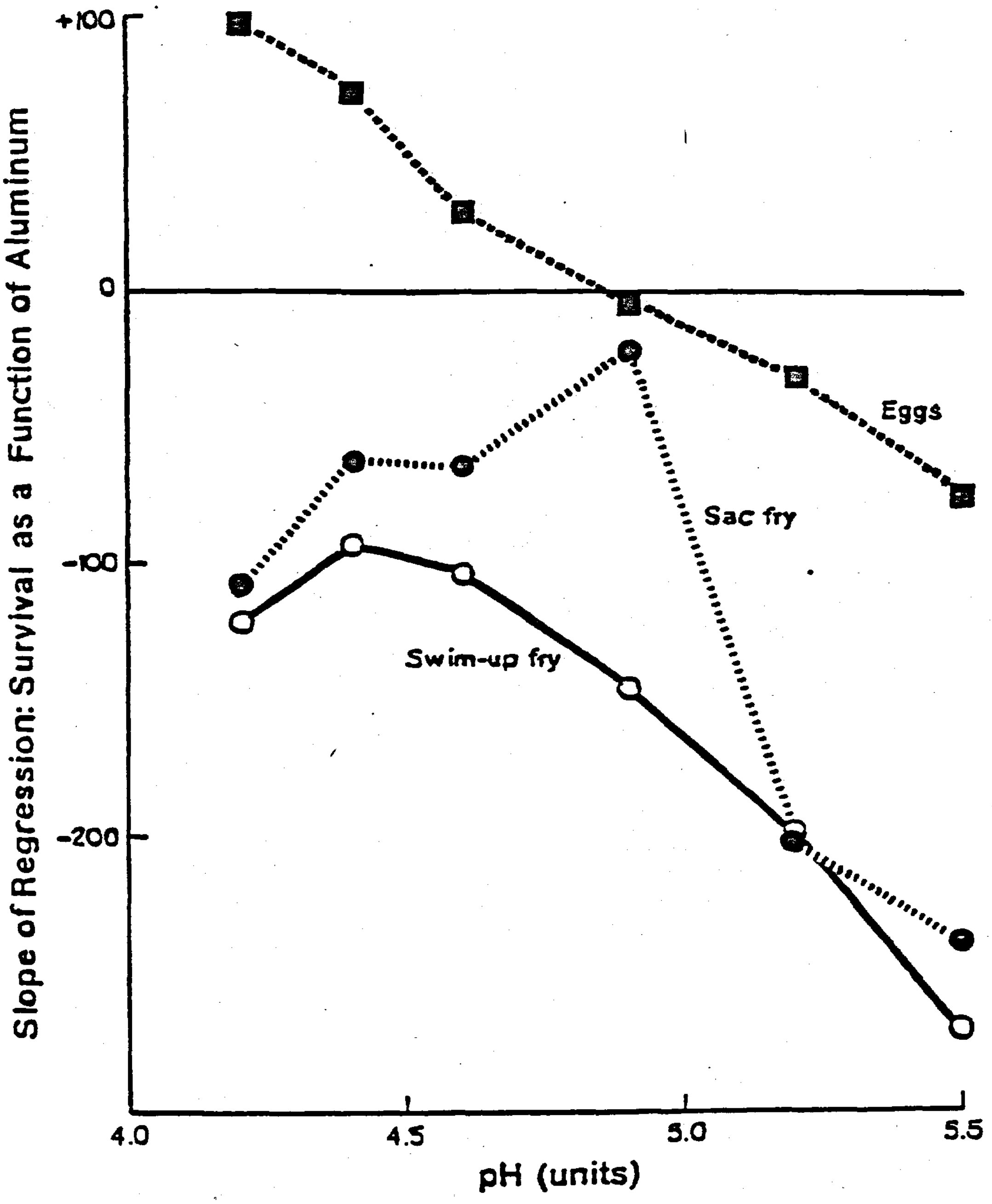


Figure 3-30 Slope of the regression line of brook trout survival (arcsin transformation) as a function of total aluminum concentration at each pH level, plotted as a function of pH level. A positive slope indicates presence of aluminum improved survival: a negative slope, detrimental effects of aluminum (Baker and Schofield 1980).

Schofield and Trojnar (1980) indicated that levels of aluminum, rather than pH alone, may be the primary factor limiting survival of brook trout stocked in acidified Adirondack lakes. Muniz and Leivestad (1980) and Schofield and Trojnar (1980) suggest that mass mortalities of fish, observed during transient episodes of acidification in the spring, are most likely a result of elevated concentrations of inorganic aluminum, mobilized from the soils by strong acids present in snowmelt water. The former study demonstrated that pH depression alone (to levels of pH 4.7-5.0) did not induce physiological stress in fish, as determined from changes in plasma chloride levels. However, associated increases in aluminum levels to 0.2 mg/l or more, were found to be sufficient to induce severe stress and eventual mortality.

Aluminum levels in streams in the Great Smoky Mountains National Park, U.S.A. (Herrmann and Baron 1980), and in the Muskoka-Haliburton area of Ontario (total aluminum levels from 1976 to mid 1978 ranged between 5 and 1000 μg/l in 60 streams), do fall within the ranges demonstrated to be lethal to fish in laboratory conditions.

However, as the laboratory studies demonstrate, the evaluation of aluminum as a toxic element in acidified waters is not a simple function of total concentration. In evaluating the survival of indigenous fish populations, one must consider the form of aluminum, the level of hydrogen ion, the fish species present and their life history stage.

3.7.9 Impacts on Fisheries in Canada and the United States

Adirondacks

The Adirondack region is one of the largest sensitive lake districts in the eastern United States, and it is also the most heavily impacted by acid precipitation. A recent inventory of Adirondack waters, classified by type of fishery supported, indicates that the brook trout fishery has been most severely affected by acidification (Pfeiffer and Festa 1980). These authors have shown that at least 180 former Adirondack brook trout ponds will no longer support populations because of acidification. Currently, 212 Adirondack lakes have a pH <5.0, and an additional 256 lakes have a pH between 5.0 and 6.0. A survey of 214 high elevation lakes in 1975 by Schofield (1976) revealed that 52 per cent had surface pH levels below 5.0, and 90 per cent of these acidified lakes were devoid of fish life (Table 3-18). These lakes are very sensitive to acidification. Comparable data collected for 40 of these lakes, from the period 1929 to 1937, indicated that only four per cent were below 5.0 and devoid of fish (Figure 3-31). Entire fish communities, consisting of brook trout, lake trout, white sucker, brown bullhead and several cyprinid species, were eliminated over the forty year

TABLE 3-18
DISTRIBUTION AND FREQUENCY OF OCCURRENCE OF FISH SPECIES COLLECTED DURING SURVEYS OF ADIRONDACKS LAKES >610 METERS ELEVATION
NUMBERS IN ( ) REFER TO EXTINCT POPULATIONS

pH	<4.5	4.5-4.99	5.0-5.49	5.5-5.99	6.0-6.49	6.5-6.99	>7.0	TOTAL
Total lakes	16	95	36	15	28	22	3	215
% of total	7.1	44.2	16.7	7.0	13.0	10.2	1.4	
No fish	16	74	2	1	0	0	0	93
%	17.2	79.6	2.1	1.1				
Fish	0	20	25	11	22	19	3	100
%		20.0	25.0	11.0	22.0	19.0	3.0	
Brook trout	0	16(26)	18(1)	11	17	17	3	82
%		19.5	21.9	13.4	20.7	20.7	3.7	
f	.80	.72	1.00	.77	.89	1.00		
Lake trout	0	0(5)	1(2)	4	2	4	2	13
%			7.7	30.8	15.4	30.8	15.4	
f			0.4	.36	.09	.21	.67	
Bullhead	0	8(8)	11(1)	5	14	9	3	50
%		16.0	22.0	10.0	28.0	18.0	6.0	
f		.40	.44	.45	.64	.47	1.00	
White sucker	0	3(1)	7(1)	8	7	8	3	36
%		8.3	19.4	22.2	19.4	22.2	8.3	
f	.15	.28	.73	.32	.42	1.00		
Creek chub	0	0(7)	5	7	5(1)	8	2	27
%			18.5	25.9	18.5	29.6	7.4	
f			.20	.64	.23	.42	.67	
Golden shiner	0	3(4)	3	1	8	3	2	20
%	15.0	15.0	5.0	40.0	15.0	10.0		
f	.15	.12	.09	.36	.16	.67		
Common shiner	0	9(2)	0(1)	3(1)	1	3	3	11
%		9.1	0	27.3	9.1	27.3	27.3	
f		.05		.27	.05	.16	1.00	
Lake chub	0	1(1)	0	2	0	1	3	7
%		14.3		28.6		14.3	42.9	
f		.05		.18		.05	1.00	
Redbreast sunfish	0	0	0	0	0	3	0	3
%						100.0		
f						.16		
Common sunfish	0	0(1)	0	1	1	2	2	6
%				16.7	16.7	66.7	66.7	
f				.09	.05	.11	.67	

From: Schofield 1976 .

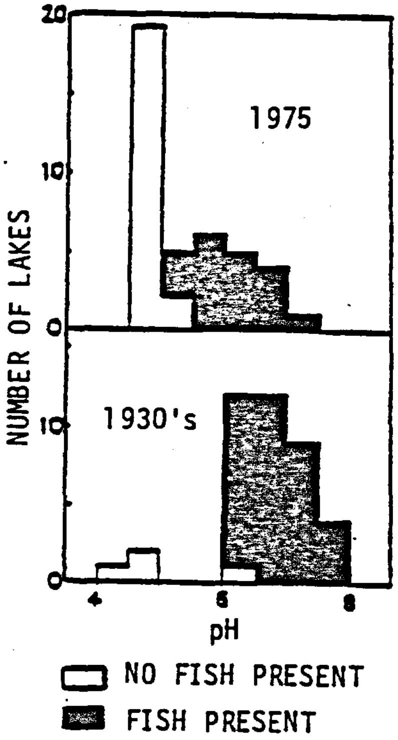


Figure 3-31 Frequency distribution of pH and fish population status for 40 high elevation lakes surveyed in the 1930s and again in 1975 (Schofield 1976).

period, in association with decreased pH. The number of fish species represented in these high elevation lakes was also observed to decline markedly below pH 5.5.

Ontario

More data on inland fisheries resource impacts from lake acidification are available from Ontario than from any other province in Canada. The case study of lakes in the La Cloche Mountain range by Beamish and Harvey (1972) is best known. These lakes have a naturally low buffering capacity and are only 65 km southwest of the Sudbury area smelters.

Some of the lakes appeared already to have lost fish populations at the time of the first survey, 1965-66; others had populations that were endangered, and still others were apparently in a healthy condition (Beamish 1976). The fish community of Lumsden Lake (one of 68 examined) has been studied for 14 years. The following chronology of fisheries losses has been assembled by Harvey (1980) from his studies with Beamish (Beamish and Harvey 1972), from Provincial Government capture records dating to the early 1960's, and from observations by local anglers and residents for some species prior to 1960:

1950's - 8 species present

1960 - last reported capture, yellow perch, *Perca flavescens* and burbot, *Lota lota*

1960-65 - sport fishery fails (pH 6.8, Sept. 1961)

1967 - last capture of lake trout, *Salvelinus namaycush* and slimy sculpin, *Cottus cognatus*

1968 - tagged population of white sucker, *Catostomus commersoni* disappears

1969 - last capture of trout perch, *Percopis omiscomaycus* and lake herring, *Coregonus artedii*

1971 - last capture of lake chub, *Couesius plumbeus* (pH 4.4, Aug. 1971)

In their study, Beamish and Harvey (1972) also reported the absence of fish in lakes near Lumsden Lake, Lumsden III, Lumsden II and O.S.A. They interpreted these observations as evidence that the factor(s) affecting the fishes of Lumsden Lake were probably widespread. They also noted that both sport and nonsport fishes had disappeared from the lakes, suggesting that exploitation was not responsible.

The loss of populations of lake trout, lake herring, white suckers and other species was attributed to increasing levels of acidity.

Historical data available for Lumsden Lake indicated that in one decade, 1961 through 1971, the lake pH had decreased from 6.8 to 4.4. pH measurements from 1961 or earlier were available for eleven other La Cloche Mountain Lakes. 1971 measurements for these lakes indicated that hydrogen ion levels had increased ten to one hundred fold in the decade.

Beamish (1974a) also examined the fish populations in O.S.A. and Muriel Lakes. He found virtually that all the fish in O.S.A. Lake had been lost and that while a variety of species were present in Muriel Lake, only the yellow perch population appeared unstressed.

A case history of another La Cloche Mountain lake, George Lake, was compiled by Beamish et al. (1975) for the years 1966 through 1973. They estimated that the pH of George Lake decreased at an annual rate of 0.13 pH units. Coincident with the reduction in lake pH, populations of lake trout, walleye, burbot and smallmouth bass were lost. In 1973, most brown bullheads, rock bass, pumpkinseeds and northern pike did not spawn.

Beamish (1976) described the acidification of waters in the La Cloche Mountains and the concomittant loss of fish populations. He also examined other possible explanations for the response of fishes in these lakes. He concluded that acidity appeared to be the principal agent stressing the fish populations, as well as controlling the concentrations of metals.

The age distribution of a population of white suckers in Crosson Lake (Muskoka-Haliburton area of Ontario) was examined by Harvey (1980). The population in Crosson Lake (pH 5.1) showed a truncated age composition (Figure 3-32) compared with the populations in less acidic Red Chalk (pH 6.3) and Harp lakes (pH 6.3). A similar loss of older fish from the white sucker population in George Lake (Harvey 1980) has been discussed previously as a symptom of acid stress.

Quebec

Quebec has large numbers of lakes which are potentially sensitive to acid inputs, but comprehensive fisheries data that might substantiate this view are unavailable at this time. Recently, Charette and Lagacé (1981) have shown that angling success in the Laurentide Park, north of Quebec City, has decreased approximately 30 per cent between 1970 and 1978. The reduction is not attributed to overfishing, as the mean weight of the catch has remained constant. The analyses on the 63 lakes for which there is pH and angling data showed that watersheds having the lowest mean lake alkalinity contained a higher frequency of lakes having abnormally low angling success.

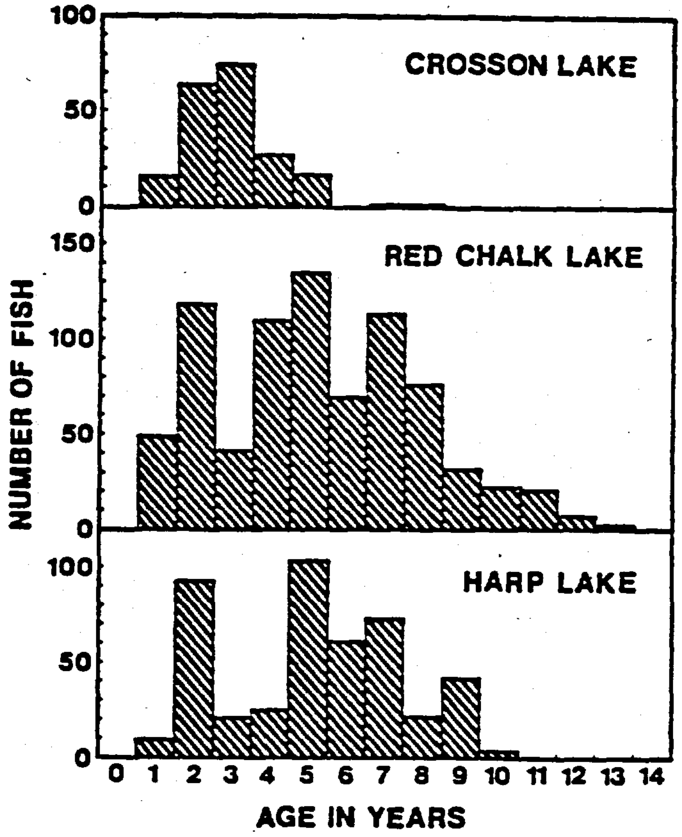


Figure 3-32 Age Composition of the White Sucker Population of three lakes in the Muskoka-Haliburton Region of Ontario (Harvey 1980).

Nova Scotia

There are thirty-seven rivers flowing through Nova Scotia for which there are records to verify that they are (or once were) Atlantic salmon rivers. For twenty-seven of these rivers, almost complete angling catch records are available (annual reports from Federal Fishery Officers) from 1936. Of these twenty-seven rivers, five have undergone major salmon stock alterations since 1936 by dam construction/removal, and/or extensive hatchery stocking. To examine the impact of acidification on angling success, the twenty-two remaining rivers were divided into two groups, based on 1980 pH levels: ten of the rivers are presently at pH <5.0 and 12 are at pH >5.0.

For the twelve rivers presently at pH >5.0, one shows a statistically significant decline in angling success since 1936, another shows a significant increase, and ten show no significant trend. Of the ten rivers with pH's <5.0, nine show significant declines, and one shows no significant trend.

To combine the data so as to form averages for the two groups, the records were first normalized by expressing each river's angling catch as a percentage of the average catch during the first five years of record (1936-40). These percentages were then summed and averaged for each of the two pH groups. The results (Figure 3-33) reveal virtually identical angling catches in the two groups until the early 1950s; after which the angling catches in rivers of pH <5 declined, while the catch in rivers of pH >5 continued to show no significant trend. Many factors other than pH (e.g. stream flows and sea survivals) also affect the angling record, but the variation from these other factors affects both groups identically. The only difference is that the angling success in rivers of pH <5 has declined since 1950 while in rivers of pH >5, it has, on average, remained the same.

There are historical water chemistry data for some of these affected rivers (Thomas 1960) from surveys performed in 1954 and 1955. In the past 25 years, the pH of the Tusket River has decreased from an annual range of 4.9-6.1 to 4.6-4.9; the Roseway from a range of 4.4-6.4 to 4.3-4.5; the Jordan River from about 5.1 to a range of 4.4-4.6; the Medway River from a range of 5.5-6.5 to 5.1-5.8; and the Clyde River has decreased from 5.0 to 4.6. Alkalinity was not detectable in the Tusket, Clyde, Roseway and Jordan rivers in 1979-80, but was measurable during Thomas' study 25 years earlier. Although Thomas (1960) sampled some of these rivers only once, his water quality data suggest that salmon reproduction in a few rivers may have been adversely affected due to acidity by the early 1950's. Even to the casual observer, some of the affected streams are strikingly different in appearance from streams with mean annual pH's above 5.0. When they were recently surveyed, in the latter part of the summer, affected stream bottoms were covered with dense

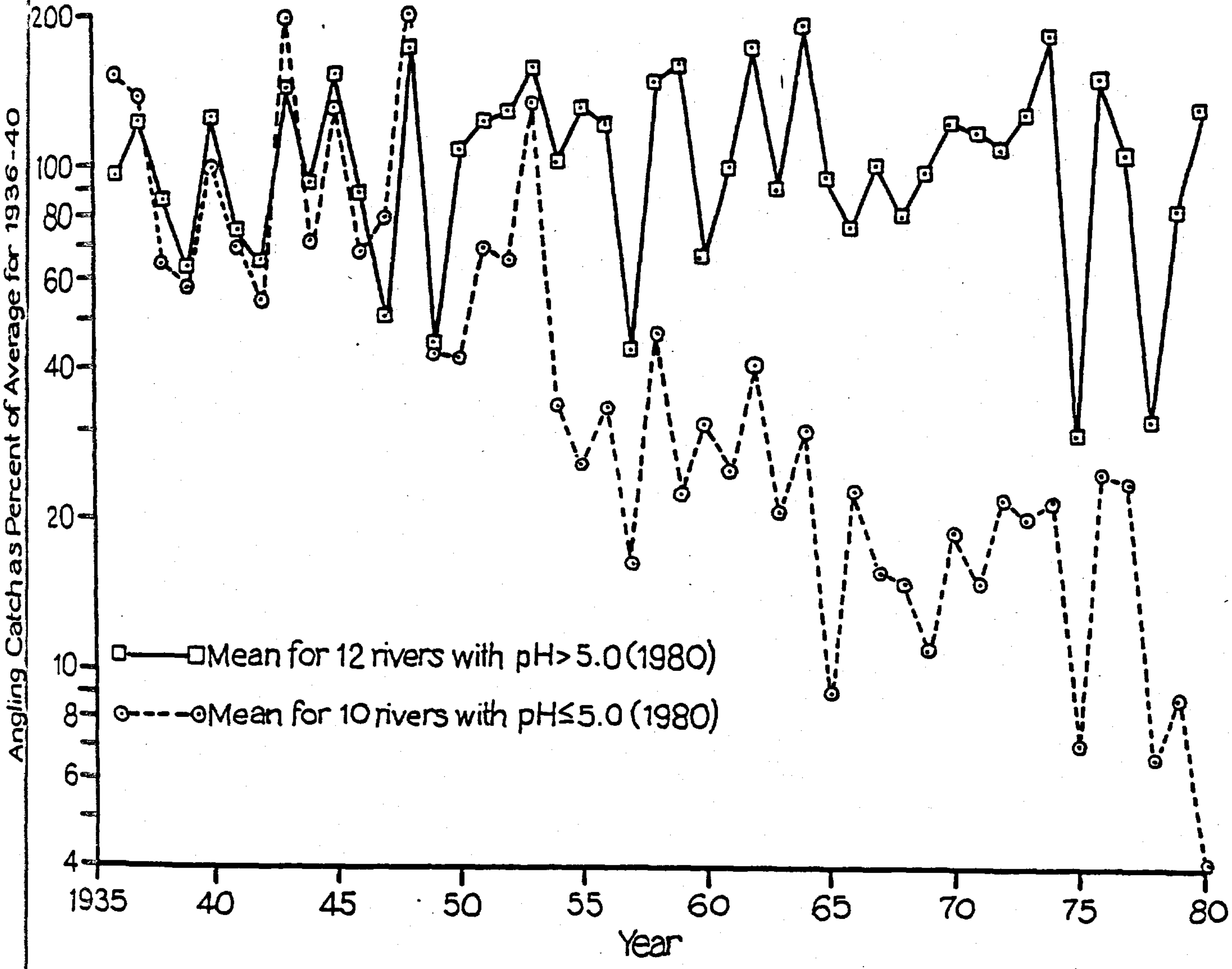


Figure 3-33 Average angling success for Atlantic Salmon in 22 Nova Scotia rivers since 1936. The data were collected from reports of federal fishery offices (from W. Watt, unpublished manuscript 1981).

mats of filamentous algae, and Sphagnum had invaded the stream channel in some areas (R.H. Peterson, personal communication).

Within Nova Scotia, the distribution of acid water is well correlated with geology (Watt 1981). Seasonal variation in the pH of acidified rivers is about 0.5 unit, with the annual minimum occurring in mid-winter, and a maximum in late summer. Historical data indicate that the local rate of acidification has been of the order of 0.3-0.4 pH units in 20 years. At present there are nine rivers with pH <4.7 which previously had salmon but now have no salmon or trout reproduction; eleven rivers are in the pH range 4.7-5.0, where some juvenile salmon mortality is probably occurring; and seven rivers are in the pH range 5.1-5.3, which is considered borderline for Atlantic salmon (Figure 3-34). The acidification threat to these twenty-seven rivers represents only 2 per cent of the total Canadian habitat potential for Atlantic salmon, but in Nova Scotia it represents 30 per cent of the available salmon potential.

One of the Nova Scotia rivers "threatened" by increased inputs of acidic precipitation, the Mersey, contains an Atlantic salmon hatchery. The Mersey watershed has poorly developed soils, and its underlying geology is Devonian granite. The mean total alkalinity of samples collected from the river in 1978-79 was always less than 0.5 mg/l, while mean pH was 5.2 with a range of 4.9-5.4. In 1954-56 the river had a mean pH of 5.8, with a range of 5.4-6.6, and a mean total alkalinity of 2.4, with a range from 1.0-4.4 (Thomas 1960). Mean sulphate values have been estimated to have increased from 1.6 mg/l in 1954-55 to 3.3 mg/l in 1978-79. These data suggest that the river is sensitive to, and has been affected by, atmospheric inputs.

During the period 1975-78, mortality of Atlantic salmon parr, reared at the Mersey hatchery, typically occurred during the 3rd and 4th weeks after first feeding. This higher-than-expected mortality was attributed to increased acidity in spring river water supplying the hatchery. In 1979, by treating the water with $CaCO_3$, the salmon fry mortality was reduced from 30 per cent to 3 per cent (Farmer et al. 1980). In 1980, the water was again treated and produced the same dramatic increase in survival of parr.

Hendrey and Wright (1976) report that "acid precipitation has devastated the salmonoid fish in southern Norway." Massive fish kills of adult salmon and trout have been reported in their river systems, usually occurring during the spring snowmelt or after heavy autumn rains. An intensive survey of 50 lakes in southern Sweden showed that inland freshwater species are also threatened. The decreases in pH have resulted in the elimination of Atlantic salmon from many Norwegian rivers in the past 20 years. Scandinavian scientists have concluded that, directly or indirectly, the principal cause of the fish losses is acidification of the waters, due to acid precipitation. If current acid loadings continue, it is

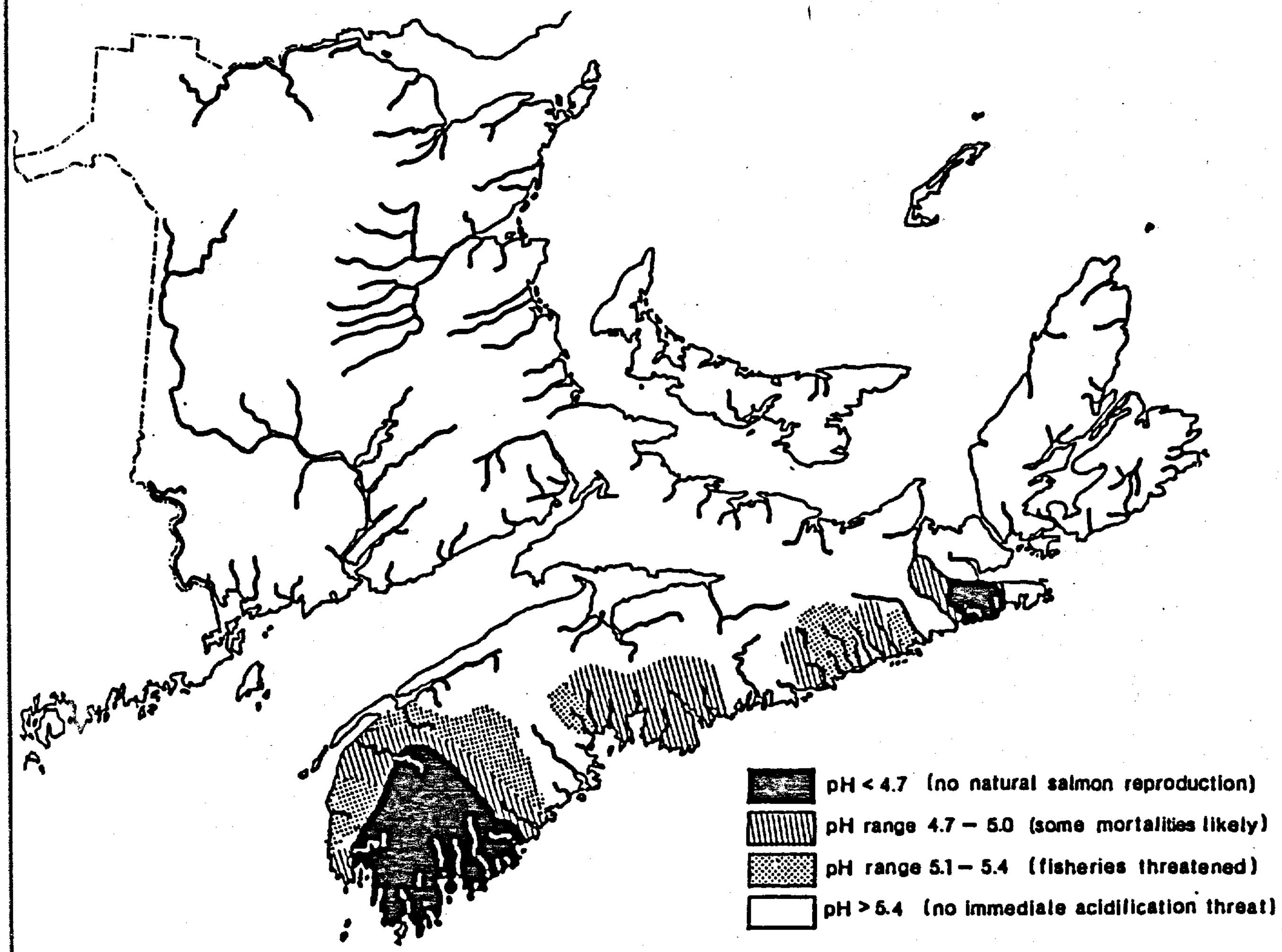


Figure 3-34 The Altantic salmon rivers of the Maritimes have been divided into 4 pH (estimated mean annual) categories based on significance to salmon reproduction. Present evidence indicates that salmon cannot reproduce at pH's below 4.7. Juvenile mortalities of 30% or more are expected in the pH range 4.0-4.7. Rivers in pH range 5.1-5.4 are considered threatened. Above pH 5.4 there is no immediate acidification concern with regard to Atlantic salmon (Watt 1981).

possible that more of the inland and Atlantic salmon fisheries in Canada will be lost. Portions of Canada's fishery resource appear to be responding in the same way as the fish stocks in Norway and Sweden.

3.7.10 Loss of Genetically Unique Fish Stocks

Loss of fish populations with specific gene characteristics from lakes and rivers appears to be an irreversible process. Over several thousand generations, most species appear to have evolved discrete stocks adapted to similar, yet discrete and specific, habitats (Loftus 1976). The basic unit of a stock is the gene pool, which is composed of a naturally sustained, genetically variable group of individuals, adapted through evolution to local environmental conditions. Man-induced stresses, (i.e., cultural eutrophication, habitat destruction, over-exploitation, species introduction and contaminants) have, separately and synergistically, reduced this genetic variability in populations of native fishes. Surface water acidification is an example of such a stress. Beamish and Harvey (1972) documented the loss of gene pools of fish in acidified lakes in Ontario. The Ontario Ministry of Natural Resources has attributed the extinction of lake trout (*Salvelinus namaycush*) in 27 lakes in the Sudbury-Temagami area to acidification (C. Olver, personal communication).

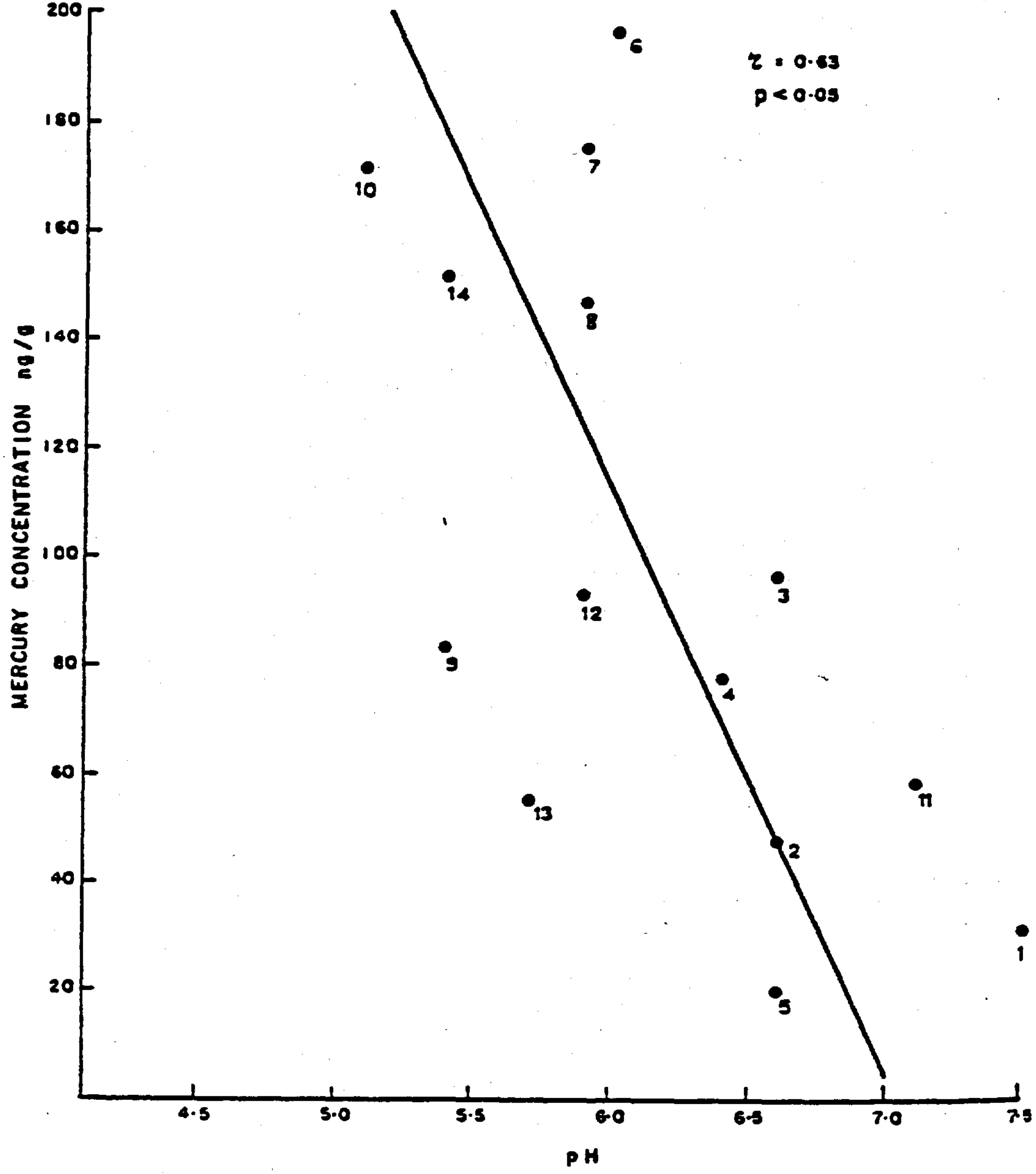
As the extinction of species has increased with the tempo of human activities, it is likely that the rate of loss of genetically discrete, locally adapted stocks has been many times greater. A naturally evolved complex of stocks appears essential to utilize fully the productive capacity of waters. Therefore, it is important to recognize and preserve stocks (Loftus 1976). Fisheries managers are now using the stock concept to allocate harvest and rehabilitate fish populations (Ricker 1972). Continued loss of discrete stocks may inhibit effective re-establishment of naturally reproducing populations in waters undergoing rehabilitation. The ramifications of these losses affect fisheries management specifically, and society in general. Genetic variability is a biological resource that must be managed (Ryman and Stahl 1981), or future opportunities for economic and recreational use of this resource will be jeopardized.

3.7.11 Mercury in Fish

Since elemental, metallic mercury can exist in the gas phase at ordinary air temperatures, it is ubiquitous in the environment. Large quantities of mercury pass between the earth and the atmosphere by natural cycling processes, which have been going on for millions of years. Therefore, the mere *presence* of mercury in any compartment of the environment does not necessarily imply any human influence. However, a considerable body of evidence exists that implicates human beings as a current major factor in the global dispersion of mercury. A recent National Academy of Science report (NAS 1978) presents evidence that human activities have, on a global scale, increased mercury emissions to the atmosphere by about 25 to 30 per cent when compared to natural emission rates. Much of this (≈40 per cent) comes from the burning of fossil fuels and ore mining activities. The intention of the U.S. to increase coal consumption by the end of this century will further increase atmospheric emissions. Coal contains, on the average, about 200 μg/g of mercury, and most of this (≈97 per cent) is emitted from stacks upon combustion (Billings and Mattson 1972). The mean residence time of mercury in the atmosphere is not accurately known but is probably in the order of several weeks to months (NAS 1978). This is ample time for long-range transport prior to deposition. These points may be of particular concern regarding any policy which embraces increased use of coal in its policy options. If all other factors were equal, one could expect such large increases in atmospheric emissions to increase the deposition rate and, hence, the concentrations of mercury in living organisms. However, increased deposition has not yet been fully substantiated, as atmospheric studies on mercury have been carried out only in a preliminary way, to date.

While no data base presently exists which explicitly shows increased atmospheric mercury deposition to biologically sensitive lakes, there is substantial evidence of the impact of pH on mercury content in fish (Landner and Larsson 1972, Brouzes et al. 1977, Hakanson 1980). Bisogni and Lawrence (1973) and Jernelov et al. (1976) have argued that one reason fish in waters of low pH contain more methylmercury than fish in waters of comparable mercury contamination, but higher pH, seems to be that acidic waters must be able to retain the monomethyl-form of mercury in solution. The main form of alkyl mercury in neutral to slightly alkaline waters is dimethylmercury, which is volatile and quite insoluble in water. Consequently, low pH waters would contain more mercury in monomethyl form, which in turn would increase the probability of the element being assimilated by fish. It is, however, important to recognize that pH is not the only variable which determines the mercury load in fish. Other factors include mercury availability, level of bioproduction, (i.e., lake trophic state), lake flushing rates and lake/watershed drainage area ratio (Hakanson 1980).

Few data exist to link mercury concentrations in fish to lake acidification. However, an increase in concentrations of mercury in fish from 1970 to 1978 is evident in some lakes in the Adirondack Mountains (C.L. Schofield, personal communication). In Ontario, Suns et al. (1980) have been sampling young-of-the-year and yearling fish for contaminant studies. Their data (Figure 3-35) demonstrate increased mercury concentrations with decreasing pH in lakes in the Haliburton area. For lakes with similar pH, the mercury was higher



LAKE #, NAME	TWP.	LAKE #, NAME	TWP.
1. Duck Lake	Minden	8. Dickie Lake	McLean
2. Little Clear Lake	Sinclair	9. Leonard Lake	Monck
3. Harp Lake	Sinclair	10. Heney Lake	McLean
4. Bigwind Lake	Oakley	11. Cranberry Lake	Guilford
5. Nelson Lake	Bowell	12. Healey Lake	McCauley
6. Chub Lake	Ridout	13. Clear Lake	Stanhope
7. Crosson Lake	Oakland	14. Fawn Lake	McCauley

Figure 3-35 Mercury concentrations in yearling yellow perch and epilimnetic pH relationships (Suns et al. 1980).

in fish from lakes with a higher ratio of drainage area/lake volume. This result implies that a quantity of mercury from either direct atmospheric deposition, or from watershed leaching, is influencing the fish concentrations. In 1980, the survey was extended to include adult bass, which are important to the sport fishery. Bass from six of the nine lakes studied had average mercury concentrations above the Canadian guideline for unlimited human consumption of 500 ng/g, and, in one lake, exceeded the U.S. guidelines of 1000 ng/g (K. Suns, personal communication).

3.7.12 Summary of Impacts on Aquatic Life from Acidification

The preceding sections have detailed the specific impact of acidification on fish, food chain organisms and ecosystems. Eilers and Berg (1981) have attempted to summarize this information in graphical form as shown in figures 3-25 and 3-26. Figure 3-25 gives the relative number of taxa of the Major Taxonomic groups as a function of pH. Figure 3-26 shows the generalized response of aquatic organisms to low pH. These figures should be used as illustrative generalized summaries, and detailed interpretations of responses should be limited to the information described above.

3.7.13 Effects of Acid Precipitation on Birds and Mammals

Only a few reports have attempted to relate acidification to changes in avian or mammalian populations. In a review paper, Almer et al. (1978) reported that, "fish-eating birds, such as mergansers and loons, have been forced to migrate from several acid lakes, with decreasing fish stocks, to new lakes with ample food supply. In this way, many territories will become vacant, and this will lead to decreasing stocks." The extent of the problem in Sweden has not been documented at this time. In another Swedish study, Nilsson and Nilsson (1978) found a positive correlation between pH and "water" bird species richness. "Water" birds were defined as those species dependent upon open water, and included a loon species, and several waterfowl and gull species. They also suggested that a reduction in young fish, a very important food source for aquatic birds, may lead to low reproductive success and local extinction in some bird species. Eriksson et al. (1980) also proposed that reduced reproduction of fish may decrease the availability of fish of the sizes appropriate to young diving water birds.

In North America, the only information on changes in aquatic bird populations comes from New York's Adirondack Mountains, and relates to the Common Loon (Gavia immer). Loon nesting densities have declined over the past 15 years (McIntyre 1979, Trivelpiece et al. 1979). During the same time fish populations in this area have also declined (Schofield 1976). To date, however, changes in loon populations in the Adirondacks have been interpreted only with respect to human disturbance, and the probable role of food depletion has not been investigated.

Effects of acid precipitation on wildlife may also be occurring as a result of increased solubility and availability of metals in acidified lakes (Suns et al. 1980, Schofield 1980). Eriksson et al. (1980) suggested this as a cause of the high mercury levels in Common Goldeneye eggs in areas of Sweden with acidified water but no industrial deposition. Studies by Nyholm and Myhrberg (1977) found impaired breeding of four species of passerines, also in Sweden. The species included Pied Flycatcher (Ficedula hypoleuca Pallas), Bluethroat (Luscinia svecica L.), Reed Bunting (Emberiza schoeniclus L.) and Willow Warbler (Phylloscopus trochilus L.). Breeding impairment was manifested as impaired eggshell structure and decreased nesting weight. Nyholm and Myhrberg (1977) and Eriksson et al. (1980) suggested that impairment was caused by uptake of Al or other trace metals from metal-contaminated aquatic insects living in acidified habitats.

Table 3-19 is a summary of potential effects on selected species of birds and mammals dependent upon the aquatic ecosystem for their food and habitat. This summary is based solely on feeding habits, as research on the impacts of acidification on vegetation structure and productivity relating to wildlife habitat is at a preliminary stage.

3.7.14 Effects on Unique Ecosystems Including Rare and Endangered Species

Documentation of acid precipitation effects on unique ecosystems and rare and endangered species is sparse at the present time. Negative effects on rare species will result in a decreased genetic diversity. Aesthetic values of affected ecosystems may be affected by changes in species composition. Many of these sites are presently National Parks or National Forests in both the U.S. and Canada and protected by federal laws. Placing an economic value on such ecosystems (and species) is difficult, but their value to society is immense.

The Boundary Waters Canoe Area Wilderness (BWCAW) of northern Minnesota has been recognized as a unique resource for many decades, as evidenced by the various laws passed since 1930 to protect its wilderness state. The attraction of the area (it attracts more recreationists than any other wilderness area in the nation) does

TABLE 3-19

AVIAN AND MAMMALIAN SPECIES MOST LIKELY TO BE INFLUENCED BY A REDUCTION IN FOOD RESOURCES DUE TO ACID PRECIPITATION, FEEDING HABITAT DURING THE BREEDING SEASON, AND ALTERNATE FOOD RESOURCES

Susceptible Food Resources	Feeding Habitat During the Breeding Season	Species	Alternate Food Resources
Fish, aquatic invertebrates, amphibians	Lakes, Rivers	Common Loon (*Gavia imuner*)	aquatic plants
		Osprey (*Pandion haliaetus*)	none
	Littoral zone	Great Blue Heron (*Ardea herodius*)	small mammals
		Belted Kingfisher (*Megaceryle alcyon*)	some terrestrial invertebrates
		Hooded Merganser (*Lophodytes culcullatus*)	some aquatic plants
		Ring-necked Duck (*Aythya collaris*)	some aquatic plants
		Common Merganser (*Mergus merganser*)	none
		American Mink (*Mustela vison*)	small mammals, birds
		River Otter (*Lontra canadensis*)	small mammals
Aquatic invertebrates	Littoral zone	Common Goldeneye (*Bucephala changula*)	fish
		Red-Breasted Merganser (*Mergus serrator*)	fish
		Black Duck (*Anas rubripes*)	aquatic plants
		Green-winged Teal (*Anas carolinensis*)	aquatic plants
		Mallard (*Anas platyrhynchos*)	aquatic plants
		Northern Pintail (*Anas acuta*)	aquatic plants
		American Wigeon (*Anas americana*)	aquatic plants
	Riparian zone	Spotted Sandpiper (*Actitis macularia*)	none
Aquatic plants	Wetlands	Muskrat (*Ondratra zibethicus*)	aquatic invertebrates
		Common Shrew (*Microsorex hoyi*)	
Aquatic invertebrates	Wetlands and Riparian zone	Common Yellowthroat (*Geothylpis trichas*)	some terrestrial invertebrates
		Bank Swallow (*Riparia riparia*)	
		Myrtle Warbler (*Dendroica coronata*)	
		Eastern Kingbird (*Tyrannus tyrannus*)	
		Blackpoll Warbler (*Pendroica straita*)	

not appear to be based on any single factor, but on a combination of related ones, such as fishing and camping in an atmosphere of wild, unpolluted landscape. However, the evergreen forests, clear water and air, rock outcrops, and shallow soils, which are the conspicuous ingredients of the BWCAW landscape, are all unusually sensitive to regionally transported pollutants. Small additions of acidity to the thin, rocky soils common in the BWCAW, coupled with geochemical weathering, can be expected to have relatively rapid and irreversible effects on outputs from the nutrient cycles of these ecosystems (Glass and Loucks 1980). These changes will affect groundwater quality and produce soil-mediated changes in cycling rates within the ecosystem.

The BWCAW is in a region comparable in vulnerability to other regions in Europe and North America which have already been severely affected by acid precipitation. Most surface waters have a poor buffering capacity, and many have a low pH (below 6.5), as well. The varied and valuable fisheries resource includes many species that have been reduced, or eliminated, by acid precipitation, elsewhere in the United States and Canada. Atmospheric acid sulphate loadings near the BWCAW are at levels associated with the onset of lake acidification in Scandinavian countries. Because of this, it is likely that the most vulnerable lakes are already being affected by acidity from atmospheric sources (Glass and Loucks 1980).

The Kejimkujik National Park, in Nova Scotia, lies in an area considered to be highly sensitive to acidic inputs, because it is composed of shallow, impoverished soils on primarily granitic and quartzite bedrock. Boulder-strewn bedrock plains and poorly drained soils are common. The effects on the salmon of this area have already been reported.

A third unique wilderness area, considered sensitive to acidic inputs, is the high-elevation system of the Adirondack Mountains. These areas consist of shallow, poorly buffered soils and contain, on the mountain tops, many arctic species rarely found in the eastern United States. Acid precipitation is known to affect the fish species of lakes in these areas (Schofield 1976), but effects on terrestrial organisms are not documented. It is of particular importance to determine the tolerance of these unique species to elevated aluminum concentrations.

Effects of acid precipitation on fish populations of the Great Smokey Mountains National Park (GSMNP) have been postulated by Herrmann and Baron (1980). Elevated aluminum concentrations (>1.0 mg/l) in GSMNP streams have been shown to have adverse effects on brook trout populations and sensitive macroinvertebrate populations. The high aluminum concentrations occur in association with acid runoff as low as pH 4.3. No studies have yet discussed the impacts of elevated aluminum concentrations on rare and endangered plant species (and other more common species) found in the southern Appalachian area, including the GSMNP.

3.8 CONSIDERATION OF EVIDENCE FOR IRREVERSIBLE IMPACTS

Researchers differ, and the evidence seems to be conflicting, as to whether the geochemical alteration of watersheds due to acidic input should be viewed as irreversible, and, if so, on what scale. Irreversibility can be viewed as a failure to recover over geologica time; but, for natural resource systems, an incomplete recovery to a prestressed or undamaged state over a few decades, for all practical purposes, may be regarded as irreversible. The following sections summarize the concepts involved and the evidence on both sides of th question.

3.8.1 Depletion of Buffering Capacity

The possiblity of irreversible reduction in buffering capacity of lakes and watersheds is one of the most serious impacts of acid deposition. Once the proton-accepting materials, which hold pH in a biologically acceptable range, are lost from the soil water and stream base-flow, free H^+ or its surrogate, Al^{3+}, rise quickly to toxic levels, seriously weakening the biota. The pH of an aquatic system is a product of a dynamic equilibrium between the system and its watershed. Large additions of acidic substances, including a mobile anion such as sulphate, have the potential to modify this equilibrium in geologically sensitive watersheds. The earlier data indicating negligible retention of sulphate and reduced alkalinities over several decades, suggests that this has occurred in a few areas.

The ability of lake and stream water to resist pH depression when acid is added, (i.e., buffering capacity) depends on its alkalinity and annual alkalinity formation. The alkalinity of the water depends on the presence of anions, or other species, which can take up protons. In most natural waters, alkalinity is largely a function of bicarbonate, but other substances, such as organic acids, are important in the low alkalinity lakes most susceptible to acidification. When lake water is titrated with acid, the change in pH per unit of added acid, (i.e., the slope) varies as successive buffers are protonated, each acceptor taking up protons in its own characteristic way. Lakes of moderate pH show successive buffering in the titration curves shown in Figure 3-36. In a whole lake system, this process is further complicated by the variable mixing processes in the lake, and the spatial and temporal changes in biological productivity, which also contribute proton uptake capacity (Zimmerman and Harvey 1979).

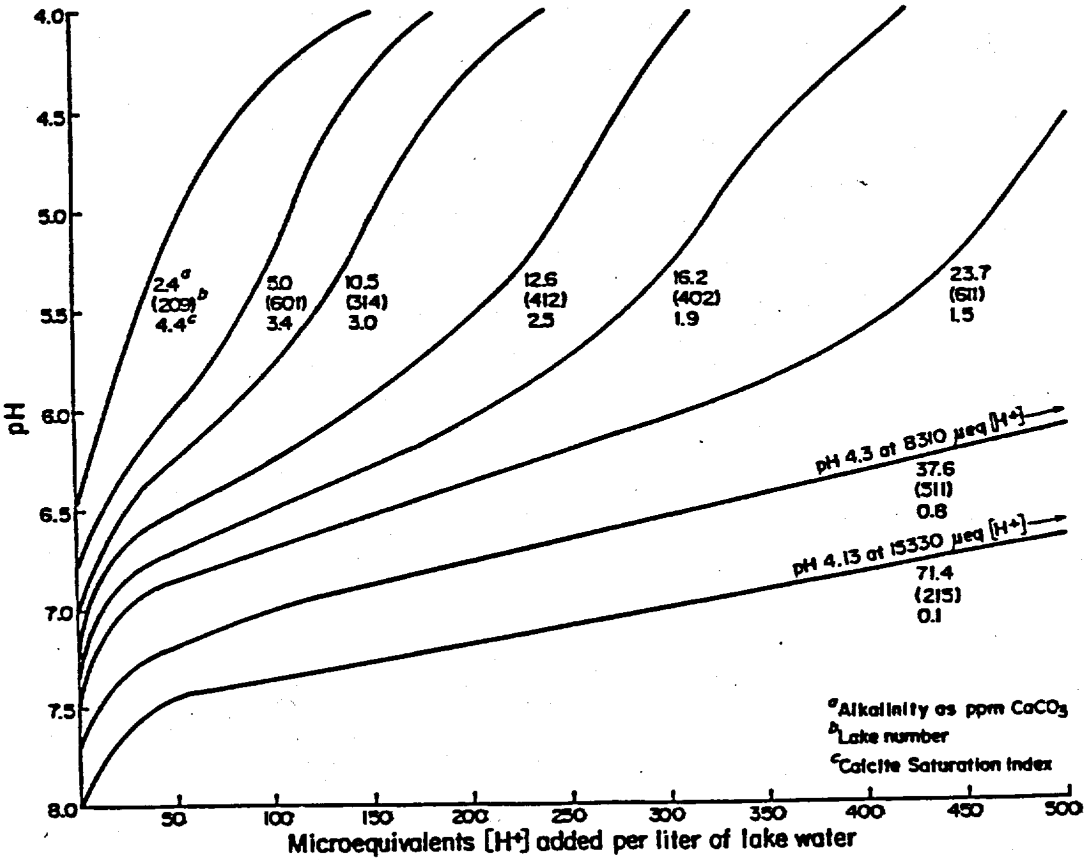


Figure 3-36 Effect of acid addition on the pH of water from selected BWCAW-VNP lakes (Glass and Loucks 1980).

When titration is considered for an entire watershed, as may be the case during sustained long-term atmospheric acid inputs, additional buffering processes can occur. Contact between protons in water and the solid buffering materials in the soil is not assured, depending on hydrologic flow patterns within both the upper ("inter-flow") and deeper soil horizons. Periods of peak runoff, when much of the "surface" water penetrates only a few centimeters into the soil, are often associated with acid flushing (low pH). This process is more likely to occur when watershed buffering is naturally low, or may have been depleted by long-term acid input. In addition, inclusion of the soil system in the buffering reactions introduces new sources of buffering which can retard pH depression in the system, but lead to the mobilization of other cations. When soil pH is less than 5.0, the displacement of aluminum from exchange sites becomes a source of buffering (where it is present); however, in the process, aluminum takes on a soluble, often toxic, form, with risks for both terrestrial and aquatic biota.

The hypothesis that acidification of surface waters by atmospheric acid inputs can be viewed as a large-scale titration has been articulated by Henriksen (1980), and supported with data from North America and Scandinavia (Wright et al. 1980). Nearly all lakes, except those dominated by acid bog drainage water, are normally bicarbonate buffered, with pH greater than 6.5. By stoichiometry, addition of acid from the atmosphere will consume alkalinity, but the pH will fall only slightly, as long as some bicarbonate remains. Long-term (more than 50 years) records of decreasing alkalinity in a water supply reservoir in the Adirondacks suggest that alkalinity has declined with continued atmospheric acid input (C.L. Schofield, personal communication). As bicarbonate and any other buffers are depleted, Henriksen suggests that lakes enter a transition phase, characterized by severe pH fluctuations (1-2 units) and associated stresses on fish and other aquatic biota. This transition phase is a time when the lake is particularly susceptible to seasonal pulses of acid, (e.g., snowmelt) and to the incomplete "mixing" of water and soil during flushing events. According to this view, a lake may exist in a transition phase until almost all bicarbonate (or other buffers) in the watershed is consumed.

However, given continued acid input, this stage is relatively ephemeral. For example, Wiltshire and Machell (1981) found that surface water pH values in Nova Scotia have a bimodal pH distribution, with the fewest lakes at pH 5.5, approximately in the middle of Henriksen's "transition phase". Scandinavian data also support these results (Wright and Gjessing 1976, Schofield 1976, Hutchinson et al. 1978). If watershed titration is occurring, then ultimately, lake pH should approach 5.0, as added H^+ depletes the bicarbonate and sulphate deposition provides the anion. As H^+ approaches higher concentrations, (lower pH), buffering occurs by aluminum, organic compounds and other proton acceptors. Although one cannot be certain, these appear to be the observed responses, and it is at this stage that fish and other biota become severely depleted or absent.

The hypothesis that a relatively irreversible titration of the chemical components of a watershed contributing to the buffering capacity, can take place, is a simplification of the complexities of lake/watershed buffering discussed in previous sections. The variety of potential sources of buffering, water flow patterns, and rates of acid deposition and flushing, all tend to make each lake/watershed system unique. However, the general pattern of observed responses is consistent with the known low buffering capacity of the geology and soils, and with present equilibrium theory for these systems. The effects can be reversed only by regeneration of buffering capacity over a period of unstressed geological weathering. The transition phase of lake acidification appears to be the last chance to halt acidification and allow normal acid-base equilibria to be established, with H^+ and Al^{3+} in a biologically tolerable range.

3.8.2 Soil Cation and Nutrient Depletion

A second, apparently irreversible, consequence of watershed titration is the loss of soil cations, particularly Ca^{2+} and Mg^{2+}, which can lead to decreases in soil fertility (Overrein et al. 1980). Likens et al. (1977) summarized the watershed level dynamics of a variety of anions and cations over an 11-year period at Hubbard Brook, New Hampshire. During this time there were net outputs of Ca^{2+}, Mg^{2+}, K^+, Na^+ and Al^{3+} at a combined rate which exceeded the rate of H^+ deposition. The difference was attributed to internal sources of H^+, although equilibrium theory suggests that smaller net losses of these cations would be accounted for by internal sources of H^+ and external sources of anions, prior to the acidification of rainfall inputs. In the 1964-1974 period, virtually all of the H^+ deposited from the atmosphere was taken up by the system, in exchange for the above cations. The extent to which these cation losses represent a significant depletion of total available material is unknown.

Similar results are reported by Harvey et al. (1981), who find cation denudation at a variety of watersheds in North America and Scandinavia. In trying to distinguish the various processes accounting for the weathering and cation export, they find that the sum of the H^+ input, bicarbonate output and NH_4^+ input usually balances the sum of the output of metal cations and nitrate input (Table 3-20). H^+ and NH_4^+ are obvious sources of hydrogen ion for exchange, and HCO_3^- output is a measure of carbonic acid weathering. Nitrate has the effect of neutralizing H^+ by generating an OH^- when it is taken up in the nitrogen cycle. If H^+, NH_4^+ and HCO_3^- in the watershed do not balance metal cations and nitrate, organic compounds are suggested as the weathering agents.

TABLE 3-20 COMPARISON OF ACID INPUT AND CONSUMPTION FOR HARP LAKE SUBWATER SHEDS ($\Sigma M = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$)[a].

Subwatershed	ΣM	$H^{+} + H_2CO_3$	$M + NO_3^{-}$	$H^{+} + H_2CO_3 + NH_4^{+}$
3	100.8	96.1	129.5	126.7
3A	110.0	99.8	126.1	131.2
4	81.6	105.3	115.0	134.8
5	100.9	94.0	134.7	124.4

[a] Numbers are averages for 2 yr (1977-1978); net mass balances are in meq m^{-2} yr^{-1}.

If cation denudation depletes the stock of nutrients of easily weathered soil, decreases in fertility can result (Abrahamsen 1980). These responses should be tied to the process of watershed titration, but the connections are unclear at this time. More data are necessary on rates of chemical transformation in the soils, and the relative roles of acid deposition, nutrient dynamics and the nutritional requirements of the plant community.

3.8.3 Loss of Gene Pools (Unique Ecosystem Components)

The most serious irreversible biological effect of acidic deposition is species extinction within sensitive regions. The organisms most threatened include amphibians, fish, crustaceans, molluscs and some aquatic insects (see previous sections). Elimination of fish populations in numerous water bodies has already occurred in Scandinavia, the Adirondacks and parts of Ontario. For these sensitive organisms, even a partial loss of populations bearing genetic characteristics intolerant to H^+, Al^{3+}, or heavy metals, can result in a relatively permanent mark on these populations. As geographic movement of these lacustrine life forms is limited, recovery of pre-stressed genetic characteristics probably can be considered only over millenia. The ecological importance of this impact will depend on the possible availability of stocks which might substitute in the impacted areas.

3.9 SULPHATE LOADING TARGETS CONSISTENT WITH PROTECTION OF AQUATIC ECOSYSTEMS

The previous sections have shown chemical and biological changes in surface water systems, including pH depression and associated effects over long-term, annual, seasonal and event-related time series. Most of the results are consistent with the explanation that they result from acidity associated with the SO_4^{2-} ion originating from atmospheric deposition. This section will consider the significance of these levels of chemical alterations, with emphasis on the levels of atmospheric input which could be viewed as having "no effect" or an "acceptable effect" on the most sensitive streams and lakes. Evaluation of a "no effect" loading threshold or "sustainable" loading rate, which may yield moderate, but "acceptable", effects, requires consideration, not only of mean trends in surface water and precipitation pH and sulphate concentration, but also of the frequency and severity of brief periods during which much of the response to the loading dose is expressed.

The following are the principal findings presented in previous sections which bear on interpreting the significance of present pollutant loadings, and the estimation of acceptable, or "target", loadings:

1. Precipitation over most of eastern North America is acidic with acid concentrations up to 100 times those expected for rainfall in equilibrium with atmospheric carbon dioxide and other natural constituents.

2. Large quantities of sulphate and nitrate are deposited with the acid in precipitation.

3. Several hundred thousand lakes in eastern North America with low alkalinities are being subjected to elevated acid loadings. Such lakes, and their associated streams, usually suffer low pH and elevated metal concentrations for short periods of time, particularly during snowmelt and other periods of heavy runoff.

4. Evidence of stressed fish populations has been observed in lakes which experience short-term low pH and elevated metal concentrations. Adult fish kills have been observed in one study lake experiencing these conditions.

5. There are numerous examples indicating that streams and lakes in Canada and the United States are losing alkalinity and becoming acidic. Fish populations, which have survived the short-term low pH conditions, will eventually be lost if the pH continues to decline to values causing reproductive failure.

6. Hundreds of lakes in eastern North America are showing serious acidification and fish populations have been lost.

3.9.1 The Relative Significance of Sulphur and Nitrogen Deposition to Acidification of Surface Waters

Results presented in the previous sections have shown that four major ions of concern in acidic precipitation, H^+, NH_4^+, NO_3^- and SO_4^{2-}, all have some potential for altering lake and stream water quality. Soil and plant interactions with nitrate ions allow the acid input from nitric acid to be largely assimilated (usually >80 per cent) by the terrestrial portion of the watershed (McLean 1981). However, in many northern and poorly buffered acid bedrock areas, biological interactions with the sulphate ion are small in comparison to the mass balance of sulphur (Harvey et al. 1981). Christophersen and Wright (1980) reported that the sulphur export from a watershed in Norway was essentially the same as the total input over the period November 1971 to October 1978. Thus, SO_4^{2-} can be viewed as a relatively conservative anion in many watersheds and, therefore, likely to show a direct relationship between concentrations observed in precipitation and those observed in lakes and streams, for basins where there are no significant geological sources or sinks of sulphur.

There are additional aspects to the issue of the dominant anion associated with the acidification of surface waters. These are:

1. the relative magnitude of SO_4^{2-} and NO_3^- in the rain and snow inputs, and their variation during the year;
2. the relative magnitude of the biological interactions of both anions in watersheds, as they are affected by biological activity at different seasons and by biomass accretion, or decomposition, over longer periods; and
3. the potential for alkalinity production in aquatic systems, through the addition of NO_3^- when N is a partially limiting nutrient for plant growth.

Data already presented here (Figures 2-6 to 2-15 [maps]) and other data presented by Galloway et al. (1980), McLean (1981) and by Harvey et al. (1981) indicate that acid sulphur inputs exceed acid nitrogen inputs over eastern Canada and the U.S. on an annual basis. The net yield of these anions to streams and lakes, however, is predominantly SO_4^{2-}, on an annual basis (Harvey et al. 1981).

Evidence that nitrate deposition is not the main driving force behind surface water acidification is given in Table 3-21 (a). Data for five streams with variable pH show that, as the acidity increases, the relative importance of nitrate declines. The median value of the H/N ratio is very low for Harp Lake 4, mainly due to the hydrogen ion concentration being so low. In Dickie Lake 5, the hydrogen ion concentration is more than an order of magnitude greater but the median H/N value has increased by 580 times. In other words, as the hydrogen ion concentrations increase, they surpass the nitrate concentrations and the pH of the streams cannot be explained by the presence of nitric acid. Table 3-21(b) gives the ratios of H/S for four of the same streams in the Dorset area of Ontario. As the pH decreases, the hydrogen ion concentrations exceed the nitrate, but are much less than sulphate (data for Dickie 5 and Red Chalk 2, are not available).

At Sagamore Lake, N.Y., nitrate concentration in runoff increased during spring pH depression, while sulphate concentrations did not (Galloway et al. 1980). There may be several reasons for the higher nitrate export observed here. These include the higher total loading (Table 2-2), differences in the pattern of various forest growth stages, and differences in topography which modify runoff patterns and, therefore, uptake by organisms in leaf litter. Still,

TABLE 3-21(a)

RATIOS OF HYDROGEN ION (H) TO NITRATE ION (N), EXPRESSED IN EQUIVALENTS PER LITRE FOR SIX STREAMS WITH VARIABLE pH IN THE DORSET, ONTARIO STUDY AREA FOR 1976, 1977, AND 1978. DATA ARE BASED ON MONTHLY AVERAGE CONCENTRATIONS, BUT COMPLETE MONTHLY RECORDS ARE NOT AVAILABLE FOR ALL STREAMS.

Stream	pH Range	H/N Range	H/N Median Value	No. of Months
Dickie 5	3.7-4.7	4.0 -278	29	28
Red Chalk 2	3.9-4.8	7.4 -133	26	24
Harp 6	4.3-6.4	0.07-17	5	24
Harp 5	4.8-6.6	0.01-50	0.4	36
Paint Lake Inlet	4.9-6.7	0.06-4.1	0.25	29
Harp 4	5.3-6.9	0.01-1.9	0.05	36

TABLE 3-21(b)

RATIOS OF HYDROGEN ION (H) TO SULPHATE ION (S), EXPRESSED IN EQUIVALENTS PER LITRE FOR FOUR STREAMS WITH VARIABLE pH IN THE DORSET, ONTARIO, STUDY AREA FOR 1976, 1977, AND 1978. DATA ARE BASED ON MONTHLY AVERAGE CONCENTRATIONS BUT COMPLETE MONTHLY RECORDS ARE NOT AVAILABLE FOR ALL STREAMS.

Stream	pH Range	H/S Range	H/S Median Value	No. of Months
Harp 6	4.3-6.4	0.003- 0.52	0.025	17
Harp 5	4.8-6.6	0.0005-0.17	0.004	36
Paint Lake Inlet	4.9-6.7	0.001- 0.08	0.015	25
Harp 4	5.3-6.9	0.0001-0.01	0.002	36

Source: W. A. Scheider, Personal communciation.

sulphate concentrations in the three study lakes here greatly exceed nitrate concentrations, even during spring runoff.

Nitrate ions which do reach the surface waters can still be taken up by aquatic plants, with resulting production of alkalinity. This has been shown to occur in one of the study lakes at the Dorset location. Reported increases in lake pH from 5.1 to 6.6 over the summer were associated with decreases in nitrate concentrations by photosynthetic processes, and this was given as the explanation for the pH increases (Harvey et al. 1981).

On balance, the evidence available, and the published interpretations of that evidence (Harvey et al. 1981, Overrein et al. 1980), lead to a conclusion that, for surface water systems, recent increases in acidity are primarily the result of increased sulphuric acid reaching these waters. In addition, the changes in SO_4^{2-} observed in surface waters are being shown to be attributable to the sulphate and sulphuric acid loading. Although nitric acid has been observed to contribute some acidity in surface waters during snowmelt, in some locations, there seems to be little theoretical or empirical evidence for anticipating any appreciable reduction in lake or stream acidification from a reduction in nitric acid inputs. Conversely, there is strong evidence that reduction in sulphate loading will reduce the observed sulphate concentrations and associated acidification of surface waters.

3.9.2 Methodologies for Estimating Target Loadings

The evidence available on the effects of acid deposition on aquatic resources indicates that present loadings are in excess of the neutralizing capacity of sensitive soils and watersheds, and that relief from these effects can be expected from a reduction in the more conservative acid ion inputs. This section, therefore, will explore the question of what levels of acid or sulphate loading would be unlikely to produce any further negative effects, i.e., a "target loading". Implicit in this concept is the idea of a single (or a series of) sulphate deposition value (as a surrogate for hydrogen ions) which would indicate a loading rate for aquatic ecosystems lying within watersheds of specifiable sensitivity.

Surface water quality alterations fall into two categories: short-term, which describes the low pH conditions during snowmelt or heavy rains, and long-term, which describes the permanent reduction in alkalinity, and the corresponding low pH values in surface waters all year long. In North America, the short-term effects are probably the most common in terms of numbers of lakes and rivers affected. While the chemistry of these effects is fairly well defined, and the biological consequences are known to be severe in some cases, overall they are not fully understood. Thus, an empirical approach to the watershed "dose/response" relationship is the only one available, at this time.

The second effect, long-term acidification, has altered large numbers of lakes in North America, but the percentage of the lakes and rivers profoundly acidified remains small. The rate of loss of alkalinity and associated increase in acidity is not yet defined beyond the fact that it seems to occur over a period measured in decades. The biological condition of the acidified lakes and streams has been relatively well defined. Consequently, this report makes use of the long-term acidification "models" developed from the most extensive data bases available, largely from Scandinavia, supplemented by North American Data, in order to derive preliminary estimates of sulphate loading targests.

The acidity and chemical composition of aquatic environments are largely controlled by: the buffering capacity of the geologic components of the basin; the effective acidity of the precipitation; and the interaction between the two. Biological processes, e.g., production and decomposition, also have an effect. Detailed models of the geochemical processes and aquatic ecosystem impacts are not fully validated at this time. Their development and application will require detailed information on basin geology, hydrology and biotic interactions, which is unlikely to be available soon for widespread application. Therefore, it is possible, at present, to determine the permissible carrying capacity of basins for acidic loadings in only a general way, using the presently observed behaviour of streams and lakes systems to derive relationships between measures of acid loading and system response. Such models are also all under continuing active development, but have advanced to the point where a preliminary application is possible, although it is important to stress that full validation remains to be achieved. Several of these models are discussed below, in order to evaluate relationships between present acid loadings and lake or stream sensitivity, as they are reflected in each approach.

Almer/Dickson Relationship

One way to summarize the relationship between lake pH and atmospheric loading of acidic pollutants is to plot observed lake pH versus sulphate loading, as summarized by Dickson (Almer et al. 1978) (Figure 3-37). Various combinations of watershed characteristics are reflected in the family of curves connecting the different sets of lake data. A larger number of curves may be envisioned, each representing lake watershed systems of comparable sensitivities, as they apparently respond to increases in atmospheric acid inputs. The curves are superficially similar to titration curves, as might be expected, and each shows buffering at high pH, then a rapid drop (as this buffering is depleted, or sulphate absorbtion capacity is exceeded) to lakes with low pH and minimal buffering. The pH in the more sensitive lakes drops sooner and more rapidly, relative to the loading of SO_4^{2-} which, in this model, is considered to be the surrogate of the acid.

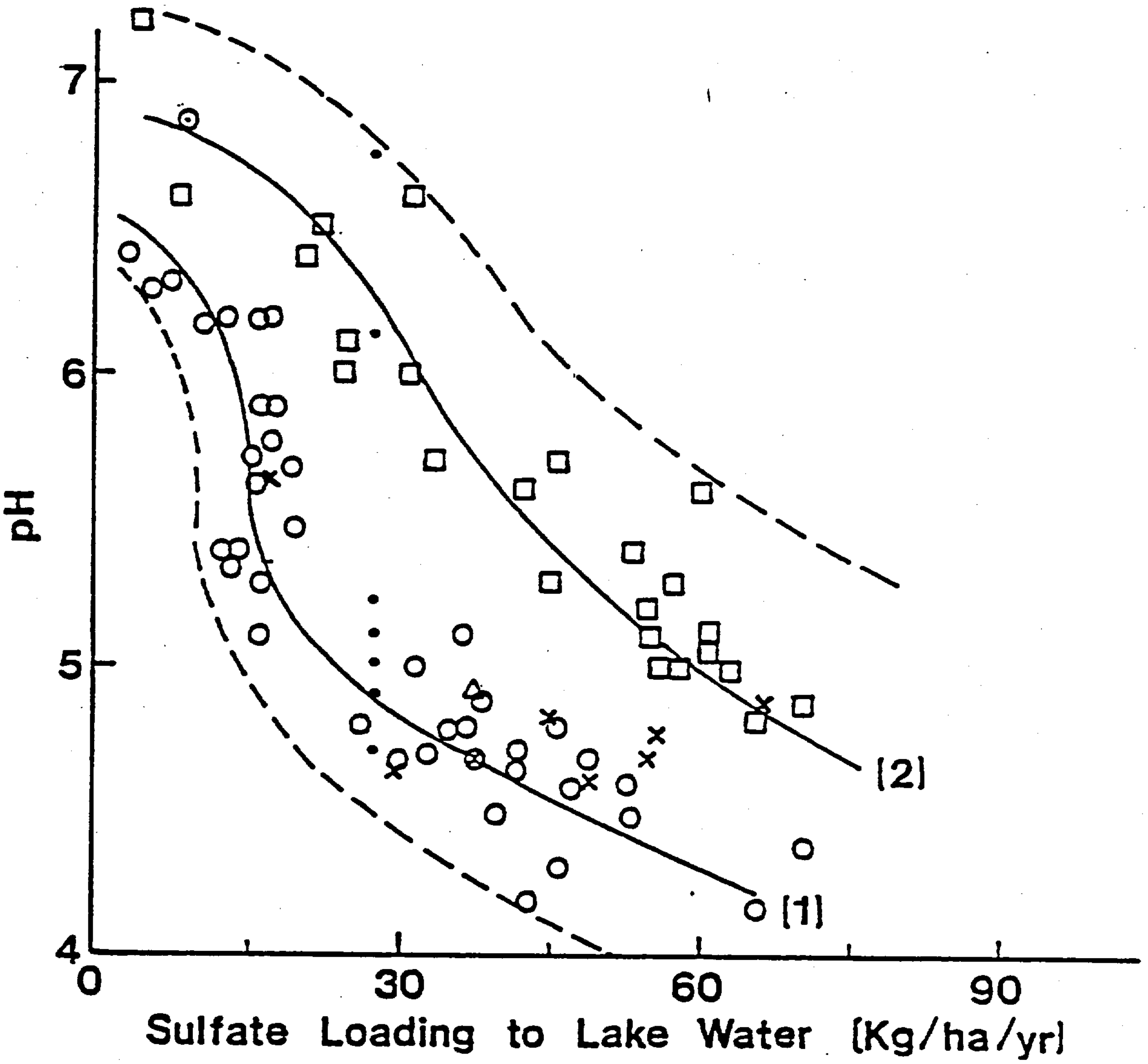


Figure 3-37 Effects of various sulphate loading rates on lake pH for lakes in very sensitive (1) and some what less sensitive (2) surroundings in Sweden. Added points are for: (•) Florida (Crisman and Brezonik 1980); (o) Como Creek (Lewis and Grant 1979); (Δ) Hubbard Brook (Likens et al. 1977); and (x) Norway (Wright and Snekvik 1978) (modified from Almer et al. 1978).

A graph of sulphate deposition versus lake pH, such as Figure 3-37, could be used to estimate lake watershed sensitivity, and thereby, acid loading tolerance, if the sensitivity response curves were defined in terms of water chemistry parameters for each watershed of interest. Unfortunately, the response curves for each family of sensitivities are not defined individually, although one may infer that they are related to the buffering capacity of the basin. The latter can be quantified through use of the calcium concentration of the waters (Henriksen 1980), or the cation denudation rate (Thompson 1981). In any case, Figure 3-37 represents the range of sensitivities found in Scandinavia, with several North American cases added, and indicates the apparent response of these aquatic regimes to sulphate loadings.

Examination of Figure 3-37 suggests that annual sulphate loadings of less than 15 to 17 kg/ha would be unlikely to degrade lakes of the type represented in curve (1). However, if the lower range of the data distribution is viewed as a "family" of the most sensitive lakes and streams, they appear to be barely free of potential acid loading effects at an annual rate of 9 to 12 kg/ha.yr. Thus, two "tolerances" can be defined, the latter associated with protection of nearly all sensitive aquatic resources, and the former designed to protect somewhat less sensitive lakes, i.e., only the portion of the "sensitive" resources that lie above curve (1) in Figure 3-37.

Since these curves were developed primarily on the basis of Swedish data, and are not actual observations of acidification responses over time, these estimates of acid loading tolerances must be viewed cautiously, for application in a North American context.

Henriksen Nomograph

Henriksen (1980) presents a model based on the concepts implicit in titration of a bicarbonate-buffered watershed/lake system with strong acid (principally H_2SO_4) from the atmosphere. In the process, bicarbonate is replaced by sulphate and lake pH can fall below 5, with consequent effects on aluminum mobilization and lake biota. These relations are basically the same as those in the Dickson work, and are further developed by Thompson (1981). The model is summarized in the nomograph (Figure 3-38), using two key measurements:

1. ambient concentrations of in-lake calcium (or Ca + Mg), as an estimator of the pre-acidification alkalinity; and

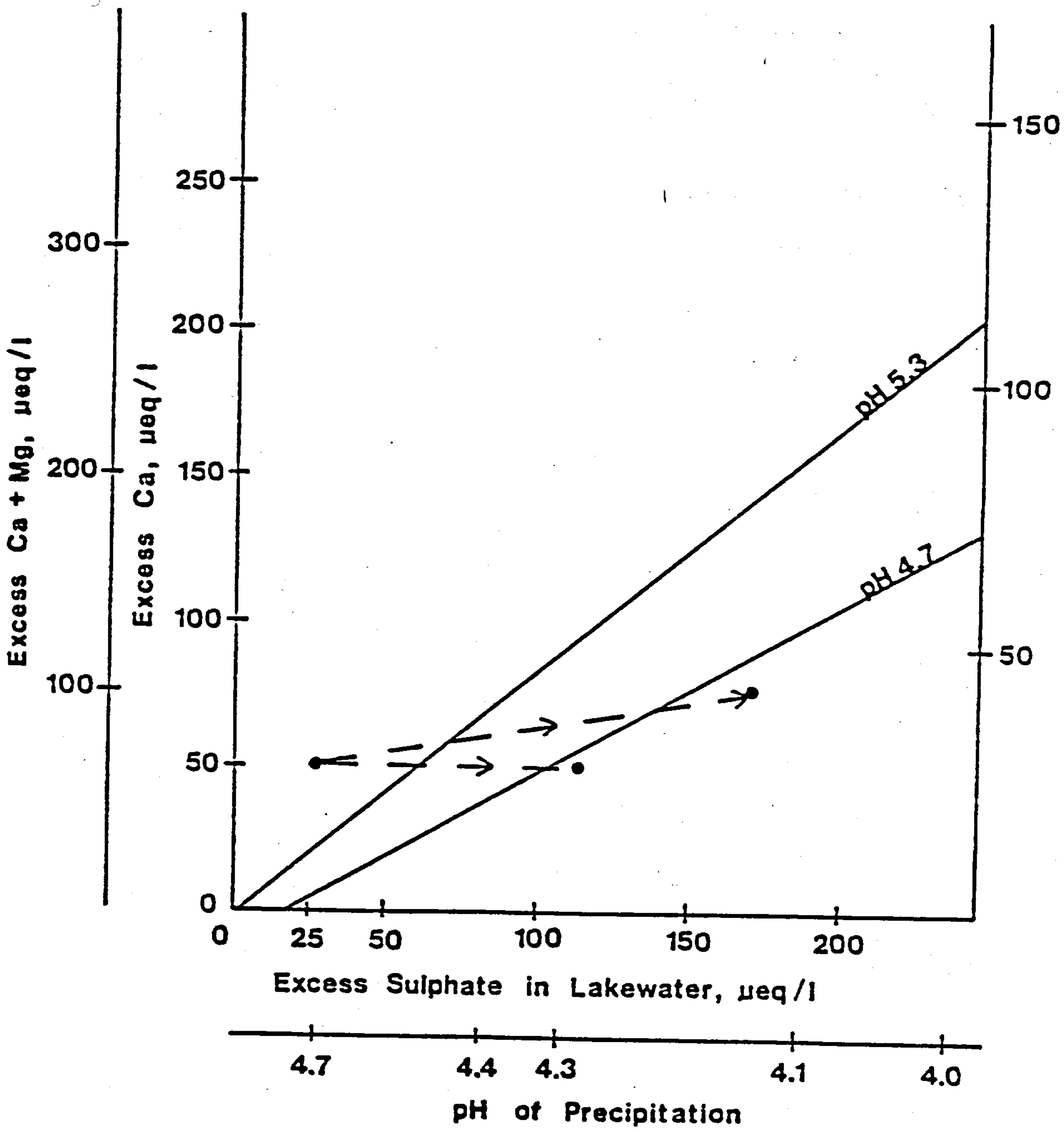


Figure 3-38 Nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations (or non-marine calcium concentration only) and the non-marine sulphate concentrations in lake water (or the weighted-average hydrogen ion concentration in precipiation) (Henriksen 1980).

2. lake sulphate concentrations (in excess of marine salt input), as an estimate of H^+ added to the system.

The resulting semi-predictive nomograph is divided into three sections:

1. bicarbonate lakes, where original alkalinity was high and/or added H^+ is low, so that the lakes remain bicarbonate buffered;

2. acid lakes, where original alkalinity was low relative to acid inputs, and all bicarbonate appears to have been depleted by the acid addition; and

3. transition lakes, in which bicarbonate appears to be undergoing reduction (or is almost depleted) and large pH fluctuations may occur during acid pulse events.

The transition phase, in which the lake apparently shifts from a bicarbonate-buffered equilibrium, at moderate pH, to an acidified system, represents the critical phase which requires prediction. Thompson (1981 and later in this report) has shown that this process is adequately represented by sulphate replacement of bicarbonate as the major anion in runoff. If cation weathering (approximated by Ca^+ plus Mg^+ in Henriksen's model) does not change in response to sulphate loading, the cation concentration of waters (or Ca^+ plus Mg^+ as its surrogate) may be used to estimate a sulphate loading which would retain a mean annual aquatic pH in the desired range. While the constancy of the cation weathering is yet to be verified due to lack of long-term records, Henriksen has shown that small changes would not have significant effect on the predictive applications.

Henriksen (1980) also derived an empirical relationahip between the sulphate concentrations of surface waters and precipitation to be:

$$SO_4(W) = -19 + 1.9\ SO_4(P)$$

where concentrations are in μeq/l, (W) refers to surface waters and (P) to precipitation. This relationship reflects the concentration of SO_4^{2-} due to evapotranspiration, and also includes the contribution of dry deposition of sulphate. The values may differ in North America, or from location to location, but are used here for purposes of estimation.

Figure 3-39 shows the distribution of lakes in Norway in terms of calcium and pH. There are numerous lakes having calcium concentrations less than 50 μeq/l. However, if this value is chosen as a limit above which lakes are to be maintained at pH greater than 5.3, then a target sulphate precipitation concentration can be derived which should protect those lakes. A distribution of North American

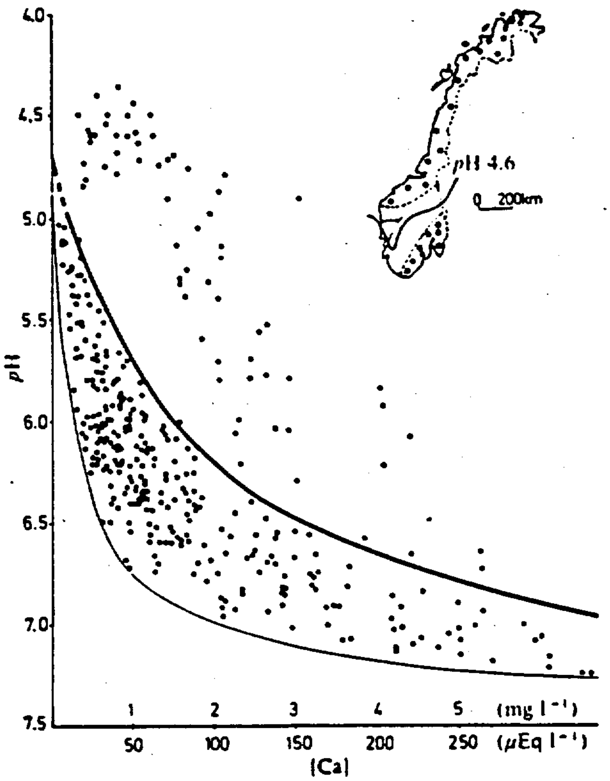


Figure 3-39 pH and calcium concentration in lakes in northern and northwestern Norway sampled as part of the regional survey of 1975; in lakes in northwestern Norway, sampled in 1977 (o), and in lakes in southernmost and southeastern Norway, sampled in 1974 (•). Southern Norway receives highly acidic precipitation (pH 4.2-4.5) and a large number of lakes have lost their fish populations, due to high acidity. Inset shows areas in which these lakes are located. Areas south of isoline receive precipitation more acidic than pH 4.6. (Henriksen 1979).

waters in relation to calcium (or to total cation concentrations) is not available, but a lower limit of 50 μeq/l would include all except the more sensitive waters, thereby possibly defining an "acceptable" SO_4^{2-} loading target.

From Henriksen's nomograph, one can calculate that a sulphate concentration in surface waters of about 60 μeq/l would permit pH to remain above 5.3, for waters having calcium concentrations greater than 50 μeq/l. Using the above relationship, this concentration in surface waters would result from a precipitation concentration of about 40 μeq/l of sulphate. If annual rainfall is 100 cm, this concentration would result in a deposition of about 20 kg/ha.yr of sulphate, which is in reasonable agreement with the estimates obtained using the Dickson nomograph to protect all but the more sensitive lakes.

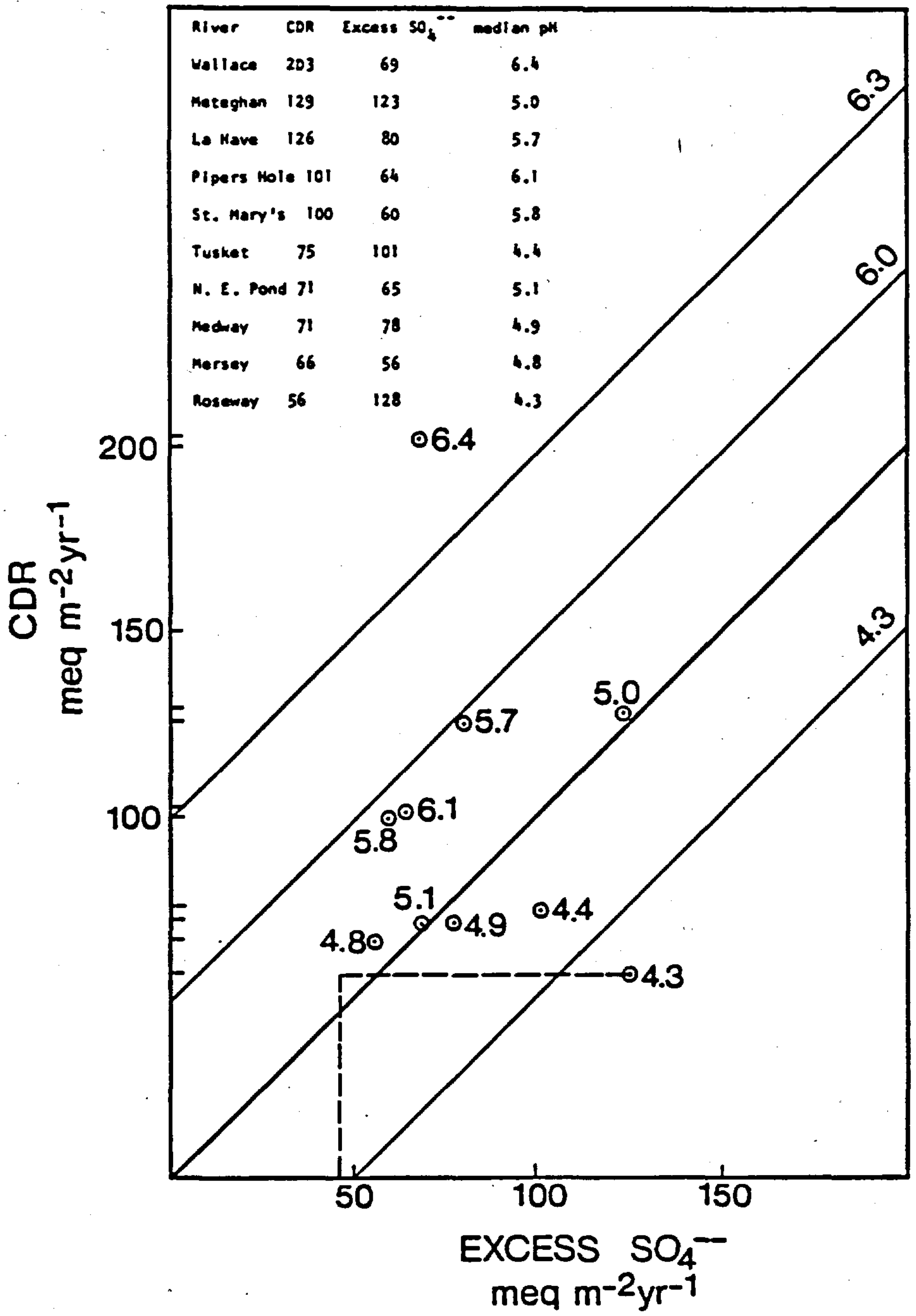
Apparently, even lower SO_4^{2-} concentrations in precipitation would be required, to protect lakes with calcium levels below 50 μeq/l. For lakes with only 25 μeq/l of calcium, protection from likely acidification (the entry level to the transition phase) would require precipitation with no more than 25 μeq/l of sulphate (12 kg/ha.yr).

Cation Denudation Rate (CDR) Model

The CDR model (Thompson 1981) relates the rate of acid (excess SO_4^{2-}) loading to the rate of major cation denudation of large watersheds, thereby predicting the mean pH of the rivers. If the rate of excess SO_4^{2-} loading is less than the CDR by 20 meq/m^2.yr (i.e., the HCO_3^- residual equals 20 meq/m^2.yr), the model predicts the result runoff water (at a yield of 1 m/yr) will have a mean pH of 5.6. As the rate of excess SO_4^{2-} loading approaches the COR, the runoff water will approach a pH of 5.1 and will carry little or no alkalinity. Figure 3-40 shows 1973 data for rivers in Nova Scotia and Newfoundland that have mean runoff rates near 1 m yr^{-1}. These rivers have a total CDR ranging from 55 to 200 meq/m^2.yr. In 1973 at least three of these rivers received excess SO_4^{2-} loads exceeding their CDR, and consequently had no alkalinity. The resulting pH was less than 5.1.

Questions have been raised as to whether atmospheric loads of strong acid alter the rates of chemical weathering in watersheds, and therefore the CDR. Comparisons of data for very soft water rivers in southern Nova Scotia between 1954-55 and 1973 (Thompson et al. 1980) show lower pH (and higher excess SO_4^{2-}) in the more recent data, but no significant change in major cation loads.

Analysis of long term monitoring data for rivers in Newfoundland shows that cation loads generally correlate well with discharge, but



River	CDR	Excess SO_4^{--}	median pH
Wallace	203	69	6.4
Meteghan	129	123	5.0
La Have	126	80	5.7
Pipers Hole	101	64	6.1
St. Mary's	100	60	5.8
Tusket	75	101	4.4
N. E. Pond	71	65	5.1
Medway	71	78	4.9
Mersey	66	56	4.8
Roseway	56	128	4.3

Figure 3-40 Cation Denudation Rate Model applied to rivers of Nova Scotia and Newfoundland (Thompson 1981).

TABLE 3-22

PERIODIC pH DEPRESSIONS OBSERVED IN STREAMS AND LAKES WITH DIFFERENT SULPHATE LOADINGS

Location	Annual Sulphate Loading kg/ha.yr(SO_4) by wet deposition	Lowest pH Observed	ΔpH Largest Difference Between Spring pH and summer or winter values	Observed Biological Effect
Panther L. ILWAS Project New York	30	4.8	2.5	No biological data available.
Tovdal R. Norway	40	pH shock suspected but no field measurements taken during the fish kill		Fish Kill (sea trout).
Haliburton Ontario (4 streams)	30	4.1	1.1	No studies.
(lake outflows)	30	4.8	1.3	A year class missing in white sucker populations one of the lakes. Limited field studies completed.
L. Timmewatten Sweden (1970)	40	4.2	0.8	Wild population of minnows have disappeared.
Sweden (1972)	40	4.3	1.1	Caged sea trout and minnows experienced 68% and 59% mortality.
Shavers Fork W. Virginia (stream)	30	5.6	0.9	Conditions caused by heavy rain. No biological studies.
Northern Minnesota streams	14	5.8	0.3-1.0	No biological studies.
Plastic Lake Ontario Inlet	30	4.0	1.7	100% mortality of caged rainbow trout.
Outlet	30	5.0	0.7	13% mortality of caged rainbow trout.
Experimental Lakes Area Kenora	10	-	0.2-0.3	No apparent biological effect.

Table 3-22 summarizes a wide range of available data, relating sulphate loading to observed pH depression and biological effects. Sulphate loadings of as little as 10 kg/ha.yr as presently observed at the E.L.A. in northwestern Ontario, are required before detrimental pH depression occurs. Much further research is needed to define the synergistic responses of biota to the pH shock and associated increases in metal elevations concentrations, and also to provide an understanding of the hydrological circumstances which control the acidic pulse occurrence.

3.9.3 Summary of Loadings and Target Loadings

The models and their indicated target loadings have been expressed in terms of sulphate loadings from wet or bulk deposition. The pH of precipitation is commonly measured, and is an important parameter related directly to short-term acid shocks. Schindler (personal communication) has suggested that precipitation pH probably should be no lower than 4.7, and that it may need to be higher to protect the most sensitive resources. He states:

> "Three studies, one in Scandinavia, one in Scotland, and one in Canada have shown that detectable decreases in pH (of lakes) are measurable where precipitation with a pH of 4.7 or less and low alkalinity lakes occur together (Watt et al. 1979; Henriksen 1980). We know from other works that where precipitation is more acidic than 4.7, aquatic damage occurs rapidly (Dillon et al. 1979, Henriksen 1980). Studies at the Experimental Lakes Area, Ontario, have shown that damage at precipitation pH values of 5.0 is not detectable so far. Preliminary evidence suggests that in sensitive areas, a precipitation pH of no less than 4.7 is desirable."

A target loading of 10 kg/ha.yr corresponds to about 20 μeq/l in precipitation for 1 meter of rain. If the sulphate were associated with an equivalent of acid, the pH would be about 4.7. The presence of bases or other anions would alter this pH value. Most of the sensitive areas of eastern North America receive precipitation in which the acid content ranges from one half to one times the sulphate content on a chemical equivalent basis (Barrie 1981). Therefore, the pH values would tend to be higher than indicated in the example given.

On the other hand, the sensitive areas in central Canada and the U.S. receive annual precipitation ranging from 0.5 to 1 meter. Thus, a 10 kg/ha.yr target loading will yield a sulphate concentration of from 20 to 40 μeq/l, with the 40 μeq/l value corresponding to a pH of 4.4, if the acid is present in an equivalent basis. The pH would range between 4.4 and 4.7, depending on the area, but would generally be higher because of the observed relationships between acid and sulphate concentrations in precipitation.

For example, measurements of bulk deposition of sulphate (wet-plus-dry fall) made at the Experimental Lakes Area (ELA) of Ontario show an average recent sulphate deposition of 10.9 kg/ha.yr and an average rainfall pH during 1974-77 of 4.86 (Glass and Loucks 1980). The presettlement pH for rainfall in this area appears to have been 5.7 (c.f. carbonic acid equilibrium, and data for 1955-56 shown by Galloway and Cowling (1978)). Data from the ELA show that 70 per cent of the nitrate and sulphate in the current rainfall is in a neutralized form and only 30 per cent is in the acid form.

Table 3-23 lists the observed sulphate loadings at several study locations and the nature of the water quality effects. Estimates of acceptable SO_4^{2-} loadings from different models are shown. A target loading of 10 kg/ha.yr appears likely to cause minimal, if any, damage to highly sensitive aquatic ecosystems. Values of 20 kg/ha.yr or more are clearly associated with degradation of the more sensitive surface waters. For the reasons developed previously, it appears reasonable to expect the extent of biological damage to decline as SO_4^{2-} loadings to presently affected areas move toward 10 kg/ha.yr. The agreement between the models and the observations is not surprising, since the models themselves are based on empirical observations from other lake sets which span the range from lake acidification to negligible effects.

Regardless of the model used to determine threshold loading values, there are variables that lie outside the purview of effects modelling. Most important is the number of lakes (placed at risk by a given "loading capacity" or "tolerance") that society may choose not to protect. Lake sensitivity is a function of geochemical processes in highly variable lakes and watersheds; abatement to a level that protects the single most sensitive stream or lake in the U.S. or Canada is probably not feasible. Once aquatic systems are inventoried, according to sensitivity measures, a cutoff point can be determined for various loading tolerances, as can the corresponding number of streams and lakes to be sacrificed. Present inventories are not sufficiently extensive to permit an unbiased estimate of tolerance profile.

To illustrate the implications of this process, and the role of predictive response models in providing options, Table 3-23 summarizes the evidence available, and Table 3-24 describes the projected consequences of SO_4^{2-} loadings by wet deposition and snow at three different intensities, using three different models of the response. The loading levels are:

1. <u>5 kg/ha.yr</u> - a level only slightly above the apparent historic levels of SO_4^{2-} deposition in northern, interior, continental land masses;

TABLE 3-23

OBSERVED SULPHATE LOADINGS AND LOADING VALUES, PREDICTED BY VARIOUS METHODS, REQUIRED TO PROTECT AQUATIC ECOSYSTEMS

SOURCE	LOADING VALUES Kg/ha.yr (SO_4^{2-})		COMMENTS
Observed Loadings	Wet/Bulk	Total	
Hubbard Brook, New Hampshire	35 (B)[1]	~55	Acidified lakes in the area
Panther Lake, Adirondacks, New York	43 (B)[2] 38 (W)[2]	62	Acidified lakes in the area
Dorset, Ontario	30 (W)[3]	42	pH depression causing fish kills
Kemjimkujik, Nova Scotia	20 (W)[3]	-	Acidified rivers. Decreased pH in lakes over a 20-30 year period.
BWCAW, Minnesota	14 (W)[4]	15[5]	Stream pH depression of 0.8 units observed
ELA, Northwestern Ontario	11 (B)[6]	-	No apparent detrimental effects observed
Indicated Minimum Effects for Loading Tolerances	Wet/Bulk	Total	
Almer/Dickson Model (see Figure 3-37)	-	~10	To protect the most sensitive waters.
	-	~16	To protect moderately sensitive waters.
Henriksen Nomograph (see Figure 3-38)	~12 (W)*	-	To protect the most sensitive waters.
	~20 (W)*	-	To protect lakes with 50 μeq/l cations, i.e., the majority of sensitive lakes.
CDR estimates for Nova Scotia Rivers (see Figure 3-40)	-	~ 7	To restore larger rivers to a pH of 5.8
	-	~20	To restore larger rivers to a pH of 5.3.
pH depression relationship (see Table 3-22)	-10 (W)	-	Required to prevent detrimental pH depression in streams and lakes.

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* Assuming 1 meter of rain per year since the model prediction is based on precipitation pH.

[1] Likens et al. 1977

[2] Johannes et al. 1981

[3] Harvey et al. 1981

[4] Glass & Brydges 1981

[5] Ragland & Wilkening 1981

[6] Glass & Loucks 1980

2. <u>15 kg/ha.yr</u> - a level reflecting somewhat elevated SO_4^{2-} deposition, and covering very large areas of the eastern and interior U.S. and Canada; and

3. <u>45 kg/ha.yr</u> - a level representative of the heavily acid SO_4^{2-} impacted regions of the eastern U.S. and Canada.

The results shown in Table 3-24 are literal interpolations of prospective responses, using the three models discussed previously. The limitations of incomplete data bases and validation steps <u>must</u> be heeded, but there is considerable consistency in the projections. Biological responses range from negligible to significant for the most sensitive streams or lakes, with SO_4^{2-} loadings ranging from 5 to 15 kg/ha.yr. Effects are less extreme in moderately to only slightly sensitive streams and lakes.

These results indicate that reductions in sulphate deposition of from 50 per cent to 75 per cent are required to protect the aquatic systems in the most heavily loaded areas of eastern North America. Furthermore, protection of the aquatic environment should be viewed as a "sliding scale", such that all reductions in sulphate deposition are likely to reduce the number of streams and lakes experiencing damage. The loading targets given here are intended to provide a basis for discussions on whether to protect all but the most sensitive surface waters, or to define some other "acceptable level" of resource alteration. The closer the actual loadings come to the targets, the fewer lakes and streams are likely to be damaged.

3.10 RESEARCH NEEDS

Although some aspects of lake and stream acidification processes are well known, the results reviewed here identify numerous gaps in the information on regional effects, and in predictive capabilities as to long-term responses. There is an immediate need, in both the United States and Canada, for improved knowledge as to the nature of geochemical alterations affecting water quality, and the associated biological effects. Considerably more research is needed on modelling the dose/response relationship and on defining target loadings, so that the most cost-effective control program can be implemented.

The list of research needs outlined below covers the same major topics as those identified within this aquatic effects section. Since they interrelate, all are considered to be of approximately equal priority for understanding each nation's risks with respect to the aquatic impacts of atmospheric deposition. Some topics may, indeed, have more importance than others when seen from regional or disciplinary perspectives. Following the list of critical research topics, arranged according to the section outline, baseline data needs are described for long-term impact assessment.

TABLE 3-24

ILLUSTRATIVE DOSE/RESPONSE/TIME RELATIONSHIPS UNDER SELECTED LOADING PATTERNS

Projected Precipitation Quality	Projected Surface Water Quality	Projected Aquatic Effects
1. SO_4^{2-} Loading: Natural to 5 kg/ha.yr and 85 cm precipitation per year:		
Annual average pH 5.2 to 6.5	Dickson Relation: Minor pH, aluminum and heavy metal changes in very sensitive lakes.	Dickson: Probably no biotic effects.
Henriksen: Annual average pH 5.0	Henriksen Nomograph: No expected changes in lake status.	Henriksen: Probably no biotic effects.
	Episode Receptor/Dose: pH depression up to 0.7 units in very sensitive systems; up to 0.25 pH units change in moderately sensitive systems.	Receptor: Possible fish mortality in some years in very sensitive systems if pH depression coincides with sensitive life stages. No biotic effects in moderately sensitive lakes.
2. SO_4^{2-} Loading: 15 kg/ha.yr and 85 cm precipitation per year:		
Annual average pH 4.6 to 4.8; single episodes to pH 4.2	Dickson: An average of 1 unit pH change for very senstive lakes; minor to no pH changes for moderately sensitive lakes.	Dickson: Fish mortality in very sensitive lakes; no known biotic effects in moderately sensitive lakes.
Henriksen: Annual average pH 4.5	Henriksen: About 30% of lakes in Norwegian study area would become acidified.	Henriksen: Potential fish mortalities in about 30% of lakes in study area due to acid conditions and elevated aluminum concentrations. Shifts in other native populations.
	Episode Receptor/Dose: About 1.0 pH unit depression during episodes in very sensitive streams; near 0.5 pH unit depression in moderately sensitive lakes.	Receptor: Fish mortality in very sensitive systems if pH depression coincides with sensitive life history stages.

TABLE 3-24 (Continued)

ILLUSTRATIVE DOSE/RESPONSE/TIME RELATIONSHIPS UNDER SELECTED LOADING PATTERNS

Projected Precipitation Quality	Projected Surface Water Quality	Projected Aquatic Effects
3. SO_4^{2-} Loading: 45 kg/ha.yr and 85 cm precipitation per year:		
	Dickson: An average of 1 to 2 unit pH changes for very sensitive lakes; 1 unit change for moderately sensitive lakes.	Dickson: Metal mobilization and elimination of sensitive species from very sensitive lakes; major shifts in populations in very sensitive lakes; partial mortality of sensitive biota in moderately sensitive lakes.
Henriksen: Annual average pH 4.08	Henriksen: Approximately 90% of lakes in Norwegian study area appear to become acidified.	Henriksen: Potential fish mortalities in 90% of lakes in study area due to acid conditions and elevated aluminum concentrations; shifts in natural populations; elimination of sensitive biota from most sensitive lakes.
	Episode Receptor/Dose: About 1.5 pH unit depression in very sensitive systems; in vicinity of 0.6 pH unit depression in slightly sensitive systems.	Receptor: Elimination of sensitive biota from very sensitive systems; major shifts in natural populations; partial mortalities in moderately sensitive systems due to heavy metal and aluminum mobilization.

* from Henriksen equations (1980)

3.10.1 Critical Research Topics

The following topic areas represent issues in which there are major information gaps, and which should be addressed by research programs, in both the U.S. and Canada, at the earliest possible date.

Element Fluxes and Geochemical Alterations of Watersheds

Three areas of research are needed here, all requiring relatively intensive study of both terrestrial (geochemical) and aquatic (hydrologic) components, mostly focused around calibrated watersheds of comparable research design and intensive data quality assurance.

1. The four ions of primary concern regarding acidification are hydrogen, ammonium, sulphate, and nitrate. Each ion reacts differently with the soil matrix and vegetation. It is necessary, therefore, to define, in specific terms, the fate and effect on surface water acidification of hydrogen, ammonium, sulphate and nitrate ions originating as atmospheric input.

   Comparison of results from calibrated watersheds with different soil and vegetation conditions is urgently needed. This report indicates that priority may have to be given to sulphur emissions control, drawing heavily on evidence that nitrogen deposition does not contribute significantly to surface water acidification, even though it contributes to precipitation acidity. The long-term necessity for a sulphur control priority needs to be established beyond doubt, as soon as possible, in order to minimize the risk of making costly errors in a control program.

2. Acid deposition results in mobilization of metals, such as aluminum, iron and manganese, from the soil particles in watersheds. Further work is needed to define the amounts and species of metals leached from watersheds and their biological consequences.

3. There is evidence that groundwater is being acidified, and that metal concentrations are elevated, in areas where snowmelt gains direct access to sandy subsoils with low acid neutralizing capacity. The effect may be seasonal, with pH values recovering during the summer, as neutralization slowly takes place. Further surveys are needed to establish the extent and characteristics of groundwater modification over time and across geographical gradients in acid loadings.

Alterations of Surface Water Quality

Two major areas of information needs have been identified in the extent and periodicity of surface water quality effects:

1. The geographic extent of surface water acidification is not yet fully documented in North America. Obvious data gaps exist in the central, southern and western U.S. and in parts of Canada. In addition, reliable data on time-trends in water quality appear to be sparse through North America, although some data have not yet been evaluated. Much of the new data needed can be obtained as part of the long-term monitoring program described below. The critical need is to begin long-term water quality measurements, in a carefully selected range of aquatic environments, as soon as possible.

2. One of the most common manifestations of acid deposition observed in eastern North America is periodic pH depression in streams and lakes, due to snowmelt or heavy rain. Since periodic low pH is a current problem for biological resources, and likely to remain so until acid deposition is reduced, the quantitative relationship between acid deposition and short-period pH depression should be determined for a broad sprectrum of aquatic environments. A dose/response relationship for episodic acute exposures to H^+ and aluminum will be a major element in defining acceptable acid loadings.

Alteration of Biotic Components

Effects on the biological components of aquatic ecosystems appear to be more poorly known than for other ecosystems. Five research topics are identified:

1. It is essential that the biological responses to various water chemistry changes induced by acid deposition, be evaluated in considerable detail to define dose/response relationships further. Studies of dose/response relationships in aquatic ecosystems should include surveys of phytoplankton, macrophytes, zooplankton, benthos and amphibians. Several species among these groups are quite sensitive to changes in pH.

   Of particular importance to the dose/response relationship is quantification of response data from indigenous species which may be vulnerable to low pH or elevated aluminum, and the pH at which effects are expressed. Special attention needs to be given to determining the pH at which species unique to certain areas are harmed and begin to show some failure in reproduction. In addition, community-level attributes of aquatic systems are likely to be sensitive to acid-induced stresses, but are difficult to determine; nevertheless, they should be understood fully. These include plankton species composition, predator-prey relationships, and trophic-state modification of lakes due to altered nutrient cycles.

2. Damage to fish populations is of particular concern because the loss of fish breaks a major link of the water/terrestrial food chain. Sport fishing is an important industry in most of the areas affected by acidic precipitation and reduction in fish supply could have serious economic consequences. Mechanisms by which low pH and high metal concentrations affect fish should be studied to improve general understanding of the toxicity phenomenon and to improve the ability to predict future effects if acidic deposition continues. Fish senistivity to H+ and metal ions should be determined, by direct bioassay, at different stages in the life cycle, concentrating on reproduction and recruitment. Behavioural or physiological changes (e.g., blood ion levels) known to be affected by sublethal acid and metal concentrations should also be evaluated. Long-term monitoring should include fish population data, as well as other measures of biological productivity.

3. Further study is needed to define the biological effects and tolerances for periodic pH depression in streams and lakes. Current work should be extended, to include the Great Lakes tributaries draining Precambrian areas. All such potentially sensitive areas in the U.S. and Canada should be surveyed, to determine whether low pH and high metal concentrations occur, and if so, whether there has been any reduction in spawning success for fish species in those tributaries.

4. Mercury concentrations in fish and other wildlife may be increased by the acidification process and/or by increased atmospheric emissions. Increased effort should be placed on measuring existing mercury concentrations and time trends throughout the wildlife food chain, as a function of lake and stream pH values. Laboratory and field studies are needed to establish the biological significance of various mercury concentrations in indigenous species of fish, birds and mammals.

5. When aquatic and/or terrestrial productivity is affected, the effect is often evidenced through the entire food chain. Thus, there is reason to believe that acidification will have an adverse effect upon food availability to the higher trophic levels of the food chain, including aquatic birdlife and mammals. The long-term effects of habitat damage on the populations of wildfowl and other wildlife should be better defined, and the losses of habitat should be quantified.

Irreversible Impacts

1. Geochemical and hydrologic principles suggest that the processes of suphate accumulations, and associated acidification of soils and surface waters, represent a large-scale titration of available alkaline substances. There is evidence

that the capacity of watersheds to provide neutralization of acids may become depleted, over long periods. Therefore, further work is needed to define the rate of acidification of surface waters, develop predictive models to quantify watershed capacity to neutralize acid over the long term, and to anticipate recovery following abatement.

The studies should include measurements on the rates of acidification of lake and stream sediments. The results of such studies are needed, to assist in setting acid loading tolerances which will be protective of the aquatic environment in the long term.

Target Loadings and Model Validation for Phase III

Much uncertainty remains as to the quantification of sulphate deposition levels ("target loadings") consistent with no further significant degradation of natural resources. Two areas of research are needed:

1. Several relationships, based on field environmental data, have been used to develop descriptive and predictive models of the acidification process. Dickson's relationship, the Henricksen nomograph, and the episodic receptor/dose relation, appear to be potentially useful empirical models which warrant comparative analysis with similar background data bases. Efforts should be made to conduct additional validation of existing and emerging model descriptions of the process of acidification.

2. Relatively detailed simulation models of the acidification process, and its effects, are being developed by several research groups. These should be evaluated, using watershed data bases from a number of intensive study sites in sensitive areas, as identified in this report. If important data are presently missing at these sites, they should be added to the measurement program, or if certain summaries are not being made, these should be added. The need is to have the most complete, quantitative long-term dose/response models evaluated fully and compared with the more empirical field relationships now in use. In support of this validation process, every effort should be made to maximize the use of existing information from all sources.

Reasonable validation of both types of models will require considerable new research. Study areas for evaluating atmospheric transport models (see Work Group II report) and loading predictors should coincide with detailed studies of sensitive receptor areas. Locations which already have some data, and which should be considered, include:

1. Experimental Lakes Area - Ontario
2. Boundary Waters Canoe Area Wilderness - Minnesota
3. Algoma Area Watershed Study - Ontario
4. Dorset-Haliburton Study Area - Ontario
5. ILWAS Project - New York
6. Laurentide Park (Lac Laflamme) - Québec
7. Kejimkujik Park - Nova Scotia
8. Hubbard Brook - New Hampshire
9. Northern Highlands Lakes - Wisconsin
10. Coweeta - North Carolina
11. Andrews - Washington

3.10.2 Long-Term Data Collection and Monitoring

The present limited ability of the scientific community to assess critically the extent of impacts from elevated acidity in precipitation, and from other components of atmospheric deposition, is a consequence of few reliable baseline observations on sensitive aquatic environments. This lack of systematic data arises, primarily, because many studies and monitoring programs were planned to define the influences of local anthropogenic development and are, therefore located near these influences. Because acidification is of greatest importance in remote areas unaffectd by local discharges, very few areas exist with any long-term baseline information.

Filling this information gap as quickly as possible should be a priority in both the U.S. and Canada. This information is needed so that positive, definitive analyses of ecosystem response to the changes in atmospheric deposition can be carried out, with extensive verification. Unless a monitoring program is in place and providing a documented time-series of system properties, there will be no significant capacity to quantify the results of either emission reductions or increases.

While a variety of data needs have been implicit throughout the aquatic effects section, certain classes of long-term measurements are needed at selected sites. Included are the following four:

1. Since a major component of aquatic research is the calibrated watershed, long-term studies of these systems should be intensified with the general objective of improving the estimates of rates of changes in water quality and biological effects relative to acid loadings (i.e., dose/response relationships), improving the understanding of the relative influence of sulphur and nitrogen loading; and establishing better measures of lake sensitivity, so that the present and potential extent of the problem can be more clearly defined.

2. Analyses should be undertaken of all available baseline studies including regional monitoring of surface water quality, plankton, fauna, soil, and vegetation records.

3. Criteria for selection of streams and lakes for new monitoring of water quality and biota should include factors related to alkanity sources, lake morphometry, watershed morphometry, groundwater inputs, vegetation cover (i.e., age of forest and community structure), surface water chemistry, groundwater chemistry, and type of biotic community (cold water, warm water etc.). The regions and lakes chosen for analysis should range from very sensitive, through moderately sensitive, to "tolerent" (reference lakes), although a geographic grid of comparable sites should also be developed. Data collected should include chemical and biological parameters identified as susceptible to change.

4. Experimental manipulations should be carried out, using adjacent watersheds with small lakes. Watershed-level experiments should include "simulated acid precipitation" additions of H^+, SO_4^{2-}, NH_4^+, NO_3^-, etc., so that long-term recovery, following termination of acid additions, can be investigated.

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SECTION 4

TERRESTRIAL IMPACTS

4.1 INTRODUCTION

A number of air pollutants, generated by various sources, cross international, state and provincial boundaries. The main pollutants which are, or have the potential to be, harmful to terrestrial ecosystems are oxides of sulphur (SO_x), oxides of nitrogen (NO_x), particulates, and secondary products, such as oxidants and acid precipitation.

Sulphur dioxide (SO_2) is emitted at phytotoxic concentrations by a large number of mainly anthropogenic sources, including power plants and smelters. Most of this SO_2 is deposited in dry forms near the sources, though some is transformed chemically in the atmosphere to other sulphur compounds. A moderate amount of SO_2 remains in the atmosphere, to be widely distributed as such. In areas remote from sources, the concentration of SO_2 near the ground is close to background levels, and not likely to cause adverse direct effects. However, SO_2 is transformed in the atmosphere through a series of reactions, into sulphuric acid (H_2SO_4), and thus contributes to the formation of the secondary pollutant, acid precipitation. Similarly, NO_x, which give rise to nitric acid (HNO_3), are likewise precursors of acid precipitation. Ozone (O_3) is also a secondary pollutant, not emitted directly, but formed in the atmosphere in the presence of sunlight, after chemical transformations of nitrogen dioxide and reactive hydrocarbons.

In summary, both acid precipitation and O_3 are long-range transported pollutants. They occur in relatively high concentrations in ambient air, at distances of hundreds of kilometers from the source of the precursor pollutants.

At this time, there is a need for improved understanding of the ecological effects of these primary and secondary pollutants on terrestrial ecosystems. Field and laboratory studies have already provided extensive documentation of the direct effects of SO_2 and O_3 on vegetation (Linzon 1981, National Academy of Sciences 1977, Rennie and Halstead 1977, Shriner et al. 1980)

It has been more difficult to determine adverse or beneficial effects of acid precipitation on plant communities. Although simulated rainfall experiments have produced some direct, (i.e., "contact") effects on plants exposed to higher than normal hydrogen-ion (H^+) loadings, direct effects have not been documented conclusively in the field for vegetation exposed to ambient precipitation (Jacobson 1980). However, several studies have demonstrated the direct effects of acid deposition on soils.

Indirect, (i.e., acting through soil, other organisms, etc.) effects of acid precipitation, and the implications thereof, are even less well known. Increases in acid deposition, it is postulated, could result in accelerated changes in the natural evolution of soils, leading to alterations in soil fertility over the long term.

Such alterations in soil chemistry could have detrimental implications for long-term sustained agricultural and forest productivity. In addition, it could have an important implication for, and linkage with, aquatic sensitivity.

This section on terrestrial effects of transboundary air pollutants is presented in three parts: (1) effects on vegetation; (2) effects on soil; and (3) sensitivity assessment.

4.2 EFFECTS ON VEGETATION

Injury to plants, resulting from exposure to atmospheric O_3, is well-known and well-documented in the literature. Visible injury is apparent, either as pigmented lesions, bleaching, topical necrosis and/or general chlorosis (Hill et al. 1970). Potential injuries resulting from direct exposure of plants to acid precipitation have variously been suggested (Cowling 1979, Cowling and Dochinger 1980, Tamm and Cowling 1976, 1977) as follows:

(1) Damage to protective surface structure such as cuticle.
(2) Interference with normal functions of guard cells.
(3) Poisoning of plant cells, after diffusion of acidic substances through stomata or cuticle.
(4) Disturbance of normal metabolism or growth processes, without necrosis of plant cells.
(5) Alteration of leaf- and root-exudation processes.
(6) Interference with reproduction processes.
(7) Synergystic interaction with other environmental stress factors.
(8) Accelerated leaching of substances from foliar organs.
(9) Increased susceptibility to drought and other environmental stress factors.
(10) Alteration of symbiotic associations.
(11) Alteration of host-parasite interactions.

In addition, acid precipitation contains plant nutrients; thus, beneficial as well as harmful effects must be considered.

4.2.1 Agricultural Crops

To permit economic analyses to be performed, data must be provided in terms of per-area change of yield of various crops, attributable to concentrations of certain pollutants or combinations of pollutants.

Farmlands of eastern North America are exposed to elevated concentrations of O_3 repeatedly during the growing season and to acid deposition from the atmosphere throughout the year. How long can agriculture continue to be exposed to acid precipitation, without significant reductions in productivity beyond those believed to be caused by O_3 alone? Can agricultural systems accept and adjust to, ad infinitum, present rates of acid deposition? These are two of the main issues that need to be addressed.

In addition, it is necessary to determine the influence of additional doses of O_3 and increases in rate of acid deposition. Will the occurrence of additional effects be gradual and demonstrable only in retrospect, and after many decades? Or will a point be reached at which small increases in dose of O_3 or acidity will produce large reductions in productivity? In other words, can we expect sudden and dramatic effects on vegetation to occur at some time in the future?

Perhaps of greatest difficulty is the necessary estimation of benefits that may accrue from reductions in O_3 concentrations and decreases in acid deposition. Resolution of this question is made particularly difficult by the possibility that nitrate (NO_3^-) and sulphate (SO_4^{2-}), supplied in rain are utilized by plants as nutrients to aid plant growth. Does the deposition of NO_3^- and SO_4^{2-} compensate for, or overcome, any deleterious effects of excess atmospheric O_3 or acid precipitation?

Three subjects must be addressed to evaluate current information: 1) Which processes in crops are subject to alteration by O_3 and acid precipitation? 2) How is evidence gathered on the responses of crops to these pollutants? 3) What are the results of recent experiments concerning the potential for beneficial and harmful effects, and for interactive effects between O_3 and acid precipitation?

Direct effect on agricultural productivity can occur through various biological mechanisms. Direct contact of O_3 and/or acids with vulnerable organs can alter assimilative processes, allocation of photosynthate, or can interfere with reproductive development. Absorption of some NO_3^- and SO_4^{2-} by foliage, on the other hand, may be of nutritional benefit, and may promote growth and development. Chemical and morphological alterations of leaf surfaces may likewise change the capacity of plants to resist disease and/or insects. Further, alterations in growth and development can modify the capacity of plants to resist other stresses, such as those related to deficiences of nutrients of soil moisture. Given these, and other, possibilities, what types of experiments have been performed to determine the effects of O_3 and acid precipitation on crops?

Three approaches have been used: 1) observations of field-grown crops; 2) experimental studies with field-grown crops; and 3) experimental studies performed with plants grown in the greenhouse or in controlled-environmental chambers. There are important advantages and limitations to each of these approaches. Field observations provide information under ambient conditions; therefore, no extrapolation from an artificial environment is required. Unfortunately, the lack of controls (unexposed plants), the multiplicity of factors that fluctuate with time, and the non-homogeneity of plants and conditions, make it difficult to draw certain conclusions concerning effects of pollutants. Field observations of effects of O_3, however, have some utility, because foliar symptoms caused by O_3 do occur in the field, there are differences in dose of O_3 from one region to another, and field diagnosis is aided by the presence of biological indicators for O_3. However, acid precipitation does not appear to have these advantages. No unequivocal examples of foliar symptoms produced by acid precipitation on field-grown vegetation have yet been reported in North America; indicator species have not yet been identified.

Experimental studies with O_3 have provided important results, indicating that reductions in yield probably occur for such crops as beans, tobacco, potatoes, onions, radishes, grapes, corn, and others (Heggestad 1980, Jacobson 1980, Reinert 1975). In general, these studies indicate that frequent exposure during the growth season to O_3 concentrations in excess of 0.1 ppm may produce yield losses of at least 20 per cent for susceptible crops (Table 4-1).

A substantial majority of presently-operating O_3 monitors, in both the United States and Canada, are in urban locations, thereby calling into question their ability to represent levels to which rural vegetation is exposed. However, some indication of the occurrence of O_3 in rural areas is given in Table 4-2, for a 200 km long south-north transect in southern Ontario. Values are for 1980, and are given as exposure-hours (for the year) in excess of 0.08 ppm (present Ontario standard) and 0.10 ppm (used in Table 4-1). In addition, maximum recorded concentrations are also given. A similar compilation (Table 4-3) is also available for selected locations in New York State, given as the number of times the standard was exceeded per year for 1978 and 1979, in relation to two standards (Hunt et al. 1981).

In contrast to results with O_3, experimental studies with simulated acid precipitation have produced both positive and negative results (Jacobson 1980, Shriner 1978). Increases and decreases in yield, as well as no significant effects, have been found, depending on concentrations of acids, plant species and cultivars, pattern and timing of rain applications, and soil, environmental, and cultural conditions (Irving and Miller 1980, Lee et al. 1981). Each species may thus have unique patterns of physiological and genetic responses to the potentially beneficial and detrimental components of acid precipitation.

Experimental studies with plants grown under controlled (or semi-controlled) conditions have demonstrated that visible foliar symptoms can be readily produced on certain crops, when pH of applied rain is

TABLE 4-1

EFFECTS OF LONG-TERM CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD, AND FOLIAR INJURY TO SELECTED PLANTS

Plant Species	Ozone Concentration μg/m^3 (ppm)	Exposure time, hr	Plant response, percent reduction from control	Reference
Lemna, duckweed	196 (0.10)	5/day, 14 days	100, flowering; 36, flowering (1 wk after exposure completed) 50, frond doubling rate	(Feder & Sullivan,1969)
Carnation	98-177 (0.05-0.09)	24/day, 90 days	50, flowering (reduced vegetative growth)	(Feder, 1970)
Geranium	137-196 (0.07-0.10)	9.5/day, 90 days	50, flowering (shorter flower lasting time, reduced vegetative growth)	
Petunia	98-137 (0.05-0.07)	24/day, 53 days	30, flower fresh wt	(Craker, 1972)
Poinsettia	196-235 (0.10-0.12)	6/day, 5 days/week, 10 weeks	39, bract size	(Craker & Feder, 1972)
Radish	98 (0.05)	8/day, 5 days/week, 5 weeks	54, root fresh wt 20, leaf fresh wt	(Tingey et al, 1971)
	98 (0.05)	8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	63, root fresh wt 22, leaf fresh wt	
Beet, garden	392 (0.20)	3/day, 38 days	50, top dry wt	(Ogata & Maas, 1973)
Bean, cultivar Pinto	255 (0.13)	8/day, 28 days	79, top fresh wt 73, root fresh wt 70, height	(Manning et al, 1971)
Bean, cultivar Pinto	290 (0.15)	2/day, 63 days	33, plant dry wt; 46, pod fresh wt	(Hoffman et al, 1973)
	490 (0.25)	2/day, 63 days	95, plant dry wt; 99, pod fresh wt	
	686 (0.35)	2/day, 63 days	97, plant dry wt; 100, pod fresh wt	
Bean, cultivar Pinto	290 (0.15)	2/day, 14 days	8, leaf dry wt	(Maas et al, 1973)
	290 (0.15)	3/day, 14 days	8, leaf dry wt	
	290 (0.15)	4/day, 14 days	23, leaf dry wt (Data available on whole plants, roots, leaves, injury, and 3 levels of soil moisture stress)	
	290 (0.15)	6/day, 14 days	49, leaf dry wt	
	440 (0.225	2/day, 14 days	44, leaf dry wt	
Bean, cultivar Pinto	440 (0.225)	4/day, 14 days	68, leaf dry wt (Data available on whole plants, roots, leaves, injury and 3 levels of soil moisture stress)	(Maas et al, 1973)
	588 (0.30)	1/day, 14 days	40, leaf dry wt	
	588 (0.30)	3/day, 14 days	76, leaf dry wt	
Tomato	392 (0.20)	2.5/day, 3 days/week 14 weeks	1, yield; 32, top dry wt; 11, root dry wt	(Oshima et al, 1975)
	686 (0.35)	2.5/day, 3 days/week, 14 weeks	45, yield; 72, top dry wt; 59 root dry wt	
Corn, sweet cultivar Golden Jubilee	392 (0.20)	3/day, 3 days/week till harvest	13, kernel dry wt; 20, top dry wt; 24, root dry wt	(Oshima, 1973)
	686 (0.35)	3/day, 3 days/week till harvest	20, kernel dry wt; 48, top dry wt; 54, root dry wt	
Wheat, cultivar Arthur 71	392 (0.20)	4/day, 7 days (anthesis)	30, yield	(Kochar, 1974)
Soybean	98 (0.05)	8/day, 5 days/week 3 weeks	13, foliar injury	(Tengey et al, 1973)
		8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	16, foliar injury 20, root dry wt	
Soybean	196 (0.10)	8/day, 5 days/week 3 weeks	21, top dry wt 9, root dry wt	
Alfalfa	196 (0.10)	2/day, 21 days	16, top dry wt	(Hoffman et al,1974)
	290 (0.15)	2/day, 21 days	26, top dry wt	
	390 (0.20)	2/day, 21 days	39, top dry wt	
Grass, brome	290-647 (0.15-0.33)(varied)	4/day, 5 days/week growing season	83, biomass	(Price & Treshow, 1972)
Alfalfa	196 (0.10)	6/day, 70 days	4, top dry wt, harvest 1 20, top dry wt, harvest 2 50, top dry wt, harvest 3	(Neeley et al, 1977)
Alfalfa	98 (0.05)	7/day, 68 days	30, top dry wt, harvest 1 50, top dry wt, harvest 2	
Alfalfa	98 (0.05)	8/day, 5 days/week 12 weeks	18, top dry wt	(Tingey & Reinert, 1975)
Pine, eastern white	196 (0.10)	4/day, 5 days/week 4 weeks (mixture of O_3 & SO_2 for same periods)	3, needle mottle (ovar 2-3 days of exposure)	(Dochinger & Seliskar, 1970)
Pine, pondernsa	290 (0.15)	9/day, 10 days	4, photosynthesis	(Miller et al, 1969)
Pine, ponderosa	290 (0.15)	9/day, 20 days	25, photosynthesis	
	290 (0.15)	9/day, 30 days	25, photosynthesis	
	290 (0.15)	9/day, 60 days	34, photosynthesis	
	588 (0.30)	9/day, 10 days	12, photosynthesis	
	588 (0.30)	9/day, 20 days	50, photosynthesis	
	588 (0.30)	9/day, 30 days	72, photosynthesis	
	880 (0.45)	9/day, 30 days	85, photosynthesis	

TABLE 4-1 (cont'd). EFFECTS OF LONG-TERM CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD, AND FOLIAR INJURY TO SELECTED PLANTS

Poplar, yellow	588 (0.30)	8/day, 5 days/week 13 weeks	82, leaf drop; 0, height	(Jensen, 1973)
Maple, silver	588 (0.30)	8/day, 5 days/week, 13 weeks	50, leaf drop; 78, height	
Ash, white	588 (0.30)	8/day, 5 days/week 13 weeks	66, leaf drop; 0, height	
Sycamore	588 (0.30)	8/day, 5 days/week 13 weeks	0, leaf drop; 22, height	
Maple, sugar	588 (0.30)	8/day, 5 days/week 13 weeks	28, leaf drop; 64, height	
Corn, sweet, cultivar Golden Midget	98 (0.05)	6/day, 64 days	9, kernel dry wt; 14, injury (12, avg. 4 yield responses)	(Heagle et al, 1972)
	196 (0.10)	6/day, 64 days	45, 25, 35 for same responses	
Pine, ponderosa	196 (0.10)	6/day, 126 days	12, root length 21, stem dry wt; 26, root dry wt	(Wilbour & Neely, 1977)
Pine, western white	196 (0.10)	6/day, 126 days	13, foliage dry wt 9, stem dry wt	
Soybean, cultivar Dare	98 (0.05)	6/day, 133 days	3, seed yield; 22, plant fresh wt 19, injury, defoliation, no reduction in growth or yield	(Heagle et al, 1974)
	196 (0.10)	6/day, 133 days	55, 65, 36 for same responses	
Poplar, hybrid	290 (0.15)	8/day, 5 days/week 6 weeks	50, shoot dry wt; 56, leaf dry wt 47, root dry wt	(Jensen & Dochinger, (1974)

(U.S. EPA, 1978)

TABLE 4-2. EXPOSURE-HOURS TO OZONE AT RURAL LOCATIONS IN SOUTHERN ONTARIO FOR 1980.

Location	Hours above 0.08 ppm	Hours above 0.10 ppm	Max. conc ppm
Merlin, Kent Co.	61	11	.137
Petrolia, Lambton Co.	39	8	.125
Huron Park, Huron Co.	41	6	.120
Tiverton, Bruce Co.	4	0	.088

(data, Ontario MOE)

TABLE 4-3. OZONE CONCENTRATIONS AT SOME LOCATIONS IN NEW YORK STATE.

		Number of times standard exceeded per year			
		Former NAAQS[1]		Current NAAQS[2]	
		1978	1979	1978	1979
Yonkers	(urban)	329	-	29	-
Whiteface Mt.	(rural)	297	300	0	0
Fredonia	(rural)	-	146	-	2
Geneva	(rural)	116	-	3	-
Ithaca	(rural)	55	-	0	-

[1] Former NAAQS = 0.08 ppm, one hour average, not to be exceeded more than one hour per year.

[2] Current NAAQS = 0.12 ppm, one hour average, not to be exceeded more than one day per year.

3.5 or less (Table 4-4). Field-grown plants may be less susceptible to the development of foliar symptoms than plants grown under controlled or semi-controlled conditions (Jacobson 1980, Shriner 1978). Further, as with O_3, foliar symptoms may not correlate closely with yield reductions (Lee et al. 1981). Recent evidence, however, suggests that generalizations concerning effects on crops from experiments with O_3 alone, or with acid precipitation alone, may under-estimate the interactive effects of exposures to these two pollutants (Jacobson et al. 1980). Further research is needed to determine if acid precipitation enhances the likelihood of actual yield reductions, in areas also experiencing repeated exposures to elevated concentrations of O_3.

In studies with soils and in studies on aquatic systems, focus has often been on relationships with mean annual deposition rates. Characteristics of individual rain events may have greater significance, in producing direct effects on agricultural crops, than such average annual rates. Although annual pH values of rain are as low as 4.0 in eastern North America, concentrations of H^+-ions (and SO_4^{2-} and NO_3^-ions) may be ten times greater than average, during individual event. The one (or several) most acid event of a growing season may have greater significance for production of direct effects on annual crops than average deposition rates.

The potential for crop damage in the field is further amplified substantially by agricultural practices. Economic constraints in any given area and year tend to result in the exposure of extensive areas of a given crop in a relatively uniform state of plant development. The onset of the cycle of flowering physiology, pollen dispersal and fertilization, and photosynthetic partitioning, could all be potentially susceptible to extensive damage over vast areas (for example, several millions of acres of soybeans in the soybean producing areas of the Mississippi River basin) from a single event, even of modest acidity. Further, a combination of events occurring, say, late in the day, when normal processes, such as stomatal closure, are keyed to light conditions, could prove critical to plant production processes.

To evaluate the economic cost of O_3 and acid precipitation to agricultural crops, answers to several questions are needed. Which crops are actually benefited by components of acid precipitation? Which crops are most susceptible to reductions in yield by exposure to O_3 and acid precipitation? Much information is available for O_3 (National Academy of Sciences 1977), but only preliminary indications are available for acid precipitation (Lee et al. 1981). The dose-response function needs to be provided with quantitative descriptions of dose of O_3, acidity, and yield that relate to actual conditions. Again, some information is available for effects of O_3 on crops, but not for acid precipitation. The influence of other parameters on these dose-response functions needs to be provided for such factors as patterns of rainfall occurrence, as they interact with stage of crop development, soil nutrient and water

TABLE 4-4 REPRESENTATIVE TOLERANCE LIMITS TO SIMULATED ACID PRECIPITATION

Species	Pollutant Concentration	Effect	Source
birch	pH 2.0 - 2.5	- foliar lesions	Abrahamsen et al. 1976
willow herb			
Scots pine			
mosses	pH 3.0		
lichens	pH 4.0	- reduced N fixation rate	Dennison et al. 1976
sunflower, bean	pH 2.7	- foliar damage	Evans et al. 1977
hardwoods	pH 2.5	- foliar damage	Haines and Waide 1980
wheat, grasses	pH 4.0	- root biomass reduction	
radish	pH 3.5	- foliar damage	Lee et al. 1980
beet	pH 4.0		
carrott	pH 4.0	- reduced yield	
mustard greens	pH 3.5	- foliar damage and reduced marketability	
spinach			
swiss chard			
tobacco	pH 3.5	- foliar damage	
lettuce			
broccoli/cauliflower	pH 3.5	- foliar damage	
cabbage	pH 3.0		
broccoli	pH 3.0	- reduced yield	
potatoes	pH 3.0	- foliar damage reduced yield	
	pH 3.5 - 4.0	- increased yield	
alfalfa	pH 3.5	- foliar damage	
	pH 3.5 - 4.0	- increased yield	
kidney beans	pH 3.2	- inhibition of parasitic organisms	Shriner 1976
oak			
conifer seedlings	pH 2.0	- foliar damage	Strifler & Kuehn 1976
mosses	pH 2.0 - 3.0	- dessication, death	Teigen et al. 1976
chrysanthemums	pH 3.0	- foliar damage and increased phosphate uptake	Tukey 1980
juniper	pH 4.0+		
yellow birch	pH 2.3 - 4.7	- pitting, curl shortening, death	Wood and Bormann 1974

1/ The average precipitation pH in eastern North America is currently greater than or equal to pH 4.0. Individual storm events may have episodes where the pH drops into the range of pH 3.0 to 4.0.

supplies, and deposition of particulate matter from the atmosphere. The modifying influence of absorption of NO_3^- and SO_4^{2-} on response to different doses of O_3 and rainfall acidity, and its significance, require clarification, so that predictions can be made for alternate futures, concerning changes in O_3 concentrations and the composition of precipitation. Finally, the critical factors determining plant susceptibility to yield reductions by O_3 and acid precipitation need to be determined, in order to extrapolate information from a few species and cultivars. When this information is provided, it may then be possible to make reasonable and reliable estimates of the economic impact of O_3 and acid precipitation on agricultural productivity.

4.2.2 Forest Ecosystems

As in the case of agricultural crops, economic evaluation of the effect on forest productivity is ultimately contingent upon the establishment of dose-response relationships, presumably between pollutant loadings, on the one hand, and some quantitative measure of growth-depression, or yield-depression, on the other.

Effects of O_3 and acid precipitation on forest trees involve several considerations which differ from those which are a matter for concern with regard to agricultural crops. Trees are perennial plants, with long lifetimes. Thus, there is greater concern with the cumulative impact of repeated exposures to O_3 and acid precipitation. Furthermore, forests are usually in areas where soil nutrient supplies are limited, and are generally not supplied with fertilizers or lime. Forests present large surface areas for interception of gaseous and particulate pollutants from the atmosphere, and these substances eventually move to the soil. Finally, the composition of precipitation as it passes through the forest system, the properties of soil, and characteristics of streams and lakes in watersheds are all, in part, affected by the nature, age, and condition of forests. Consequently, the effect of O_3 and acid precipitation on forests could also have important secondary impacts which are initiated by direct effects on trees.

In general, many tree species indigenous to North America are classified as susceptible to O_3 damage. Direct injury to tree foliage by O_3 has been demonstrated repeatedly in experimental situations (Table 4-1), and in nature as well. Concentrations of O_3, at least in some forested areas, are sufficient to cause injury (Skelly 1980). These effects of O_3, can alter the productivity, successional patterns, and species composition of forests (Smith 1980).

Concerning acid precipitation, attention is first drawn to one line of "direct" evidence, being the historic pattern of forest growth, as revealed in the growth rings. In a controversial study, based on a substantial analysis of growth rings of Scots pine and Norway spruce trees, growing in spatially-intermixed "more-susceptible" and "less-susceptible" regions in south Sweden, Jonsson and Sundberg (1972) concluded that "acidification cannot be excluded as a possible cause of the poorer growth development, and may be expected to have had an unfavourable effect on growth within the more susceptible regions". Other Scandinavian researchers, however, have not been able to uncover similar trends. Strand (1980), for example, in a large study in Norway, was unable to "find definite evidence that acid precipitation has had an effect on the growth of the trees". Studies of a similar type in North America have been, for the most part, of limited scope. Cogbill (1976), having examined historic patterns of growth rings in two forest stands, one a beech-birch-maple woods in New Hampshire, the other a spruce woods in Tennessee, observed that "no regional, synchronized decrease in radial increment was evident in the two mature stands studied". Johnson et al. (in prep.), however, noted both an abnormal decrease in growth of pitch pine on the New Jersey pine barrens, and a strong statistical relationship between stream pH (an index of precipitation pH) and growth.

Experimental evidence from studies of the action of acid precipitation on tree parts does indicate, however, that, under regimes of high acid dosing, direct damage, such as foliar lesions, can be produced (Table 4-4).

A potential impact of acid precipitation may occur indirectly through the soil, and in particular, in relation to the complex natural circulation of elements upon which forest vegetation depends, known as the nutrient, or biogeochemical, cycle. Rodin and Bazilevich (1967) describe this cycle of elements as "The uptake of elements from the soil and the atmosphere by living organisms, biosynthesis involving the formation of new complex compounds, and the return of elements to the soil and atmosphere with the annual return of part of the organic matter or with the death of the organisms". Interrelationships in the cycle are such that a change in one part of the system, if not counteracted, could ultimately produce changes throughout.

Generally, forests are relegated to soils which are of low fertility or, for some other reason, unsuited to agriculture. Further, in contrast to agricultural practice, ammendments such as fertilizers or lime are little-used in forestry practice. First, however, what evidence is there that nutrient availability is of significance in forest growth in eastern North America?

Deficiencies of nitrogen (N) are common in forests of the temperate and boreal regions. Appreciable response to N-fertilizer has been reported frequently, particularly for conifers on upland sites in both the acid rain zone of eastern Canada (Foster and Morrison 1981), and in Scandinavia (Malm and Moller 1975, Moller 1972). In a small number of fertilizer field trials carried out with conifers in Canadian forests, phosphorus (P), potassium (K), calcium (Ca) or magnesium (Mg) fertilizers did appear to elicit responses, though only when demand for N was first met (Foster and Morrison 1981, Morrison et al. 1977).

Growth of red pine and other conifers has been shown to be limited by K and Mg deficiency in restricted areas of New York State (Heiberg and White 1951, Leaf 1968, 1970, Stone 1953), and Quebec (Gagnon 1965, Lafond 1958, Swan 1962).

The generally-held association of base-rich with more fertile soils and base-poor with less fertile soils (well-demonstrated in agricultural situations) has been investigated with forest species and soils in only a limited number of instances. Pawluk and Arneman (1961) associated better growth of jack pine on sites in Minnesota and Wisconsin with several soil factors which could be considered acid rain sensitive, including cation exchange capacity (CEC), exchangeable K and percent base saturation. Also with jack pine, Chrosciewicz (1963), in northern Ontario, associated better growth with soils rich in basic minerals (and presumably richer in exchangeable in bases). Hoyle and Mader (1964), studying foliage contents, noted a high degree of correlation between Ca content and height growth of red pine in western Massachusetts. Similarly, Lowry (1972), with black spruce across a wide range of sites in eastern Canada, noted relationships between site index, on the one hand and foliage N, P, Ca, and to a lesser extent, Mg concentrations, on the other.

Studies of Adirondack forest soils (Lee et al. 1979) indicate that Ca and Mg levels in strongly acid soils limit growth of certain deciduous trees. Leaching of these elements from forest soils, as a result of high SO_4^{2-} mobility (Mellitor and Raynal 1981), may cause a chronic decrease in nutrient status of certain soils.

Since nutrient availability is a significant growth-limiting factor for many forest ecosystems, the concern is that acid precipitation will interfere with uptake and cycling of various elements. First, acid precipitation may promote increased leaching of essential foliar constituents, such as K, Ca and Mg, as a function of both acid-related surface disintegration and mass exchange by H^+ ions.

Both wet and dry precipitation undergo chemical alteration on contact with leaves, both on the surface, and, indirectly, within cellular tissue. The nature of the leachate or throughfall depends upon plant characteristics, such as tree species and leaf morphology; stand characteristics, such as age and stocking; and site conditions, including precipitation rate, distribution and chemical composition. Input/output analyses and element budgets, with particular reference to acid precipitation, have been described by various authors (Lakhani and Miller 1980, Mayer and Ulrich 1980, Tukey 1980). Generalizations are difficult, because of the wide range of environmental (soil, water, climate) conditions.

Not all elements are leached equally, and, although all plant parts can be leached, young leaves are less suceptible to leaching than mature foliage (Tukey 1980). Some elements, such as K, leach readily from both living and dead parts. Elements such as Ca leach more slowly.

Leaves only need to be wetted to initiate leaching, with further increases in precipitation having little additional effect. As cation removal increases over time, it is suggested that only with adequate nutrient supply are plants able to withstand brief, frequent rain events. Based on preliminary studies under spruce, it appears that leaching of Ca and Mg is pH dependent in the range pH 7.0 to 3.0.

Some researchers have found that throughfall from deciduous forest exhibits increased pH and higher Ca and Mg concentrations, when compared to the incident precipitation. In other instances, the opposite has been found. In studies of two hardwood species (sugar maple and red alder), little difference in throughfall chemistry was reported (Lee and Weber 1980). Stemflow from birch species shows increased acidity, relative to the incident precipitation (Abrahamsen et al. 1977). Beneath coniferous canopies, throughfall pH generally decreases, relative to precipitation in open areas, although concentrations of Ca and Mg, as well as many other dissolved ions, may increase (Horntvedt and Joranger 1976). This ion enrichment is due to both washout of dry deposits and canopy leaching. It has been reported that 90 per cent and 70 per cent of the H^+ in precipitation was retained in the forest canopy, in New Hampshire northern hardwood (Hornbeck et al. 1977) and Washington Douglas-fir (Cole and Johnson 1977) forests, respectively. Leaching of low molecular weight organic acids from the canopy may decrease the pH of throughfall (Hoffman et al. 1980).

Spruce canopies may filter dry pollutants from the atmosphere better than deciduous canopies. This cleansing action is attributed, in part, to the presence of spruce needles throughout the winter, during which SO_2 is dissolved in water films adhering to their surfaces. Subsequent removal of these deposits accounts, in part, for difference in chemical composition of the throughfall.

Contact of precipitation with vegetation results in repartitioning of chemical components, in that substances in precipitation can be absorbed by the foliage, and substances in and on the foliage can be leached and recycled, to the same plant or nearby plants. The direction of this exchange depends on the availability for exchange of a given component within each system, and permeability of plant surfaces to either uptake or egress. Throughfall studies demonstrate an enrichment of inorganic ions in the precipitation after contact with vegetation, with increasing losses of cations as the H^+ ion concentration in simulated precipitation increases. Laboratory experiments have demonstrated leaching of a wide variety of organic substances, including growth regulators, amino acids, carbohydrates and organic acids.

In summary, several processes may be affected when rainfall passes through a forest canopy. Substances residing on and in foliage are removed. These processes occur, not only with acid precipitation, but also with non-acid precipitation. Certain elements are leached more rapidly than others, especially when rainfall is acidic, and differences exist between species and stages of leaf development in rates of leaching. Leaching results in a marked change in the chemistry of precipitation before it reaches the soil. Dry deposits removed from leaf surfaces and substances lost from foliar tissues may neutralize, or may enhance, acidity, and concentrations of inorganic substances may increase considerably. More rapid transfer of elements to the soil provides opportunities for enhanced uptake and recycling by trees. Moreover, soil processes may also be affected by these deposits. Several pathways exist by which changes to precipitation occurring in the forest canopy can affect the chemistry of water transported through the terrestrial ecosystem and into streams and lakes. These are discussed further in other sections of this report.

Acid precipitation may affect health and/or productivity of forest, or other, vegetation through other than direct channels, or through effects on nutrition.

Whether there is a relationship, or not, between the occurrence of serious forest tree diseases, such as Scleroderris canker of conifers or scale insect Nectria canker of beech, and precipitation acidification in North America, is unknown. Research efforts are just beginning to evaluate the possible role of acid precipitation in the predisposition of trees to disease infection and insect attacks. Further, the behavior of plant litter and soil-occurring facultative saprobes, which may exhibit plant pathogenic tendencies under acidification, requires evaluation.

4.3 EFFECTS ON SOIL

Soils vary widely with respect to their properties (physical, biological, chemical and mineralogical), support different vegetation communities, are subjected to different cultural practices, are situated in different climatic zones, and are exposed to a broad spectrum of acid loadings. Thus caution must be exercised in generalizing from findings indicated herein. Further, there are various offsetting mechanisms, which may influence effects of increased precipitation acidity, and which, likewise, vary with soil properties, vegetation types, climatic regimes and cultural practices. Also, movement of water through natural soils involves not simply uniform capillary and gravitational processes but, at times, considerable moisture flow, may be directed overland as overland flow, or may be channelized in the soil in root channels, with reduced opportunity for equilibration. Thus, results from in situ studies may, at times, be at variance with theoretical calculations.

In the discussion which follows, the documented and hypothesized effects of acidic deposition on soils are described under the following headings:

1) Effects on Soil pH and Acidity
2) Impact on Mobile Anion Availability, Base Leaching, and Cation Availability

3) Influence on Soil Biota and Decomposition-Mineralization Activities
4) Influence on Phosphorus Availability
5) Effects on Trace Element and Heavy Metal Mobilization and Toxicity
6) Impact on Clay Minerals and CEC

4.3.1 Soil pH and Acidity

It has been hypothesized that atmospheric deposition of strong acids and acid-forming substances may increase the rates of soil acidification in unmanaged forest soils. Increases in soil acidity are generally accompanied by decreases in the availability of several essential macro-nutrient elements, including Ca, Mg, K, N, and P. In addition, soil acidification can also lead to mobilization of certain pH-dependent trace elements (e.g., aluminum (Al), manganese (Mn), zinc (Zn), and iron (Fe)), sometimes to the point of toxicity. For reference, Table 4-5 presents an overview of the soil elements and reactions which may be affected by changes in acidity.

The process of soil acidification primarily involves the replacement of exchangeable basic cations (Ca, Mg, K, Na, NH_4^+) by H^+ and, at lower pH ranges, Al^{3+} ions. The chemistry of soil acidification is relatively well understood, and has been described by Jenny (1961), Wiklander (1973/74, 1975, 1980), Bache (1980), and Nilsson (1980). The common range of pH for soils in humid regions is about pH 5.0 to 7.0, with the preferred range for cultivated soils being pH 6.0 to 7.0. Many forested soils, particularly under coniferous cover, fall within the range pH 4.5-5.5 in the mineral horizons, with surface organic layers commonly exhibiting pH's in the range 3.5 to 4.5. For reference, Table 4-6 presents the terms used in soil science to describe soil acidity.

Various field and laboratory experiments have been conducted to examine the effects of acidic deposition on soil acidity. Results have indicated that artificial acid rain at pH's below 4 can lead to measurable decreases in soil pH (Abrahamsen et al. 1976, Bjor and Teigen 1980, Stuanes 1980). For example, simulated acid rain inputs of pH 4.0 and below to spruce podzol soils in Norway caused soil acidification of the O, A, and B horizons (Abrahamsen et al. 1976). In some cases, the soil pH depression, over time, amounted to 0.5 pH units.

In spite of the many experimental studies, it has been difficult to determine, under natural field conditions, the comparative contributions of anthropogenic versus soil-derived acids to soil acidification. The necessary control conditions have simply not been available to permit an unequivocal assessment. Natural soil acidification, it is to be remembered, is an ongoing process in humid regions. Its impoverishing action is compensated for, in part, by weathering of primary minerals, if present, and, where vegetated, by

TABLE 4-5 ACIDITY RELATED REACTIONS INFLUENCING AVAILABILITY OF SEVERAL ELEMENTS

Elements(s)	Type of Reaction
N	Chiefly biological - biochemical;nitrifying bacteria decline with declining pH, thus ammoniacal-N predominates over nitrate-N; reduces mineralization.
P	Phosphate fixation reactions.
K, Ca, Mg	Chiefly mass displacement of absorbed bases by H+ and Al ions.
Fe, Mn	Chiefly dissolution of hydroxides in acid solution; organic status, redox important particularly for Fe.
Al	pH regulated solubility of Al-oxy and hydroxy compounds.

TABLE 4-6 TERMS USED FOR DESCRIPTION OF SOIL ACIDITY

TERM	pH RANGE (IN WATER)
Neutral	6.6 - 7.3
Slightly Acid	6.1 - 6.5
Medium Acid	5.6 - 6.0
Strongly Acid	5.1 - 5.5
Very Strongly Acid	4.5 - 5.0
Extremely Acid	Below 4.5

biological cycling of elements. Thus, atmospheric acid inputs must be assessed within the context of natural acid production in ecosystems. For example, significant H^+ ion production occurs in medium acid to neutral soils (pH 5.5 to 7.0), due to formation of carbonic acid from CO_2 released by decomposition and root respiration (Johnson 1980). Cole and Johnson (1977) found that carbonic acid contributed approximately twice as much H^+ to the soil as precipitation, in a Douglas-fir ecosystem receiving precipitation 3 to 4 times more acid than normal (weighted average annual pH, 4.9). However, a drop in pH to 4.0, about 30 times more acid than normal, such as occurs in the most heavily impacted areas of eastern North America (Cogbill and Likens 1974), would result in H^+ inputs far in excess of that produced by carbonic acid. In more acid soils (pH less than 5.5), such as podzols developed under coniferous forests, organic acids contribute significantly to natural soil acidification. It is not as yet known what role anthropogenic acidification will have in these ecosystems. Presumably, extremely acid soils will experience the least change of pH. However, very low pH events could result in further acidification.

Sollins et al. (1980) proposed a comprehensive scheme for calculating H^+ ion budgets in forest ecosystems, based upon measured mass balances of cations and anions within the nutrient cycles. Andersson et al. (1980) used this model to obtain H^+ ion budgets for forest ecosystems in Sweden, West Germany, and Oregon. In the heavily impacted Solling site in West Germany, their analysis shows that atmospheric H^+ ion inputs are small (approximately 10 per cent) compared to net internal flows. Ulrich (1980), using essentially the same approach, stressed input-output balances to assess the long-term net acidification of soils, because of internal compensations of H^+ production and consumption by uptake and mineralization processes. He also pointed out important spatial considerations within the soil profile. For instance, H^+ - consuming ammonium (NH_4^+) mineralization might occur in litter layers, whereas H^+ - producing NH_4^+ uptake occurs in mineral soil layers at the same time. Some indication of orders of magnitude of H^+ ion contribution by softwood, versus hardwood, forest, and their relationship to anthropogenic loading, were provided (Ulrich 1980). Total H^+ ion input was determined as about *ca* 0.81 keq/ha, of which 0.79 keq/ha was considered man-made. A beech canopy generated an additional *ca* 0.58 keq/ha; a spruce canopy, an additional 2.28 keq/ha. This evidence suggests that, as mean pH of rainfall declines below pH 4, its contribution to the H^+ ion balance is not insignificant, even in comparison to spruce forest H^+ ion production, thus hastening the process of podzolization.

As noted earlier, the adverse effect of soil acidification results chiefly from the influence of changed pH on other processes, such as soil biochemical reactions and N availability, organic matter turnover, mobilization of trace elements, and transformation of clay minerals.

4.3.2 Impact on Mobile Anion Availability and Base Leaching

Acidification and soil impoverishment involve the displacement of basic cations (i.e., K, Ca, Mg, Na, etc.) from exchange surfaces, and their replacement by H^+ and Al^{3+} ions, and the establishment of new exchange/solution equilibria (Wiklander 1973/74, and others). Under natural conditions, two sets of processes seem to be involved. First, there are exchange processes whereby H^+ ions displace base cations from the exchange surface; and second, there are the processes whereby the exchanged ions are transported within the soil column under the influence of mobile anions (Johnson and Cole 1976, 1977).

Soils vary widely in ability to retain cations, i.e., CEC and the relative degree of saturation of the CEC with bases, the latter being referred to as base saturation. Total CEC (permanent and pH dependant) of a productive soil under cultivation, in humid regions, might range from 15-30 meq/100 g, and occasionally higher, in the surface horizons, and to much less in the subsoil. In coniferous podzols, the CEC of the humus layer may be high, but, beneath it, values decrease abruptly with depth. It is presumed that the loss, particularly of those base cations of nutritive value (chiefly K, Ca, Mg), could be accelerated under acid precipitation, with attendant adverse impacts on forest growth.

Various "simulated acid rain" leaching experiments are described in the literature (Abrahamsen et al. 1976, Abrahamsen and Stuanes 1980, Lee and Weber 1980, Morrison 1981, Overrein 1972, Roberts et al. 1980, Singh et al. 1980). In some controlled irrigation experiments, Ca and Mg appear to be the most affected and K the least affected (Abrahamsen 1980, Hovland et al. 1980, Ogner and Teigen 1981, Wood and Bormann 1976). To some extent, this may reflect the relative amounts of these cations on soil exchange sites, but the rate of increase in K depletion seems to be consistently below that for Ca or Mg under acid irrigation as well (Abrahamsen 1980, Ogner and Teigen 1981, Wood and Bormann 1976). The relative lack of response in K may also be due to the greater plant requirements for K, as opposed to Ca or Mg, and possibly also to fixation of K in 2:1 clays.

In some cases, the accelerated cation leaching has led to net depletion of available cations in the rooting zone. Significant reductions of base saturation percentage were noted in the O and A horizons in Norwegian spruce podzol soils, following applications of simulated acid rain with a pH of 3.0 or lower (Abrahamsen 1980).

By way of qualification, it should be noted that soil acidification and decreases in base saturation do not always occur concurrently. Under natural soil acidification by humic acids, production of humus increases CEC, but does not increase the cation content (Kononova 1966). Soil pH and base saturation will thus decrease without a corresponding reduction in exchangeable base content (Ulrich 1980). Similarly, with anthropogenic acidification, soil pH and base saturation may decrease, with no corresponding net nutrient loss. This occurs if the soil is actively adsorbing both H^+ and SO_4^{2-}, which would increase CEC over time (Johnson and Cole 1977). In addition, decreases in base saturation and pH in soils subjected to leaching losses of base cations, can be offset, to some extent, by acid-induced increases in soil weathering (Johnson 1980).

Much of the potential impact of atmospheric deposition stems from the input of the mobile SO_4^{2-} anion to soils. Whereas the mobility of bicarbonate or organic anions may be severely limited in many acid or clay-rich northern soils, SO_4^{2-} anions may be very mobile in these same soils. It has been shown that atmospheric H_2SO_4 inputs overwhelm natural leaching processes, in some New Hampshire Spodosols, caushing perhaps a threefold increase in the natural rate of cation denudation, and marked increases in the leaching of soluble inorganic Al. In New Hampshire subalpine coniferous soils, anthropogenic SO_4^{2-} anions supplied 76 per cent of the electrical charge balance of the leaching solution, while Al and H^+ were the dominant cations in solution (Cronan 1980, Cronan et al. 1978, Cronan Schofield 1979). In contrast, some soils (chiefly those rich in Fe and Al sesquioxides) exhibit a substantial capacity to adsorb SO_4^{2-}, and thus demonstrate a considerable initial resistance to base leaching by anthropogenic H_2SO_4 (Johnson and Cole 1977, Johnson and Henderson 1979, Morrison 1981, Roberts et al. 1980, Singh et al. 1980). In general terms, this implies that the effect of acid precipitation on soil cation leaching is highly dependent upon the mobility of the anion associated with the acid - whether it be SO_4^{2-}, NO_3^-, or an organic anion (Cronan 1980, Johnson and Cole 1980, Seip 1980). This is due to the requirement for charge balance in the soil solution, a necessary condition that precludes the leaching of cations without associated mobile anions. Soils low in free Fe and Al, or high in organic matter (the latter appears to block sulphate adsorption sites [Johnson et al. 1979, 1980]), are therefore generally susceptible to leaching by H_2SO_4 (e.g., Cronan et al. 1978). Where SO_4^{2-} adsorption does occur, such as in highly weathered soils in Tennessee, S accumulation can be beneficial in three ways: (1) prevention of cation leaching by H_2SO_4, by immobilization of the SO_4^{2-} anion; (2) creation of new cation exchange sites; and (3) the release of OH^- from adsorption surfaces (Johnson et al. in prep.). It follows that, when SO_4^{2-} exchange sites are fully occupied, cation leaching will commence. On Walker Branch Watershed, 48 per cent of total S to input accumulates in the soil, whereas only 13 per cent accumulates in vegetation (Johnson and Henderson 1979, Shriner and Henderson, 1978). Along the same lines, one might expect the NO_3^- in acid precipitation to contribute to net cation leaching only in those systems where NO_3^- is mobile. Because of the N-limited status of many forests, most NO_3^- tends to be accumulated by plants during the growing season and tends not to contribute to cation leaching.

4.3.3 Influence of Soil Biota and Decomposition/Mineralization Activities

It has been postulated that atmospheric deposition of strong acids may adversely affect soil biota and decomposition acitivities, either directly, through soil acidification, or indirectly, through trace metal mobilization and toxicity. Laboratory experiments and observations on soils in close proximity to pollutant sources provide information on changes which occur in soil biota, as a result of increased acid precipitation. Observations indicate decreases in total numbers of soil bacteria and actinomycetes, and some relative increase in presence of fungi; although, under conditions of very high loading, fungi have been reported less abundant. Generally, total numbers of enchytraeids have not been affected (except under extreme conditions), though differential species responses have been reported (Abrahamsen et al. 1976, 1977, Alexander 1980, Baath et al. 1980).

The available evidence concerning the effect of acidity on organic matter breakdown and soil respiration is not conclusive (Rippon 1980, Tamm et al. 1977). However, the weight of evidence from decomposition experiments, to date, suggests that acid deposition may retard organic matter decomposition. Studies (Baath et al. 1979, 1980, Francis et al. 1980, Lohm 1980, Tamm et al. 1976) have noted decreased decomposition or carbon mineralization in soils and litter exposed to artificial acid rain inputs at pH's below 3.5 to 3.0. Meanwhile, other studies have shown little or no effect (Abrahamsen 1980, Hovland et al. 1980). Clearly, the results are dependent, in part, on the soil type and on the severity of the simulated acid rain treatment.

In some soils, there are indications that acid precipitation may alter humic/fulvic acid dynamics. While moderate acidity may aggregate humic acid particles, it may lead to dissolution and mobilization of fulvic acids. In soils like Podzols, which contain appreciable quantities of fulvic acid, substantial losses could potentially occur in moderate acidic leaching.

Besides carbon cycling, there is concern that acid deposition may have adverse effects on N cycling patterns and processes. In this case, there are actually two potential sides to the issue: (1) the possibility that acid deposition may decrease N mineralization and availability; and (2) the possibility that atmospheric inputs of anthropogenic N compounds may provide a fertilizer effect, by increasing the amount of available N. Tamm (1976) predicted short-term increases in N availability and tree growth, due to net N losses from ecosystems. In support, Ulrich et al. (1980), in Germany, resampled soils over a thirteen-year period and showed significant accumulations of N-poor organic matter in the forest floor of a 120 year-old beech forest. This was interpreted as a condition which could lead to internal H^+ production, immobilization of N, and mobilization of soluble Al^{3+}. Other studies, by Francis et al. (1980) and Alexander (1980), have shown that ammonification and nitrification may be decreased markedly in soils exposed to artificial rain at pH's approaching 3.0. However, several studies have demonstrated increased N availability, at least during the initial stages of H_2SO_4 input (Abrahamsen 1980, Ogner and Teigen 1981, Roberts et al. 1980), and this has produced minor growth increases in situations where N is limiting (Abrahamsen 1980, Tamm and Wiklander 1980, Tveite and Abrahamsen 1980). Whether this increase in N availability is due to change in microbial activity, or to the acid catalyzed hydrolysis of labile soil N, is unknown as yet. In either event, the results of Norwegian studies in which both N availability and NO_3^- leaching were stimulated by H_2SO_4 inputs, strongly suggest that contrary to earlier predictions (Tamm 1976), nitrification can be stimulated by acid inputs as well. This has definite negative long-term implications for forest N and cation status, if NO_3^- production exceeds plant uptake, resulting in net ecosystem N and cation loss.

4.3.4 Influences on Availability of Phosphorus

Like N, phosphorus (P) is an essential element for plant life. In soil, P occurs in both inorganic and organic compounds. It is utilized from the soil solution by plants chiefly, though not entirely, as the (inorganic) orthophosphate anion. The availability of P to plants is determined to a large extent by the ionic form in which it is present. In soil solutions of low pH, available P is present largely as $H_2PO_4^-$; as pH increases, HPO_4^{2-} predominates. In strongly acid mineral soils, $H_2PO_4^-$-ions may react with solubilized Fe, Al and Mn compounds and be precipitated as the insoluble metal, hydroxyphosphate. Also, under conditions of increasing acidity, $H_2PO_4^-$ tends to react with the insoluble drous hy oxides of Fe, Al and Mn, and in more weathered soils it may become fixed on silicate clays, through the process of anion exchange.

4.3.5 Effects on Trace Element and Heavy Metal Mobilization and Toxicity

A further by-product of increased soil acidity, and anion availability, appears to be the mobilization of certain metals, such as Al, Mn and Fe. At low concentrations, Mn and Fe serve as essential nutrients for the growth of higher plants; however, in excess, they can be detrimental to growth. Plant species vary in their susceptibility to certain metals. A case in point is Al, where differential responses to elevated levels have been demonstrated. Many factors affect tolerance/susceptibility, including soil pH, NH_4^+ versus NO_3^- nutrition, Al exclusion processes, Ca and P nutrition, and organic Al complexes (Foy et al. 1978). Plant species known to be sensitive to Al include barley, sugarbeet, corn and alfalfa.

Experiments with soil in lysimeters (Abrahamsen et al. 1976) indicate increased loss of Al in relation to increased acid input. Simulated acid precipitation experiments in Norway showed more leaching of Al from a semipodzol at "rain" pH of 4.5 than at pH 5.6. Cronan and Schofield (1979) also reported increased mobilization of Al in some New Hampshire podzols, as a result of atmospheric H_2SO_4 inputs. Increased availability of Al in terrestrial ecosystems may cause the immobilization of P (Abrahamsen 1980). Ulrich et al. (1980), reported a marked increase between 1966 and 1973, and a levelling-off after that, of both Al and Fe ions in the equilibrium soil solution of a beech woods soil in Germany. It was suggested that Al concentrations were reaching levels toxic to tree roots in these beech forests.

Concerning other trace elements, in sufficient concentration, several are toxic to higher plants. In restricted areas, vegetation may be stunted or absent, due to toxicity of metals such as nickel (Ni) (Foy et al. 1978). In a well-known study on serpentine-derived soils in Czechoslovakia, Nevmec (1954) attributed the failure of plantations of pine and various hardwood species to excessive levels of Ni, chromium (Cr) and cobalt (Co). Plantation failure was considerably reduced by fertilizing with lime and diabase dust. Around Sudbury, Canada, Ni and Cu added as dustfall from smelters are maintained in acidified soils in concentrations sufficiently high to be toxic to vegetation (Hutchinson and Whitby 1974, 1976). Any possibility of mobilizing trace metals through decreasing soil pH by acid rain, thus, has implications for forest productivity. Interestingly, studies by Tyler (1978) showed that lead (Pb) is not readily leached from surface soils by acid precipitation inputs. Although the solubility of this element increases with decreasing pH, most soils contain sufficient organic matter to tie up the Pb as insoluble organic-Pb complexes in the soil matrix.

The effects of increased metal mobilization may be even more deleterious to aquatic life than to terrestrial vegetation communities. Substantial leaching of Al from soils into groundwater, then to streams and lakes, has been observed under field conditions in zones of very high impingement (Cronan and Schofield 1979, Dickson 1978).

4.3.6 Impact on Clay Minerals and CEC

Clay minerals are major inorganic components of soils, and the types of clay minerals generally found in soils are characteristic of parent materials and climate. In recently glaciated terrain, clays are formed by comminution of micaceous and other soft minerals to clay size. In older glaciated soils, or in soils formed in residual substrate, clay minerals are largely secondary products, produced by chemical weathering. Clay minerals have a considerable influence on physical, chemical and biological activities in soils, because of their large surface area and structural characteristics.

It has been postulated that acid deposition may have an important impact on some soils, by causing clay degradation and reductions in CEC. This could occur through accelerated weathering of clay mineral lattices, or through increased formation of hydroxy Al interlayers in expansible clay minerals. The aluminated phases of expansible clay minerals are present in a wide variety of soils (Bryant and Dixon 1964, Carstea 1968, Rich and Obenshain 1955), and are thought to be a common weathering product of mica schists in acid soils (Rich and Obenshain 1955, Sawhney 1960) and in glacial till (Jackson 1963).

Sawhney (1968) noted that the process of alumination may cause the CEC of vermiculite to diminsh threefold. There is currently a need for further research, to determine whether acid rain may accelerate these processes of clay degradation.

4.4 SENSITIVITY ASSESSMENT

In the present report, soil is taken as the unconsolidated mineral material on the surface of the earth which serves as a natural medium for land plants.

Accelerated changes in the natural evolution of soils may occur as a result of an increase in the rate of acidification and associated nutrient impoverishment. These changes hold important implications for long-term, sustained forest/agricultural productivity, and for aquatic sensitivity. (See also discussion under Section 3.5 - Aquatic Ecosystems Sensitive to Acidic Deposition). Recent discussions have indicated that the assessment of terrestrial sensitivity must consider, and distinguish among, those aspects of the terrestrial ecosystem which have an effect on forest and agricultural productivity, on the one hand, and aquatic sensitivity, on the other (Cowell et al. 1981).

4.4.1 Implications for Forest Productivity

Acid precipitation may cause increases as well as decreases in forest productivity (Abrahamsen 1980, Cowling and Dochinger 1980). The net effect on forest growth depends upon a number of site-specific factors, such as nutrient status and amount and composition of atmospheric acid input. In cases where nutrient cations are abundant and S or N are deficient, moderate inputs of acid may actually increase forest growth. At the other extreme, acid precipitation in sufficient amounts may reduce productivity, on sites with adequate N and S but deficient in cations. In either case, the nutritional costs and benefits of acid precipitation are highly dependent upon the quantities of nutrient capital and nature of the acid inputs involved.

As previously indicated, deficiencies of N are common in forests of the temperate and boreal regions. Inputs of NO_3^- (as well as NH_4^+ and other forms of N) may improve forest productivity, in the short term (Abrahamsen 1980). In the longer term, however, any improvements in N-status may be offset by loss of nutrient cations through accelerated soil leaching (Johnson et al. in prep., Tveite 1980). The same general concepts apply to SO_4^{2-} deposition but S deficiencies are much lower than N requirements. Therefore, any benefits of SO_4^{2-} deposition are of limited geographical distribution and probably occur, to a maximum degree, at lower H_2SO_4 input levels than occur currently in most of eastern North America (Evans et al. in prep.).

The criteria for sensitivity to leaching by H_2SO_4 are different from those for HNO_3. The mobility of NO_3^- is related to biological immobilization within the ecosystem. This is rapid and efficient in N-deficient systems. The mobility of the SO_4^{2-} anion is controlled to a greater degree by inorganic chemical processes within the soil, (i.e., adsorption to free Fe and Al oxides, Johnson and Cole 1980). Therefore, sensitivity maps for cation leaching must differentiate between H_2SO_4 and HNO_3 inputs. The following analysis considers only H_2SO_4 inputs, since these dominate over HNO_3 throughout much of eastern North America. Therefore, biological immobilization of HNO_3 (as well as its potential benefits on N-deficient forest ecosystems) is not considered here. Coote et al. (1981) have considered nitrogen transformations, in assessing the effect of acid precipitation in agriculture soils.

There are a number of factors which can interact with acid input to affect forest productivity. The complexity of the problem requires the adoption of an ecosystem approach to understanding terrestrial sensitivity. The key factors for three levels of sensitivity of changes in forest cation nutrient status to H_2SO_4 deposition are given in Table 4-7. These are not the only factors involved in determining terrestrial sensitivities, based on nutrient status (and thus forest productivity). Rather, they represent some fundamental soil characteristics which are measureable, and for which sensitivity criteria can be assigned.

This sensitivity rating scheme does not account for one important criterion, namely, the relative contributions of anthropogenic acids and natural, internally-produced acids in forest ecosystems. If anthropogenic acid adds only a small increment to the natural acid production of a forest ecosystem, the site cannot be considered sensitive to cation-leaching by acid precipitation, regardless of other soil chemical and physical criteria. Unfortunately, it is not yet possible to quantify internal acid production without considerable effort, and the data are not available for sensitivity mapping using this criterion. Furthermore, atmospheric inputs may change through time, requiring continual re-evaluation of sensitive vs non-sensitive areas. Such an analysis is beyond the scope of the present study. Therefore, the rating scheme outlined below makes the assumption that atmospheric acid inputs significantly add to, or exceed, natural, internal acid production. However, more research is needed to show where this assumption is acceptable or unacceptable.

The main factors included in the current assessment are exchangeable bases, SO_4^{2-} adsorption capacity, soil depth, and underlying materials.

Where the soil depth is less than 25 cm, the presence or absence of carbonate in the underlying materials, either subsoil or bedrock, is considered. A soil depth of 25 cm is considered important, because this includes the zone of maximum root concentration, hence, nutrient uptake. It also corresponds primarily with the organic and eluviated

TABLE 4-7 SENSITIVITY TO CHANGES IN FOREST CATION NUTRIENT STATUS

TERRESTRIAL FACTORS	LOW	MODERATE	HIGH
Soil Chemistry			
i) Exchangeable Bases	>15 meq/100g	6 to 15 meq/100g	<6 meq/100g
Surrogate: Combinations of pH in water (or % Base Saturation) and one of (a) Family Particle Size	clayey, >pH 5.0 loamy, >pH 5.5 all calcareous soils	clayey, pH 4.5 to 5.0 loamy, pH 5.0 to 5.5 sandy, >pH 5.5	clayey, <pH 4.5 loamy, <pH 5.0 sandy, <pH 5.5
or (b) Texture	clay, silty clay, sandy clay (>35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam, loam (10 to 35% clay)	silt sandy loam, loamy sand, sand (<10% clay)
or (c) Cation Exchange Capacity	>25 meq/100g	10 to 25 meq/100g	<10 meq/100g
ii) SO_4^{2-} Adsorption Capacity	high sulphate adsorption: low organic matter AND high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$		low sulphate adsorption: high organic matter AND/OR low Al_2O_3 and/or Fe_2O_0 & Fe_3O_4
Soil Depth*	>25 cm	>25 cm	<25cm*
* If soil depth is less than 25 cm, Underlying Material is incorporated			
Underlying Material			
i) Parent Material	carbonate bearing	non-carbonate bearing	non-carbonate bearing
ii) Bedrock Material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with non-carbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, meta-equivalents	granite, granite gneiss, orthoquartzite, syenite

horizons of the profile. In addition, exchangeable base content is considered a better measure of sensitivity than CEC or pH alone (Cowell et al., 1981).

The three levels of sensitivity for exchangeable bases are taken from Wang and Coote (1980). These values incorporate a loading factor, which assumes a loss by elaching of 25 per cent of the exchangeable bases over 25 years, under an acid leading impact of 60 kg/ha $CaCO_3$ equivalent.

SO_4^{2-} adsorption capacity is considered important for determining sensitivity, but little empirical data are available to establish limits. In those soils which have a demonstrated capability for adsorbing SO_4^{2-} to the soil sesquioxide surfaces (low organic matter, high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$), the mobility of cations is reduced. Cations generally only appear in quantity in leachates when SO_4^{2-} moves through the profile. Thus high SO_4^{2-} adsorption corresponds to a lower sensitivity to acid precipitation.

In terms of forest productivity, it is presumed that extremely low pH soils (pH 4.5) are still sensitive to H^+ ion inputs, in that, while acidification per se may proceed only slowly, loss of limited cation reserves may be significant, however small the loss may be. Basic to the determination of effects on forest productivity, then, is the assumption that the reduced availability of basic cations, because of replacement in the soil by H^+, is detrimental to forest growth.

Any failure to establish cause/effect relationships may only reflect an insensitivity of methods used or, given the very wide range of forest and forest soil conditions versus the small number of studies, simply the lack of thorough investigation. The general restriction of commerical forest production to less productive sites, coupled with new harvesting technology, where more of the tree is removed from the site, thus reducing the availability of nutrients for recycling, and the difficulty of applying lime, may increase the vulnerability of long term forest growth to acid precipitation. Interestingly, while Ca deficiency per se is not a general feature of forest sites, several independent studies of nutrient removals, associated with intensive harvesting, have pinpointed the possibility of depleting this element on marginal sites over the long term (Boyle and Ek 1972, Boyle et al. 1973, Weetman and Webber 1972).

4.4.2 Implications for Agricultural Productivity

Agricultural areas do not usually include the shallower soils which would be more sensitive to impacts from acid precipitation. The effects of fertilization and liming of agricultural soils will generally mask any direct effects of acid precipitation on the soil. In addition, acid precipitation could help offset S deficiencies in some soils. The wide ranges in both soil properties and intensities of soil management result in a great variation in potential for significant effects on agricultural soils. However, the current state of knowledge suggests that the implications of air pollution for agricultural soils are that direct effects will be minimal, even in those situations where greatest impact would be expected.

As for direct effects on crops, there is, as yet, no conclusive documentation of such impacts occurring in the field as a result of acid precipitation. However, experimental evidence does exist for a number of effects on crop species, including loss of nutrients from foliage by leaching, predisposition of plants to attack by pests, inhibition of N fixation, injury to plant surfaces, and reduced yield. Under experimental conditions, simulated acid rain of pH 4 or below has caused certain effects (see earlier discussion). However, great variation in sensitivity among species has been noted. The timing of acid precipitation events, as was stressed earlier, may be more important in looking at effects on agricultural crops. Generally, what happens during the growing season is of primary concern, but within the growing season itself, there may be critical times. For a particular crop, there will be large areas at the same stage of growth at the same time. The significance of these relationships has not been determined, and further work is required before their importance will be understood.

4.4.3 Terrestrial Sensitivity Mapping for Eastern North America

Figures 4-1 and 4-2 are maps showing sensitivity to changes in forest cation nutrient status as a result of acid deposition, for areas in eastern North America. They were interpreted using the Ecodistrict data base for Canada (Cowell et al. 1981) and the Geoecology data base for the United States (Olson et al. 1980). The evaluations have been made using the criteria suggested in Table 4-7.

Figure 4-3 shows the criteria evaluation procedure for sensitivity to changes in forest cation nutrient status for Canada. The information base does not permit strictly comparable criteria or their surrogates within eastern Canada, or between Canada and United States. However, an attempt has been made to integrate factors in as comparable a fashion as the various data bases would allow.

Eastern Canada

The map of eastern Canada (Figure 4-1) was prepared using the Ecodistrict data base (Cowell et al. 1981). As described in Section 3

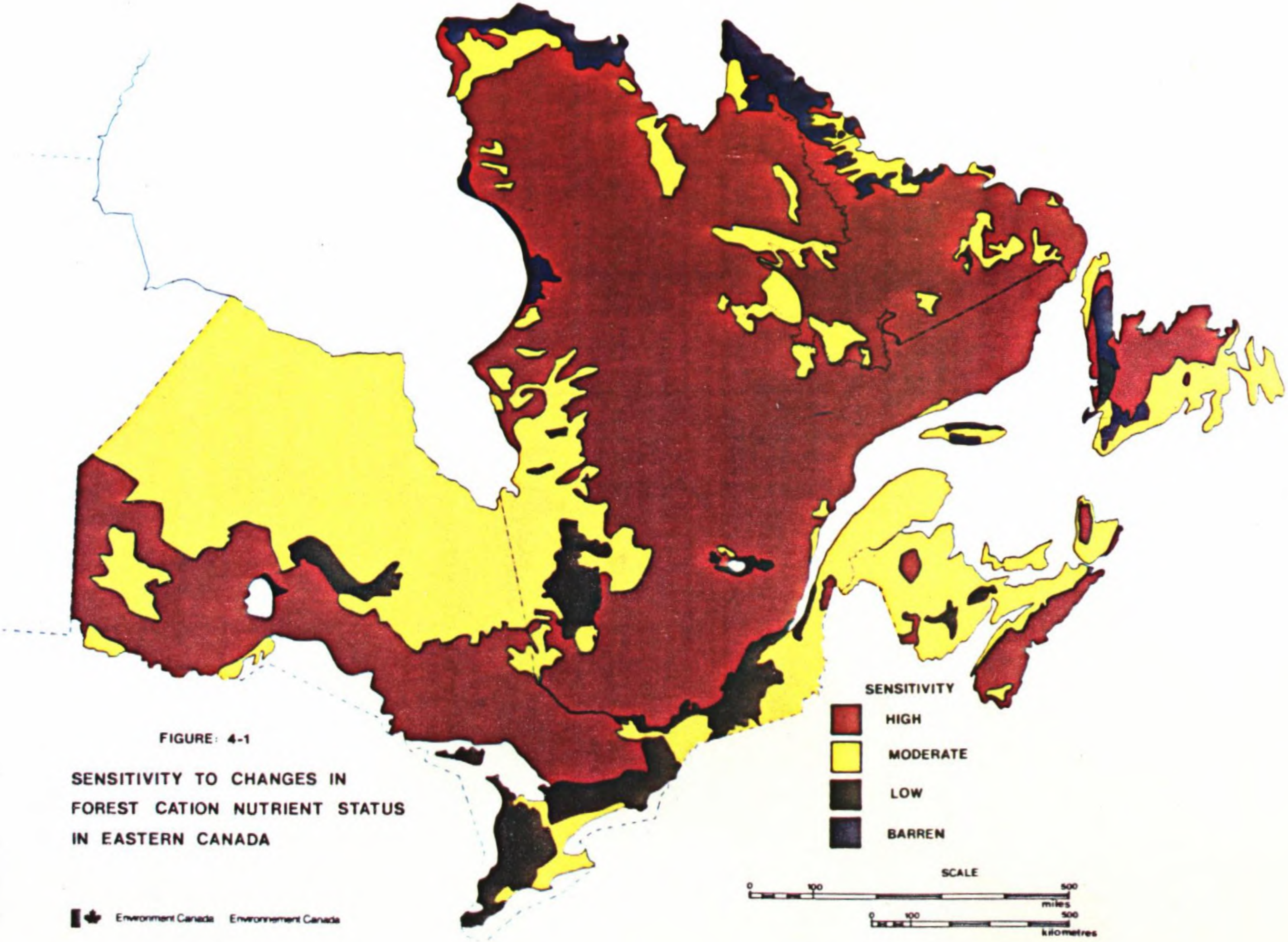

FIGURE: 4-1

SENSITIVITY TO CHANGES IN FOREST CATION NUTRIENT STATUS IN EASTERN CANADA

Environment Canada Environnement Canada

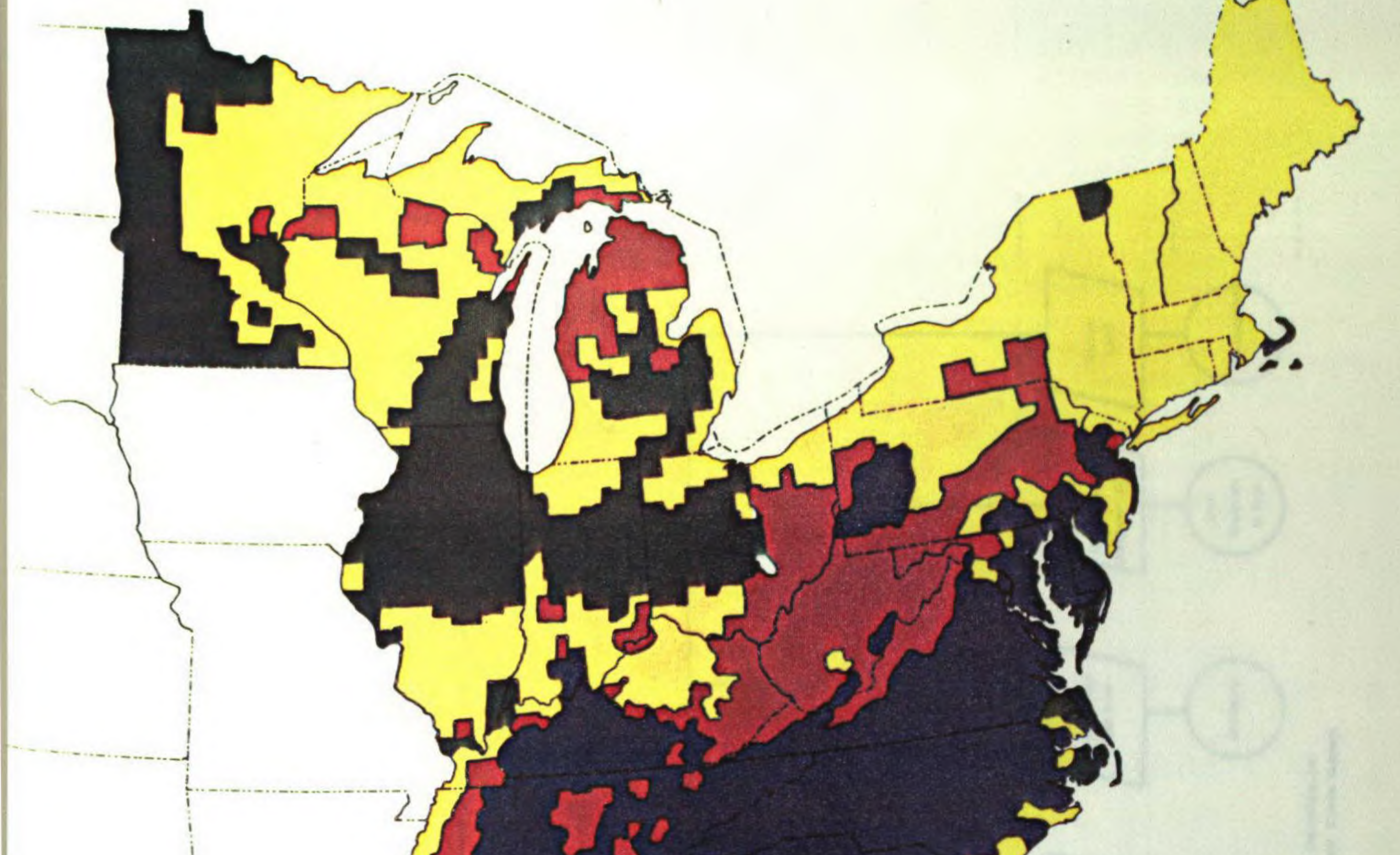

FIGURE: 4-2

SENSITIVITY TO CHANGES IN FOREST CATION NUTRIENT STATUS IN THE EASTERN UNITED STATES

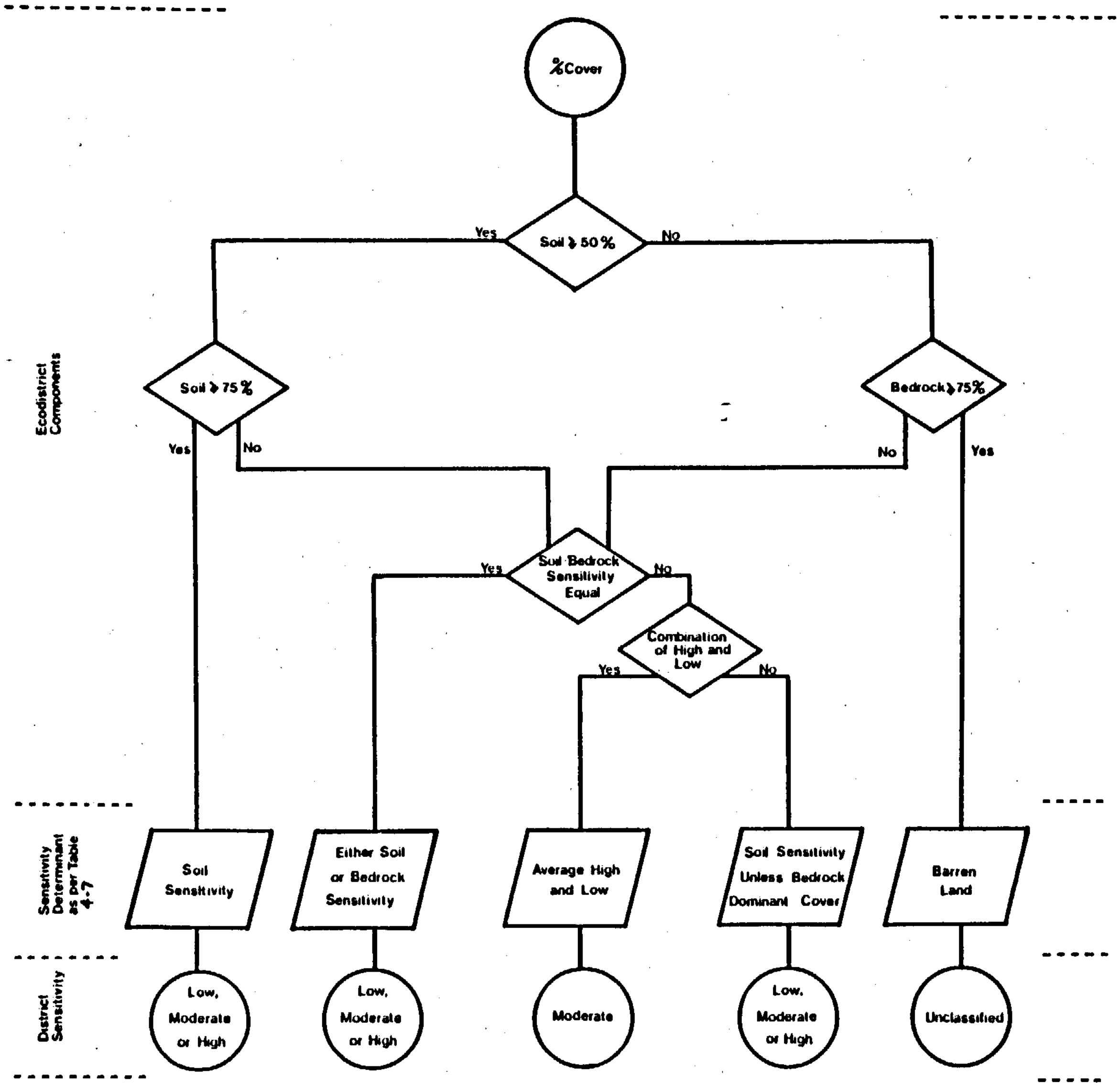

Figure 4-3: Ecodistrict Criteria Evaluation Procedure for Sensitivity to Changes in Forest Cation Nutrient Status for Eastern Canada

ecodistricts are units of land characterized by a distinctive pattern of relief, geomorphology, vegetation, soils, water and land. They are interpreted using LANDSAT colour imagery, existing mapping, and ecological survey data. The Ecodistrict data base includes information on soil properties, bedrock geology, drainage, vegetation and water bodies. At present, it incorporates existing data, and thus the form of the data varies somewhat from region to region. However, the sensitivity criteria were integrated using a common format to maintain a level of consistency and comparability (Cowell et al. 1981). Figure 4-3 shows the criteria evaluation procedures which denote high, moderate and low sensitivity for each of aquatic input sensitivity and changes in forest nutrient cation status, respectively.

Bedrock geology sensitivity was assigned according to Table 4-7, and relatively good geological mapping is available for all of eastern Canada. In Ontario, soil depth and soil petrography (estimated carbonate content) are well defined south of 50°N latitude and were taken from Hills (1960) and other sources. Elsewhere, texture, soil great group and parent material were used as surrogates for soil chemistry, and soil depth was taken from ecological land survey data, soil capability mapping and field knowledge. Ecodistricts dominated by peatland terrain were assigned a moderate soil sensitivity, because they have a high cation exchange capacity, but are mostly low in base saturation. It is not known exactly how these soils are affected by acid deposition.

Eastern United States

The map of the eastern United States (Figure 4-2) was produced at the Oak Ridge National Laboratory, using county-level data on soils from the Geoecology data base (Olson et al. 1980, 1981). This map was determined by total exchangeable base content and sulphate adsorption capacity (Table 4-7). Soil depth and underlying materials were not incorporated in this analysis, because of the small number of counties mapped as having shallow soils, and because of questions regarding the completeness of the Conservation Needs Inventory mapping of non-agricultural areas (Section 3).

Olson et al. (1981) also produced maps of sensitivity, based on several of the other soil factors listed in Table 4-7. Exchangeable bases were used in the final maps because these, along with SO_4^{2-} adsorption, are the preferred soil parameters to determine terrestrial sensitivities (Cowell et al. 1981). Table 4-8 shows average chemical properties for counties within each sensitivity level.

Chemical and physical soil characteristics employed in the analysis are average values, taken from published information, representing the A horizons (upper 20-25 cm) of each great soil group (Klopatek et al. 1980, Olson et al. 1981). Proportions of soil types within counties were estimated from the 1:7,500,000 scale soil map of the United States (USGS 1970). As in the case of eastern Canada, no

TABLE 4-8 AVERAGE SOIL SURFACE CHARACTERISTICS AND STANDARD DEVIATIONS OF COUNTIES CLASSIFIED AS TO THEIR POTENTIAL FOR NUTRIENT CHANGES RELATED TO ACID RAIN. THE HIGH (SULPHATE) CLASS HAS HIGH SULPHATE ADSORPTION CAPACITY BUT IS LOW IN EXCHANGEABLE BASES, CATION EXCHANGE CAPACITY, BASE SATURATION, pH, CLAY CONTENT and ORGANIC MATTER.

	Soil sensitivity							
	Low		Moderate		High(sulphate)		High	
Number of counties	265		462		625		306	
Percentage of counties	16		28		38		18	
Percentage of counties in commercial forest (>30%)	12		57		96		87	
Exchangeable bases (meq/100g)	23	6	9	2	3	1	4	1
Cation exchange capacity (meq/100g)	31	17	19	7	9	2	12	3
Base saturation (%)	79	15	52	15	29	7	39	8
pH	6.0	.6	5.2	.5	4.9	.2	4.9	.3
Clay content (%)	24	6	17	5	10	3	12	5
Organic matter (%)	6	2	6	3	3	1	4	2

allowance has been made in the interpretation for land management effects in agricultural areas. However, the majority of counties in the moderate and high categories have more than 30 per cent commercial forest (Table 4-8).

Sulphate adsorption was estimated on the basis of known characteristics of great soil groups (Olson et al. 1981). Of particular interest, for mapping purposes, were soils that had high sensitivity, based on exchangeable bases, but were known to adsorb SO_4^{2-}. These areas were mapped as a separate class in Figure 4-2. It is not certain how effective SO_4^{2-} adsorption is in lessening effects on forest nutrient cation status. This is because most nutrient uptake takes place within the upper 25 cm of the profile, whereas SO_4^{2-} adsorption occurs at deeper levels (Johnson and Henderson 1979). However, these areas are considered to have lower sensitivity than the exchangeable base status would indicate. It should be noted that the capacity of the soil to adsorb SO_4^{2-} is not unlimited, and could be exceeded in areas of high anthropogenic acid loading.

Discussion

These maps are an approximation of sensitive areas, based on a fairly strict definition of sensitivity, applied using small-scale polygon-format data. Polygons, at this scale (Ecodistrict or County), are not as spatially accurate as individual overlays of bedrock geology or soil chemistry, but provide a convenient framework for integrating more than one coverage. Because criteria are selected on the basis of predominance of occurrence in a county or ecodistrict, the whole polygon is assigned a sensitivity based on dominant characteristics. Thus, depending on the size of individual polygons, real boundaries may be somewhat modified. This explains, in part, why sensitivity levels do not always correspond across the international boundary. Generally, in these cases, one can expect to find a change near the border, but the polygons (Ecodistrict or County) are not small enough to show its exact location.

To improve the interpretations, the next step will be to use more accurate soil chemistry and depth data for the U.S. This could be accomplished with Soil Conservation Service county level soil survey data. The Canadian data base requires much improved soil chemistry information from non-agricultural areas. Once this has been achieved, it will be necessary to carry out more spatially accurate computer mapping and analysis, in those areas of high or moderate sensitivity experiencing high atmospheric loadings of H_2SO_4. Only when this stage has been reached can the most significant comparisons be made, that is, between terrestrial/geographic characteristics and watershed chemistry.

4.5 RESEARCH NEEDS

The following list does not confer an order of priority; rather, the ordering reflects the general progression of the foregoing chapter from INTRODUCTION through SENSITIVITY ASSESSMENT.

1. Improved resolution (spatial and temporal) of current wet and dry deposition patterns in both the United States and Canada.

2. Improved projection of wet and dry deposition within designated areas of United States and Canada.

3. Improved information on capture and fate of dry S and N within principal terrestrial ecosystem types.

4. Determine tree and crop species exposed to greatest risk of reduction in productivity by acid precipitation. Determine plant characteristics associated with susceptibility/tolerance to O_3 and acid precipitation.

5. Determine quantitative relationships between dose-response acid precipitation and productivity of trees and crops.

6. Determine extent to which dose-response relationships are altered by presence of O_3, deposition of particulates, soil nutrient and moisture supplies, and pattern and timing of precipitation events with respect to stages of plant development. Identify stages of vulnerability of agricultural crops and/or forest vegetation, particularly to episodic wet and/or dry deposition.

7. Determine degree to which uptake of metals, particularly aluminum, is increased by exposure to acid precipitation.

8. Interaction of acid stress with other abiotic and with biotic stresses on terrestrial plants. Determine whether incidence of common diseases and insect infestations is likely to be affected by acid precipitation and ozone.

9. Develop a standardized biological indicator of acid precipitation, having known relationships to changes in productivity of trees and crops.

10. Identification of beneficial as well as injurious effects of various components of acid pollution, with particular reference to rate relationships for principal terrestrial ecosystem types, that is, determine effects of H^+, SO_4^{2-}, and NO_3^-, separately and combined, on forest nutrient status. (This is a problem of quantifying benefits of SO_4^{2-} and NO_3^- inputs vs detriment of H^+-deposition and net overall effect on forest ecosystems at current and projected input levels.)

11. Quantification, based on actual field observations, of natural H^+-ion production and consumption rates for the principal terrestrial ecosystem types, and the clear distinction of anthropogenic and natural H^+ ion production, that is, obtain more information on natural internal acid production and leaching for a variety of forest ecosystems. (This must be used in a full, comprehensive analysis of acid rain effects on soil leaching of metal cations and transfer to aquatic ecosystems.)

12. Improved information, based on actual field observations on a representative range of soil types, on impact of acid deposition on sensitive biochemical and/or chemical processes, and the general identification of sensitive soil types to various pollutants and pollutant combinations.

13. Determine major factors affecting soil SO_4^{2-} adsorption capacity, and how they vary among soil orders and/or major soil types.

14. Improved information, based on actual field observation on a representative range of mainly natural soils, on impact of acid deposition on soil biota, soil mineralogy and soil organic matter.

15. Improved understanding of relationships between forest productivity and acid sensitive properties of soils.

16. Consideration of the long-term site impoverishment potential of continued acid deposition, in the light of trends in forest management toward more rapid growth, shorter rotations and full-tree, or even whole-tree, harvesting.

17. Improved system of mapping terrestrial sensitivity, hopefully incorporating extant data bases, to allow further identification of key sensitive areas.

18. Improved soils information base, including also such factors as depth to carbonate and sulphate adsorption capacity, particularly in remote areas.

19. Mitigative measures for correcting acidity impacts.

4.6 CONCLUSIONS

1. Field and laboratory studies with O_3 that indicate reductions in yield may occur for various tree species and such crops as beans, tobacco, potatoes, onions, radishes, grapes, and corn. Frequent exposures, during the growth season, to O_3 concentrations in excess of 0.1 ppm have produced yield losses of as much as 20 per cent for susceptible species.

2. Although simulated rainfall experiments have produced some direct effects on plants exposed to higher than normal H^+ concentrations, direct effects have not been documented conclusively in the field for vegetation exposed to ambient precipitation.

3. Experiments with simulated acid precipitation and O_3 have demonstrated greater plant growth reduction from the two together than would be expected from the results of their individual effects.

4. Individual precipitation events which occur during critical growth stages (e.g., during flowering or pollination) offer amplified potential for damage to agricultural crops.

5. Direct effects of acid precipitation on soils have been shown to increase SO_4^{2-} movement and increase the rate of nutrient cation denudation. However, some soils exhibit a substantial capacity to absorb SO_4^{2-} and resistance to nutrient cation leaching.

6. The terrestrial system's influence on the acid component of precipitation has important implications for the aquatic ecosystem.

7. Multi-factor data bases have been employed, to develop maps of eastern North America which depict the sensitivity of various areas (down to the county level for the U.S. and ecodistricts in Canada) to impacts from acid precipitation.

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SECTION 5

HEALTH AND VISIBILITY

5.1 INTRODUCTION

A complete assessment of the health implications of U.S./Canadian transboundary air pollution would encompass the full range of current pollution concerns, including photochemical oxidants, sulphur and nitrogen oxides, particulate matter, and associated toxic substances. Although future phases may address these air quality concerns, this report will focus on potential health effects associated with the transboundary deposition of acidifying substances.

Available information gives little cause for concern over direct health effects from acid deposition. The pH of acidic precipitation is generally well within the range normally tolerated by the skin and gastro-intestinal tract. Although high levels of SO_2, NO_2, and acid aerosols are reported in urban areas, no studies have been found which suggest adverse effects from dry deposition on the skin.

Evidence does suggest, however, that inhalation of high levels of such substances may produce respiratory and other internal disease (EPA 1980, NAS 1978a), and one early epidemiological study (Gorham 1958) even reported an (inverse) statistical association between bronchitis mortality and the pH of winter precipitation in Great Britain. In this case, precipitation acidity was probably an index of acid precursor air quality, since a plausible mechanism for causality does not exist.

A full discussion of the effects of direct inhalation of atmospheric acids is beyond the scope of this report. The circumstances in which inhalation of airborne acids might be implicated, as causative agents, are most likely to occur in areas of high pollution sources and population densities, in addition to areas receiving atmospheric inputs from distant sources. The attribution of adverse health effects specifically to acid aerosols is complicated by the copresence of other pollutants, including particulate matter and photochemical oxidants.

Health effects which may be associated with acidic deposition can be both indirect and direct in nature. Based on the readily accessible literature, several areas of potential impact are: (1) contamination of edible fish by toxic materials, principally mercury; (2) leaching and corrosion of watersheds and storage and distribution systems, leading to elevated levels of toxic elements; and (3) inhalation of deleterious substances, especially photo-oxidants and acid aerosols, which may lead to increased morbidity, and perhaps mortality.

5.2 HEALTH

5.2.1 Contamination of Edible Fish

Some evidence suggests that acid deposition may alter the biogeochemical cycle of metals, including mercury (Brosset and Svedung 1977, Jensen and Jernelov 1972, Schindler et al. 1980, Tomlinson 1978). Poorly buffered waters in areas remote from any point source of discharge of mercury have been found to contain fish with elevated levels of mercury. Landner and Larson (1972) first noted an inverse relationship between water pH and methyl mercury content of fish in certain Swedish lakes. Scheider et al. (1978) found that the mercury content of walleye from 21 Ontario lakes was significantly higher for lakes where alkalinity was less than 15 mg/l (as $CaCO_3$), as opposed to lakes with higher alkalinities. According to Tomlinson et al. (1979), fish from poorly buffered lakes and rivers in Quebec, New Brunswick, Minnesota, New York, and Maine also contain elevated mercury.

The mechanisms by which acid deposition might increase fish mercury content are not known, but most likely involve both biological and chemical processes. The principal forms of mercury of interest are elemental (Hg^o), dimethyl mercury ($(CH_3)_2Hg$), mercuric mercury (Hg^{2+}), and monomethyl mercury (CH_3Hg^+). Jensen and Jernelov (1972), and several other investigators, have shown that inorganic mercury can be methylated in both aquatic and terrestrial ecosystems. One hypothesis, attempting to explain the relationship between pH and mercury, holds that monomethyl mercury formation is at low pH (<7), while dimethyl mercury forms at higher pH (>7) (Jensen and Jernelov 1972, Tomlinson et al. 1979). Dimethyl mercury has a high vapour pressure, is relatively insoluble, and is thus largely released to the atmosphere. Methyl mercury uptake by fish in lakes having these pH regimes is thus minimized. Lakes with lower pH produce proportionately larger amounts of monomethyl mercury, which is efficiently taken up by biota. The reduced availability of young fish containing low mercury levels, and increased foraging activity by larger predator fish, both characteristic of acidified lakes, increase the bioaccumulation of methyl mercury in larger fish. Recent experiments by Mayfield (1980) found a very poor correlation between mono- and dimethyl mercury versus pH. The mechanisms leading to increased mercury burdens in fish are undoubtedly much more complicated, and probably include additional considerations, such as the complexity of the food chain, redox conditions, inorganic and organic sequestering agents, watershed to lake area ratio (Suns et al. 1980), and rate of atmospheric mercury input. Using calculations from Brosset and Svedung (1977), Tomlinson et al. (1980), and Brouzes et al. (1977), it has been hypothesized that acid-containing clouds and rains should effectively remove methyl mercury from the atmosphere. The surface of acidified lakes should also be an effective sink for the dry deposition of methyl mercury. Once removed, methyl mercury would then be more likely to stay in solution in acidified waters. This scenario is shown in Figure 5-1, which illustrates the distribution of mercury in waters of three different acidities. Again, recent evidence suggests that the process is much more complicated (Barton et al. 1981). These authors could detect no dimethyl mercury in air from measurements taken at several locations in Ontario. Thus, while the exact mechanisms responsible for the observed elevated levels of mercury in fish from acidified lakes remain obscure, fish are harvested from these lakes, and present a potential health hazard to humans. The extent to which acid deposition may have contributed to mobilization, or retention, of mercury in fish, is speculative.

Presently the mercury content of fish tested in the affected areas is often more than the U.S. F.D.A. recommended levels of 0.50 μg/g. If the situation is not changed then it would appear that the mercury content of fish will continue to rise as lake pH drops (Figure 5-2).

Another critical factor in this regard is that the bioaccumulation of mercury is related to the species' trophic level. The larger pisciverous fish are known to have greater concentrations of mercury in the tissues than the planktivors (Philips et al. 1980). These fish are also the most prized sport fish, and make up the majority of the yearly catch eaten. Little research has been directed at mammals inhabiting areas of elevated mercury levels. One study by Wren et al. (1980) suggests that terrestrial species have a demethylating process, which can reduce the amount of toxic organic mercury in their bodies.

5.2.2 Contamination of Drinking Water

Acid deposition can increase the concentration of toxic metals in drinking water by: (1) increasing the deposition of metal in soluble forms (e.g., mercury); (2) leaching of metals from the watershed and from sediments; and (3) acid corrosion of materials used in reservoirs and drinking water distribution systems.

Again, no clear evidence of health effects arising from the consumption of drinking water, contaminated with metals from acid deposition, have been reported in the literature, but some potential problems have been identified. In New York State, water from the Hinkley reservoir has become acidified to such an extent, that lead concentrations in drinking water at the top exceed the maximum levels for human use, (50 μg/l) recommended by the New York State Department of Health (Turk and Peters 1977).

Groundwater may also become acidified in poorly buffered areas (Cronan and Schofield 1979); for example, it has been reported

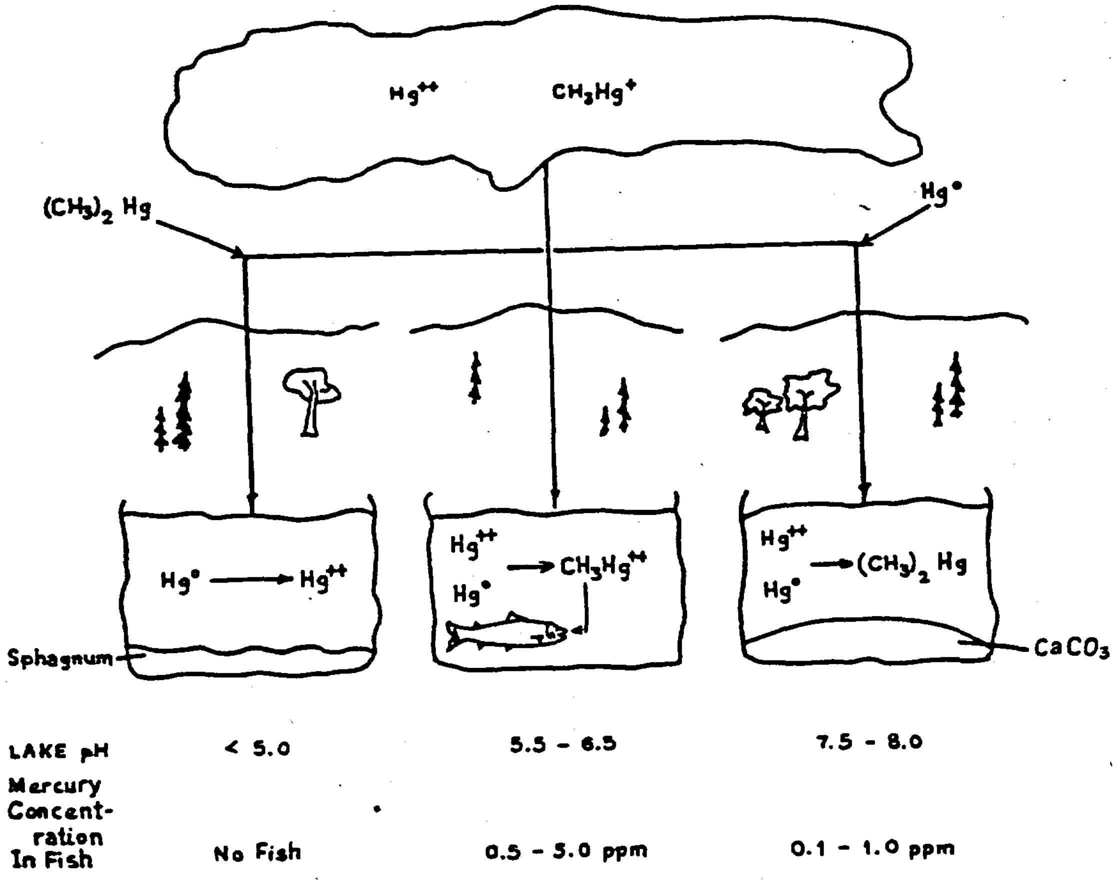

Figure 5-1. Varying effects of lake pH on the distribution of mercury in ecosystems (Tomlinson 1978).

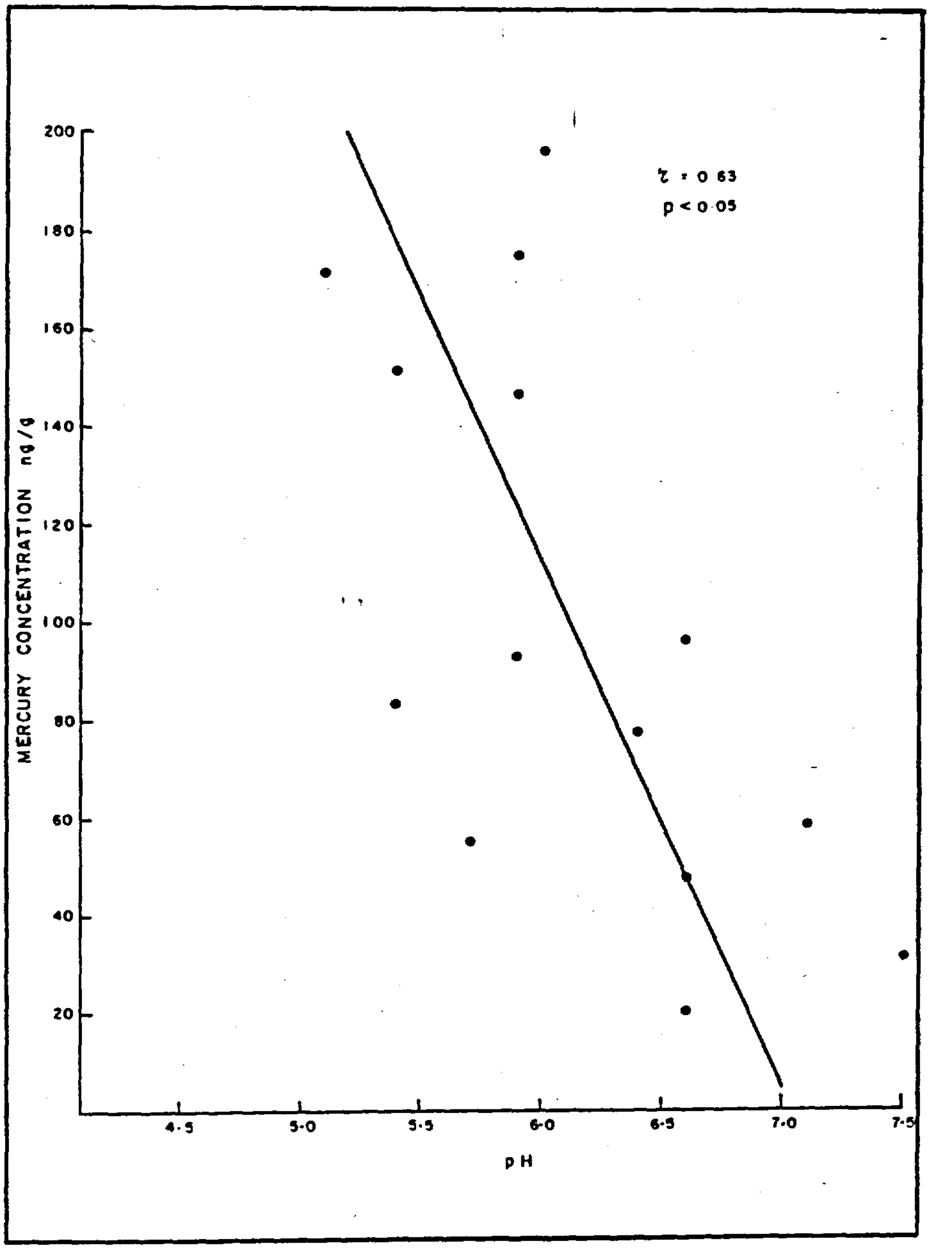

Figure 5-2. Mercury in Yearling Yellow Perch and Epilimnetic pH Relationships (Suns et al. 1980).

that, in Sweden, some well water has become acidified to the extent that substantial corrosion of household plumbing has occurred (Hultburg and Wenblad 1980). An occurrence of this kind could lead to increased levels of such metals as aluminum, zinc, copper, lead and cadmium in drinking water.

Groundwater Quality in Ontario

Many wells in the Precambrian area of Ontario are located in proximity to shallow bedrock, so the potential for acidification exists. The first field surveys were carried out in 1980 in the Muskoka-Haliburton area. A total of eighty-five groundwater samples were field-tested, and twenty-eight samples were analyzed, for major ions and some trace metals, in the laboratory. Groundwater was sampled in July from shallow springs and wells, from both bedrock and overburden formations. Eleven of the eighty-five samples had pH values less than 6.0, with the lowest value being 5.2. October sampling of five of the low pH wells resulted in only one sample with a pH value less than 6.0, suggesting that groundwater pH may fluctuate during the year. The lowest recorded pH of 5.2 was from a shallow well, servicing a permanent home near Bracebridge, Ontario. The owner has lived there about 10 years, but during the last three years has experienced water supply equipment failure, which has been attributed to acidic water reaching the system.

Altered Groundwater Chemistry in the Adirondack Region

The New York Department of Health has undertaken studies of acid precipitation effects on drinking water in the Adirondack Mountains of New York State. They have concluded that acid precipitation in the Adirondack region of New York is affecting the quality of drinking water, to such an extent that violations of drinking water standards could occur. In spring waters, the leaching of metals from natural bedrock or overburden can produce elevated metal concentrations. High concentrations are found in homes using metal piping in the distribution system, particularly if the lines are used intermittently.

Sharpe et al. (1980) provide significant information on the effects of deposition of lead and cadmium, as well as acid deposition, on the quality of drinking water from cisterns in Clarion County, Pennsylvania. Wet and dry deposition of lead and cadmium resulted in solutions which were in the same order of magnitude as recommended United States drinking water limits (50 μg/l and 10 μg/l respectively). Lead levels in tap water from cisterns were much higher than those found in the source water; about 16 per cent of the households sampled had tap water levels in excess of the United States drinking water standard. The investigators concluded that the increase in tap water lead levels resulted from acid corrosion of the lead solder in the joints in the cistern and plumbing. Thus, cistern water users are at special risk in areas of high acid deposition.

There is a time dependence for the initiation of adverse health effects resulting from drinking water contaminated with metals at, or approaching, the concentrations listed in Table 5-1. For example, brief episodic excursions of lead over the recommended standard, associated with snowmelt derived acidity in water from small lakes or streams, is not likely to be of major concern. Longer or continual consumption of water containing lead levels 25 μg/l could be of concern (NAS, 1977), although the actual standard for drinking water lead levels in the United States and Canada is 50 μg/l.

5.2.3 Sensitive Areas and Populations at Risk

Areas

In summary, the following areas will be particularly sensitive to health hazards from contaminated fish and drinking water:

1. poorly buffered lakes and streams (with a viable fish population);
2. watersheds with unusual accumulations of metals in sediments or soils;
3. areas which lack drinking water treatment facilities; and
4. areas with substantial lead plumbing.

Populations

The following populations will be susceptible to health hazards resulting indirectly from atmospheric deposition:

1. those dependent on fish from acidified waters as a major dietary staple;
2. those with elevated mercury or lead blood levels from other exposures;
3. women of childbearing age, and children; and
4. those dependent on cisterns as a primary source of drinking water.

TABLE 5-1

CANADIAN AND UNITED STATES DRINKING WATER GUIDELINES FOR TOXIC METALS (µg/1)

	Canadian	United States
Lead	50	50
Mercury	1	2
Cadmium	5	10
Copper	1000	1000
Zinc	5000	5000
Arsenic	50	50
Selenium	10	10

5.2.4 Data Needs and Research Requirements

Work is required to delineate the following factors, related to the effects of acid deposition on human health:

1. levels and species of metals in edible fish in the U.S.A. and Canada;
2. levels and species of metals in drinking waters of the U.S.A. and Canada;
3. levels of human tolerance for mercury in fish;
4. data to characterize and identify sensitive areas and receptors more fully;
5. deposition rates of acid from acidic precursors, such as sulphur and nitrogen oxides; and
6. effects on health from episodic and long-term exposures to acidic pollutants in most sensitive receptors.

5.2.5 Inhalation of Deleterious Substances

Recently, evidence has been gathered which indicates that even low level exposure to certain respirable substances can prove harmful to human health. Specifically, photochemical air pollutants have come under close scrutiny, especially ozone (O_3). Ozone is a secondary gaseous pollutant, formed as a result of photochemical reactions of volatile organic chemicals and nitrogen oxides. Therefore, the formation and transportation of ozone is limited by the production of NO_x and suitable environmental conditions.

Ozone is a deep lung irritant, capable of causing death from pulmonary edema in serious cases. Sublethal exposures produce substernal tightness, irritation of mucous membranes, dry cough, and headache. The lethality of ozone is influenced by factors other than concentrations and length of exposure. Young animals are more susceptible, and elevated temperatures, increased relative humidity and exercise all increase its toxicity (Casarett and Doull 1980). Ozone is also believed to be radiomimetic, and these effects are thought to be long lasting and perhaps irreversible. There is also some evidence that previous exposures to O_3 may impart some form of tolerance. Hackney et al. (1977) demonstrated significant differences in the reactivity of subjects from Los Angeles versus subjects from Toronto, suggesting that the individuals from Los Angeles had built up tolerance to O_3.

As with other toxicants, the individual health of a person has an effect on the results. People in poor health, or the aged, especially those with respiratory afflictions, are particularly sensitive to low level exposures.

Ozone is especially toxic when found in combinations with other respiratory irritants. Grose et al. (1980) found that 0.10 ppm O_3, combined with 0.22 ppm H_2SO_4 aerosol, significantly decreased tracheal ciliary activity, while 0.10 ppm O_3 alone had no effect. In fact, the decrease in activity was greater than that observed with H_2SO_4 alone. There are also preliminary data which indicate that mixture of ozone and sulphur dioxide (SO_2) at low concentrations produce more severe effects than either gas does separately (N.R.C. 1975)

Ozone produces eye, nose and throat irritation in the 0.1 - 0.15 ppm range (Ferris 1978), and the American Lung Association (1977) states that significant health effects are found when ozone levels are above 0.37 ppm. Goldsmith and Nadel (1969) found consistent increases in airway resistance after 1 hr. exposures of 1.0 ppm., while other researchers found similar results with lower O_3 concentrations and longer exposure times (Kerr et al. 1975, Young et al. 1964). Table 5-2 illustrates some effects at different exposure levels.

In summary, brief exposures to ozone can be linked to alterations in pulmonary function, and at low levels O_3 produces eye, nose and throat irritation. If chronic exposure produces tolerance, then brief episodic excursions of high O_3 concentrations will have a more profound effect on human health than long term low level exposures. On the other hand, the radiomimetic properties of ozone may produce significant health effects even at low dosage levels. Therefore, it would seem prudent to limit all O_3 exposures to below threshold levels (0.10 ppm), to maintain a suitable margin of safety.

Nitrogen oxides, another photochemical irritant, are primarily derived from internal combustion engines, and NO is rapidly converted to NO_2 in the atmosphere. However, once NO_2 is formed, it is then converted to HNO_2 in a relatively short time period. A recent National Air Pollution survey (1980) indicates that NO_2 concentrations are highest during the year from January to July, but concentrations do not exceed existing Canadian guidelines. Ozone levels, conversely, achieve maximum readings from April to July, and the annual mean concentration exceeds maximum acceptable levels at several locations, predominantly in Eastern Canada.

Nitrogen dioxide, like ozone, is a deep lung irritant and can produce pulmonary edema in severe cases. Both short- and long-term exposures to NO_2 enhance susceptibility to infections. Due to the relatively low levels of NO_2 in Canada and the lack of concrete epidemiological data, current standards seem adequate to protect

TABLE 5-2 EFFECTS OF OZONE IN MAN (WALDBOTT. 1973)

Concentration	Duration	Symptom	Observer
0.05 to 0.1 ppm	Immediate	Odor noticeable	Jaffe
0.1 to 1.0 ppm	2 weeks	Odor; shortness of breath; headache	Wilska
		Visual disturbances	Lagerwerff
0.6 to 0.8 ppm	2 hours	Substernal cough, irritation in trachea	Young and others
0.94 ppm	1½ hours	Cough; dyspnea, exhaustion	Jaffe
0.1 to 1.0 ppm	1 hour	Increased airway resistance	Goldsmith and Nadel

GOLDSMITH, J.R. and NADEL, J.A. (1969) J. Air Pollut. Cont. Ass. 19: 329-330.
JAFFE, L.S. (1968) Arch. Environ. Health 16: 241-255.
LAGERWERFF, J.M. (1963) Aerospace Med. 34: 479-486
WILSKA, S. (1951) Acta Chem. Scand. 5: 108-118
YOUNG, W.A. et al (1964) J. Appl. Physiol. 19: 765-768

human health. The most significant effect produced by transported NO_x may be the conversion to nitric acid and subsequent deposition.

Sulphur oxides and related particles are also important respiratory irritants. As with nitrogen oxides, the levels of SO_2 associated with transboundary transport between the U.S. and Canada are relatively low, and current standards seem adequate to protect human health. Some concern has been expressed, however, over regional transport of sulphur containing fine particles, including sulphuric acid, sulphates and associated substances. The effects of general particulate matter and sulphur oxides have been reviewed recently by Ware et al. (1981), Holland et al. (1979), and Spassoff (1981) and are the subject of a revised criteria document currently being finalized by the U.S. EPA. These reviews suggest that it would be inappropriate to single out sulphates as the only significant component of the sulphur - particle complex. Until ongoing standard reviews and perhaps additional research is conducted, it appears that attainment and maintenance of the current U.S. and Canadian standards for particulate matter would provide reasonable public health protection.

To the extent that transboundary transport contributes significantly to violations of such standards (an issue for Workgroup III to resolve), the matter should be the subject of the bilateral discussions. Presently the U.S. standards are 25 $\mu g/m^3$ annual geometric mean total suspended particles (TSP) and the maximum 24 hour level is 260 $\mu g/m^3$. The U.S. is considering the possibility of new standards based on particle size. No changes in the maximum acceptable levels for suspended particulate matter are anticipated in Canada (annual geometric mean, 70 $\mu g/m^3$; 24 hour mean, 120 $\mu g/m^3$).

5.3 VISIBILITY

5.3.1 Identification of Key Effects on Visibility

The effect of transboundary pollution on visibility is directly related to air quality, rather than deposition. The particulate phase precursors to acid deposition (mostly sulphuric acid aerosol and various ammonium sulphate aerosols) play a major role in atmospheric visibility. Available data suggest that nitrates exist predominantly in the vapour phase, and are, for the most part, of little consequence to visibility in eastern North America. However, for isolated point sources, visible brown plumes from NO_2 have been reported at distances of 100 km from the source (Menlo 1980).

The ability to define, monitor, model, and control anthropogenic visibility impairment is dependent on current scientific and technical understanding of the factors which affect atmospheric visibility. Because visibility involves the human perception of the physical environment, evaluation of the effects of air pollution on visibility must include specification of the process of human visual perception, and quantification of the impact of air pollution on the optical characteristics of the atmosphere.

From a scientific and technical point of view, deterioration of visual air quality is probably the best understood, and most readily measured, effect on air pollution. However, many important uncertainties and limitations exist in available knowledge. Significant implications of current understanding of vision in the atmosphere may be summarized as follows (EPA 1979).

(1) Visibility impairment is caused by the scattering and absorption of light by suspended particles and gases. Fine solid or liquid particles (atmospheric aerosols) and, to a lesser extent, nitrogen dioxide, are the most important anthropogenic causes of degraded visual air quality. Air molecules, weather variables and natural emissions also effect visibility.

(2) Light scattering and light absorbing pollutants reduce the amount of light received from viewed objects, and scatter ambient or 'air' light into the line of sight. This scattered air light is perceived as haze. Because these effects vary with the wavelength of light, discolouration can result. Extinction (b_{ext}) is a measure of light scattering and absorption.

(3) These effects can be quantified or approximated through use of theoretical mathematical treatments and experimentally derived pollutant/optics relationships.

(4) The perceptibility of pollution effects on light depends on human eye/brain responses. Studies of the eye/brain response to contrast indicate that typical observers can detect a 0.02 (2 per cent) or greater contrast between large, dark objects and the horizon sky. Assuming this threshold contrast, visual range, the farthest distance at which a large black object can be seen against the sky, is related to extinction by the Koschmeider equation:

$$Vr = \frac{3.9}{b_{ext}}$$

The overall impact of aerosol haze is to reduce visual range and contrast, and to change colour. Visually, the objects are 'flattened', and the aesthetic value of a vista can be degraded, even though the distances are small relative to the visual range. Much of the scenic value of a vista can be lost, when the visual range is reduced to a distance that is several times the greatest line-of-sight range in the scene (Charlson et al. 1978).

Aerosol haze can also degrade the view of the night sky. Star brightness is diminished by light scattering and absorption. Perception of stars is also reduced by an increase in the brightness of the night sky, caused by scattering of available light. In or near urban areas, night sky brightness is significantly increased by particle scattering of artificial light. The combination of extinction of starlight and increased sky brightness markedly decreased the number of stars visible in the night sky at fine particle concentrations of 10-30 $\mu g/m^3$ (Leonard et al. 1977).

As noted above, available empirical information suggests that fine particulate sulphates play a major role in visibility reduction. Direct measurements and statistical analyses indicate that fine sulphate aerosols account for 30-60 per cent of visibility reduction, related to fine particles, in areas as diverse as the northeastern United States, Los Angeles, and the southwest Mountain States. However, other fine particule constituents are also important, and can dominate light scattering and absorption in various regions (EPA 1979).

Studies of trends in eastern U.S. airport visibility indicate that, while winter visibilities improved in some northeastern locations, overall eastern visibility declined. Summer, often the season of best visibility in the early 50's, currently provides the worst. From 1948 to 1974, summertime haze (extinction) increased by more than 100 per cent in the central eastern states, by 50-70 per cent in the Midwest and the eastern Sunbelt States, and by 10-20 per cent in the New England area. Although the results of airport surveys should be viewed with caution, the results are consistent from site to site (Figure 5-4).

Comparable data should be available soon for eastern Canada (Husar et al. 1979).

Very close parallels have been noted between the geographical/seasonal features of airport visibility trends, and the geographical/seasonal features of trends in atmospheric sulphate concentrations, sulphur dioxide emissions, and coal use patterns. These parallels provide strong circumstantial evidence that the historical visibility changes in the east were caused, at least in part, by trends in sulphate concentrations and sulphur dioxide emissions.

Episodes of regional scale haziness have been observed, in the eastern United States and Canada. Examination of airport data,

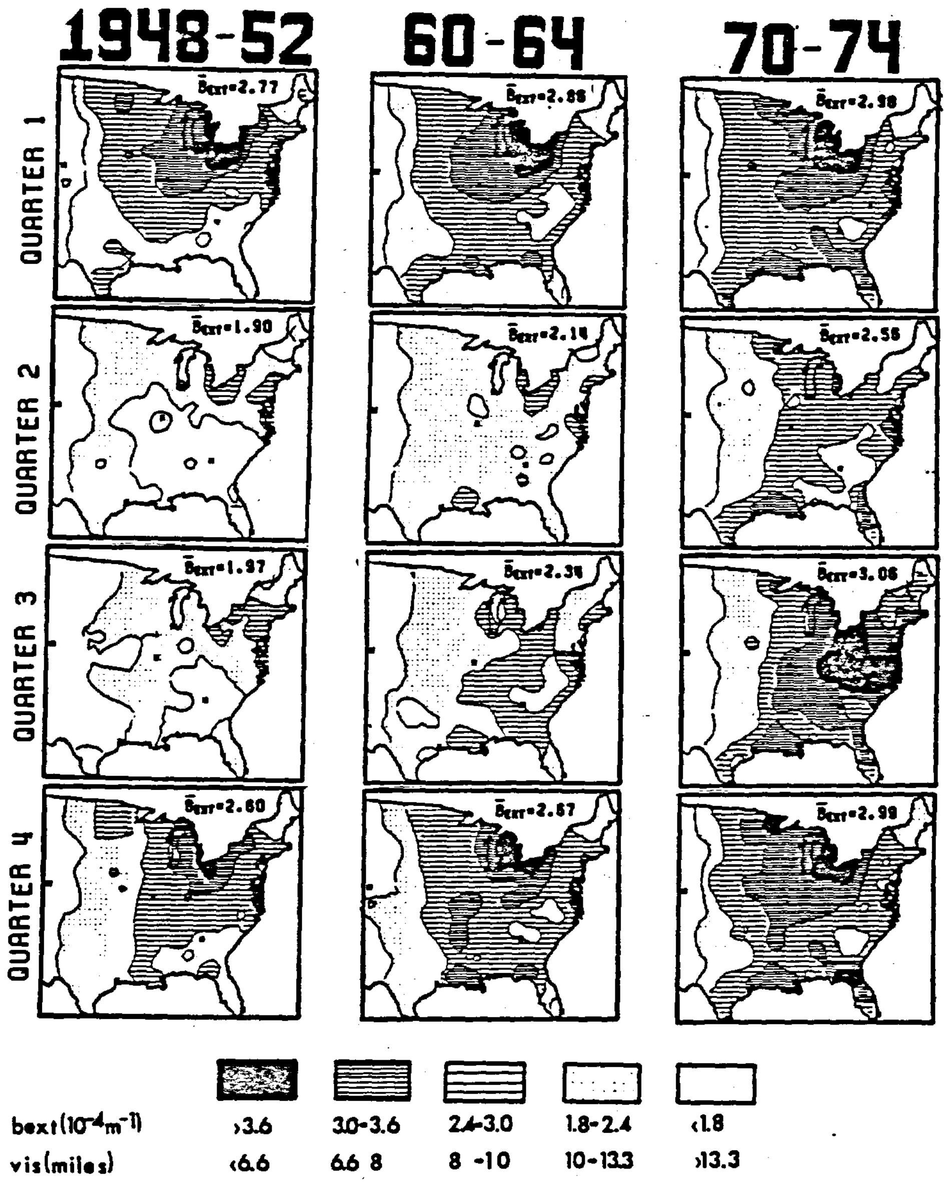

Figure 5-3. Seasonal and spatial distribution of long-term trends in average airport visibilities for the eastern United States (Husar et al. 1979)

pollution measurements and satellite photography indicates that these haze air masses move across eastern North America in the manner of high pressure systems, causing significant visibility reductions in areas with little or no air pollutant emissions.

5.3.2 Assessment of Impacts

As note above, visibility in the northeastern U.S. and Canada shows strong seasonal trends, with periodic episodes of intense haze moving across large regions several times each summer. In addition to the obvious adverse aesthetic effects, when fine particles and humidity combine to reduce visual range below three miles, aircraft operations are curtailed.

Figure 5-5 illustrates the relationship between fine particle loadings and visual range. At high background loadings, small increments make only small changes in visibility. Humidity strongly enhances the effects of fine sulphates, as shown in Figure 5-6. This relationship is derived from regressions of form:

$$b_{ext} = b_o + \frac{0.04\ (\text{sulphate})}{(1 - RH)}$$

When background conditions are understood, this can be used to relate predicted sulphate levels to resulting visual range. On the other hand, actual impacts must be derived from the results of regional modelling runs.

5.3.3 Sensitive Areas and Populations

Clean areas such as found in western North America, are the most sensitive to visibility degradation. In the U.S., the Clean Air Act affords special protection to visibility in 156 'Class I' areas, including national parks and wilderness areas. Many of these Class I areas are located near the U.S./Canadian border and one (Roosevelt-Campobello) in Canada. However, any area, urban or rural, with normal viewing distances of a mile or more may be affected by episodic regional haze, carrying acid precursor substances.

Assessment of the relative value of visibility in urban, versus rural, areas is beyond the scope of this report.

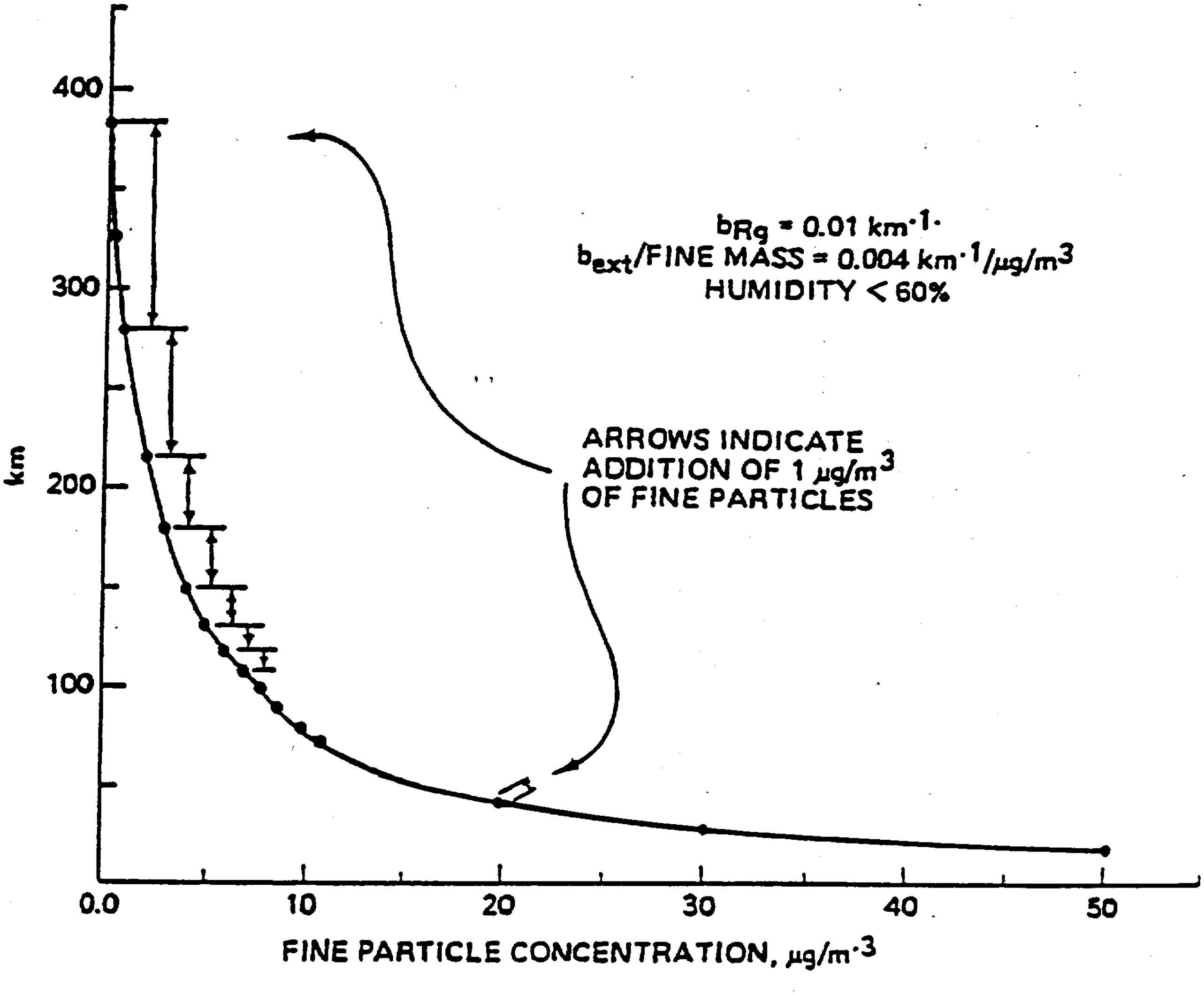

Figure 5-4. Effects of fine particle increments on calculated visual range (EPA 1979).

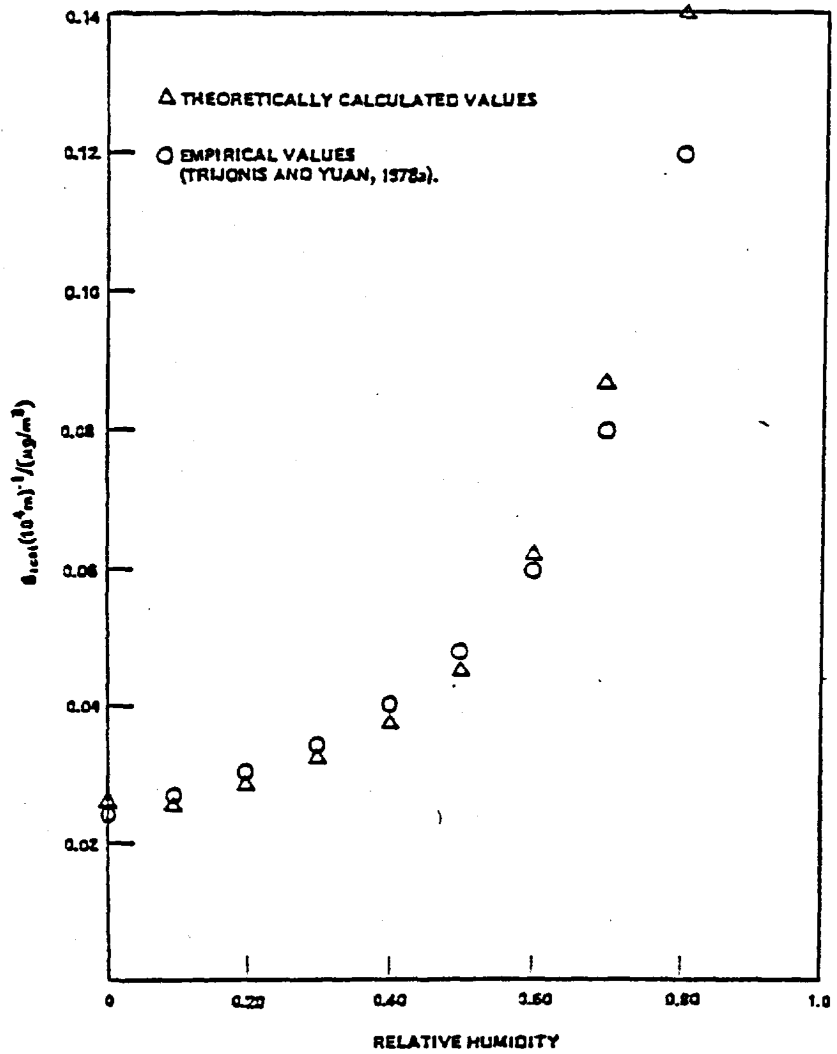

Figure 5-5. Light-scattering per unit mass of sulphate aerosol as a function of relative humidity (Latimer et al 1978).

5.3.4 Data Needs/Research Requirements

The following instruments are required to complete work related to the effects of atmospheric deposition on visibility:

1. output or regional modelling groups;
2. decision on how to treat aesthetic effects of long-term transport of air pollutants.

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SECTION 6

EFFECTS ON MAN-MADE STRUCTURES

6.1 INTRODUCTION

Previous sections of this report have focused substantially upon the effects of pollutants on sensitive receptors in remote wilderness areas. In the present section, the receptors, man-made structures, are usually co-located with the pollutant sources. The separation of pollutants from near or intermediate sources and distant sources, as defined earlier, is nearly impossible to achieve, particularly once pollutants such as SO_2 have been oxidized to sulphates, the more stable secondary product. This distinction is further impaired by the significant difference between concentrations (and potential effects) from local sources, on the one hand, and long-range sources, on the other: normally, the atmospheric load from local sources completely masks the low concentrations arriving from far upwind, except in those cases where there are few or no local emissions.

In the context of corrosion processes, however, the distinction is academic, since damage in general would be reduced through a reduction in concentrations of the major agents, regardless of the distance these pollutants had travelled to the deposition site.

Consideration of damage will be limited to exterior surfaces, not only because the wet deposition of pollutants and surface wetting by rain, dew and snow are primarily to these exteriors, but also because the concentrations of corrosive gases, such as sulphur dioxide, ozone and nitrogen oxides, are usually much higher outdoors than inside buildings.

There has been some success in relating damage to economic costs, particularly in the case of sulphur dioxide, perhaps the most important corrosive agent. Direct costs of duplication, replacement, or protection can be calculated. However, the economic analyses have not been as successful in several other areas. These areas include the determination of the amount, distribution and economic value of a certain material in use; the extent of deterioration associated with pollution damage for a specific material; and the quantification of replacement factors, including replacement for aesthetic reasons and non-replacement because of obsolescence. Clearly, replacement factors can involve social variables, including education, fashion, pride, etc. Another difficulty associated with economic analysis concerns quantifying economic loss due to damage to a cultural heritage. This task is often impossible. Perhaps this valuation is irrelevant, however, in the same sense as the valuation of a remote wilderness lake or a fish species is irrelevant.

6.2 OVERVIEW

Acid deposition, oxidants, gases and particulates contribute to the accelerated degradation of materials. Plastics, elastomers, paints and organic coatings are degraded by oxidation, by acids and by acid-catalyzed polymer decomposition. Particulates adversely affect the appearance of surfaces and can cause the retention of aggressive chemical species. For example, on metals, particulates containing soluble inorganic salts or absorbed corrosive gases, can create local electrochemical cells of high activity.

Many metallic construction materials are adversely affected by acid deposition, through increased dissolution of protective surface oxides, or of the metal itself. Oxidants are thought to be less damaging to metals and, in some cases, have been shown to lower metallic corrosion rates. Certain specialized metallic electronic components have been shown to be very sensitive to certain pollutants, particularly SO_x species.

Masonry materials exhibit a wide range of responses to pollutants. Carbonate-containing materials, such as limestone or marble, are very susceptible to attack by acid deposition. Recent studies have shown that these materials can be attacked by atmospheric sulphur dioxides through several mechanisms. The oxidation of sulphur dioxide to sulphuric acid can be catalyzed by chemical means (metallic ions, particularly Fe^{2+}, or carbon), or by micro-organisms. The resulting sulphate ion reacts with the calcium carbonate of the stone to form calcium sulphate (gypsum). Also, bacterial action upon granite has been observed.

Other masonry materials, particularly those containing large amounts of silicates, (e.g., concrete), are more resistant to most acidic atmospheric pollutants. Wood materials in construction are generally resistant to weak acid deposition, but are attacked by oxidants.

As the effects of air pollutants on materials become better understood, it will be possible to perform cost/benefit analyses, and to develop policy guidelines relating to the amounts of pollutant loading which can be tolerated. Some attempts have already been made in this direction. However, for the case of historic structures it is not always possible to provide an objective economic assessment of damage, as is the case for degradation occurring in pristine wilderness areas which are ecologically sensitive.

It is recognized that the architectural and sculptural expressions of our two heritages are a non-renewable resource of the most precious sort. Historic structures and monumental statuary represent the most visible aspects of historical and cultural evolution. In the United States, legislative recognition of the value of this cultural heritage, giving a mandate for its preservation, began in 1906, with the passage of the Antiquities Act, and continues to this day, with the passage of the Historic Preservation Act Amendments of 1980. The 1916 Organic legislation of the National Park Service gives a mandate for the conservation of "...'historic objects'...to provide for the enjoyment of the same in such a manner and by such means as will leave them unimpaired for the enjoyment of future generations."

In Canada, similar legislative action has been taken in the Archeological Sites Protection Act, and in the 1953 Historic Sites and Monuments Act.

Preservation of original material is intrinsic to maintaining the cultural value of architectural and sculptural works. The patina of history cannot be replicated. Natural materials incorporated into man-made structures cannot, in most cases, be duplicated today.

The sources of supply for historic building materials are limited, if not extinct. Quarries have been exhausted, and stands of first growth timber are scarce. The pool of skilled craftsmen and artisans, able to extract and shape these materials, is diminishing. As in the case of many sensitive ecological systems which are being altered, degradation of certain man-made structures is an irreversible process. For these reasons, the monuments of our cultures must be distinguished from natural and economic resources in studying the effects of atmospheric depositions. Measures of the net loss by deterioration must embrace aesthetic and historical contributions, and not rely on monetary scales alone. Trade-offs made in mitigating the impact of air pollutants should address the preservation of the qualities that constitute the significance of the monument.

Notwithstanding these qualifications, it is possible to make reference to economic assessments of corrosion damage attributed to air pollutants. A recent study, completed by the Council for Environmental Quality, has estimated that the cost of damage, due to corrosion of buildings and fabrics in the United States, is of the order of \$2 billion per year. The cost of damage to natural ecosystems and crops, for example, is additional.

A second report, released by the Organization for Economic Cooperation and Development (OECD), indicates that, for the eleven European countries studied, based on an expected production of 24.4 million metric tons in 1985, the resulting benefit of a 50 per cent reduction in SO_2 emissions, in terms of reduced damage, would be of the order of \$1.16 billion per year. In this case, the benefit is based on corrosion of metals only, and excludes limestone and sandstone structures, since no exact dose/response relationships are available, between deposition of sulphur compounds on these materials and corrosion rates. Nor is the loss due to impoverishment of a cultural heritage assessed.

Additional information on economic consequences of air pollution is contained in papers by Haynie (1980a), Yocum and Upham (1977) and Spence and Haynie (1972). These examples are but a few of the many documents which are available, which examine the economic consequences of a wide variety of atmospheric pollutants. In these instances, dose/response relationships are obtained by relating the concentrations present in the atmosphere to the degree of damage observed or measured. The more difficult task, noted earlier, of relating this damage to costs (implied duplication, protection or replacement), has not yet been satisfactorily completed.

6.3 ASSESSMENT OF EFFECTS

As mentioned above, the assessment of deterioration, due to pollutants transported over long distances, is confounded by the impact of pollution produced locally. For instance, in northern climates, corrosive effects due to atmospheric pollution may be masked, in winter, by the impact of road salt ($CaCl_2$ and/or NaCl), which is particularly corrosive to metals. These salts can also damage porous masonry building components, through mechanisms similar to those discussed earlier for gypsum. Any assessment of the impacts of atmospheric pollutants on man-made structures must take into consideration several complicating factors. To start with, not all building materials are durable, even in the absence of atmospheric deposition. Hence, it is important to differentiate between expected weathering, and accelerated deterioration attributable to atmospheric deposition.

In the following section, effects associated with some of the more important pollutants will be discussed. It is understood that the pollutants are delivered to the corrosion site in either wet or dry form, that is, during a precipitation event, or during a dry period. The dry deposition may occur in particulate or gaseous form.

6.4 MECHANISMS

Chemical/physical corrosion processes are those most extensively discussed in the literature. It is suggested that SO_2 is the primary species causing damage to materials exposed to the atmosphere (Boyd and Fink 1974, Harker et al. 1980, Kucera 1976, Mansfeld 1980, Mikhailovskii and Sanko 1979, OECD 1979, Yocum and Upham 1977).

In the case of zinc, dose/response relationships for SO_2 have been developed (Haynie 1980a, 1980b, Haynie and Upham 1970), while the impact of acidic precipitation is not well understood. The pH value of precipitation is probably a significant factor in the case of zinc and copper, which develop protective coatings of basic carbonates or oxides (Guttman and Sereda 1968, Mattsson and Holm 1968). At pH near 4, the protective coating may be rapidly dissolved, exposing the metal (Allaino-Rossetti and Narabelli 1976, Gettens 1964).

To date, there have been few studies which provide estimates of the relationship between degrees of deterioration and atmospheric deposition. Monitoring of air quality indices, as well as meteorological variables, particularly temperature and humidity, has been scanty. The taxonomy for describing and measuring the deterioration of metal, architectural, and sculptural material, is not yet universally established.

As indicated earlier, a complicating feature, in assessing damage related to acidic precipitation and pollutants carried from great distances, is the confounding impact of local pollution sources. In the case of sulphur dioxide, the conversion rate to sulphate in the atmosphere is slow, of the order of 3 per cent per hour. If local SO_2 emissions, deposited on local buildings, are subsequently oxidized to sulphate, it is impossible to distinguish the local source from the sulphate deposited by acidic precipitation, and originating from sources several hundred kilometers upwind. Hence, all dry materials that have fallen upon a surface during a dry period may directly cause corrosion, or may lead to enhanced corrosion, once a surface is wetted.

There is little information relating corrosion rate and available NO_x. Haynie (1980a) assessed corrosion rates of steels by NO_x, SO_2 and ozone under varying relative humidity, temperature and wind-speed conditions. A recent paper by Byrne (1980) suggests that the corrosion of aluminum is very much more influenced by the presence of NO_x than by that of SO_2. In addition, the author suggests that SO_2 may be able to reduce nitrogen oxides to nitrogen gas in the presence of a catalytic surface, such as Al_2O_3.

On the other hand, HNO_3 has a very deleterious effect on most metals, more so than H_2SO_4 or HCl (McLeod and Rogers 1968). In addition, metal nitrate salts tend to be more soluble than the sulphate salts, which means that nitrate corrosion products could be readily washed from surfaces, exposing fresh metal to attack, while sulphate products could remain on the surface to inhibit further corrosion. Also, when some corrosion products are washed out of masonry surfaces, very damaging efflorescence can occur.

Future implications of HNO_3 corrosion are serious, when taken in the context of NO_x emissions predicted for the next 20 years. It is expected that these will increase significantly (Altshuller and McBean 1980). The conversion of NO_x to nitric acid, during its residence in the atmosphere, is not well understood, but more and more attention is now being focused on nitrogen chemistry and its contribution to acidic precipitation. When this nitric acid in the rain is deposited with chloride-containing species (in marine environments, for example), the corrosive potential is greatly increased.

While there is some speculation that ozone may reduce the corrosive potential of SO_2 (Haynie and Upham 1971), the direct corrosive effects of ozone on paints, elastomers and plastics are well known (Haynie et al. 1976, Spence and Haynie 1972, Yocum and Upham 1977).

Considerable work is currently underway, to examine the processes involved in the deterioration of natural masonry materials, such as limestone, marble and sandstone. In all cases, the stone provides varying amounts of calcium carbonate; acidic water reacts with the available calcium carbonate to form gypsum ($CaSO_4$) (La Gauri and Holden 1981). Other sulphates, such as Na_2SO_4, are also formed. surface dissolution, and the further dissolving of mortar between building stones, can lead to weakening of the structure as well as the deterioration of the surface.

Sulphates are very soluble materials. In the case where $CaSO_4$ is formed on sandstone, the high porosity of the sandstone provides an open structure for the internal development of gypsum crystals, which can exert extremely large pressures in the porous stone, and lead to internal disintegration (Arnold 1976, Brann and Wilson 1970, Spedding 1969, Thompson and White 1974, Weaver 1980).

Since the gypsum solution can migrate over the total surface, it is possible for this type of deterioration to occur at sites where rain has not contacted the building. The chemical formation of gypsum, and other salts, is often observable as an efflorescence, or build-up of inorganic, crystal-like scales on the surface.

There is little information on the effects of atmospheric ammonia on the corrosion of materials. However, it has been suggested that ammonia may be a major indirect contributor to the early stages of atmospheric corrosion (Ross and Gallaghan 1966). Ammonia, along with other species, can combine with water to lower the surface tension. In consequence, a larger portion of the material surface can be wetted, and become, therefore, more susceptible to attack by atmospheric pollutants.

Biological weathering has been proposed recently as a major contributor to deterioration. Bacteria on the surface of buildings draw sulphur dioxide (SO_2) from the atmosphere; the microbe's metabolic system converts the gas into sulphuric acid which it uses as a digestive fluid (Babick and Stotzky 1978, Hansen 1980, Winkler 1977). The digestive fluid attacks the calcium carbonate in the limestone, marble and sandstone, liberates carbon dioxide, the microbe nutrient, and thus, produces calcium sulphate as a by-product. Similar destructive reactions can occur on granite, where carbonate-containing dust can support the same initial reactions. Once initiated, the bacterial digestive fluid can attack the granite silicate structure (Winkler 1973).

Other studies have claimed that all deterioration can be attributed to chemical and physical (mechanical) processes, and that biological aggression is negligible (Fassina 1978, Torroca 1981).

6.5 IMPLICATIONS OF TRENDS

It is anticipated that, over the next 20 years, NO_x emissions into the atmosphere will increase in the order of 35 per cent. During the same period, it is expected that SO_2 emissions will remain the same, or increase slightly, based on current energy utilization projections. Under these circumstances, it is anticipated that the nitric acid in rain will substantially increase, with large potential effects in terms of materials deterioration.

Since the pollutants causing corrosion and deterioration may be delivered to the material in either wet or dry form, it is of interest to examine the consequences of episodicity. It has been shown that, in some instances where most of the deposition occurs in dry form, the occurrence of rain may, in fact, be beneficial, even if the rain is acidic, since it performs a washing function, removing the collected deposition of corrosive materials from previously dry surfaces. In the event that the site receives regular acidic rain, it is the wet deposition which delivers the main corrosive load to the materials site.

Hence, it is both the chemistry of the material being deposited, and episodicity of deposition, which must be taken into consideration in assessing the potential for damage. In this regard, it is of interest to consider the consequences of a light shower falling upon a surface which has been dry for some time. If only wetting occurs, the activation of accumulated dry deposits can lead to serious corrosion damage.

Another example of episodicity is the occurrence of spring snowmelt, after a subzero period of many months. In this case, all the pollutants delivered, either by the snow or in dry form, are available for dissolution from the snow pack. Since most of the pollutants are selectively leached from the pack with the first 10-25 per cent of melt water, the resulting fluid could be very corrosive. If the snow has been accumulating on buildings, or if surface runoff flows down the sides of foundations, considerable damage may result.

6.6 SUSCEPTIBLE MATERIALS AND THEIR DISTRIBUTION

All types of man-made structures show some sensitivity to air pollution. Metals are most affected by acidic species, which can cause dissolution of the metal or protective surface films. Organic materials, that is, plastics, paints, elastomers, and wood, are attacked by acids and oxidants (Spence et al. 1972). Masonry materials are affected by gases and acids and, perhaps, indirectly by bacterial growth that depends on the availability of pollutants, such as SO_2.

Several cases of specific damage to masonry structures at well documented sites are noted in the literature. In the cases of the Acropolis and the Cologne Cathedral, the deteriorated structures are being subjected to extremely high local levels of pollution.

1. The Elgin Marbles, transported to the British Museum at the end of the 18th Century, can be viewed as a control group for measuring atmospheric effects on the buildings of the Acropolis in Athens, Greece (Skonlikidis et al. 1976, Spence and Haynie 1972). The preserved state of the protected museum marbles contrasts sharply with the sculptures which, until recently, remained in situ.

2. The Cathedral in Cologne, West Germany, has suffered much deterioration from its urban-industrial environment (Luckat 1976, Seneviratne 1976). In contrast, Ludwig II's Neuschwanstein Castle, built of stone from the same quarry at the same time that Cologne Cathedral's 200-year building program was completed, offers a real-world controlled sample. The stone at Neuschwanstein shows no sign of deterioration, in contrast to the crumbling stone of the Cathedral. Atmospheric sulphate deposition at Neuschwanstein averages 6-8 $mg/m^2/day$ (22-29 kg/ha/yr), compared to 130 $mg/m^2/day$ (475 kg/ha/yr) in the Cathedral area.

3. A recent study in Ottawa, Canada, has documented the consequences of both material dissolution and internal fracturing of sandstone buildings (Weaver 1980). Acid deposition is causing release of pollutants trapped in the stone in past years, causing increased damage. Ottawa is essentially a non-industrial city, with an annual average pH of rain of less than 4.2.

4. The Environmental Protection Agency (U.S.) has a study underway to assess the effects of acid rain on marble gravestones that mark military graves in the United States (Baer 1980). These stones, provided by the Veterans Administration, are obtained from only two or three quarries, and have been placed in over 100 national cemeteries throughout the country, since veterans first were eligible to receive them (1873). The stones provide two sets of chemically uniform indicators (granite, marble), which have recorded, over precise periods of time, the effects of corrosion at each site.

Surface corrosion of bronze statuary is another example where the major concern is focused on the maintenance of a tangible heritage, which is being subjected to the effects of atmospheric deposition. As is the case with buildings, the distribution is concentrated essentially in urban centres. The sculptured shape is the key value, rather than the structural material itself; corrosion of the sculptured surface is tantamount to loss of the cultural value of the statue.

Protective coatings applied to both monuments and buildings are treated as sacrificial finishes. If weathering of the finish or coating accelerates with increased pollutant deposition, then the cycle for renewal can be adjusted. At present, however, sacrificial coatings for masonry structures are not viable. Attempts to shield threatened masonry structures with protective coatings have not generally been successful; they are subject to failure in adhesion and often cause spalling of the substrata material. With regard to statuary, coatings must not only meet corrosion requirements, but also maintain aesthetic qualities.

As noted, the great majority of buildings, structures and statuary, which are being subjected to the deteriorating process associated with atmospheric transport and deposition, are found in urban areas. Hence, a delineation of sensitive areas will be dominated by industrial and demographic distributions, rather than geographic features.

6.7 DATA NEEDS AND RESEARCH REQUIREMENTS

Although the examination of the corrosion of materials is a well established discipline, dose-response relationships, taking account of atmospheric variables as well as agent concentrations, are rather poorly documented. While some gross relationships are understood, work is required to delineate the following specific factors:

1. constituents which are active on selected materials (e.g., the impact of ammonia on the corrosion of carbon steels, low-alloy steels and copper alloys);

2. effect of background levels of chloride ions and carbonyl sulphide (Gradel et al. 1981) on the corrosion of materials;
3. the role of particulates in materials degradation;
4. the role of sulphates in the corrosion of materials, compared to the better understood role of SO_2;
5. effects of episodic, in contrast to continuous, moisture and temperature cycles;
6. effects of biological activity on building materials containing carbonate species, on surfaces exposed to carbonate-containing dusts, and on metals and alloys;
7. neutralizing agents which may be available in the atmosphere and which have not yet been monitored in precipitation network studies;
8. dose-response relationships for a range of corrosive agents and surfaces, determined in field and controlled environments, and in laboratory models;
9. the synergistic relationships between different corrosive agents;
10. the role of electrophoretic effects produced in porous stone by the absorption of strong electrolyte solutions;
11. soil sensitivity and underground corrosion; and
12. stress corrosion cracking of Al and Cu alloys by a number of agents.

Many of these needs were discussed by Yocum and Grappone in a report to the Electric Power Research Institute (1976).

In addition to these areas of study, which have not yet been adequately addressed, there are certain data sets which would be useful in the development of a final report:

1. estimates of wet and dry chloride deposition (since chloride plays a very important synergistic role, with nitric and sulphuric acid, in corrosion processes);
2. estimates of pollutant loads on susceptible structures, giving relative contributions by local sources and distant sources; and
3. data from the EPA tombstone study, which is now underway in the United States.

6.8 METHODOLOGIES

Testing of materials, to deterimine their resistance to atmospheric corrosion or degradation, is conducted at a number of established sites around the world (Committee G-1 1968). Approximately fifteen of these sites are in the United States, east of the 100th meridian, with additional sites being maintained on a priorietary basis by individual organizations. The sites are typically characterized as ural, urban, industrial, or marine, to reflect the perceived quality of the environment at each site. Meteorological and air quality monitoring have not generally been performed at these sites. Recently, measurements of temperture, rainfall, humidity, wind speed and direction, solar radiation, SO_2 and chloride ioin concentration, were begun at the marine stie at Kure Beach, North Carolina (F.L. La Que Corrosion Laboratory). There has been, however, no evidence to suggest that acid deposition, nitrogen oxidesd, oxidants, particulate matter and ammonia are being measured at any of the other material test sites.

In 1980, a temporary monitoring station was established at the Bowling Green U.S. Customs House, in New York City, as a joint NPS-EPA contribution to the Nation-Committee on Challenges to a Modern Society monitoring project (Livingston 1981). The objectives of this study are to:

1. intercompare site specific measurements (including various distances from the street) with the permanent Manhattan monitoring station measurements;

2. correlate these measurements with material deterioration; and

3. determine the efficacy of a variety of instruments for measuring material effects.

The station is monitoring acid precipitation deposition with a continuous sulphur dioxide analyser, lead peroxide and caustic plates. Nitrogen oxide and ozone also are being measured with a continuous analyser. Rainwater samples are collected and analysed for pH and ionic concentration, both before and after contact with building materials, in order to measure rate of attack. Particulate deposition studies are estimating the mass particulates concentrations of nitrates, sulphates and trace elements. An integrated deposition measure is made with the IRMA device (Immission Rate Measuring Apparatus) developed in Germany. Ammonia is not being measured.

Over the years, certain aspects of materials testing in the atmosphere have been incorporated into standards by the American Society for Testing and Materials (ASTM), to estimate or minimize some of the more obvious uncertainties. For the atmospheric corrosion of metals, these range from the preparation, cleaning and evaluation of specimens, to the way tests are conducted and data are recorded (ASTM-Part 10 1980). Several methods have been developed to characterize pollutant levels in the atmosphere, for example, sulphur dioxide, using lead peroxide candles (ASTM-Part 26 1977). A standard for measuring time-of-wetness for surfaces exposed to the atmosphere has been prepared in draft form (ASTM G-01.04.01 1980, Sereda, Croll and Slade 1980). An ASTM task group was recently established for calibrating the corrosiveness of the atmosphere at test sites (Baker 1980, Baker and Lee 1980).

The characterization of time-dependent meteorological air quality and acid deposition variables at test sites, and the correlation of these variables with the response of materials to their environment, while clearly relevant to atmospheric corrosion and degradation, has long been recognized as a complex and challenging task. Such an effort has usually been considered unnecessary where, as in most cases, the primary goal of atmospheric testing has been to determine the relative performance of a series of materials and, thereby, to establish criteria for their selection, improvement, and preservation in a particular environment. Many studies of this type have been made on a variety of metallic and non-metallic materials.

Among the earliest departures from the strategy of comparative testing were studies, led by Larrabee and Coburn (1962), and pursued on a broader scale by ASTM Committee G-1, to measure the corrosiveness of the atmosphere at different test sites for selected metal alloys. Underlying this interest was the desire for a fundamental understanding of the interactions between materials and atmospheric constituents, so that the performance of materials could be predicted, based on properties of the material and of the atmosphere. Such a concept implies a dose-response function which defines the relationship between the rate of corrosion or degradation and:

1. the concentration of reactants in the atmosphere and on the material surface;
2. the nature and disposition of reaction products; and
3. meteorological and environmental factors which affect the intensity of exposure to the reactants and the fate of the products.

The dose-response function quantifies the material-environment interaction, and provides the fundamental basis for the development of economic damage functions used for damage (benefit) prediction, and for designing pollution control strategies (Benarie 1980, Gillette 1975, Hershaft 1976, Liu and Yu 1976, Mansfeld 1980).

In laboratory studies of the mechanism, kinetics, and thermodynamics of materials corrosion and degradation processes, and of the effect of specific atmospheric constituents on these processes, experimental conditions are well controlled, and a wide variety of sampling and analytical techniques are available (Duncan and Spedding 1973a, 1973b, Haynie, Spence, and Upham 1976, 1978, Spence and Haynie 1974). A typical experimental approach is to vary the dose rate of one pollutant while holding other variables constant, and study the response of the material. In the case of metals, studies of this type are usually done for relatively short times, compared to the time required to form a steady-state corrosion film. Hence, they are often limited to simple conditions, involving corrosion initiation on a bare, or slightly oxidized, metal surface. This approach is adequate for establishing specific details of the responses of materials to pollutant dose rates. It has not, however, been effective for describing the performance of materials in atmospheric exposures, where the permutation and interaction of environmental and meteorological variables is complex and constantly shifting over time.

By far the greatest amount of work on atmospheric corrosion, and the degradation of materials, has involved field exposures at regional test sites, where the effects of exposure are clearly defined by changes in the character and properties of the material (Haynie and Upham 1970, 1971, Kucera 1976, Mansfeld 1980, Spence and Haynie 1972, Upham and Salvin 1975, Winkler 1978). Short- and long-term effects can be observed; effects in 'different' environments are readily obtained for analysis and interpretation. On the other hand, the local environmental conditions are obviously variable, and it is difficult to determine cause-and-effect relationships from regional meteorological/environmental data (Haynie 1980a, Sereda and Ashton 1981).

Moreover, the evidence, from studies in Europe and North America, is that the meteorological and materials data obtained at specific sites is not generally transferable and applicable to sites at other locations. This is because of differences not only in the composition of pollutants but, perhaps more importantly, a consequence of differences in the properties of the "same materials". For example, bricks may be made from clay with widely different chemical composition, may be fired at different temperatures and for different lengths of time, or may be treated with different glazes. All these variations have an influence on the ultimate impact of atmospheric components. Finally, when making comparisons between exposures at different sites, it is important to consider, for example, the orientation and pitch of the samples and their elevation above ground (ASTM-Part 10 1980). Inconsistencies in these variables may lead to differences in response which cannot be accounted for.

An essential difficulty, particularly for heavily used test sites (such as Kearny, N.J., State College, PA, and Kure Beach, N.C.), has been the absence of air quality and acid deposition data which could be correlated with atmospheric corrosion and degradation data. Most often, such data have been obtained from a nearby monitoring or weather station, where conditions may or may not correspond to those at the test site (Haynie 1980a, Haynie and Upham 1970, 1971, Mansfeld 1980).

The analysis of field test data, to determine the sensitivity of materials to environmental factors, is largely empirical; the fundamental reactions and interactions have so far proved to be too complex to be treated otherwise. Three basic approaches have been taken for corrosion data. Haynie, and others (Haynie et al. 1978, Haynie and Upham 1971, Legault and Pearson 1978, Mansfeld 1980, Yocum and Grappone 1976), utilize a 'power' function, which describes how the corrosion rate varies over time as the corrosion film ages. The rate constant is modified by exponential factors, which define the effect of specific atmospheric constituents. Cramer et al. (1980) employ a similar approach, but use an algebraic factor, related to the composition of the corrosion film, to modify the rate constant. In the second approach, Guttman and Sereda (1968), and others, have expanded the material response function as a Taylor series, for a specific exposure time, and determined the coefficients for the lower-order terms by a least- squares fit of the data. The data do not generally warrant more than a few linear and interaction terms. In the third approach, Knotkova-Cermakova et al. (1978) apply feedback principles to the mathematical analysis, whereby the corrosion rate for the present, and all previous times, is thought to influence the corrosion rate in the future by its effect on the growth and aging of the corrosion film.

Of these approaches, the third appears the most satisfying, from a mechanistic viewpoint. Applications of the first have been quite useful for extrapolating experimental results, while the second more readily identifies, for any given exposure time, the important variables and interactions at a specific site. However, owing to the essential non-linearity of the response function, results obtained by the second approach for different test sites are not generally comparable, and should not be used for interpolating to other conditions.

Analysis of most field test data, by any of these approaches, has suffered from the lack of environmental and meteorological measurements, specific to the exposure site and to the exposure time. It is generally recognized that there must be a shift away from this position, and that meteorological, acid deposition and air quality instrumentation should be incorporated into field materials experiments. In this way, the key atmospheric and meteorological effects on materials can be determined, to provide an accurate assessment of the impact of acid deposition on materials corrosion and degradation.

6.9 ASSESSMENT OF ECONOMIC DAMAGE

Estimates of the financial losses attributable to air pollution, if accompanied by appropriate statements of uncertainty and of assumptions, are useful even if the range of error is fairly large. This is especially true now, in view of increased interest in balancing costs of regulation against benefits. Cost is a measure of material, energy and labour consumption. Premature consumption of products wastes limited natural resources and consumes labour in non-productive tasks. While this may create jobs, it does not contribute to an improved standard of living. Instead, it contributes to inflation, and hastens the time when certain resources become scarce.

The task of estimating the damage costs for the effects of long-range transported air pollution involves many variables, some of which are difficult, or quite expensive, to quantify, and some of which relate only indirectly to costs. At this time, the values of many of these variables can only be estimated, since no hard data are available. Thus, present economic assessments are rough and imprecise.

The literature on effects of pollutants on materials describes various approaches to determining costs of extra maintenance, earlier replacement, and more frequent painting, resulting from air pollutants and acidic deposition (for reviews, see Haynie 1980c, Yocum and Grappone 1976, Yocum and Upham 1977). These studies typically involve broad assumptions about the kinds of materials which are exposed, in a given area. No study has produced completely satisfactory results, and estimates of costs vary widely.

The assessment of economic damage attributable to air pollution depends on many factors, including: (a) knowing the rates of deterioration (physical damage) which can be expected for a material when it is exposed to an environment which contains known levels of air pollutants and particulates, and, also, knowing what the deterioration rate would be in the absence of the pollutants, so that the incremental costs of air pollution (Yocum and Grappone 1976) and, hence, the dose-response relationship, can be determined; (b) knowing the distribution of the material in the environment, including how the material is used and whether or not it is protected or exposed; (c) having accurate data on pollutant loadings coincident with the material distribution; and (d) being able to predict human response to materials damage. This latter component includes not only the recognized variability regarding how and when decisions are made to clean, paint, or replace, but also, how decisions are made to select substitute materials which may offer improved performance, and to what extent structures are replaced prior to the time significant damage would have occurred, due to pollutants.

It is possible to obtain fairly firm dose-response numbers for a few types of materials, including chain link fencing, galvanized roofing, and electric power transmission towers. Damage functions for these materials are well known, and economic assessments have been made. Using air pollution dispersion models (ENAMAP, ASTRAP, etc.), predictions can be obtained for rates of wet and dry deposition. Calculating from these rates, and the damage functions, one obtains damage rates. In cases where a material is part of a work of art, or has other cultural value, it is difficult to assign an economic value. Some attempts have been made to estimate damage costs, using renovation and repair costs as a surrogate for cultural value. Although this approach neglects the loss of artistic value originally present in the structure or object, which cannot be quantified, at least it allows the costs of restoration, a mitigating measure, to be compared with other control measures.

The validity of cost estimation is dependent on the precision of estimates of the amount and value of the materials which are exposed. The quantities of certain materials, such as chain link fencing, galvanized guttering and roofing, distributed throughout the environment have been shown to be directly proportional to the population density. In other studies, the amount of material exposed has been calculated by determining the amount produced during a period equal to the standard "use-life of that material", and the application of an "exposure factor", to account for the uses to which the material is put. Recent estimates for centre city areas are in fair agreement with the production volume approach. Production data can be found in "Census of Manufacturers" issued at three to four year intervals by the U.S. Department of Commerce. The production-volume/exposure-factor methodology often involves some arbitrary judgments in the selection of exposure factors, and in the analysis of production data. However, until more surveys of exposed material are made or better statistics are found, from which the exposed material can be estimated, assessments can only be based upon this approach. Thus, it is possible to obtain production data and to convert these to exposed surface area per capita, for the metals and painted metals. The variability of these estimates reflects the uncertainty in these factors. For building materials, the statistics or record on restorations and repairs are the primary data base. Data of this sort may be difficult to obtain. The National Park Service of the U.S. keeps records of maintenance and upkeep costs of monuments. Historical preservation organizations and foundations can provide restoration cost data for certain historical areas, such as Annapolis, Md., or the Georgetown area of Washington, D.C. However, such data are inherently difficult to interpret.

Human response to the corrosion or deterioration is the least well documented aspect of material damage. Assumptions of human optimal response can be made, using, for reference, the response that is economically optimal. For example, the economically optimal interval for repainting painted steel and the associated costs (which would be a function of prevailing wage structure, and thus a function of geographical location) can be determined, with the cost of actual human response assumed to be some multiplicative factor greater than one. For galvanized roofing, the human optimal response in many cases is to do nothing, i.e., let it corrode to the point where it is no longer useful and replace it. In this case, the cost due to pollution is the accelerated replacement frequency. In fact, some galvanized roofing, perhaps most, is never painted. The economically optimal response may be to paint after some corrosion has occurred, the optimal interval being based on the exposed lifetime. The least-cost option for wire is probably to replace it. The economically optimal human response is probably not representative of the actual human response. However, the actual response is unknown. The economically optimal response provides a useful basis for the economic assessment, in that it yields at least an order of magnitude and a frame of reference from which aggregate human response behaviour assumptions can be made. Again, the literature may reveal the range of parametric assumptions made concerning the materials, and this would give values for the assessment and a range of variability or uncertainty which can be carried forward.

The economic assessments possible today are crude. In the future, as damage functions for new and old construction materials are determined, and as methodologies for determining materials distribution are refined, the range of uncertainty in the aggregate cost of pollution-induced materials damage will be narrowed. These determinations and refinements should be accorded high priority in research and development planning.

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SECTION 7

THE FEASIBILITY OF ESTIMATING THE ECONOMIC BENEFITS OF CONTROLLING THE TRANSBOUNDARY MOVEMENT OF AIR POLLUTANTS

7.1 INTRODUCTION

7.1.1 Purpose

This report presents a review of the relevant methods of estimating the monetary value of benefits associated with environmental protection efforts to deal with the long range transport of air pollution (LRTAP) problems. An important part of the development of environmental policy strategies is an understanding of the relationship of benefits and costs. The focus of this paper is on techniques to estimate benefits.

The objectives of this report are threefold. The first is to present an overview of economic methodologies, which can be, or have been, used to estimate the monetary benefits associated with LRTAP control. In undertaking this review, the underlying theory is presented and the applicability and limitations of each technique to the LRTAP receptor categories are evaluated.

The second objective is to recommend the most appropriate techniques for deriving monetary values for the increased goods and services due to reductions in LRTAP. In so doing, the report reviews data requirements, practicality of the methods, and the extent to which the methods capture the full measure of benefits.

Finally, the third objective is to present this material in a brief and readable form, which is readily understood by colleagues in other disciplines involved in the study of LRTAP effects, but without a rigorous or extensive knowledge of economics. It is hoped that this review will provide an understanding of techniques of economic analysis, and indicate the nature of the information and data needed from scientific research to apply the economic methods leading to strategy appraisal.

There is a relatively large body of literature on environmental economics and benefit/cost analysis. Our purpose here is to summarize the current state of the art of the valuation of benefits associated with LRTAP control recognizing that there is sufficient, if not complete, agreement on this.

This review draws upon published works in an attempt to synthesize theory and application. In particular, A. Myrick Freeman's book The Benefits of Environmental Improvement (1979), The Costs and Benefits of Sulphur Oxide Control (1981) and preliminary investigations by Thomas D. Crocker for the U.S. Environmental Protection Agency, have served as important references.

7.1.2 Background

Neither physical science studies of the effects of deposition alone, nor engineering and cost studies of abatement and mitigation technologies, will suggest appropriate levels for precursor emission controls or acid deposition. Governments and the public are faced with choosing among varying levels of damages, effects and costs of control and mitigation, rather than "damages or no damages".

In a world of pervasive markets, prices alone would be sufficient means of conveying information about the most appropriate mix of damages, effects and costs of pollution control. Prices would indicate relative scarcities and provide incentives for allocation of resources to the place and time in which they will have the most value. The most valuable allocation is called, in economic parlance, an efficient allocation.

Since there is not a world of pervasive markets, economists, in dealing with resource allocation issues, attempt to simulate ones with benefit/cost analysis. They attempt to assign monetary values, which the gainers and losers would assign, to some change in resource allocation. The algebraic sum of these dollars is then used in determining the necessary level of intervention. If there is a net benefit from intervention, then the new resource allocation is said to be more efficient. The analysis thus shows the benefits of the intervention to society, and conversely, the costs if steps are not taken.

Consequently, benefit/cost analysis is useful when decision makers want to duplicate the results of a world which reflects individual values and preferences. It is limited, however, in that it usually gives an incomplete accounting of value, and thus it is best seen as an aid to decision making. At a minimum, it constitutes a systematic and practical framework for organizing data and for making evaluations and comparisons.

Other methods and criteria have been suggested, for assessing the environmental effects of resource development projects, or for evaluating environmental protection strategies such as arbitrary weighting procedures, overlay maps, quality and enjoyment indices. These are, for the most part, descriptive, and generally do not provide a consistent, well-developed theory which links human preferences and value systems to physical effects being described. Moreover, these non-economic techniques do not provide a systematic and non-arbitrary means of weighting the various physical and environmental consequences and effects.

In order to compare the various types of incommensurable entities, such as changes in crop yield and fish catches, transformations must be made to cast these different entities, where possible, into comparable units. In addition, the various physical effects must be given weights, to indicate their relative value to society. Monetary units admirably perform this dual function of providing comparable weighting units.

A fundamental focus of this paper is to determine the feasibility of applying monetary valuations to non-marketed goods, services and attributes, such as aesthetics, human health and life, ecological relationships and recreational enjoyment. The difficulty of assigning monetary values to these environmental attributes is recognized, the impossibility is not.

It is important to recognize that the monetary value of goods and services affected by environmental quality is not simply the willingness-to-pay on the part of the users of the goods and services. In fact, economists have identified several not necessarily mutually exclusive dimensions of value: (a) <u>activity</u> value which is derived from the direct use of goods and services affected by environmental quality; (b) <u>option</u> value which is derived from the possibility that people might use these goods and services in the future; and (c) <u>legacy or bequest</u> value which is derived from the desire of people to leave to their descendants a given level of environmental quality. An accurate measure of the value of many goods and services affected by environmental quality would reflect all these dimensions, where appropriate. For example, the value of the unique trout fishery in the Adirondacks includes activity value from those who now use it or would, if, there were not LRTAP; option value from those who might use it in the future; and legacy value from those who want to ensure that their children could enjoy the area in its pristine state in the future.

At this point, a brief discussion of terminology is appropriate. The terms "damages", "costs" and "benefits" are frequently used interchangeably in reference to LRTAP effects on the environment. It is the choice of a reference point which more clearly determines their specific meanings. "Benefits" are the gains from preserving existing environmental quality and from restoring or improving a degraded area. Since our reference point is a degraded environment, we will describe the reduction or mitigation of LRTAP effects as benefits. "Damages" are the mirror image of benefits if, and only if, the path of environmental degradation is comparable to environmental improvement. The reference point in this case is a relatively clean environment, and thus pollution effects constitute "damages" or "damage costs". Continued or increased emissions, in a somewhat polluted environment, are also likely to have effects which would be considered as damages.

For the purpose of this paper, we have attempted to be consistent in our use of the terms. The word "costs" is used primarily in reference to LRTAP control or abatement efforts. Benefits are the gains associated with pollution reduction or prevention, given our reference point of an environment already affected by pollution. Our economic measure of benefits is, therefore, the value which people place on reducing the effects of LRTAP, and our purpose is to indicate how monetary values might be assigned to the physical effects resulting from LRTAP abatement.

7.1.3 Emission-Benefit Relationship

The relationship between residual emissions, such as SO_x and NO_x, and monetary benefits is complex, and varies among receptor categories. In general, however, the relationship consists of three primary linkages: (1) the relationship between emission discharges and ambient environmental quality; (2) the relationship between ambient environmental quality and the direct and indirect effects on people (the dose-response); and (3) the relationship between direct and indirect effects on people and the economic value of these effects (user value). The linkages between the various elements can be represented in a simple quadrant diagram in Figure 7-1.

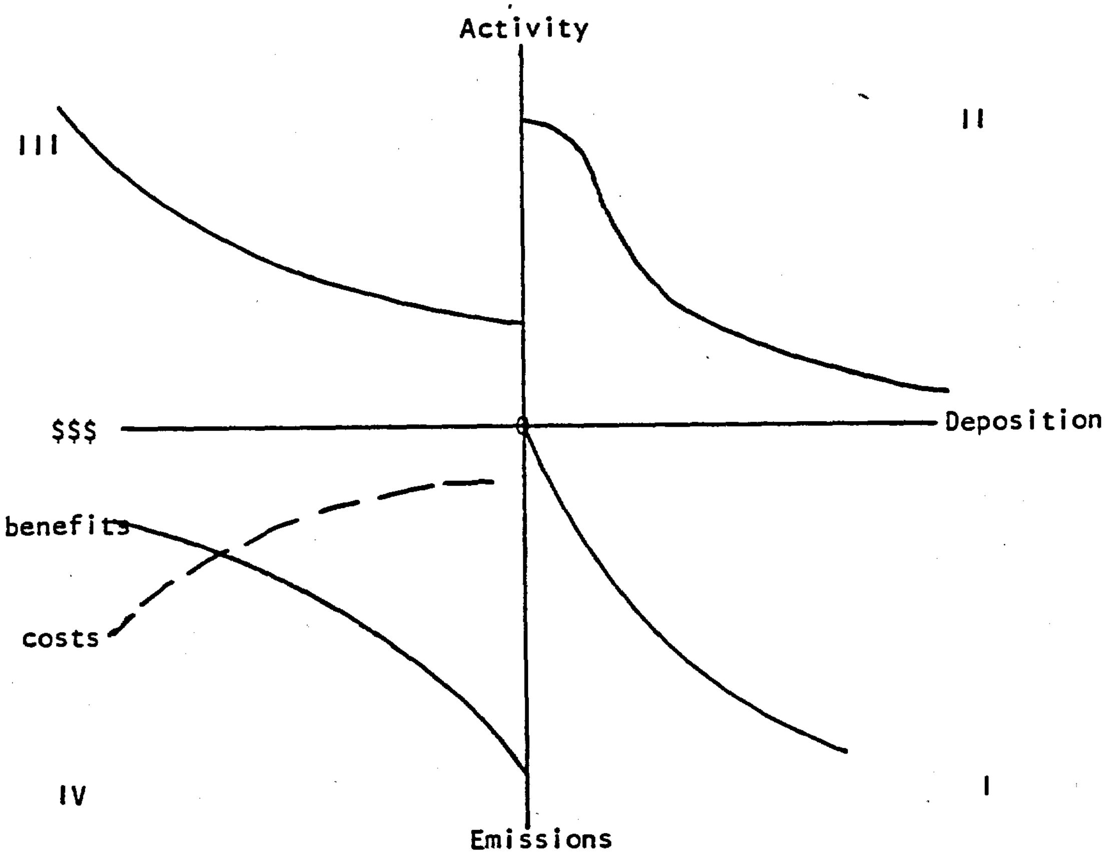

Figure 7-1 Relationship between emissions and economic effects.

Quadrant I shows a transformation function which relates emission levels to deposition (used here as inverse for environmental quality). In the case of acid deposition, long range transport models are being used to show the spatial and temporal relationship between SO_2 emissions and sulphate and total sulphur deposition.

Quadrant II shows a functional relationship between deposition (or environmental quality) and activity levels. This relationship between emissions and activity levels, is very complex and varies considerably with the receptor category.

In the case of sports fishing, the relationship in the diagram is a gross simplification of the linkage between sulphur deposition and days of sports fishing activity. The actual linkages go as follows:

(1) sulphur deposition to change in pH (and metal ions) which varies with the buffering capacity (or sensitivity of the waterbody);

(2) pH to fish population, distinguished if possible into rough, warm and cold water species; and

(3) fish population by species type and number of days of recreational fishing for particular species. This assumes that the stock of fish is independent of fishing pressures.

Where the effects are direct, as in human health, the function in quadrant II illustrates the relationship between ambient environmental quality, (e.g., sulphate concentrations) and human mortality.

Quadrant III relates activity to dollar values. The relationship is direct; as activity increases, its economic value increases. This function could illustrate the relationship between activities and both its primary and secondary economic value.

In the fourth quadrant, a benefits function can be drawn which relates the dollar value of benefits to particular LRTAP emission levels by following a given level through each quadrant. Thus, the total benefits are the integral under the curve. In addition, this quadrant can be used to show a control cost function (shown in dashed lines in Figure 7-1).

While this quadrant diagram illustrates the linkages in a very simplified way, in fact, the functions are not as straightforward. In each quadrant, there is an element of <u>uncertainty</u>, which may be small or large, and thus total uncertainty is compounded. Uncertainty may result from inaccuracies in measurement, or the use of assumptions in the face of limited data.

Let us say, for example, that the best estimate of the relationship between emissions and deposition, (i.e., the transformation function) is represented by a range, for which the upper limit is A and the lower limit is B. The benefits range in quadrant IV is no longer a curve, but the area WXYZ shown in Figure 7-2, where the range of benefits at emission level, a, is Z to Y. If the functions in quadrants II and III are similarly presented as ranges, the total benefits area in quadrant IV becomes an even larger area.

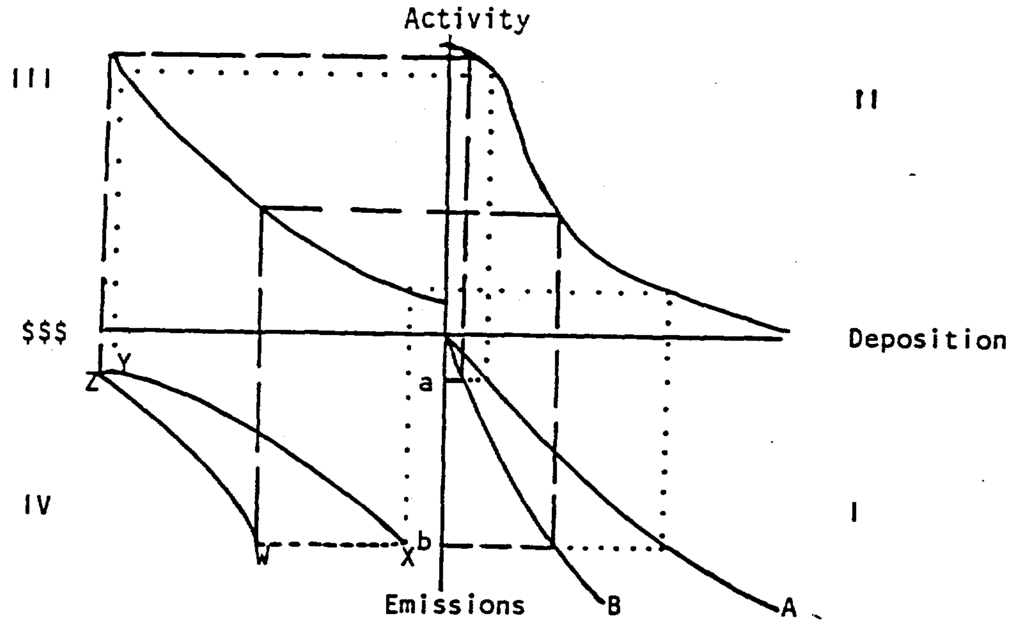

Figure 7-2 Variation in effects due to different emission-deposition relationships.

In the case of LRTAP, economic methodologies for assigning monetary values to benefits are reviewed for the categories in Table 7-1.

Table 7-1 ACTIVITY CATEGORIES

1.	Aquatic	a. commercial
		b. recreational
		c. ecosystem
2.	Terrestrial	a. agricultural
		b. forest
		c. ecosystem
3.	Man-made buildings, structures and artifacts	
		a. materials
		b. historic
4.	Water Systems	a. treatment
		b. materials
5.	Human Health	a. morbidity
		b. mortality
6.	Visibility	a. aesthetic

The critical link in this process is the relationship between dose and response (Quadrant II). Until more results are forthcoming which relate damages to various levels of LRTAP, it will be difficult to provide reliable estimates of the economic values of the benefits of LRTAP reduction.

7.1.4 Efficiency and Equity Considerations

The physical damages of LRTAP result in reduced economic welfare for society. Conversely, the reduction of these damages offsets these welfare losses, which may not be shared equally by all members of society. The decision by government to intervene or not to intervene thus has both efficiency and equity implications.

The concept of economic efficiency or efficiency effects reflects the fact that it is often possible to reallocate resources, e.g., by spending more or less on environmental protection, in ways which will bring about an increase in the net value of production or output to society. This output encompasses goods and services provided by the environment, as well as those produced by man and sold in markets. Increases in this net value of output result in an increase in economic welfare.

Changes in economic welfare which are associated with environmental damages, or with environmental protection activities, may, under certain circumstances, be measured by changes in the monetary values assigned by all individuals affected by an action. Thus, a reallocation of resources and efforts will increase efficiency, if it results in an increase in the social value of goods and services produced by the economy (or by natural environments), as indicated by individuals' demand for them.

The equity impact relates to the redistribution of economic welfare amongst individuals. These individuals can be further divided into groups, regions, countries, or generations. The simplest way in which to view this impact is to examine the changes in the distribution of monetary income which result from alternative strategies.

A wide variety of individuals, of differing nationality, income and social class, and generation, are potentially affected by LRTAP effects and LRTAP abatement alternatives. Some individuals, due to location in source or sensitive receptor regions, or having a preference for goods and services related to air quality in these regions, may be more significantly affected than others by social choices to abate or not to abate LRTAP. A decision to maintain existing air quality management practices produces gains to individuals who use the environment for production (as an employee or shareholder of firms in source regions), and consumption (e.g., use of automobiles in source regions) purposes; or consume the products and services of LRTAP-source firms. Damages are imposed on those individuals who use the environment for production (e.g., agriculture) and consumption activities (e.g., water-based recreation in acid-sensitive lakes); or consume the products and services of LRTAP-affected firms. The roles of gainers and losers are, of course, reversed if LRTAP abatement is contemplated.

An issue of considerable importance which has been given little or no consideration, is the effect of LRTAP on property rights, insofar as the adverse effects of pollutants result in the involuntary surrender of rights to both common pool resources (e.g., airsheds) and individual property, or the usurpation of these rights. For example, residents in both Canada and the United States involuntarily give up some of their rights to clean air, or lakes with fish populations, to the coal-burning utilities and the nonferrous smelting industry. Within one political jurisdiction, the surrender of these rights from one area to another, for the use of others, may be considered an acceptable transfer, if it is determined (by concensus or voting) that the collective good of the nation or region is enhanced. However, regions or nations may not share any collective good that may result from the transfer, and there is no forum for arriving at a concensus between two nations, other than negotiation and bargaining.

Thus, redistribution effects and property rights among groups, regions, or generations may have significance for social welfare, depending upon the relative weights attached to individuals, countries, or generations, and whether or not compensation is actually paid to those affected by the changes.

The compensation principle adds further complications to the property rights issue, because it is unlikely that compensation will be paid between losers and gainers. In using benefit/cost analysis, a particular course of action is often deemed worthwhile, if the gains to the gainers would be sufficient to compensate the losers. If compensation does not take place, and the distributional weights are important, efficiency conditions may not be satisfied. Thus, the lack of mechanisms or incentives to preserve or compensate the rights of others may result in an economically inefficient allocation of resources.

The assignment of implicit or explicit welfare weights has been subject to significant criticism. Steiner (1975) notes that data and analytical problems severely limit the ability to trace the eventual distribution of economic effects to individuals, as tax payers, resource suppliers, and consumers. The development of implicit welfare weights from past governmental decisions also requires the assumption that elected officials had full knowledge of the magnitude and composition of the economic effects, when decisions were made (Freeman 1969). The ability of elected government officials to generate an optimal set of equity weights which would be stable over time has also been questioned (Steiner 1977, Haveman 1967).

Some agreement does exist, however, among applied welfare theorists, as to the treatment of distributional effects. A display of the distributional consequences of social choices is recommended as a supplement to the statement of economic efficiency impacts (Haveman and Weisbrod 1975, McKean 1958, Mishan 1971). Some analysts have also recommended that the display process be taken a step further, by presenting a series of welfare-weighted calculations using alternative weighting functions (Eckstein 1961). The distributive consequences of alternative weights can then be easily identified. Freeman (1969) outlines a more formal process, whereby each government agency spells out program objectives and recommended weighting functions. These weighting functions would then be reviewed and approved by the central budget agency (e.g., Office of Management and Budget, or Treasury Board), to ensure weighting consistency among programs and relative to overall governmental priorities. Present federal project evaluation procedures of the Canadian Treasury Board (1976) and U.S. Water Resources Council guidelines (1980) basically conform to the display format for distributional consequences recommended in the literature. Our purpose here is to point out that redistributive effects are associated with most of the benefits of LRTAP control, and these should also be taken into consideration.

7.2 BENEFITS: CONCEPTUAL APPROACHES

This chapter distinguishes between primary and secondary monetary benefits associated with changes in activities. Primary benefit is the willingness of society to pay for goods and services resulting from changes in environmental quality, or the compensation required to restore welfare to original levels. The willingness to pay on the part of consumers is described graphically as an area under a demand curve, and in economic parlance is called consumer surplus. The willingness to pay on the part of producers is described graphically as an area above a supply curve, and in economic parlance is called producer surplus, or rents. (For those readers unfamiliar with economics, we have included an Appendix describing a few key concepts of economic theory). Most of this section will describe the three basic approaches, market, imputed market and non-market, for estimating willingness to pay on the part of consumers and producers. Secondary monetary benefits are changes in the levels of economic activity among regions. Some will gain, while others lose. At a national level, these are not usually contributions to economic efficiency, but are rather transfers from one region to another. They are nonetheless important at the regional level.

7.2.1 Primary Benefits

Market Approach

In many cases, the value of a change induced by an improvement of environmental quality can be ascertained by direct observation of a change in the market.

For example, a reduction in LRTAP which results in an improvement in environmental quality may produce increases in crop yields and commercial fish catches. The benefits of a change in environmental quality include the total value of price changes to consumers and net income to producers. In the following paragraphs, we will present a few techniques for estimating these changes.

The Net Factor Income approach provides a measure of the change in producer's income, resulting from change in output due to improved environmental quality. Here, it is important to specify the dose-response relationship, so that the change in output (as measured by yield, catch, etc.) can be determined. Assuming that the increase in output does not affect price, then the change in income is calculated by multiplying output change by the relevant market price. If the output change is sufficiently significant that price falls, the new price should be used.

Partial Budgeting is a technique similar to net factor income. It estimates the extent of benefits from environmental improvement, by calculating the effects on key portions of a budget of a representative (e.g., farm) enterprise. Expansion factors can then be used to extrapolate the effect on the enterprise to the effect on the industry, or on a specific crop or kind of livestock. Examples of this technique are in use in Economics and Statistics Services, USDA, to estimate economic gains from production and sales of a certain crop because of reduced insect damage, or agricultural losses to farms and ranches from strip mining of coal.

Perfect Substitutes is another technique to be used where a change in environmental quality requires less of other productive inputs. This situation is best illustrated where decreases in LRTAP deposition result in reduced use of lime to treat drinking water or maintain lake water pH. The value of benefits is measured by the cost savings for lime.

There are some important qualifications, which affect the extent to which these market methods under- or over-estimate the value of benefits. The first of these problems concerns the use of "partial equilibrium" analysis in making estimates of price and quantity changes. All other variables relevant to demand and supply of goods and services are assumed not to change. However, the availability of substitutes is an important determinant of demand, which may well be altered by the effects of acid deposition. The *a priori* implications of change in these aspects can be noted, but the empirical verification of these hypotheses is, in some cases very difficult. Finally, although the market price may be used as the relevant measure of unit value, where government support, or other policies which influence prices, is in effect, use of this (supported or other) price will overstate the value of benefits.

Imputed Market Approach

Where there are no organized markets for the goods or services of the environment, (e.g., visibility) or for goods affected by quality (e.g., recreation), a number of imputed market approaches are available for deriving or inferring their monetary value.

The Property Value Method is an imputed market approach which has been used to value environmental benefits. Economists have long been interested in the relationship between property values and levels of environmental quality. It is suggested that variations in the level of environmental quality will affect the value of otherwise similar properties (Ridker 1967, Ridker and Henning 1967). The value obtained should reflect tangible and intangible values of environmental quality, insofar as these are perceived by individuals in the property market. This facet may pose problems in the case of LRTAP. Since these effects are not well understood, the property market may not be able accurately to reflect the adjustment. Given these concerns, the property value method is not considered an appropriate method to measure the benefits of LRTAP reduction.

Hedonic Price or Demand Analysis is a more general application of this specific property value technique. A demand function for a public good is estimated through a two step procedure. First, the implicit price of environmental quality is estimated, based on property value (in the case of visibility), or travel cost (in the case of recreation). Then the implicit prices are compared with variations in environmental quality, to determine a demand function. However, only under a particular but rather broad set of circumstances is the demand function so derived an accurate measure of willingness to pay for environmental quality.

Complementary Expenditures is yet a third imputed market technique. The most frequently used expenditure, variation in travel cost, is the basis for imputing the value an individual places on a recreation experience. The maximum expenditure of an individual is the basis for deriving a demand curve. Other expenditures, such as expenses for fishing equipment, might, but have not yet, been used to impute values.

Risk Premiums are now the imputed market technique most frequently used in valuing mortality. These risk premiums can be, among other things, wage differentials among occupations, and insurance premiums. The technique could possibly be used to value changes in morbidity as well, but foregone wages and medical costs are the more common valuation approach.

Non-Market Approach

A third major approach to valuation is a direct enquiry to individuals about their willingness to pay for changes in environmental quality. Information is obtained through an interview method, whereby respondents are asked to reveal their preferences for environmental services. In some cases, such as visibility changes, this approach is an alternative to another major approach, such as imputed market; in other cases, where no markets exist, for estimating option value, it is the only approach for valuation.

The Bidding Game is one non-market approach to preference revelation. The technique consists of constructing an artificial (i.e., contingent) market and simulating market transactions. The inteviewer/auctioneer presents the respondents with a set of possible states or contingencies for the relevant environmental service. The respondent is asked to assign a price, or asked whether he or she agrees to a price for each possibility, which reflects his or her valuation. The auctioneer enters into a bidding process to determine if the respondent would pay (receive) a higher (lower) price than that stated initially. The process continues until the auctioneer has determined the highest (lowest) bid.

Rank Ordering is a second non-market technique. It requires similar information about hypothetical environmental situations to the bidding game, plus additional information, including some measure of the costs or price of a visit. Individuals are asked to rank the hypothetical situations from the least to the most desirable. These rankings reveal trade-offs among the environmental services, other attributes of an area and price of admission. These trade-offs form the basis for estimating the value of various levels of environmental quality.

The major issues involved in these techniques relate to three categories of bias: hypothetical, strategic, and information. They are summarized in Rowe and Chestnut (1981), but are briefly discussed here.

Hypothetical bias refers to the fact that the hypothetical nature of the question may not ellicit accurate bids. In order to minimize the hypothetical bias, it is essential that the scenario which is defined for the respondent be as real and credible as is possible. Otherwise, the respondents may feel that the game, being totally hypothetical, is not really relevant. In this case, they may not treat the interview seriously, and hence fail to reveal true bids.

Strategic bias is introduced, if the respondents have an incentive to conceal their true preferences, in order either to avoid payment (be a free rider) or to influence the outcome. Strategic behaviour is defined by Brookshire et al. (1976) as occurring when respondents attempt to impose their preferences on others, by bidding in such a way as to influence the mean bid, and hence the outcome. The survey must be designed so as to minimize the influence of these biases.

Information or starting point bias refers to the extent to which the information provided to respondents may, and can, influence their bids.

7.2.2 Secondary Benefits

The approaches described above are techniques for the valuation of the primary (efficiency) benefits associated with a particular commodity or service. The benefits of environmental improvement are, however, not limited to a particular good. Changes in income to producers, in terms of crop or forest products, could have important impacts on jobs and income, in regions where these activities are a part of the economic base. Similarly, changes in sports fishing activity will affect the overall sector. These effects will be more significant in areas where these activities form a greater proportion of the economic base. Since these secondary benefits will accrue to different economic sectors, and to various geographic regions, analysis on a sectoral/regional scale provides an additional measure of welfare change.

Various regional economic analysis techniques are available to account for secondary benefits. They measure the effects on spending and re-spending patterns (multipliers), and the direct, indirect, and induced effects on other economic sectors (linkages), and, in turn, on the overall level of economic activity in the region (Bender 1975, Conoposk 1978).

Although the change in the overall level of economic activity due to LRTAP may be a transfer from one region or country, the effect of the transfer is important to that region or country. Thus, an analysis of these secondary effects is an important part of the total estimate of benefits.

7.3 BENEFIT ESTIMATION TECHNIQUES

The literature on benefit estimation techniques offers several approaches for transforming effects of LRTAP on various receptors into dollar values. These have been broadly categorized into three groups, by their reliance on market, imputed market and non-market mechanisms for the generation of value information. This section examines the appropriateness of each technique for the various LRTAP receptor categories and the methodology employed, and comments on its specific application to the valuation of benefits, associated with LRTAP abatement benefits, for each of the identified receptor categories.

In considering which techniques are most appropriate to LRTAP, several factors are relevant. The benefit estimation techniques should have a solid theoretical basis, i.e., consistent with economic theory. Although the techniques have theoretical consistency, it is important that the empirical implementation be practical, in terms of data and computational requirements.

The techniques selected should minimize the degree of uncertainty and contentiousness associated with the results. Application of the most appropriate technique to a receptor category, and a clear statement of assumptions and conditions, are essential for credible results.

The results must be obtained at a reasonable cost. For example, survey design must balance practicality and cost with reliability of results. It is not feasible to interview every member of society. Instead, it is necessary to interview representative sample groups, drawn from the population.

These criteria are not independent of each other. An analyst is forced to make trade-offs or concessions. Ultimately, the desired result may be summed up as: obtain the most useful results at reasonable cost for the purpose at hand.

7.3.1 Aquatic

Recreational Fishery

The conceptually correct procedure for estimating the value to users of changes in recreational fishing, is to estimate the willingness-to-pay for each site. Willingness-to-pay is a function of socio-economic characteristics, the quality of the recreational experience at the site and at substitute sites, and the (travel and other expenditure) cost to get to the site and substitute sites (Freeman 1979).

A demand curve, which graphically summarizes willingness-to-pay, for an individual site, would relate the number of fishing days to the prices of this experience, assuming no changes in income and tastes. The demand curve for a given lake is given in Figure 7-3. If the price of admission to the lake is OA per day, the quantity consumed will be OX_1. The value of the recreation site, given the initial level of water quality, is the consumer surplus, as measured by the area ABC. If no admission is charged, i.e., price is zero, then consumer surplus is the area under the demand curve, that is, $OBCD_1$.

Now, if acid deposition is reduced and water quality improves, the demand curve will shift to the right (D_2). The net economic benefit is the increase in willingness-to-pay, as measured by the area between the two demand curves, BDEC. The net benefit is the increased value to existing users, as well as the value to the new users.

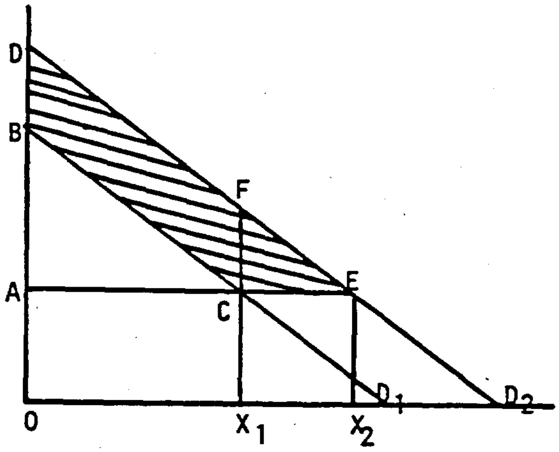

Figure 7-3: Change in demand due to water quality improvement

The problem with this theoretical approach is that most recreational fisheries charge a zero price, or nominal entrance fee. Where there is no fee or variation in market price, a market approach to valuation is impossible.

One imputed market approach is the Clawson-Knetsch travel-cost method, which infers behavioural responses to price changes (reflected by differences in travel cost). This method is site specific, estimating demand for a particular park or lake, and not the fishing activity itself. This method is done by circumscribing a recreational fishing site with a series of concentric zones. For each zone, travel costs and visitation rates are calculated, based on a survey of the origin of visitors.

Four limitations of this technique are the assumptions that all travel costs are incurred for the purpose of visiting the specified site, that travel time can be correctly valued, that only present users are accounted for, and that response to a change in quality cannot be inferred from a single site. The second can be handled by using a shadow price to value time, but will result in different values, depending on the assumptions used. The third can be handled by surveying non-users within the region, to determine their response to water quality improvements at a given site. The fourth requires data on a number of sites of varying quality. This method is, however, more complex if there are several recreation sites which are substitutes, such as is likely with the effects of LRTAP. In this case, the demand for any one site is a function of prices and distances to other competing sites.

A second imputed market approach, the property value technique, has seldom been applied to changes in water quality, due to the difficulties in correctly accounting for the interaction of water quality and distance from water on property values, and the fact that it ignores the value of changes in water quality to recreationists who do not own property in the vicinity of the lake or stream. This technique is not recommended for a valuation of benefits of environmental improvement for a recreational fishery for these reasons. In addition, data for other "imputed markets approaches" are more readily available and it is doubtful that, in the absence of solid information on dose-response relationships, the property market would be able to reflect adequately the pervasive effects of LRTAP.

A third imputed market approach is the participation model. The technique relates participation in specific recreation activities by a given population to the socio-economic characteristics of that population, and to the supply of recreation opportunities available, to develop estimates of quantity. If participation equations for specific populations are estimated, it is possible to predict the increase in participation to be expected with an increase in fishing opportunities or ambient water quality. The value of a recreation day of particular type must be inferred by other methods, (such as travel cost). Then one component of recreation benefits, the value to new users, can be estimated by multiplying the increase in recreation days (quantity) by the assumed value per day (price) (see Figure 7-3). The limitations of this approach are that it does not capture the utility associated with the current level of use (quantity X_1), that is the area BDFC in Figure 7-3, and there is considerable uncertainty about the value assigned to a recreation day.

A probabilistic participation model is perhaps the best technique for accounting for a broad range of locations, accessibilities, and fish types, affected by changes in reductions in acid deposition, and the interacting adjustments made by recreational fishermen to the additions of available water bodies (Russell 1981). This method requires:

1. Estimation of two types of probability-of-participation equations:

   a. The probability that a randomly chosen member of the U.S. or Canadian population is an angler at all;

   b. The probability that a randomly chosen angler spends at least some time in a year fishing for a particular species.

2. Estimation of an equation predicting the number of days of fishing per year engaged in by anglers for various fish species.

The equations could be estimated using data on existing water availability. Next, changes in the probabilities and days of participation could be projected, for a condition under which additional bodies of water were made available for fishing, due to reductions in acid deposition. Fishing days in this future state, less fishing days in the present case, would give the projected increase in fishing by type of fishing. The increase in days for each type of fishing would then be valued at the appropriate figure for consumer surplus per day. It should be noted, however, that the application of this technique to the benefits of reduced LRTAP effects is complex given its data requirements.

The major limitation in applying this technique, as with many others, is in relating changes in total sulphur or sulphate deposition to changes in water available, by species type. The aquatic effects work group would have to provide an inventory of existing water bodies, differentiated by susceptibility to acid deposition and general species type (rough, warm water and cold water). In addition, they would have to provide dose-response data, i.e., different deposition levels (kg of wet sulphate per ha per year) that would permit the survival of fish populations by species type for each water regime, in the following format:

Species Type	Lake Type		Fish Population Surviving
	Susceptible (little buffer)	Very Susceptible (no buffer)	
rough	≤15 ± 5 kg/ha/yr	≤10 ± 4 kg/ha/yr	≥90%
warm water	≤15 ± 5 kg/ha/yr	≤10 ± 4 kg/ha/yr	≥90%
cold water	≤10 ± 2 kg/ha/yr	≤5 ± 2 kg/ha/yr	≥90%

Without this type of information, or another similar approximation, we cannot accurately estimate the economic value of a change in recreational fishing due to a change in acid deposition.

For recreational fisheries, a contingent market approach, using surveys, can be used. The approach attempts to elicit values of how respondents think they would behave if a proposed water quality change were to occur in a hypothetical situation. There is some skepticism about these approaches, primarily because they assume that individuals are capable of predicting and willing to predict, accurately their response behavior to a hypothetical situation. In addition, the accuracy of the results may be questioned, due to information, strategic or starting point biases as discussed in Chapter II.

Two limitations of all the above techniques are their failure to capture option and legacy values of the recreational fishery or the aquatic ecosystem, and the emphasis on valuation of a particular activity, rather than the economic sector, i.e., recreation and tourism, which is based on recreational fishing (i.e., secondary benefits).

Commercial Fishery

The conceptually correct approach for valuation, in the case of commercial fisheries, requires estimation of producers' responses and market effects. In the simplest case, assume that only a few commercial fishermen benefit from a reduction in acid deposition. If the fishery is being appropriately managed to maximize net economic yield, the benefit of reducing acid deposition is equal to the market value of the increased yield, net of any changes in expenditure on variable factors of production. In the case of existing fisheries, there would be little variable cost change, outside of shifting fishing grounds or shifting from less desirable to more desirable species.

In a more realistic case, the value of restoring a commercial fishery will depend upon several variables, unique to a given situation. If, as is most likely, there is free access to the fishery, since it is a common property resource, producer surplus would accrue to the existing fishermen only in the short run. This surplus would attract additional fishermen to the fishery, which would reduce it to zero. If the change in the commercial catch is significant, then there would be a need to estimate price effects (consumer surplus) as well.

In addition, restoration of a commercial fishery in economically depressed areas could conceivably be sufficient to strengthen a region's economic base, and hence income and employment. Maintaining the regional population would prevent negative external effects upon the rest of society, because of the higher congestion levels in urban areas due to migration from depressed fishing areas. Some of the secondary benefits can be estimated, using a regional income and employment model.

The specificity of the dose-response relationship between reductions in LRTAP deposition and increases in commercial fish populations and catches will determine the reliability of any estimates of the benefits to this economic sector.

Aquatic Ecosystem

Any valuation of the benefits of reducing acid deposition should reflect the value of all changes in the aquatic ecosystem, rather than just recreational and commercial fisheries. Changes in salamander and loon populations could result from reduced acid deposition, and these changes could affect activity, option and existence values. Limitations in dose-response functions and the absence of economic studies in this area will make it difficult to measure these values. Insofar as they are excluded, the total benefits will be underestimated.

7.3.2 Terrestrial

Agriculture

The conceptually correct procedure for valuing changes in the agricultural sector is the determination of changes in producer's and consumer's surplus, due to a change in environmental quality. The changes in the surpluses depend upon costs of production, demand, and market structure. Since knowledge of these parameters suggests that most of the benefits of reducing LRTAP effects will accrue to producers, benefits may be estimated from observed or predicted changes in net income of certain factor inputs. The change in net income accrues as profit to the farmer, or as surplus income to the fixed factor of production.

In the case of acid deposition, where there is limited information about effects on agricultural productivity, a frequently satisfactory estimate of the change in net factor income will be obtained from the product of changes in crop yields multiplied by market prices. For this procedure to be a reasonable estimate of benefits, there must not be government intervention to support the price of affected crops, nor changes in expenditures for other production inputs. In addition, it would be assumed that producers have neither undertaken mitigation measures, e.g., liming, nor changed cropping patterns, in response to acid deposition.

If acid deposition is shown to have a measurable impact on some crops across a large geographic area, then it is recommended that consideration be given to changes in prices as well as yield. Given that many agricultural crops have inelastic demand curves, that is, a small change in quantity demanded results in a larger proportionate change in price, accounting for price effects would considerably improve the total estimate of benefits, and indicate the distribution of benefits between producers and consumers.

Forestry

The conceptually correct procedure for estimating the value of changes in the forestry sector is similar to the agriculture sector, using a market approach. Since knowledge of production, demand, and market structure suggest that the benefits of reducing acid deposition will accrue to producers, benefits may be estimated from observed or predicted changes in net factor income.

In the case of acid deposition, a frequently satisfactory technique to estimate the change in net factor income is to use the change in timber yield multiplied by the market value differentiated by species and product. Moreover, it presumes that the demand for forest products is highly inelastic, i.e., insensitive to price changes. For the forestry sector, the procedure is less complex than in the agriculture sector, because there is less government intervention and known use of mitigation measures or changes in tree planting patterns, due to acid deposition.

Ecosystem

Any valuation of the benefits of reducing acid deposition should reflect the value of all changes in the terrestrial ecosystem, rather than just agricultural and forestry activities. Change in nutrient composition of soils is a major change, which may not be immediately captured by changes in yields in the agriculture and forestry sectors. This change, as well as changes in terrestrial animal populations, would affect, to some degree, activity, option and existence values. Although these are best measured by means of a survey, it is unlikely, given the dearth of dose-response information, that individuals would be able to assign accurate options or values to the terrestrial ecosystem.

7.3.3 Water Supply

The conceptually correct procedure for valuing a reduction in the direct effects of acid deposition on water supplies, is the reduction of treatment cost. These changes in treatment costs are a first approximation, as long as they do not change other forms of producers activities, cause substitutions among factor inputs, or change prices of outputs.

Although the use of changes in treatment costs is recommended as a benefit measure, there may be problems in making an empirical estimate. The problem lies in correctly assigning a percentage of liming costs to the mitigation of acid deposition effects. Even if there were no acid deposition, industries and municipalities would probably continue their current treatment practices of balancing the pH of water. Consequently, we would provide at best only an upper bound on benefits by assigning all liming costs in areas of high acid precipitation to acid deposition.

7.3.4 Effects on Buildings and Structures

The conceptually correct procedure for valuing the reduction in the effects of acid deposition on commonly used materials, is the annual equivalence of the present value difference in life cycle costs of production processes. The difference is appropriate for reductions in deposition which extend the useful life of materials (including water supply systems), reduce maintenance or repair costs, or eliminate the need for higher initial costs for damage resistant materials.

The recommended approach would use the annual equivalence of difference in life cycle costs for commonly used material. Annual equivalence would be calculated in a two step procedure (Maler and Wyzga 1976). The first step estimates the present value of the difference in the stream of current replacement costs, before and after acid deposition. The second step calculates the annual equivalent flow of the present value of the reduction in damages.

Benefit estimation for commonly used materials requires information about changes in rates of deterioration (dose-response) or maintenance, and distribution of susceptible materials. Thus, information is essential to the determination of the value of benefits.

While the life cycle cost approach values the benefits of reduced repair and replacement costs, it does not capture the historical value of buildings and monuments. This is an intangible, nonmonetary value, which can best be determined by a willingness-to-pay survey of viewers for the aesthetics of less damaged structures and statues. This method will, however, result in an underestimate of total value, insofar as it fails to capture option and legacy values. A second and important limitation of the contingent valuation method is due to the lack of a proven approach. Although surveys have been tested and validated in other areas, such as recreation and visibility, additional research would be required prior to their application to derive historical values.

7.3.5 Human Health

Mortality

The conceptually correct procedure for estimating the value of reductions in the probability of death or increases in longevity, is what an individual must be paid to accept additional risk. This willingness-to-pay, when aggregated over many individuals, is usually referred to as the value of statistical life, or the value of a statistical death avoided. It is simply a shorthand way to represent the total amount of benefits enjoyed by all the population which benefits from risk reduction.

One approach for estimating the willingness to pay to avoid a statistical death, is to observe human behavior in risky situations. Most empirical estimates, which have been reviewed by Bailey (1980), examine wage differentials among occupations with varying degrees of risk; one empirical estimate used individual choice with respect to seat belt use. The values (1978 dollars) found in the former studies (wage differentials) ranged from approximately $250,000 (Thaler and Rosen 1976) to $5.0 million (Smith 1974); the value found in the seat belt study was approximately $313,000 (Blomquist 1979).

Other approaches for estimating the value of human life include total lifetime earnings, court awards, and surveys. Current economic thinking questions these approaches, on theoretical and empirical grounds.

Neither the behavioural nor the survey approach captures the willingness-to-pay of relatives or close friends. One study (Needleman 1976) indicates that including others' willingness to pay could increase the statistical value of life by 25-100 per cent. Although this study measured willingness to pay, it differed from the behavioural approach in one significant respect. It placed a value on a known human life, whereas the behavioural approach assigns a value to an improvement in safety for each of a large number of individuals.

Review of the significant behavioural studies could provide high and low limits for the range of values of a statistical death avoided, and is therefore the approach recommended for valuing the effects associated with LRTAP. However, no monetary estimates are possible unless there is an agreed upon dose-response relationship.

Morbidity

The conceptually correct procedure for estimating the value of reductions in morbidity is also what an individual must be paid to accept additional risk. Individuals must be paid a certain amount to accept lost time at work, or restricted activity days. A more complete analysis would ask, in addition, what an individual must be paid if he had to accept a career change as a result of an accident.

Unfortunately, there are few behavioural studies and surveys which provide us with estimates of willingness to accept risk. In lieu of this information, average daily earnings (not wage differentials by occupation) for those in the labour force can be used as an empirical value, with the recognition that not all morbidity results in lost earnings (paid sick leave and sickness on non-working day), and that earning measures do not reflect pain and discomfort.

The value of changes in morbidity would partially follow the lower bound estimates of Freeman (1979). Morbidity could be measured either by work days lost or restricted activity days. The work days lost measure applies only to people in the labour force. Restricted activity days applies to all people of all ages and includes degrees of illness and incapacitation which are not severe enough to result in absence from work. Work days lost and restricted activity days could alternatively be valued at $20 per day and $40 per day to provide a range, the latter being the (U.S.) average gross daily earning in the private non-agriculture sector in 1978.

7.3.6 Visibility

The conceptually correct procedure for valuing changes in visibility is to estimate the willingness-to-pay in each region (Rowe and Chestnut 1981). The demand curve for an individual site would relate the number of days of satisfactory visibility to the price of these days, assuming no changes in income and tastes, etc. (Figure 7-4). If the number of days of satisfactory visibility is OA, the value of visibility, given the initial level of visibility, is the entire area under the demand curve, because there is no expenditure for visibility.

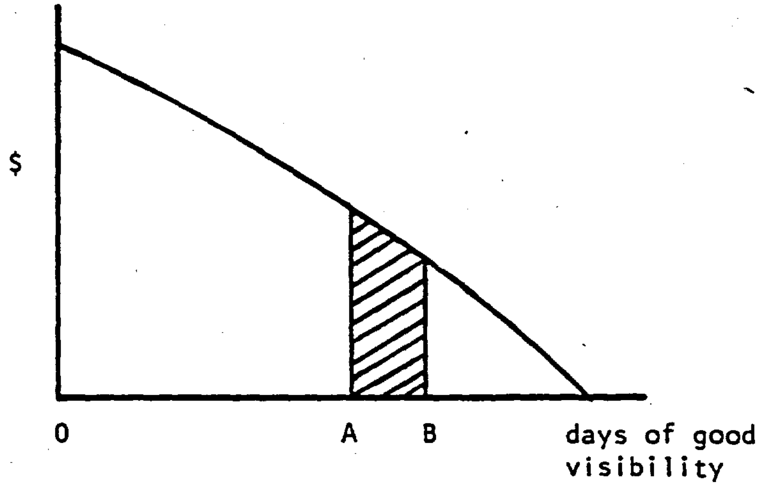

Figure 7-4 Change in demand due to visibility improvement

Now, if LRTAP is reduced and visibility improves, using a dose-response relationship specified by the effects group, the number of days of satisfactory visibility will increase. This results in a movement along the demand curve. The net economic benefit is the increase in willingness-to-pay as measured by the entire area under the demand curve.

The problem with this theoretical approach for valuing visibility, as with many environmental goods, is due to its special status as a "public good." There are no markets for which prices and demand curves can be directly obtained. Thus, imputed market and non-market approaches are proposed as valuation techniques in this field.

The imputed market approach (hedonic prices/demand analysis) uses existing market data, in cases where the selection of a market good may vary with visibility levels, such as the choice of residential location. This approach further assumes that the intensity of these also requires that technical measures of pollution concentrations or visibility levels are reasonable representations of the environmental attributes that individuals value, and that these measures can be used to identify that part of an individual's behaviour attributable to the component of environmental quality being studied.

The non-market approaches (Bidding Game, Rank Ordering) attempt to elicit values through surveys of how respondents think they would react to a proposed visibility change. In contrast to the market approaches, non-market approaches do not attempt to infer values of a component of environmental quality from observation of individuals' actual behaviour in response to a change in environmental quality. Instead, individuals are asked to predict how they would behave, or have behaved, in response to a change in environmental quality. Bias of values determined by this method may be due to the level of information conveyed to respondents. This approach presupposes that a particular change in environmental quality can be described to the respondents, usually with photographs and verbal descriptions, in a way that corresponds to what their perceptions of the actual experience would be. For example, it is assumed that a photograph of the Grand Canyon, obscured by pollution, will elicit a response that corresponds to what the response to the actual situation would be. This type of approach also assumes that individuals are capable of predicting, and willing to predict, accurately their response behavior to a hypothetical situation that they may or may not ever actually have experienced.

It is recommended that a review of empirical studies on the value of visibility be undertaken to provide a range of values for various regions, and for urban and rural areas.

7.3.7 Summary

The following table provides a summary of methods and their applicability to the various LRTAP affected receptor categories. The 'X' denotes that the method can be used, whereas X denotes the method which is recommended as most appropriate. It should be noted that the methods capture only the primary values, and that regional econometric analysis is necessary to draw out the secondary economic effects (jobs and income), in a given sector and in a specific area.

TABLE 7-2 - SUMMARY OF METHODS

	Market		Imputed Market			Non-Market
	Factor Income	Substitutes	Travel Cost	Property Value	Observed Behaviour	Survey
A. Aquatic						
1. Sports Fishery			X		X	X
2. Commercial Fishery	X					
3. Ecosystem						X
B. Terrestrial						
1. Crops	X			X		
2. Forests	X			X		
3. Ecosystem						X
C. Buildings, Structures						
1. Materials	X			X		
2. Historic						X
D. Water Systems		X				
E. Health						
1. Morbidity					X	
2. Mortality					X	
F. Visibility				X		X

7.4 QUALIFICATIONS, CONCLUSIONS AND RECOMMENDATIONS

This section has provided a review of methods which can be employed, to determine the primary economic benefits of LRTAP reduction on specific receptor categories, as well as the secondary economic effects.

7.4.1 Qualifications

Although numerous limitations and qualifications have been noted, with respect to specific methods or issues, there are three significant qualifications which are relevant to LRTAP-related environmental effects. They are:

1. Lack of Dose-Response Relationship Information;
2. The Difficulty of Capturing All Benefit Values; and
3. Treatment of Irreversibilities and the All or Nothing Feature.

Dose-Response Relationship

The need for data from the Effects Groups for the various receptor categories has been stressed at several points. It is, however, such an important prerequisite to the estimation of benefits that it is reviewed again here. Although some data are available, what is needed is a clear statement of changes in output, e.g., water availability with fish populations as related to LRTAP effects (i.e., changes in pH). This must be further extrapolated over geographical areas, and over the short and long term, to derive estimates of total quantity changes.

These information needs, by receptor category, are summarized in Table 7-3. In the absence of these data, meaningful benefit estimates are often impossible.

Inclusion of All Values

A second concern is the extent to which the methods recommended will fully capture the value of the benefits. Some methods can provide at best, a partial measure, since they cannot capture option and legacy values. Although their exclusion results in an underestimate, determination of the actual size of this underestimate is difficult. Some economists think the underestimates are large in situations dealing with unique assets, or major changes in an entire geographical region, such as New England. The matter is further complicated by the issue of property rights, discussed under equity consideration. Thus, one should be cautious in assuming that any benefit figure is a reflection of the full value to society. This may be less of a concern, if the values which can be measured are sufficient to indicate the desired choices.

TABLE 7-3 SUMMARY OF PHYSICAL SCIENCE DATA NEEDED FOR BENEFIT EVALUATION

	Inventory	Dose-Response
A. Aquatic		
1. Sports Fishery	water availability by susceptibility, geographical area and species type	change in fish population with varying deposition levels
2. Commercial Fishery	water availability by susceptibility, geographical area and species type	change in fish population with varying deposition levels
3. Ecosystem	species diversity, numbers	changes in species diversity and numbers
B. Terrestrial		
1. Agricultural Crops	crop pattern by geographical area	change in marketable yield with varying deposition levels
2. Forests	cover type, age, stocking and size by geographical area	change in marketable yield with varying deposition levels
3. Ecosystem	species diversity, numbers	changes in species diversity and numbers
C. Buildings, Structures		
1. Material	geographical distribution by type of material and by use	deterioration rate as a function of total sulphur
2. Historic	geographical distribution by type of material	deterioration rate as a function of total sulphur
D. Water Systems	geographical distribution of systems on susceptible water bodies	change in lake/stream intake pH
E. Health		
1. Morbidity	population	sickness per $\mu g/m^3$ SO_4^{2-}
2. Mortality	population	deaths per $\mu g/m^3$ SO_4^{2-}
F. Visibility	population	change in km of visibility per $\mu g/m^3$ SO_4^{2-}

Irreversibilities and the All or Nothing Feature

The possibilities that the physical dose-response relationships, with respect to LRTAP deposition, may be irreversible, and that the rate of damage may not be monotonically related to deposition, called the all or nothing feature, or non-convexities, constitute additional limitations to conventional economic analysis.

First, it has been suggested that once a certain level of damage has occurred, reduction in LRTAP may not result in an improvement in environmental quality. Hence, the effects of LRTAP may be irreversible, (i.e., certain species may never be restored). If so, current market or inferred prices will substantially understate the value of these resources to society. From the perspective of benefit valuation, this would suggest that it is imperative that option, existence, and legacy values be included in the estimates.

Second, it has been suggested that the dose-response relationship is such that, after a certain level of pollution, the rate of damages declines (Crocker and Forster 1981). Such would be the case where most of the fish are gone, and further pollution has little or no impact. This feature of non-convexity would suggest that benefits of LRTAP control are much higher, and increase at a more rapid rate, if the environment is relatively unpolluted. Once the rate of damages starts to decline, the benefits of abatement would be commensurately lower. This suggests that there are significant benefits of immediate LRTAP control, and lower benefits if control and abatement take place after significant damage.

7.4.2 Conclusions and Recommendations

This paper has attempted to provide an overview of techniques of deriving the economic value of benefits associated with LRTAP abatement. There is a large body of economic literature which deals more thoroughly with the intricacies of the theory, and is replete with numerous empirical studies. Many of the latter have not, however, dealt specifically with the effects of LRTAP.

Three conclusions arise from the material presented here.

(1) There are several techniques which can be applied to determine the primary economic benefits associated with a particular activity category, bearing in mind that the values are underestimated since they fail to include option and legacy values. However, the lack of data on dose-response relationships limits the application of these techniques at this time.

(2) The value of the benefits can be further estimated for specific economic sectors, and hence regions, to derive an estimate of the impacts in various geographical areas.

(3) It is evident that more economic research is required. Economic techniques have yet to be rigorously tested in some sectors, such as historical value, and are limited in their treatment of option and legacy values, and in dealing with the issue of property rights.

In light of this, we recommend that:

(1) The participation model be applied, on a US/Canada basis, to sports fishing, to determine the value of primary benefits, due to LRTAP reduction. This is because dose-response data are available for the aquatic receptor, and because the current geographically - specific studies now being undertaken tend to ignore substitution among fishing sites.

(2) Regional economic analysis be undertaken, to derive the secondary value of the recreation and tourism sector in areas of the U.S. and Canada affected by LRTAP (e.g., Adirondacks and Muskoka-Haliburton), due to the concerns expressed about the effects on the economies of these areas.

(3) Further research be initiated to apply the survey (contingent market) methodologies to the derivation of primary benefit values of visibility in the eastern U.S. and Canada, and to historical sites, because of the lack of information about these values.

(4) Further research be undertaken to obtain sound estimates of materials damages.

(5) Further work be undertaken with respect to the issues relating to property rights, as these are an important part of the distributional aspect of the long range transport of pollutant.

(6) Additional investigation (conceptual thinking) be undertaken on the relationship between activity and other (option and legacy) values for the various receptor categories, in order to derive a sense of the underestimate of the total benefits, due to the omission of the latter values.

We anticipate that the results of the studies would give small numbers in relationship to the potential benefits of LRTAP reduction. We base this on the OECD results (1981), which found that aquatic effects were only a small percentage of the total benefits of sulphur reductions, and that very small increases in agricultural and forestry yields would generate a very large benefit estimate. Moreover, if a control program directed at LRTAP includes reductions in NO_x (ozone) levels, which have demonstrable and significant effects on agricultural output, the benefits are likely to be substantial.

7.5 APPENDIX A - REVIEW OF RELEVANT ECONOMIC CONCEPTS

Two basic economic concepts which provide a measure of changes in social welfare (satisfaction) are consumer's surplus and producer's surplus. Changes in these measures are regarded as being the most theoretically relevant indicators of social welfare loss or gain, resulting from specific activities or events.

7.5.1 Consumer's Surplus

Traditional economic theory presumes that the individual consumer is the best judge of his own personal well-being or utility, given currently available information. If an individual is made better off, other things being equal, then his social well-being or welfare is increased.

The individual consumer allocates his money income across the various commodities in such a fashion that he maximizes his welfare or utility. In general, his desired purchase of a commodity will depend upon his tastes, the prices of all goods, and his income.

The demand curve graphically represents the relationship between the desired purchase of a commodity and its price (or the willingness-to-pay). For each additional unit, the consumer is willing to pay less than for the previous unit. Hence, the curve slopes down to the right. This is called the ordinary demand curve or the Marshallian demand curve. If we assume that more of the good will be purchased at lower prices if prices fall (a "normal" good), then a consumer's ordinary demand curve is represented in Figure 7-5.

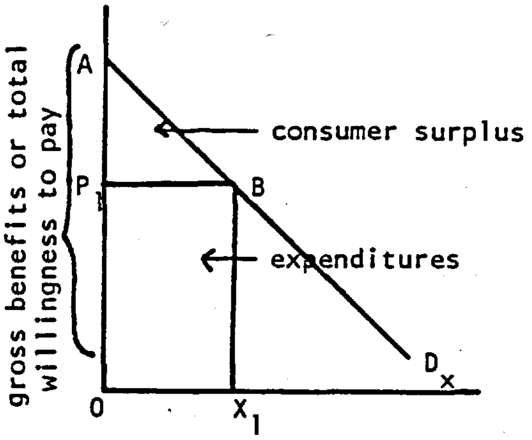

Figure 7-5 Measure of consumer surplus.

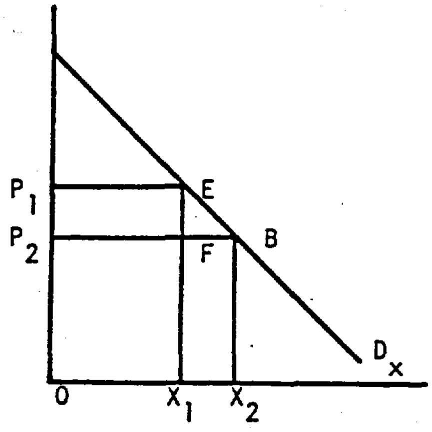

Figure 7-6 Change in consumer surplus.

A point on the demand curve is the maximum price that the individual would be willing to pay for a specified amount of good, and is noted by an ordered pair (x, p). Alternatively, for a given price p, x represents the most the consumer would willingly purchase. A maximum price exists for every potential consumption level for the good, and is given as the relevant p-point on the demand curve.

Suppose that the commodity sells in the market for P_1 and the consumer purchases X_1. The consumer's expenditure on x is P_1 X_1 (price times quantity). The triangular area denoted P_1AB, which lies above the expenditure rectangle OP_1BX_1 is what economists call the Consumer's Surplus. It is a surplus, since it represents a saving to the individual in terms of what he would have been prepared to pay for levels of consumption smaller than X, as shown by the associated prices on the demand curve. Instead of paying the maximum price for each level of commodity x, the consumer pays P_1 for all units. If all of the savings are added up, then we obtain the area P_1AB. Since the price is given in money units, consumer surplus is a monetary measure. The area OP_1BX_1, plus the area P_1AB (consumer expenditure plus consumer surplus), is a measure of the gross benefits to the individual of consuming X_1 units. Consumer's surplus is the net benefit to the individual consuming x^o units, that is, total willingness-to-pay minus expenditure.

Changes in the value of consumer's surplus are a measure of the welfare associated with the activity which caused the change. Consider the case in which the price of the commodity falls from P_1 to P_2 due to an environmental improvement as illustrated in Figure 7-6. At price P_2, the consumer can both purchase more of the commodity, and pay less per unit. In addition, his consumer's surplus is increased by the trapezoidal area P_2P_1EB. This geometric area represents a monetary measure of the welfare effect associated with the price change.

Consumer's surplus can be estimated for an individual, using observed price and quantity data. However, instead of estimating individual demand curves, economists use aggregated data and estimate market demand curves. Market demand curves are obtained by aggregating individual demand curves, that is, adding up horizontally (along the quantity axis). This implies that tastes and preferences can be aggregated across individuals. If, however, individuals have different incomes, or if the distribution of income is altered significantly, then aggregations can lead to biases in estimates. Simple linear summation of these demand curves is inadequate. One must, then, resort to Engel curves.

There are two alternative monetary measures of the effects of a price change, known as equivalent and compensating variation (denoted as EV and CV respectively), which can be translated into a change in income. Under the circumstances where a decrease in LRTAP effects results in a price decrease, EV and CV can be defined as follows:

Compensating Variation is the change in income, given the price decrease, which maintains the consumer's original utility. CV is equal to the income which would be withdrawn to offset the price decrease.

Equivalent Variation is the change in income which, given the original price, would leave the consumer's satisfaction or utility unchanged if price decreases. An increase in income equal to EV would be given to the consumer to maintain welfare.

While EV and CV are technically the more correct measures of welfare change, they are difficult to estimate, and the value of consumer surplus, which is closely related to CV and EV, is easier to measure and is therefore recommended for this analysis.

Public Goods

In the above discussion, we assumed that commodity x was traded in an organized market at a non-zero price. The impact of LRTAP on the price of a particular commodity was subsequently considered. This scenario is, of course, an over simplification. Now let us consider a certain commodity which is a "public good" such as an environmental commodity (e.g., clean air), which is not traded in an organized market (but not, of course a zero value to society). The levels of this environmental commodity are assumed to be outside the control of the individual. Hence, the overall level of consumer welfare depends not only upon prices of market commodities and money income, but also upon the level of environmental commodities he consumes.

Where there are no markets, and hence no prices, it is difficult to derive a demand curve, and it is done through other means, as discussed in sections II and III. Again, the measure of consumer's surplus is the area under the demand curve, and in this case, the total area since the price is zero. The change in consumer surplus would be measured by the change in quantity if, for example, visibility increases due to reduced LRTAP, as shown in Figure 7-7.

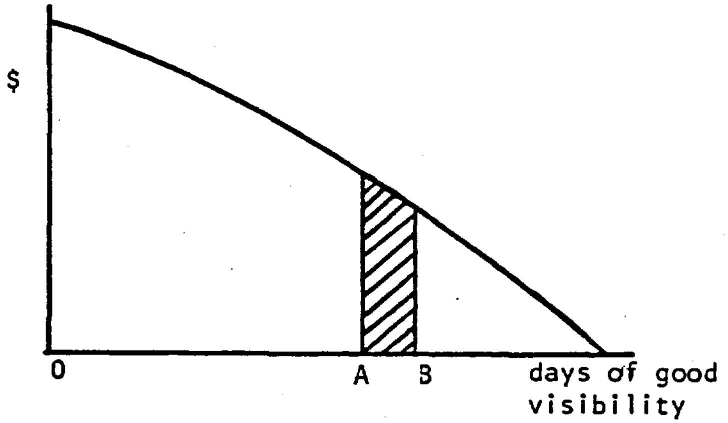

Figure 7-7 Change in demand due to visibility improvement.

While willingness-to-pay is used to determine demand curves, this is not the real test of the value of visibility, although it is an easier measure. The change in quantity has affected consumer utility, and the consumer effectively enjoys an increase in income.

We can therefore obtain a monetary measure of the welfare change, by considering the change in income which will have the same impact as the change in environmental quality. Here there are two measures — compensating and equivalent surplus (denoted as CS and ES), depending upon which welfare position is used for the initial starting point for comparison.

Compensating surplus is the change in income which results in the same level of utility, given the change in quantity. Equivalent surplus is a change in income which produces a change in utility equal to the change in quantity, at the original quantity level. These measures are shown graphically in Figure 7-8.

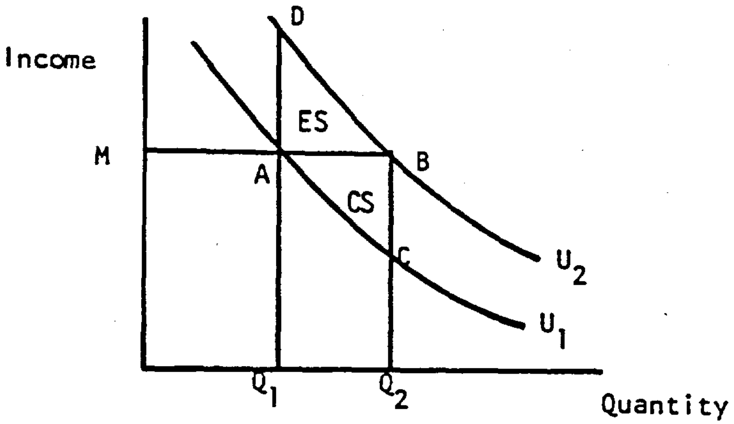

Figure 7-8 Compensating and equivalent surplus.

7.5.2 Producer's Surplus

The discussion thus far has been concerned with consumer's surplus as one measure of economic welfare. It is possible to define an analogous concept for producers in the economy. This is called producer's surplus. The concept of consumer's surplus is defined with respect to the consumer's demand curve. Producer's surplus is defined with respect to the producer's supply curve of the relevant commodity. Figure 7-9 presents a supply curve, which presumes that more of the output will be produced as price rises. Higher prices are required to cover increased production costs at higher output levels.

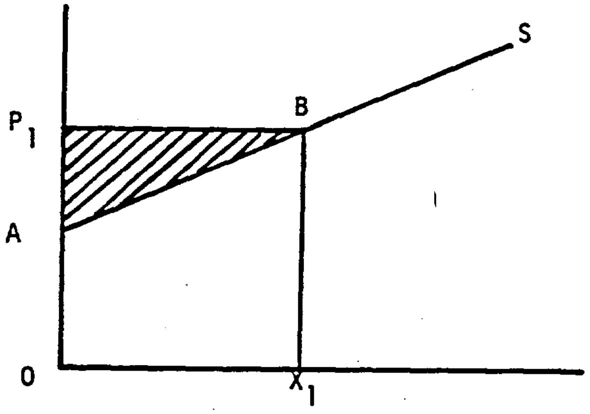

Figure 7-9   Producer's surplus.

In Figure 7-9 a point (X_1, P_1) on the supply curve can be given two interpretations. For a given price P_1, the output X_1 is the largest that the firm is prepared to supply at that price. Or, for a given output X_1, the price P_1 is the minimum price that the firm will accept for supplying X_1. In the market, all units sell for the same price, hence the producer gains on all unit levels lower than the total sale, because the market price exceeds the minimum he needs. This gain is called producer's surplus, and is represented by the area AP_1B in Figure 7-9 - the area above the supply curve bounded by the market price.

Changes in the value of this producer's surplus are interpreted as a measure of welfare change. This change causes a supply shift from S to S_1, due, for example, to an increase in crop yields from reduced LRTAP, and is illustrated in Figure 7-10.

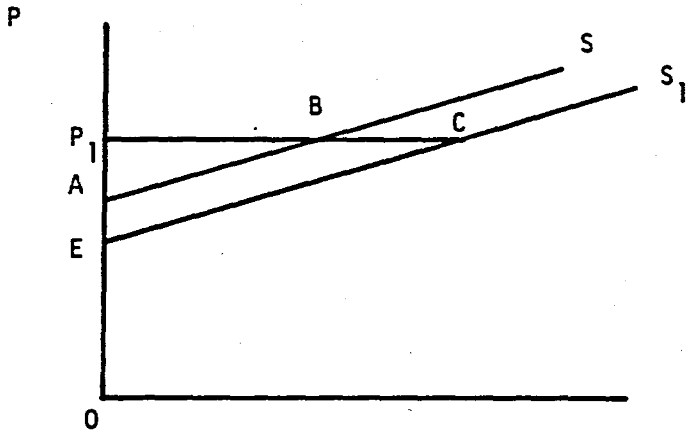

Figure 7-10   Change in producer's surplus due to change in supply.

The area ABCE represents the welfare gain to the producer caused by a shift in the supply curve from S to S_1. The minimum price required to supply each level of output is now lower, and is everywhere further from the market price received by the producer.

Changes in net social welfare caused by LRTAP effects on marketable commodities can be determined by examining the net change in consumer's and producer's surpluses. Suppose, for example, that the reduction of LRTAP deposition results in an increased supply of some product. The supply curve has then shifted to the right from S to S_1, while the demand curve for the product remains stationary at D, as shown in Figure 7-11.

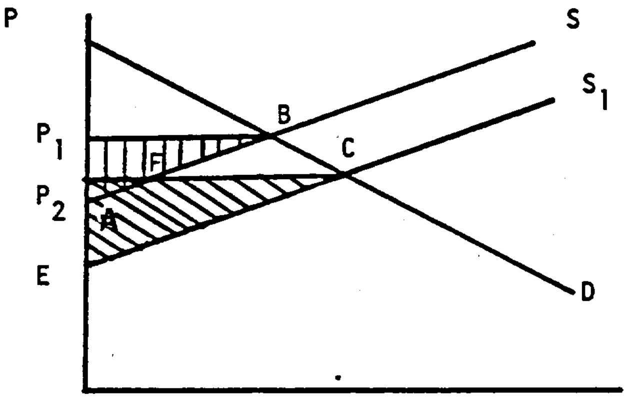

Figure 7-11 Hypothetical change in producer's surplus due to reduction in LRTAP deposition.

The area EP_2C is the new producer's surplus, caused by the price fall due to the supply increase, compared to AP_1B at the original supply and price levels. Producer's surplus changes for two reasons. The producer's surplus is increased by EAFC as a result of increased production at lower cost, with a given market price. Producer's surplus decreases by P_2P_1BF a result of market pressures decreasing output prices and stimulating production. The net change in surplus is therefore ABCE.

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